O.V. Perlova [1], I.S. Ivanova [1], Yu.S. Dzyazko [2], M.O. Danilov [2], I.A. Rusetskii [2], G.Ya. Kolbasov [2]

SORPTION OF U(VI) COMPOUNDS ON INORGANIC COMPOSITES CONTAINING PARTIALLY UNZIPPED MULTIWALLED CARBON NANOTUBES

[1] Odessa I.I. Mechnikov National University
2 Dvoryanska Str., Odesa, 65082, Ukraine, E-mail: olga_perlova@onu.edu.ua
[2] Vernadsky Institute of General and Inorganic Chemistry of National Academy of Sciences of Ukraine
32/34 Academician Palladin Avenue, Kyiv, 03142, Ukraine

Unlike ion-exchange resins, inorganic sorbents possess high selectivity towards heavy metal ions and stability against ionizing radiation. However, sorption on these materials is rather slow. Moreover, sorption capacity strongly depends on the solution pH. In order to improve sorption properties of inorganic ion-exchangers, composites containing advanced carbon materials are obtained. Regularities of sorption of U(VI) compounds from low-concentrated aqueous solutions (up to 0.1 mmol dm^{-3} of uranium) on hydrated zirconium dioxide and zirconium hydrophosphate are considered. The sorbents were modified with partially unzipped multiwalled carbon nanotubes (PUMWCNTs). Sorption isotherms were obtained and analyzed. They obey Dubinin-Radushkevich model indicating sorption sites, a size of which is comparable with that of ions being sorbed. As found, the sorption mechanism is ion exchange. The effect of the solution pH on the sorption rate of U(VI) ions and capacity of inorganic ion-exchangers and their composites has been considered. Carbon additions increase sorption capacity of zirconium dioxide and zirconium hydrophosphate, when the initial pH of one-component solution is 3–4 and 5–7 respectively. Under these conditions, U(VI)-containing cations are removed from the solution practically completely. The rate of sorption obeys the model of chemical reaction of pseudo-second order, when uranium is removed from one-component solution. PUMWCNTs slow down sorption on zirconium dioxide and accelerate it on zirconium hydrophosphate. The dependence of the pseudo second order equation constants on the pH of U(VI) solutions was analyzed. The reaction of the first order occurs, when the solution contains also Ca^{2+} and Mg^{2+} ions. Regeneration was carried out using HNO_3 and $NaHCO_3$ solutions: the rate-determining stage of desorption is particle diffusion. It has been shown that one-component ZHP can be regenerated with a $NaHCO_3$ solution practically completely. The most suitable solution for U(VI) desorption from ZHP-PUMWCNTs composite is a 1 M HNO_3 solution.

Keywords: Uranium(VI) compounds, hydrated zirconium dioxide, zirconium hydrophosphate, partially unzipped multiwalled carbon nanotubes, sorption

INTRODUCTION

The sources of soluble uranium(VI) compounds in ground and mining water as well as in natural and artificial water reservoirs are uranium-containing minerals, the products of coal combustion, emission of power plants, waste water of granite processing plants and so on [1]. Uranium and its compounds are toxic since they are common cell venom besides their radioactivity [2]. Similarly to other heavy metal ions, they are irreversibly bound to proteins, primarily with sulfide groups of amino acids, disrupting their function. Activity of ferments is depressed first of all. With chronic intoxication, the kidneys are attacked. Disorders of the hematopoiesis and nervous system are also possible.

The maximal allowable concentration of soluble compounds of hexavalent ^{238}U isotope is 0.015 mg·dm^{-3} (this isotope is the most widespread). It has been recommended by the US Environmental Protection Agency that the ^{238}U concentration in drinking water is 20 µg·dm^{-3} [3].

In order to recovery small amounts of U(VI) from water, adsorption and ion exchange methods are usually used, since these techniques reduce the uranium content lower the maximal allowable concentration [4]. Moreover, no solid insoluble wastes are formed as a result of water processing. A number of sorbents are applied to U(VI) recovery, for example TiO_2 [5], hydroxyapatite [6], Fe_2O_3 [7], polymer [8–11] and polymer-inorganic composites [12–16].

Some approaches are applied to enhance sorption capability of materials: impregnation with alginate [5, 6], coating of inorganic particles with carbon [6] or polymer [7].

Nowadays such advanced carbon nanomaterials as oxidized graphene (GO) [17–19], multiwalled carbon nanotubes (MWCNT) [20], graphene-like materials obtained by unzipping MWCNT [21], aerogel prepared from the MWCNT-GO composites [22]. The advantages of these materials are adsorption capacity in a wide range of pH and no effect of ionic strength on this parameter. The disadvantage is fine dispersion that makes impossible to use MWCNT and GO as fillers of adsorption columns.

In order to avoid these difficulties, carbon nanomaterials are inserted into synthetic polymer [23–25], biopolymer [26–28] or inorganic [29–31] matrices. Among these matrices, inorganic ion exchangers like hydrated oxides or hydrophosphates of multivalent metals occupy special position [32–35], since they can be obtained in a form of large granules. The inorganic compounds are stable against ionizing radiation – it means they can be used many time for U(VI) sorption followed by regeneration of sorbents. Earlier the GO-containing composites based on hydrated zirconium dioxide (HZD) [29, 36, 37] and zirconium hydrophosphate (ZHP) [29] have been obtained. GO nanoribbons produced from nanotubes, and GO nanosheets obtained from graphite using Hummers' methods were used as a modifier. Comparing with one-component HZD, the composites possess higher sorption capacity towards heavy metal cations [37]. The optimal GO content that provides large size of granules and their mechanical durability has been found [29, 36]. The effect of GO on U(VI) uptake is more expressed in the case of the composite based on ZHP [29]. However, main regularities of sorption and desorption of U(VI) compounds on HZD and ZHP-based composites were not investigated, though they were mentioned very briefly. The aim of this work was to find the effect of PUMWCNTs on U(VI) sorption-desorption depending on different experimental conditions, such as acidity and composition of the solution.

EXPERIMENTAL

The methods of the synthesis of PUMWCNTs and related composites are described in detail in [29]. Briefly: MWCNTs (8–15 layers) have been acquired from the "TM Spetzmash" LTD. Their specific surface area was 130 m^2g^{-1}. The nanotubes were unzipped in a concentrated H_2SO_4 solution using $K_2Cr_2O_7$ as an oxidant [38]. Aqueous suspension of PUMWCNTs (2.8 mg cm^{-3}) was obtained in this manner. Sol of insoluble zirconium hydroxocomplexes was synthesized similarly to [39]. Then a mixture of sol (100 cm^3) and suspension (90 cm^3) was activated with ultrasound for 5 min at 30 kHz using a Bandeline bath (Bandeline). The mixture was gradually added to saturated NaOH solution, the hydrogel granules were washed with a 1 M NH_4OH solution and deionized water, and dried under ambient conditions. As a result, HZD-PUMWCNTs hybrid composite was obtained. In order to synthesize pure HZD, only sol was used for hydrogel deposition. ZHP-based composite and one-component ZHP were deposited by means of a 1 M H_3PO_4.

The samples were characterized as described in [29]. Additionally, the total capacity of sorbents towards Na^+ (all samples) and Cl^- (HZD-based samples) was determined. A 1 M NaCl solution was previously acidified with a HCl solution or alkalized with a NaOH solution down (up) to the predetermined pH value. Then the solution was passed through the column filled with sorbent. The passage was stopped when the solution pH at the inlet and outlet of the column was equal. The sorbent was removed from the column, washed with deionized water and divided into two portions. The first of them was treated with a 0.1 M HCl solution, Na^+ ions were determined in the effluent with a PFM-4U flame photometer. The second portion was treated with a 0.1 M NaOH solution. The content of Cl^- ions in the alkaline solution was determined using an ELIS-131Cl selective electrode. Mixed solutions containing 0.1 mol dm^{-3} NaCl and 0.1 mol dm^{-3} NaOH or HCl were used to determine total ion exchange capacity of the sorbents.

U(VI)-containing solution was prepared from uranyl acetate salt, then the solution was acidified with HNO_3 down to pH 2. Further portions of the liquid were alkalized with a NaOH solution up to pH 3, 4, 5, 6, 7 and 8. For all cases, the sorbent dosage was 2 g·dm^{-3}. The U(VI) concentration in the solutions before and after sorption was determined after uranium transformation into a complex with Arsenazo III

[40]. A Shimadzu UV-mini1240 spectro-photometer (Shimadzu, Japan) was applied for the analysis, which was performed at 670 nm.

Neutral solutions (pH 7) were used for obtaining sorption isotherms at 25 °C. The initial concentration of U(VI) was 5–25 mg·dm^{-3}.

Sorption rate was investigated as follows. The sorbent was inserted into flasks, the solution containing 25 mg·dm^{-3} of U(VI) was added. The initial pH of the solutions was within the interval of 2–8. The flasks were shaken intensively with a Water Bath Shaker Type 357 system (Elpan, Poland). After predetermined time, the solution probe (1 cm^3) was taken.

The degree of ion removal from the solution (R_s) and sorption capacity (A) were calculated as:

$$R_s = \frac{C_i - C}{C_i} \times 100\% \quad , \tag{1}$$

$$A = \frac{V_s(C_i - C)}{m}, \tag{2}$$

where C_i and C are the initial and equilibrium concentration respectively, V_s is the solution volume, m is the sorbent mass.

For regeneration of the samples loaded with U(VI) at pH 6, such solutions as 0.1 M NaHCO$_3$, 0.1 M and 1 M HNO$_3$ were used. Desorption rate was investigated. The regeneration degree (R_d) was estimated from the formula:

$$R_d = \frac{C_d}{C_i - C} \times 100\%, \tag{3}$$

where C_d is the effluent concentration, C is the equilibrium concentration of the U(VI)-containing solution after sorption.

The rate of uranyl sorption from neutral solution, which was prepared using tap water, was also studied. Initially water contained Ca^{2+} (1.2 mmol dm^{-3}) and Mg^{2+} (0.5 mmol dm^{-3}).

RESULTS AND DISCUSSION

As shown earlier [29, 36], the content of GO or PUMWCNTs of 2 % is optimal: it provides formation of rather large granules, which could be used in sorption columns. On the other hand, the optimal combination of mechanical durability and sorption properties is realized namely under this amount of carbon additions [36]. The data regarding morphology, porous structure and functional groups of PUMWCNTs and composites are given in [29]. In this work, it has been found that X-ray pattern for PUMWCNTs is typical for GO-like materials, which contain several layers: typical broad reflex is located below $2\theta = 26.02°$ (reflex for graphite). The reflex for PUMWCNTs is expressed as a shoulder of the peak for SiO$_2$ of a capillary, where the sample is placed. As found, PUMWCNTs cover primary particles of HZD and ZHP. Similarly to GO, PUMWCNTs contain epoxy- carboxyl and phenolic groups. When the PUMWCNTs are in composites, these groups are masked with vibrations attributed to HZD and ZHP.

Main characteristics of the sorbents, which were determined in [29], are summarized in Table 1. The method of nitrogen adsorption-desorption was applied to porosity investigations. According to this method, specific surface area of PUMWCNTs was 230 m^2·g^{-1}, the volume of micro- and mesopores is 0.07 and 0.39 cm^3·g^{-1} respectively. Comparing with PUMWCNTs, HZD is characterized by higher microporosity and lower mesoporosity. Carbon additions to HZD increase the volume of mesopores and decrease microporosity. Lower micro- and mesoporosity as well as smaller value of surface area are attributed to ZHP as compared with PUMWCNTs. They increase these magnitudes for the ZHP-based composite.

HZD contains −OH functional groups, the point of zero charge of this material is about 7 (Fig. 1 *a*). The groups are mainly protonated in acidic region and dissociated in alkaline media releasing H$^+$. As a result, anions are preferably sorbed from acidic solutions. In alkaline media, mainly cations are sorbed. The pH value that corresponds to PZC can be found from the intersection of the curves 1 and 3 of Fig. 1 *a*. As shown, the PZC is realized in neutral media. Regarding PUMWCNTs, carboxyl groups are responsible for sorption in weakly acidic and neutral regions [41]. Additions of PUMWCNTs results in a shift of point of zero charge (PZC) to acidic region (intersection of curves 2 and 4). This is due to −COOH groups (their dissociation is about pH 3 for GO [41]). Moreover, the PUMWCNTs increase sorption capacity towards cation and depress anion sorption on HZD. The data are in agreement with the results reported in [37, 41] for the HZD-based composites containing oxidized graphene (the data are given for Pb^{2+} [37] and Na$^+$ [41] cations, HCrO$_4^-$ [37] and Cl$^-$ [41] anions).

As opposite to HZD, ZHP possesses cation exchange properties. The dependence of cation exchange capacity on the solution pH shows 2 semi-waves (Fig. 1 *b*). The first of them corresponds to −OPO$_3$H$_2$ groups, the next semi-wave is also related to them and additionally to (−O)$_2$PO$_2$H groups. As seen, the height of the second semi-wave is insufficiently higher. It means that dihydrophosphate groups dominate. The composite containing PUMWCNTs shows higher Na$^+$ sorption at pH > 2.3 comparing with one-component ZHP indicating the effect of PUMWCNTs additions (Fig. 1).

Table 1. Characteristics of sorbents

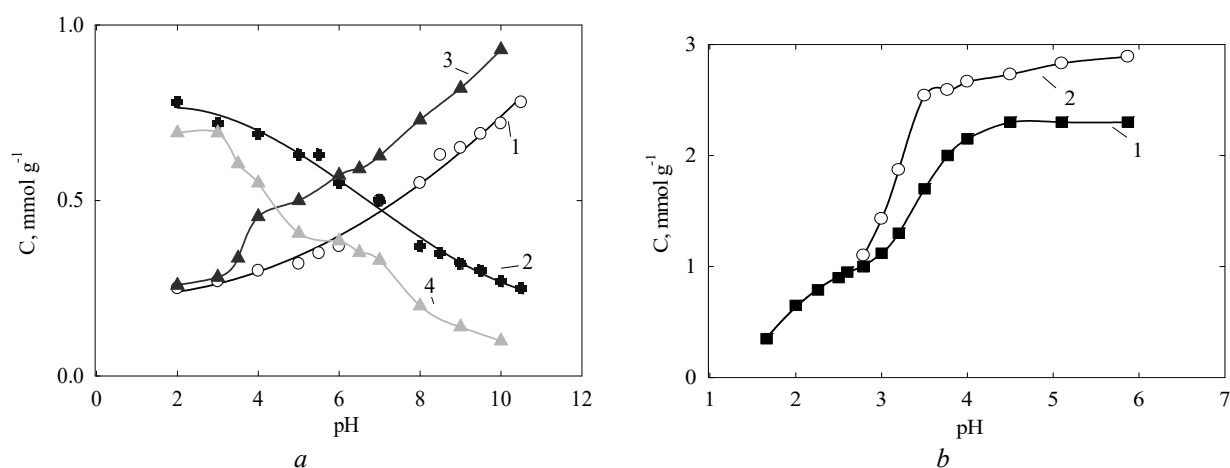| Sample	Size of dominated granules, mm	Pore volume, cm^{3}g^{-1}		Specific surface area, m^{2}g^{-1}	Total ion exchange capacity, mmol g^{-1}	
		micropores	mesopores		Na$^+$	Cl$^-$
HZD	0.40	0.11	0.02	338	1.10	1.15
HZD- PUMWCNTs	0.25	0.08	0.03	280	1.35	0.9
ZHP	0.80	0.06	0.02	165	2.30	–
ZHP- PUMWCNTs	0.30	0.07	0.03	190	2.95	–

Fig. 1. Dependence of sorption capacity of HZD (*a1*, *a3*), HZD-based composite (*a2*, *a4*), ZHP (*b1*) and its composite (*b2*) on the pH of NaCl solution passed through the column. Ions: Na$^+$ (*1, 2*) and Cl$^-$ (*3, 4*)

In general, the growth of total cation-exchange capacity is about 25 % due to only 2 % of the carbon modifier.

Sorption of U(VI) is affected by not only functional groups, but also by speciation of the ionic forms of uranyl cations. Regarding nitrate media, uranyl ions are in cationic or neutral forms: their state strongly depends on the solution acidity (Fig. 2). At low pH, UO$_2^{2+}$ cations dominate. Increasing pH results in formation of hydrolysis forms, mainly UO$_2$(OH)$^+$ (pH 4–8) and UO$_2$(OH)$_2$ (pH > 5) [43]. More complex diagram is given in [44], where additional forms are pointed. However, their content is rather small. The maximal amount of (UO$_2$)$_2$(OH)$_2^{2+}$ and (UO$_2$)$_4$(OH)$_7^+$ species is 15 % (pH 5) and 10 % (pH 7) respectively.

Let us consider the features of U(VI) sorption on one-component inorganic sorbents and their composites. Sorption isotherms were obtained at pH$_i$ 7 (here pH$_i$ is the initial pH value of the solution). As follows from Fig. 1, carbon additions improve sorption on ZHP and depress U(VI) uptake in the case of HZD. The isotherms obey Dubinin-Radushkevich (DR) model [45] (Fig. 3):

$$ln\,A = ln\,A_{DR} - \frac{R^2T^2}{E^2}\left[\,ln\left(1+1/C\right)\,\right]^2, \qquad (4)$$

where A_{DR} is the constant, E is the adsorption energy. These data are summarized in Table 2. As seen, the E values are within the interval of 8–16 kJ·mol⁻¹ indicating ion exchange mechanism of sorption. Higher A_{DR} constants were found for the composites containing PUMWCNTs than those for one-component sorbents. It should be stressed that the A_{DR} looks unrealistic comparing with the magnitudes of sorption capacity. It means, sorption from the solutions, the concentration of which is less than 0.1 mol·dm⁻³, involves so called "strong sorption centers", which are loaded first of all. Their size is comparable with that for hydrated uranyl ions.

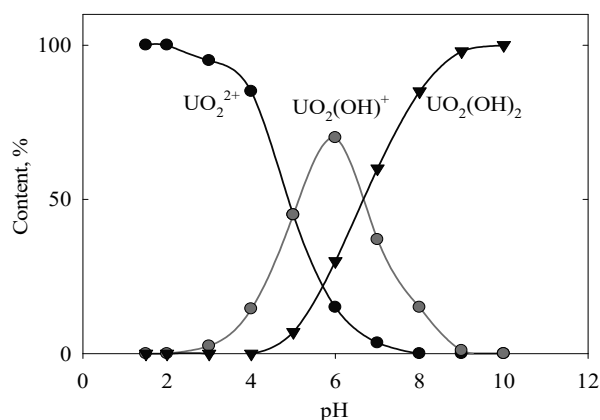**Fig. 2.** Uranium speciation in nitrate solution, $C_U = 0.2$ mmol·dm⁻³. The diagram was plotted according to [43]

When the sorption mechanism is ion exchange, double-charged hydrated ion is placed between two hydrated functional groups. For instance, a diameter of $UO_2(H_2O)_5^{2+}$ ions is 2.16 Å [46], radius of –OH groups (they are attributed to HZD, phosphate and carboxyl groups) is 1.58 Å, diameter of water molecules is 2.57 Å (H_2O molecules are near –OH functional groups). Thus, the optimal distance between –OH groups, which contain one water molecule, is about 10 Å. When ion exchange is accompanied by complex formation, –OH groups are in coordination environment of uranium-containing ion. According to literature data, U(VI) ions form complexes with functional groups of hydrated oxides [47] and hydrophosphates [48, 49] of multivalent metals. Complex formation with functional groups of GO has been also proved [17]. In this case, only the sizes of uranium-containing ion and –OH group are taken into consideration: the optimal distance between functional groups is ≈ 6.4 nm.
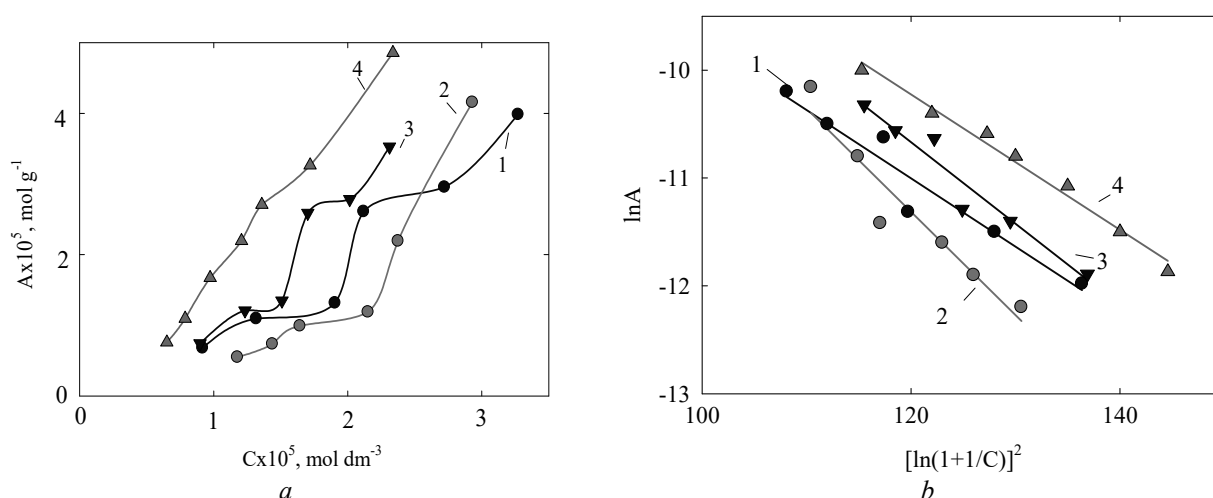

Fig. 3. Isotherms of U(VI) sorption on HZD (*1*), HZD- PUMWCNTs (*2*), ZHP (*3*), ZHP-PUMWCNTs (*4*): original data (*a*) and application of DR model (*b*). The initial pH of the solution was 7

Table 2. Application of DR models to sorption of U(VI) compounds (the *L* values are given for double charged functional groups in the case of ZHP and its composite)

Sample	A_{DR}, mol g^{-1}	E, kJ mol^{-1}	L, Å		
			pH 2	pH 4	pH 7
HZD	0.03	9.87	15.96	14.97	11.84
HZD- PUMWCNTs	1.18	8.01	14.53	10.16	8.45
ZHP	0.20	9.03	6.75	7.40	6.90
ZHP- PUMWCNTs	0.94	10.10	7.24	7.10	6.70

We can estimate the distance between dissociated functional groups according to the expression [50]:

$$L = \sqrt{\frac{qS}{AF}} \qquad (5)$$

where q is the charge of electron, A is the exchange capacity, S is the specific surface area, F is the Faraday constant. Regarding composites, the L value can be considered as an average magnitude. In the case of HZD and its composite, only cation-exchange groups were considered. When functional groups are double-charged ($-OPO_3H_2$), the distance between them can be calculated as $L = \sqrt{\frac{zqS}{AF}}$, where z is the charge number. The results are summarized in Table 2. Here the L magnitude was calculated.

Normally, the distance between cation-exchange groups becomes shorter, when pH increases. However, we observe the enlargement of the L value for ZHP for $-OPO_3H_2$ groups due to distorting effect of hydrophosphate groups. The optimal distance between functional groups is realized in the case of ZHP and its composite with PUMWCNTs.

Besides the E value, other confirmation of ion exchange mechanism is a change of the solution pH. Fig. 4 *a* illustrates the equilibrium pH (pH$_e$) as a function of initial value. A dashed straight line corresponds to the equality of initial and equilibrium pH. Location of the curves in the upper region of the plot indicates alkalization of the equilibrium solution. The data in the bottom region mean acidification. The coincidence of experimental data with the pH$_e$ − pH$_i$ curve points no change of pH. In the case of HZD, the pH$_e$− pH$_i$ curve is shifted to the upper region: the shift is most noticeable within the pH$_i$ interval of 3–5. No sufficient change of acidity has been found under higher initial pH.

Alkalization of equilibrium solution is more pronounced for HZD-based composite containing PUMWCNTs. Regarding HZD, alkalization at pH 3–5 is due to preferable anion sorption. No change of pH occurs in neutral media, where adsorption of colloidal UO$_2$(OH)$_2$ species is possible. At the same time, sorption isotherm, which was obtained at pH$_i$ 7, obeys Dubinin-Radushkevich (DR) model [29]. Within the framework of this model, the E constant is 9.6 kJ·mol^{-1} indicating ion exchange mechanism of U(VI) sorption on HZD. It means preferable sorption of ionic forms of U(VI). The equality of pH$_i$ and pH$_e$ within the interval of 6–8 is due to the equivalent exchange of cations (mainly UO$_2$(OH)$^{+}$ and Na^{+}) and anions (NO$_3^{-}$ and Ac^{-}). Regarding HZD-based composites, more intensive alkalization is observed. As known, graphene-like materials depress sorption of anions on HZD [37, 42]. Maximal possible concentration of acetate anions in equilibrium solution is 0.2 mmol·dm^{-3}, the pH of the sodium acetate solution is 7.5. Other reason of alkalization is interaction of carbon additions with O$_2$ dissolved in water: this causes formation of surface oxygen-containing groups [51].

The distance between the functional groups of HZD-based composite is in 1.5 times smaller comparing with HZD within the pH interval of 4–7 (see Table 2). As a result, the A_{DR} constant is almost in 40 times higher for the composite.

Regarding ZHP and its composite, acidification occurs at pH$_i$ 4–8 (ZHP) and 3–8 (ZHP-based composite). However, a change of the L value is insufficient. As a result, the A_{DR} magnitude for the composite is smaller only in 4.7 times in comparison with one-component ZHP.

Let us consider the effect of pH on sorption rate. Figs. 4 *b–d* illustrate the dependences of removal degree of U(VI) compounds on time. The data obtained for different initial pH are

given for ZHP-GO composite (Fig. 4 *b*). In the region of insufficient dissociation of phosphorus-containing and carboxyl groups (pH 2), the R_s value is minimal. Increasing pH improves sorption: R_s = 75–90 % within the pH interval of 3–8. Kinetic curves, which were obtained at pH 2 (functional groups of carbon additions are not dissociated) and pH 4 (functional groups of the modifier are dissociated), are also given in Figs. 4 *c, d* for all samples. In general, the

removal degree of U(VI) compounds reaches 50 % or more after 3 h. When dissociation of −COOH, −OH or phosphate groups is insufficient, PUMWCNTs depress U(VI) sorption. Under higher pH, involvement of carboxyl groups to sorption increases the removal degree of uranium in comparison with unmodified ZHP.
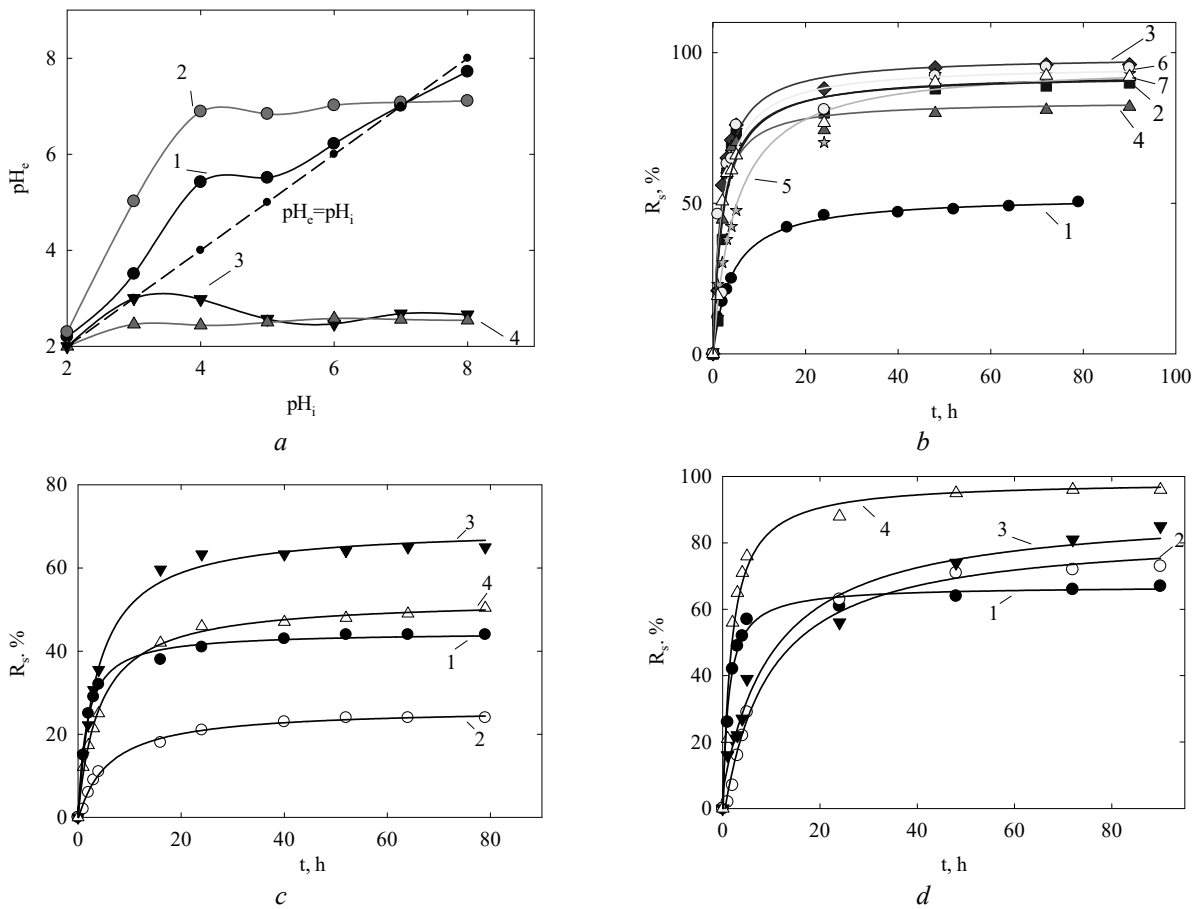

Fig. 4. Equilibrium pH of U(VI)-containing solution as a function of its initial pH (*a*), degree of U(VI) removal as a function of time (*b, c, d*). Sorbents: HZD (*a1, c1, d1*), HZD- PUMWCNTs (*a2, c2, d2*), ZHP (*a3, c3, d3*), ZHP- PUMWCNTs (*a4, b, c4, d4*). Initial pH: 2 (*b1, c*), 3 (*b2*), 4 (*b3, d*), 5 (*b4*), 6 (*b5*), 7 (*b6*), 8 (*b7*)

As found, the model of pseudo-second order proposed by Ho and McKay describes the results most adequately (Fig. 5 *a*) [52]:

$$\frac{t}{A} = \frac{1}{K_2 A_\infty^2} + \frac{1}{A_\infty} \cdot t , \qquad (6)$$

where K_2 are the rate constants, A_∞ is the sorption capacity under equilibrium conditions. The correlation coefficient was 0.98–0.99. The

concentration of U(VI) (0.1 mol·dm^{-3}) is much smaller than the content of functional groups of the sorbents. This gives a possibility to consider the interaction of sorbed ions with functional group as a reaction of "pseudo-order". The interaction can be formation of U(VI) complexes with functional groups of PUMWCNTs [17], HZD [47] and ZHP [48, 49].

The constants of eq. (6) are plotted in Fig. 5 *b–e*. As seen, theoretical A_∞ data are in a good agreement with experimental magnitudes. The HZD-based composite demonstrates higher sorption capacity at pH_i 3–4 comparing with one-component HZD. The growth of capacity is 20–50 % evidently due to the involvement of carboxyl groups to ion exchange. Under higher pH, HZD removes U(VI) practically completely. At the same time, sorption capacity of the composite containing PUMWCNTs is less under these conditions evidently due to more considerable alkalization of the equilibrium solution. As a result, the content of $UO_2(OH)^+$ ions, which are capable to exchange, decreases (see Fig. 2).
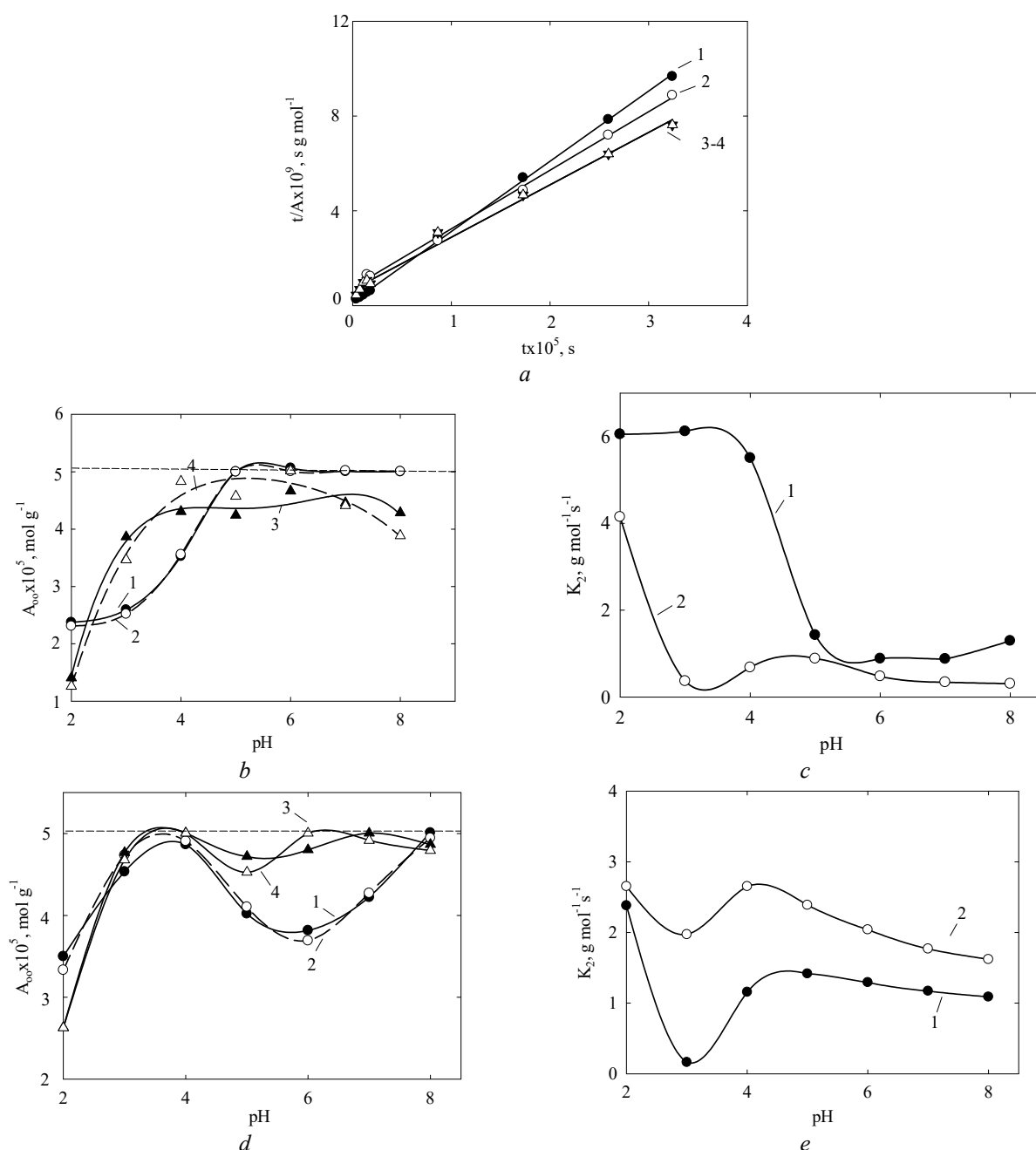

Fig. 5. Application of the model of pseudo-second order to sorption of U(VI) on HZD (*a1*, *b1-2*, *c1*), HZD-based composite (*a2*, *b3-4*, *c2*), ZHP (*a3*, *d1-2*, *e1*) and ZHP-based composite (*a4*, *d3-4*, *e2*). Dependences: the *t/A* value on time (*a*), A_∞ (*b*, *d*) and K_2 (*c*, *e*) constants on the initial pH of U(VI)-containing solution. A_∞ constant: theoretical (*b1*, *b3*, *d1*, *d3*) and experimental (*b2*, *b4*, *e2*, *e2*) values. Horizontal dashed lines indicate maximal possible sorption capacity taking into consideration the content of U(VI) in the solution
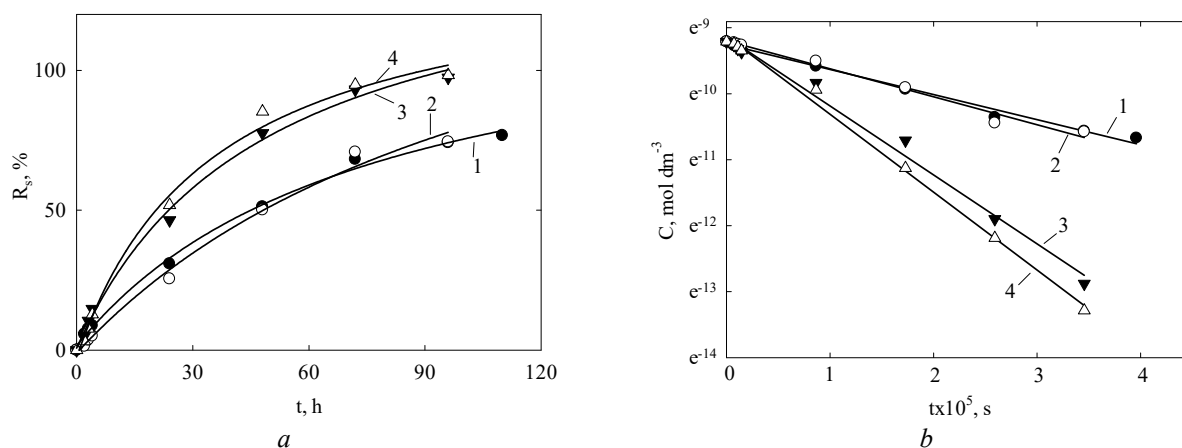
Fig. 6. Sorption of U(VI) cations from tap water on HZD (*1*), HZD-based composite (*2*), ZHP (*3*), ZHP-based composite (*4*): degree of U(VI) removal as a function of time (*a*), application of the model of first order (*b*)

The maxima of the $pH_e - pH_i$ curves for HZD and its composite can be explained by the transformation of $UO_2^{2+} \rightarrow UO_2(OH)^+$ (as a rule, double-charged ions are sorbed preferably). This transformation evidently causes slightly expressed maxima of the $A_\infty - pH_i$ curve for the composite.

In the case of ZHP-based composite, it shows an increase of sorption capacity up to 40% within the interval of pH_i 5–7 comparing with one-component ZHP. The effect of PUMWCNTs is not pronounced at pH 2–4.

It should be noted, that PUMWCNTs slow down sorption on HZD and accelerate it on ZHP (Figs. 5 *c, e*). It means the strongest interaction of U(VI)-containing cations with dihydrophosphate groups (the lowest K_2 value has been found namely for ZHP). The weakest interaction is for hydroxyl groups of HZD. Carboxyl groups of PUMWCNTs occupy the intermediate position. The extremes of the $K_2 - pH_i$ curves are due to sorption of different ionic forms of U(VI). In all cases, the strongest effect of PUMWCNTs on sorption rate is observed at pH 2–4, when dissociation of functional groups is depressed sufficiently.

When U(VI) cations are sorbed from the solution containing also Ca^{2+} and Mg^{2+} ions, sorption rate is described by the model of first order (Fig. 6) [53]:

$$\ln C = \ln C_i - K_1 t . \tag{7}$$

Here K_1 is the constant. It means, considerable part of functional groups is occupied by hardness ions. As a result, the amount of ions in the solution is not in great abundance in relation to functional groups, which are capable to react $UO_2(OH)^+$ (UO_2^{2+}) $\rightarrow H^+$, $UO_2(OH)^+$ (UO_2^{2+}) $\rightarrow Ca^{2+}$, $UO_2(OH)^+$ (UO_2^{2+}) $\rightarrow Mg^{2+}$. The interaction of sorbed ions with functional groups cannot be related to the reaction of "pseudo-order".

It should be noted that both ZHP and its composite remove U(VI) cations practically completely. In general, no sufficient effect of carbon additions on sorption capacity of HZD and ZHP has been found. However, the additions accelerate sorption: the K_1 value increases comparing with one-component sorbent (Table 3). In all cases, the C_i value is in a good agreement with experimental magnitude $(0.1 \text{ mmol·dm}^{-3})$.

At last, let us consider desorption of U(VI) compounds. As seen from Fig. 7 *a*, PUMWCNTs slightly deteriorate the regeneration of uranium-containing cations from HZD, when a 0.1 M HNO_3 solution was used. At the same time, the carbon addition improves ZHP regeneration. It is also valid for more concentrated acid (Fig. 7 *b*). These data are in agreements with Figs. 4 *c, e*. Indeed, the interaction of functional groups with sorbed ions in acidic solutions becomes weaker in the order: HZD > PUMWCNTs > ZHP.

In the case of a $NaHCO_3$ solution, the carbon addition depresses regeneration (Fig. 7 *c*). It means stronger interaction of U-containing ions with carboxyl groups (PUMWCNTs) in alkaline media comparing with hydroxyl (HZD) and phosphate groups (ZHP). It should be noted, that the regeneration occurs completely only for one-

component ZHP. Desorption can be complicated by the formation of insoluble $UO_2(OH)_2$ compound, which is precipitated inside granules.

Among different theoretical approaches, the model of particle diffusion has been found to be the most suitable. If the rate-determining stage of sorption is diffusion inside granules, it is valid for exchange of ions with different mobility [54]:

$$F = \left[1 - \exp(\pi^2(f_1(\alpha)t + f_2(\alpha)t^2 + f_3(\alpha)t^3)\right]^{0.5} \quad (8)$$

Here F is the degree of the process completion, α is the ratio of the self-diffusion coefficients of ions to be exchanged. As follows from (8),

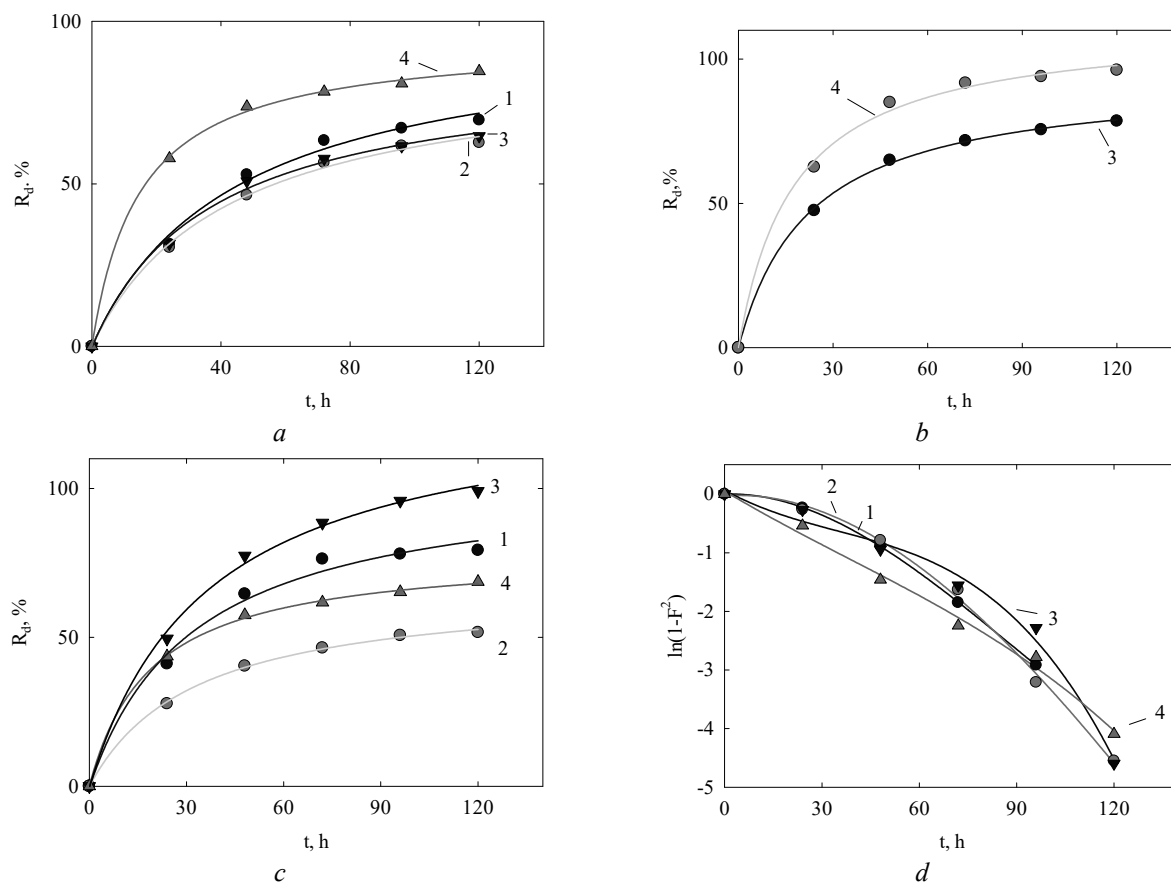$$\ln(1 - F^2) = \pi^2(f_1(\alpha)t + f_2(\alpha)t^2 + f_3(\alpha)t^3) \quad (9)$$

Fig. 7. Desorption of U(VI) from HZD (*1*), HZD-based composite (*2*), ZHP (*3*), ZHP-based composite (*4*): regeneration degree as a function of time (*a-c*), application of particle diffusion model (*d*) – dependence of $\ln(1-F^2)$ value on time. Solutions: 0.1 (*a, d*) and 1 M (*b*) HNO₃, 0.1 M NaHCO₃ (*c*)

Table 3. Application of the model of the first order to sorption of U(VI) from tap water

Sample	C_i, mmol dm^{-3}	$K_I \times 10^6$, s^{-1}
HZD	0.0989	3.81
HZD-PUMWCNTs	0.1042	4.23
ZHP	0.1103	10.45
ZHP-PUMWCNTs	0.1114	11.80

The $\ln(1 - F^2) - t$ plot is approximated with a cubic polynomial (Fig. 7 *d*) indicating particle diffusion as a rate-determining stage. The

effective diffusion coefficient (*D*), which is attributed to exchange of ions with different mobility, can be calculated as [54]:

$$D = 0.03 \frac{r^2}{t_{1/2}}, \qquad (10)$$

where r is the granule radius, $t_{1/2}$ is the half-time of exchange. The D and $t_{1/2}$ data are shown in Table 4 (a radius of dominated granules is given in Table 1). In all cases, the carbon addition slows down regeneration. However, the regeneration of ZHP-composite occurs practically completely in a 1 M HNO$_3$ solution

(HZD is partially dissolved under these conditions). Higher regeneration degree (comparing with ZHP) is achieved also in a 0.1 M HNO$_3$ solution.

In order to regenerate HZD-based composite with the acid solution, desorption has to be carried out twice. It should be noted that one-component ZHP can be regenerated with a NaHCO$_3$ solution practically completely.

Table 4. Application of the particle diffusion model to sorbent regeneration

Sorbents	1 M HNO$_3$			0.1 M HNO$_3$			0.1 M NaHCO$_3$		
	R_d, %	$t_{1/2}$, h	$D \times 10^{14}$, m^{2}s^{-1}	R_d, %	$t_{1/2}$, h	$D \times 10^{14}$, m^{2}s^{-1}	R_d, %	$t_{1/2}$, h	$D \times 10^{14}$, m^{2}s^{-1}
HZD	–	–	–	70	25.14	4.42	79	19.5	5.70
HZD- PUMWCNTs	–	–	–	62	22.3	1.95	52	20	2.17
ZHP	78	16	27.78	65	41	10.84	98	22	20.22
ZHP- PUMWCNTs	98	14	4.46	85	12	5.21	69	19	32.89

CONCLUSIONS

Comparing with one-component sorbents, hybrid composite from HZD modified with PUMWCNTs shows higher sorption capacity towards U(VI)-containing ions in the media, the initial pH of which is 3–4. ZHP-based composite is effective within the pH interval of 5–7. Comparing with polymer ion-exchangers, for instance FIBAN fibrous materials [55, 56], the sorption rate on inorganic ion-exchangers is slower. However, the carbon additions accelerate sorption on ZHP from one-component solution. Both sorption capacity and sorption rate are affected by dissociation degree of functional groups on the one hand, and also by the speciation of U(VI) ions on the other hand. In all

cases, the PUMWCNTs accelerate sorption from the solutions, which contain hardness ions. The sorbents can be regenerated with a 0.1 M HNO$_3$ solution: no sufficient deceleration of HZD regeneration due to PUMWCNTs is observed. The composite has to be regenerated 2 times in order to achieve complete desorption degree. The most suitable solution for U(VI) desorption from ZHP-PUMWCNTs composite is a 1 M HNO$_3$ solution.

The composites can be used for U(VI) removal from radioactive liquid wastes, where polymer ion exchangers are destroyed. ZHP-based composite can be also applied to removal of uranium from water, which contains also hardness ions.

Сорбція сполук U(VI) неорганічними композитами, що містять частково розкриті вуглецеві нанотрубки

О.В. Перлова, І.С. Іванова, Ю.С. Дзязько, М.О. Данилов, І.А. Русецький, Г.Я. Колбасов

Одеський національний університет імені І.І. Мечникова
вул. Дворянська, 2, Одеса, 65082, Україна, olga_perlova@onu.edu.ua
Інститут загальної та неорганічної хімії ім. В.І. Вернадського Національної академії наук України
просп. Академіка Палладіна, 32/34, Київ, 03142, Україна

На відміну від іонообмінних смол, неорганічні сорбенти мають високу селективність відносно іонів важких металів та стійкість до іонізуючих випромінювань. Однак сорбція на цих матеріалах досить повільна. Крім того, їхня сорбційна ємність суттєво залежить від pH розчинів. З метою покращення сорбційних властивостей неорганічних сорбентів одержують композити, що містять вуглецеві матеріали. Встановлено закономірності сорбції сполук урану(VI) з низькоконцентрованих водних розчинів (до 0.1 ммоль дм$^{-3}$ урану) на гідратованому діоксиді цирконію і гідрофосфаті цирконію, а також на даних сорбентах, модифікованих частково розкритими вуглецевими нанотрубками. Отримано і проаналізовано ізотерми сорбції. Встановлено, що вони описуються моделлю Дубініна-Радушкевича. Запропоновано механізм сорбції (іонний обмін) із зазначенням сорбційних центрів, розмір яких є порівняним з розмірами іонів, що сорбуються. Показано, що при pH розчинів 3–4 добавки вуглецю збільшують сорбційну здатність гідратованого діоксиду цирконію, а при pH 5–7 – гідрофосфату цирконію. За цих умов уранвмісні катіони практично повністю виділяються з однокомпонентних розчинів. Під час вилучення урану з таких розчинів швидкість сорбції підпорядковується кінетичній моделі псевдодругого порядку, причому частково розкриті вуглецеві нанотрубки уповільнюють сорбцію на діоксиді цирконію і прискорюють її на гідрофосфаті цирконію. Проаналізовано залежність констант кінетичного рівняння псевдодругого порядку від pH урановмісних розчинів. Сорбція урану з розчинів, що містять також іони Ca^{2+} і Mg^{2+}, описується кінетичним рівнянням першого порядку. Регенерація проводилася з використанням розчинів HNO$_3$ і NaHCO$_3$. Встановлено, що швидкість десорбції урану з поверхні досліджених сорбентів лімітується швидкістю внутрішньої дифузії. Показано, що однокомпонентний гідрофосфат цирконію практично повністю регенерується розчином NaHCO$_3$. Найкращим реагентом для десорбції U(VI) з композиту на основі гідрофосфату цирконію є 1 M розчин HNO$_3$.

Ключові слова: сорбція, сполуки урану(VI), гідратований діоксид цирконію, гідрофосфат цирконію, частково розкриті вуглецеві нанотрубки

REFERENCES

1. Hoover J., Gonzales M., Shuey C., Barney Y., Lewis J. Elevated arsenic and uranium concentrations in unregulated water sources on the navajo nation, USA. *Exposure Health.* 2017. **9**(2): 113.
2. Bjørklund G., Semenova Yu., Pivina L., Dadar M., Rahman M., Aaseth J., Chirumbolo S. Uranium in drinking water: a public health threat. *Arch. Toxicol.* 2020. **94**(5): 1551.
3. Hakonson-Hayes A.C., Fresquez P., Whicker F. Assessing potential risks from exposure to natural uranium in well water. *J. Environ. Radioact.* 2002. **59**(1): 29.
4. Bhalara P.D., Punetha D., Balasubramanian K. A review of potential remediation techniques for uranium(VI) ion retrieval from contaminated aqueous environment. *J. Environ. Chem. Eng.* 2014. **2**(3): 1621.
5. Basu H., Pimple M.V., Saha S., Patel A., Dansena C., Singhal R.K. TiO$_2$ microsphere impregnated alginate: a novel hybrid sorbent for uranium removal from aquatic bodies. *New J. Chem.* 2020. **44**(10): 3950.
6. Saha S., Basu H., Rout S., Pimple M.V., Signal R.K. Nano-hydroxyapatite coated activated carbon impregnated alginate: A new hybrid sorbent for uranium removal from potable water. *J. Environ. Chem. Eng.* 2020. **8**(4): 103999.
7. Galhoum A.A., Eisa W.H., IbrahimEl-Tantawy El-Sayed I.E.T., Tolba A.A., Shalaby Z.M., Mohamady S.A., Muhammad S.S., Hussien S.S., Akashi T., Guiba E. A new route for manufacturing poly(aminophosphonic)-functionalized poly(glycidyl methacrylate)-magnetic nanocomposite - Application to uranium sorption from ore leachate. *Environ. Pollut.* 2020. **264**: 114797.
8. Youssef W.M., Sheikh A.S.E., Ahmed S.H., Morsy A. Polyacrylic acid/polyaniline composite as efficient adsorbent for uranium extraction from nuclear industrial effluent. *J. Radioanal. Nucl. Chem.* 2020. **324**: 87.

9. Shelar-Lohar G., Joshi S. Comparative study of uranium and thorium metal ion adsorption by gum ghatti grafted poly(acrylamide) copolymer composites. *RSC Adv.* 2019. **9**(70): 41326.

10. Moghaddam R.H., Dadfarnia S., Shabani A.M.H., Tavakol M. Synthesis of composite hydrogel of glutamic acid, gum tragacanth, and anionic polyacrylamide by electron beam irradiation for uranium(VI) removal from aqueous samples: Equilibrium, kinetics, and thermodynamic studies. *Carbohydr. Polym.* 2019. **206**: 352.

11. Liu J., Zhao C., Yuan G., Dong Y., Yang J., Li F., Liao J., Yang Y., Liu N. Adsorption of U(VI) on a chitosan/polyaniline composite in the presence of Ca/Mg-U(VI)-CO₃ complexes. *Hydrometallurgy*. 2018. **175**: 300.

12. Pan D., Fan Q., Fan F., Tang Y., Zhang Y., Wu W. Removal of uranium contaminant from aqueous solution by chitosan@attapulgite composite. *Sep. Purif. Technol.* 2017. **177**: 86.

13. Haggag E.S.A., Abdelsamad A.A., Masoud A.M. Potentiality of uranium extraction from acidic leach liquor by polyacrylamide-acrylic acid titanium silicate composite adsorbent. *Int. J. Environ. Anal. Chem.* 2020. **100**(2): 204.

14. Dzyazko Yu.S., Perlova O.V., Perlova N.A., Volfkovich Yu.M., Sosenkin V.E., Trachevskii V.V., Sazonova V.F., Palchik A.V. Composite cation-exchange resins containing zirconium hydrophosphate for purification of water from U(VI) cations. *Desalin. Water Treat*. 2017. **69**: 142.

15. Perlova N., Dzyazko Y., Perlova O., Palchik A., Sazonova V. Formation of Zirconium Hydrophosphate Nanoparticles and Their Effect on Sorption of Uranyl Cations. *Nanoscale Res. Lett.* 2017. **12**: 209.

16. Perlova O., Dzyazko Yu., Halutska I., Perlova N., Palchik A. Anion exchange resin modified with nanoparticles of hydrated zirconium dioxide for sorption of soluble U(VI) compounds. *Springer Proc. Phys*. 2018. **210**: 3.

17. Li Z., Chen F., Yuan L., Liu Y., Zhao Y., Chai Z., Shi W. Uranium(VI) adsorption on graphene oxide nanosheets from aqueous solutions. *Chem. Eng. J.* 2012. **210**: 539.

18. Wang C.L., Li Y., Liu C.L. Sorption of uranium from aqueous solutions with graphene oxide. *J. Radioanal. Nucl. Chem.* 2015. **304**(3): 1017.

19. Zhao G.X., Wen T., Yang X., Yang S.B., Liao J.L., Hu J., Shao D.D., Wang X.K. Preconcentration of U(VI) ions on few-layered graphene oxide nanosheets from aqueous solutions. *Dalton Trans.* 2012. **41**(20): 6182.

20. Sun Y., Yang S., Sheng G., Guo Z., Wang X. The removal of U(VI) from aqueous solution by oxidized multiwalled carbon nanotubes. *J. Environ. Radioact.* 2012. **105**: 40.

21. Wang Y., Wang Z., Gu Z., Yang J., Liao J., Yang Y., Liu N. Tang J. Uranium(VI) sorption on graphene oxide nanoribbons derived from unzipping of multiwalled carbon nanotubes. *J. Radioanal. Nucl. Chem*. 2015. **304**: 1329.

22. Gu Z., Wang Y., Tang J., Yang J., Liao J., Yang Y., Liu N. The removal of uranium(VI) from aqueous solution by graphene oxide–carbon nanotubes hybrid aerogels. *J. Radioanal. Nucl. Chem.* 2015. **303**: 1835.

23. Li S., Yang P., Liu X., Zhang J., Xie W., Wang C. Graphene oxide based dopamine mussel-like cross-linked polyethylene imine nanocomposite coating with enhanced hexavalent uranium adsorption. *J. Mater. Chem. A.* 2019. **7**(28): 16902.

24. Song S., Wang K., Zhang Y., Wang Y., Zhang C., Wang X., Zhang R., Chen J., Wen T., Wang X. Self-assembly of graphene oxide/PEDOT:PSS nanocomposite as a novel adsorbent for uranium immobilization from wastewater. *Environ. Pollut.* 2019. **250**: 196.

25. Liu H., Zhou Y., Yang Y., Zou K., Wu R., Xia K., Xie S. Synthesis of polyethylenimine/graphene oxide for the adsorption of U(VI) from aqueous solution. *Appl. Surf. Sci.* 2019. **471**: 88.

26. Peng W., Huang G., Yang S., Guo C., Shi J. Performance of biopolymer/graphene oxide gels for the effective adsorption of U (VI) from aqueous solution. *J. Radioanal. Nucl. Chem.* 2019. **322**: 861.

27. Radhakrishnan A., Nahi J., Beena B. Synthesis and characterization of multi-carboxyl functionalized nanocellulose/graphene oxide-zinc oxide composite for the adsorption of uranium(VI) from aqueous. *Mater. Today: Proc.* 2020. https://doi.org/10.1016/j.matpr.2020.05.249

28. Hu X., Wang Y., Yang J.Q., Li Y., Wu P., Zhang H., Yuan D., Liu Y., Wu Z., Liu Z. Synthesis of graphene oxide nanoribbons/chitosan composite membranes for the removal of uranium from aqueous solutions. *Front. Chem. Sci. Eng.* 2020. **14**: 1029.

29. Perlova O.V., Dzyazko Yu.S., Palchik A.V., Ivanova I.S., Perlova N.O., Danilov M.O., Rusetskii I.A., Kolbasov G.Ya., Dzyazko A.G. Composites based on zirconium dioxide and zirconium hydrophosphate containing graphene-like additions for removal of U(VI) compounds from water. *Appl. Nanosci.* 2020. **10**: 4591.

30. Yang A., Zhu Y., Huang C.P. Facile preparation and adsorption performance of graphene oxide-manganese oxide composite for uranium. *Sci. Rep.* 2018. **8**: 9058.

31. Ali A.H. Potentiality of zirconium phosphate synsized from zircon mineral for uptaking uranium. *Sep. Sci. Technol.* 2018. **53**(14): 2284.

32. Tatarchuk T., Shyichuk A., Mironyuk I., Naushad M. A review on removal of uranium(VI) ions using titanium dioxide based sorbents. *J. Molec. Liq.* 2019. **293**: 111563.

33. Kapnisti M., Noli F., Misaelides P., Vourlias G., Karfaridis D., Hatzidimitriou A. Enhanced sorption capacities for lead and uranium using titanium phosphates; sorption, kinetics, equilibrium studies and mechanism implication. *Chem. Eng. J.* 2018. **342**: 184.

34. Wang Y., Zeng D., Dai Y., Fang C., Han X., Zhang Z., Cao X., Liu Y. The Adsorptive Ability of 3D Flower-Like Titanium Phosphate for U(VI) in Aqueous Solution. *Water, Air, Soil Pollut.* 2020. **231**: 464.

35. Mu W., Yu Q., Zhang R., Li X., Hu R., He Y., Wei H., Jian Y., Yang Y. Controlled fabrication of flower-like α-zirconium phosphate for the efficient removal of radioactive strontium from acidic nuclear wastewater. *J. Mater. Chem. A.* 2017. **5**(46): 24388.

36. Dzyazko Yu.S., Ogenko V.M., Shteinberg L.Ya., Bildyukevich A.V., Yatsenko T.V. Composite adsorbents including oxidized graphene: effect of composition on mechanical durability and adsorption of pesticides. *Him. Fiz. Tehnol. Poverhni.* 2019. **10**(4): 432.

37. Dzyazko Yu.S., Ogenko V.M., Volfkovich Yu.M., Sosenkin V.E., Maltseva T.V., Yatsenko T.V., Kudelko K.O. Composite consisting of hydrated zirconium dioxide and graphene oxide for removal of organic and inorganic components from water. *Him. Fiz. Tehnol. Poverhni.* 2018. **9**(4): 417.

38. Danilov M.O., Rusetskii I.A., Slobodyanyuk I.A., Dovbeshko G.I., Kolbasov G.Y., Strubov Y.Y. Synthesis, properties, and application of graphene-based materials obtained from carbon nanotubes and acetylene black. *Ukr. J. Phys.* 2016. **7**(1): 3.

39. Dzyazko Y.S., Volfkovich Y.M., Sosenkin V.E., Nikolskaya N.F., Gomza Yu.P. Composite inorganic membranes containing nanoparticles of hydrated zirconium dioxide for electrodialytic separation. *Nanoscale Res. Lett.* 2014. **9**(1): 271.

40. Kadam B.V., Maiti B., Sathe R.M. Selective spectrophotometric method for the determination of uranium(VI). *Analyst.* 1981. **106**(1263): 724.

41. Szabo T., Tombacz E., Illes E., Dekany I. Enhanced acidity and pH-dependent surface charge characterization of successively oxidized graphite oxides. *Carbon.* 2006. **44**(3): 537.

42. Myronchuk V., Zmievskii Y., Dzyazko Y., Rozhdestveska L., Zakharov V., Bildyukevich A. Electrodialytic whey demineralization involving polymer-inorganic membranes, anion exchange resin and graphene-containing composite. *Acta Periodica Technologica.* 2019. **50**: 163.

43. Nazarenko V.A., Antonovich V.P., Nevskaya E.M. *Hydrolysis of metal ions in diluted solutions.* (Moscow: Atomizdat, 1964). [in Russian].

44. Gapel G., Cormelis R., Caruso J.A., Crews H., Heumann K.G. *Handbook of elemental speciation II. Species in the environment, food, medicine and occupational health.* (Chichester, UK: Wiley, 2005).

45. Rieman W., Walton H. *Ion Exchange in Analytical Chemistry.* (Oxford, New York, Toronto, Sydney, Braunschweig: Pergamon Press, 1970).

46. Persson I. Hydrated metal ions in aqueous solution: How regular are their structures? *Pure Appl. Chem.* 2010. **82**(10): 1901.

47. Maya L. Sorbed uranium(VI) species on hydrous titania, zirconia, and silica gel. *Radiochim. Acta.* 1981. **31**(3–4): 147.

48. Almazan-Torres M.G., Drot R., Mercier-Bion F., Catalette H. Den Auwer C., Simoni E. Surface complexation modeling of uranium(VI) sorbed onto zirconium oxophosphate versus temperature: Thermodynamic and structural approaches. *J. Colloid Interface Sci.* 2008. **323**(1): 42.

49. Zakutevskyy O.I., Psareva T.S., Strelko V.V. Sorption of U(VI) ions on sol-gel-synthesized amorphous spherically granulated titanium phosphates, *Russ. J. Appl. Chem.* 2012. **85**(9): 1366.

50. Volfkovich Y.M. Influence of the electric double layer on the internal interface in an ion exchanger on its electrochemical and sorption properties. *Soviet Electrochem.* 1984. **20**(5): 621.

51. Kinoshita K. *Carbon: Electrochemical and Physicochemical Properties.* (New York: Wiley, 1988).

52. Ho Y.S., McKay G. Pseudo-second order model for sorption processes. *Process Biochem.* 1999. **34**(5): 451.

53. Rai G. *Chemical kinetics.* (New Delhi: Goel Publishing House, 2010).

54. Helfferich F. *Ion Exchange.* (New York: Dover, 1995).

55. Sazonova V.F., Perlova O.V., Perlova N.A., Polikarpov A.P. *Colloid J.* 2017. **79**(2): 270.

56. Perlova O.V., Sazonova V.F., Perlova N.A., Polikarpov A.P. Sorption of uranium(VI) compounds by fibrous cation exchanger FIBAN K-1 from acidic media. *Water: Chemistry and Ecology.* 2016. **3**: 53. [in Russian].