

# Preparation and use of humic coatings covalently bound to silica gel for Np(V) and Pu(V) sequestration

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## Abstract

Alkoxysilylated humic derivatives were used to create covalently bound humic coatings on silica gel. The corresponding reaction was conducted in an aqueous milieu that was feasible due to the water solubility of these derivatives. The alkoxysilylated humic derivatives were obtained by alkoxysilylation of leonardite humic acid (HA) and hydroquinone-modified HA (HQ) with enhanced redox properties. The silica gel coated with covalently bound HA and HQ was tested for sequestration of aqueous Np(V) and Pu(V) under anaerobic conditions. Greater sequestration with respect to Pu(V) (up to 97%) as compared to Np(V) (up to 60%) was demonstrated for samples of silica gel coated with HA and HQ, whereas sorption of both actinides on pure silica gel did not exceed 20%. Results provide bench-scale proof that alkoxysilylated humic derivatives can be used as reagents for the in situ installation of permeable reactive barriers designed to remediate actinide-contaminated groundwater.

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## 1. Introduction

The most commonly applied technology for treatment of groundwater contaminated with toxic substances including metals and radionuclides is “pump and treat”, followed by disposal or re-injection of treated groundwater. This process is costly and inefficient due to difficulties arising from the ineffective capture of contaminated groundwaters and the sorption of contaminants on mineral surfaces [1]. A permeable reactive barrier (PRB) is an alternative technology to “pump & treat” systems. A PRB is a subsurface wall of reactive permeable medium emplaced across the flow path of a contaminant plume [2]. A typical PRB is costly to install but economical to maintain. Much of the installation cost is related to excavation of aquifer material that is then replaced with reactive porous media [3]. PRBs are filled with different reactive materials such as metals or metal-

based catalysts for degrading volatile organics, chelators or ion exchangers for immobilizing metal ions, nutrients and oxygen for microorganisms to enhance bioremediation, or other agents [4].

Humic substances (HS) have shown promise as refractory and as inexpensive reactive components for PRB [5,6]. HS are ubiquitous in the environment and comprise the most abundant pool of non-living organic matter [7]. Leonardite is the most widely used raw material for production of commercial humic preparations followed by other low-rank coals, peat, and sapropel. Macromolecules of HS consist of a hydrophobic aromatic backbone that is highly substituted with functional groups (mostly carboxyls and hydroxyls) [8]. This structure enables humics with hydrophobic, redox, ion exchange, and chelating properties. As a result, HS play an important role in the environmental behaviour of actinides (An). The elevated fraction of oxygen donor groups within the humic molecule fosters the formation of stable complexes with actinides [9,10]. The order of increasing complex strength is  $AnO_2^+ < An^{3+} < AnO_2^{2+} < An^{4+}$  [9]. Hence, the strongest complexes are formed by HS with tetravalent actinides.

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However, when metal loading approaches 5–10% of the total ionized carboxylate concentration, coagulation of HS–An(IV) complexes occurs. Below this percentage, actinide–HS complexes are mobile in flow-through porous medium [10–12]. HS have been shown to reduce metals with estimated reduction potentials of 0.5–0.7 V [13]. This range is consistent with the redox potential of hydroquinone which suggests quinonoid structures are responsible for the redox properties of humic materials [14,15]. In the context of this study, it is of particular importance to stress that HS can reduce Pu(VI/V) to Pu(IV), Np(VI) to Np(V) [16,17], and that several investigations report enhanced sorption of actinides on humics-rich solids (silts and bottom sediments) [18,19]. Thus, humic PRBs could be an effective innovation in groundwater remediation. A two step *in situ* method of installing humic PRBs is described by Balcke et al. [20]: in the first step the mineral support is coated with iron(III) and in the second humic polyanions are immobilized. Unfortunately, the metal-bridges used to form the HS-coating are highly sensitivity to variations in pH and  $E_h$ ; consequently, the practical utility of this *in situ* method remains in question.

The objectives of this study were: (1) to develop a new approach for preparing stable humic coatings which are covalently bound to mineral support; and (2) to assess the performance of these coatings in sequestering actinides in high valence states. To prepare covalently bound humic coatings under aqueous conditions, we used novel humic derivatives with surface active alkoxyethyl (Si–OAlk) groups incorporated into the humic backbone as described in our previous publication [21]. These derivatives adsorb irreversibly on mineral support by forming Si–O–Si or Si–O–M bonds with OH-containing mineral surfaces. This precludes facile mobilization of the humic coating and any contaminants entrapped within that coating. Pu(V) and Np(V) were used as model actinides. They represent the dominant dissolved species of Pu and Np in natural waters [9], which possess the highest mobility in the environment; hence, pose a significant environmental threat and challenge for groundwater clean up.

## 2. Experimental

### 2.1. Materials

Parent and modified leonardite humic materials (HA and HQ, respectively) were used for preparing alkoxyethyl-derivatives as described in [21]. Leonardite humic acids (HA) used for further modifications were isolated from commercially available potassium humate (Powhumus™) 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 desiccator over P<sub>2</sub>O<sub>5</sub>. The obtained HA were modified with hydroquinone using formaldehyde condensation at a monomer: HA ratio of 100 mg per 1 g as described by Perminova et al. [22]. The corresponding sample was kindly provided by A.N. Kovalenko. The resultant HQ-derivative possessed a higher redox capacity: 1.1 mequiv./g as compared to 0.6 mmol/g measured for the parent HA [22]. Reagent grade (Acros Ltd.) 3-amino-propyltrimethoxysilane (APTS) was then used to derive both HA-APTS and HQ-APTS.

Reagents of analytical grade were used for the following purposes: 0.5 M HCl and NaOH were used to prepare humic derivatives; KH<sub>2</sub>PO<sub>4</sub> and

Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O were used to prepare 0.03 M buffer solution. Silica gel 60 (Merck) with specific surface area of 540 m<sup>2</sup>/g was used as a mineral support for immobilization of humic derivatives.

### 2.2. Study of sorption ability of humic derivatives

The sorption of HA-APTS and HQ-APTS onto SiO<sub>2</sub> was studied by the method of isotherms. For this purpose, solutions of HA derivatives at concentration ranges of 0.01–5 g/L (for HA-APTS) and 0.01–2.5 g/L (for HQ-APTS) were prepared in 0.03 M phosphate buffer at pH 6.8 and 10 mL aliquots were added to 0.1 g of silica gel. A decrease in concentration of either HA derivative ( $C_{HS}$ ) in the test solution was measured using UV–vis spectrophotometry.

### 2.3. Methods of preparation and characterization of the humic coating immobilized on silica gel

Aqueous solutions of HA-APTS and HQ-APTS were prepared by dissolving a weight of dry derivative in a few drops of concentrated NaOH followed by dilution with 0.03 M phosphate buffer at pH 6.8. Concentrations of humic derivatives in solution were 5 g/L for HA-APTS and 2.5 g/L for HQ-APTS. An aliquot (0.1 L) of each solution was added to 1 g of silica gel and stirred until sorption equilibrium was reached. The time required to establish sorption equilibrium was 72 h. A decrease in concentration of HA derivatives in the solution was detected spectrophotometrically at 254 nm. Samples of silica gel with APTS-humic derivatives immobilized were centrifuged and washed repeatedly with distilled water. Next, these samples (HA-APTS–SiO<sub>2</sub> and HQ-APTS–SiO<sub>2</sub>) were dried in vacuum desiccator over P<sub>2</sub>O<sub>5</sub> during 52 h.

Elemental analyses (C, H, N) were performed using Carlo Erba Strumentazione analyzer. Ash content was determined by manual combustion.

FTIR spectroscopy was used to characterize the structures of silica gel with immobilized APTS-humic derivatives. Prior to analysis, the above described samples were dried under reduced pressure ( $3 \times 10^{-3}$  mBar) at 50 °C. Dried samples were mixed with KBr (spectroscopic grade, 1:100) and pressed into pellets. FTIR spectra were recorded at 64 scans with a resolution of 4 cm<sup>-1</sup>.

### 2.4. Preparation of stock solutions of Np(V) and Pu(V)

Experiments on actinide sequestration were conducted under anoxic conditions in the dark and in a glove box filled with argon gas of high purity. The initial Pu(IV) solution was obtained from RIAR (Dimitrovgrad, Russia) as a mixture of Pu-238, Pu-239 and Pu-242 isotopes with the isotopic ratio by activity of 0.946 Pu-238, 0.038 Pu-239, and 0.017 Pu-242. Pu(V) was prepared according to the technique described by Saito and Choppin [23]. For this purpose, a solution of Pu(IV) was evaporated two times with concentrated HClO<sub>4</sub> until wet salts were obtained and then dissolved in 1 M HNO<sub>3</sub>. After an addition of 2 mL KBrO<sub>3</sub>, the plutonium solution was heated in a boiling water bath during 3 h until the bromine vapors disappeared. Completeness of Pu oxidation was controlled spectrophotometrically by monitoring absorbance maxima of Pu(IV) and Pu(VI) as described by Milyukova et al. [24]. Once oxidation was completed (a lack of Pu(IV) absorbance), a 20 µL aliquot of Pu(VI) solution was diluted with 20 mL of distilled water. Next, 0.22 mL of 30% H<sub>2</sub>O<sub>2</sub> was added as a reducing agent. The reaction mixture was kept under room temperature for 1 h. An aliquot of the obtained solution (50 µL) was diluted with distilled water (1.5 mL), acidified with 3.3 M HCl (0.6 mL) and purified from admixtures of Pu(IV) and Pu(VI) using extraction with 6.7% di-(2-ethylhexyl)-phosphoric acid (HDEHP) in toluene (1 mL) as described in [25]. Reaction yield (conversion of Pu(IV) to Pu(V)) was determined by measuring the activity of water and organic phases using liquid scintillation counting; the accounted yield was 85%. The prepared stock solution of Pu(V) had a concentration of  $1.46 \times 10^{-7}$  M.

The initial <sup>237</sup>Np solution was purchased from RIAR (Dimitrovgrad, Russia) in the form of Np(V)O<sub>2</sub><sup>+</sup> in 1 M HNO<sub>3</sub> with a concentration of  $1.4 \times 10^{-2}$  M. Radiochemical purity of <sup>237</sup>Np solution was controlled using alpha-spectrometer equipped with Si-surface barrier detector (Model 7401, Canberra Ind., Australia). Neptunium concentration was measured using a liquid scintillation counter (LSC, TriCarb2700TR, Canberra Ind., Australia). Prior to these experiments, the daughter <sup>233</sup>Pa was separated from <sup>237</sup>Np by solvent extraction using 0.5 M 1-(2-thenoyl)-3,3,3-trifluoroacetone (TTA) in toluene as described

in [26]. The pentavalent oxidation state of neptunium was confirmed using solvent extraction technique [25]. The concentration of Np(V) stock solution was  $1.87 \times 10^{-3}$  M.

### 2.5. Batch experiments on Np(V) and Pu(V) sequestration by immobilized humic derivatives

All sorption experiments were conducted under batch conditions in an inert atmosphere (argon gas) and in a glove box. All reagents including MilliQ distilled water, HClO<sub>4</sub> and NaOH solutions were bubbled with argon gas to remove oxygen prior to use. Plastic centrifuge tubes were used for preparing test solutions. A known mass of tested sorbent was introduced into the tube, added with 20 mL of deoxygenated MilliQ water, and spiked with 50  $\mu$ L of Np(V) or Pu(V) stock solutions. The pH of the prepared solution was adjusted using HClO<sub>4</sub> or NaOH. The centrifuge tubes were then sealed, shaken, and stored in a dark glove box over the entire duration of the experiments (8–10 days). Solutions were periodically sampled to monitor the kinetics of Np and Pu sequestration by tested sorbents. Initial concentrations of Np(V) and Pu(V) in the prepared solutions were  $4.68 \times 10^{-6}$  and  $4.9 \times 10^{-9}$  M, respectively. Experiments with Np(V) were conducted at pH 4.5, and the tested sorbent masses were 40 and 70 mg for HA-APTS–SiO<sub>2</sub> and HQ-APTS–SiO<sub>2</sub>, respectively. Experiments with Pu(V) were conducted at three pH values: 3.5, 4.6, and 7.7, and the mass of HA-APTS–SiO<sub>2</sub> tested was 7 mg. The mass of silica gel tested as a reference material (non-modified with humics) for both Np and Pu experiments was 100 mg. Experimental solutions were periodically sampled to measure neptunium and plutonium content using solvent extraction with liquid scintillation counting [23].

## 3. Results and discussion

### 3.1. Sorption of humic derivatives onto silica gel

The APTS-humic derivative sorption isotherms on silica gel are shown in Fig. 1a and b for leonardite HA (HA) and its hydroquinone-enriched derivative (HQ), respectively. Both isotherms were characterized with inflection points in the region of 1.4 g/L, which is close to the critical micelle concentration of humic substances of 3–7 g/L [27,28] that could cause multilayer sorption to take place on the surface of silica gel at concentrations exceeding 1.4 g/L. Thus, we applied the Langmuir model to the first section of these isotherms (up to inflection point) to estimate maximum sorption and the adsorption constants for derivatives tested. The following equation was used to fit the experimental curves:

$$\theta = \frac{m(\text{HS})}{m(\text{SiO}_2)} = \frac{KC(\text{HS})}{1 + KC(\text{HS})},$$

where  $K$  is the sorption constant,  $\theta$  the sorption capacity,  $m(\text{HS})$  the mass of HS (mg) sorbed onto sorbent used (SiO<sub>2</sub>),  $m(\text{SiO}_2)$  the mass of SiO<sub>2</sub> used in the sorption experiment (g) and  $C(\text{HS})$  is the equilibrium concentration of HS in solution (mg/L).

Table 1  
Content of elements in silica gel coated with the immobilized APTS-humic derivatives

HS sample	Description	Content of elements (mass%)			Bound amount of HA (mg HS/g SiO <sub>2</sub> )
		C	H	N	
HA-APTS–SiO <sub>2</sub>	Leonardite HA on SiO <sub>2</sub>	9.2	4.23	0.78	242
HA-APTS–SiO <sub>2</sub> (water)	Same sample washed with distilled water	9.2	4.19	0.77	240
HQ-APTS–SiO <sub>2</sub>	Hydroquinone-enriched HA on SiO <sub>2</sub>	3.3	0.62	0.45	100
HQ-APTS–SiO <sub>2</sub> (water)	Same sample washed with distilled water	3.3	0.61	0.45	100

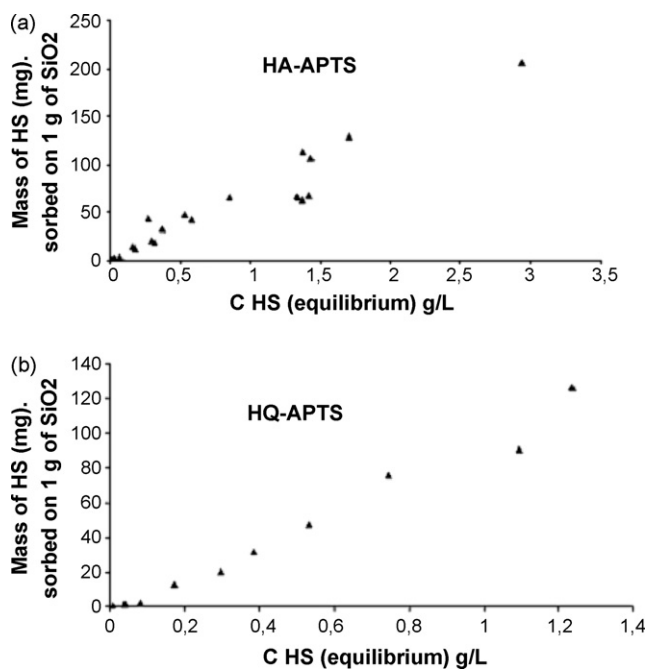


Fig. 1. Sorption isotherms of humic derivatives on silica gel: (a) HA-APTS, (b) HQ-APTS.  $C(\text{HS})$  stands for equilibrium concentration of humic derivative in solution (0.03 M phosphate buffer, pH 6.8). Initial concentrations of HA-APTS and HQ-APTS are 5 and 1.5 g/L, respectively.

The resultant values of maximum sorption capacity ( $\theta_{\text{max}}$ ) were 0.15 and 0.52 g HS per 1 g SiO<sub>2</sub> for HA and HQ, respectively. Sorption constants ( $K$ ) were 677 and 185 mL/g for HA and HQ, respectively. Both alkoxy-silylated derivatives exhibited high sorption affinities for silica gel.

### 3.2. Immobilization and characterization of the humic coatings on silica gel

To obtain the samples of silica gel with covalently bound humic coatings, the sorption of humic derivatives was conducted at the highest concentration tested: 5 g/L for HA-APTS and 2.5 g/L for HQ-APTS. A portion of the silica gel with immobilized HS was then washed with distilled water to remove labile humic material and both samples were analyzed for organic carbon, hydrogen, and nitrogen contents. Results shown in Table 1 indicate HA-APTS and HQ-APTS sorption on silica gel was practically irreversible: that is the content of carbon did not change after several washings with distilled water. Of particular importance was the high amount of organic carbon immobilized onto silica gel: 9.2% for HA-APTS and 3.3% for HQ-APTS.

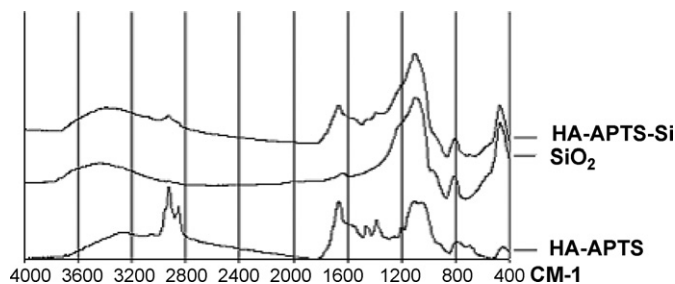


Fig. 2. FTIR spectra of silica gel, HA-APTS and HA-APTS-SiO<sub>2</sub> measured in KBr pellets.

This corresponded to 240 and 100 mg of immobilized HS per 1 g of silica gel for HA and HQ, respectively Table 1.

The method presented here exceeded substantially other immobilization techniques described in the literature (see, e.g. review publication by Koopal et al. [29]). Comparison of results from this study with that reported elsewhere (Table 2) show the new method immobilized 2–10 times more humic material. In addition, all previously reported methods lead to reversible sorption of HS, whereas the new approach generated an irreversibly bound coating in a one-step process and without subsequent washings.

Samples of silica gel with irreversibly bound humic material were characterized using FTIR spectroscopy. FTIR spectra of pure silica gel, HA-APTS and HA-APTS-SiO<sub>2</sub> are shown in (Fig. 2). For silica gel, the following assignments were made: the broad band at 3500 cm<sup>-1</sup> – Si-OH stretching vibrations, the band at 1640 cm<sup>-1</sup> –OH bending vibrations from the adsorbed water, strong bands in the range from 1250 to 1000 cm<sup>-1</sup> – Si-O-Si asymmetric stretching vibrations, and the band at 900–750 cm<sup>-1</sup> – Si-OH bending [30]. For the spectrum of HA-APTS, the bands at 2940–2845 cm<sup>-1</sup> were assigned to –CH<sub>2</sub>– groups, at 1690 cm<sup>-1</sup> – to Schiff bases, and at 1400 and 3360–3180 cm<sup>-1</sup> – to amide bonds. The FTIR-spectrum of HA-APTS-SiO<sub>2</sub> exhibited bands typical to both HA-APTS and SiO<sub>2</sub> and to the chemical bonds formed during the immobilization procedure: 3500–3200 cm<sup>-1</sup> (Si-OH and C-OH stretching vibrations, stretch vibrations of H-bonded OH and amide bands), 2924 cm<sup>-1</sup> (asymmetric stretch vibrations of CH<sub>2</sub> and CH<sub>3</sub>), 2875 cm<sup>-1</sup> (symmetric stretch vibrations of CH<sub>2</sub> and CH<sub>3</sub>) and 1710–1610 cm<sup>-1</sup> (Schiff bases, water bending vibrations, aromatic C=C stretch, H-bonded carbonyl groups and the asymmetric COO stretch). Strong bands at

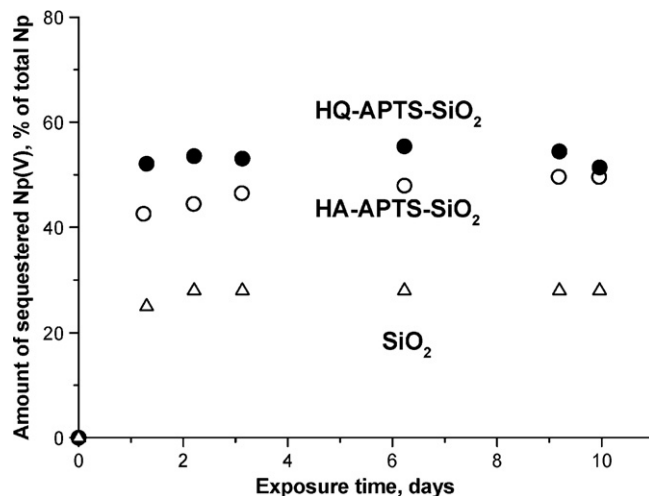


Fig. 3. Sequestration kinetics of Np(V) in the presence of pure SiO<sub>2</sub>, SiO<sub>2</sub> with covalently bound leonardite humic acid (HA-APTS-SiO<sub>2</sub>) and their hydroquinone-enriched derivative (HQ-APTS-SiO<sub>2</sub>); C<sub>tot</sub>(Np)=4.68 × 10<sup>-6</sup> M, pH 4.5, mass/volume ratios for HA-APTS-SiO<sub>2</sub> and HQ-APTS-SiO<sub>2</sub> are 3.5 and 2.0 g/L, respectively.

1250–1000 cm<sup>-1</sup> (Si-O-Si) and 900–750 cm<sup>-1</sup> (Si-OH) from the silica gel itself mask other information. Very similar interpretations were made for HQ-APTS-SiO<sub>2</sub>.

### 3.3. Np(V) and Pu(V) sorption onto silica gel coated with immobilized humic derivatives

Fig. 3 shows the sequestration kinetics of Np(V) by pure SiO<sub>2</sub>, HA-APTS-SiO<sub>2</sub> and HQ-APTS-SiO<sub>2</sub> at pH 4.5. It can be seen both forms of immobilized humics sorbed Np(V). Transient sorption plateaus after the second day of exposure. The sequestration performance of the hydroquinone-enriched derivative (HQ) was slightly better than the non-modified leonardite material (HA): the amount of sequestered neptunium was 55% for HQ versus 45% for HA.

Corresponding results for Pu(V) are shown in Fig. 4. Sorption of Pu(V) onto pure silica gel did not exceed 10–20% in the pH range from 3.5 to 7.7 over the test duration. Humic-modified silica gel sequestered ~75% of Pu after the first day of exposure at pH values of 7.7 and 4.6. The percentage of sequestered plutonium further increased with exposure time and then stabilized after 100 h to levels of 97 and 90% at pH values of 4.6 and 7.7, respectively. It should be noted here that we used con-

Table 2

Amounts of reversibly and irreversibly sorbed HS on silica gel using different immobilization methods (from [29]) as compared to those obtained in this study

Method	Ads <sup>a</sup>	EDC <sup>b</sup>	DMF <sup>c</sup>	Gly <sup>d</sup>	HA-APTS <sup>e</sup>
Bound amount of HS before washing with 0.1 M NaCl, pH 10 (mg HS/g SiO <sub>2</sub> )	65	107	124	60	242
Bound amount of HS after washing with 0.1 M NaCl, pH 10 (mg HS/g SiO <sub>2</sub> )	42	56	72	16	240 <sup>f</sup>

<sup>a</sup> “Ads” stands for immobilization of HS onto APTS-modified silica gel in the aqueous phase without further heating by adsorption (Ads) mechanism.

<sup>b</sup> EDC stands for immobilization method based on HS binding to SiO<sub>2</sub> modified with APTS in the presence of *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDS).

<sup>c</sup> DMF stands for binding of HS to APTS-modified silica gel at high temperature in the anhydrous solvents (e.g. DMF).

<sup>d</sup> Gly stands for binding of HS to APTS-modified silica gel via glutaric aldehyde.

<sup>e</sup> HA-APTS stands for binding of HA-APTS derivative to silica gel in 0.03 M phosphate buffer at pH 6.8 at room temperature as described in this publication.

<sup>f</sup> Washing was conducted using distilled water.



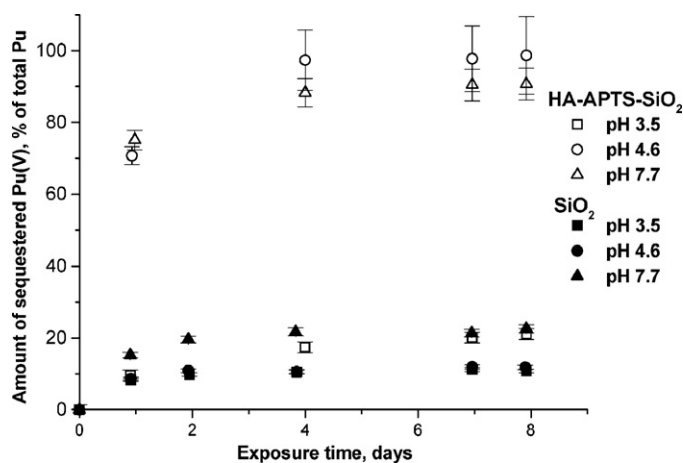


Fig. 4. Sequestration kinetics of Pu(V) by SiO<sub>2</sub> with covalently bound leonardite HA (HA-APTS-SiO<sub>2</sub>) at different pH values;  $C_{\text{tot}}(\text{Pu}) = 4.90 \times 10^{-9}$  M, mass/volume ratio for HA-APTS-SiO<sub>2</sub> is 0.345 g/L.

centration of Pu ( $4.9 \times 10^{-9}$  M), which was much lower than its solubility limit [31]. This lead us to believe that the greater sequestration obtained here resulted from Pu sorption to immobilized humics rather than sedimentation of hydrolyzed forms. Substantially lower sequestration efficiencies were observed for immobilized humics (up to 20%) at the lowest tested pH of 3.5. This corroborates well with previous findings of lower sorption affinities for Pu under acidic conditions [32] which may be due to less complexation with humics at low pH values.

Results shown in Figs. 3 and 4 indicate that it is reasonable to estimate equilibrium particle–water partition coefficients ( $K_d$ ) for the sorbents using data after 100 h of exposure. It is then useful to compare these partition coefficients to those reported for natural geosorbents. As follows from Fig. 3,  $K_d$  values for Np(V) ranged between  $3 \times 10^2$  and  $5 \times 10^2$  mL/g for both sorbents. There was no substantial benefit detected from the humic material enriched with quinonoid units. At the same time, measured  $K_d$  values were an order of magnitude higher as compared to those of pure silica gel (30 mL/g). It can be expected that  $K_d$  values for Np would increase with pH. This is surmised from the data shown for Pu(V) in Fig. 4.

Pu partition coefficients for the humic-coated silica gel were approximately  $8 \times 10^3$ ,  $3 \times 10^4$  and  $1.9 \times 10^5$  mL/g for pH values of 3.5, 7.7 and 4.6, respectively. These coefficients (in particular, those for pH 4.6 and 7.7) fell within the upper range of  $10^2$  to  $10^5$  mL/g previously reported for natural geosorbents [31–34]. For soils, Glover et al. [35] measured plutonium partition coefficients for 17 samples from 9 different sites of which 7 were located on U.S. DOE facilities. For measurements conducted at an initial plutonium concentration of  $10^{-8}$  M, which is close to the concentration used in this study,  $K_d$  ranged between 80 and  $2.2 \times 10^3$  mL/g. Bell and Bates [36] reported soil values of plutonium  $K_d$  from 32 to  $7.6 \times 10^3$  mL/g. These soils were from the Sellafield and Drigg sites in England and their texture ranged from clay to sand. Data showed plutonium adsorption varied with pH, giving a maximum adsorption at pH 6. A number of studies published much higher plutonium partition coefficients varying from  $1 \times 10^3$  to  $1 \times 10^6$  mL/g for river, oceanic,

and lake sediments. Duursma and coworkers calculated a  $K_d$  of  $1 \times 10^4$  mL/g for marine sediments [37,38]. Studies by Mo and Lowman [39] on plutonium-contaminated calcareous sediments in aerated and anoxic seawater medium yielded  $K_d$  values from  $1.64 \times 10^4$  to  $3.85 \times 10^5$  mL/g. The latter were very close to those obtained in our studies.

Hence, the synthesized humics-coated silica gels were as effective in sequestering Pu as the most efficient natural geosorbents. This finding would appear to justify further research on development of an innovative groundwater remediation technology that would use alkoxysilylated humic derivatives for the *in situ* installation of humic PRBs [21]. The alkoxysilylated humic derivatives, as opposed to non-modified native humic material, were shown here to form covalent bonds with mineral surfaces in water. Humic PRBs would be created by injecting solutions of alkoxysilylated derivatives directly into contaminated aquifers using a fence row of wells. The injected humics would form an organic coating on mineral surfaces of aquifer materials, and thus, creating a “humic curtain” capable of sequestering actinides from contaminated groundwater. The effectiveness of humic PRB would depend on pH; although, the optimal pH for sequestering mobile plutonium(V) appeared to exist within the environmentally relevant range of 4.5–7.7. Further work, however, is needed to develop and test humic PRBs under environmental conditions before the technology can be brought into practice. Detailed kinetic, batch, and flow-through studies should be conducted to define physical–chemical and technological parameters of the processes involved including humic reagent loadings, hydraulic residence times, and other parameters needed to design and optimize the humic PRB performance under natural subsurface conditions.

#### 4. Conclusion

The results of this study provide proof of a concept for developing a new groundwater remediation technology based on a use of alkoxysilylated humic derivatives. Under aqueous conditions, silica gel was coated with an irreversibly bound layer of alkoxysilylated humic derivatives. The resultant sorbent displayed significantly elevated sequestration efficiencies for Np(V) and Pu(V). Both contaminants pose a major threat to the environment due to their high mobility. The immobilized humic sorbent can be expected to perform well under anoxic conditions and at neutral or slightly acidic pH.

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