Sorption of ^{90}Sr by a T-3K carbonate-containing zirconium dioxide

Anna V. Voronina[1] · Nadezhda V. Belokonova[1] · Anna K. Suetina[1] · Vladimir S. Semenishchev[1]

Abstract

A physicochemical properties of carbonate-containing zirconium hydroxide T-3K sorbent as well as selective ^{90}Sr sorption from natural waters were studied. It was shown that sorbent consist of ZrO_2 (46.39%), Na_2O (1.78%) and Al_2O_3 (1.42%) as the major components in microporous carbonate-containing zirconium hydroxide where sorption of ^{90}Sr occurs due to formation of sparingly soluble strontium carbonate. Affinity of the T-3K sorbent for alkaline earth ions corresponded to the reverse trend of carbonates solubility: $Sr > Ba > Ca \gg Mg$ and maximum strontium sorption was observed at pH 7–10. Distribution coefficients of strontium were $(1.3 \pm 0.1) \times 10^3$ mL/g for low mineralized water with calcium content of 16 mg/L and 95 mL/g for seawater; static exchange capacity of the sorbent was 30.4 ± 0.5 mg/g.

Keywords Natural water · Liquid radioactive waste · Strontium-90 · Carbonate-containing zirconium hydroxide · Sorption

Introduction

Despite prevention measures, anthropogenic radionuclides are still released into the environment resulting in contamination of soils and water bodies [1]. Among the main sources of water bodies pollution by artificial radionuclides are nuclear weapon tests [2, 3], daily work of enterprises treating irradiated nuclear fuel [4] as well as nuclear accidents [5]. Isotopes of cesium and strontium play the leading role in pollution of natural water bodies and ^{90}Sr is one of the most dangerous one due to its relatively long half-life (29.12 years), high affinity to bone tissue and high beta energy of its progeny ^{90}Y. Presence of ^{90}Sr in liquid radioactive waste as well as its release into natural waters makes it necessary to search for methods of effective separation of ^{90}Sr from various aqueous solutions with the aim of radiochemical analysis or deactivation. This process is complicated because of interference from alkaline earth cations presenting in both radioactively contaminated natural waters and liquid radioactive waste. Concentration of calcium in natural waters varies within 1–100 mg/L in surface waters, up to 10–250 mg/L

in underground waters and up to 600 mg/L in salt lakes and seawaters [6–12].

A number of sorbents based on various sparingly soluble compounds are developed for elimination of strontium from natural waters and liquid radioactive waste. Among sparingly soluble compounds used in these sorbents, there are granulated and modified manganese dioxide including mesoporous manganese dioxide and birnessite [13–17], titanium hydroxide [18], calcium and magnesium phosphates and hydrophosphates [19], zirconium phosphate [20, 21] as well as titanosilicates [14, 22–24]. Possibility of using the sorbents for strontium preconcentration in methods of radiochemical analysis of aqueous samples is evaluated for some of these sorbents [25–29].

Granulated inorganic sorbents seem to be the most prospective for decontamination of radioactively contaminated waters. These sorbents provide distribution coefficients of strontium within 10^2–10^4 mL/g, and their static exchange capacity may reach several hundred mg/g. Possibility of their use should be determined by their cost, availability (commercial or lab sample) and enough mechanical strength for exploitation in column conditions. Extraction chromatographic resins highly selective for strontium have found application in analysis of aqueous samples. Bezhin et al. [29] reported a possibility of using various granulated inorganic sorbents for determination of radiostrontium in seawater samples. A sorbent Modix (SPE Eksorb Ltd) is chosen as

✉ Anna V. Voronina
av.voronina@mail.ru

[1] Department of Radiochemistry and Applied Ecology, Ural Federal University, 19, Mira Street, Yekaterinburg, Russia 620002
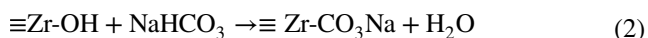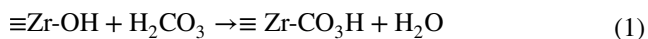
the most promising one, however the development of an analytical method is still in progress.

Strontium carbonate is another one sparingly soluble salt of strontium. Despite is has a higher solubility than strontium phosphate, the study of strontium sorption by carbonate-containing sorbents is also interesting. Solubility product of strontium carbonate is intermediate between the respective values for strontium sulfate and phosphate: $SrSO_4 > SrCO_3 > Sr_3(PO_4)_2$. This work is aimed to a study of physicochemical and sorption properties of a carbonate-containing zirconium hydroxide (T-3K sorbent produced by JSC Inorganic Sorbents, Russia), selectivity of strontium sorption as well as a possibility of using this sorbent for preconcentration of ^{90}Sr from fresh water and seawater and for decontamination of aqueous media.

Experimental

The T-3K sorbent was an inorganic polymeric material with amorphous structure, which was synthesized via sol–gel method as white spherical granules. The sorbent can be easily used in column conditions due to its spherical form, chemical stability and mechanical strength. The grain size of the sorbent was 0.4–1.0 mm, bulk density was 1.05 g/mL and the mechanical strength was at least 5 MPa.

The method of synthesis of the T-3K sorbent included treatment of gel spheres of the hydrated zirconium dioxide (T-3 sorbent) by sodium hydrocarbonate solution [30]. According to the producer's data, chemical reactions of the surface modification can be described by the following Eqs. (1), (2):

$$\equiv Zr\text{-}OH + H_2CO_3 \rightarrow \equiv Zr\text{-}CO_3H + H_2O \tag{1}$$

$$\equiv Zr\text{-}OH + NaHCO_3 \rightarrow \equiv Zr\text{-}CO_3Na + H_2O \tag{2}$$

According to the suggestions of the developers, its chemical composition is surface-modified hydrated zirconium dioxide, $Zr(OH)_{3.5}(NaCO_3)_{0.5}$ [30].

The study of physicochemical properties of the T-3K sorbent

Physicochemical properties of the T-3K sorbent were studied in comparison with the respective properties of the T-3 sorbent. Analysis of element composition of the sorbent was performed using an ARL QUANT'X (USA) energy dispersive X-ray fluorescence spectrometer (the detection limit is 10 ppm, relative error is 10–20%). Infrared spectrum of the sorbent was obtained using Vertex-70 IR-Raman spectrometer with RAM-II device (Bruker, Germany). To make interpretation of the IR spectrum easier, we have additionally obtained the IR spectrum of the hydrated zirconium dioxide (a T-3 sorbent), which is the raw material for synthesis of the T-3K sorbent.

Surface area of the sorbents was determined by the method of low temperature nitrogen sorption using the Nova 1200e high-speed surface area analyzer (Quantachrome, USA). Temperature of degassing was 100 °C, the degassing length of time was 2 h, and the sorbent weight was 250 ± 5 mg.

The effect of pH on strontium sorption by the T-3K sorbent

The dependence of strontium sorption on pH was studied using a weakly mineralized water (tap water) with addition of 1 mg/L of stable strontium and spiked with ^{90}Sr as a radiotracer (the activity concentration was 10 kBq/L). Sorbent weight/solution volume ratio was 50 mg per 30 mL. Time of the phases contact was 1 week. Tap water was stored and filtered before the experiments to eliminate iron hydroxide colloids. Concentration of stable strontium was adjusted by addition of $SrCl_2$ solution with known concentration. The pH was adjusted by addition of HCl or NaOH solutions. Measurements of ^{90}Sr were performed using a semiconductor alpha/beta radiometer UMF-2000 (Doza, Russia) after equilibrium ^{90}Y ingrowth. The degree of strontium sorption S was calculated in accordance with the Eq. (3):

$$S = \frac{I_{in} - I_{end}}{I_{in} - I_b}, \tag{3}$$

where I_{in}, I_{end} are initial and final count rates of the solution, cpm; I_b is background count rate, cpm.

The effect of Ca²⁺ and Na⁺ concentrations on strontium sorption

In the experiments, distilled water with addition of various concentrations of Ca^{2+} and Na^{+} ions was used. Concentrations of ions were adjusted to the concentration range typical for natural surface and ground waters and soil solutions by addition of $CaCl_2$ and NaCl solutions. Concentrations of calcium varied from 1 to 300 mg/L, pH values in solutions before sorption were 5.6 ± 0.1. Concentrations of sodium varied from 0.02 to 230 mg/L, pH values in solutions before sorption were 6.5 ± 0.1. Strontium concentration was adjusted to 1 mg/L in all solutions by addition of $SrCl_2$ solution with a known concentration. Temperature of the solution was 22 ± 1 °C. The sorbent weight was 50 mg and the solution volume was 30 mL. The experiments were performed in three replicates. Time of phase contact was 1 week. Chemical composition of natural waters as well as strontium and calcium concentrations in the solutions before

and after sorption were determined using the NexION 350X mass spectrometer with inductively coupled plasma. Data treatment was performed using TotalQuant software. Distribution coefficients of strontium and calcium K_d (mL/g) were calculated according to the Eq. (4):

$$K_d = \frac{S}{1 - S} \cdot \frac{V}{m},\qquad(4)$$

where S is degree of sorption, dimensionless; V is volume of the solution, mL; m is weight of the sorbent, g.

Separation factor R (Sr/Ca) was calculated according to the Eq. (5):

$$R = \frac{K_d(\text{Sr})}{K_d(\text{Ca})},\qquad(5)$$

where K_d (Sr) is the distribution coefficient of strontium, mL/g; K_d (Ca) is distribution coefficient of calcium, mL/g.

Study of selectivity of strontium sorption by the T-3K sorbent over alkaline and alkaline earth ions in weakly mineralized water and seawater

Sorption of strontium from weakly mineralized (tap) water and seawater (Mediterranean Sea). Sorbent weight/solution volume ratio was 500 mg per 100 mL. Time of phase contact was 1 week. Concentrations of alkaline and alkaline earth elements were determined by ICP-MS. Distribution coefficients of the alkaline and alkaline earth elements as well as Sr/Metal separation factors were calculated as described above.

Sorption of ^{137}Cs was studied using low mineralized water with concentration of stable cesium of 0.01 mg/L, which was adjusted by addition of CsCl solution with known concentration. Sorbent weight/solution volume ratio was 50 mg per 30 mL. Time of phase contact was 1 week. Activity concentration of ^{137}Cs radiotracer was 20 kBq/L. Measurements of ^{137}Cs were performed using a semiconductor alpha/beta radiometer UMF-2000 (Doza, Russia).

The isotherms of strontium sorption

The isotherms of strontium sorption were obtained using tap water and seawater (Mediterranean Sea) with addition of 10^{-9}–3 g/L of stable strontium; ^{90}Sr was used as a radiotracer. Time of phase contact was 1 week to determine equilibrium sorption characteristics. The sorbent weight was 50 mg and the solution volume was 30 mL.

Measurements of ^{90}Sr were performed using a semiconductor alpha/beta radiometer UMF-2000. Mathematical treatment of the linear sections of the isotherms performed using the least squares method; the slope of the linear sections and distribution coefficients of strontium were calculated.

Study of ^{90}Sr desorption from the T-3K sorbent

Desorption of ^{90}Sr from the T-3K sorbent nu acidic solutions was studied under batch conditions. The effects of acid type (HCl or HNO$_3$), acid concentration and time of phases contact were studied. The sorbent was loaded by ^{90}Sr under batch conditions for 1 week contacting 500 mg with 100 mL of a solution. After loading, the sorbent was washed with distilled water, dried at a room temperature and then contacted with 10 bed volumes (BV) of the stripping solutions. Samples aliquots were collected after time intervals within 24 h, analyzed, and the degree of desorption was calculated.

Results and discussion

### Chemical composition and porosity of the T-3K sorbent

Table 1 shows chemical composition (as element oxides) of the T-3 and T-3K sorbent. The content of zirconium hydroxide (after water deduction) was 46% for the T-3K sorbent and 61% for the T-3 sorbent; the data agree with certificate data for these sorbents. All other oxides were as trace impurities. For example, sodium content in the T-3K sorbent was 1.78% and aluminum content was 1.42%.

The transmittance IR spectrum of the T-3 and T-3K sorbent is given at Fig. 1.

A wide adsorption band at 2800–3700 cm^{-1}, which is typical for stretching vibrations of OH$^-$ groups [31], was observed in the IR spectrum. The adsorption peak at 1635 cm^{-1} was conditioned by bending vibrations of absorbed water molecules [32]. Presence of absorbed carbon dioxide molecules was confirmed by spectral adsorption bands at 2364 cm^{-1} (asymmetric stretching vibration) and 668 cm^{-1} (symmetrical bending vibration) [33]. The sharp peaks at 2859 cm^{-1} and 2924 cm^{-1} indicated vibrations of the Zr–O bond [34]. In contrast to the T-3 sorbent,

Table 1 Chemical composition (as element oxides) of the T-3K sorbent, %wt

Element oxide	ZrO$_2$	Na$_2$O	Al$_2$O$_3$	CuO	TiO$_2$	FeO	CaO	K$_2$O
T-3K	46.39	1.78	1.42	0.032	0.004	0.024	0.012	0.06
T-3	61.30	3.25	0.017	0.077	0.206	0.004	0.123	0.01

Fig. 1 Transmittance IR spectrum of the T-3K sorbent
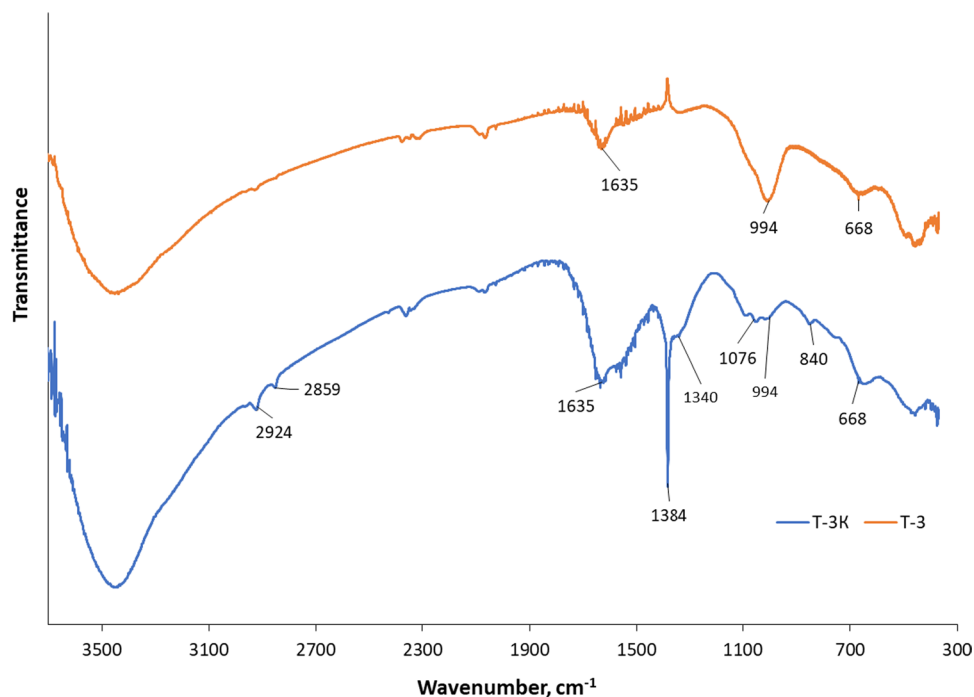
the IR spectrum of the T-3K contains the absorption peaks at 1384 cm^{-1}, 1076 cm^{-1} and 840 cm^{-1} indicating vibrations of the CO$_3$ group [35]. Adsorption peaks at 1080, 1040 and 845–850 cm^{-1} correspond to various types of surface carbonate groups [36]. The adsorption peak at 1390 cm^{-1} indicates the presence of the CO$_3^{2-}$ group [36], the peaks series at 1080–1030 cm^{-1} and 1337 cm^{-1} can be associated with bidentate carbonates on the surface of zirconium dioxide [36–38].

Table 2 shows the parameters of the pore structure of the T-3 and T-3K sorbents being determined by the low temperature nitrogen adsorption method.

Figure 2 presents the isotherm of nitrogen adsorption and size distribution of micropores for the T-3K sorbent.

The isotherm of nitrogen adsorption was Type I of Langmuir's isotherm. The isotherm was convex relative to the P/P_0 axis and the amount of adsorbate approached the limit as P/P_0 increased to 1. This type of isotherm is basically typical for microporous materials. The analysis of micropores distribution of the T-3 и T-3K sorbent was performed using the V-t method. The results have shown that the T-3 sorbent was a micropore sorbent with the surface are of 144 ± 7 m^2/g. Chemical modification of the T-3 sorbent by carbonate resulted in a decrease of its porosity as well as the area and volume of micropores. The contribution of external surface increased after modification.

Figure 2 showed a very narrow micropores distribution T-3K sorbent. The average diameter of micropores was 1.5–2 nm, the volume of micropores was $(9.6 \pm 1.0) \times 10^{-3}$ cm^3/g and the area of micropores was 14 ± 1 m^2/g. Thus, the sorbent was mainly microporous with a small contribution of mesopores with the average diameter of 2–5 nm. The volume of mesopores was $(9.3 \pm 0.9) \times 10^{-4}$ cm^3/g. The effective diameter of pores was 3.1 ± 0.3 nm. The surface area of the sorbent was determined using the BET method. This value was 95 ± 5 m^2/g and it was mainly conditioned by the contribution of external surface area (81 ± 4 m^2/g). Therefore, we suggest that reactions of the sorbent with strontium should occur mainly on the surface of the sorbent.

Table 2 The parameters of the pore structure of the sorbents

Sorbent	BJH method (nitrogen desorption)			BET method	V-T method		
	Surface area, m^2/g	Pore volume, cc/g	Pore diameter, nm	Surface area, m^2/g	Micropore volume, cc/g	Micropores area, m^2/g	Surface area, m^2/g
T-3K	1.09 ± 0.05	$(9.3 \pm 0.9) \times 10^{-4}$	3.1 ± 0.3	95 ± 5	$(9.6 \pm 1.0) \times 10^{-3}$	14 ± 1	81 ± 4
T-3	0.41 ± 0.02	$(3.2 \pm 0.2) \times 10^{-4}$	3.0 ± 0.2	144 ± 7	$(5.0 \pm 0.3) \times 10^{-2}$	52 ± 3	92 ± 5

Fig. 2 Isotherm of nitrogen adsorption (**a**) and differential distribution of micropores size (**b**) for the T-3K sorbent

a

b
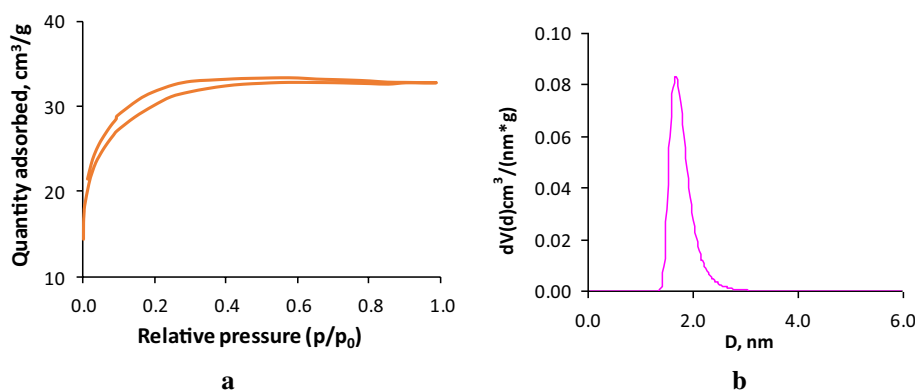
The study of pH effect on strontium sorption by the T-3K sorbent

Figure 3 shows the pH dependence of the degree of strontium sorption by the T-3K sorbent.

The sorbent possessed buffer capacity that resulted in pH shifting to pH 7–8 during sorption of strontium at the initial pH range of 4–10. Because of this significant buffer capacity, we have failed to obtain experimental points at the pH range of 4–6 even after triple acidification of the solution during 3 days of sorption. The dependence showed a decrease of strontium sorption by the T-3K sorbent with the decrease of pH value that is typical for weak acid cation exchangers. The maximal sorption of strontium achieved at pH 7–10; distribution coefficient of strontium was $K_d = (2.08 \pm 0.04) \times 10^3$ mL/g. Thus, the working pH range for the T-3K was optimal for strontium separation from seawater and fresh waters.

The study of selectivity of strontium sorption by the T-3K sorbent in presence of alkaline and alkaline earth elements

Selectivity of strontium sorption by the T-3K sorbent over the major components of natural waters was studied. Figure 4 shows t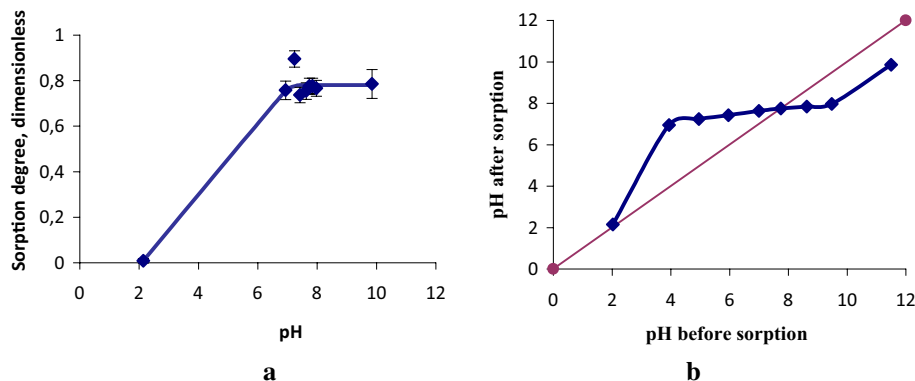he dependences of distribution coefficients of Sr and Ca as well as Sr/Ca separation factors on calcium concentration in the solution. The maximal distribution coefficients of Sr and Ca achieved in solutions at calcium concentration up to 1 mg/L; the respective values reached 1.5×10^5 and 1.5×10^4 mL/g respectively. The maximal Sr/Ca separation factor reached 13 giving a possibility of selective separation of strontium from calcium.

In case of calcium concentration in the solution more than 50 mg/L, distribution coefficients of Sr and Ca remained nearly invariable: lg K_d (Sr) = 4.2 ± 0.2 mL/g and lg K_d (Ca) = 3.9 ± 0.3 mL/g The average Sr/Ca separation factor was 2.0.

Figure 5 presents the dependence of strontium distribution coefficient on sodium concentration in the solution. Increase of sodium concentration resulted in a decrease of strontium distribution coefficient at sodium concentrations up to 0.0001 mol/L (2.3 mg/L); however, the K_d value was invariable (lg K_d (Sr) = 3.8 ± 0.1 mL/g) at higher concentrations of sodium.
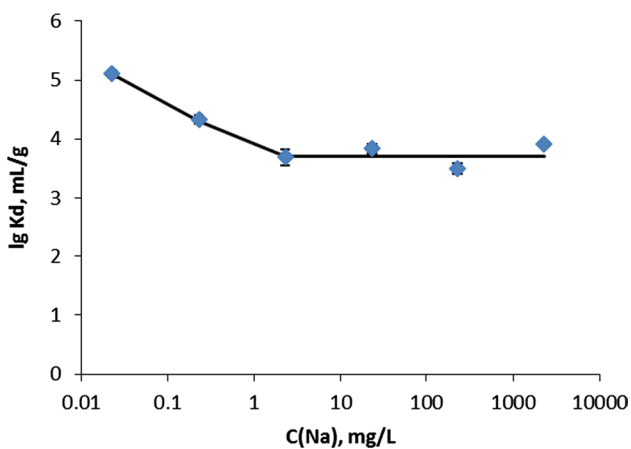
A high distribution coefficient of strontium in presence of significant amounts of sodium and calcium allows using the T-3K sorbent for both strontium preconcentration from natural waters in radioanalytical schemes and decontamination of radioactively polluted natural waters and liquid radioactive waste from strontium radionuclides.

Fig. 3 The effect of pH in strontium sorption by the T-3K sorbent: **a** the dependence of sorption degree on pH; **b** the dependence of pH after sorption on the pH value in the solution before sorption

a

b
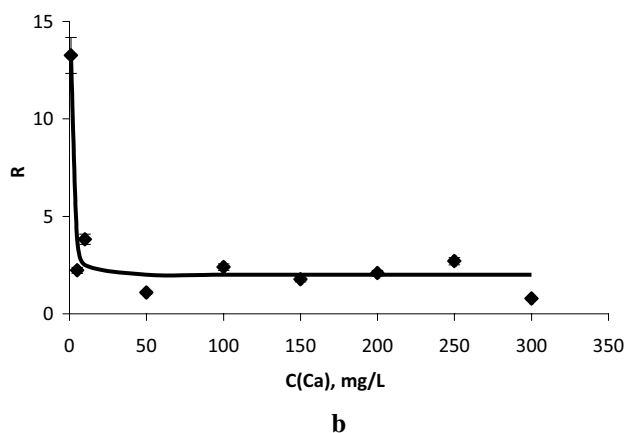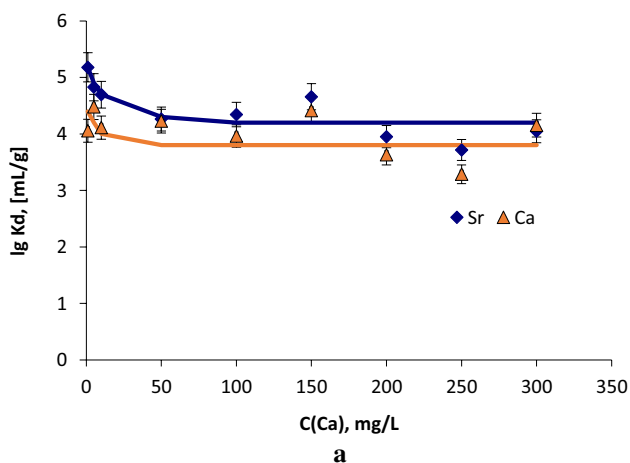
Fig. 4 The effect of calcium concentration on distribution coefficients of Sr and Ca (**a**) and Sr/Ca separation factor (**b**). Concentration of stable strontium was 1 mg/L

Fig. 5 The effect of sodium concentration on distribution coefficient of Sr. Concentration of stable strontium was 1 mg/L

Table 3 Concentrations of major alkaline and alkaline earth ions and parameters of their sorption by the T-3K sorbent

Cation	Concentration, mg/L	Distribution coefficient K_d, mL/g	Separation factor R (Sr^{2+}/M^{2+})
Low mineralized water (tap water)			
Na	3.96	Increase of sodium concentration in the solution was observed*	
K	1.2	97	227.6
Ca	14.3	2.4×10^3	8.9
Mg	7.2	1.7×10^3	12.8
Sr	0.85	2.2×10^4	–
Ba	0.03	1.9×10^3	11.9
Seawater (Mediterranean Sea)			
Na	14,400	< 6	–
K	135	< 4	–
Ca	158	36	2.6
Mg	646	< 6	–
Sr	3	95	–
Ba	0.01	< 4	–

*This increase of sodium concentration in the solution after sorption can be explained by exchange of ions from the solution by sodium from the sorbent resulting in sodium release into the solution

Sorption of strontium from low mineralized and seawater was studied under batch conditions. Table 3 shows concentrations of major alkaline and alkaline earth ions and parameters of their sorption by the T-3K sorbent.

It is obvious that selectivity of sorption of various cations by the T-3K was conditioned by solubility of respective carbonates. Sodium and potassium carbonates possess high solubility resulting in low sorption of these ions. According to literature data [39], solubility products of alkaline earth carbonates follow in the series: $MgCO_3 = 7.9 \times 10^{-6}$; $CaCO_3 = 4.4 \times 10^{-9}$; $SrCO_3 = 5.3 \times 10^{-10}$; $BaCO_3 = 4.9 \times 10^{-9}$. Affinity of the T-3K sorbent for alkaline earth ions corresponds to the reverse trend of carbonates solubility: $Sr > Ba > Ca \gg Mg$. Some deviation from this trend was observed in case of barium that can be probably explained by its low concentration in natural waters. Thus, the sorbent shows the highest selectivity for strontium among alkaline earths due to the lowest solubility product of strontium carbonate. Therefore, the sorbent provides selective separation in the pairs Sr/Mg, Sr/Ca and Sr/Ba allowing good strontium sorption from waters with elevated calcium content.

Separation factors of Sr/Ca obtained in both low mineralized water and seawater with natural concentrations of alkaline and alkaline earth elements were like those obtained

in pure CaCl$_2$ solutions (see Fig. 4). Iron, potassium, magnesium, and barium were not separated from seawater.

Selective preconcentration of strontium is preferable for development of a method for determination of ^{90}Sr in natural waters. Among the main radionuclides interfering ^{90}Sr measurement by beta radiometry is ^{137}Cs, which is a long-lived beta emitting radioactive contaminant presenting natural waters together with ^{90}Sr. In case of ^{137}Cs sorption by the T-3K sorbent, this radionuclide will contaminate the measuring source resulting in a systematic error of measurement of ^{90}Sr activity. However, cesium carbonate is a well soluble compound; therefore, considering mechanism of ions sorption by the T-3K, sorption of cesium is expected to be low.

Sorption of ^{137}Cs by the T-3K sorbent was studied in comparison with the T-3 sorbent under the same experimental conditions. The T-3 sorbent has OH$^-$ groups as the sorption sites and thus it shows very weak selectivity for cesium. The distribution coefficient of cesium for the T-3 sorbent was 30 mL/g, and the static exchange capacity was 0.5 mg/g. The experimental test of ^{137}Cs sorption by the T-3K sorbent from low mineralized water under batch conditions has shown that the degree of cesium sorption was very near to error of measurement, $S = 0.13 \pm 0.10$. Chemical modification of the T-3 sorption with sodium bicarbonate with the aim of increasing its selectivity for strontium resulted in replacing the OH$^-$ groups by –CO$_3$H and –CO$_3$Na groups (see Eqs. 1 and 2) and thus in depression of the ability to adsorb cesium. As it was shown above, chemical modification resulted in a decrease of the surface area of the sorbent and in an increase of the contribution of the external area. Therefore, the T-3K sorbent provided selective separation of strontium from ^{137}Cs.

The study of strontium sorption from natural water with various salt content

Isotherms of strontium sorption were also obtained for both T-3 and T-3K sorbent. The T-3 sorbent did not separate strontium from weakly mineralized water. Among nine solutions with various strontium concentrations in the experiment, the degrees of strontium sorption in two points were 0.07 ± 0.02 and 0.09 ± 0.04 at initial concentrations of strontium of 10^{-6} and 10^{-1} mg/L respectively. At the same time, sorption of strontium was nearly zero in other seven solutions. In contrast to the T-3 sorbent, the T-3K showed well selectivity for strontium.

Isotherms of strontium sorption by the T-3K sorbent from low mineralized water (pH 7.5 ± 0.1) and seawater (pH 8.0 ± 0.1) are presented at Fig. 6.

The isotherm of strontium sorption by the T-3K sorbent from weakly mineralized water was treated using the
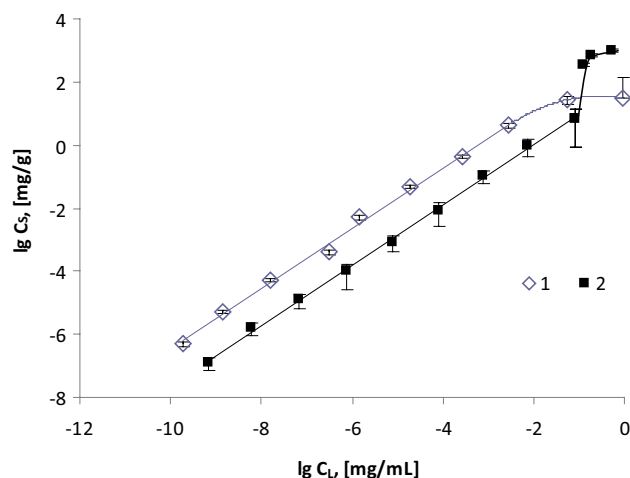
Fig. 6 Isotherms of strontium sorption by the T-3K sorbent from low mineralized water (1) and seawater (2). C_L is concentration of strontium in the equilibrium liquid phase and C_S is concentration of strontium in the equilibrium solid phase

mathematical models by Henry, Langmuir, Freundlich and Dubinin–Radushkevich for quantitative description of the results.

The Langmuir isotherm equation is [40]:

$$C_s = \frac{K_L \cdot C_L \cdot \Gamma_\infty}{1 + K_L \cdot C_L} \tag{6}$$

where C_s is equilibrium strontium concentration in the sorbent, mg g^{-1}; C_L is equilibrium strontium concentration in the solution, g L^{-1}; Γ_∞ is static exchange capacity (SEC) of the sorbent (sorption capacity after total saturation), mg g^{-1}; K_L is Langmuir's constant, L g^{-1}.

The Freundlich isotherm equation is [41]:

$$C_s = K_F \cdot C_L^{1/n} \tag{7}$$

where K_F is Freundlich's constant, L kg^{-1}; n is a parameter.

The Dubinin–Radushkevich isotherm equation is [42]

$$C_s = \Gamma_\infty \exp(-k \cdot \varepsilon^2), \tag{8}$$

where k is a constant depending on the energy of adsorption, mol^2/kJ^2; ε is chemical potential, kJ/mol; R the molar gas constant, 8.31 J/(mol K); T is the temperature, K.

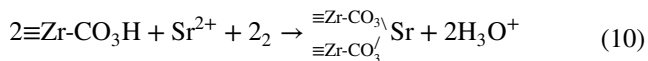$$\varepsilon = RT \ln(1 + 1/C_L) \tag{9}$$

The isotherms of sorption were plotted in linear coordinates and then treated using the least squares method; quantitative characteristics of the isotherms were determined. The equations were transformed into linear appearances, and the values of the respective constants were calculated (Table 4).
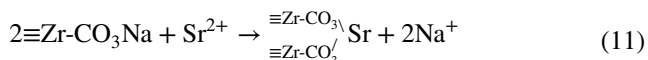
Table 4 Parameters of adsorption isotherms

Linear form of equation	Model constant	Value of the constant
Henry's equation $\lg C_s = \lg K_d + \lg C_L$	$\lg K_d$, mL/g	3.1 ± 0.4
	K_d, mL/g	$(1.3 \pm 0.1) \times 10^3$
	R^2	0.9966
Langmuir's model $\frac{C_L}{C_s} = \frac{C_L}{\Gamma_\infty} + \frac{1}{K_L \cdot \Gamma_\infty}$	Γ_∞, mg/g	30.4 ± 0.5
	K_L, mL/mg	78 ± 27
	R^2	0.9997
Freundlich's model $\ln C_s = \ln K_F + (1/n) \ln C_L$	K_F, (mg/g)·(mL/mg)$^{1/n}$	233 ± 59
	$1/n$	0.85
	n	1.2 ± 0.1
	R^2	0.9793
Dubinin–Radushkevich equation $\ln C_s = \ln \Gamma_\infty - k \cdot \varepsilon^2$	k, mol^2/kJ^2	$(5.9 \pm 0.9) \times 10^{-2}$
	Γ_∞, mg/g	9 ± 6
	R^2	0.9671

According to the correlation coefficients obtained, the Langmuir's model was the most suitable model for treating the isotherm of strontium sorption by the T-3K sorbent from weakly mineralized water over the entire concentration range studied. This indicates the ion exchange mechanism of sorption. The Henry's model was also adequate at low concentrations of strontium. Henry's distribution coefficient of strontium was 1.3×10^3 mL/g, the static exchange capacity of the sorbent was 30.4 ± 0.5 mg/g.

Considering the dependences of strontium sorption on pH and concentrations of other cations, ion exchange is the most probable mechanism of strontium sorption by the T-3K sorbent. Since the T-3 sorbent did not adsorb strontium, we suggested that the T-3K sorbent adsorbed strontium due to its carbonate phase. Hydrogen of the hydrocarbonate group exchanges by strontium resulting in formation of sparingly soluble strontium carbonate on the surface of zirconium dioxide. The reaction of interaction of the sorbent with strontium can be presented as following (10):

$$2{\equiv}Zr\text{-}CO_3H + Sr^{2+} + 2_2 \rightarrow \begin{smallmatrix} {\equiv}Zr\text{-}CO_3 \backslash \\ {\equiv}Zr\text{-}CO_3^/ \end{smallmatrix} Sr + 2H_3O^+ \qquad (10)$$

Strontium exchange by sodium also occurs (11):

$$2{\equiv}Zr\text{-}CO_3Na + Sr^{2+} \rightarrow \begin{smallmatrix} {\equiv}Zr\text{-}CO_3 \backslash \\ {\equiv}Zr\text{-}CO_3^/ \end{smallmatrix} Sr + 2Na^+ \qquad (11)$$

Exchange of sodium by strontium was confirmed by mass spectrometry; a significant increase of sodium concentration was observed in the solution after sorption.

Bezhin et al. [29] suggested another mechanism of strontium sorption by the T-3K sorbent; however, this suggestion seems to be doubtful because the authors stated that the T-3K sorbent is a hydrated zirconium dioxide rather than carbonate-containing zirconium dioxide as

we have shown above. We have tested the T-3 sorbent (hydrated zirconium dioxide) and found it did not uptake strontium.

The isotherm of strontium sorption from seawater had a linear appearance at strontium concentrations up to 100 mg/L pointing to the fulfillment of Henry's law. The T-3K sorbent separated strontium at these concentrations due to the ion exchange mechanism. At the same time, the isotherm had different appearance at the concentrations above 100 mg/L. This can be explained by a change of the sorption mechanism from ion exchange to precipitation of strontium carbonate in the pore space of the sorbent. This suggestion is confirmed by low solubility product of $SrCO_3$ (5.3×10^{-10}). The value of distribution coefficient of strontium from seawater (Mediterranean Sea) was 85 ± 25 mL/g that agrees well with the respective value of 1.1×10^2 mL/g being obtained in the experiments with simulated seawater [21]. According to the mathematical treatment of the sorption isotherm, the value of static exchange capacity for strontium in seawater was 7 mg/g. However, the sorption isotherm showed that the capacity of the T-3K sorbent for strontium may reach up to 980 mg/g (the maximal value of C_s) at strontium concentration in a solution of more than 100 mg/L probably due to a mechanism of strontium carbonate precipitation in the pore space of the sorbent. This feature of the sorbent allows using it for treating contaminated seawater containing strontium radionuclides or liquid radioactive waste based on seawater.

The study of strontium desorption

Desorption of strontium from the T-3K sorbent by various acidic solutions was studied under batch conditions to define the most suitable type and concentration of stripping solution. Figure 7 shows the dependences of the degree of
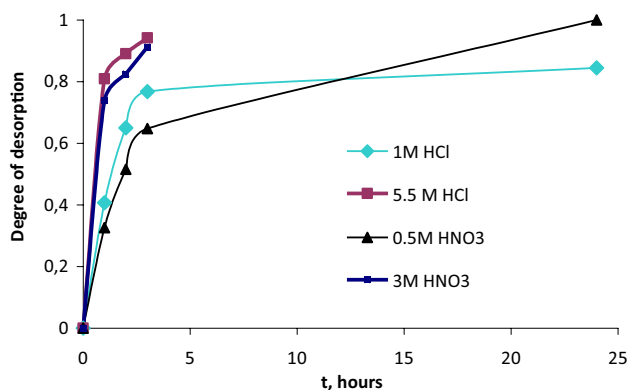
Fig. 7 The dependences of strontium desorption from the T-3K sorbent on time of the phases contact

strontium desorption from the T-3K sorbent by hydrochloric and nitric acid solution on time of the phases contact.

Nitric acid appeared unsuitable for strontium desorption since a turbidity of the solution because of destruction of the sorbent was observed even after 1 h of the phases contact. Hydrochloric acid solutions with the concentrations of 2, 3 and 5.5 mol/L were unsuitable too for the same reason. For example, destruction of the sorbent during desorption of strontium by 2 M HCl resulted in an increase of zirconium concentration in the solution that corresponded to leaching of 23% of zirconium from the T-3K sorbent. Thus, 1 M HCl was chosen as the most suitable stripping solution for strontium. The degree of strontium desorption after 3 h was 77%. The longer time of the phases contact is not recommended because a turbidity of the solution was observed after 24 h.

Conclusions

Physicochemical and sorption properties of the T-3K carbonate-containing zirconium hydroxide sorbent were studied. It was shown that the sorbent is a microporous carbonate-containing zirconium hydroxide consisting of ZrO_2 (46.39%), Na_2O (1.78%), Al_2O_3 (1.42%) as the major components excluding water.

The T-3K sorbent did not adsorb ^{137}Cs. Affinity of the T-3K sorbent for alkaline earth ions corresponded to the reverse trend of carbonates solubility: $Sr > Ba > Ca \gg Mg$. The maximal sorption of strontium achieved at pH 7–10 allowing for successful strontium separation from various aqueous solutions such as seawater and fresh waters, radioactively contaminated industrial waters and liquid radioactive waste. Distribution coefficient of strontium from low mineralized water was $K_d = 1.3 \times 10^3$ mL/g and the static exchange capacity of the sorbent was 30 mg/g. Sr^{2+}/Ca^{2+} separation factor depended on calcium concentration in the solution; this value was 9.3 in case of tap water with calcium

content of 14.3 mg/L. Separation factors of strontium and other alkaline earth ions were determined for sorption from low mineralized water and seawater. Distribution coefficient of strontium was invariable ($\sim 6.3 \times 10^3$ mL/g) at sodium concentration in the solution ≥ 0.0001 mol/L.

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