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New Sorbents Based on Polyacrylonitrile Fiber and Transition Metal Ferrocyanides for ^{137}Cs Recovery from Various Composition Solutions

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Featured Application: New sorbents based on polyacrylonitrile fiber and transition metal ferrocyanides can be used for ^{137}Cs selective sorption from technological solutions (liquid low- and intermediate-level waste; seawater containing radioactive waste; wastewater), as well as from natural waters (fresh and saltwater) with the purpose of radioecological monitoring.



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Abstract: For the first time, new sorbents based on polyacrylonitrile (PAN) fiber and transition metal ferrocyanides were obtained. The main difference between the obtained sorbents and the existing ones is the stage of preliminary preparation of the initial support by converting it into the forms PAN-Fe(OH)₃ or PAN-MnO₂, due to which additional ion exchange groups (carboxyl, carbonyl, etc.) are formed, which increases the amount of ferrocyanide fixed to the support. The best components and conditions for the synthesis of new sorbents were determined (concentration (0.1–0.2 mol/L), as well as pH (1 for sorbents based on PAN-Fe(OH)₃, and 1–5—PAN-MnO₂) of potassium ferrocyanide solution, concentration of transition metal salts (0.02 mol/L), temperature conditions). The influence of the studied solution composition (pH, concentration of Na⁺, K⁺, NH₄⁺ ions) on the cesium distribution coefficients during its recovery by the obtained sorbents was assessed. The possibility of cesium recovery from solutions with pH 1–9 containing macro quantities of cations was demonstrated. The sorbents derived were characterized by modern structural methods such as infrared spectroscopy, thermogravimetric analysis, and scanning electron microscopy with EDS analysis. A study of the trace amount sorption of ^{137}Cs was carried out in comparison with commercially available highly efficient sorbents (FNS-10 and Termoksid-35), and it was shown that the resulting sorbents are not inferior to industrial ferrocyanide sorbents and can be used for ^{137}Cs selective sorption from technological solutions and natural waters.

Keywords: cesium; ^{137}Cs ; sorption; polyacrylonitrile fiber; transition metal ferrocyanides

1. Introduction

During the operation of nuclear fuel cycle enterprises, a significant amount of radioactive waste of various chemical and radionuclide compositions is generated, the main part

of which is liquid radioactive waste of low and medium levels of activity. They pose a great environmental hazard due to their significant volume and high total activity, as well as the possibility of uncontrolled spread in emergencies and, as a consequence, environmental pollution [1]. In addition, despite the efforts made to localize radioactive substances as a result of nuclear defense programs implementation, the functioning of nuclear fuel cycle enterprises, as well as the occurrence of emergencies, radionuclides enter the environment, significantly changing the natural radioactivity of soils, natural waters, and bottom sediments, which causes serious environmental threats requiring urgent measures [2].

Radionuclide ^{137}Cs , whose half-life is 30.1 years [3], is characterized by high migration ability in the external environment, as well as ease of integration into food chains. It is intensively sorbed by soil and bottom sediments and is found in water mainly in the ion form. Entering the human body, cesium is distributed relatively evenly, which leads to an almost uniform irradiation of organs and tissues. Constant systematic monitoring of ^{137}Cs activity in natural waters makes it possible to identify new and relevant sources of radioactive contamination [4]. In addition, to determine the accumulation coefficients of a given radionuclide in aquatic organisms, it is necessary to have information about its content in water.

In this regard, the urgent task is to develop new methods for ^{137}Cs selective recovery from low- and intermediate-level waste, as well as methods for ^{137}Cs radioanalytical monitoring in environmental objects. To solve the problem of isolating and concentrating cesium from technological and natural waters of various compositions with low radionuclide content, high salt content, and the presence of significant amounts of isomorphic potassium and sodium, sorption methods can be used. Due to the increased interest in the problem of sorption and concentration of ^{137}Cs from liquid media of complicated composition, all over the world, there is a continuous search, development, and improvement of sorption materials with characteristics such as high selectivity to the radionuclide, sorption efficiency, mechanical and chemical strength, as well as simplicity of production and low cost.

Thus, for ^{137}Cs sorption, a selective resorcinol–formaldehyde resin (RFR) was proposed [5], the advantage of which is the possibility of its repeated use after the stages of radionuclide elution and regeneration. A composite material based on RFR with different contents of barium silicate was created, tests of which showed that an increase in the concentration of barium silicate leads to a decrease in cesium distribution coefficients [6]. High values of cesium distribution coefficients, when recovered from acidic, neutral, and alkaline media, were also obtained on sorbents based on sodium titanate [7,8].

The most widely used sorbents for the ^{137}Cs recovery are those based on ammonium phosphomolybdate (AMP) [9,10] and transition metal ferrocyanides [4,11]. Various supports are impregnated with phosphomolybdate: PAN fiber (AMP-PAN) [9], silica gel (AMP-SiO₂) [10], and others. However, it should be noted that sorbents based on AMP are prone to adsorption of ^{40}K , which leads to an overestimation of the result of measuring ^{137}Cs activity; therefore, sorbents based on transition metal ferrocyanides are preferable [4]. Transition metal ferrocyanides can be used to extract ^{137}Cs in pure form [12] or deposited on a support: PAN fiber (KNiFC-PAN) [4,13,14], silica gel (SiO₂-KMCHCF [15], FSS [16], FC-Cu-EDA-SAMMS [17]), aluminosilicates (Niket-k) [18,19], chitin-containing materials (FFCG-SO₄-FC [20], Mikoton-Cs [21], CFC Zn-K, CFC Cu-K, CPC Ni-K [22]), hydrated zirconium dioxide (Thermoxide 35) [16,23,24], activated carbon (C/NiHCF, C/InHCF, C/CuHCF) [25], cellulose support (Anfezh [16,19,26], Uniket [18], NKF-C [27,28], FN and FN-50 [19,29]), natural minerals (diatomite (FND) [19,24], tripolite [30], clinoptilolite (NPF-CL) and quartz-glaucinite concentrate (NPF-GL) [23,31,32]) and others. Zeolite–imidazole frameworks [33], mesoporous silica gels [34], aerogels [35], and hydrogels [36], which showed high sorption characteristics in cesium recovery, should be mentioned as new promising supports. However, their widespread use is hampered by commercial unavailability. In addition, under dynamic conditions, these sorbents have high hydrodynamic resistance and do not allow for achieving high transmission rates of the test solution.

The use of natural raw materials, including renewable ones, as a support can significantly reduce the cost of sorbents in industrial production. Most often, natural biopolymers are used in the form of cellulose raw materials. However, it should also be noted that the sorbents obtained from natural cellulose initially contain ^{137}Cs radionuclides up to 36.3 mBq/g, which complicates their use in the concentration and determination of ^{137}Cs in environmental objects, including natural waters [31].

The physicochemical properties of the support (matrix), in particular the presence of functional exchange groups, determine the peculiarity of the transition metal ferrocyanide fixation on an inert support. Fixation of the ferrocyanide active phase on supports that do not have ion exchange properties occurs due to adhesion or mechanical fixation of transition metal ferrocyanide crystals. If the support contains functional groups, additional electrostatic interaction of ferrocyanide particles with them takes place [37–39]. Modification of ion exchange resins is one of the first methods for the synthesis of composite sorbents [40]. A feature of such material synthesis is the need for sequential processing of the ion exchange resin with solutions of transition metal salts and potassium ferrocyanide. Sorbents obtained by immobilizing transition metal ferrocyanides on supports that do not contain functional exchange groups can be obtained either by sequential treatment of the supports with solutions of transition metal salts and potassium ferrocyanide [23,32] or directly by modification with transition metal ferrocyanide [41,42], which greatly simplifies synthesis.

Fibrous sorbents impregnated with transition metal ferrocyanides, which, due to their developed specific surface area, have increased kinetic parameters of the ion exchange process [43], ensuring complete sorption of ^{137}Cs at increased flow rates of the test solution, are of great interest. Due to these characteristics, as well as the simplicity of the production method, this type of material can be considered the most promising. This is especially true for radioecological monitoring of natural objects when passing large volumes of natural water samples with a low content of ^{137}Cs through the sorbent is necessary. Owing to the high throughput rate under expeditionary conditions, it is possible to process a greater number of samples, which will make it possible to receive a more detailed distribution of ^{137}Cs in considered objects.

Unfortunately, fibrous sorbents are currently not available for use due to the lack of established industrial production in Russia. However, it should be noted that in foreign studies, sorbents based on PAN fiber—KNiFC-PAN—have become widespread for ^{137}Cs sorption [4,14]. Therefore, this work is aimed at obtaining and comprehensively studying highly efficient fibrous sorbents based on transition metal ferrocyanides.

2. Materials and Methods

2.1. Materials

PAN fiber produced by Moscow Wool Spinning Factory OJSC (Moscow, Russia), which is pure 100% polyacrylonitrile without oxygen, with a thread thickness of 19 microns, was used as a support for sorbent production.

Sodium hydroxide, sodium nitrate, iron(III) chloride, ammonia, nitric acid, potassium ferrocyanide, cobalt(II) chloride, nickel(II) chloride, copper(II) chloride, zinc(II) chloride (ReaChem JSC LLC, Moscow, Russia), potassium permanganate (NevaReaktiv LLC, St. Petersburg, Russia) were qualified as chemically pure for analysis.

To prepare calibration and test solutions, a standard sample solutions CRM (Certified Reference Materials of solutions of metal ions) 0160:2004 [44] (Ormet LLC, Ekaterinburg, Russia) was used.

Seawater was sampled in the Sevastopol Bay of the Black Sea (sampling point coordinates: 44.62128, 33.56376). Salinity—18.1‰, pH—7.8. The composition of the sampled seawater is presented in detail in our previous study [16].

Seawater samples were filtered through nitrocellulose membrane filters with a pore size of 0.45 μm and a diameter of 47 mm (ZAO Vladisart, Vladimir, Russia).

2.2. Method of Support Preparation

Preliminary preparation of the initial PAN fiber was carried out using two methods, by precipitating iron(III) hydroxide with ammonia on pre-hydrolyzed PAN (converting PAN to the form PAN-Fe(OH)₃) and by treating it with potassium permanganate (converting PAN to the form PAN-MnO₂). These techniques and the conditions for their implementation are described in detail in our previous works, presented in [45,46], respectively.

During the preliminary preparation of PAN fiber, additional ion exchange groups (carboxyl, carbonyl, etc.) are formed, which is confirmed by the IR spectra given in [45,46]. This increases the amount of ferrocyanide mounted onto the support at the next stages of sorbent production.

2.3. Method of Sorbent Production

Schemes for obtaining sorbents are presented in Figure 1.

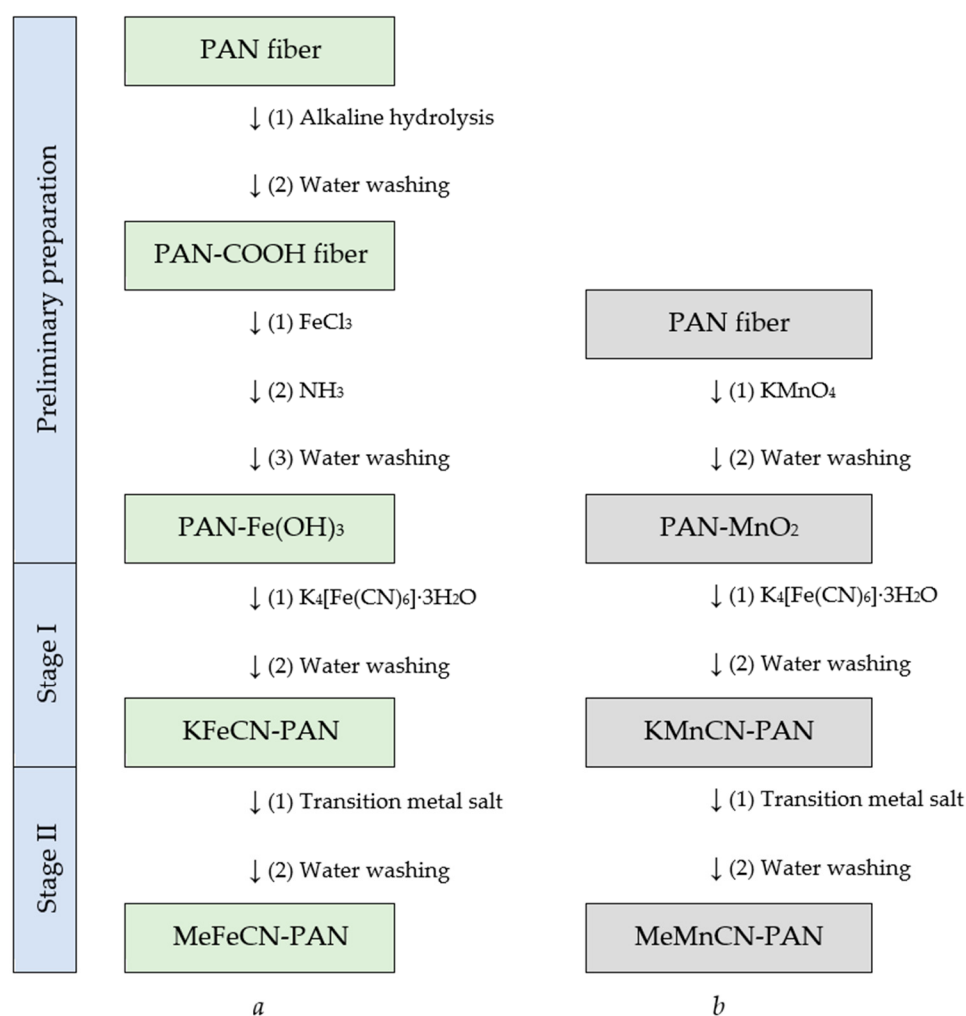


Figure 1. Schemes for the production of fibrous ferrocyanide sorbents: (a) based on fiber prepared by precipitation of iron(III) hydroxide with ammonia; (b) based on fiber treated with potassium permanganate.

To obtain sorbents at the first stage, the pre-prepared PAN fiber was kept in a weakly acidic solution of potassium ferrocyanide under various conditions (concentration of potassium ferrocyanide, pH of the potassium ferrocyanide solution, temperature). After this, the fiber was washed with distilled water until a clear washing solution was achieved and dried at room temperature or in a stream of warm air.

Then, at the second stage, the fiber was kept in a solution of a transition metal salt (iron, cobalt, nickel, copper, or zinc) under various conditions (transition metal salt concentration, temperature). The produced sorbent was washed with distilled water till the clear washing solution and also dried at room temperature or in a stream of warm air.

Summary data on the synthesis of sorbents using various materials and synthesis conditions are given in Table 1.

Table 1. Summary data on the synthesis of sorbents.

Synthesis Conditions		CoFeFC-PAN	NiFeFC-PAN	CuFeFC-PAN	ZnFeFC-PAN	FeMnFC-PAN	CoMnFC-PAN	NiMnFC-PAN	CuMnFC-PAN	ZnMnFC-PAN
Support	PAN-Fe(OH) ₃	+	+	+	+	–	–	–	–	–
	PAN-MnO ₂	–	–	–	–	+	+	+	+	+
Stage I	Solution of K ₄ [Fe(CN) ₆]	C, mol/L	0.05	+	+	+	+	+	+	+
			0.1	+	+	+	+	+	+	+
			0.2	+	+	+	+	+	+	+
			0.35	+	+	+	+	+	+	+
			0.5	+	+	+	+	+	+	+
		pH	1	+	+	+	+	+	+	+
			1.2	+	+	+	+	+	+	+
			1.5	+	+	+	+	+	+	+
			2	+	+	+	+	+	+	+
			2.5	+	+	+	+	+	+	+
			2.9	+	+	+	+	+	+	+
			3.5	+	+	+	+	+	+	+
			4.2	+	+	+	+	+	+	+
			5	+	+	+	+	+	+	+
	t _I , °C	25	+	+	+	+	+	+	+	+
		50	+	+	+	+	+	+	+	+
		80	+	+	+	+	+	+	+	+
Stage II	Solution of FeCl ₃ , mol/L	0.01	–	–	–	+	–	–	–	–
		0.02	–	–	–	+	–	–	–	–
		0.05	–	–	–	+	–	–	–	–
		0.1	–	–	–	+	–	–	–	–
	Solution of CoCl ₂ , mol/L	0.01	+	–	–	–	+	–	–	–
		0.02	+	–	–	–	+	–	–	–
		0.05	+	–	–	–	+	–	–	–
		0.1	+	–	–	–	+	–	–	–
	Solution of NiCl ₂ , mol/L	0.01	–	+	–	–	–	+	–	–
		0.02	–	+	–	–	–	+	–	–
		0.05	–	+	–	–	–	+	–	–
		0.1	–	+	–	–	–	+	–	–
	Solution of CuCl ₂ , mol/L	0.01	–	–	+	–	–	–	+	–
		0.02	–	–	+	–	–	–	+	–
		0.05	–	–	+	–	–	–	+	–
		0.1	–	–	+	–	–	–	+	–
	Solution of ZnCl ₂ , mol/L	0.01	–	–	–	+	–	–	–	+
		0.02	–	–	–	+	–	–	–	+
		0.05	–	–	–	+	–	–	–	+
		0.1	–	–	–	+	–	–	–	+
	t _{II} , °C	25	+	+	+	+	+	+	+	+
		50	+	+	+	+	+	+	+	+
		80	+	+	+	+	+	+	+	+

2.4. Analysis of the Obtained Sorbents by Structural Methods

IR spectra of the produced sorbents were recorded on a Spectrum 1000 spectrometer (Perkin Elmer, Waltham, MA, USA) using KBr tablets.

Thermogravimetric analysis of materials was carried out using a differential thermal analyzer DTG-60H (Shimadzu, Kyoto, Japan). The analysis was carried out in an argon atmosphere, with a heating rate of 10 °C/min.

Images of the structure of the materials under study were obtained by scanning electron microscopy using a Carl Zeiss CrossBeam, the XB 1540 device (Zeiss Int., Oberkochen, Germany), with an attachment for energy dispersive analysis.

2.5. Sorption of Cesium Ions

The sorption of cesium ions was carried out according to the method presented in [25]. A sample of the sorbent weighing 0.1 g, weighed with an accuracy of 0.0001 g, was continuously mixed with 20 mL of the test solution for 48 h. After that, the sorbent and solution were separated by filtration through a “white tape” filter paper, and the concentration of cesium in the filtrate was determined. Each experiment was repeated at least three times.

As a liquid phase, solutions of sodium nitrate with a concentration of 0.1 and 1 mol/L, pH 6, and in seawater of the composition given in Section 2.1 with a cesium concentration of 10–20 mg/L, were used. According to [24], these sodium nitrate solutions are recommended for assessing the sorption properties of sorbents concerning cesium.

Quantitative determination of cesium concentration in solutions was carried out on a KVANT-2 atomic adsorption spectrophotometer (Kortek LLC, Moscow, Russia) in the emission mode in an acetylene air flame at a wavelength of 852.1 nm. The error in determining cesium averaged 1% and did not exceed 2%.

The cesium distribution coefficient was determined by equation [9,47]

$$K_d = \frac{C_0 - C}{C} \cdot \frac{V}{m}, \quad (1)$$

where C_0 is the concentration of cesium in the initial solution, mg/L; C —cesium concentration in the filtrate, mg/L; V —volume of solution, mL; m —sorbent mass, g.

2.6. Sorption of Trace Amounts of ^{137}Cs

Experiments on the sorption of ^{137}Cs microquantities were carried out under static conditions by continuously mixing a sample of air-dry sorbent weighing about 0.05 g, weighed with an accuracy of 0.0001 g with 20 mL of solution for 24 h.

Then, the mixture was filtered through a “white tape” paper filter and the specific activity of ^{137}Cs in the filtrate was determined by the direct radiometric method using the SKS-50M spectrometric complex (Green Star Technologies, Moscow, Russia). Based on analysis results, the distribution coefficient values of the corresponding radionuclide were calculated using equation [24,48]

$$K_d = \frac{A_0 - A}{A} \cdot \frac{V}{m} \quad (2)$$

where A_0 and A are, respectively, the specific activity of the ^{137}Cs radionuclide in the initial solution and the filtrate, Bq/L.

The solutions studied were 0.1 and 1 mol/L solutions of sodium nitrate with pH 6 and seawater of the above composition.

Before the start of the experiments, indicator amounts of ^{137}Cs radionuclide in an amount of about 10^5 Bq/L were added to the solution and kept for 3 days at room temperature to achieve equilibrium of the various ionic and radioactive forms of solution components.

3. Results and Discussion

3.1. Selection of Optimal Materials and Conditions for Sorbent Synthesis

To obtain sorbents with the best cesium sorption performance, it was necessary to select the components and conditions for the synthesis of these sorbents, namely the concentration of potassium ferrocyanide, the pH of the potassium ferrocyanide solution, the transition metal salt and its concentration, and the synthesis temperature.

3.1.1. Assessment of the Effect of Potassium Ferrocyanide Concentration and pH

When obtaining sorbents, the prepared support was treated at the first stage with a solution of potassium ferrocyanide with different concentrations and at different pH levels. Two types of sorbents were obtained:

- KFeFC-PAN—sorbents based on potassium ferrocyanide and fiber prepared by precipitation of iron(III) hydroxide with ammonia (PAN-Fe(OH)_3);
- KMnFC-PAN—sorbents based on potassium ferrocyanide and fiber treated with potassium permanganate (PAN-MnO_2).

Figure 2 shows the dependences of the cesium distribution coefficients on the concentration of potassium ferrocyanide in a solution with pH 1, used in the preparation of sorbents.

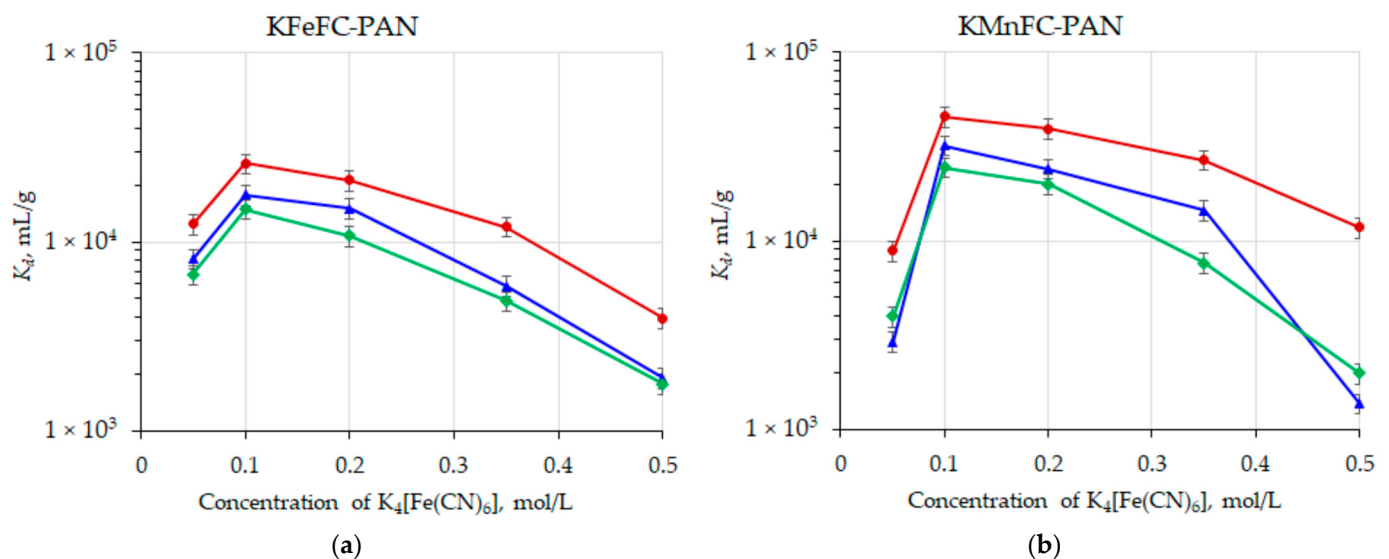


Figure 2. Dependences of the cesium distribution coefficients upon sorption from 0.1 (●) and 1 (◆) mol/L solutions of sodium nitrate with pH 6 and seawater (▲) on the concentration of potassium ferrocyanide solution used at the first stage in sorbent preparation: (a) KFeFC-PAN; (b) KMnFC-PAN.

From the data obtained, it is seen that in both cases the optimal concentration of potassium ferrocyanide solution is 0.1–0.2 mol/L, which generally corresponds to data from other studies on the production of sorbents based on ferrocyanide [26,49].

Thus, according to [26], at high content of potassium ferrocyanide in the initial modifying solution, an unstable solid phase of variable composition is formed ($\text{KFe}[\text{Fe}(\text{CN})_6] \cdot n\text{K}[\text{Fe}(\text{CN})_6]$, where n is a variable value depending on the concentration of $\text{K}_n[\text{Fe}(\text{CN})_6]$ in the initial solution), which, unlike normal and mixed iron(III) ferrocyanides, is soluble in water. Therefore, in cases of its formation, a certain fraction of iron(III) ferrocyanide passes from the solid phase into solution, which is the reason for the decrease in the sorption capacity of ferrocyanide ions during the modification process.

Figure 3 shows the dependence of distribution coefficients of cesium on the pH of a potassium ferrocyanide solution with a concentration of 0.1 mol/L used in the preparation of sorbents.

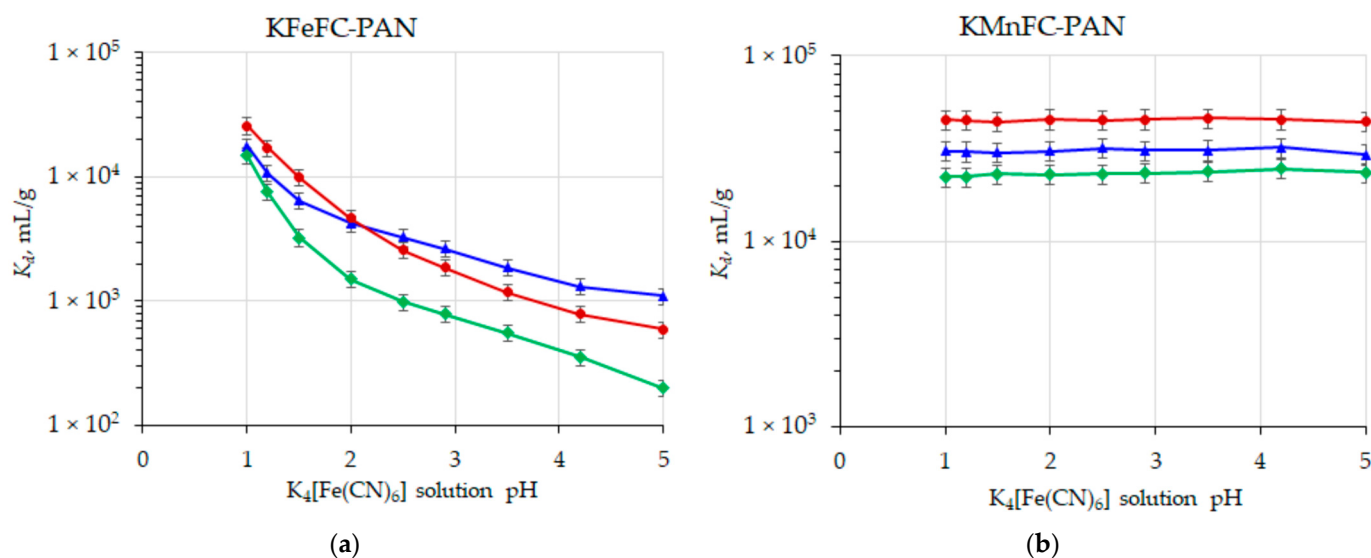


Figure 3. Dependences of the cesium distribution coefficients upon sorption from 0.1 (●) and 1 (◆) mol/L solutions of sodium nitrate with pH 6 and seawater (▲) on the pH of potassium ferrocyanide solution used at the first stage in sorbent preparation: (a) KFeFC-PAN; (b) KMnFC-PAN.

For sorbents obtained based on PAN fiber prepared by precipitation of iron(III) hydroxide with ammonia (PAN-Fe(OH)₃) [45], it was found that the best cesium distribution coefficients are achieved when using a ferrocyanide solution with pH of 1–1.5.

This is explained by the fact that at this pH, iron(III) hydroxide dissociates according to the main type [50]. At high pH, the dehydroxylation of iron(III) hydroxide is insignificant, so the modification of the fiber is less active. The data acquired coincide with the conclusions reached when obtaining the Anfezh sorbent [26]. The production of sorbents at a pH of less than 1 was not carried out, because according to [26], under these conditions, peptization of the sorbent occurs, accompanied by the transition of part of the ferrocyanide component into a solution.

In the case of using PAN fiber treated with potassium permanganate, the sorption characteristics of the resulting sorbents do not depend on the pH of the potassium ferrocyanide solution in the range from one to five, which is consistent with the data of other researchers [49].

3.1.2. Assessment of the Influence of Transition Metal Salt Type and Concentration

At the second stage of the synthesis, solutions of cobalt(II), nickel(II), zinc(II), copper(II), and iron(III) chlorides with a concentration of 0.01–0.1 mol/L were used for subsequent processing of sorbents. Pre-treatment of the prepared PAN-Fe(OH)₃ and the PAN-MnO₂ fiber (first stage of synthesis) was carried out with a 0.1 mol/L solution of $K_4Fe(CN)_6$ with pH 1.

Results obtained for sorbents based on KFeFC-PAN (PAN fiber prepared by precipitation of iron(III) hydroxide with ammonia PAN-Fe(OH)₃, followed by treatment with potassium ferrocyanide) and KMnFC-PAN (PAN fiber treated with potassium permanganate PAN-MnO₂, followed by treatment with potassium ferrocyanide) are shown in Figures 4 and 5, respectively. More detailed dependences of the cesium distribution coefficients on the concentration of the transition metal salt, taking into account the concentration of potassium ferrocyanide used in the preparation of sorbents, are given in Supplementary Materials in Figures S1 and S2.

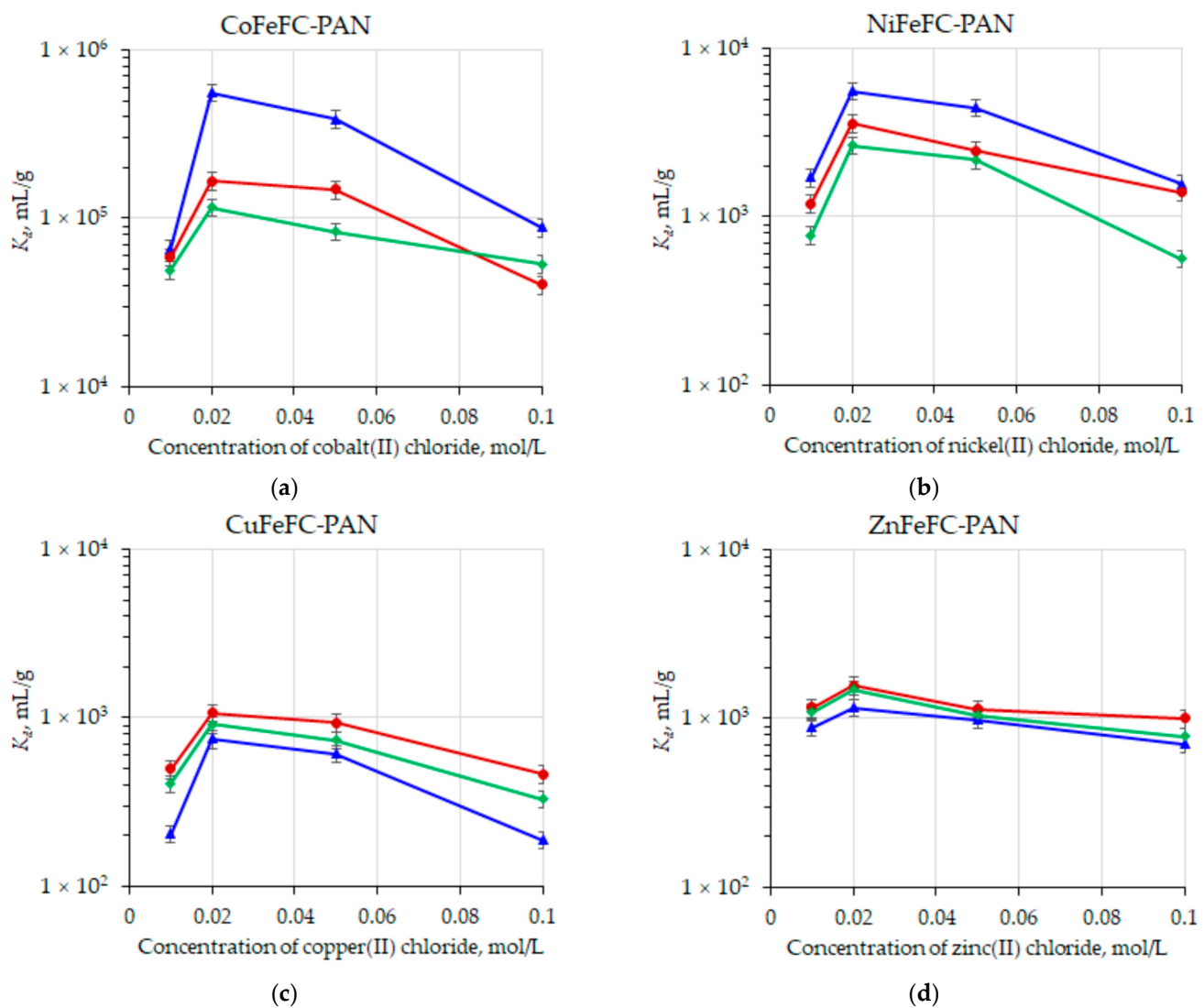


Figure 4. Dependence of the cesium distribution coefficients upon sorption from 0.1 (●) and 1 (◆) mol/L solutions of sodium nitrate with pH 6 and seawater (▲) on the concentration of the transition metal salt used in sorbent preparation: (a) CoFeFC-PAN, (b) NiFeFC-PAN, (c) CuFeFC-PAN, (d) ZnFeFC-PAN.

It was found that for sorbents based on PAN fiber prepared by precipitation of iron(III) hydroxide with ammonia (PAN-Fe(OH)₃), the best cesium distribution coefficients are achieved when cobalt(II) chloride is used for modification with a concentration of 0.02 mol/L—CoFeFC-PAN sorbent.

For sorbents based on fiber treated with potassium permanganate (PAN-MnO₂), the best cesium distribution coefficients are achieved at a concentration of cobalt(II) chloride of 0.02–0.05 mol/L and iron(III) chloride of 0.02 mol/L—sorbents CoMnFC-PAN and FeMnFC-PAN, respectively.

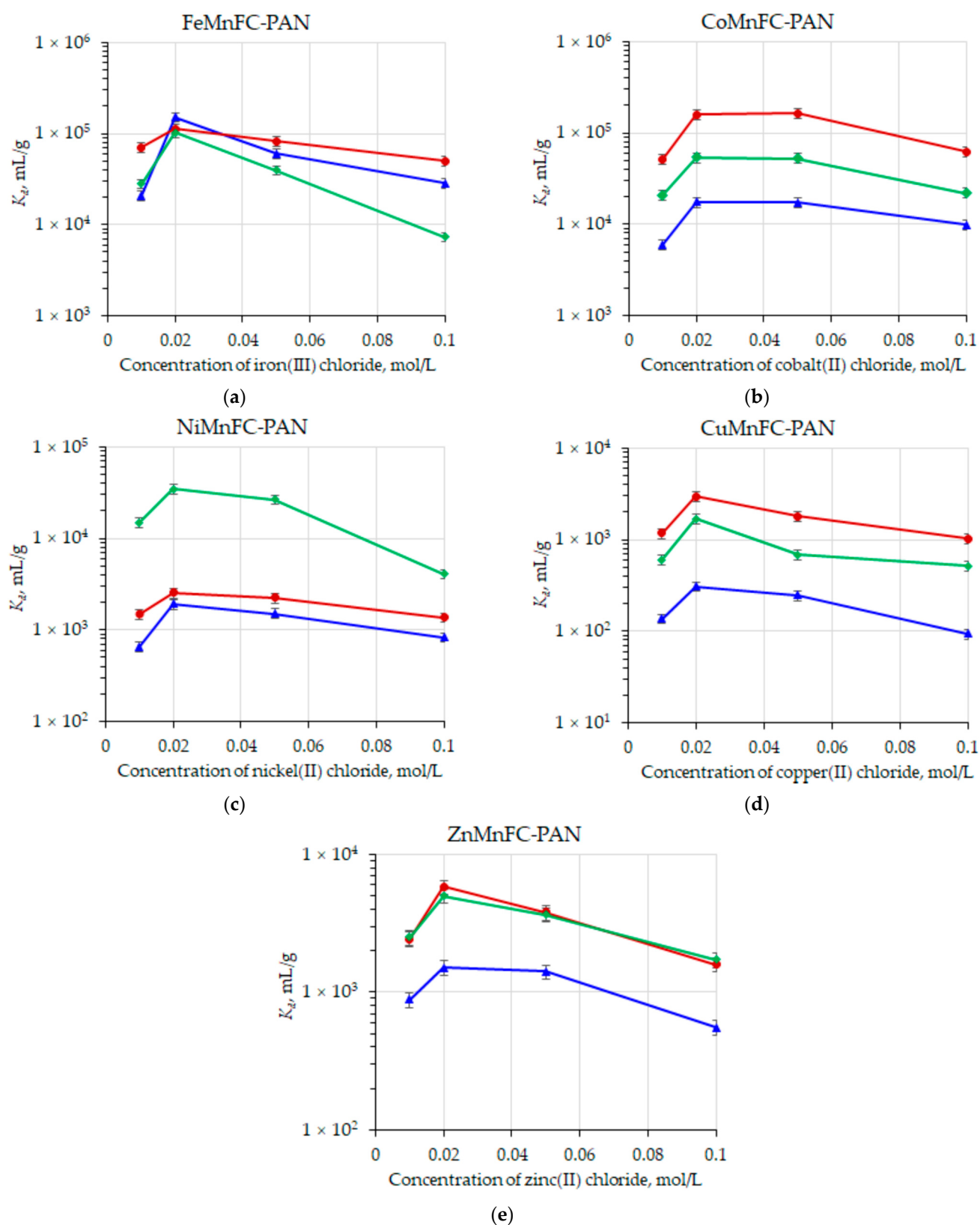
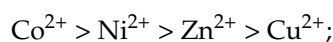


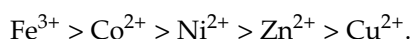
Figure 5. Dependence of the cesium distribution coefficients upon sorption from 0.1 (●) and 1 (◆) mol/L solutions of sodium nitrate with pH 6 and seawater (▲) on the concentration of the transition metal salt used in sorbent preparation: (a) FeMnFC-PAN, (b) CoMnFC-PAN, (c) NiMnFC-PAN, (d) CuMnFC-PAN, (e) ZnMnFC-PAN.

In general, the degree of influence of the transition metals used on the cesium sorption can be expressed as follows:

- for sorbents based on PAN-Fe(OH)₃ support:



- for sorbents based on PAN-MnO₂ support:



The analysis of work [38] devoted to the study of sorbents based on transition metal ferrocyanides shows that sorption characteristics largely depend on the type of transition metal in the inorganic phase. At the same time, various authors [13,38] obtained different series of decreases in the capacity of ferrocyanide sorbents concerning cesium. The authors associate such discrepancies with the peculiarities of the formation and binding of the matrix surface with the sorption-active phase, the properties of which depend on the method of composite sorbent obtaining [37,38].

3.1.3. Assessment of Synthesis Temperature Influence

The effect of synthesis temperature was assessed at the first and second stages of sorbent production—modification with potassium ferrocyanide and modification with a transition metal salt. The synthesis was carried out at room temperature (22–25 °C), as well as at 50 and 80 °C using an IR-1M3 rotary evaporator (LOIP, St. Petersburg, Russia).

The effect of reaction mixture temperature on the sorption-active properties of the materials produced was assessed in different variations, in particular under the influence of temperature only at the first stage, only at the second stage, and also at both stages.

It was found that synthesis temperature does not affect the sorption properties of the materials produced; the obtained cesium distribution coefficients differ within the error. The results obtained are shown in Supplementary Materials in Table S1.

Further studies were carried out on sorbents that showed the best sorption characteristics—CoFeFC-PAN, CoMnFC-PAN, and FeMnFC-PAN.

3.2. Structure of the Obtained Sorbents

The obtained sorbents were studied by structural methods using infrared (IR) spectrometry, thermogravimetric (TGA) analysis, and scanning electron microscopy (SEM) with energy dispersive analysis (EDS).

In the IR spectra of the obtained sorbents (Figure 6), peaks in the range of 2000–2150 cm^{−1} are visible, corresponding to the C≡N group coordinated with the metal, which indicates the presence of a complex ion [Fe(CN)₆]^{4−} [51].

In the region of 3200–3500 cm^{−1}, there is a wide absorption of the carboxyl group as well as of hydroxyl groups [52]. The absorption peak at 1730 cm^{−1} can be associated with stretching vibrations of the carbonyl group [53], which in turn is formed due to partial oxidation of the polymer chain during the fiber modification process.

The absorption bands in the region of 2940 cm^{−1} and 1450 cm^{−1} belong to the methyl and methylene groups of the polymer chain [53]; their positions are identical in the IR spectra.

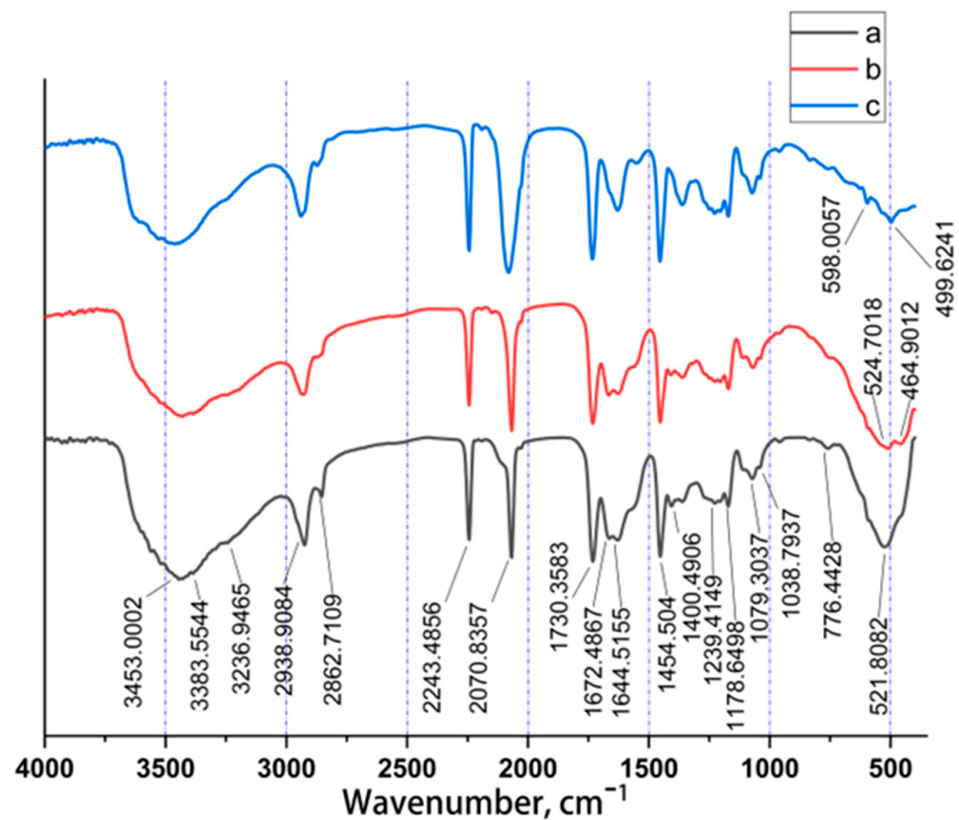


Figure 6. IR spectra of sorbents: (a) CoFeFC-PAN; (b) CoMnFC-PAN; (c) FeMnFC-PAN.

Figure 7 shows the thermograms of obtained fibrous sorbents that have the following features. Heating to 300 °C was accompanied by a slight weight loss up to 6% for the CoFeFC-PAN sorbent (based on fiber prepared by precipitation of iron(III) hydroxide with ammonia) and up to 15% for FeMnFC-PAN and CoMnFC-PAN sorbents (based on fiber treated potassium permanganate); up to 200 °C, the heating corresponded to the process of dehydration of crystallization in molecular water [54]. When heated to 300 °C, two parallel processes probably occurred: the beginning of the cyclization of PAN, as well as the removal of crystallization and molecular water [54]. Also, at the stage from 290 to 450 °C for all samples, an increase in the rate of weight loss was observed, which is characterized by thermal-oxidative destruction of mixed transition metal ferrocyanides, with a maximum rate at 350 °C and 390 °C. At this stage, the complex ion $[\text{Fe}(\text{CN})_6]^{4-}$ decomposed with the formation of ferrites and transition metal oxides with the release of presumably cyanogen [55].

At temperatures above 400 °C, there was a sharp decrease in the mass of the sample and an increase in the calorific value of the product as the temperature rose, which is associated with further carbonization and burnout of the organic residue [56]. With further heating to 800 °C, the weight curve gradually reached a plateau.

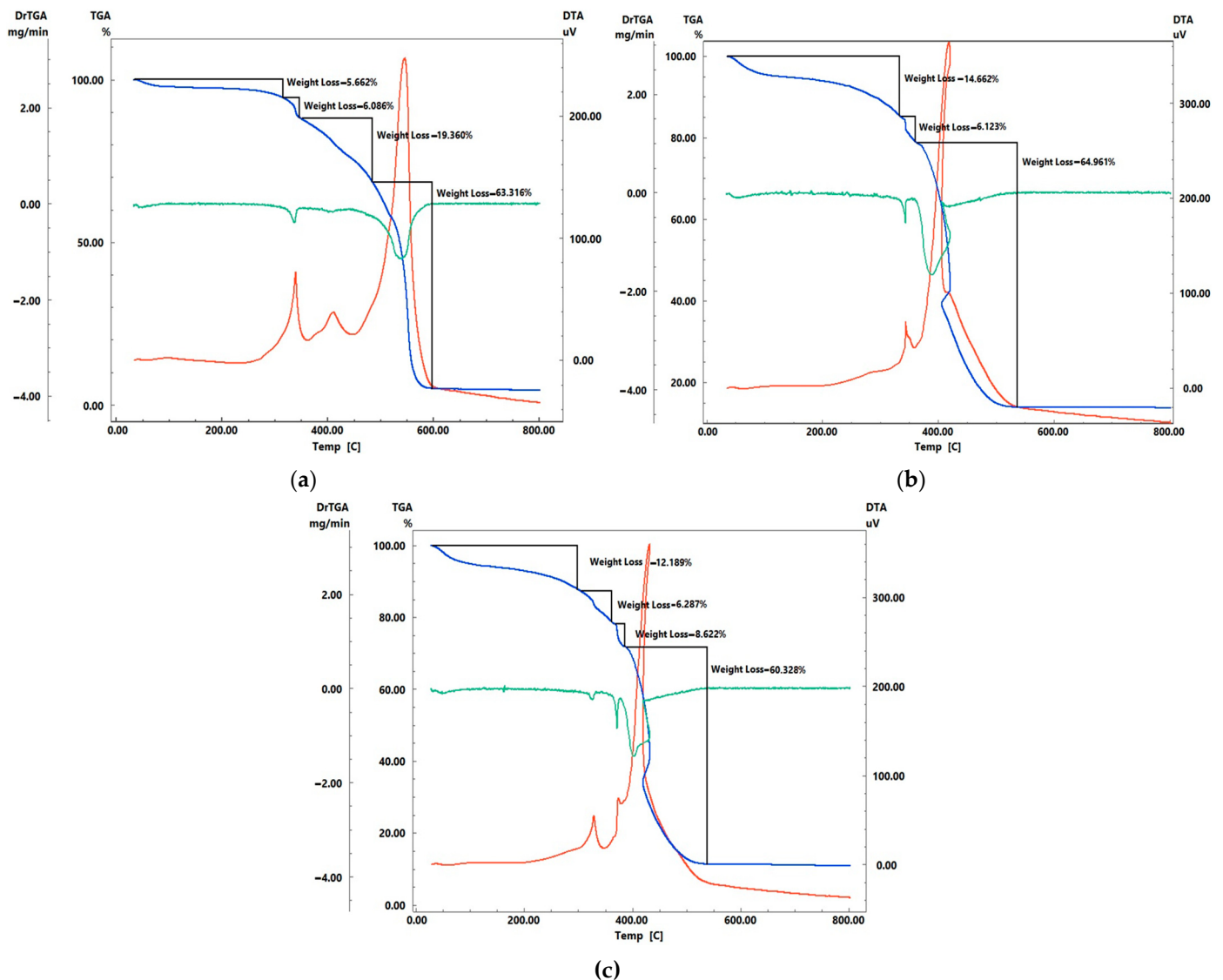


Figure 7. Thermograms of the obtained sorbents: (a) CoFeFC-PAN; (b) CoMnFC-PAN; (c) FeMnFC-PAN (heating rate—5 °C/min; lines: blue—mass change curve; red—DTA curve; green—derivative of the DTA curve; black—areas of significant drop in mass in a certain temperature range, a description of which is given below).

The SEM image of fibrous sorbents (Figure 8) shows the presence of interlayer spaces in which the formation of coarse-grained deposits occurs during the modification of PAN fiber. In addition, the formation of deposits also occurs on the entire surface of individual fibers, which is confirmed by the results of EDS analysis (Figure 9).

Also, using energy dispersive analysis (Figure 9), the distribution of elements on the surface of composite materials was assessed, and the results obtained are presented in Table 2. It was found that during the formation of the ferrocyanide layer, the distribution of all components of the mixture occurs evenly, regardless of synthesis conditions.

Table 2. Elemental composition of the surface of the resulting sorbents.

Sorbent	Fe, %	Mn, %	Co, %	K, %	C, %	O, %	N, %
CoFeFC-PAN	26.75	—	5.44	3.54	28.86	17.24	18.17
CoMnFC-PAN	7.55	15.23	4.89	4.01	32.97	15.32	20.03
FeMnFC-PAN	9.68	33.37	—	4.41	32.38	8.63	11.53

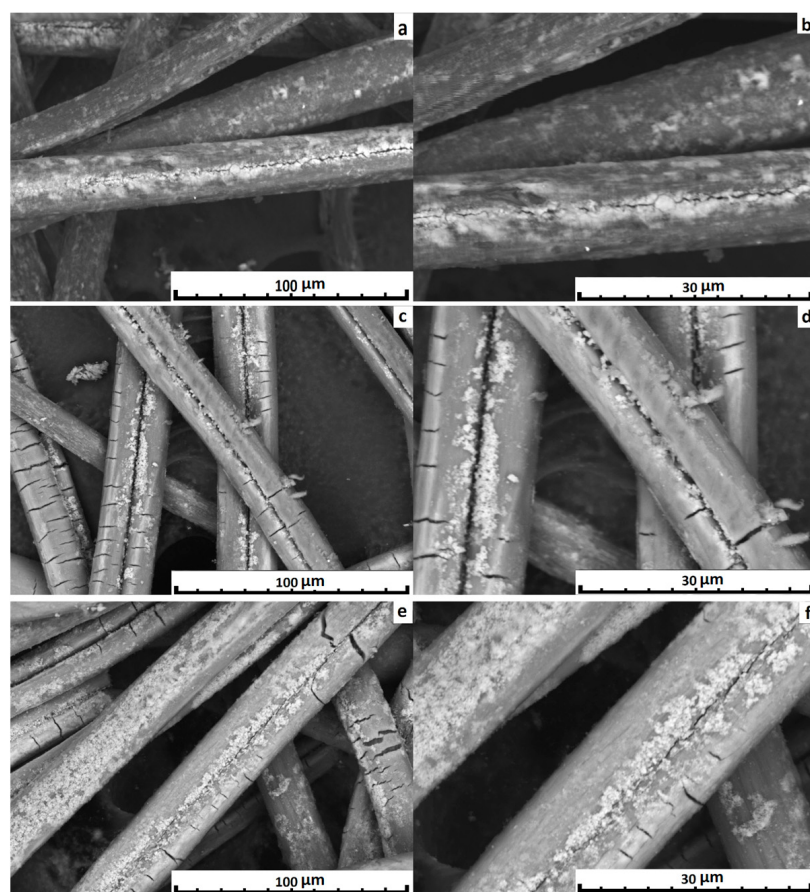


Figure 8. SEM images: (a,b)—CoFeFC-PAN; (c,d)—CoMnFC-PAN; (e,f)—FeMnFC-PAN (100–30 μm).

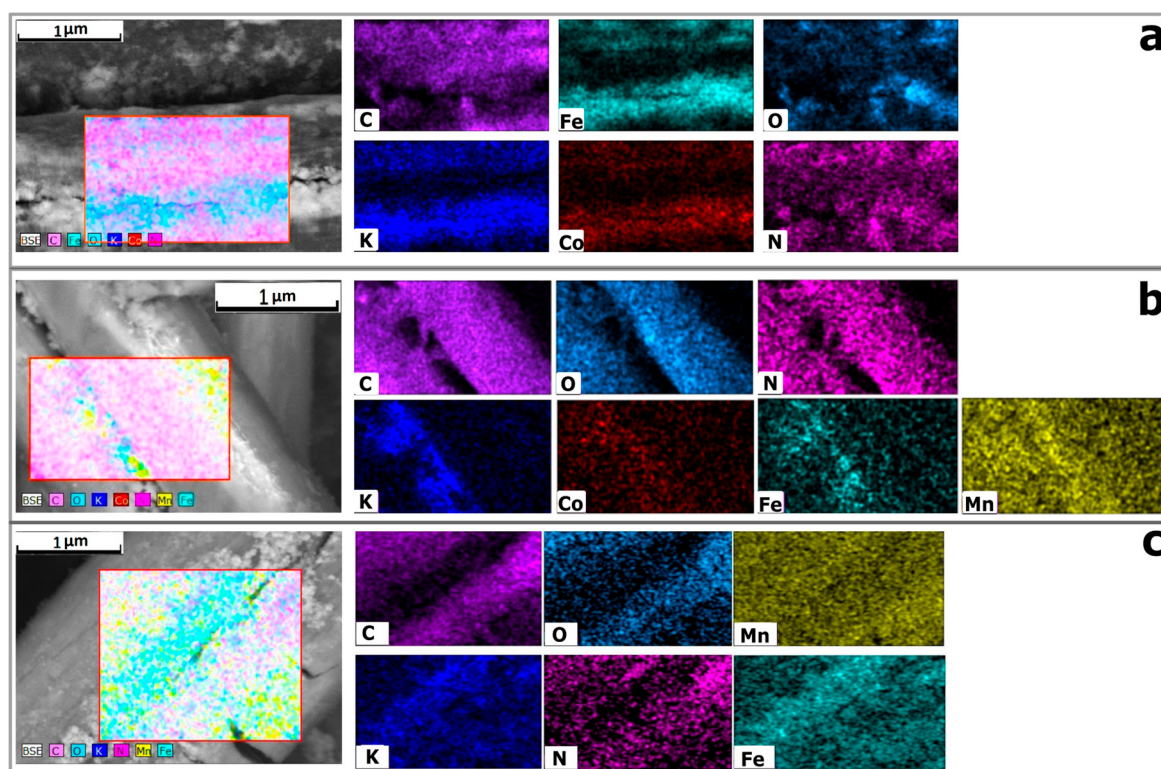


Figure 9. EDS analysis: (a) CoFeFC-PAN; (b) CoMnFC-PAN; (c) FeMnFC-PAN.

3.3. Sorption of Trace Amounts of ^{137}Cs

To obtain comparative characteristics of the studied samples under similar conditions, ^{137}Cs sorption was carried out on the following sorbents:

- FNS-10—sorbent based on nickel–potassium ferrocyanide deposited on silica gel (TU 2641-003-51255813-2007. Manufacturer: Institute of Physics and Chemistry of the Russian Academy of Sciences, Moscow, Russia);
- Termoksid-35—spherogranulated inorganic sorbent based on nickel ferrocyanide and zirconium hydroxide (TU 6200-305-12342266-98. Manufacturer: JSC “Inorganic Sorbents” (former NPF “Termoksid”), Zarechny, Russia).

The values of the obtained distribution coefficients of ^{137}Cs on various sorbents during sorption from model solutions of the composition mentioned above are given in Table 3.

Table 3. Elemental composition of the surface of obtained sorbents.

Sorbent	K_d ^{137}Cs (mL/g) for Various Sorbents in Solution of		
	0.1 mol/L NaNO_3	1.0 mol/L NaNO_3	Seawater
CoFeFC-PAN	$(1.4 \pm 0.4) \times 10^5$	$(1.0 \pm 0.2) \times 10^5$	$(5.3 \pm 1.7) \times 10^5$
CoMnFC-PAN	$(1.5 \pm 0.7) \times 10^5$	$(4.5 \pm 0.1) \times 10^4$	$(2.0 \pm 0.2) \times 10^4$
FeMnFC-PAN	$(7.4 \pm 0.3) \times 10^4$	$(1.1 \pm 0.3) \times 10^5$	$(1.6 \pm 0.3) \times 10^5$
FNS-10	$(8.4 \pm 0.3) \times 10^4$	$(7.3 \pm 0.2) \times 10^4$	$(1.1 \pm 0.3) \times 10^4$
Termoksid-35	$(1.2 \pm 0.4) \times 10^5$	$(8.1 \pm 0.2) \times 10^4$	$(3.1 \pm 0.3) \times 10^4$

The results presented in Table 3 show that in all studied media, the CoFeFC-PAN sorbent has the highest sorption characteristics concerning ^{137}Cs , that is, not inferior to the best industrial ferrocyanide sorbents.

In addition, it should be noted that previously, under similar conditions, when extracting from 0.1 and 1 mol/L solutions of sodium nitrate with pH 6 [19,24] and seawater [16], a large number of sorbents of various types were tested: organic ion exchange resins, natural and synthetic aluminosilicates and zeolites, oxyhydrates, phosphates, titanosilicates, ferrocyanide sorbents, carbon sorbents. Papers [16,19,24] present detailed comparative tables of ^{137}Cs distribution coefficients. When comparing our results with those presented, it is seen that the effectiveness of obtained sorbents is not inferior to the effectiveness of existing materials. For example, the maximum determined distribution coefficients are $(6.8 \pm 0.6) \cdot 10^4$ mL/g and $(6.1 \pm 0.4) \cdot 10^4$ mL/g for ferrocyanide sorbents Anfezh and FD-M based on cellulose support. For the obtained sorbents, CoFeFC-PAN and FeMnFC-PAN, the distribution coefficients are greater than 10^5 mL/g, which indicates their promise for marine expeditionary research.

3.4. Selection of Optimal Conditions for Cesium Sorption

The study on the cesium sorption efficiency from solutions of various compositions (pH, concentration of Na^+ , K^+ , NH_4^+ ions) with the sorbents obtained in this work was also carried out.

The following results assessment of the effect of solution pH on cesium sorption were obtained, presented in Figure 10.

Based on the results of assessing the influence of solution pH, it is seen that the produced ferrocyanide sorbents are characterized by the independence of cesium distribution coefficients from pH in the range from one to eight, which is associated with the high selectivity of the ferrocyanide phase to cesium. At the same time, a decrease in the distribution coefficients of cesium in an alkaline medium at pH above nine was observed for sorbents, associated with peptization and partial destruction of the ferrocyanide phase. Overall, the results show that the sorbents obtained are potentially suitable for the sorption and concentration of cesium from liquid media in the pH range from one to nine.

Figure 11 shows the results of assessing the dependence of the cesium sorption efficiency on the type and concentration of the cation, which can have a significant competing effect.

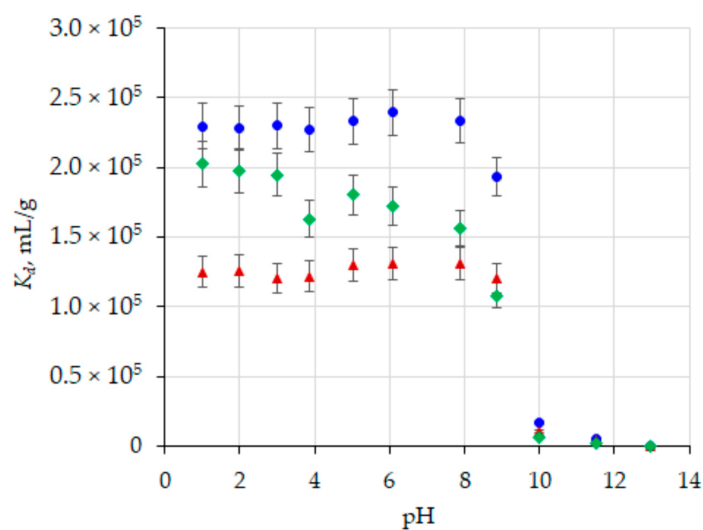


Figure 10. Dependence of cesium distribution coefficients during sorption by produced sorbents CoFeFC-PAN (●), FeMnFC-PAN (▲), and CoMnFC-PAN (◆) on the pH of the test solution.

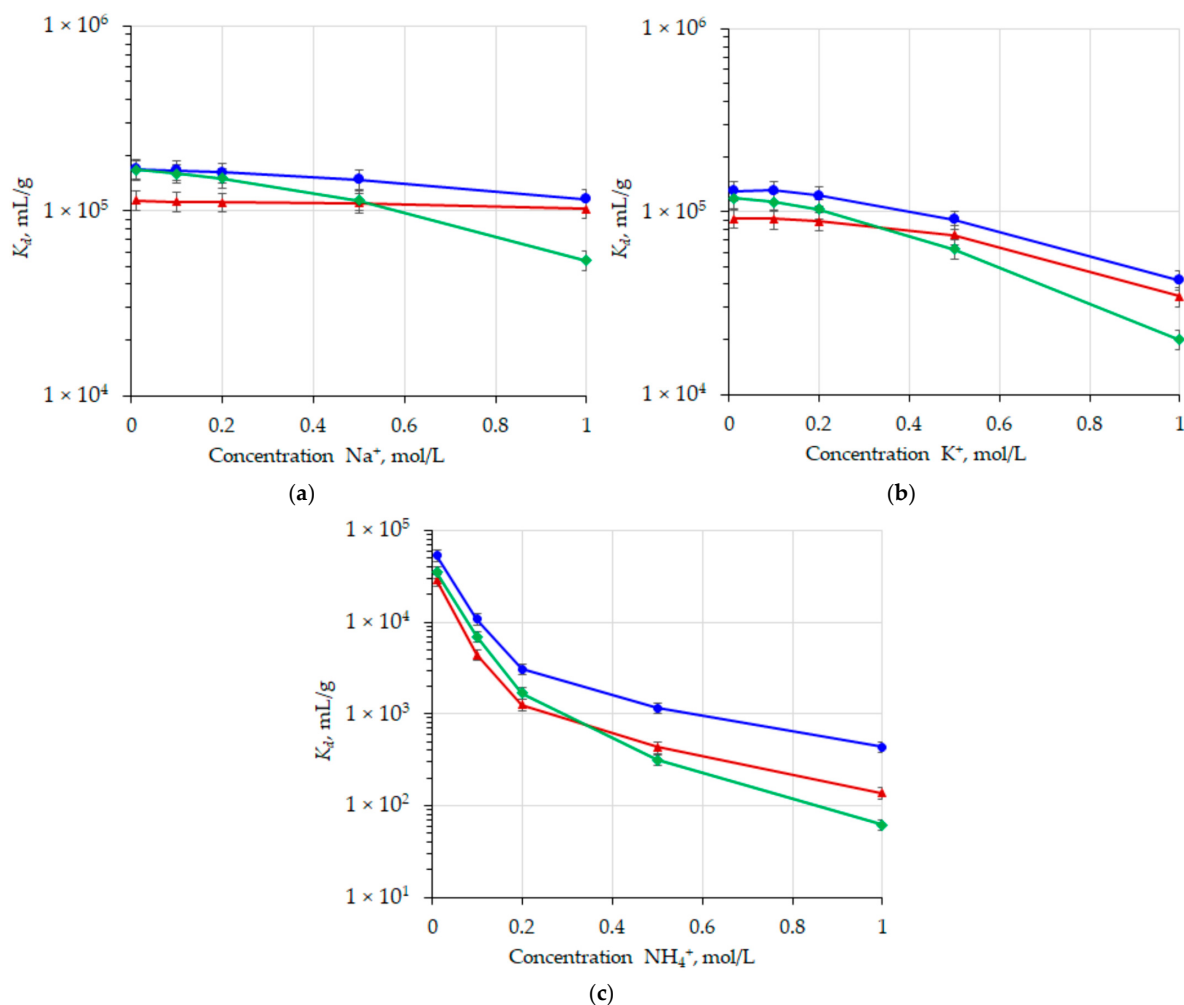


Figure 11. Dependence of the cesium distribution coefficients during sorption by produced sorbents CoFeFC-PAN (●), FeMnFC-PAN (▲), and CoMnFC-PAN (◆) on the presence of cations in the test solution: (a) sodium; (b) potassium; (c) ammonium.

It is seen that the results obtained are in good agreement with the literature data on the sorption of alkali metal and ammonium ions by transition metal ferrocyanides [57]. A decrease in the values of cesium distribution coefficients is expressed in the series of cations present: $\text{Na}^+ > \text{K}^+ > \text{NH}_4^+$. Ferrocyanides sorb alkali metal ions due to the zeolite effect, which is more pronounced the closer the diameter of the sorbed ion is to the cross-sectional dimensions of the channels in the ferrocyanide structure. The maximum zeolite effect is observed for the Cs^+ cation; the NH_4^+ ion is closest in size to the Cs^+ ion. Thus, the effective diameter of the hydrated Cs^+ cation is 0.25 nm; for comparison, the diameter of the NH_4^+ ion is also 0.25 nm, K^+ —0.3 nm, Na^+ —0.4–0.45 nm; therefore, the NH_4^+ ion has a greater effect on Cs^+ sorption than the cations of other elements under consideration [58].

4. Conclusions

During our work, sorbents based on PAN fiber and transition metal ferrocyanides were synthesized for ^{137}Cs sorption from natural and technological environments. It was shown that the best sorption characteristics were obtained at a concentration of potassium ferrocyanide solution of 0.1–0.2 mol/L and pH—1 for sorbents based on PAN fiber prepared by precipitation of iron(III) hydroxide with ammonia (PAN-Fe(OH)₃), and pH 1–5 for sorbents based on PAN fiber treated with potassium permanganate (PAN-MnO₂).

For sorbents based on PAN-Fe(OH)₃ fiber, the best cesium distribution coefficients were achieved when cobalt(II) chloride with a concentration of 0.02 mol/L was used for modification (CoFeFC-PAN sorbent); for sorbents based on PAN-MnO₂ fiber, the best cesium distribution coefficients were achieved when cobalt(II) chloride with a concentration of 0.02–0.05 mol/L (CoMnFC-PAN sorbent) and iron(III) chloride with a concentration of 0.02 mol/L (FeMnFC-PAN sorbent) were used for modification PAN. The independence of the properties of obtained sorbents from the temperature regime in the range of 25–80 °C is shown.

The studied structure of the obtained materials using infrared spectroscopy, thermogravimetric analysis, and scanning electron microscopy with energy dispersive analysis showed that during the formation of the ferrocyanide layer, the distribution of all components of the mixture occurs uniformly, regardless of the synthesis conditions. In the IR spectra of the obtained sorbents, peaks in the range of 2000–2150 cm^{−1} correspond to the C≡N group coordinated to the metal, which indicates the presence of a complex ion $[\text{Fe}(\text{CN})_6]^{4-}$.

When studying the influence of solution composition (pH, concentration of Na^+ , K^+ , NH_4^+ cations), it was shown that the synthesized sorbents could be used to recover and concentrate cesium from liquid media in the pH range from one to nine containing macro quantities of sodium, potassium and ammonium ions. The presence of the NH_4^+ cation has the greatest effect on the cesium sorption; the influence of Na^+ is minimal.

The sorption of ^{137}Cs microquantities by the obtained sorbents was studied, the effectiveness of the obtained sorbents was shown in comparison with known adsorbents of various brands, and the possibility of using the obtained sorbents for the recovery and concentration of ^{137}Cs from seawater was demonstrated.

In the course of further research, a more detailed study of the physicochemical parameters of cesium sorption is planned using the obtained materials, namely sorption and desorption kinetics, isotherms, selectivity, and sorption dynamics in solutions of complex chemical composition. In addition, ^{137}Cs sorption efficiency from large volumes (up to 250 L) of natural water will be assessed at different flow rates of the test solution. During the expedition, radioanalytical monitoring of ^{137}Cs in surface seawater samples will be performed using the obtained sorbents.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app14020627/s1>, Figure S1: Dependence of cesium distribution coefficients upon sorption from 0.1 (a,d,g,j) and 1 mol/L (b,e,h,k) solutions of sodium nitrate with pH 6 and seawater (c,f,i,l) on the concentration of potassium ferrocyanide (0.05 (▲), 0.1 (●), 0.2 (◆), 0.5 (■)) and the concentration of the transition metal salt used in the preparation of sorbents: (a–c)—CoFeFC-PAN,

(d–f)—NiFeFC-PAN, (g–i)—CuFeFC-PAN, (j–l)—ZnFeFC-PAN; Figure S2: Dependence of cesium distribution coefficients upon sorption from 0.1 (a,d,g,j,m) and 1 mol/L (b,e,h,k,n) solutions of sodium nitrate with pH 6 and seawater (c,f,i,l,o) on the concentration of potassium ferrocyanide (0.05 (▲), 0.1 (●), 0.2 (◆), 0.5 (■)) and the concentration of the transition metal salt used in the preparation of sorbents: (a–c)—FeMnFC-PAN, (d–f)—CoMnFC-PAN, (g–i)—NiMnFC-PAN, (j–l)—CuMnFC-PAN, (m–o)—ZnMnFC-PAN; Table S1: Cesium distribution coefficients during sorption from a 0.1 mol/L sodium nitrate solution with pH 6 and seawater depending on synthesis temperatures at the first and second stages of the synthesis of several sorbents.

Author Contributions: Conceptualization, N.A.B.; methodology, N.A.B., E.A.T., V.V.M. and I.G.T.; validation, N.A.B. and V.V.M.; formal analysis, I.G.S., V.A.R. and N.A.N.; investigation, I.G.S., V.A.R., N.A.B., N.A.N. and V.S.Y.; resources, N.A.B., V.V.M. and V.S.Y.; data curation, I.G.S., V.A.R., N.A.N., E.A.T. and V.S.Y.; writing—original draft preparation, I.G.S., N.A.B., E.A.T., V.V.M. and I.G.T.; writing—review and editing, all authors; visualization, I.G.S., V.A.R., N.A.B. and E.A.T.; supervision, N.A.B. and I.G.T.; project administration, N.A.B.; funding acquisition, N.A.B. All authors have read and agreed to the published version of the manuscript.

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