Synthesis of mesoporous silica-tethered phosphonic acid sorbents for uranium species from aqueous solutions

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Abstract

One-pot synthesis of highly ordered SBA-15 type silica-tethered phosphonic acid at weakly acidic pH (3.75) allows for higher loading of phosphonic functionality (up to 33%) without significant deterioration of the mesostructure. In this synthesis sodium metasilicate was used instead of tetraethylorthosilicate. The resulting samples featured high specific surface areas (362-533 m²/g) and well developed mesoporosity. The hexagonal structure and high concentration of phosphonic acid groups (1.0-3.0 mmol/g) in the synthesized samples were established by XRD, TEM, EDS and elemental analysis methods. Since inexpensive sodium metasilicate was used as a source of silica, these materials can be of interest for large scale applications. Experimental studies of the synthesized materials showed that they are effective for extraction of trace uranium species under weak basic conditions (pH 8.3), which are relevant for practical use such as uranium extraction from seawater.

Keywords: Mesoporous silica, block copolymer templating, phosphonic acid-modified silica, uranium recovery from seawater

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1. Introduction

The formation of functionalized ordered mesostructures that provide a quick access of the sorption centers to metal ions is of great importance from practical point of view. However, this process is complicated in the case of sorbents with high loading of complexing groups. Mann and co-authors showed [1,2] that the preservation of the spatial ordering in mesoporous materials is possible when the synthesis gel possesses less than 20% (molar) of the organosilane used for introducing the desired organic functionality. Moreover, the removal of template by extraction from the ordered mesophase leads occasionally to the structural deterioration; note that in this case alkylammonium surfactants under alkaline conditions were used. It is known that the synthesis under alkaline conditions leads to mesoporous structures with relatively thin pore walls that reduce their mechanical stability. The use of block copolymer templates such as Pluronic P123 instead of alkylammonium surfactants allows for the synthesis of mesoporous structures with relatively thick pore walls, which enhance the hydrothermal and mechanical stability of the resulting mesostructures [3,4]. Similarly as alkylammonium surfactants, the block copolymers can form different types of mesostructures depending on the experimental conditions. Specifically, the self-assembly of silica species in the presence of block copolymer P123 under acidic conditions usually leads to the formation of hexagonally ordered mesostructures [3-6]. At low pH, the protonated poly(ethylene oxide) segments of P123 and silica species are attracted through weak electrostatic interactions mediated by the negatively charged chloride ions; the presence of silica species induces the formation of cylindrical aggregates at concentrations below the critical micelle concentration [7].

The use of tetraethoxysilane (TEOS) together with trifunctional silanes $(\text{RO})_3\text{SiR}'$ having a functional group (R') in the initial reaction medium permits one-step attachment of R' groups on the surface of pore walls. However, the incorporation of a high concentration of these functional groups leads to the formation of a bimodal structure, and ultimately also to irregular (amorphous) structure [8,9]. In this case mesopores with small diameters are formed (for example, pore width = 3.5 nm [8]), which is not typical for block copolymer-templated materials such as SBA-15. Moreover, the concentration of functional groups in these samples was in the range of 0.5 mmol/g (ordered mesostructure) - 1.00 mmol/g (disordered mesostructure) [9]. It should be noted that the one-pot synthesis was carried out in strong acidic media so not all complexing groups like amines could be incorporated under such conditions. In addition, alkoxysilanes are expensive reagents. So there is a question: is it possible to replace the aforementioned expensive precursors with cheaper ones such as sodium silicate. The price of the final sorbent is an important factor for its large-scale

applications. Note that the replacement of hydrochloric acid with other catalysts or adjustment of the reaction medium pH in the range of 3-5 could cause the formation of materials with disordered porosity [10-13]. According Brinker [14] and Hook [15] the rate of hydrolysis of TEOS at pH below 4 is higher than the rate of its polymerization. Thus, an increase in pH speeds up the polymerization and slows down TEOS hydrolysis. So, the hydrolyzed silicate species gather around the micelles, which lead to the formation of wormlike structures. Thus, nanofoam-type materials are formed at pH = 5 and higher [10]. Earlier Imai et al. also showed that the change in pH can cause the transformation of these structures [16].

It is known that phosphonic acid groups form stable complexes with lanthanides and actinides. Therefore, materials with phosphonic acid functionality are widely used for extraction and separation of lanthanides and actinides. [17-27]. There are many reports on the sorption of uranium species from aqueous phases by phosphorus-containing sorbents. After analysis these reports one can note that a wide range complexing groups on the surfaces of different nature has been used. This is especially true for phosphonic or phosphoric acids functionalites; for instance, organosilicas functionalized with phosphorus-containing alkoxysilanes [19,21,25,26], polystyrene resin with ethylenediamine-tris(metylenphosphonic) acid [23], chitosan - tripolyphosphate [24], silica functionalized with orthophosphoric acid [27] and so on. However, there is difficult to find material, which would be effective and prepared in a simple way using inexpensive precursors.

In this work we report the block copolymer-templated synthesis of mesoporous organosilica from inexpensive sodium metasilicate under weak acid conditions (acetic acid). Diethylphosphatoethyltriethoxysilane (DPTS) was chosen for incorporation of P-containing functional groups, because its hydrolysis in acidic medium causes the formation of P-containing oligomers $[\equiv\text{Si}(\text{CH}_2)_2\text{P}(\text{O})(\text{OH})_2]_n$ [28]. The amount of DPTS in the synthesis gel was varied to study its effect on the porosity and mesostructural ordering. These materials were examined as potential sorbents for recovery of uranium from seawater.

2. Experimental

2.1. Chemicals

Sodium metasilicate, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (Sigma, USA); diethylphosphatoethyltriethoxysilane, $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$ (DPTS, 95%, Gelest, USA); poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) Pluronic P123 block copolymer, $(\text{EO}_{20}\text{RO}_{70}\text{EO}_{20})$, 99%, BASF, USA); concentrated acetic acid, CH_3COOH (99.7%, Aldrich, USA); ethanol (absolute); uranyl nitrate $(\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$, Aldrich, USA); sodium

chloride (NaCl, Aldrich, USA); and sodium bicarbonate (NaHCO₃ Aldrich, USA) were used as received in the synthesis and testing of P-containing mesoporous silica materials.

2.2. Preparation of P-containing mesoporous silica samples

Sample 1 was obtained by using the Na₂SiO₃·9H₂O/DPTS molar ratio = 10:1. 0.25 cm³ of DPTS was pre-hydrolyzed in 7.36 cm³ of concentrated acetic acid at 80°C for 6 hours using reflux condenser and oil bath; next the mixture was cooled down to room temperature. The solution of template (0.8 g of Pluronic P123 block copolymer in 13 cm³ of water) was added to the solution of DPTS. Separately, 2.276 g (0.008 M) of sodium silicate was dissolved in 10 cm³ of water, and added to the reaction mixture. Next, the resulting suspension was left on oil bath for 1 h at 40°C. Finally, the mixture was paced in microwave for 2 h at 40°C with magnetic stirring on and switched to 10 h at 100°C without stirring. The resulting precipitate was filtered and air-dried for a day. Polymeric template was removed by boiling twice the sample in acidified ethanol (30 cm³ per 1 g of mesophase) under stirring for 12 hours. The final sample was filtered, dried under vacuum at 50°C for 3 days.

Note that the above recipe is analogous to that reported in [29]; the difference is in the acidic conditions used. The samples synthesized in this work were prepared at lower pH (acetic acid) instead of HCl, which was used in [29].

Analogous samples were obtained by the same procedure using the following Na₂SiO₃·9H₂O/DPTS molar ratios: 10:2 (sample 2), 10:3 (sample 3), and 10:4 (sample 4).

2.3 Measurements

The small angle XRD patterns were recorded over a range of $0.50 < 2\theta/^{\circ} < 2.5$ on a PANanalytical. Inc. X'Pert Pro (MPD) MultiPurpose Diffractometer with Cu_{Kα} radiation (0.1540 nm) using an operating voltage of 40 kV and 40 mA, 20s step time and 0.01 step size. Microscope glass slides were used as sample supports. All materials were manually ground prior to the XRD analysis and the measurements were performed at room temperature.

For morphology investigation and elemental composition determination, a FEI Tecnai G2 F20 transmission electron microscope (TEM) supplied with an EDS detector was used. Samples for TEM analysis were dispersed in ethanol by ultrasonication at a moderate concentration (~5 wt. %). A Lacy carbon coated, 200-mesh, copper TEM grid was dipped into the sample suspension and then dried under vacuum at 60°C for 3 h prior to analysis. The EDS spectra were collected at 30% of detector dead-time and 3 min acquisition times.

SEM photomicrographs taken by scanning electron microscope JSM-6060 LV (JEOL, Japan).

Elemental analysis of the samples for C, P, H was performed in the certified IOC Laboratory of National Academy of Science (Ukraine). The accuracy was $\pm 0.2\%$. Thermogravimetric (TG) analysis was performed on a TA Instruments TGA 2950 analyzer with $10^\circ\text{C min}^{-1}$ heating rate.

IR reflectance spectra in the region $4000\text{--}400\text{ cm}^{-1}$ were recorded under ambient conditions on a spectrometer Thermo Nicolet Nexus FTIR with diffuse reflection using the prefix "SMART Collector" with a resolution of 8 cm^{-1} . Samples were mixed with KBr (Aldrich) in a ratio of 1:20. Prior IR measurements the samples were dried under vacuum.

Textural properties of the synthesized samples were evaluated from the nitrogen adsorption-desorption isotherms obtained with ASAP 2010 volumetric analyzers manufactured by Micrometrics, Inc. (Norcross, GA). Adsorption isotherms were measured at -196°C in the interval of relative pressures from 10^{-6} to 0.995 using ultra high purity nitrogen from Praxair Distribution Company (Danbury, CT, USA). Before analysis, samples were degassed under vacuum in the port of the adsorption instrument for 2 h at 110°C until the residual pressure dropped to 6 or less μmHg . The Brunauer–Emmett–Teller (BET) [30] surface area was evaluated using adsorption data in the range of 0.05–0.2 p/p_0 , whereas the single-point total pore volume was estimated at 0.98 p/p_0 [31]. Pore-size distributions together with the maximum pore diameters (d_m) were determined by Kruk–Jaroniec–Sayari (KJS) method [32] based on the Barrett–Joyner–Halenda (BJH) algorithm [33].

2.4. Uranium sorption experiments

Uranium sorption experiments were conducted analogously as in [34] using simulated seawater prepared by dissolving 17 mg of uranyl nitrate ($[\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$), 25.6 g of sodium chloride (NaCl) and 193 mg of sodium bicarbonate (NaHCO_3) in 1 L of DI water. Next, 50 mg of the silica-based sorbent was shaken in 50 mL of the uranium containing solution for 24 hrs, followed by filtration. The quantification of the remaining uranium in solution was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis.

3. Results and discussion

The geometry of mesopores for block copolymer-templated silica samples is primarily determined by the structure of micelles in solution and synthesis conditions (chemical properties of the template, composition of synthesis gel, aging conditions, etc.) [35–38].

Pluronic P123 forms rod-like micelles under acidic conditions [1], the surface of which attracts the products of hydrolysis of TEOS and trifunctional silanes that condense during hydrothermal treatment to form a solid mesostructure. The self-assembly synthesis was carried out under weak acidic conditions (acetic acid; pH = 3.75); at this pH a wormlike mesostructure is formed by P123 block copolymer [10, 39].

The small angle XRD patterns of the synthesized powder-like products are shown in Fig. 1. As can be seen from this figure all of them except sample 1, which has the smallest concentration of functional groups, exhibit a single reflection at 0.8-0.85 $2\theta^\circ$, typical for wormlike mesostructures with uniform pores or weakly ordered mesostructures [1,36,37].

Fig. 1. Powder X-ray diffraction patterns of phosphonic acid-functionalized SBA-15-type mesoporous silicas prepared by using different $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ /DPTS molar ratios: 10:1 (sample 1), 10:2 (sample 2), 10:3 (sample 3), and 10:4 (sample 4).

The XRD pattern of the extracted sample **1** contains three well-defined reflections at 2θ (100) – 0.8° , (110) – 1.4° and (200) – 1.6° , corresponding to the hexagonal structure and indicates well-ordered derived material. This pattern is typical for mesoporous materials SBA-15 type ($p6m$ symmetry group). The spatial ordering of mesoporous silica decreases with increasing DPTS concentration in the reaction solution. Thus, the X-ray diffraction patterns of the samples **2-3** have no reflections indexed as (110) and (200); the sample **2** features only a low-intensity shoulder in the range of $1.4 - 1.6$ $2\theta/^\circ$. A relative intensity of the main reflection (100) gradually decreases from the sample **1** to **2**, **3**, and **4** with increasing DPTS amount used in the synthesis (Fig. 1).

Data obtained by X-ray diffraction analysis have been confirmed by TEM analysis. So, the TEM image of the sample **1** (Fig. 2a) clearly indicates the presence of hexagonal ordering of mesopores. Some elements of hexagonal system are also visible on the image of the sample **2** (Fig. 2b).

The distances between the centers of the pores for the samples **1** and **2** represent 8.7 and 10.5 nm, respectively. However, the further increase in the concentration DPTS contained in the synthesis gel causes a significant deterioration of the mesostructural ordering. Thus, only some ordered domains can be found on the TEM images of the sample **3** (Fig. 2c), but the TEM images of the sample **4** do not show ordered domains (Fig. 2d).

Fig. 2. TEM images of the samples **1** (a), **2** (b), **3** (c) and **4** (d), obtained by TEM and EDS diagram (e) for the sample **2** from one point of its surface.

Previous reports [1, 2] on the synthesis of ordered organosilica mesostructures show that it is extremely difficult to preserve the mesostructural ordering for the synthesis gels containing over 20-25% of organosilane with a hanging organic group, especially larger one. Note that the content of DPTS in the mixture used for synthesis of the sample **3** is about 33%. It is noteworthy that a previous study [10] of the pH effect on the mesostructure formation in the presence of P123 shows that at pH 3.6 the MSU-3 type mesostructure (sample S12 in [10]) was confirmed by TEM and XRD analysis. It should be mentioned that the samples **1-4** were synthesized at similar pH but the MSU-3 type structures were not observed.

The EDS analysis of mesoporous functionalized silica (sample 2) reveals the presence of silicon and phosphorus (see Fig. 2e). Since the concentration of functional groups is not very high, then the signal intensity of phosphorus is low. The presence of the phosphorus-containing functionality in the samples studied was additionally confirmed by elemental analysis (see Table 1).

Table 1. Data of elemental analysis for the synthesized samples.

Sam ple	%C	%H	%P	%Si	Si/P	c_m mmol/g	c_s mmol/m ²	c group/nm ²
1	6.9	3.0	3.0	30.3	11.2 (11.0)	1.0 (1.3)	0.0024	1.4
2	10.5	4.4	5.5	27.2	5.5 (6.0)	1.9 (2.0)	0.0036	2.1
3	14.6	4.4	7.5	24.8	3.7 (4.3)	2.6 (2.8)	0.0050	3.0
4	17.0	4.9	8.4	21.0	2.6 (3.5)	3.0 (3.1)	0.0083	5.0

Notes: the values listed in the last three columns represent concentrations of phosphonic groups expressed in mmol/g (c_m), mmol/m² (c_s) and group/nm² (c); these values were calculated by using elemental analysis data for phosphorus (atomic %P); values in parentheses were calculated on the basis of the synthesis gel composition.

The percentage of phosphorus in the samples obtained by elemental analysis was used to calculate the concentration of phosphorus-containing groups (see the values listed in the last three columns of Table 1). The concentration of these groups increases in the following order: from sample **1** to sample **4**, i.e., with increasing DPTS amount in the synthesis gel. This increase is expected due to the decrease in the value of Na₂SiO₃/DPTS. The values of the ligand concentration calculated on the basis of %P (by elemental analysis) are not significantly different from those obtained on the basis of the synthesis gel composition (see Table 1).

According to data of elemental analysis the weight loss (the percentage of organic component in the samples **1-4**) was calculated. Based on the content of elements in the samples the weight loss data are: ~19.3 % for the sample **1**, 21.7 % - sample **2**, 30.2 % - sample **3**, and 37.2 % - sample **4**. Clearly the trend of the increasing weight loss in relation to the synthesis gel composition is observed. A little bit larger weight loss as compared to the expected one can be explained by the presence non-hydrolyzed ethoxy groups, and in the case of the sample **1** by the presence of carboxyl groups in the structure due to some entrapment of acetic acid in the structure (see IR below).

The SEM images of the synthesized samples are shown in Fig. 3. The morphology of these samples is not typical for typical SBA -15 type materials. The majority of particles are irregular and their size is less than 10 microns. The primary structure consists of irregular disc-type particles of 1-2 μm as in the case of sample **1** as shown in Fig. 3a.

Fig. 3. SEM images of the samples studied **1** (a), **2** (b), **3** (c, e) and **4** (d, f)

These discs are packed into agglomerates and form a secondary structure. In the case of the sample **2** the particles of spherical shape slightly larger (Fig. 3b) are mainly observed. Samples **3** and **4** (Fig. 3c, d) after magnification show agglomerated objects (Fig. 3e, f) composed of smaller primary particles. Thus, an increase in the DPTS amount in the reaction mixture affects significantly the morphology of the synthesized samples. As compared to the morphology of the samples with similar composition, obtained in the presence of hydrochloric acid instead of acetic acid [29], one can argue that the acidity of the medium

have a significant effect on the morphology of these materials. Therefore, even in the case of microwave-assisted synthesis the agglomeration of primary particles into a solid structure is not prevented.

Chemical identification of the surface layer of the synthesized materials was carried out by IR spectroscopy. Shown in Figure 4 are the IR spectra of the samples studied. The intensive absorption band at $1060\text{--}1193\text{ cm}^{-1}$ can be assigned to $\nu_{\text{as}}(\text{Si-O-Si})$ of polysiloxane skeleton [40,41], which is displayed at high frequencies as a shoulder. Indeed, an intensive shoulder in this band is visible for the samples **1-3**, which in the case of the sample **4** (with the highest concentration of functional groups) becomes an individual band at 1207 cm^{-1} (see Fig. 4).

Fig. 4. IR spectra of the samples studied.

This shoulder certainly refers to the absorption band $\nu(\text{P=O})$ of the P-containing groups that is present at 1241 cm^{-1} on the spectrum of initial DPTS. It is shifted to low frequencies by about 35 cm^{-1} (Fig. 4a-d) indicating the participation of P=O groups in hydrogen bonds [40]. This hydrogen bond can be formed by water molecules, as indicated on the IR spectra of all samples at $\sim 1630\text{ cm}^{-1}$ by absorption band characteristic for the deformation vibrations of H_2O , and above 3000 cm^{-1} by a broad and intense absorption band due to stretching vibrations of OH groups of water molecules. However, in the spectrum of the sample **1**, except for the absorption band at 1641 cm^{-1} , there is an absorption band of medium intensity

at 1723 cm^{-1} (Fig. 4). These absorption bands are characteristic of stretching vibrations of COOH groups [41]. Thus, in the case of the sample **1** the presence of residues of acetic acid, as it was suggested by the data of elemental analysis is confirmed by IR analysis.

The results of elemental analysis of the resulting samples indicate the overestimated values of the carbon content. The IR spectra of these samples suggest that can be primarily caused by the presence of $-(\text{CH}_2)_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)(\text{OH})$ fragments in these samples. Thus, there is a group of bands of low intensity at the $1360\text{-}1480\text{ cm}^{-1}$ and $2910\text{-}2990\text{ cm}^{-1}$ (Fig. 4). The last can be related to the stretching vibration $\nu_{\text{s,as}}(\text{CH})$, while the absorption bands at $1352\text{-}1378$, 1390 , $1445\text{-}1460$ and $1479\text{-}1482\text{ cm}^{-1}$ can be attributed to $\omega(\text{CH}_2)$, $\delta_{\text{s}}(\text{CH}_3)$, $\delta_{\text{as}}(\text{CH}_3)$ and $\delta(\text{CH}_2)$ ethoxygroups. The band of medium intensity, which corresponds to vibrations $\delta(\text{Si-CH}_2)$ is identified in this region at $1413\text{-}1420\text{ cm}^{-1}$ [40].

Thus, one can conclude that the surface layer containing phosphonic acid residues – $(\text{CH}_2)_2\text{P}(\text{O})(\text{C}_2\text{H}_5\text{O})_2$, which are slightly hydrolyzed; there is a tendency to incorporate acetic acid species into the polysiloxane framework, especially that with low content of functional groups (sample **1**) as indicated by IR spectra (Fig. 4) and elemental analysis data.

Analysis of the DTG profiles for the sample **4** before and after removal of the polymeric template (Fig. 5, curves **4'** and **4**, respectively) clearly shows that in the first case an intense peak in the range of $250\text{-}350^\circ\text{C}$ reflects thermodegradation of P123 block copolymer. The efficiency of removal of polymeric template from mesostructure with acidified ethanol was confirmed by the absence of this peak in the aforementioned range for the sample after extraction of the template. The same peak is absent in the DTG curves for the others samples (Fig. 5, curves **1-4**). It is evident that traces of extracting solvent and physically adsorbed water are removed up to 120°C (2-4%).

Fig. 5. DTG and TG (inset) curves for the samples **1-4** and **4'** after and before the removal of polymeric template, respectively.

The weight loss at higher temperatures is proportional to the concentration of the introduced functional groups, which is reflected by a peak on the DTG curves in the range of temperatures between 275 °C and 450°C. The decomposition of organic groups at the aforementioned temperature range is reflected by 11-19% weight loss for the samples **1-4**, and about 22 % weight loss for the sample **4'**. The DTG curve for the sample **1**, the IR spectrum of which indicated the presence of acetic acid is quite interesting (Fig. 5, curve 1). It is obvious that its presence should be reflected by an additional peak in the range 150-250°C and the peak at 275-450°C is shifted to slightly higher temperature range, 350-500°C. Note also that the total weight loss for the sample **1** is larger than that for the sample **2**. The peak about 3-5% at the 500-700°C can be attributed to the condensation of the neighboring silanol groups to form siloxane bonds.

Low-temperature adsorption-desorption isotherms of nitrogen recorded for all samples are type IV according to the IUPAC classification (Fig. 6a) [31,42]. However, the capillary condensation for the sample **4** with the highest content of functional groups is less steep and the hysteresis loop is elongated, which is an indication that pores are non-uniform (broad pore size distribution), and consequently the mesopores are disordered. In

this case, the pore size distribution (PSD) shows two peaks with maxima corresponding to 3.3 and 6.4 nm, respectively (Fig. 6b). The isotherm recorded for the sample **1** is typical for SBA-15 (Fig. 6a) with a steep capillary condensation step, which generates narrow PSD (uniform mesopores) with distinct maximum of about 8.9 nm.

In 2002 Van der Voort and others reported a new type of SBA-15 silica with plugged pores known as PHTS [43,44]. The PHTS materials possess microporous inclusions inside cylindrical mesochannels. Thus, the PSD peak at ~ 3 nm on the pore distribution curve (Fig. 6b) for the sample **2**, the intensity of which increases with higher concentration of organic groups (samples **3** and **4**), can be associated with the formations of plugs in mesopore channels in addition to the complimentary fine pores existing in the SBA-15 mesostructures [45]. The formation of bimodal porous structures is characteristic for the polymer templating synthesis at lower pH (3.5-4) [10].

Fig. 6. Nitrogen adsorption-desorption isotherms (panel a) and the corresponding pore size distributions calculated from adsorption branches of the isotherms obtained by KJS method (panel b).

A comparison of the adsorption and structural parameters for the samples studied is shown in Table 2. One can argue that in the case of the samples **2** and **3** the value of the specific surface area is significant affected by contribution of fine micropores. However,

there is a general trend for the samples studied; namely, the pore volume and pore diameter decrease with increasing content of functional groups (Table 2).

Table 2. Parameters of the porous structure for the synthesized materials

Sample	TEOS/ DPTS	S_{BET} , m ² /g	V_s , cm ³ /g	d_m , nm
1	10:1	417	0.66	8.9
2	10:2	533	0.55	6.9
3	10:3	515	0.56	6.9
4	10:4	362	0.40	6.4

Mesopore diameter d_m calculated at the maximum of the second peak of the PSD curves; the first peak indicates the presence of complementary fine pores (micropores and small mesopores).

It is known that the cationites with phosphonic acid residues [46,47] form stable complexes with ions of rare earth elements and uranium. Similarly, the mesoporous silicas studied have been decorated with phosphonic acid functionalities that are stable in aqueous solutions. Therefore, it is worthy to test these materials for adsorption of uranium species from aqueous solutions. According to some authors [48] the existence of uranyl ions UO_2^{2+} is possible at $\text{pH} \leq 2.5$. Our previous studies have been focused on adsorption of uranyl ions at $\text{pH} = \sim 2-2.5$ [21,49]. At higher pH values (between 2 and 8) more complex ions such as $\text{UO}_2(\text{OH})^+$, $\text{U}_2\text{O}_5^{2+}$, and $\text{U}_3\text{O}_8^{2+}$, are present in aqueous solutions [50]. However, a very challenging and practically important task is the extraction of uranium species present in sea water. Under sea water conditions ($\text{pH} \sim 8.3$) uranium is at oxidation state (VI) mainly in the form of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ and about 10% of $\text{UO}_2(\text{OH})_3^-$ [48,51]. If suitable sorbents are developed, the extraction of the aforementioned uranium species from seawater ($\text{pH} \sim 8.3$) could be a feasible alternative to its recovery from ores, which is a laborious process involving acid or base treatments, precipitation and purification steps. According to Sekiguchi and co-workers [52] the state of soluble uranium species in seawater is mainly influenced by CO_2 concentration and pH. Therefore, $\text{HCO}_3^-/\text{CO}_3^{2-}$ buffer present in seawater facilitates the formation of uranyl tricarboxylate complex $[\text{UO}_2(\text{CO}_3)_3]^{4-}$. This complex is stable at $\text{pH} \sim 8.3$ and readily decomposes into two different species such as $[\text{UO}_2(\text{CO}_3)_2]^{2-}$ and $[\text{UO}_2(\text{CO}_3)]$ in the pH ranges of 6-8 and 5-7, respectively [52]. Adsorption of uranium species on the samples studied was

performed at pH analogous to that in sea water; the corresponding adsorption capacity data are listed in Table 3.

Table 3. Uranium adsorption data for the samples studied.

sample	adsorbent mass used (mg)	volume of solution used (mL)	U adsorption capacity (g-U/kg-ads)	% of U adsorbed
1	13.5	100	24.1	40.7
2	12.7	200	54.5	43.3
3	12.4	200	11.5	8.9
4	13.3	200	10.9	9.1

As can be seen from Table 3 the values of uranium adsorption capacity obtained for the samples **1** and **2** are very high; the adsorption capacity obtained for the sample **2** is almost twice larger, which is not surprising because the concentration of phosphonic acid groups in this sample is about twice larger too (Table 1). These organosilica materials possess relatively uniform mesopores with ordered domains, which are easily accessible for relatively large uranium species present in a model aqueous solution that resembles the sea water conditions. The sample **3** possesses the surface area similar to that of the sample **2**, but contains about 30% more of phosphonic acid groups. In comparison to the sample **3**, the sample **4** exhibits even more phosphonic acid groups but its surface area is smaller, 352 m²/g versus 515 m²/g (sample **3**). Since both samples **3** and **4** possess much more phosphonic acid groups than the sample **2**, one could expect higher uranium adsorption capacities for the former samples. Table 3 shows that this is not the case. The adsorption capacity for the samples **3** and **4** is about 11 g of U per kg of the adsorbent; this value is almost four times smaller than that obtained for the sample **2**. As it was mentioned above, the former samples possess plugged mesopores, which is reflected by bimodal shape of PSD, and fine disordered pores (including micropores), which can limit accessibility of some porous domains to the relatively large uranium species. In addition, due to the high concentration of phosphonic acid groups in the samples **3** and **4**, and the polymeric nature of the surface layer as well as the presence of plugged pores, some organic groups are simply inaccessible to the relatively large uranium species. This inaccessibility can even rise after binding initial uranium species, which block access to other uranium species. This study shows that while a large concentration of phosphonic acid groups is an important factor for adsorption of uranium species under sea water conditions, an equally important factor is the presence of accessible mesoporous network without plugs and pore constrictions, which can exclude some porous domains for uranium species.

4. Conclusions

Synthesis of ordered phosphorus-containing materials of SBA-15 type at weak acidic conditions (pH ~ 3.75) is improved. The resulting materials featured surface areas of 363 - 533 m²/g, pore volumes of 0.40-0.66 cm³/g, and mesopore widths of 6.4-8.9 nm. The concentration of phosphonic acid groups in these samples varied from 1.0 to 3.0 mmol/g. Since inexpensive sodium metasilicate was used as a source of silica, these materials can be prepared on a large scale for various adsorption applications. For instance, one of the samples exhibited the surface area of 533 m²/g, pore volume of 0.55 cm³/g, mesopore width of 6.9 nm, and phosphonic acid concentration of 2.0 mmol/g, which was shown to be optimal for adsorption of uranium species from aqueous solutions (pH = 8.3 to mimic sea water conditions); at these conditions about 55 g of uranium per kg of the adsorbent was recorded, which illustrates high adsorption capacity of these materials for uranium species.

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