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REMOVAL OF URANYL CATIONS FROM IRON-CONTAINING SOLUTIONS USING COMPOSITE SORBENTS BASED ON POLYMER MATRIX

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Some technologies of uranium recovery from minerals involve hydrochloric acid where cationic forms of uranyl ions dominate. The work is devoted to development and testing of sorbents for removal of uranium(VI) from liquid wastes containing also an excess of Fe(III) ions. Organic-inorganic ion-exchangers based on gel-like strongly acidic resin containing zirconium hydrophosphate have been proposed for this purpose. The theoretical approach, which allows us to control a size of incorporated particles, has been applied to modification of the resin with the inorganic constituent. The results of TEM show that the samples contain mainly aggregates of nanoparticles (300 nm) or simultaneously aggregates (200 nm) and agglomerates (several microns). The synthesized organic-inorganic ion-exchangers contain from 10 to 50 mass. % of zirconium hydrophosphate. Composition and structure of the ion-exchangers affect their sorption properties. Sorption of U(VI) from modeling solutions containing also HCl and Fe(III) ions was researched under batch conditions. The initial pH of the solution was within the interval of 2–4, the sorbent dosage was 2–10 g/dm³. Simultaneous sorption of U(VI) and Fe(III) species was shown to occur, the removal of Fe(III) species is faster and more complete. Increasing of the sorbent dosage and the solution pH results in improvement of the efficiency of uranium (VI) removal and increase of the exchange rate. Sorption degree of uranyl cations reaches about 90 % after 3 h at pH 2 and the sorbent dosage of 10 g/dm³. When the sorbent dosage is 5 g/dm³ and the solution pH is 4 the sorption degree reaches 100 % for the composite containing 10 % of the inorganic constituent. The sorption degree is lower for the materials containing higher amount of zirconium hydrophosphate. The rate of sorption has been found to obey mainly particle diffusion model. The models of chemical reaction of pseudo-first or pseudo-second order can be also applied. The composites show mainly higher sorption capacity towards U(VI) at pH 2, the pristine resin demonstrates higher capacity towards Fe(III) under these conditions. The organic-inorganic ion-exchangers can be recommended for polishing of liquid wastes which are formed during monazite processing.

Keywords: gel-like strongly acidic resin, zirconium hydrophosphate, sorption, uranium(VI) compounds

INTRODUCTION

The problem of uranium recovery not only from ore [1], but also from unconventional raw-stuff [2] is of current interest. According to the Red Book of the IAEA, the alternative sources of uranium are phosphates (including phosphorites as well as monazites containing rare-earth elements (50–60 %), thorium (4–12 %) and uranium (up to 1 %)), non-ferrous metal ores, carbonatites, black shales and lignite (brown

coal). Uranium can be recovered from these minerals as a minor by-product.

Monazites are considered as an additional resource base of uranium [3], which is recovered simultaneously with basic components, such as rare earth elements and thorium [4, 5]. Up to 10 kg of uranium can be obtained from 1 ton of monazite. One stage of monazite concentrate processing involves formation of acidic multicomponent diluted solutions containing not only uranyl cations, but also an excess of Fe(III)

[6–8]. It is similar also for phosphorites. The valuable and toxic components, such as uranium compounds, must be removed from the liquid wastes. It is necessary in order to use these compounds further on the one hand and to solve ecological problems on the other hand. Among effective and ecologically pure methods, adsorption and ion exchange are considered as attractive techniques [9–16].

A number of sorbents has been proposed for selective removal of uranium compounds from multicomponent solutions: clays, which are modified by hydrated oxides of titanium and aluminium [10], unicellular algae [11] or complexing agent [12], anion-exchange resins [13, 14], particularly benzimidazole-type materials [13], complex composites including double hydroxides [15, 16] modified by graphene [15] or polysulfide [16]. An overwhelming majority of materials are suitable only for sorption of U(VI) anions. Nevertheless, monazite processing involves hydrochloric acid [6–8]. As a result, uranyl cations are formed in the effluent [6, 17]. This approach allows one to separate uranium from thorium, which is one of the main components of monazite. Extraction [18] and ion exchange are used for separation [19]. In the last case, separation of uranium from thorium is carried out by means of control of the acid concentration. Unmodified clays can sorb U(VI) cations [20] due to amphoteric properties of these natural materials (as a rule, modification enhances sorption of anions). However, the sorption process is rather slow, the sorbents tend to destruction in acidic media during regeneration. Strongly acidic cation exchange resins can be considered as the most attractive sorbents of uranyl cations due to their high ion exchange capacity, regeneration without destruction, capability to sorb cationic species in a wide pH interval [21]. In order to provide selectivity of the resins towards toxic ions, such as Pb(II) [22], Ni(II) [23, 24], Cd(II) [23, 25], they were modified with zirconium hydrophosphate (ZHP). Earlier we have proposed this type of composite, which contains a low amount of the inorganic constituent, as a sorbent for uranyl cations [26]. Sorption of these species was researched mainly for one-component solutions. As expected, the ZHP amount in the polymer and a type of the incorporated particles will affect sorption. The aim of the work was to elucidate the interrelation

between these factors and removal of uranyl cations from combined solutions.

EXPERIMENTAL

Following reagents of CP grade were used: $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (Chemapol, Czech Republic), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 7\text{H}_2\text{O}$, HCl (1.19 g/cm³), H_3PO_4 (1.87 g/cm³). The reagents were produced by Cherkassy State Plant of Chemical Reagents, Ukraine).

Gel-like strongly acidic cation-exchanger (Dowex HCR-S resin produced by Dow Chemical, USA) was used for investigations. Porous structure of this polymer matrix [23, 25], particularly its transformation in non-aqueous solvent [26], has been researched in details earlier [23, 25]. Before the modification, the resin was treated with acetone, this sample is called as “pristine resin” and marked as CR. ZHP was inserted into the polymer matrix by means of immersion in a 1 M ZrOCl_2 solution followed by washing with a 0.01 M HCl solution and ZHP deposition with H_3PO_4 similarly to [26]. This procedure was repeated 1 (CR-1) and 7 (CR-3) times. The procedure of CR-2 obtaining was similar to that for CR-1 (one-time modification), however, the stage of washing with hydrochloric acid was excluded.

A size of air-dry grains (300 particles for each sample) was determined using a Crystal-45 optical microscope (Konus, USA). The content of ZHP (after removal of the precipitate from outer surface of grains) was estimated as a growth of mass. TEM images were obtained using a JEOL JEM 1230 transmission electron microscope (Jeol, Japan). Before the investigations, the samples were pretreated as described in [23–25]. The content of phosphorus and zirconium in the samples was analyzed with an X-Supreme8000 XRF (X-ray fluorescence) spectrometer (Oxford Instruments, UK).

Multicomponent modeling solution of following composition (mol/dm³) were prepared: U(VI) (2.1×10^{-4}), Fe(III) (4.5×10^{-3}), HCl (0.02). Initial value of the pH was 2. Uranium(VI) is mainly in the form of UO_2^{2+} [17] under these conditions, Fe^{3+} (85 %) and $[\text{FeOH}]^{2+}$ (15 %) species [27] coexist in the solution. The solutions of pH 3 and 4 were also applied to the research. The pH was corrected by adding of a 0.1 M KOH solution and controlled with an I-160 MI pH-meter (Izmeritel'naya tekhnika LTD, RF). Increasing in the pH from 2 to 4 causes no

significant change of uranyl cations [17]. Simultaneously the content of Fe^{3+} decreases down to 30 % (pH 3) and 0 (pH 4) [27]. The amount of $[FeOH]^{2+}$ grows up to 50 % (pH 3) and falls down to 15 % further (pH 4). At the same time, the content of $[Fe(OH)_2]^+$ increases up to 20 % (pH 3) and 85 % (pH 4).

Sorption was investigated under static conditions at 20 ± 2 °C. The sorbent mass was 0.1–0.5 g, the solution volume was 50 cm^3 . Preliminarily weighted samples of air-dry sorbent swelled in deionized water. Agitation was performed using a Water bath shaker type 357 (Elpan, Poland) at 150 rpm. After predetermined time, the solid phase was separated from the liquid, which was analyzed later. U(VI) and Fe(III) were determined with a photometric method as a complex with Arsenazo III [28] and sulfosalicylic acid [29] respectively.

Sorption degree of metal ions (S) was estimated as:

$$S = \frac{C_0 - C}{C_0} \times 100, \% \quad (1)$$

where C_0 and C are the concentration of U(VI) or Fe(III) in the solution before and after sorption, respectively. Sorption capacity (A) was calculated according to the expression:

$$A = \frac{C_0 - C_p}{C_0} \times \frac{V}{m}, \quad (2)$$

where V is the solution volume, m is the weight of the sorbent.

RESULTS AND DISCUSSION

A size of the particles incorporated into the polymer depends on modification procedure. As shown earlier, the particles, a radius (r) of which is lower than [26]:

$$r = \frac{\beta V_m \sigma}{RT \ln \frac{K_{SP, CatAn}}{C_{CatAn, \infty} \left(C_{HAn} - \frac{(A + [Cat^+]_{ad}) V_i}{V_{HAn}} \right)}}, \quad (3)$$

are dissolved and re-precipitated, when an insoluble compound like ZHP ($CatAn$ salt) is deposited in ion exchange polymer. Here $C_{CatAn, \infty}$ is the concentration of oversaturated solution of insoluble salt (extremely small value), β is the shape factor of particles, V_m is the molar volume

of insoluble salt, σ is the surface tension of solvent, R is the gas constant, T is the temperature, K_{SP} is the solubility product, C_{HAn} is the precipitant (H_3PO_4) concentration, A is the ion exchange capacity of the polymer, $[Cat^+]_{ad}$ is the concentration of additionally sorbed electrolyte (if the polymer impregnated with a $ZrOCl_2$ solution is not washed, this value corresponds to equilibrium concentration of this solution), V_i and V_{HAn} are the volumes of ion-exchanger and precipitant respectively.

According to formula (3), a decrease of ion exchange capacity of the polymer or concentration of additionally sorbed electrolyte causes a reduction of the

$$\frac{K_{SP, CatAn}}{C_{CatAn, \infty} \left(C_{HAn} - \frac{(A + [Cat^+]_{ad}) V_i}{V_{HAn}} \right)}$$
 magnitude.

Thus, formation of larger particles is favorable thermodynamically in the case of $CR-1$ and $CR-3$, which were free from additionally sorbed $ZrOCl_2$ before ZHP precipitation. Indeed, this is true for the polymer phase: a size of particles (aggregates of nanoparticles) is up to 300 nm in the case of $CR-3$ (Fig. 1).

Smaller aggregates (up to 200 nm) were found for $CR-2$. The particles are stabilized by pore walls, which prevent agglomeration. These pores, where location of these particles is possible due to steric factor, are free from functional groups and contain hydrophobic parts of hydrocarbonaceous chains [23–26]. However, the $CR-2$ sample contains not only aggregates, but also dendritic agglomerates of micron size, which are formed in structure defects of the resin. These large particles are deposited from the additionally sorbed electrolyte. The agglomerates provide the largest grains of this ion-exchanger as well as the highest ZHP content (Table 1).

Primary nanoparticles are mainly elliptical, they are larger for the $CR-1$ and $CR-3$ ion-exchangers: a length of major axis is up to 100 [26, 30] and about 50 nm respectively. Indeed, further modification of the $CR-1$ composite involves the matrix with smaller exchange capacity (lower A value). This is due to partial substitution of the polymer by ZHP on one hand and ion exchange inertness of the inorganic constituent in strongly acidic media on other hand.

The *CR-2* sample shows smaller primary nanoparticles (up to 20 nm) due to a presence

of additionally sorbed electrolyte in large pores of the polymer before ZHP precipitation.

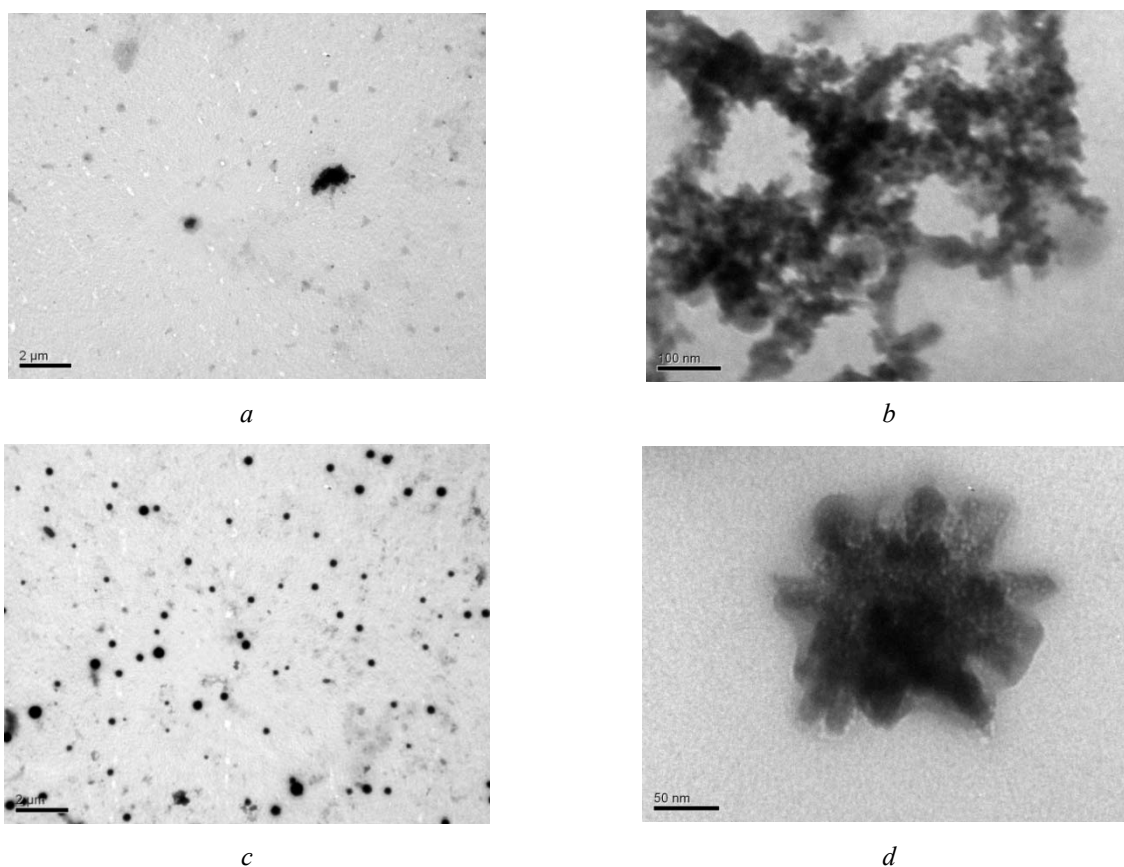


Fig. 1. TEM images of *CR-2* (*a*, *b*) and *CR-3* (*c*, *d*) composites

Table 1. Characteristics of sorbents

Sample	Modification features		ZHP morphology		ZHP amount, mass %	Molar ratio of Zr:P	Grain diameter, mm
	Cycles	ZrOCl ₂ before ZHP precipitation	Dominant particles (size, nm)	Size of nanoparticles, nm			
<i>CR</i>	–	–	–	–	0	–	0.53
<i>CR-1</i>	1	Removed	Aggregates (up to 200-300 along minor axis)	≈50	10	1:0.30	0.63
<i>CR-2</i>	1	Not removed	Aggregates (up to 200) and agglomerates (several microns)	≈20	50	1:0.43	0.88
<i>CR-3</i>	7	Removed	Aggregates (up to 300)	≈80	15	1:0.25	0.64

The aggregates are characterized by minimal content of phosphorus (*CR-1* and *CR-3*). Indeed, H₂PO₄[–] and HPO₄^{2–} species of the precipitant are co-ions, their penetration into the polymer phase is difficult, since the resin contains micropores, where –SO₃H groups are located [23–26]. Diffusion parts

of intraporous electric double layers are overlapped preventing movement of co-ions. Moreover, the aggregates are an additional barrier against them. Thus, the lowest phosphorus content has been found for *CR-3*. Agglomerates in structure defects evidently provide higher amount of phosphorus

(CR-2), since structure defects are opened for co-ions.

Composition and structure of the ion-exchangers affect their functional properties. Fig. 2 illustrates kinetic curves of U(VI) and Fe(III) sorption for the time (t) interval of 0–30 h. In some cases, the longer period was necessary for equilibrium, these regions of kinetic curves are not shown. As seen, the removal of Fe(III) species is faster and more complete.

In general, U(VI) cations are heavier, larger and less hydrated than Fe(III), lower limiting

molar conductivity (λ_i^0) is attributed to them (Table 2). The diffusion coefficient (D_i^0) can be calculated as $\frac{RT\lambda_i^0}{|z_i|F^2}$ [31]. Here F is the Faraday constant, z_i is the charge number. As seen from Table 2, uranyl cations are less mobile. The results are in an agreement with literature data, which consider the effect of hydration energy of ions on their sorption [32].

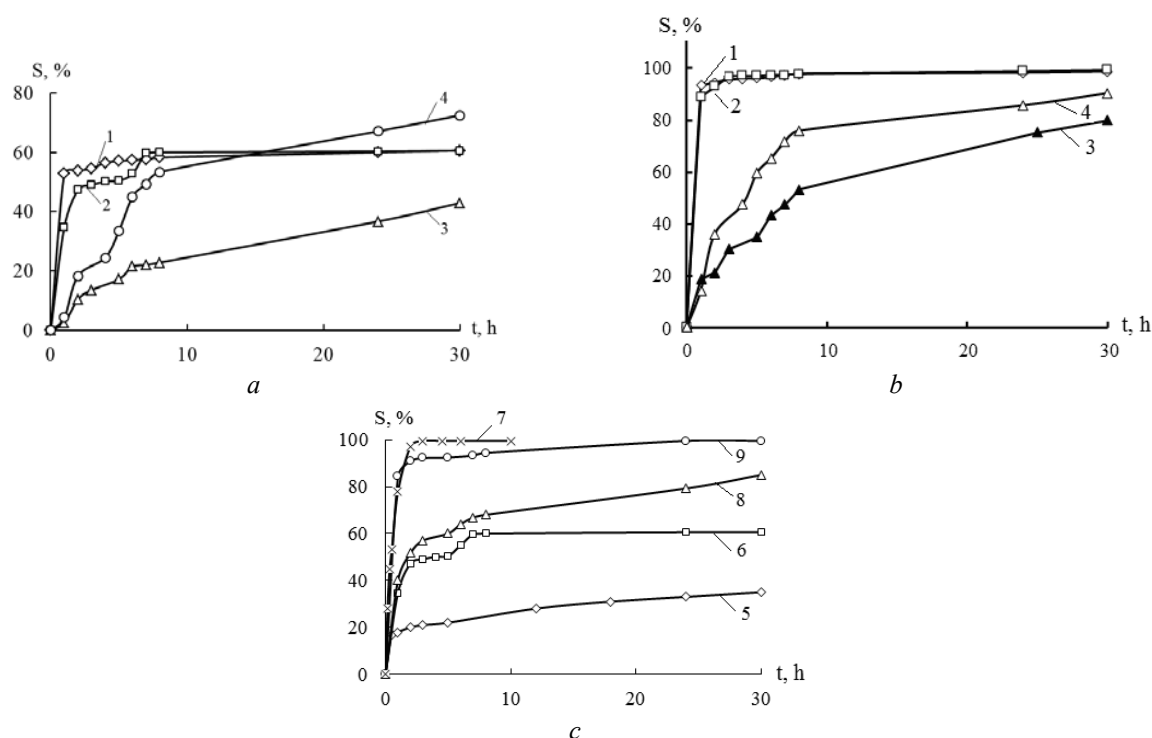


Fig. 2. Sorption degree of U(VI) (a, c) and Fe(III) (b) cations from multicomponent solutions as a function of time. Different sorbents were used (a, b): CR (1), CR-1 (2), CR-2 (3), CR-3 (4), the solution pH was 2, the sorbent dosage was 5 g/dm³. The CR-1 sample was used (c), its dosage was varied: 2 (5), 5 (6, 7), 7.5 (8), 10 (9) g/dm³, the initial pH was 2 (5, 6, 8, 9) or 4 (7)

Moreover, both uranyl and Fe(III) cations form complexes with SO_4^{2-} and H_2PO_4^- ligands in a solution. Formation of the complexes is also possible in ion-exchangers contain the same groups. This slows down a movement of species inside the ion-exchanger grains but improves sorption capacity. Confirmation of this assumption requires additional investigations.

The rate of ion exchange for different ions and sorbents can be compared using such parameter as half-exchange time ($t_{1/2}$). This parameter is given in Fig. 3 as a function of ZHP

content in the polymer for different sorbent dosage. As seen, the ion exchange rate increases with an increasing in sorbent dosage.

According to trivial approach, the rate of ion exchange is expressed as dn/dt , where n is the amount of sorbed ions. The flux of species is determined as $(1/S) \times (dn/dt)$. Here S is the area of the sphere, which corresponds to front of ions inside particles (particle diffusion) or to bound of hydrodynamically immobile layer of the solution at the particle surface (film diffusion). On the other hand, the flux obeys Fick's law as

$DS \text{ grad } C$. It means $dn/dt=DS \text{ grad } C$. In other words, the rate of sorption increases with a

growth of the S value, i.e. with an increasing in sorbent dosage.

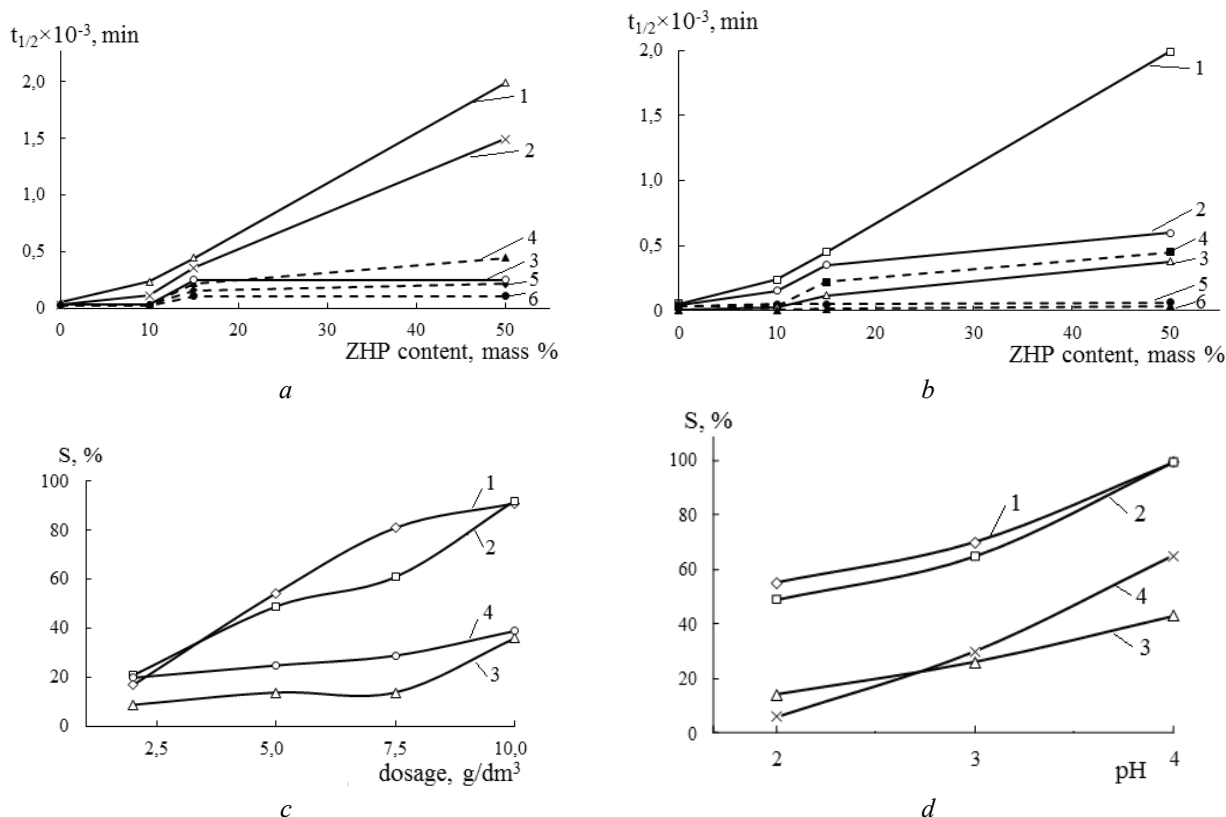


Fig. 3. Half-time of U(VI) (1-3) and Fe(III) (4-6) exchange as a function of ZHP content in the polymer (a, b), sorption degree of U(VI) after 3 h as a function of sorbent dosage (c) and initial pH of the solution (d). Sorbent dosage was 5 (a: 1, 4; b: 1, 4; d), 7.5 (a: 2, 5) and 10 (a: 3, 6) g/dm³, the initial pH of the solution was 2 (a, b: 1, 4, c), 3 (b: 2, 5), 4 (b: 3, 6)

Table 2. Physicochemical characteristics of ions in aqueous solutions

Parameter	UO ₂ ²⁺	Fe ³⁺	References
Ion radius, nm	0.186; 0.325*	0.067	[33, 34]
λ_i^0 , S×m ² /mol	0.0032	0.0068	[33]
$D_i^0 \times 10^{10}$, m ² /s	4.26	6.03	–
Standard entropy of hydration, J/(mol×K)	–33.5	–621.7	[35]
Standard enthalpy of hydration, kJ/mol	–1161.5	–5744.2	[35]
Change of the solvent entropy, J/(mol×K)	–106.3	–385.8	[35]
Complexes with SO ₄ ²⁻	pK ₁ =3.0 pK _{1,2} =5.4 pK _{1,2,3} =7.3	pK ₁ =3.5	[36]
Complexes with H ₂ PO ₄ ⁻	pK ₁ =2.7 pK _{1,2} =4.2	pK ₁ =4.2 pK _{1,2} =7.2	[36]

* radii of minimum and maximum van der Waals projections of an uranyl ion onto the plane

In general, incorporated ZHP particles slow down exchange of both Fe(III) and U(VI) species evidently due to transformation of porous structure of the polymer constituent [23–26, 30], increase in grain size and interaction of ions with functional groups of ZHP. However, the *CR-1* sample shows the same $t_{1/2}$ values as the pristine resin, when the sorbent dosage is maximal. This parameter is practically the same for the *CR-2* and *CR-3* ion-exchangers in the case of U(VI) sorption under these conditions. This indicates either slower diffusion in grains of *CR-3* (particle kinetics) or lower $grad C$ magnitude (particle or film kinetics). Sorption rate of Fe(III) is slightly dependent on dosage of these samples.

Increasing in the solution pH causes acceleration of sorption process, moreover, the $t_{1/2}$ values for Fe(III) and U(VI) become close to each other. The *CR-1* sample shows practically similar rate of Fe(III) and U(VI) species at pH 4. If the rate-determining stage is particle diffusion, the acceleration can be a result of higher concentration gradient inside sorbent grains. Indeed, the highest sorption degree of uranyl cations is reached at pH 4 (see Fig. 2 c). Regarding Fe(III), the increase of sorption rate can be a result of a reduction of charge number of the species due to their hydrolysis in the solution.

Sorption degree of uranyl cations reaches about 90 % after 3 h, when the sorbent dosage is 10 g/dm³ (*CR*, *CR-1*). This value is lower for the materials containing ZHP with small phosphorus content (*CR-3*) and large agglomerates (*CR-2*). The *CR* and *CR-1* samples remove U(VI) from the combining solution more completely than *CR-3* and *CR-2* after 3 h at pH 4.

A very important task is to improve the uptake of uranyl cations under an excess of iron(III) ions. Sorption from multicomponent solution is due to not only $UO_2^{2+} \rightarrow H^+$ and $Fe^{3+} \rightarrow H^+$ exchange, but also due to substitution of Fe^{3+} , $FeOH^{2+}$ and $Fe(OH)_2^+$ species by UO_2^{2+} . A ratio of $A_{\infty,U} / A_{\infty,Fe}$ (where A_{∞} is the equilibrium capacity at $t \rightarrow \infty$) is given in Fig. 4 a as a function of ZHP content in the polymer. In general, an increasing in sorbent dosage provides preferable U(VI) sorption. It is especially typical for the pristine resin and the sample with 10 % of the inorganic constituent. At the same time, the separation capability of the *CR* and *CR-1* ion-exchangers is practically similar: no influence of ZHP on selectivity is observed (Fig. 4 b). The $A_{\infty,U} / A_{\infty,Fe}$ ratio increases with a growth of the pH. This is probably due to sorption of hydrolyzed $Fe(OH)_2^+$ and $FeOH^{2+}$ species, they can be exchanged for UO_2^{2+} easier than Fe^{3+} .

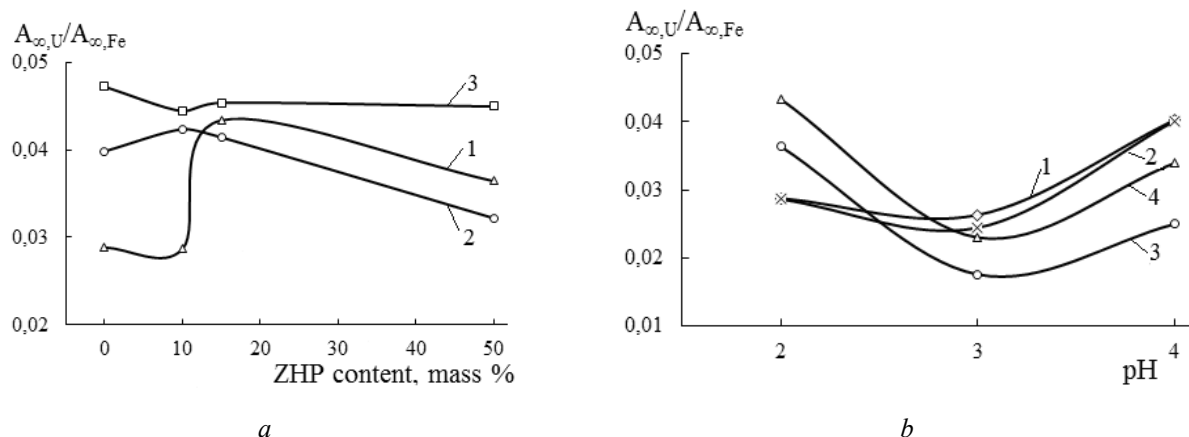


Fig. 4. The ratio of $A_{\infty,U} / A_{\infty,Fe}$ as a function of ZHP content in the composites (a) and pH of the solution (b). Sorbent dosage was: a – 5 (1), 7.5 (2), 10 (3) g/dm³, b – 5 g/dm³. The initial pH of the solution was 2 (a). Sorbents: b – *CR* (1), *CR-1* (2), *CR-2* (3), *CR-3* (4)

Alternately, larger amount of ZHP (CR-2 and CR-3) promotes preferable sorption of uranyl at pH 2, where exchange capability of the inorganic constituent is insignificant [25]. This can be caused by a formation of selective sorption sites in the polymer constituent due to squeezing of pores containing functional groups [23]. From this point of view, the aggregates of ZHP nanoparticles influence this formation stronger than large agglomerates. These sites could be attractive for sorption of doubly charged FeOH^{2+} species at pH 3 providing a decrease of the $A_{\infty,U} / A_{\infty,Fe}$ ratio. Further increase of uranyl uptake can be caused by a growth of the content of $\text{Fe}(\text{OH})_2^+$ ions in the solutions at pH 4 and their easier interchange with UO_2^{2+} . Moreover, the contribution of ZHP to sorption capacity of the composite becomes more significant [25].

Regarding selectivity, an advantage of the CR-2 and CR-3 samples is realized at pH 2. This advantage over the pristine resin disappears at higher pH.

Let us make some quantitative estimates. The experimental data in Fig. 2 were calculated using models of diffusion [32] and chemical reactions [37]. The rate of film diffusion was simulated [32] as:

$$\ln(1 - F_s) = -K_f t, \quad (4)$$

where F_s is the degree of the process completion ($F_s = S / S_\infty$, here S and S_∞ are the sorption degree under predetermined time and $t \rightarrow \infty$), K_f is the constant of film diffusion, which is related to diffusion coefficient in the solution as [32]:

$$K_f = \frac{3D_f}{r_0 \cdot \delta \cdot K_d}, \quad (5)$$

where r_0 is the radius of sorbent grain; δ is the thickness of hydrodynamically immobile layer of the solution at the grain surface, K_d is the distribution coefficient.

Particle diffusion was simulated according to Boyd-Adamson-Myers equation [32]:

$$\ln(1 - F_s) = \ln \frac{6}{\pi^2} - K_p t, \quad (6)$$

where K_p is the constant of particle diffusion. This value is related to diffusion coefficient in particles as:

$$K_p = \frac{\pi^2 D_p}{r_0^2}. \quad (7)$$

Equation (6) is valid at $F_s > 0.7$. The K_p and K_f constants were determined from slopes of the $\ln(1 - F_s) - t$ curves. Since both film and particle diffusion are described by a kinetic equation of the first order, it is valid:

$$t_{1/2} = \frac{\ln 2}{K}. \quad (8)$$

$$\text{Thus, } D_f = \frac{0,23r_0 \cdot \delta \cdot K_d}{t_{1/2}} \quad (\text{film diffusion})$$

$$\text{and } D_p = \frac{0,07 \cdot r_0^2}{t_{1/2}} \quad (\text{particle diffusion}).$$

Since hydrodynamical parameters are not defined under static conditions, the order of the δ value can be approximately estimated using literature data from the mass transport coefficient ($k = D / \delta$). When a solution is passed fast through the packed bed of Dowex HCR-S resin, the order of this coefficient is 10^{-5} m/s for Ni(II) ions ($D_f = 6.49 \times 10^{-10}$ m²/s) [38]. This approximately corresponds to conditions of continuous shaking. Thus, the order of the solution film thickness is assumed to be ≈ 10 μm .

The results for certain experiments are given in Fig. 5 a and Table 3. The sorption rate is determined by particle diffusion, since $K_p \ll K_f$ (the dosage is 5 g/dm³). In the case of higher dosage (10 g/dm³), the constants are comparable (CR-2 and CR-3) and the order of D_f values is realistic. At the same time, the order of particle diffusion coefficient is 10^{-13} m²/s. According to literature data for ion-exchange resins of the same cross-linkage ($\approx 8-10$ %), $D_f = 1.65 \times 10^{-12}$ m²/s (sorption of sulfate complexes on Amberlite IRA 400 anion-exchanger) [39], 1.76×10^{-13} m²/s (sulfate complexes and Dowex-1 anion-exchangers [40]). Thus, the data obey particle diffusion (CR, CR-1)

or both particle and film diffusion (CR-2 and CR-3).

In order to ascertain a contribution of chemical reaction to ion exchange, the models [37] of pseudo-first:

$$\ln(A_\infty - A) = \ln A_\infty - K_1 \times t \quad (9)$$

and pseudo-second order:

$$\frac{t}{A} = \frac{1}{K_2 A_\infty^2} + \frac{1}{A_\infty} \times t, \quad (10)$$

were applied. Here K_1 and K_2 are the rate constants.

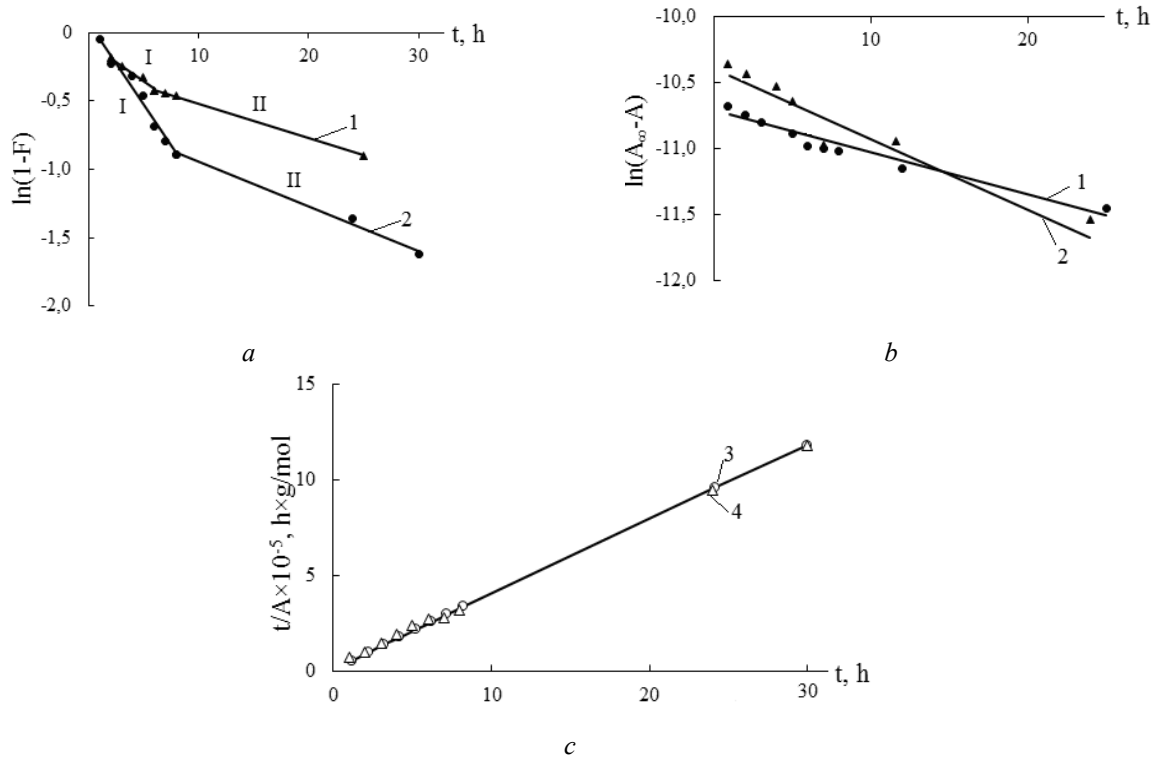


Fig. 5. Application of diffusion models (a), models of pseudo-first (b) and pseudo-second (c) order to U(VI) sorption on CR-2 (1), CR-3 (2), CR (3), CR-1 (4). The sorbent dosage is 5 g/dm³, the initial pH of the solution is 2. Regions (a): I – film diffusion; II – particle diffusion.

Table 3. Application of diffusion models to U(VI) sorption on the pristine and composite materials

Sample	$r_0 \times 10^4$, m	Film diffusion			Particle diffusion		
		$K_f \times 10^5$, s ⁻¹	$D_f \times 10^{10}$, m ² /s	R_c^2	$K_p \times 10^5$, s ⁻¹	$D_p \times 10^{13}$, m ² /s	R_c^2
Sorbent dosage of 5 g/dm³							
CR	2.66	30.80	≈1.72	0.969	2.35	1.70	0.999
CR-1	3.19	18.33	≈1.18	0.930	3.33	3.43	0.931
CR-2	4.42	1.56	≈0.12	0.942	0.88	1.75	0.952
CR-3	3.18	3.33	≈0.22	0.968	0.90	0.93	0.990
Sorbent dosage of 10 g/dm³							
CR	2.66	–	–	–	7.00	5.05	0.909
CR-1	3.19	–	–	–	2.00	2.07	0.907
CR-2	4.42	4.66	≈0.80	0.982	4.45	8.83	0.999
CR-3	3.18	9.50	≈1.94	0.997	3.00	3.10	0.999

According to Table 4 and Figs. 5 *b, c*, sorption of Fe(III) and also U(VI) (*CR-2, CR-3*) is described by the model of pseudo-first order. In the case of *CR, CR-I*, the rate of Fe (III) and U(VI) sorption is simulated by the model of pseudo-second order (experimental and calculated A_{∞} values are close to each other, the correlation coefficients, R_c^2 are high). These models provide different mechanisms of interaction with functional groups [31]. Thus, ion exchange is complicated by chemical

interaction of Fe(III) and uranyl ions with one (*CR-2, CR-3*) or two functional groups (*CR, CR-I*). In other words, it is an indirect sign indicating a presence of one (the sample with content of zirconium hydrophosphate is 15 and 50 mass. %) or two (the sample 15 % of the inorganic constituent and the pristine resin) $-\text{SO}_3\text{H}$ or phosphorus-containing group in the coordination arrangement of Fe(III) or UO_2^{2+} . A confirmation of this assumption requires additional investigations.

Table 4. Models of chemical reactions for Fe(III) and U(VI) sorption

Sample	$A_{\infty} \times 10^5$, mol/g (experimental)	Pseudo-first order			Pseudo-second order		
		$A_{\infty} \times 10^5$, mol/g (calculated)	$K_1 \times 10^5$, s ⁻¹	R_c^2	$A_{\infty} \times 10^5$, mol/g (calculated)	K_2 , dm ³ /(mol×s)	R_c^2
Fe (III)							
Sorbent dosage of 5 g/dm³, pH 2							
<i>CR</i>	88.1	5.8	6.0	0.961	88.3	2.9	0.999
<i>CR -I</i>	88.6	7.5	6.5	0.759	88.7	2.6	0.999
<i>CR -2</i>	71.4	70.4	1.3	0.978	86.3	0.05	0.985
<i>CR -3</i>	87.4	87.3	5.2	0.989	91.7	0.07	0.989
Sorbent dosage of 7.5 g/dm³, pH 2							
<i>CR -0</i>	59.5	1.7	14.8	0.966	60.0	30.9	0.999
<i>CR -I</i>	59.5	26.3	21.7	0.904	60.0	2.2	0.999
<i>CR -2</i>	56.5	50.6	4.7	0.929	62.0	0.12	0.996
<i>CR -3</i>	58.4	58.0	7.1	0.944	66.0	0.11	0.992
Sorbent dosage of 10 g/dm³, pH 2							
<i>CR</i>	44.5	0.4	5.7	0.980	45.0	55.8	0.999
<i>CR -I</i>	44.6	0.2	5.0	0.996	45.0	105.5	0.999
<i>CR -2</i>	44.3	42.5	12.3	0.979	56.0	0.02	0.990
<i>CR -3</i>	44.5	45.0	25.2	0.969	48.0	0.42	0.987
U(VI)							
Sorbent dosage of 5 g/dm³, pH 2							
<i>CR</i>	2.54	0.43	37.0	0.961	2.55	38.0	0.999
<i>CR -I</i>	2.54	0.63	31.7	0.952	2.63	13.8	0.999
<i>CR -2</i>	2.60	2.26	10.2	0.989	2.56	0.82	0.864
<i>CR -3</i>	3.79	3.04	15.2	0.901	4.38	0.54	0.813
Sorbent dosage of 5 g/dm³, pH 4							
<i>CR</i>	4.50	2.59	40.3	0.921	4.75	27.7	0.999
<i>CR -I</i>	4.48	4.88	50.8	0.988	5.06	11.7	0.997
<i>CR -2</i>	2.81	2.23	7.67	0.948	2.94	6.17	0.999
<i>CR -3</i>	4.15	3.06	5.67	0.891	4.40	2.83	0.999
Sorbent dosage of 7.5 g/dm³, pH 2							
<i>CR</i>	2.37	1.08	76.7	0.912	2.80	15.3	0.999
<i>CR -I</i>	2.52	1.41	35.2	0.937	2.33	8.94	0.999
<i>CR -2</i>	1.88	1.73	13.7	0.997	1.93	1.17	0.922
<i>CR -3</i>	2.34	2.44	43.3	0.996	1.95	1.00	0.997
Sorbent dosage of 10 g/dm³, pH 2							
<i>CR</i>	2.10	3.15	70.2	0.909	2.11	65.8	0.999
<i>CR -I</i>	1.98	1.82	86.7	0.827	2.12	3.67	0.999
<i>CR -2</i>	2.00	1.97	46.7	0.983	2.53	0.33	0.959
<i>CR -3</i>	2.01	2.26	90.3	0.992	2.60	43.5	0.987

CONCLUSIONS

As predicted theoretically, the removal of additionally sorbed electrolyte ($ZrOCl_2$ solution) before ZHP precipitation causes formation of small aggregates in the ion exchange polymer. The aggregates are evidently located in pores containing hydrophobic parts of hydrocarbonaceous chains. In this case, ZHP contains low amount of phosphorus. Further modification of the composite results in formation of smaller ZHP particles containing lower phosphorus amount. Agglomerates are formed from additionally sorbed electrolyte in structure defects of the polymer, the inorganic constituent is characterized by the highest phosphorus content.

The ion-exchangers were applied to removal of toxic and valuable component, such as uranyl ions, from the solutions containing also an excess of Fe(III). Comparing of the results obtained with data of [26, 30], it is possible to see that Fe(III) species slow down sorption of U(VI) cations. This is evidently caused by U(VI)→Fe(III) exchange. A growth in the solution pH from 2 to 4 improves uranyl

sorption, though ion exchange is complicated by chemical reactions with functional groups.

The sample containing the minimal amount of ZHP shows similar sorption behavior as the pristine resin. The advantage of this composite over the unmodified ion-exchanger is facilitated regeneration and, as a result, longer life-time [26, 30]. Practical application of this sorbent is recommended, where it is necessary to remove uranyl ions as completely and faster as possible.

U(VI) sorption on the composites with higher content of the inorganic constituent is slower, smaller sorption degree is realized. This is independent on a type of dominated particles (aggregates or agglomerates), the content of phosphorus also plays no significant role. These ion-exchangers sorb preferably U(VI) at pH 2, they can be recommended for predominant recovery of these cations from acid media, particularly from wastes of monazite processing. In order to accelerate sorption, the smallest fraction of the pristine resin should be used for modification. Large dosage of these composites is recommended for U(VI) recovery.

Вилучення катіонів уранілу із залізовмісних розчинів з використанням композитних сорбентів на основі полімерної матриці

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Роботу присвячено вивченню закономірностей сорбції катіонів уранілу на орґано-неорґанічних іонітах, які отримували модифікуванням гідрофосфатом цирконію гелевої сильнокислотної іонообмінної смоли. Для модифікування використовували теоретичний підхід, що дало змогу регулювати розмір інкорпорованих частинок. Сорбенти містили, в основному, агрегати наночастинок (300 нм) або одночасно агрегати (200 нм) та агломерати (декілька мікрон). Сорбцію U(VI) із модельних розчинів, що містили також HCl і надлишок Fe(III), досліджено у статичних умовах в інтервалі pH 2–4 і при дозуванні сорбентів 2–10 г/дм³. Встановлено, що швидкість сорбції описується переважно моделлю внутрішньої дифузії та моделями хімічної реакції псевдопершого (вміст гідрофосфату цирконію у зразках – 15 та 50 мас. %) та псевдодругого порядку (зразок із вмістом неорґанічної складової 10 мас. % та вихідна смола). Зразки із вищим вмістом модифікатора сорбують переважно U(VI) при pH 2, а з нижчим – при pH 4.

Ключові слова: *гелевий сильнокислотний катіоніт, гідрофосфат цирконію, сорбція, сполуки урану(VI)*

Извлечение катионов уранила из железосодержащих растворов с использованием композитных сорбентов на основе полимерной матрицы

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Работа посвящена установлению закономерностей сорбции катионов уранила на органо-неорганических ионитах, полученных модифицированием гидрофосфатом циркония гелевой сильнокислотной ионообменной смолы. Для модифицирования использовали теоретический подход, что дало возможность регулировать размер инкорпорированных частиц. Сорбенты содержали, в основном, агрегаты наночастиц (300 нм) или одновременно агрегаты (200 нм) и агломераты (несколько микрон). Сорбцию $U(VI)$ из модельных растворов, содержащих также HCl и избыток $Fe(III)$, исследовали в статических условиях в интервале pH 2–4 и при дозировке сорбентов 2–10 г/дм³. Установлено, что скорость сорбции описывается преимущественно моделью внутренней диффузии и моделями псевдопервого (содержание гидрофосфата циркония в образцах 15 и 50 масс. %) и псевдоторгового порядка (образец с содержанием неорганической составляющей 10 масс. % и исходная смола). Образцы с более высоким содержанием модификатора сорбируют преимущественно $U(VI)$ при pH 2, а с более низким – при pH 4.

Ключевые слова: гелевый сильнокислотный катионит, гидрофосфат циркония, сорбция, соединения урана(VI)

REFERENCES

1. Gupta C., Singh H. *Uranium Resource Processing: Secondary Resources*. (Berlin, Heidelberg, New York: Springer-Verlag, 2003).
2. Schnell H. An Overview of uranium production from unconventional resources. In: *Nuclear Fuel Cycle and Materials. Uranium Production Cycle*. Proc. Technical Meeting On Uranium from Unconventional Resources (November 4-6, 2009, Vienna, Austria).
3. Chaki A. Unconventional uranium resources - Indian scenario. In: *Nuclear Fuel Cycle and Materials. Uranium Production Cycle*. Proc. Technical Meeting On Uranium from Unconventional Resources (November 4-6, 2009, Vienna, Austria).
4. Zhu Z., Pranolo Y., Cheng Ch.Y. Separation of uranium and thorium from rare earths for rare earth production. *Miner. Eng.* 2015. **77**: 185.
5. Lapidus G.T., Doyle F.M. Selective thorium and uranium extraction from monazite: II. Approaches to enhance the removal of radioactive contaminants. *Hydrometallurgy*. 2015. **155**: 161.
6. Wickleder M.S., Fourest B., Dorhout P.K. Thorium. In: *The Chemistry of the Actinide and Transactinide Elements*. (Netherlands: Springer, 2006).
7. Kaplan G.E., Uspenskaya T.A., Zarembo Yu.I., Chirkov I.V. *Thorium, its Raw Resources, Chemistry and Technology*. (Moscow: Atomizdat, 1960). [in Russian].
8. Zelikman A.N., Korshunov B.G. *Metallurgy of Rare Metals*. (Moscow: Metallurgiya, 1991). [in Russian].
9. Zaganiari E.J. *Ion Exchange Resins in Uranium Hydrometallurgy*. (Paris: Books on Demand France, 2009).

10. Pilipenko I.V., Kovalchuk I.A., Kornilovich B.Yu. Synthesis and sorption properties of montmorillonite intercalated with aluminum and titanium polyhydroxocomplexes. *Him. Fiz. Tehnol. Poverhni*. 2015. **6**(3): 336. [in Russian].
11. Tobilko V., Lypskyi V., Kovalchuk I., Spasonova L., Kornilovich B. Biosorption of uranium on immobilized microalgae. *Pol. J. Chem.* 2008. **82**(1–2): 249.
12. Bogolepov A.A., Pshinko G.N., Kornilovich B.Yu. The impact of complexing agents on the processes of sorption treatment of waters containing uranium. *J. Water Chem. Technol.* 2007. **29**(1): 9.
13. Kitagaki T., Kaneshiki T., Nomura M., Suzuki T. Uranium separation from a simulant fuel debris solution using a benzimidazole-type anion exchange resin. *J. Nucl. Sci. Technol.* 2016. **53**(10): 1639.
14. Zagorodnyaya A., Abisheva Z., Sharipova A., Sadykanova S., Akcil A. Regularities of rhenium and uranium sorption from mixed solutions with weakly basic anion exchange resin. *Miner. Process. Extr. Metall. Rev.* 2015. **36**(6): 391.
15. Tan L., Wang Yu., Liu Q., Wang J., Jing X., Liu L., Liu J., Song D. Enhanced adsorption of uranium(VI) using a three-dimensional layered double hydroxide/graphene hybrid material. *Chem. Eng. J.* 2015. **259**: 752.
16. Ma Sh., Huang L., Ma L., Shim Yu., Islam S.M., Wang P., Zhao L.-D., Wang Sh., Sun G., Yang X., Kanatzidis M.G. Efficient uranium capture by polysulfide/layered double hydroxide composites. *J. Am. Chem. Soc.* 2015. **137**(10): 3670.
17. Gapel G. *Speciation of actinides. Handbook of elemental speciation II. Species in the environment, food, medicine and occupational health.* (Chichester, UK: Wiley, 2005).
18. Peppard D.F., Mason G.W., Gergel M.V. The mutual separation of thorium, protoactinium, and uranium by tributyl phosphate extraction from hydrochloric acid. *J. Inorg. Nucl. Chem.* 1957. **3**(6): 370.
19. Alhassanieh O., Abdul-Hadi A., Ghafaa M., Aba A. Separation of Th, U, Pa, Ra and Ac from natural uranium and thorium series. *Appl. Radiat. Isot.* 1999. **51**(5): 493.
20. Tsunashima A., Brindley G.W., Bastovanov M. Adsorption of uranium from solutions by montmorillonite; compositions and properties of uranyl montmorillonites. *Clays Clay Miner.* 1981. **29**(1): 10.
21. Rao T.P., Metilda P., Gladis J.M. Preconcentration techniques for uranium(VI) and thorium(IV) prior to analytical determination—an overview. *Talanta*. 2006. **68**(4): 1047.
22. Zhang Q., Pan B., Zhang S., Wang J., Zhang W., Lu L. New insights into nanocomposite adsorbents for water treatment: A case study of polystyrene-supported zirconium phosphate nanoparticles for lead removal. *J. Nanopart. Res.* 2011. **13**: 5355.
23. Dzyazko Yu.S., Ponomaryova L.N., Volkovich Yu.M., Trachevskii V.V., Palchik A.V. Ion-exchange resin modified with aggregated nanoparticles of zirconium hydrophosphate. Morphology and functional properties. *Microporous Mesoporous Mater.* 2014. **198**: 55.
24. Dzyazko Yu.S., Ponomaryova L.N., Rozhdestvenskaya L.M., Vasilyuk S.L., Belyakov V.N. Electrodeionization of low-concentrated multicomponent Ni^{2+} -containing solutions using organic-inorganic ion-exchangers. *Desalination*. 2014. **342**: 52.
25. Dzyazko Yu., Rozhdestvenska L., Palchik A., Lopicque F. Ion-exchange properties and mobility of Cu^{2+} ions in zirconium hydrophosphate ion exchangers. *Sep. Purif. Technol.* 2005. **45**(2): 141.
26. Dzyazko Yu.S., Perlova N.A., Perlova O.V., Ponomaryova L.N., Volkovich Yu.M., Palchik A.V., Trachevskii V.V., Belyakov V.N. Organic-inorganic ion-exchanger containing zirconium phosphate, for extracting uranium compounds (VI) from aqueous solutions. *Him. Fiz. Tehnol. Poverhni*. 2016. **7**(2): 119. [in Russian].
27. Hoffmann P. *Speciation of Iron. Handbook of elemental speciation II. Species in the environment, food, medicine and occupational health.* (Chichester, UK: Wiley, 2005).
28. Khan M.H., Warwick P., Evans N. Spectrophotometric determination of uranium with arsenazo-III in perchloric acid. *Chemosphere*. 2006. **63**(7): 1165.
29. Liang W.A., Zhang Z.Y., Zou S.F. Ultraviolet derivative spectrophotometric determination of trace iron with sulfosalicylic acid. *Fenxi Kexue Xuebao*. 1997. **13**: 145.

30. Perlova O.V., Dzyazko Yu.S., Perlova N.A., Sazonova V.F., Palchik A.V. Sorption of cations UO_2^{2+} on the polymeric ion exchanger modified with zirconium hydrogen phosphate. *Voprosy khimii i khimicheskoi technologii*. 2016. **2**: 150. [in Russian].
31. Atkins P.W. *Physical Chemistry*. (Oxford: Oxford University Press, 1998).
32. Helfferich F. *Ion Exchange*. (New York: Dover, 1995).
33. Ravdel A.A., Ponomareva A.M. (Eds.) *Short Handbook of Physicochemical Variables*. (Leningrad: Khimiya, 1983). [in Russian].
34. Yaroshenko N.A., Sazonova V.F., Perlova O.V., Perlova N.A. Sorption of uranium compounds by zirconium-silica nanosorbents. *Russ. J. Appl. Chem.* 2012. **85**(6): 849.
35. Krestov G.A. *Thermodynamics of ionic processes in solutions*. (Leningrad: Khimiya, 1984).
36. Lurie Y.Y. *Handbook of Analytical Chemistry*. (Moscow: Khimiya, 1989).
37. Zhao G., Wu X., Tan X., Wang X. Sorption of heavy metal ions from aqueous solutions: a review. *Open Colloid Sci. J.* 2011. **4**: 19.
38. Dzyazko Yu.S. Purification of a diluted solution containing nickel using electrodeionization. *Desalination*. 2006. **198**(1–3): 47.
39. Streat M., Takel G.N.J. Anion exchange kinetics of uranium in sulphate media. *J. Inorg. Nucl. Chem.* 1981. **43**(4): 807.
40. Barnes C.D., da Silva Neves R.A., Streat M. Anion exchange of uranium from aqueous sulphuric acid solutions: diffusion kinetics. *J. Appl. Chem. Biotechnol.* 1974. **24**(12): 787.

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