Investigation of Sr uptake by birnessite-type sorbents from seawater

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Abstract

Sorption of micro- and microamounts of Sr from seawater has been studied using granulated Na-birnessite. Distribution coefficients of 90 Sr in the natural seawater are $0.8-1.2 \times 10^3$ ml g⁻¹, in the model seawater they are $1.6-1.8 \times 10^3$ ml g⁻¹. Application of Na-birnessite was shown to be prospective in sorption–desorption–regeneration regime. In dynamic sorption conditions, over 150 bed volumes of seawater can be purified till 5% breakthrough occurs at feed rate 10 BV h⁻¹. Na-birnessite can be used for 90 Sr radionuclide removal from liquid radioactive wastes containing seawater.

Keywords Manganese oxide · Strontium-90 · Seawater · Radioactive liquid waste

Introduction

Nowadays, countries as Japan, South Korea and China actively build and operate nuclear power plants (NPPs). Some NPPs situated in the coastal zone use seawater for direct cooling thus setting up possible risks. E.g., in case of an accident, huge amounts of liquid radioactive wastes (LRW) of complex chemical composition can be formed and hazardous man-made radionuclides can be brought into the ocean as happened in 2011 on Fukushima-1 NPP [1, 2]. Besides, operating and shutting down nuclear submarines and vessels equipped with nuclear power generators are under way that inevitably cause accumulation of LRW of low activity level containing seawater (SW) [3, 4].

The most hazardous man-made radionuclides are ^{137,134}Cs and ⁹⁰Sr, which possess high migration ability and easily fit into biochemical cycles. The milestone of processing low-active LRW is transferring them into industrial wastes by preliminary concentrating ¹³⁷Cs and ⁹⁰Sr via

Andrei Egorin andrey.egorin@gmail.com various methods [5, 6]. If 137 Cs can be easily removed by ferrocyanide sorbents or by resorcinol–formaldehyde resins, removal of 90 Sr, especially from solutions with high contents of Mg²⁺ and Ca²⁺, is still an urgent issue [7].

To remove Sr from liquid medium various sorbents are used: synthetic and natural zeolites, barium silicate and sorbents based on titanium and manganese oxides [8–17].

Although natural and synthetic zeolites are widely applied as sorption materials, their low selectivity does not allow removing ⁹⁰Sr from SW [8, 9]. Only monolith Zeolite A can be an alternative to the immobilized beds of sorbent. Despite the high capacity with respect to Sr (5.1 mg-eq g⁻¹) in dynamic conditions the breakthrough occurs after 50 bed volumes [10].

Sorption-reagent materials based on barium silicates are another group of sorbents showing high selectivity to Sr^{2+} ions [11] due to peculiar sorption mechanism [12, 13]. Their main drawbacks are low hydromechanical stability and irreversible sorption that limits using these materials in sorption–regeneration cycles [18].

Sorbents based on hydrated titanium oxides and titanates of alkaline metals (SrTreat sorbent) were shown to be good at removing ⁹⁰Sr from alkaline solutions with high Na⁺ content (58 g L⁻¹) [14, 17]. There is also known a commercial sorbent T-5 and its modification T-55, sorption properties of which were studied in the presence of Ca²⁺. Mean K_d value of ⁹⁰Sr in the range of Ca²⁺ concentration



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0.05–110 g L⁻¹ is 500 ml g⁻¹ and 320 ml g⁻¹ for T-5 and T-55 sorbents, respectively. Sorbent based on titanosilicates of alkaline metals "IONSIV IE-911" can be used for simultaneous removal of ¹³⁷Cs and ⁹⁰Sr from mineralized media with high Na⁺ content. However, titanosilicates can hardly be implemented for ⁹⁰Sr removal from SW due to low selectivity [9, 11, 19].

Manganese oxides attract much interest as sorption materials for Sr removal from complex saline media including SW. Materials based on hydrated manganese oxides and its mixtures with titanium oxides are well known. It is noteworthy that sorption on manganese oxides proceeds reversibly, therefore making possible their repeatable use in sorption–regeneration cycle. Manganese oxides are known to enhance Sr uptake with the increase of solution pH [20, 21]. In Hasany et al. [20] this is addressed to hydrolysis of Sr²⁺ in liquid medium according to the scheme (1):

$$\mathrm{Sr}^{2+} + \mathrm{H}_2\mathrm{O} \leftrightarrow \mathrm{Sr}(\mathrm{OH})^+ + \mathrm{H}^+$$
 (1)

Alkaline medium shifts the equilibrium to the right followed by sorption of $Sr(OH)^+$ on the surface of the manganese oxide sorbent. However, such hydrolytic sorption occurs only if the sorbent possesses functional OH-group. Acidic medium suppresses hydrolysis followed by reduction of the sorption values that can be used to elute absorbed strontium [20].

Selectivity of hydrated manganese oxides increases in the row $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$ that implies removing ⁹⁰Sr from solutions containing even Mg²⁺ and Ca²⁺ ions. In the work [8] that studied different materials, sorbents based on hydrated and dehydrated oxides (ISMG, ISMP-1 sorbents) were the most efficient in the seawater. To date there are sorbents based on manganese oxides that were successfully used for processing liquid radioactive wastes from 90Sr. E.g., in FSUE IE "Mayak", ISM-S and ISM-SP sorbents, which are hydrated manganese oxide sorbents, allowed processing more than 2000 bed volumes of moderately mineralized LRW [15, 16]. Specific type of hydrated Mn and Ti oxide sorbents [22, 23] appeared to be efficient in processing highly active LRW from the Savannah River Site with the total mineralization of 400 g L^{-1} and Na⁺ being the main constituent. However, Ca²⁺ ions suppress the Sr sorption by these materials, thus limiting implementation of these sorbents for seawater decontamination [22, 23].

The most interesting Sr sorbents are layered and tunnel manganese oxides. Birnessite is a layered manganese oxide and can be considered as an efficient sorbent for Sr removal in presence of chemically close elements. Birnessite is a precursor for producing tunnel manganese oxides [24] and can be easily obtained using available methods and equipment. In Gray et al. [25] sorption capacity of K-birnessite with respect to alkali-earth metals was shown to increase with the size contraction of hydrated cation, while Ca and Mg exchange proceeds only by 50% [26]. In Dyer et al. [27] there were demonstrated two types of sorption cites for birnessite: A cites—binding alkali and alkali-earth metals, B cites—binding Co^{2+} , Zn^{2+} , Cu^{2+} and Mn^{2+} ions.

Tunnel manganese oxides, todorokite and cryptomellan, can be obtained by birnessite autoclaving at 140–170 °C for several days [28–30]. Sorption by manganese oxides with tunnel structure is governed by ion-sieve effect, i.e. ion retention occurs if pore diameter and effect cation radius are comparable [24]. These materials have satisfactory selectivity towards Sr even in the presence of Mg²⁺ and Ca²⁺ [31, 32].

Manganese oxides are fine powders that cannot be used in dynamic sorption regime. To overcome this, manganese oxide should me mixed with binding agent or it is applied on a mechanically stable matrix, thus complicating the sorbent's production. Possible binding agents or matrixes are SiO₂ [33], methylmethacrylate [34], alginate [35], fibers of chitosan-melanin complexes [36] and polyurethane foam [37]. More than 100 m³ of LRW with activity of 89–257 Bq ml⁻¹ was processed by composite sorbent with polyurethane foam used as a support.

Brief analysis of references has shown that most of the materials for Sr removal are low effective in the solution of complex salinity like SW. In some cases, despite high efficiency, Sr sorption can proceed irreversibly that excludes repeatable usage of the sorbents. Key-point of the modern safe management of LRW consists in minimizing volume of radioactive wastes (RW) that are sent to be fixed. That is why to implement an efficient technology for LRW processing one needs materials with high selectivity and ability to be repeatedly used in sorption-elution-regeneration cycle. Obtained radionuclide eluate then could be evaporated to a minimal volume. Fairly simple synthesis without autoclaving, well known sorption properties and satisfactory selectivity to Sr make birnessite the most preferable material to solve the mentioned technological problem.

Despite the great number of works related to birnessite sorbent, there is no information on application of this material for removing ⁹⁰Sr from seawater in dynamic conditions. The work studies sorption-selective characteristics of granulated sorbent Na-birnessite and investigates the process of ⁹⁰Sr removal from seawater in dynamic conditions of sorption-desorption-regeneration cycle regime.

Experimental

Materials and reagents

Potassium permanganate (KMnO₄), sodium hydroxide (NaOH), hydrogen peroxide (H₂O₂) (25–30%), hydrochloric acid (HCl) and strontium (stable) chloride (SrCl₂ × 6H₂O) were purchased from Nevareaktiv, Russia. All chemicals were of analytical grade and used without additional purifications. Carrier free radio-strontium (⁹⁰Sr) was obtained from Institute for Physics and Power Engineering named after A. I. Leypunsky as a chloride in 1 M hydrochloric acid solution and was diluted before use.

Seawater (SW) used in this work was collected from Amur Bay basin (Primorskiy krai, Russia) and was preliminary filtered through the Whatman "Blue Ribbon" filter with 3 μ m pores. Simulated SW (S-SW) was prepared according to Kester et al. [38]. Main characteristics of the liquid media used in the work are given Table 1.

A series of model solutions with different content of Mg^{2+} and Ca^{2+} were used in the work (Table 1, solutions MS-1, MS-2, MS-3, MS-4). In the first case we prepared a series of solutions without Ca^{2+} and with various Mg^{2+} content (0.002–2.4 g L⁻¹), in second, on the contrary, we prepared solutions without Mg^{2+} but with various Ca^{2+} content (0.004–4 g L⁻¹). We used solutions either with stable Sr isotope with concentration 50 mg L⁻¹ (MS-2, MS-4) or the radionuclide ⁹⁰Sr with activity 1000 Bq ml⁻¹ (MS-1, MS-3).

Synthesis of materials

Sorbent was obtained by interaction between 10 g of KMnO₄ and 250 ml of concentrated H₂O₂. Brown

Table 1 Characteristics of liquid media used in the work

Component	S-SW Concen	SW tration (g	MS-1 g L ⁻¹)	MS-2	MS-3	MS-4
Na ⁺	11	8.4	11		11	
K^+	0.4	0.4	0.4		0.4	
Mg^{2+}	1.3	1.2	0.002-2.4		0	
Ca ²⁺	0.41	0.4	0		0.004–4	
Sr ²⁺	0.008	0.007	0.0002	0.05	0.0002	0.05
$\mathrm{SO_4}^{2-}$	2.7	n/m ^a	2.7		2.7	
Cl^{-}	19.4		15-22		15-22	
HCO_3^-	0.14		0.14		0.14	
Br^{-}	0.07		0.07		0.07	
H ₃ BO ₃	0.026		0.026		0.026	
F^{-}	0.001		0.001		0.001	

^an/m-not measured

precipitate was filtered under vacuum and washed with 250–500 ml of deionized H₂O and then dried at 75 °C for 6 h. Obtained product was ground and held in 3 M solution of NaOH, *m/V* ratio 0.1–0.15 g ml⁻¹ for 24 h. The part of material was dried at 105 °C for 6 h, the obtained sorbent is denoted as MnO₂(105). After that the material was annealed at 500 °C in air for 6 h, heating rate 8.3 °C/min. Final sorbent formed granules of irregular shape, black color with characteristic metal luster and bulk weight of 1.56 g ml⁻¹. Material was denoted as MnO₂(500).

Material denoted as $MnO_2(500)HNa$ was obtained via the following procedure. Sorbent $MnO_2(500)$ (0.2 g) was put into column of 5 mm in diameter and then it was consequently fed up with 0.5 M solution of HCl and 1 M solution of NaOH at a rate of 10 bed volumes per hour (BV h⁻¹). After that, the material was washed with 50 ml of water and dried.

Sorption of Sr in static conditions

Sorption of Sr in static conditions was carried out under continuous stirring of the sorbent and liquid media in polypropelene 10 ml cylinder at a rate of 20–30 rounds per minute on the vertical rotary shaker for 24 h, m/V— 0.001 g ml⁻¹, sample mass—0.01 g. Initial activity of the solutions was 1000 Bq ml⁻¹. Liquid medium was separated from sorption material via decantation followed by filtration through the "Blue Ribbon" filter fixed in the Swinnex filter holder (2.5 cm in diameter). Then we measured residual activity and calculated distribution coefficient of ⁹⁰Sr (K_d) or the sorption of stable isotope (S%).

Distribution coefficient of ⁹⁰Sr was evaluated by formula (2):

$$K_{\rm d} = \frac{A_0 - A_1}{A_1} \times \frac{V}{m} \tag{2}$$

 90 Sr (%) sorption was calculated by formula (3):

Sorption% =
$$\left(1 - \frac{A_1}{A_0}\right) \times 100$$
 (3)

where A_0 —initial activity of the liquid medium (Bq ml⁻¹) or the initial concentration of Sr (mg L⁻¹), A_1 —residual activity of liquid medium after sorption (Bq ml⁻¹) or equilibrium concentration of Sr (mg L⁻¹), V—volume of liquid phase after sorption (ml), *m*—sorbent's mass (g).

Sorption isotherm was obtained using S-SW series of solutions with various initial Sr^{2+} concentrations. Sorption time was 7 days.

Sorption of Sr in dynamic conditions

Sorbents characteristics were studied in dynamic conditions using repeated sorption-elution-regeneration cycles. Prior to the experiment 1 ml of the sample was held 1 day in the liquid medium of SW or S-SW. Then the sorbent was transferred to a glass column with inner diameter 0.5 cm through which seawater containing 90 Sr (1000 Bq ml⁻¹) radiolabel was passed at a rate of 10 columns per hour $(BV h^{-1})$. To determine sorbent dynamic exchange capacity we used S-SW solution containing stable Sr of concentration 50 mg L^{-1} to reduce the time of the experiment. Decrease of strontium sorption efficiency up to 95% or lower we considered as a breakthrough. Retained Sr was eluted by 0.5 M HCl solution fed with 10 BV h^{-1} speed. After that the sorbent was regenerated with 100 ml of 1.0 M solution of NaOH, washed with 30 ml of distilled water and used in the next sorption cycle.

Sorption (%) under dynamic conditions was calculated by using the formula (3). Desorption of 90 Sr was calculated by the formula (4):

Desorption% =
$$\left(\frac{\sum_{1}^{i} V \times A_{1}}{A_{x} + A_{x-1}}\right) \times 100$$
 (4)

where A_1 —eluate activity (Bq ml⁻¹), V—eluate's volume (ml), A_x —activity of ⁹⁰Sr retained during sorption (Bq), A_{x-1} —residual activity of ⁹⁰Sr from previous cycle (Bq), *x*—cycle's ordinal number, *i*—eluate's fraction ordinal number.

Equipment

Content of ⁹⁰Sr in seawater samples was determined on a liquid scintillation alpha–beta spectrometric radiometer Tri-Carb 2910 TR (Perkin Elmer, USA). Element's content in the SW was evaluated using atomic absorption flame spectroscopy on a Thermo Solar AA M6 ("Thermo Electron Corporation", USA). XRD analysis was carried out on a D8 ADVANCE diffractometer, XRD-patterns were recorded in the 2θ range $3-85^\circ$ with 0.02° step and sampling time of 0.6 s per point. Phase composition was identified using "MATCH!" software and Crystallography Open Database (COD). Surface morphology was investigated by the means of scanning electron microscopy (SEM) on a device Carl Zeiss Crossbeam 1540-XB (Germany).

Results and discussion

Materials' notation, their sorption characteristics as well as sodium and potassium content are given in Table 2.

High selectivity with respect to removed cation is one of the most important characteristics of a sorbent used for processing highly mineralized liquid media, like seawater, from ⁹⁰Sr. Table 2 (columns 6, 7) presents values of $K_{\rm d}$ ⁹⁰Sr obtained in SW and S-SW and indicating some trends. E.g., with the increase of annealing temperature from 105 to 500 °C efficiency of radionuclides removal increases by more than 1.5. Probably, this is caused by formation of evident crystal phase of birnessite at higher temperatures. Preliminary sequential washing of the samples with HCl and NaOH also increases the Sr uptake efficiency. Such results can be explained by the fact that treatment of manganese oxide with NaOH does not allow full substitution of K by Na. However, treatment of the final sorbent with HCl solution removes K followed by its full substitution by Na after NaOH treatment. The hypothesis is proved by chemical analysis of the samples presented in Table 2 (columns 4 and 5) showing initial manganese oxide to have high K content. Sample washed with HCl and NaOH as well as the sample after three sorption-elutionregeneration cycles contains practically no potassium. Ivanets et al. [32] showed mesoporous manganese oxide removes Sr in 0.1 M solution of NaCl better than in distilled water, thus proving Na-form birnessite to be more efficient in scavenging Sr.

XRD patterns of the $MnO_2(105)$, $MnO_2(500)$, MnO₂(500)HNa are presented on Fig. 1. Materials are characterized by low crystallinity that complicates precise phase identification. However, obtained XRD patterns allows expecting several phases, mainly K- and Na-birnessite (see legend on Fig. 1).

SEM images of manganese oxide surface are given on Fig. 2. It can be seen that original samples are monolith granules of irregular shape (Fig. 2a, b), but sequential treatment of them with HCl and NaOH changes surface morphology (Fig. 2c–e) probably improving sorption-selective characteristics. It is noteworthy that sequential purging of HCl and NaOH leads to mass loss of the material (5% in average) evidencing the sorbent's dissolution and increasing specific surface area from 9.4 to $12 \text{ m}^2 \text{ g}^{-1}$ (see Table 2). Despite the material's dissolution it can be still used in dynamic conditions, because three cycles of sorption–regeneration have no effect on sorbent's granulation (Fig. 3f–h).

Even though materials based on manganese oxides effectively retain Sr in the presence of Na⁺ [22], it is obvious that sorption is greatly affected by Ca²⁺ and Mg²⁺ ions that are close chemical counterparts of Sr. Table 3 presents results of Sr sorption (stable isotope and ⁹⁰Sr) from model solutions containing Ca²⁺ and Mg²⁺ in various concentrations. Obviously, Ca²⁺ ions cause the most negative influence on Sr uptake. However, in model solution containing Ca²⁺ 0.4 g L⁻¹ value K_d ⁹⁰Sr are high enough

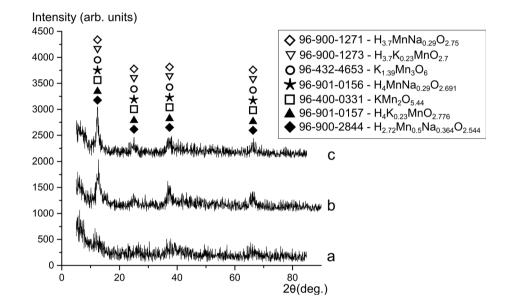
Table 2	Sorbents'	notation	and	their	sorption	characteristics
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Notation	Temperature of thermal treatment	Treatment with HCl + NaOH	ω(Na ⁺) [wt%]	ω(K ⁺) [wt%]	$K_{\rm d} {}^{90} {\rm Sr} \ ({\rm ml} \ {\rm g}^{-1})$		Specific surface
					SW	S-SW	area $(m^3 g^{-1})$
MnO ₂ (105)	105	_	n/m ^b	n/m	520	950	13.4
MnO ₂ (500)	500	-	4.1	4.37	890	1690	9.4
MnO ₂ (500)HNa	500	+	6.06	0.34	1240	1830	12
$MnO_2(500)SR^a$	500	+	5.49	0.31	n/m	n/m	n/m

^aSample MnO₂(500)HNa after three cycles of sorption-elution-regeneration

^bn/m-did not measured

Fig. 1 XRD patterns of synthesized samples,
(a) MnO₂(105), (b) MnO₂(500),
(c) MnO₂(500)HNa



indicating high selectivity of the sorption material and its applicability for radionuclides removal from seawater.

Isotherm of Sr sorption from S-SW by $MnO_2(500)$ HNa sorbent is given on Fig. 3. Fitting was carried out using classical Langmuir equation and SigmaPlot software (ver. 13.0). Isotherm is presented as a variable of removed Sr (Adsorbed Sr, mg g⁻¹) depending on its equilibrium concentration (equilibrium, mg L⁻¹). Evaluated saturation sorption value is 8.8 mg g⁻¹ (Sr/sorbent). Evaluated capacity is comparable with the values for commercial ion-exchange resin Sr Resin (Eichrom Technologies Inc [39] μ TrisKem International [40]). However, such values of sorption capacity can be achieved only in acidic media. Taking into account full exchange and total Sr content in SW, sorbent's capacity before breakthrough should exceed 1000 bed volumes.

In fact, sorption of Sr from the S-SW with the particular concentration of the ion (50 mg L^{-1}) in dynamic conditions reached 9.16, 7.82, 6.85 mg g^{-1} (Sr/sorbent) in the first, second and third cycles, respectively (Fig. 4a). Such

capacity reduction can be caused by gradual material's dissolution. After three cycles, the height of sorption layer reduced by 20%. Solubility can be explained by disproportionation of Mn^{+3} in the acidic medium into Mn^{+4} and Mn^{+2} [41].

While removing microquantities of ⁹⁰Sr from real SW, sorbent's capacity with respect to Sr content reduces and does not reach the maximal value. Capacity reduction is due to organic pollutants and organic carbon in the SW leading to reduction of Mn to lower oxidation states.

⁹⁰Sr uptake from SW is peculiar due to low efficiency of radionuclides removal in the first cycle (Fig. 4, curve 1) caused by the sorbent's turning on into the operating regime, transition into Na-form and formation of developed surface. Second and third cycles show sorbent's capacity to exceed 150 bed volumes, while changes of the sorbent's color or filtrate coloring were not revealed.

Elution curves of ⁹⁰Sr retained from real SW in dynamic conditions are given on Fig. 5a . Although obtained results evidence instable elution of radionuclide, residual ⁹⁰Sr

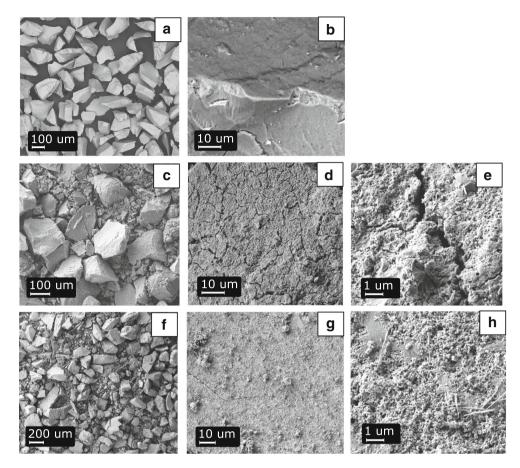


Fig. 2 Surface of the manganese sample: a, b $MnO_2(500)$, c–e $MnO_2(500)HNa$, f–h $MnO_2(500)SR$

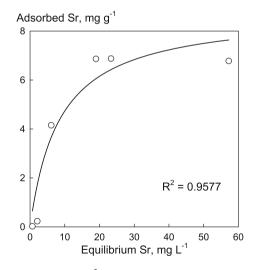


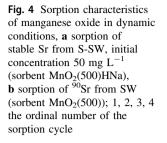
Fig. 3 Isotherm of Sr^{2+} sorption from S-SW (sorbent $MnO_2(500)HNa$)

activity in the sorbent is not higher than 4% of the total activity removed by the sorbent after 4 cycles. Treatment with NaOH is followed by insignificant desorption of residual 90 Sr (Fig. 5b) reaching 0.9, 1.1, 0.7 and 0.02% from the total activity retained in the cycle.

Table 3 Influence of concentration of Ca^{2+} and Mg^{2+} ions on Sr sorption (sorbent $MnO_2(500)HNa)$

	Solution	Concentration of Ca^{2+} (g L^{-1})				
		0.004	0.04	0.4	4	
S (%)	MS-2	98.1	97.5	59	2	
$K_{\rm d} {}^{90}{\rm Sr} \ ({\rm ml} \ {\rm g}^{-1})$	MS-1	40,200	13,700	1900	700	
		Concentration of Mg^{2+} (g L ⁻¹)				
_		0.002	0.02	0.24	2.4	
S (%) $K_{\rm d} {}^{90} { m Sr} ({ m ml} { m g}^{-1})$	MS-4 MS-3	98.7 189,800	97.7 54,300	91.1 22,000	82 6100	

Synthetic organic complexants like EDTA as well as oxalate salts salts are used both as cleansing agents and as a part of deactivating mixtures and washing means on nuclear power plants. That is why we studied sorptionselective characteristics of the sorbent in static conditions in the presence of Trilon B and oxalate ion (Table 4). Oxalate-ion was shown to have no effect on sorption-selective properties of the material based on manganese



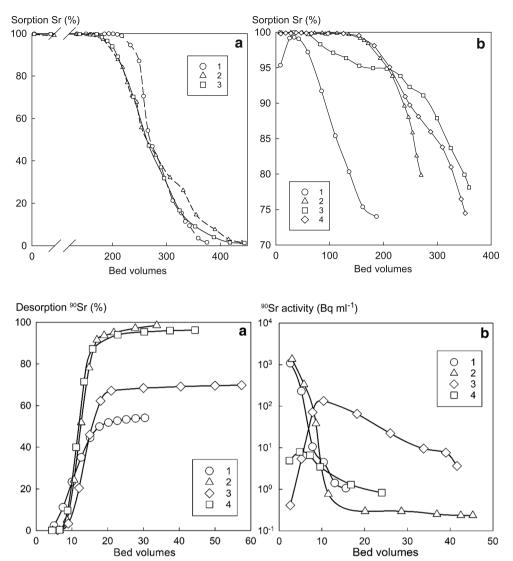


Fig. 5 Desorption of ⁹⁰Sr, **a** elution by 0.5 M HCl solution, **b** sorbent's regeneration by 1.0 M NaOH solution

Table 4Influence of organic complexing agents on sorption-selective
characteristics of the sorbent based on manganese oxide ($MnO_2(500)$)

	Trilon B concentration (g L^{-1})				
	0	0.17	1.7	17	
$\frac{K_{\rm d}^{90} \text{Sr (ml g}^{-1}) \text{ in S-SW}}{K_{\rm d}^{90} \text{Sr (ml g}^{-1}) \text{ in SW}}$	1746 822	958 574	801 445	665 424	
	$C_2 O_4^{2-}$ concentration (g L ⁻¹)				
	0	0.04	0.4	4	
$K_{\rm d} {}^{90}{\rm Sr} \ ({\rm ml} \ {\rm g}^{-1}) \ {\rm in} \ {\rm S}{\rm -}{\rm SW}$ $K_{\rm d} {}^{90}{\rm Sr} \ ({\rm ml} \ {\rm g}^{-1}) \ {\rm in} \ {\rm SW}$	1653 893	1689 908	n/m* n/m*	n/m* n/m*	

*n/m-did not measured

oxide. However, concentrations of oxalate-ions higher than 0.04 g L^{-1} in SW and S-SW lead to formation of insoluble precipitates of calcium and magnesium followed by coprecipitation of ⁹⁰Sr.

Presence of Trilon B negatively affects sorption-selective characteristics of the sorbent, probably due to formation of stable Mn-EDTA complexes and material's structure distortion. E.g., Trilon B was shown to have a negative influence on sorption characteristics of materials based on manganese oxides [20, 27].

Conclusions

Obtained sorption material for 90 Sr removal from seawater has been obtained via interaction of KMnO₄ and H₂O₂ followed by NaOH treatment and annealing. Final sorption material is a low crystallized layered modification of manganese oxide, namely Na–K-birnessite. HCl treatment of birnessite followed by NaOH regeneration has been shown to improve efficiency of Sr uptake by the sorbent from seawater and simulated solutions. Presence of Ca²⁺ ions downgrades sorption efficiency of birnessite sorbent. Nevertheless, even at the concentration of Ca 0.4 g L^{-1} the mean coefficient of ⁹⁰Sr distribution is 1.9×10^3 ml g⁻¹, therefore allowing the use of the material seawater treatof ⁹⁰Sr ment. Distribution coefficients are $0.8-1.2 \times 10^3 \text{ ml g}^{-1}$ in natural seawater, $1.6-1.8 \times 10^3$ ml g⁻¹ in simulated seawater and the evaluated value of maximal capacity is 8.8 mg g⁻¹. In dynamic regime, material is mechanically stable and preserves granulation. However, under long term operation, the dynamic exchange capacity of the sorbent reduces due to its dissolution. That is why long term material's exploitation requires regular addition of new sorbent. The mean volume of seawater fed before the breakthrough of 90 Sr is 150 bed volumes at the filtration rate 10 BV h⁻¹. Presence of Trilon B makes the material less efficient due to its decomposition, which is why purified LRW should not contain organic complexing agents. The material described herein should be used for processing liquid ⁹⁰Sr wastes containing seawater from radioactive radionuclide.

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