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Features of equilibrium uranium sorption on the fibrous carboxylated sorbent FORPAN from carbonate-containing solutions simulating seawater

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Abstract

Objectives: The purpose of this work is to study and identify the features of the equilibrium sorption of uranium from carbonate-containing solutions on a fibrous sorbent obtained (at the St. Petersburg Institute of Textile and Light Industry named after S. M. Kirov) by synthesizing carboxylated polyacrylonitrile (PAN) fiber with formaldehyde, with the common name of FORPAN.

Experimental: The equilibrium sorption of uranium by the carboxylated fibrous sorbent FORPAN from carbonate-containing solutions simulating seawater was studied in the range of initial concentrations ($3.36 \cdot 10^{-5}$ – $7.13 \cdot 10^{-4}$ mol/l) and temperatures (293–338 K) at pH = 7.85. It was found that during the contact of the fiber with the carbonate-containing uranium solution, a sharp decrease in the pH of the solution and the cleavage of the tricarboxylate uranyl complex occur due to the protolysis of carboxyl groups. Based on mathematical processing (using the least squares method) of the dependences of the equilibrium distribution coefficients of uranium (ml/g) on the equilibrium concentration of uranium in solution (mol/ml) at different temperatures, a generalized equation was obtained that made it possible to calculate the capacity of the fiber for uranium (mol/g) during its sorption from model solutions prepared based on Caspian Sea water in the range of studied concentrations and temperatures, as well as to calculate the capacity of the FORPAN sorbent relative to uranium in Caspian Sea water ($1.22 \cdot 10^{-5}$ mol/g = $2.9 \cdot 10^{-3}$ g/g) and the distribution coefficient of uranium in seawater ($1.6 \cdot 10^4$ ml/g) at $T = 293.3$ K.

Conclusions: Based on the conducted studies of the features of equilibrium sorption of uranium from model carbonate-containing solutions and the results obtained, FORPAN fiber can be recommended for the extraction uranium from dilute carbonate-containing solutions of natural waters, in particular from Caspian Sea water, with a uranium content of $2.5 \cdot 10^{-6}$ mol/l, in the range of relatively low temperatures of 293–307 K.

Keywords: Sorption, Uranium, Fibrous sorbent, Carbonate-containing solutions, Thermodynamics

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1. Introduction

Ocean water is a virtually inexhaustible source of many elements, particularly uranium, copper, and cobalt, whose oceanic abundances are estimated at $4.2 \cdot 10^9$, $4.1 \cdot 10^9$, and $7.6 \cdot 10^7$ tons, respectively. Ocean water is promising not only for its inexhaustibility but also for its technological feasibility – its constant composition and potential for comprehensive use.

Attention to the ocean as a source of uranium is driven by the depletion of terrestrial reserves and the intensive development of nuclear energy. Given the trace concentrations of uranium in seawater ($\sim 3 \mu\text{g/l}$) against the backdrop of its highly mineralized, complex salt composition, the need to select selective sorbents using highly effective methods for concentrating this element is of undeniable practical interest [1, 2]. Sorption methods are currently showing promise [3]. The authors used FIBAN C-1 (cation exchanger) and FIBAN AC-22V (aminocarboxyl polyampholyte) fiber ion exchangers under dynamic settings to determine various features of the sorption, extraction, and concentration of uranyl ions from model nitrate solutions. It was demonstrated that a high uranium sorption rate is coupled with effective uranium (VI) extraction and concentration. The following quantitative aspects of uranium sorption under dynamic conditions were computed: sorption rate, uranium content in the sorbent phase, dynamic exchange capacity, and overall dynamic exchange capacity.

The possibility of using many types of sorbents for these purposes has been investigated so far: natural and synthetic ion exchangers, complexing, modified, composite, and others. The efficiency of radionuclide extraction depends on the sorbent's selectivity in the presence of inorganic and organic components contained in aqueous media [4–7]. Thus, the authors [4] synthesized a new sorbent, 4XADMnO (Amberlite XAD-4 modified with manganese dioxide nanoparticles), to improve the sorption of UO_2^{2+} ions in aqueous media from low-level radioactive waste and characterized it using EDX, XRD, and FTIR analysis. It was established that the developed sorbent was successfully used for the sorption of UO_2^{2+} ions for safety purposes.

By adding hydrated zirconium dioxide to a gel-like anion-exchange resin, the authors [6]

created organic-inorganic sorbents. Throughout the experiment, the solvent's surface tension, temperature, and solution concentration were all changed. Particles of different sizes are more common in the polymer matrix depending on the production technique. Research on the sorption of anionic uranyl complexes revealed that pseudo-first- or pseudo-second-order chemical reaction models describe the sorption rate. Compared to the original resin, samples altered with tiny particles ($< 300 \text{ nm}$) show a greater sorption rate. Particle size reduction makes it easier for the sorbents to regenerate chemically.

When selecting a sorbent, it is necessary to consider: high sorption capacity and selectivity; good kinetic and mechanical properties in multiple sorption-regeneration cycles; and, most importantly, the sorbent's low cost.

According to numerous studies, sorbents based on metal oxides meet most of these requirements. In particular, titanium dioxide, as a sorbent, is distinguished by its radiation and chemical stability in acidic and alkaline solutions, and as an ion exchanger, it exhibits a satisfactory exchange rate, which is important when working in a column configuration. Hydrated titanium dioxide has been studied in considerable detail for a number of years as a sorbent for extracting uranium from seawater. It should be noted that mixed titanium oxide sorbents exhibit the best sorption characteristics, due to the introduction of an inert additive in the form of zirconium oxide (6 %) and others during synthesis, which has a significant impact on the change in the sorption properties of titanium dioxide (almost doubling its kinetic and equilibrium characteristics, significantly altering all energy parameters of the sorption process [8–12]).

For the selective concentration of radionuclides from neutral natural waters, complexing sorbents with phosphoric acid, amidoxime, hydroxamic, iminodiacetate, and other groups are also used, which are capable of binding radionuclides into corresponding complex compounds and effectively isolating them from natural waters with a high salt content and in the presence of natural ligands [13].

Currently, the sorption extraction of metals from solutions using fibrous sorbents, characterized by good kinetic properties and high element distribution coefficients during

sorption, allows them to be successfully used for the concentration and separation of trace elements from natural waters and other solutions, under both static and dynamic conditions [14]. The developed surface, providing good sorption and kinetic properties of fibrous sorbents, distinguishes them from granular sorbents, since they are convenient for practical use both in static conditions (a small amount of sorbent is required, especially when there is no need to regenerate the sorbent), and in a dynamic, columnar version, for concentrating microelements from large volumes of solutions, when after sorption the elements are usually eluted and then analyzed [15, 16].

Neutron activation sorption (NAS) is performed directly on the sorbent without elution or degradation, which increases the speed of the method and reduces contamination by foreign impurities.

The selection of the sorbent and sorption conditions ensures the separation of trace elements from large quantities of macroelements. Separation of elements using fibrous sorbents is based on differences in the sorbent's selectivity for metals, which in turn is due to differences in the stability of the complexes formed by metals in the sorbent phase.

The selectivity of a sorbent is determined primarily by the nature of its functional and analytical groups. The selective properties of sorbents are characterized by selectivity series. The presence of carboxyl groups determines the complexing properties of the ion exchanger. Metal ions such as Zn, Cd, Pb, Cu, U, and others form complexes of varying strength with acetate ions. For example, the strength of monoacetate complexes increases in the following order: $Zn^{2+} < Cd^{2+} < Pb^{2+} < Cu^{2+} < UO_2^{2+}$. According to Gregor, the strength of polyacrylate complexes increases in approximately the same direction. Interestingly, the strength of sulfate complexes of these metals is virtually identical.

A visual expression of sorbent selectivity is the dependence of element distribution coefficients on pH and component concentration.

The presence of complexing groups in ion-exchange fibers leads to an increased affinity of these ion exchangers for metal ions; such compounds exhibit specific properties and are highly selective for individual metal ions.

The most effective uranium sorbents known to date contain amidoxime (AO) or imide-dioxime (H_3JDO) functional groups capable of binding uranyl ions (UO_2^{2+}). This is the form in which uranium is most commonly found in seawater. Polyacrylonitrile (PAN) fibers are grafted with an H_3JDO group, which is selective for the uranyl ion. The adsorption capacity of such modified polymers can exceed 4 grams of uranium per gram of adsorbent [17]. Although the use of functional AO groups has significantly improved uranium extraction efficiency and is considered the most promising approach for extracting uranium from seawater, implementing these functional AO groups is a complex and expensive process. Furthermore, the effectiveness of these groups is significantly impacted by exposure to other ions. Furthermore, since these adsorbents are primarily available as powders or nanoparticles, their regeneration after uranium extraction is difficult.

Not all known uranium-adsorbing materials can be used in the industrial extraction of uranium from seawater, as they often bind more strongly to vanadium ions (VO^{5+}), the concentration of which in water exceeds the uranium content [18]. In order to comprehend the remarkably strong and selective vanadium binding by polyamidoximes, the authors of this research provided a thorough investigation combining *ab initio* modeling with thermochemical titration and XAFS spectroscopy. The adsorbent's cyclic imidodioxime group creates a special nonoxide complex called V^{5+} , which has the highest stability constant yet seen for V^{5+} species, even though the open-chain amidoxime functional groups do not bind vanadium. Vanadium is only bound by imidodioximes, according to XAFS data of the adsorbents after they were submerged in seawater. The observed fundamental results, according to the scientists, can help explain the widespread accumulation of vanadium in certain marine animals and offer suggestions for additional optimization of the selectivity of amidoxime-based sorbent materials. This is very expensive because it is necessary to separate the uranium from the vanadium after sorption.

Researchers from the Oak Ridge National Laboratory and the Lawrence Berkeley National Laboratory, led by A. Ivanov and Jan Arnold, turned their attention to siderophores (iron-transport

proteins). This class of chelating compounds with nitrogen and oxygen donor groups, used by some species of bacteria and fungi as reservoirs for sequestering excess iron, is considered a potential ligand for binding *f*-elements, which include uranium [19]. The authors synthesized an artificial siderophore: bis[hydroxy(methyl) amino]-4-mordoline-1,3-triazine (H_2BHT). They then modified the ethylene-acrylic acid copolymer by binding this ligand to it. Despite the relatively low capacity of the material, 0.1 g of uranium per 1 g of sorbent, the vanadium content did not affect uranium sorption, indicating that H_2BHT is more selective for uranium ions than for vanadium ions. Further work in this direction is underway [20–22]. In order to extract uranium from seawater, the authors [20] thoroughly reviewed materials developed between 2000 and 2016. They focused on recent advancements in the field of inorganic materials, polymeric adsorbents, and related research on amidoxime, and nanostructured materials like metal–organic frameworks, porous organic polymers, and mesoporous carbon materials. The difficulties of doing accurate and repeatable uranium adsorption tests were also covered in the article, along with the standardization of parameters required to guarantee accurate comparison of various adsorbents. The history of uranium extraction from saltwater and current research in this field are briefly described in Review [22]. The coordination chemistry of the project is described in full in the paper, along with the functional groups found on common polymer sorbents and their low-molecular-weight analogs. Uranium selectivity in comparison to other metals, especially vanadium, is still difficult to achieve, and future solutions will need techniques for both quantitative evaluation of bond strength and selectivity.

Among the most recent achievements, the works of the authors [23–25] are noteworthy. The scientists have developed a series of new porous materials with specific pores and functional groups (hydroxyl, carboxyl, amidoxime, phosphate, etc.) that are highly selective for uranium. The active groups, when coordinated in these porous materials, form specific sites for binding uranium, which, compared to other ions, have a higher affinity and selectivity for uranyl ions (UO_2^{2+}).

Along with studies of the properties of traditional sorbents, adsorption-photocatalytic and adsorption-electrocatalytic materials are being studied, containing both specific adsorption sites and photocatalytic or electrocatalytic fragments in their frameworks. These innovative strategies enable the conversion of uranyl ions into sorbable solid products (such as UO_2 or $Na_2O(UO_3 \cdot H_2O)$), which increases the highly efficient extraction of uranium, as well as their resistance to biofouling. The development of such porous materials represents a breakthrough in the field of selective uranium extraction from seawater [23].

Since the efficiency of uranium extraction depends on the presence of active adsorption sites in adsorbents, maximizing the utilization factor of binding sites is necessary to improve the sorption capacity. For this purpose, microredox reactors operating on the principle of $Cu(I) \rightarrow Cu(II)$ conversion are introduced into the sorbent (containing both amidoxime and carboxyl groups), which activates the regeneration of inactivated binding sites. This sorbent has a high adsorption capacity of 962.4 mg-U/gAds, excellent ability to resist fouling, and excellent uranium absorption (14.62 mg-U/gAds) from natural seawater in 56 days. These indicators allow us to consider the sorbent the best among high-performance materials for uranium sorption from seawater [24].

An effective sorbent for uranium extraction from seawater has been synthesized by introducing amidoxime groups (AO) and grafted polyamides (PA) onto the Ti_3C_2 surface using a simple, one-step hydrothermal method. The absorption of $[UO_2(CO_3)_3]^{4-}$ by the Ti_3C_2 -AO-PA sorbent is characterized by fast reaction kinetics (approximately 120 min), excellent sorption capacity (81.1 mg/g at pH 8.3), significantly high selectivity (32.8 mg-U/gAds), and excellent antibacterial properties against contamination (92.8 %).

X-ray absorption spectra (XPS) and density functional theory (DFT) computational studies also demonstrated the high extraction capacity of Ti_3C_2 -AO-RA for uranium, primarily due to the complexation of AO and NH_2 with $[UO_2(CO_3)_3]^{4-}$. These findings suggest that the Ti_3C_2 -AO-RA sorbent is promising for the rapid and selective adsorption of uranium from real seawater [25].

These latest advances demonstrate that uranium extraction from seawater is a promising approach for ensuring a continuous supply of uranium fuel for nuclear power.

The problem of creating efficient inorganic and fibrous sorption materials with sufficient mechanical strength, acceptable kinetics, and high sorption capacity remains relevant. The use of sorption materials is hampered by the lack of a wide range of options, as well as by insufficient understanding of the thermodynamics, kinetics, and mechanism of sorption.

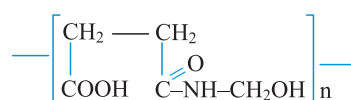
This study aims to investigate the equilibrium sorption of uranium by FORPAN fibrous sorbent (synthesized at the S. M. Kirov St. Petersburg Institute of Textile and Light Industry) from carbonate-containing solutions simulating seawater over a wide range of concentrations ($3.36 \cdot 10^{-5}$ to $7.13 \cdot 10^{-4}$ mol/l) and temperatures (293 to 338 K). The study also includes calculating a generalized thermodynamic equation for uranium sorption by FORPAN fiber under these conditions.

2. Experimental

The studies were conducted using model solutions prepared using natural Caspian Sea water (with a uranium content of $2.5 \cdot 10^{-6}$ mol/l). For analytical control and experimental convenience, uranium-233, previously purified from decay products, was added as a radioactive indicator, along with various amounts of natural uranium in the form of a tricarboxylate-uranilate complex to study sorption over wide ranges of temperatures (293–338 K) and concentrations ($3.36 \cdot 10^{-5}$ ÷ $7.13 \cdot 10^{-4}$ mol/l). The main requirement for the model solutions is the stability of the concentration and forms of existence of uranium under conditions of carbonate-bicarbonate equilibrium. The technique [26, 27] of preparing solutions with subsequent pH stabilization by bubbling air through the solutions and adjusting the pH with 0.01 M HCl and Na_2CO_3 solutions made it possible to obtain solutions with stable (for at least two years) uranium concentration and pH. The selected pH of the solutions (~ 7.85) corresponded to the pH measurements of seawater. Uranium in the model solutions, as in seawater, was in the ion-soluble form $[\text{UO}_2(\text{CO}_3)_3]^{4-}$. Radioactive indicator methods, as well as spectrophotometric methods with the Arsenazo-

III reagent, were used to determine the uranium content in solutions and sorbent samples. Monitoring of α -radioactivity measurements was carried out using a 2154-1-1M PROTOKA device.

The kinetics of uranium sorption were carried out earlier [1] using the limited volume method on the fibrous sorbent FORPAN with the structural formula of the unit:



The experiments were carried out in a glass reaction vessel equipped with an electric stirrer and thermostat. At set intervals, at a given temperature (293, 308, 323, or 338 K), 10 ml of a uranium solution of a specified concentration, along with 0.01 g of air-dried fiber, were introduced into the vessel. The start time of the experiment was recorded. At set intervals, 0.025 ml samples of the solution were removed from the reaction vessel and analyzed for uranium content using the α -radiometric method.

Based on the initial concentration of uranium in the solution at each moment in time, the concentration of uranium in the solution at a given time τ ($C_{p,\tau}$), the amount of sorbed uranium in the solid phase ($C_{m,\tau}$) and the value of the distribution coefficient of uranium in the system at a given time ($K_{d,\tau}$) were calculated using the formulas:

$$C_{p,\tau} = C_{p,init} \frac{J_{p,t}}{J_{p,init}}, \quad (1)$$

$$C_{T,\tau} = \frac{C_{p,init} \cdot V}{m} \left(1 - \frac{J_{p,\tau}}{J_{p,init}} \right), \quad (2)$$

$$K_{d,\tau} = \frac{V}{m} \left(\frac{J_{p,init}}{J_{p,\tau}} - 1 \right), \quad (3)$$

where $J_{p,init}$ and $J_{p,\tau}$ are the initial and determined α -radioactivity of the solution after a specified time, imp; $C_{p,init}$ and $C_{p,\tau}$ are the initial uranium concentration and the concentration at a specified time in the solution, mol/l; V is the volume of the solution, ml; m is the mass of the sorbent, g.

All kinetic dependences were satisfactorily described by the generalized Avrami-Erofeev-Kolmogorov kinetic equation using the Sakovich relation [1]. The equation parameters were processed using the least squares method.

Important information about sorption processes can be obtained by studying the thermodynamics of sorption of a given substance based on the temperature dependences of equilibrium distribution coefficients or sorption isotherms at different temperatures. Based on experimental data, uranium sorption by FORPAN fiber changed insignificantly over time upon reaching equilibrium between the “top” and “bottom” phases over a period of $1.4 \cdot 10^4$ s. This allowed the distribution coefficients (K_d) presented in Table 1 to be considered equilibrium, and the values of C_p and C_T were assumed to be equilibrium and designated $C_{p,\infty}$ and $C_{T,\infty}$, respectively.

Below in Fig. 1, based on the experimental results of Table 1, the dependences of the equilibrium distribution coefficients of uranium ($K_{d,\infty}$, ml/g) on the equilibrium concentration of uranium in solution ($C_{p,\infty}$, mol/ml) at various temperatures are shown. By extrapolating these dependences to any given equilibrium concentration of uranium in solution, an equation of the form can be obtained for each of them:

$$\ln K_{d,\infty} = a + b \ln C_{p,\infty}, \tag{4}$$

where $K_{d,\infty}$ is the equilibrium distribution coefficient of uranium in the system, ml/g, parameters a and b are constant values for a given pH value of the initial solution, calculated by mathematical processing using the least squares method (given in Table 2).

Uranium in seawater is dissolved as a stable tricarbonat-uranilate complex at $\text{pH} > 7.5$, with a carbonate ion content greater than $n \cdot 10^{-6}$ M. At carbonate ion content less than $n \cdot 10^{-6}$ M and $\text{pH} < 7.5$, it dissociates due to the formation of high concentrations of bicarbonate ions in solution, which do not interact with uranium.

The content of HCO_3 groups was determined using Reznikov’s method, modified for the conditions of our experiment [28], the results of which are presented in Table 3.

The calculation of the entropy and enthalpy values of the uranium sorption process on the FORPAN fiber under study was carried out from the experimental results of the dependence of the equilibrium distribution coefficient of uranium on

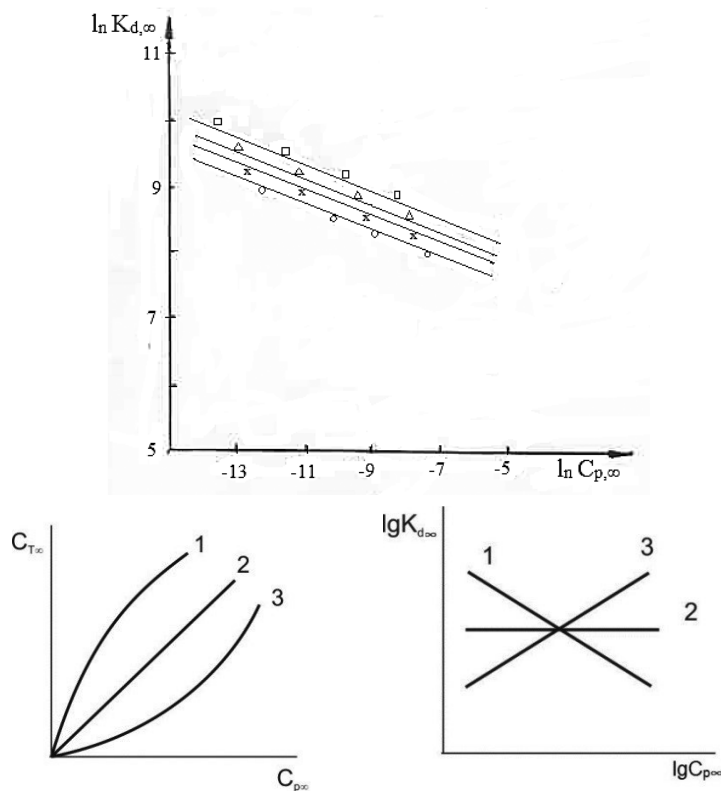


Fig. 1. Uranium sorption isotherm as a function of the equilibrium distribution coefficients ($K_{d,\infty}$) ml/g versus the equilibrium uranium concentration in solution ($C_{p,\infty}$, mol/l) using FORPAN fiber: 1 – 293 K; 2 – 308 K; 3 – 323 K; 4 – 338 K

Table 1. U²³³ sorption from model solutions with C_{s,init.} = (3.36·10⁻⁵ – 7.13·10⁻⁴) mol/l polyampholyte

Sorbent, structural formula of the unit, active groups	Brief characteristics of the sorbent, SEC, mol/g	Initial concentration of the solution, C _{s,init} mol/l	K _{d,∞} , ml/g				Equilibrium time, t _{∞,C}
			Temperature, K				
			293	308	232	338	
$ \begin{array}{c} \text{FORPAN} \\ \text{O} \\ \parallel \\ \text{COOH}-\text{C}- \\ \\ \text{NHCH}_2\text{OH} \\ \\ \text{O} \\ \parallel \\ \text{COOH}, \text{C}-\text{NH} \end{array} $	Obtained by synthesis of carboxylated PAN fiber with formaldehyde, COE _{NaOH} = 2.0	3.36·10 ⁻⁵	6670	11195	21764	32260	1.4·10 ⁴
		1.15·10 ⁻⁴	4496	7336	13068	16224	
		2.7·10 ⁻⁴	2165	3544	4124	8773	
		7.13·10 ⁻⁴	1232	1881	2342	3149	

Table 2. Parameters of the equation $\ln K_{d,\infty} = a + b \ln C_{p,\infty}$ (4) for four concentrations at a given temperature. Capacities (mol/g) calculated with the generalized parameters of equation (6)

Fiber	T, K	ln K _{d,∞} , mol/g	ln C _{p,∞} , mol/l	pH C _{p,∞}	Parameters of equation (4)		The value of capacity according to the equation (6)	
					a	b	ln C _{B,∞}	mol/g
FORPAN	293	8.79	-12.13	5.1	3.72	-0.42	-10.87	1.9·10 ⁻⁵
		8.4	-10.77	7.22			-10.07	4.2·10 ⁻⁵
		7.68	-9.36	7.32			-9.25	9.6·10 ⁻⁵
		7.12	-8.05	7.42			-8.49	2.1·10 ⁻⁴
	308	9.3	-12.8	5	4.14	-0.41	-11.14	1.45·10 ⁻⁵
		8.97	-11.19	7.7			-10.23	3.2·10 ⁻⁵
		8.17	-9.95	7.8			-9.52	7.3·10 ⁻⁵
		7.54	-8.31	8.22			-8.60	1.8·10 ⁻⁴
	323	9.99	-13.43	5.1	3.64	-0.47	-11.38	1.1·10 ⁻⁵
		9.48	-11.71	7.7			-10.43	2.9·10 ⁻⁵
		8.34	-10.75	7.45			-9.90	4.2·10 ⁻⁵
		7.76	-8.45	7.85			-8.60	1.8·10 ⁻⁴
	338	10.38	-13.80	4.9	4.03	-0.45	-11.47	1.0·10 ⁻⁵
		9.69	-9.77	7.3			-9.29	91·10 ⁻⁵
		9.08	-8.48	7.7			-8.59	1.8·10 ⁻⁴
		8.05	-8.79	8.32			-8.44	2.1·10 ⁻⁴

The average values of the parameters \bar{a} and \bar{b} of the equation (4) $a = (3.88 \pm 0.3)$; $b = -0.43 \pm 0.038$

Table 3. Uranium sorption from model carbonate-containing solutions on FORPAN fiber at T = 293.15 K. Results of determination of bicarbonate ion and uranium content in solutions and sorbents

Initial concentration of uranium in solutions, mol/l	3.36·10 ⁻⁵	1.15·10 ⁻⁴	7.13·10 ⁻⁴
pH of the initial solution	7.85	7.87	7.89
The concentration of uranium in the equilibrium solution after sorption, mol/l	4.4·10 ⁻⁶	2.09·10 ⁻⁵	3.21·10 ⁻⁴
Concentration of uranium in the sorbent, mol/g	2.92·10 ⁻⁵	9.41·10 ⁻⁵	3.95·10 ⁻⁴
pH of the equilibrium solution	5.1	7.2	7.38
Concentration of HCO ₃ ⁻ ion in the initial solution, mol/l	1.04·10 ⁻³	5.25·10 ⁻³	3.01·10 ⁻²
Concentration of HCO ₃ ⁻ ion in solution after sorption, mol/l	1.96·10 ⁻³	6.41·10 ⁻³	4.16·10 ⁻²

temperature. These dependences were obtained for various initial uranium concentrations in solutions with a pH of 7.85 and are shown in Figure 2.

3. Results and discussion

The dependence $\ln K_{d,\infty} \rightarrow \ln C_{p,\infty}$ presented in Fig. 1 is similar to [29] the accepted representation of an isotherm of the $C_{T,\infty} \rightarrow C_{p,\infty}$ type, which can be successfully replaced by a representation in logarithmic coordinates, which makes it possible to easily, using extrapolation, estimate the capacity of the sorbent at any equilibrium concentration of the element in the solution for any form of sorption isotherm.

The calculated values of the uranium sorption isotherm parameters from model solutions are presented in Table 2.

By further mathematical processing of the values of the parameters a and b of equation (4) from temperature ($a \rightarrow \frac{1}{T}$ and $b \rightarrow \frac{1}{T}$), a generalized equation was derived that made it possible to calculate the equilibrium distribution coefficient K_d (ml/g) associated with temperature and the equilibrium concentration of the solution (mol/l), as well as the capacity of the fiber for uranium (mol/g) during its sorption from model solutions of seawater with pH 7.85–7.9 in a wide range of equilibrium concentrations of uranium in the solution ($1.0 \cdot 10^{-4}$ – $1.0 \cdot 10^{-9}$ mol/l) and

temperatures (293–338 K):

$$\ln K_d = (5,271 - 0,72 \ln C_{p,\infty}) - (437,68 - 89,52 \ln C_{p,\infty}) / T. \tag{5}$$

Based on equation (5), we can write:

$$\ln C_{T,\infty} = (-5,271 + 0,28 \ln C_{p,\infty}) + (437,68 + 89,52 \ln C_{p,\infty}) / T. \tag{6}$$

Substituting into equation (6) the value of the uranium concentration in the water of the Caspian Sea, $2.5 \cdot 10^{-6}$ mol/l, we obtain the value of the capacity for seawater ($C_{T,S,W}$):

$$\ln C_{p,S,W} = -12.89$$

$$C_{T,S,W} = 1,22 \cdot 10^{-5} \text{ mol/g} = 2,9 \cdot 10^{-3} \text{ l/g} \tag{7}$$

Uranium sorption from natural waters and carbonate systems actively occurs with the participation of both anion exchangers and cation exchangers. However, under the same conditions, the absorption of uranium by cation exchangers is explained by the authors [30] by the fact that the presence of an ion exchanger shifts the equilibrium between the carbonate complex and the products of uranyl ion hydrolysis. It is necessary to take into account the participation of the HCO_3^- ion in the carbonate equilibria system, which are interconnected with the pH of the solution, and determine the binding of uranium

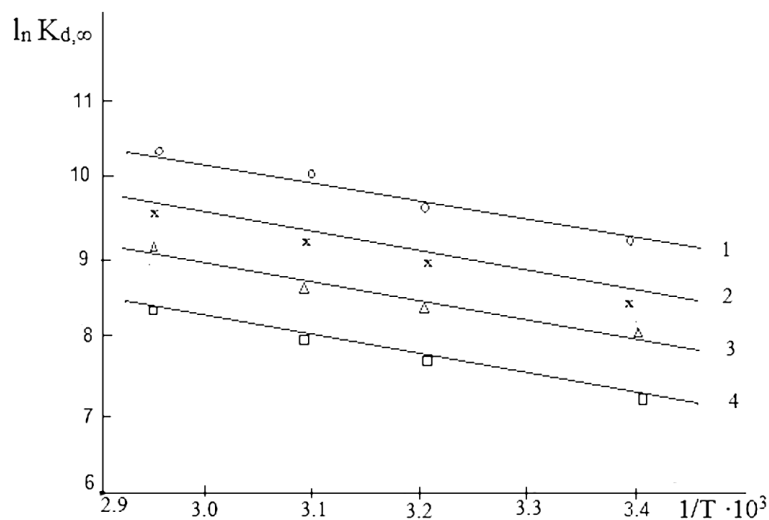
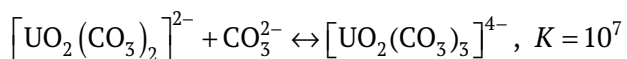
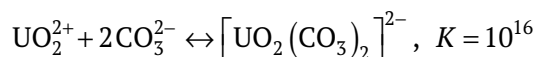


Fig. 2. Temperature dependences of the equilibrium distribution coefficient for uranium sorption using FOR-PAN fiber at different initial uranium concentrations in solution: 1 – $3.36 \cdot 10^{-5}$ M; 2 – $1.15 \cdot 10^{-4}$ M; 3 – $2.73 \cdot 10^{-4}$ M; 4 – $7.14 \cdot 10^{-4}$ M

into uranyl carbonate complexes according to the reactions:



A comparison of the equilibrium constants for these reactions shows that, in the region of near-neutral and alkaline pH values, even a slight excess of carbonates above stoichiometric values is sufficient for the virtually complete binding of uranium into uranyl carbonate anions [31].

The carboxyl groups of FORPAN fiber, being acidic in nature and subject to the mechanism of carboxyl cation dissociation [32], partially or completely dissociate depending on the pH of the solution and are responsible for the sorption of uranium as a result of ion exchange. The amino groups are the basic groups, responsible for the formation of coordination bonds during sorption in a slightly acidic medium with a pH of 3–5. Taking this into account, the appearance of a negative charge in alkaline media and a positive charge in acidic media for FORPAN fiber can be represented by the following reaction equations:



At the initial moment of contact of the fiber with a carbonate-containing solution with a pH of 7.85, the fiber is charged negatively due to the protolysis of the carboxyl group according to reaction (a), which results in a decrease in the pH of the solution and the cleavage of the tricarbonat uranium complex. In this case, the ion-exchange activity of the COOH groups is evident, and in solutions with neutral and slightly alkaline pH, the formation of stable carboxyl complexes of uranium is possible. In more acidic environments, carboxyl groups are protonated and are unable to form strong bonds with uranium, while in an alkaline environment, uranium can form complex compounds, including hydroxide complexes $\text{UO}_2(\text{OH})_2$ and $\text{UO}_2(\text{OH})_3$, which can compete with carboxyl complexes. As a result of the shift of the pH environment

to the region of low pH values (~ 5–5.5), the process begins to proceed according to reaction (b), during which two types of bonding of the ligand groups of the fiber (ionic and coordination) occur, since in an acidic environment the amino group protonates and acquires a positive charge, turning into an ammonium ion ($-\text{NH}_3^+$), capable of participating in complex formation, however, in an alkaline environment it loses a proton and becomes neutral, which inhibits the further process of complex formation, or desorption of the complex may occur, which is reflected in the shift in the equilibrium between the forms of existence of uranium in the presence of fiber [33].

The experimental data obtained show that during the period of contact between the solution and deprotonated fiber from weakly alkaline and acidic solutions, sorption is characterized by high distribution coefficients (Table 1), which can be attributed to an increase in the HCO_3^- content in the solution. The observed increase in the solution concentration and pH, as well as a decrease in uranium sorption (reaching equilibrium), confirm the lack of correlation between uranium and carbonate ions in the fiber. As the uranium concentration and solution pH increase, the process proceeds with an increase in the ion-exchange mechanism.

A similar phenomenon in the sorption process was also discovered in [34] during a study of uranium(VI) sorption on goethite using X-ray absorption spectra (EXAFS), where in the presence of carbonate ions in the solution, an increase in uranium sorption was detected at low pH with the formation of complexes: $(> \text{FeOH})_2\text{UO}_2(\text{H}_2\text{O})$; $\text{FeOCO}_2\text{UO}_2$ and $(> \text{FeOH})_2\text{UO}_2\text{CO}_3$, which were desorbed with an increase in the pH of the solution and were not recorded by the EXAFS spectra. Taking these complexes into account, the authors developed a thermodynamic model of surface complexation on goethite, corresponding to their experimental data on uranium sorption from aqueous solutions.

To study the thermodynamics of the process of uranium sorption from carbonate-containing solutions simulating seawater, the equation was first processed:

$$\ln K_d = A - B \frac{1}{T} \quad (8)$$

using the least squares method for various initial concentrations $3.36 \cdot 10^{-5} \div 7.13 \cdot 10^{-4}$ mol/l in the form of a dependence of $\ln K_d - \frac{1}{T}$ on each temperature (293, 308, 323, 338 K). By further processing the parameters A and B from the initial concentration in the form $(A - \ln C_{p,init}) (B - \ln C_{p,init})$, where $A = A' + B' [A = (-1.17) + (-2.17)]$ and $B = B' + B'' [B = 1276.7 + 472]$, generalized values of the parameters were obtained for any initial concentration:

$$A = A' + A'' \ln C_{p,init}, \quad (9)$$

$$B = B' + B'' \ln C_{p,init}. \quad (10)$$

As a result of mathematical processing of the entire set of obtained dependencies, a generalized semi-empirical thermodynamic equation was derived that relates the equilibrium distribution coefficient of uranium in the system ($K_{d,\infty}$), the initial concentration, and the temperature of the sorption experiment in the form:

$$\ln K_d = A' + A'' \ln C_{p,init} - \frac{B' + B'' \ln C_{p,init}}{T}. \quad (11)$$

Substituting the calculated values of the parameters into equation (11), $A' + A'' \ln C_{p,init} = (-1.17) + (-1276.7) \ln C_{p,init}$ and $B' + B'' \ln C_{p,init} = (2.17) + 472 \ln C_{p,init}$ a generalized equation of thermodynamics for the process of uranium sorption from model solutions of seawater in a wide range of initial uranium concentrations $3.36 \cdot 10^{-5} - 7.13 \cdot 10^{-4}$ mol/l and temperatures (293–308 K) at pH 7.85 for FORPAN fiber was obtained:

$$\ln K_d = (-1.17) + (-1276.7 \cdot \ln C_{p,init}) - (2.17 + 472 \cdot \ln C_{p,init}) / T. \quad (12)$$

The value of the uranium distribution coefficient in the water of the Caspian Sea ($K_{d,S.W}$) with a concentration of $2.5 \cdot 10^{-6}$ mol/l ($\ln C_{p,S.W} = -12.89$) at $T = 293.3$ K, calculated using equation (12), is equal to $\ln K_{d,S.W} = 9.7$ $K_{d,S.W} = 1.6 \cdot 10^4$ mol/l.

The values of the parameters $A = A' + A'' \ln C_{p,init}$ and $B = B' + B'' \ln C_{p,init}$ of equation (12) correspond to the parameters of the known relationship:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT}, \quad (13)$$

Where K_d is the equilibrium distribution coefficient of uranium in the system, ml/g; ΔS is the entropy of the uranium sorption reaction, J/mol deg; ΔH is the enthalpy of the uranium sorption reaction, J/mol; R is the universal gas constant, equal to 8.3143 J/mol deg; T is the experimental temperature, K.

The following formula was used to calculate the change in Gibbs free energy:

$$\Delta G = \Delta H - T \Delta S. \quad (14)$$

As can be seen from Table 4, the enthalpy value $\Delta H < 0$ is negative, i.e., the process is exothermic, with heat release. The heat of reaction for uranium sorption by the fiber under study is estimated to be in the range $-28 \div -40$ kJ/mol. These values are significantly lower than the heat of chemisorption reactions ($50 \div 80$ kJ/mol) and are close to the enthalpies characteristic of ion-exchange reactions, i.e., the process of uranium sorption from carbonate-containing solutions by FORPAN fiber proceeds via an ion exchange mechanism, along with complexation.

4. Conclusions

Based on a study of the fundamental principles of equilibrium uranium sorption by the fiber, it was established that the experimentally determined uranium distribution coefficients in the temperature range of 293–338 K are in equilibrium. It was found that during the period of fiber contact with a carbonate-containing uranium solution, the pH of the solution sharply decreases to 7.86, and the tricarbonat uranium complex decomposes due to protolysis of carboxyl groups. This period is characterized by high uranium distribution coefficients and an increase in HCO_3^- in the solution, confirming the lack of correlation between uranium and carbonate ions in the fiber.

The capacity of the fiber for uranium (mol/g) was calculated during its sorption from model solutions prepared based on Caspian Sea water in the range of studied concentrations and temperatures, and the capacity of the FORPAN sorbent relative to uranium in Caspian Sea water ($1.22 \cdot 10^{-5}$ mol/g = $2.9 \cdot 10^{-3}$ g/g) and $K_{d,S.W} = 1.6 \cdot 10^4$ ml/g at $T = 293.3$ K was also calculated.

Table 4. Parameters of equation (8) for different initial concentrations of model solutions and the values of enthalpy, entropy and Gibbs free energy of the uranium sorption reaction on FORPAN fiber ($T = 298.16$ K), calculated based on the generalized parameters $A = A' + A'' \ln C_{p,init}$; $B = B' + B'' \ln C_{p,init}$

$C_{p,init}$ mol/l	$\ln C_{p,init}$	$A = A' + B' \ln C_{p,init}$	$B = A'' + B'' \ln C_{p,init}$	$A^{gener.} = A' + A'' \ln C_{p,init}$	$B^{gener.} = B' + B'' \ln C_{p,init}$	ΔS J/mol-degree	ΔH J/mol	ΔG kJ/mol
$3.36 \cdot 10^{-5}$	-10.3	20.907	-3584	13148	-4859	109.32	-40400	-72.998
$1.15 \cdot 10^{-4}$	-9.1	18.609	-2887	11610	-4293	96.535	-35694	-64.477
$2.73 \cdot 10^{-4}$	-8.2	17.350	-2843	10462	-3868	87.015	-32162	-58.1
$7.13 \cdot 10^{-4}$	-7.2	14.009	-2013	9237	-3415	76.801	-28394	-51.292

A generalized semiempirical thermodynamic equation for uranium sorption by the fiber under study was obtained. It relates the equilibrium distribution coefficient of uranium in the system, the initial concentration, and the temperature of the sorption experiment under given conditions. The parameters of this equation made it possible to calculate the entropy, enthalpy, and Gibbs energy of uranium sorption by FORPAN fiber. The enthalpy values ($\Delta H < 0$) are negative, indicating an exothermic process with the release of heat. The heat of reaction for uranium sorption by the fiber under study is estimated at values in the range of $-28 \div -40$ kJ/mol. These values turned out to be significantly lower than those for chemisorption processes, i.e., they are more consistent with ion-exchange processes, along with which complex formation also occurs.

Based on the conducted studies of the features of equilibrium sorption of uranium from model carbonate-containing solutions and the results obtained, FORPAN fiber can be recommended for the purpose of extracting uranium from dilute carbonate-containing solutions of natural waters, in particular, from the water of the Caspian Sea, with a uranium content of $2.5 \cdot 10^{-6}$ mol/l, in the range of relatively low temperatures of 293–308 K.

Author contributions

M. A. Rahimli – concept, writing, and scientific editing of the article; S. R. Mamedova – research and participation in literature analysis, and preparation of figures and tables.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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