

Application of the de Job method in the evaluation of the stoichiometry of uranyl phosphate complexes sorbed on bentonite

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ARTICLE INFORMATION



DOI: 10.5155/eurjchem.7.1.42-48.1348

Received: 23 October 2015

Received in revised form: 05 December 2015

Accepted: 05 December 2015

Published online: 31 March 2016

Printed: 31 March 2016

KEYWORDS

Uranium
 Bentonite
 Phosphates
 Job method
 Sorption spectra
 Uranyl phosphate complexes

ABSTRACT

For the first time, the continuous variation method was applied for the evaluation of the stoichiometry of uranyl phosphate complexes sorbed on bentonite. Sorption of $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in the presence of $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ from 0.001 mol/L solutions led to the appearance of maxima in the sorption peaks of U(VI) and P(V) ions at molar ratios of $[\text{U(VI)}]/[\text{P(V)}]_s = 1.4, 3.3, 3.6$ and $1.2, 1.7$. It is suggested, based on complementary XRD and XPS data, that the UO_2HPO_4 complex is located on aluminols ($\equiv\text{Al-OH}$) whereas the $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ complex is precipitated in the interlamellar space of bentonite. The participation of $(\text{UO}_2)_3(\text{OH})_5^{+}$ and $(\text{UO}_2)_4(\text{OH})_7^{+}$ species in the formation of U(VI) surface complexes is suggested, based on the deconvolution of sorption spectra of U(VI) on the bentonite in the presence of phosphates.

Cite this: *Eur. J. Chem.* **2016**, *7*(1), 42-48

1. Introduction

Due to its practical importance, the problem of uranium surface complexes has been extensively studied [1]. There is a demand for the introduction of new sorbents, which could effectively bind uranium ions and prevent their emission to the aqueous environment. Uranium is found in nuclear wastes as well as in groundwater near uranium mines [2]. Among the different methods used for uranium removal, such as ion exchange, solvent extraction, membrane filtration, coagulation-filtration, reverse osmosis, hyperfiltration and electro-dialysis, sorption plays a prominent role owing to the low cost of the materials used. Phosphate complexes of U(VI) formed on the surface of different sorbents such as alumina, ferrihydrite and silica, evidently improve U(VI) sorption [3-13]. Our aim is to present a new method of characterization of the stoichiometry of surface complexes based on the sorption. It is common knowledge in coordination chemistry that the continuous variation method, alternatively called the de Job method, is a simple tool for the evaluation of complexes formed in the equilibrium phase, i.e. aqueous or non-aqueous complexes. The main assumption of this method is that the measured feature of a complex, for example its UV-VIS absorbance in a solution, has a maximal value at a characteristic metal/ligand ratio, when the concentrations of metal

and ligand change continuously and at the same time their sum is kept constant [14]. In the present work, the availability of the method of continuous variation in a sorption system was investigated. When the sum of U(VI) and phosphate ion concentrations P(V) is fixed but their mutual proportion changes, the observed sorptions of U(VI) and P(V) should reach their characteristic maximum values at particular $[\text{U(VI)}]/[\text{P(V)}]_s$ ratios for their concentrations in the sorbent phase. The occurrence of U(VI) and P(V) peaks at the different values of $[\text{U(VI)}]/[\text{P(V)}]_s$ would result only from the formation of at least two surface complexes of U(VI) with phosphate ligands. A full characterization of the complexes formed is possible if different, complementary methods are used. For this reason, we applied X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) methods to describe the sorption products obtained. We believe that the success of the continuous variation method in relation to uranyl ions would allow its future application in systems with other ions. One should remember that evaluation of the stoichiometry of the complexes formed, measured directly, is the first, very important step in the recognition of a complexation scenario. Identification of this stoichiometry based on the fit of experimental data to the different sophisticated equations defining the formation constants of surface complexes is risky.

2. Experimental

2.1. Reagents

Sodium bentonite was prepared from the product delivered by Sigma-Aldrich, by equilibration of 5 g bentonite with 100 cm³ of NaCl (Sigma-Aldrich, 99.99% purity) solution (1 mol/L) through 24 h. The sodium form of bentonite was washed several times by water to remove the rest of sodium chloride. The presence of chlorides in washing solution was checked argentometrically. After filtration the solid residue was dried in air.

2.2. Equilibrium sorption data

The sorption isotherms of U(VI) were determined by contacting a 0.1 g sample of Na-clay with 100 cm³ of a UO₂(CH₃COO)₂·2H₂O + Na₂HPO₄·7H₂O solution (Lachema, n.p., Brno, p.a., Sigma-Aldrich) at concentrations of 0.0001-0.0010 mol/L for U(VI) and P(V), respectively. The sum of U(V) and P(V) concentrations was always 0.001 mol/L. The pH of the mixture was controlled by 0.1 mol/L acetate buffer (CH₃COOH + CH₃COONa). The following parameters were maintained: a mechanical shaker WU-4, shaking speed 170 oscillations/min, shaking time 6 h, and temperature 22 °C. After shaking, the samples were left to stand for 12 h and were then passed through filter paper (Filtrak 390, Polish Chemical Reagents) and centrifuged at 10,000 rpm for 15 min (Med. Instruments). The initial and the equilibrium concentrations of U(VI) in the aqueous phase were determined by the Arsenazo(III) method [15], whereas the equilibrium concentrations of phosphate ions P(V) in the aqueous phase were measured spectrophotometrically by the phosphomolybdic method [15].

The concentrations of U(VI) and P(V) ions in the bentonite phase (*c_s*) in mol/g were calculated from the relationship:

$$c_s = (C_0 - C_{eq})V/m \quad (1)$$

where *c_s*, *c₀*, and *c_{eq}* denote the concentrations of U(VI) and P(V) ions in the sorbent phase, the initial solution, and the equilibrium solution, respectively. The symbols *V* and *m* designate the volume of solution in dm³ and mass in g, respectively.

2.3. X-ray diffraction data

The samples for X-ray powder diffraction analysis were obtained by shaking 0.1 g Na-bentonite with 100 cm³ of a mixture of UO₂(CH₃COO)₂·2H₂O and Na₂HPO₄·7H₂O at their constant sum concentration of 0.002 mol/L and a variable [U(VI)]/[P(V)] molar ratio of 0.4-18. After 6 h, the mixture was centrifuged, and the solid residue was dried in the air.

The XRD spectra were registered using the Empyrean apparatus (Panalytical Co.) with CuKα radiation (λ = 1.54178 Å) obtained using a focusing mirror and generated by a Cu anode device operating at 40 kV and 40 mA in conjunction with a one-dimensional line positional detector. The ICDD diffraction database was used for the identification of peaks in the spectrum.

2.4. X-ray photoelectron spectroscopy data

The samples for the analysis of X-ray photoelectron spectroscopy spectra were prepared by shaking 1.5 g of Na-bentonite with 100 cm³ of a 0.002 mol/L UO₂(CH₃COO)₂·2H₂O solution or with a mixture of 0.002 mol/L of UO₂(CH₃COO)₂ and Na₂HPO₄·7H₂O (0.002 mol/L) at pH = 4 or 7 (symbols of samples: U4, UP4, U7, UP7). After 6 h, the mixtures were centrifuged, and the solid residue was dried in the air. The same procedure was applied for the samples with different proportions of U(VI) and P(V) in the initial solution. The

concentration of U(VI) was 0.002 mol/L, whereas the concentration of P(V) changed according to the series 0.0002, 0.001, 0.002, 0.005 mol/L. The symbols of the respective samples were: UP0.0002, UP0.001, UP0.002, and UP0.005.

The U4f XPS spectra were recorded on an ESCA apparatus with a multidetection electron analyzer Scienta R4000 (produced by VG Scienta) in the fixed analyzer transmission mode. An unmonochromatized AlKα source (1253.6 eV) with a voltage of 12 kV and an emission current of 30 mA was employed. Powdered samples were placed on a molybdenum sample holder and submitted to a vacuum of 5 × 10⁻⁹ mbar. The U4f spectra were fitted, using CASA XPS software, with a Gaussian-Lorentzian peak shape after subtraction of the background with a Shirley baseline; the uranium 4f spin-orbit coupling was maintained at 10.8 eV, and the component ratio (U4f5/2)/(U4f7/2) was constrained to 0.75. The typical error associated with binding energies was +/- 0.3 eV.

3. Results and discussion

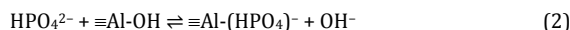
3.1. Sorption isotherms

Sorption isotherms of U(VI) and P(V) ions on bentonite in the presence of phosphate are given in Figure 1. There is an evident improvement in U(VI) and P(V) sorption in the bi-component system compared with the mono-component systems. It seems, however, that P(V) peaks refer to the similar complexes independent of the pH. Their position is located at initial solution *c₀* = 0.0005 mol/L. The U(VI) peak has changed its position from *c₀* = 0.0006 to 0.0008 mol/L. The enhancement of the U(VI) peak (when the bi-component system is compared with the mono-component ones) is easily recognizable for pH = 4.7 and is significantly weakened for pH = 6.6.

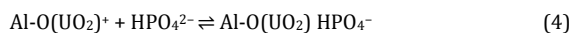
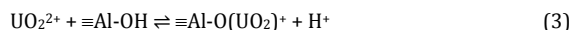
The positions of the maxima of U(VI) and P(V) sorption are shown in Figure 2. At pH = 4.7, the sorption maximum for U(VI) appears at the molar ratio of U(VI)/P(V) = 1.4, whereas for pH = 5.4 and 6.6 at the molar ratios of 3.3 and 3.6, respectively. It is interesting that the peaks related to P(V) sorption appear at U(VI)/P(V) = 1.2, 1.2, 1.7 for pH = 4.7, 5.4 and 6.6, respectively. It is rather certain that at least two different complexes are present in the sorbent phase, i.e. ones with a higher and ones with a lower content of U(VI) ions.

The formation of (UO₂)₃(OH)₅⁺ and (UO₂)₄(OH)₇⁺ is well-documented [16]. They can locate on silanols ≡Si-OH or aluminols ≡Al-OH. The role of phosphate ions in the whole complexation scenario is, however, problematic. The precipitation of (UO₂)₃(PO₄)₂·4H₂O in the bentonite interlayer space results in a sorption maximum at [U(VI)]/[P(V)]_s = 1.4.

Some kind of interaction of (UO₂)₃(OH)₅⁺ and (UO₂)₄(OH)₇⁺ cations, present in the equilibrium aqueous phase (Figure 3), with HPO₄²⁻ ions and at the same time with silanols or aluminols would lead to the appearance of surface complexes with U(VI)/P(V)_s = 3.3 and 3.6. Phosphate ions probably play a bridging role between oligomeric uranyl hydroxy complexes. The whole complexation process is, however, more complicated. It is rather certain that phosphate ions sorb on the surface of bentonite via an exchange reaction [11]:



As a consequence, uranyl ions would locate on the aluminum-phosphate complex, forming Al-(HPO₄)UO₂⁺ species at a molar ratio of U(VI)/P(V) = 1, which may explain the position of the observed peaks of P(V) sorption for pH = 4.7 and 5.4 at [U(VI)]/[P(V)]_s = 1.2. An alternative complexation reaction involves the sorption of uranyl ions on aluminols with subsequent coordination of phosphate ions:



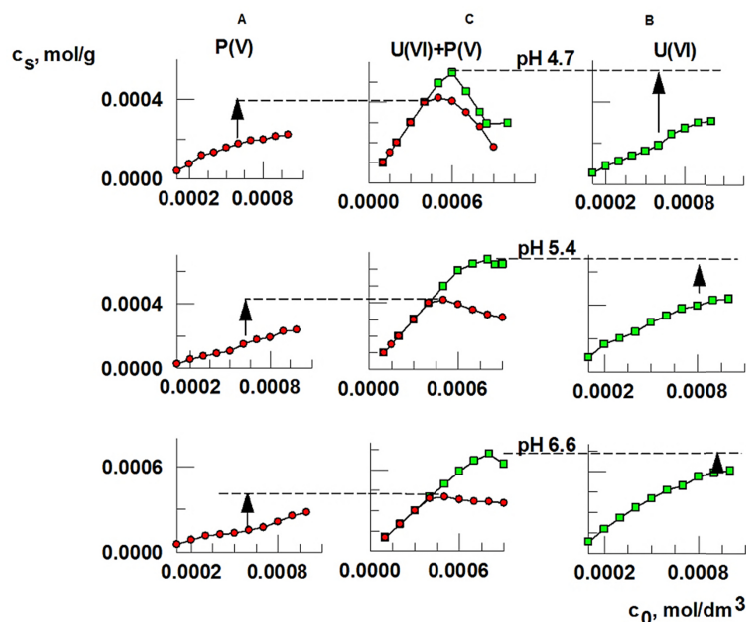


Figure 1. The sorption isotherms of U(VI) ions on bentonite in the presence of phosphate ions (A - a monocomponent system, U(VI) alone; B - a monocomponent system, P(V) alone; C - a bicomponent system, U(VI) + P(V)); In all systems, 0.1 mol/L acetate buffer was used at pH = 4.7, 5.4 and 0.05 mol/L CH_3COONa was used at pH 6.6; c_s - concentration of U(VI) and P(V) in the sorbent phase, c_0 - initial concentration of U(VI) and P(V) in the aqueous phase).

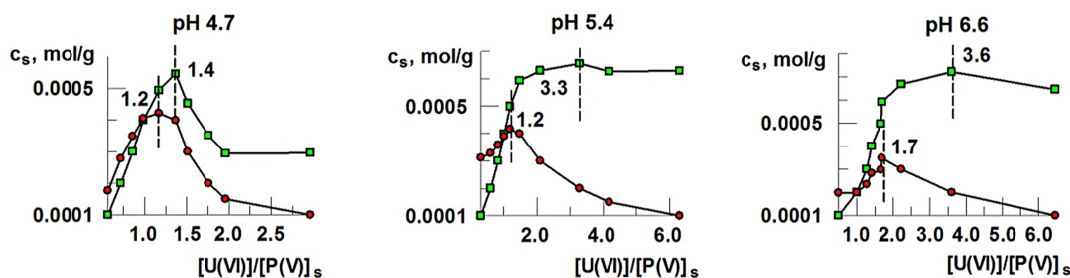


Figure 2. Sorption of U(VI) and P(V) ions vs. molar ratio $[\text{U(VI)}]/[\text{P(V)}]_s$ in the sorbent phase.

The location of the uranyl phosphate complex on surface silanols $\equiv\text{Si-OH}$ is rather minimized, since the exchange reaction (2), is preferred for aluminols owing to the higher basicity of aluminols compared to silanols.

In turn, the lack of U(VI) distinct sorption enhancement at pH = 6.6 (when the bicomponent mixture is compared to the monocomponent ones) provides evidence for the coexistence of some kind of U(VI)-phosphate complexes with U(VI) surface species which do not contain phosphates. A more detailed analysis of the U(VI) sorption isotherms is given in Figure 4.

The sorption peaks of U(VI) were deconvoluted using Peak Fit Programme (AISN Software Inc., Version v4), based on the well-known second derivative method and the Gaussian procedure [17], which is very often applied in spectroscopy for characterization of different spectra. The general assumption of the method is based on the distribution of the absorption bands around discrete energies. The probability of an absorption band is randomly distributed in energy, and an absorption band can be modelled with a Gaussian distribution, where the random variable is energy. According to the method presented in this work, a crude approximation can be made about the probability of U(VI) sorption being randomly distributed in the $[\text{U(VI)}]/[\text{P(V)}]_s$ ratio, which allows U(VI)

sorption peaks to be modelled with a Gaussian distribution using the following relationship:

$$c_s = a_0 \times \exp[-1/2 \times (([\text{U(VI)}]/[\text{P(V)}]_s - a_1)/a_2)^2] \quad (5)$$

where a_0 , amplitude; a_1 , center; a_2 , width (standard deviation).

In other words, the maxima on the sorption isotherm correspond to specific $[\text{U(VI)}]/[\text{P(V)}]_s$ values characteristic of U(VI) surface complexes. For this reason, the term sorption spectra can be used without exaggeration. Three peaks can be observed in the U(VI) sorption spectra for the stoichiometries 0.89, 1.31 and 1.85 at pH = 4.7. Only two peaks referring to the stoichiometries 1.61, 3.83; 1.93 and 3.5 are visible at pH = 5.4 and 6.6, respectively. For this reason it can be concluded that the equilibria defined by equations (2-4) exist unequivocally only at pH = 4.7. For all the pHs, the precipitation of uranyl phosphate and the participation of $(\text{UO}_2)_3(\text{OH})_5^+$ and $(\text{UO}_2)_4(\text{OH})_7^+$ oligomeric species in the formation of surface complexes with phosphate ions is unquestionable. The fractional numbers characterizing the stoichiometries correspond to the occurrence of different surface complexes, for example, the stoichiometry 1.3 relates to the predominance of a mixture of 1 and 2 stoichiometry's.

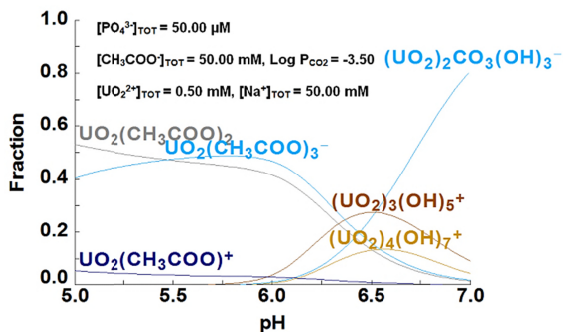


Figure 3. Molar fractions of different U(VI) complexes in the aqueous phase (based on Medusa software [16]; species formed in the sorbent phase are excluded from calculation; TOT- overall concentration of species in the aqueous phase, pCO₂- partial pressure of CO₂ in air).

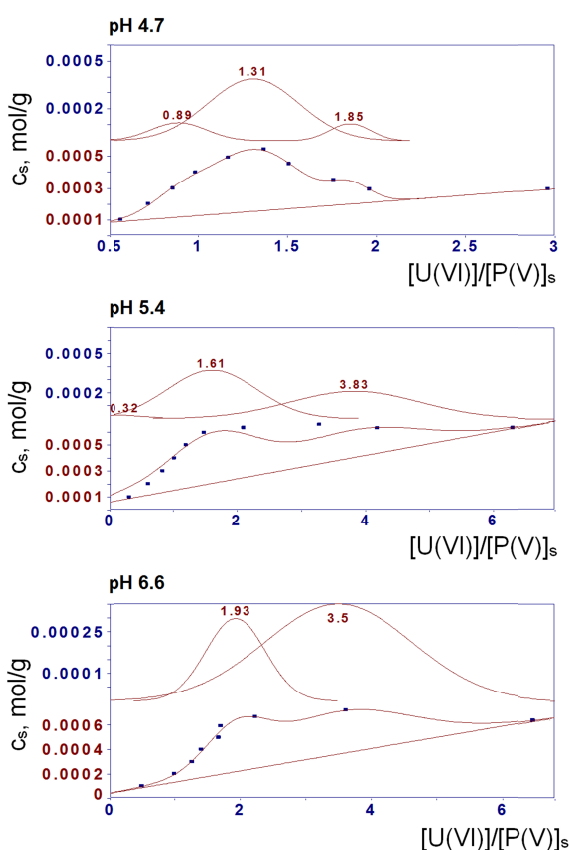


Figure 4. Sorption spectra of U(VI) at different pH values (top- results of the deconvolution, bottom- the best fit of *c_s* with the experimental points).

Finally, it is worth examining how U(VI) sorption intensifies for different pH values when the bicomponent system is compared with the monocomponent ones (Figure 5). The value of intensification *I* was evaluated according to the relationship:

$$I = \frac{c_s}{c_{s(m)}} \quad (5)$$

where *c_s* and *c_{s(m)}* refer to the sorption of U(VI) in the system with phosphates and without phosphates, respectively, obtained for the same initial concentration of U(VI). Two peaks were found in the band of dependence: *I* vs. [U(VI)]/[P(V)]_s, for

[U(VI)]/[P(V)]_s = 1.04 and 1.29, respectively, at pH = 4.7. This leads to the conclusion that at this pH the affinity of the UO₂HPO₄ complex for bentonite was the highest when compared with the other forms of U(VI) complexes. At pH = 5.4, three peaks were observed at [U(VI)]/[P(V)]_s = 0.97, 1.54, 2.82; this means that, at this acidity, the precipitation of (UO₂)₃(PO₄)₂·4H₂O in the bentonite phase and the formation of higher complexes with the participation of (UO₂)₃(OH)₅⁺ and (UO₂)₄(OH)₇⁺ species prevailed among over the other mechanisms of U(VI) ion transfer from the aqueous to the sorbent phase. At pH = 6.6, U(VI) sorption was intensified for [U(VI)]/[P(V)]_s = 1.83, 2.91, which provides evidence for the further shift of the surface complexation equilibria in the direction of common sorption of (UO₂)₃(OH)₅⁺, (UO₂)₄(OH)₇⁺ and HPO₄²⁻ ions on the surface of bentonite.

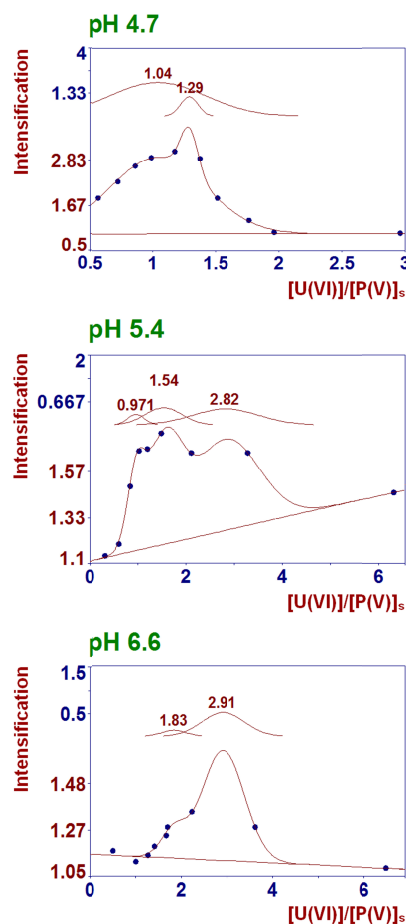


Figure 5. Intensification of U(VI) sorption on bentonite under the influence of phosphates (top- results of the deconvolution, bottom- the best fit of *I* with the experimental points).

3.2. X-ray diffraction spectra

The XRD spectra of the bentonite samples loaded with U(VI) ions and phosphates are given in Figure 6 and 7. In the vicinity of bentonite peak appears a distinct peak referring to a phosphate complex of U(VI) at 2θ = 9.9°, originating, most probably, from precipitated uranyl phosphate; this peak disappears at [U(VI)]/[P(V)]_s = 4 and 9 for pH = 5.4 and 4.7, respectively. Apart from that, a group of peaks in the range of 2θ = 12-28°, is visible for the molar ratios [U(VI)]/[P(V)]_s from 0.25 to 1.50, which also originate from the precipitated (UO₂)₃(PO₄)₂·4H₂O.

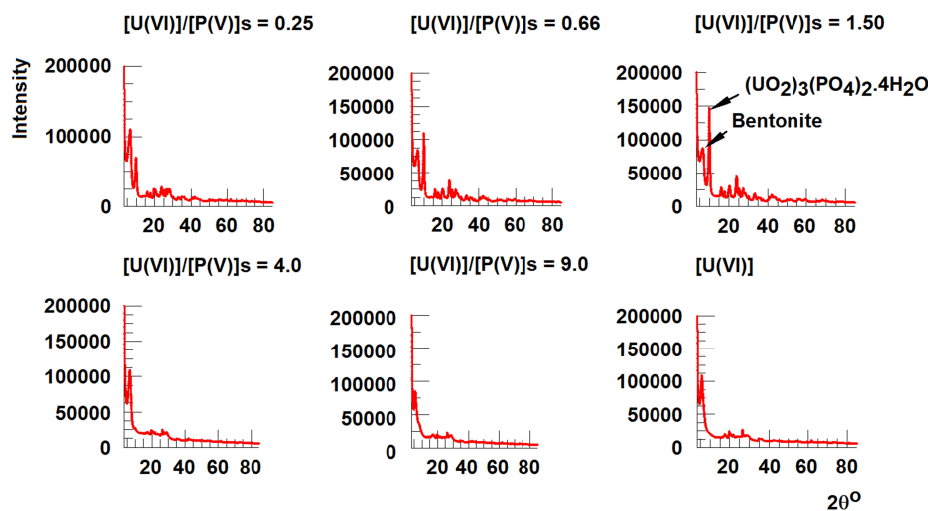


Figure 6. XRD spectra of bentonite loaded with U(VI) + P(V) mixture (pH = 4.7; the numbers denote the molar ratio $[U(VI)]/[P(V)]_s$).

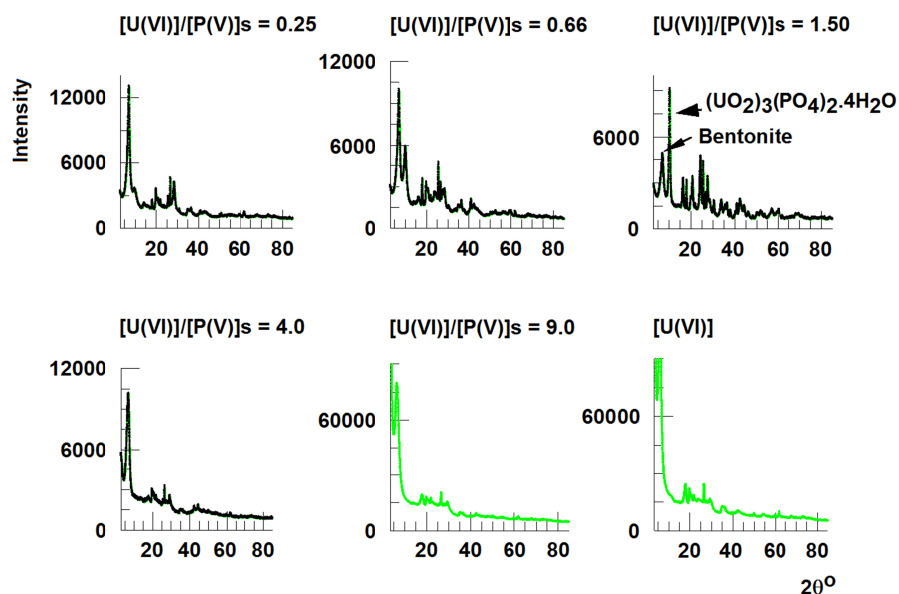


Figure 7. XRD spectra of bentonite loaded with U(VI) + P(V) mixture (pH = 5.4; the numbers denote the molar ratio $[U(VI)]/[P(V)]_s$).

It is interesting that no uranyl phosphate precipitation is observed for the samples with higher $[U(VI)]/[P(V)]_s$ molar ratios, which is in disagreement with solubility rules. It is worth inspecting the molar fractions of the different species formed in the U(VI) + P(V) mixture for the system with no sorbent phase (Figure 8). One can observe that for the high excess of U(VI) ions, precipitation of uranyl phosphate is evident in the whole pH range, jointly with $UO_2(OH)_2 \cdot 2H_2O$.

The observations made in the sorption experiment may result from the fact that, thermodynamically, the formation of some kind of U(VI) surface complex is more favorable than the precipitation of uranyl phosphate.

3.3. X-ray photoelectron spectra

When the pH was kept at 4 or 7, the corresponding U4f5/2, U4f7/2 XPS spectra (Figure 9 and 10) were fitted with two components [18]. The experiment was repeated with the

different combinations of U(VI) and P(V) concentrations. The positions of the particular peaks are given in Table 1.

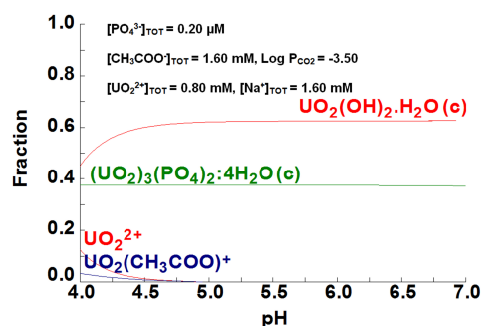
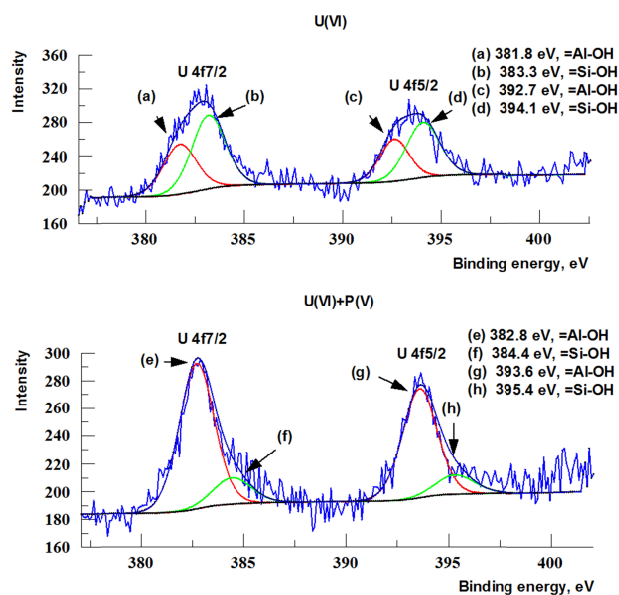
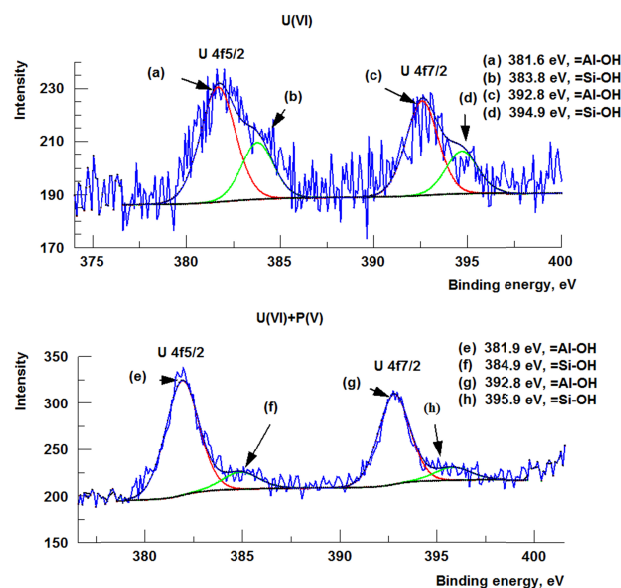


Figure 8. Molar fractions of species formed in the U(VI) + P(V) mixture for the system with no sorbent (calculations based on Medusa freeware [16]).

Table 1. Peak positions (in eV) and areas (in %) in the XPS spectra of U-loaded bentonite samples (symbol. pH_{eq} denotes the equilibrium pH of aqueous phase during loading of bentonite with U(VI) and P(V)).

Sample	=Al-OH	Unrecognized peak	=Si-OH	pH_{eq}
U4	381.8; 40.2%		383.3; 59.8%	5.13
U P4	382.8; 83.6%	384.4; 16.4%		5.34
U 7	381.6; 68.0%		383.8; 32.0%	7.83
UP7	381.9; 85.9%	384.9; 14.1%		7.88
UP0.0002	381.5; 78.9%	384.9; 21.1%		6.36
UP0.001	381.1; 71.8%	384.4; 28.2%		7.38
UP0.002	381.7; 74.5%	384.5; 25.5%		7.74
UP0.005	380.5; 68.9%		383.4; 31.1%	7.81

**Figure 9.** XPS spectra of bentonite loaded with U(VI) and U(VI) + P(V) mixture at pH = 4.**Figure 10.** XPS spectra of bentonite loaded with U(VI) and U(VI) + P(V) mixture at pH = 7.

Introduction of phosphate to the sorption system results in an enlargement of the peaks: 381.8, 381.6 eV, probably corresponding with a U(VI) phosphate complexes sorbed on aluminol sites and decrease of the peaks: 383.3, 383.8 eV as a result of minor role of silanol sites in phosphates

immobilization. This may be a response to the formation of a UO_2HPO_4 complex or a result of some kind of interaction of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ species with surface groups. The 4f-orbital binding energy of 382.7 eV, found for the sample obtained at pH = 4 (symbol UP4), corresponds strictly with the value 382.9

eV observed by Drot *et al.* for U(VI) sorbed on thorium diphosphate/phosphate [19].

The peaks referring to binding energies higher than 384 eV have not been recognized. We can only presume that they relate to U-O bonds in triuranium heptaoxide U₃O₇ [20]. In turn, the peak 380.5 eV in the sample with an excess of phosphates, referring to pH = 7.81, can be identified as an uranyl polyhydroxo complex (UO₂)_x(OH)_y^{2x-y} sorbed on surface aluminols [21].

4. Conclusions

The experimental results obtained in this study lead to the following conclusions:

1. The continuous variation method can serve as a preliminary test for the evaluation of the stoichiometry of U(VI)-P(V) surface complexes. The approximate character of the method is evident for pH = 6.6, when the free U(VI) hydroxy complexes are anchored on the sorbent surface parallel to the uranyl phosphate complexes. This difficulty can be eliminated by analyzing the intensification I of U(VI) sorption when the system with phosphates is compared with that without phosphates. The interaction of (UO₂)₃(OH)₅⁺ and (UO₂)₄(OH)₇⁺ species with HPO₄²⁻ ions is evident.
2. Phosphate anions evidently improve the sorption of U(VI) ions on bentonite owing to the formation of ternary complexes among aluminol sites, U(VI) and phosphate anions HPO₄²⁻. This fact can be exploited in the construction of engineering barriers used for the isolation of nuclear waste repository sites from the natural environment [22,23]. The stoichiometries of these complexes, i.e. their U(VI)/P(V)_s molar ratios, are 1.2, 1.4; 1.2, 3.3; 1.7, 3.6 for pH = 4.7, 5.4 and 6.6, respectively. Deconvolution of the sorptive spectra of U(VI) results in the presumption about the stepwise evolution of the surface complexes formation with pH, where UO₂HPO₄, (UO₂)₃(PO₄)₂·4H₂O, (UO₂)₃(OH)₅⁺, (UO₂)₄(OH)₇⁺ species interact with the surface sites of bentonite.
3. X-ray photoelectron spectroscopy allows one to diagnose the participation of silanol and aluminol groups in the complexation of U(VI) ions in the absence and presence of phosphates.
4. X-ray diffraction data confirm the precipitation of (UO₂)₃(PO₄)₂·4H₂O in the interlayer space of bentonite.

Acknowledgements

The research was carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the Operational Program Development of Eastern Poland 2007-2013 (Contract No. POPW 01.03.00-06-009/11-00), equipping the laboratories of Biology and Biotechnology, Mathematics, Physics and Informatics, and Chemistry for studies of biologically active substances and environmental samples.

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