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Retention and chemical speciation of uranium in a wetland on the Savannah River Site

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Abstract

Uranium speciation and retention mechanism onto Savannah River Site (SRS) wetland sediments was studied using batch (ad)sorption experiments, sequential extraction desorption

tests and U L₃-edge X-ray absorption near-edge structure (XANES) spectroscopy of contaminated wetland sediments. U was highly retained by the SRS wetland sediments. In contrast to other similar but much lower natural organic matter (NOM) sediments, significant sorption of U onto the SRS sediments was observed at pH <4 and pH >8. Sequential extraction tests indicated that the U(VI) species were primarily associated with the acid soluble fraction (weak acetic acid extractable) and NOM fraction (Na-pyrophosphate extractable). Uranium L₃-edge XANES spectra of the U-retained sediments were nearly identical to that of uranyl acetate. The primary oxidation state of U in these sediments was as U(VI), and there was little evidence that the high sorptive capacity of the sediments could be ascribed to abiotic or biotic reduction to the less soluble U(IV) species. The molecular mechanism responsible for the high U retention in the SRS wetland sediments is likely related to the chemical bonding of U to organic carbon.

Keywords: Wetland sediments, uranium, chemical speciation, retention

1. Introduction

Uranium (U) has been found to accumulate in wetlands in areas where U-rich rock formations are present ([Zielinski et al., 1987](#)). Based on such observations, natural and constructed wetlands have been used as a cost-effective means to immobilize U from U mines and processing facilities ([Noller et al., 1994](#)). Thus, it is important to understand the biogeochemical behavior of U in wetlands so that the wetlands can be more efficient and effective for the remediation and reclamation of U-contaminated sediments (e.g., U mine and milling sites, nuclear waste storage sites, and fuel cell rod storage basins). Possible pathways for

long term U immobilization in wetlands include the chemical and/or microbial reduction of soluble U(VI) ions to fairly insoluble U(IV) species (Kalin et al., 2005; Lovley et al., 1991; Noubactep et al., 2006; Turick et al., 2008), mineral precipitation, sorption onto NOM (Wan et al., 2011), ion exchange or sorption to sediment minerals (Akber et al., 1992; Dong et al., 2012; Grybos et al., 2007), and accumulation in plants (Hinton et al., 2005; Knox et al., 2008).

The Savannah River Site (SRS) in Aiken, SC includes several (former) uranium processing facilities. As a result of their operations, U has entered the surrounding environments through accidental and purposeful discharges. For example, approximately 45,000 kg of depleted U was released into Tims Branch and its associated wetlands between 1958 and 1980 and approximately 70% of the U still remains in the stream and associated wetland sediments of this waterway (Bertsch et al., 1994; Evans et al., 1992; Pickett, 1990).

The U desorption distribution coefficients (K_d values) of SRS contaminated wetland sediments has been measured to be quite large, ranging from 170 to 6493 mL g⁻¹ (Kaplan and Serkiz, 2001). NOM has been demonstrated to control the availability of U in the contaminated sediments within the Steed Pond basin (a basin within Tims Branch; Sowder et al., 2003). Bertsch et al. (1994) reported the *in situ* characterization of chemical speciation of U in the sand fraction of a SRS sediment sample using micro X-ray absorption spectroscopy, which appeared to indicate the presence of U(VI). Given these initial observation that much of the U may naturally exist in the U(VI) form, the remediation technologies of the contaminated SRS sediments with apatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}, \text{F})_2$) (Arey et al., 1999; Kaplan et al., 2004; Seaman et al., 2001), humic acid (Wan et al., 2011), native trees (Hinton et al., 2005), natural hyper-accumulators, for example, the netted chain fern (*Woodwardia areolata*) (Knox et al., 2007), and microbial metabolites (Turick et al., 2008) have been evaluated.

However, the tendency of U to enter the mobile phase and become available to local biota or be transported from the contaminated area has not been well quantified. The chemical speciation of U and the molecular mechanism responsible for the high retention in the SRS wetland sediments reported by [Kaplan and Serkiz \(2001\)](#) are not sufficiently well understood. Additional information is also needed to facilitate the development of *in situ* treatment and remediation strategies of U-contaminated SRS wetland sediments. The objective of this work was to identify: (1) the chemical speciation of U; and (2) the molecular mechanisms responsible for the high U retention in SRS wetland sediments ([Kaplan and Serkiz, 2001](#)). The general approach was to conduct laboratory batch tests to measure U sorption as a function of pH with SRS uncontaminated wetland sediments, and then to use sequential extraction and U L₃-edge XANES spectroscopy to evaluate the U speciation of the batch samples and field U-contaminated sediments.

2. Materials and methods

2.1 Artificial groundwater

The recipe for an artificial groundwater (AGW) solution was based on the monitoring survey results for uncontaminated groundwater samples at the SRS ([Strom and Kaback, 1992](#)). Briefly, the AGW has a pH of ~6.0, electrical conductivity of 0.026 mS cm⁻¹, turbidity of <1 NTU, 1.25 mg L⁻¹ Na, 0.25 mg L⁻¹ K, 0.93 mg L⁻¹ Ca, 0.66 mg L⁻¹ Mg, 5.51 mg L⁻¹ Cl, and 0.73 mg L⁻¹ SO₄, which mimics the non-impacted SRS subsurface groundwater conditions ([Li et al., 2012](#)).

2.2 SRS wetland sediments

Contaminated and uncontaminated surface sediment samples (0 to 0.15 m depth below the leaf-litter level) were collected from the TNX wetland site, which is adjacent to a pilot-scale nuclear facility that released processing wastes including U and Th into an unlined seepage basin between 1958 and 1980. The basin contents entered the adjacent wetland by subsurface flow and overland flow. The characteristics of the contaminated and uncontaminated sediments are summarized in Table 1 ([Kaplan and Serkiz, 2001](#)). The mineralogy of both the contaminated and uncontaminated sediments was characterized by primary silica sand, and lesser kaolinite, hydroxy-interlayered vermiculite, illite and gibbsite.

2.3 Batch experiments

Batch U(VI) sorption experiments as a function of pH (2.5-10) were set up at a constant total U(VI) concentration (2×10^{-5} M) in AGW solution with or without 0.1M NaNO₃ under ambient atmospheric CO₂ ($P_{\text{CO}_2} = 10^{-3.5}$ atm) and temperature (22 °C). About 0.1 gram of the uncontaminated sediment and 10 mL solution were added into a 15 mL polypropylene centrifuge tube while exposed to air. The resulting solids concentration was 10 g L⁻¹. After spiking 0.1 mL of the U stock solution (2×10^{-3} M uranyl nitrate, pH 3.6, Eh 433 mV) and then pH adjustment using 0.1 M NaOH or 0.1 M HNO₃ solution, the suspensions were placed on a shaker for 96 hour sorption reaction. For some batch experiments, all tubes were open to atmospheric CO₂ twice per day and 30 minutes each time to promote the solution equilibrium with atmospheric CO₂. The pH values were adjusted daily until the pH shifts were <0.1 pH unit (a Radiometer Copenhagen PHM 95 pH meter). Each suspension was filtered using 0.2 µm Nylon membrane syringe filters.

The filtrate was acidified with 2% HNO₃ and analyzed for U by inductively coupled plasma mass spectrometry (ICP-MS). The extent of U sorption to the sediments was calculated using a distribution coefficient, K_d value, which is a U concentration ratio of sediment to solution. The K_d values (mL g⁻¹) were calculated using equation 1:

$$K_d = \frac{C_0 - C}{C} \times \frac{V}{M} \quad (1)$$

where C₀ and C are the initial and final U concentrations in solution, respectively, V is the volume of the solution (mL) and M is the mass of the sediment (g).

2.4 Sequential extraction

Sequential extraction of contaminated and U-sorbed uncontaminated sediments was carried out using the method of Miller et al. (1986), which is a modification of ASTM D3974-81 (ASTM 1999) literature protocols (Baston et al., 1994; Kaplan and Serkiz, 2001; Miller et al., 1986; Sowder et al., 2003) and summarized in Table 2.

2.5 U L₃-edge XANES measurements

U L₃-edge XANES spectra of the contaminated sediment (<53 μm fraction) and the U-sorbed uncontaminated sediments (<53 μm batch) were collected using the Hard X-ray MicroAnalysis beamline (06ID-1) at the Canadian Light Source (CLS) (Jiang et al., 2007). The 50-100 mg air-dried powder sample was pressed into a disk pellet with a 6.3 mm diameter and sealed by Kapton

tape. The beamline was equipped with Si(111) double crystal monochromators and Rh mirrors. The monochromators were calibrated using the first inflection point at 17038 eV of the K-edge of yttrium metal foil that was mounted between two N₂-filled ionization chambers downstream of the sample. The U L₃-edge XANES spectra of all sediment samples and uranyl acetate standard (diluted in silica powder to ~500 mg kg⁻¹ U) were collected using a 32-element solid state Ge fluorescence detector. The spectrum of UO₂ standard was collected using transmission mode. Eight layers of aluminum foils were used to eliminate Fe signals, and a Sr-3 solid state filter to screen other impurity signals near U L₃-edge. The storage ring was operated at 140-200 mA during the experimental measurements. The U L₃-edge XANES spectra were recorded in the energy range of 17000-17470 eV, and processed using Athena. All the collected spectra were background removed and normalized.

3. Results

3.1 Retention and chemical species of U in the contaminated SRS wetland sediment

The sequential extraction results of the contaminated (285 mg kg⁻¹ ²³⁸U) and uncontaminated (0.57 mg kg⁻¹ ²³⁸U) sediments are summarized in Table 3. For the contaminated sediment, U was primarily associated with acid soluble and organic carbon fractions, and to a much smaller extent with the amorphous Fe/Al oxide, crystalline Fe/Al oxide, and structural fractions. Fig. 1 shows the U L₃-edge XANES spectra of the contaminated sediment (<53 μm fraction), black NOM particles that were separated from the contaminated sediment and ground to <53 μm, and two standards, uraninite (UO₂) and uranyl acetate, in the energy range of 17150-17300 eV only. With regard to the standards, three distinctive features distinguish the uraninite (U(IV)) from the

uranyl acetate (U(VI)) spectra as marked in Fig. 1: 1) the U L₃-edge peak is sharper and shifts toward lower energy by 2.5 eV for U(IV) than U(VI); 2) there is a “shoulder” at ~17188 eV for U(VI); 3) the peak at ~17215 eV is sharper and stronger for U(IV) than U(VI). The spectra of the contaminated sediment (filled circles) and its NOM particles (empty squares) are essentially indistinguishable and overlap directly on the uranyl acetate standard spectrum (dash line). These results indicated that the U species in the contaminated sediment is U(VI), without detectable U(IV), and the U(VI) species is likely bonding to organic carbon. On-going extended X-ray absorption fine structure (EXAFS) measurements are underway to confirm the nature of the U binding environment in these samples.

3.2 Retention of U onto the uncontaminated sediment

The sorption percentages and K_d values of U onto the uncontaminated SRS wetland sediment versus pH are shown in Fig. 2A and 2B, respectively. For batches 1 and 2, the U sorption profiles were repeated as two separate and identical experiments (AGW). For batch 3, the AGW was amended with 0.1 M NaNO₃; the sorption profile was largely indistinguishable from the results in batches 1 and 2, indicating that ion exchange was likely not a major mechanism for the U uptake. For batch 4 which was open twice a day to promote equilibrium conditions with atmospheric CO₂, the U sorption profile again was not notably different from batches 1, 2, or 3. Batches 5 through 7 were designed for the comparison of particle size effects, and they indicated a general expected trend that greater sorption occurred in the smaller fraction (<53 μm) for batch 5 and 7, and less sorption occurred in the larger size fraction (53 μm to 250 μm) for batch 6. This trend was especially apparent at lower pH levels.

In general, the U sorption profiles with the wetland sediment were similar to those with other pure phase minerals (Cheng et al., 2004; Hsi and Langmuir, 1985; Payne et al., 1998; Waite et al., 1994; Wan et al., 2011) and sediments (Dong et al., 2012; Wan et al., 2011). However, this wetland sediment had two distinguishing aspects with its U sorption trends. First, at pH >8, the U sorption percentages or K_d values were much higher than those measured with other solid phases (Hsi and Langmuir, 1985; Payne et al., 1998; Waite et al., 1994). Decreasing sorption in this elevated pH range is commonly attributed to the formation of uranyl-carbonate complexes (Bernhard et al., 2001; Brooks et al., 2003; Duff and Amrhein, 1996; Kalmykov and Choppin, 2000). In our batch experiments, the solutions inside the 15 mL centrifuge tubes might be not in a complete equilibrium with atmospheric CO₂, even though the tubes were open to atmospheric CO₂ twice per day and 30 minutes each time. Second, at pH <4, the U sorption was also much higher than for other systems (Hsi and Langmuir, 1985; Payne et al., 1998; Waite et al., 1994). This may be attributed to the presence of high concentrations of NOM in these wetland samples. Uranyl and NOM form strong bonds, including at low pH levels (Wan et al., 2011). This may partially explain why at pH < 4, the U sorption was much higher onto the fraction of <53 μm sediment than onto the 53-250 μm fraction, because the former may contain much more NOM than the latter, in addition to the particle size effect.

3.3 Chemical speciation of U in the U-sorbed uncontaminated sediment

The U-sorbed uncontaminated sediments (batch 4 in Fig. 2) were further studied using sequential extraction. The total sorption profile (open diamonds) and the sequential extraction profile of U sorbed onto each fraction of this sediment are shown in Fig. 3. The retained U is

primarily associated with acid soluble and organic fractions, and lesser amounts were associated with the structural, amorphous Al/Fe oxide, structural Al/Fe oxide, and aqueous soluble fractions. These results are in strong agreement with the sequential extraction results from the contaminated sediment (Table 3).

The U L₃-edge XANES spectra of the U sorbed uncontaminated sediments (batch 5 in Fig. 2), in comparison with that of uranyl acetate (empty circles) and the uncontaminated sediment without U sorption (dash line), are shown in Fig. 4. A very weak signal was recorded for the uncontaminated sediment (0.57 mg kg⁻¹ ²³⁸U), indicating that U L₃-edge XANES can detect the U signal to the sub mg kg⁻¹ level in such sediments, but the recorded spectrum does not provide as much structural or chemical information as spectra derived from samples with greater U concentrations. All the U L₃-edge XANES spectra of the sediment samples, which are also nearly identical to the uranyl acetate spectra, suggesting, but not confirming, that the sorbed U species is almost exclusively U(VI), and is likely bonding to carbon in its second coordination shell.

4. Conclusions

U is highly retained in the SRS wetland sediments, which was not affected by higher ion strength (0.1 M NaNO₃) solutions. The U species in the SRS wetland sediments were U(VI), without detectable U(IV). Chemical or microbial reduction and ion exchange with sediment minerals are unlikely pathways for the U retention in the SRS wetland sediments. The U sorption onto the SRS wetland sediments might also play a limited role in the U retention, especially at the lower pH condition. The retained U was associated with acid soluble and organic fractions of the wetland sediments, and the U L₃-edge XANES spectra of the retained U are nearly identical

to that of uranyl acetate (U(VI)). These results might indicate that the molecular mechanisms for the high U retention onto the SRS wetland sediments would be either chemical sorption or bonding with NOM-like humate colloids (Wan et al. 2011) or accumulation in the wetland plants (Hinton et al., 2005; Knox et al., 2008) that constituted a significant source of the NOM in the SRS wetland sediments.

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Table 1 Characteristics of the SRS contaminated and uncontaminated sediments

	Contaminated sediment	Uncontaminated sediment
pH ^a	4.53	4.16
Organic carbon, mg kg ⁻¹	1427	1395
Fe oxide ^b , wt%	0.09	0.01
Sand, wt%	53	79
Silt, wt%	22	16
Clay, wt%	19	6
²³⁸ U, mg kg ⁻¹	285	0.57
²³⁸ U desorption K _d , mL g ⁻¹	1297	n/a
^a 1:1 solid/deionized water ratio ^b Analyzed using Na dithionite-sodium citrate-citric acid extraction, reported as Fe ₂ O ₃ . n/a = not available.		

Table 2. Sequential extraction protocols (Baston et al., 1994; Miller et al., 1986)

Steps	Reagents	Fractions	pH	Extraction time (hrs)
1	Artificial ground water	Aqueous	5.5	16
2	0.44 M acetic acid (CH ₃ COOH)+0.1 M Ca(NO ₃) ₂	Acid soluble	2	8
3	0.1 M Na pyrophosphate (Na ₄ P ₂ O ₇)	Organic	10	24
4	0.175 M ammonium oxalate (NH ₄) ₂ C ₂ O ₄ +0.1 M oxalic acid (H ₂ C ₂ O ₄)	Amorphous Fe/Al oxides	3	4 in dark
5	0.29 M Na dithionite in 0.15 M sodium citrate + 0.05 M citric acid buffer	Crystalline Fe/Al oxides	5	0.5 in 50 °C
6	1 part HNO ₃ , 3 parts HCl, 1 part H ₂ O	Structural	<<1	48 in 80 °C water bath

Table 3. Retention of U in the whole contaminated sediments from sequential extraction

	Contaminated sediment #1		Contaminated sediment #2	
	²³⁵ U	²³⁸ U	²³⁵ U	²³⁸ U
Acid extractable (% fraction)	44	36	27	25
Organic fraction (% fraction)	51	37	70	57
Amorphous Fe/Al oxides (% fraction)	0	6	0	3
Crystalline Fe/Al oxides (% fraction)	5	3	3	2
Structural (% fraction)	0	17	0	14
Total U concentration, (mg kg ⁻¹)	2.13	285	1.81	329

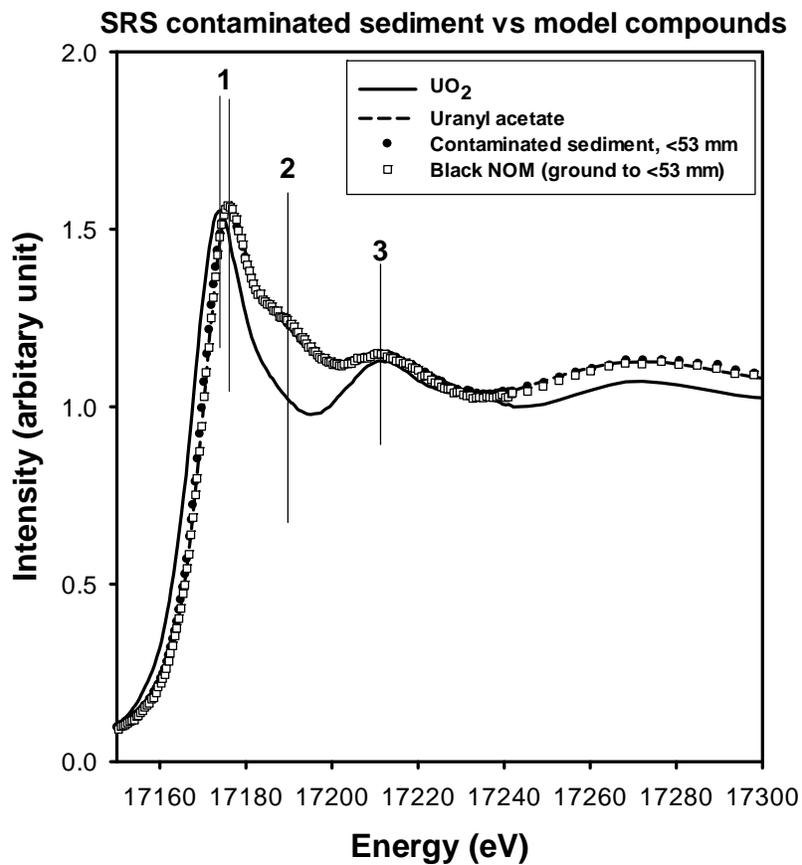


Fig. 1. U L_3 -edge XANES spectra of contaminated sediment (<53 μm ; filled circles), its black NOM (<53 μm ; empty squares), in comparison with the spectra of uraninite (U(IV)) (solid line) and uranyl acetate (U(VI)) (dash line).

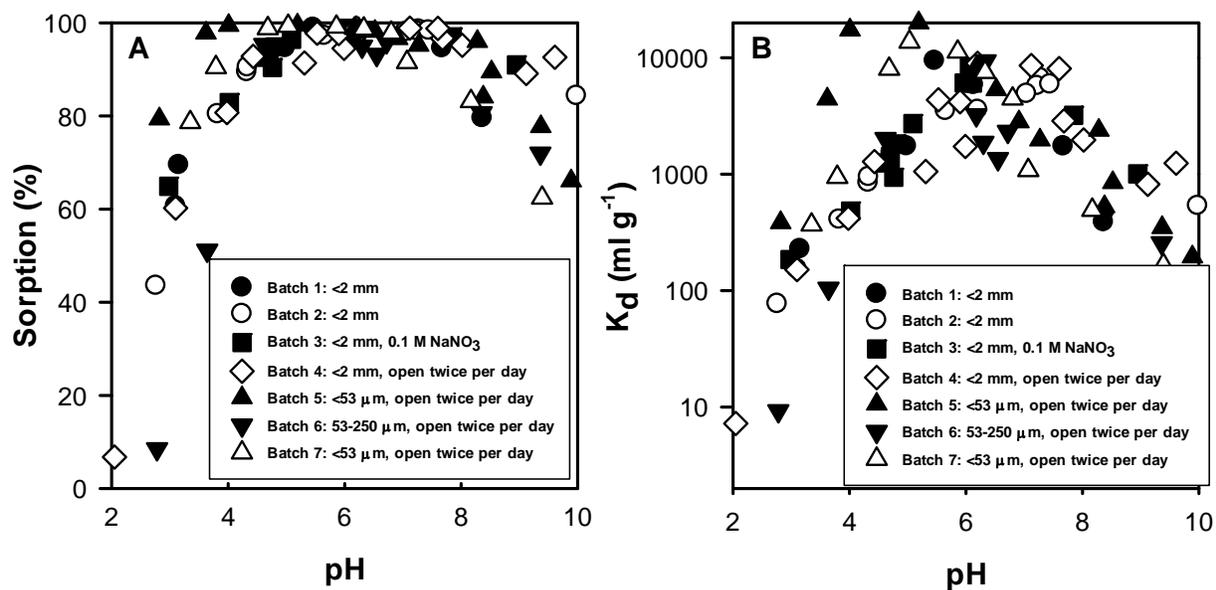


Fig. 2. Sorption percentages (A) and K_d values (B) of U onto the uncontaminated wetland sediment versus pH. Batches 1-3 were just open for the pH adjustment daily, but batches 4-7 were opened twice daily, 30 minutes each time.

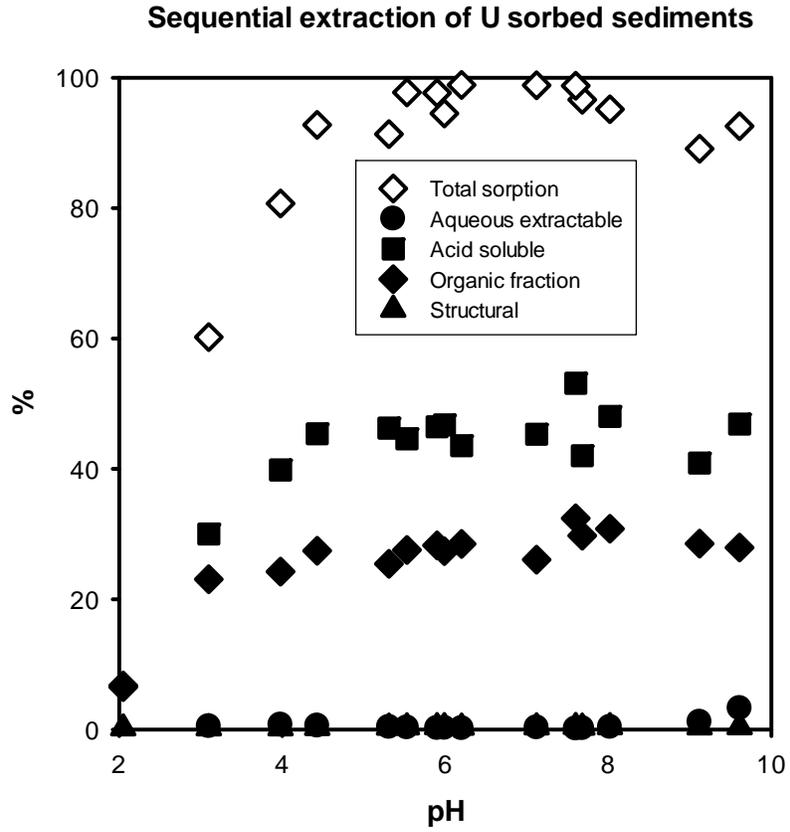


Fig. 3. Sequential extraction of U-sorbed uncontaminated sediments (batch 4 in Fig.2).

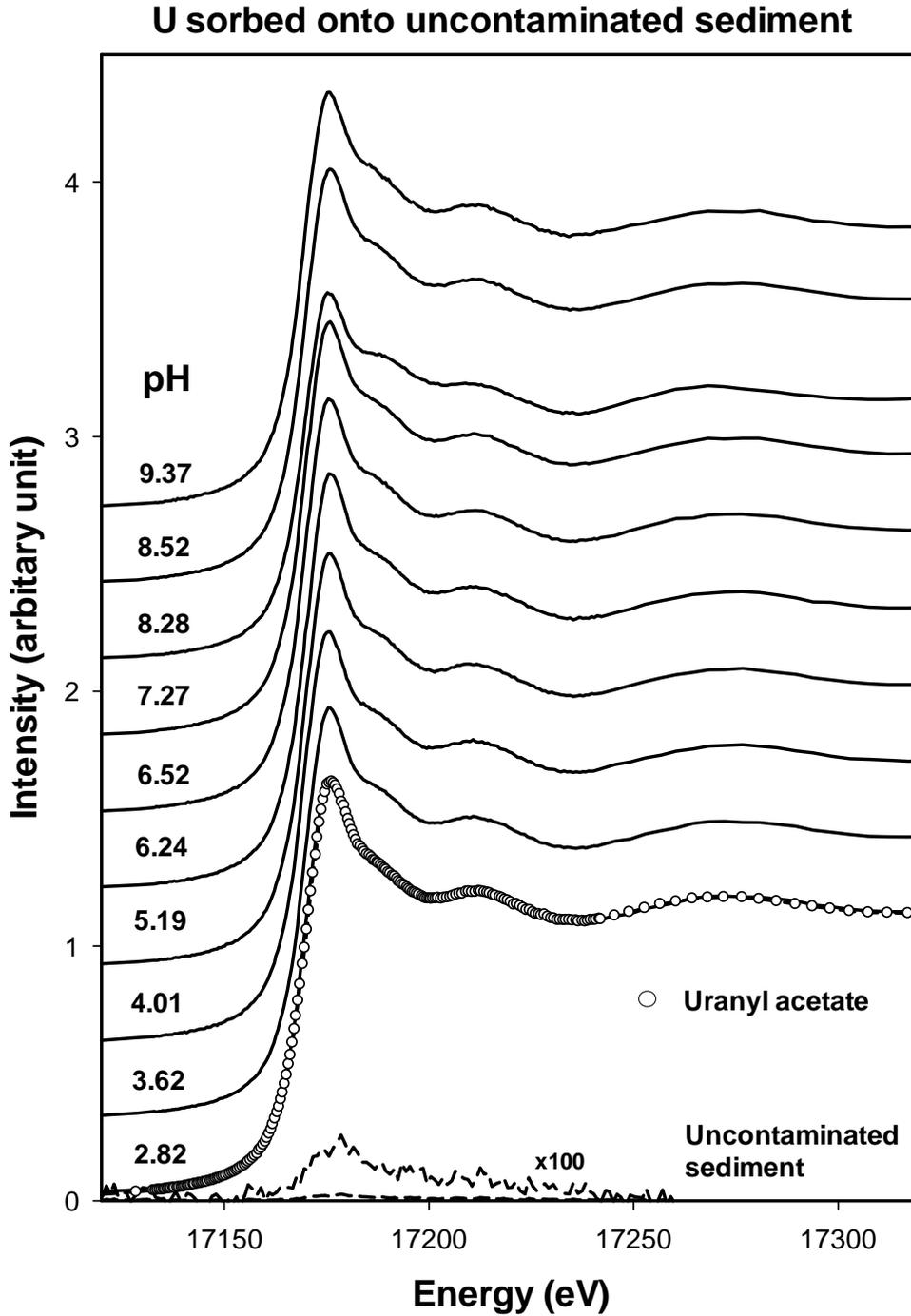


Fig. 4. U L₃-edge XANES spectra of uncontaminated sediment (dash line) and its U-sorbed samples in the pH range of 2.8-9.4 (batch 5 in Fig. 2). The spectrum of uranyl acetate is shown as empty circles for comparison.