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Sorbents Based on Polyacrylonitrile Fiber for Complex Recovery of Artificial ^{137}Cs and Natural Radionuclides from Natural Media

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Abstract: Sorbents based on polyacrylonitrile fiber, containing ferrocyanides of transition metals and manganese oxides (CoMn-PAN and FeMn-PAN) or iron(III) hydroxide (CoFe-PAN) in their structure were obtained, as confirmed by the results of X-ray diffraction and energy-dispersive analyses. The selectivity of the obtained sorbents was investigated, along with their ability to sorb Cs, Ba (as an analog of Ra), P, and Be from various natural media, including river water and seawater with varying salinity of 18.2 and 33.8 ‰. The data show that the sorbents are universal for the recovery of artificial ^{137}Cs and natural radionuclides from the natural environments, including complex salt composition (seawater). Researching the obtained sorbents during marine expeditions confirmed the efficiency of the obtained materials based on transition metal ferrocyanides and manganese oxides (CoMn-PAN and FeMn-PAN) for the sorption of ^{137}Cs, ^{7}Be, ^{210}Pb, ^{210}Po, ^{226}Ra, ^{228}Ra, and ^{234}Th. Additionally, the sorbent based on transition metal ferrocyanides and iron(III) hydroxide (CoFe-PAN) was effective for the sorption of ^{137}Cs, ^{7}Be, ^{32}P, ^{33}P, ^{210}Pb, ^{210}Po, and ^{234}Th. Based on the obtained results, methods for comprehensively determining artificial ^{137}Cs and natural radionuclides using these sorbents were developed.

Keywords: sorption; sorbents; ^{137}Cs; natural radionuclides; selectivity; river water; seawater

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1. Introduction

The concentration of artificial and natural radionuclides from natural media makes it possible to solve several important fundamental and practical problems in ecology [1,2], radioecology [3–5], and oceanology [6–8].

Artificial radionuclide levels allow us to determine the radioecological condition of natural media [9,10], while natural ones allow us to study the processes occurring in nature. The isotope ^{7}Be is an indicator of fundamental processes associated with vertical transport in the ocean [11,12], while ^{32}P and ^{33}P are markers of phosphorus biodynamics, which allows us to obtain a more complete picture of the state of the studied water area [13,14]. Isotopes ^{226}Ra and ^{228}Ra indicate processes associated with the flow of freshwater into marine waters, particularly submarine groundwater discharge [15,16]; and ^{210}Pb, ^{210}Po with ^{234}Th, reflects the sedimentation parameters and flows of suspended particulate matter and particulate organic carbon [17,18].

Sorption materials have become widely used for concentrating radionuclides from natural media [19]. However, the search for optimal materials and methods continues. Of particular interest are sorbents that enable the simultaneous concentration of a range of radionuclides. This simultaneous sorption of several radionuclides allows for the determination of them within a single sorbent sample. For example, measuring a sorbent sample using gamma spectrometry can reveal the activity of ^{7}Be, ^{137}Cs, ^{210}Pb, ^{226}Ra, ^{228}Ra, and ^{234}Th, which are identified by different photopeaks [20].

So far, many sorbents have been developed for the recovery of artificial radionuclides [21–24], some of which allow for the simultaneous recovery of several radionuclides [25–36]. Most of these materials are designed to recover ^{137}Cs and ^{90}Sr. Thus, of great interest is a composite material based on resorcinol–formaldehyde resin and barium silicate [25], intended for the combined sorption of ^{137}Cs and ^{90}Sr from seawater. The efficiency of this materials toward ^{90}Sr is increased with a higher barium silicate content, but it decreases for ^{137}Cs. This behavior is associated with the selectivity of barium silicate for ^{90}Sr: the higher its content in the sorbent, the better the ^{90}Sr removal efficiency. The developed sorption materials exhibit moderate purification coefficients at high flow rates in filter devices, allowing for the purification of large quantities of water contaminated with ^{137}Cs and ^{90}Sr radionuclides.

In the works [26,27], Grushicheva E.A. et al. proposed the use of clinoptilolite and tripoli for the sorption of ^{137}Cs and ^{90}Sr under static conditions. It has been demonstrated that these materials exhibit high sorption parameters. For clinoptilolite, the degree of recovery of ^{137}Cs and ^{90}Sr was more than 96 and 86%, respectively, and the distribution coefficients were more than $(8 \pm 2) \times 10^3$ mL/g and $(4 \pm 1) \times 10^3$ mL/g, respectively. For tripoli, the degree of recovery was more than 93 and 98%, respectively, and the distribution coefficients were more than $(1 \pm 0.2) \times 10^3$ mL/g and $(3 \pm 1) \times 10^3$ mL/g, respectively.

In the work [28], Nikiforov A.F. et al. showed that finely dispersed aluminosilicate sorbents Ekozol-401 and Miksorb effectively and quickly recover ^{137}Cs and ^{90}Sr from natural media. The maximum distribution coefficients of ^{137}Cs and ^{90}Sr for the Ecozol-401 were $(2.9 \pm 0.9) \times 10^4$ mL/g and $(1.4 \pm 0.2) \times 10^3$ mL/g, respectively, and for the Miksorb sorbent, they were $(2.7 \pm 0.7) \times 10^4$ mL/g and $(2.7 \pm 0.5) \times 10^3$ mL/g, respectively.

Additionally, for the sorption of radionuclides ^{137}Cs and ^{90}Sr, synthesized magnetic potassium zinc hexacyanoferrate(II) was used [29]. The maximum removal values for this sorbent are achieved within the first 5 to 15 min, with up to 97.2% of ^{137}Cs and 35.8% of ^{90}Sr being absorbed. This suggests a higher selectivity of the sorbent for ^{137}Cs. Additionally, a significant advantage of this composite sorbent is its capability to be separated from the solution using an external magnetic field.

A sorbent based on titanium(IV) oxohydroxophosphates can be used for the removal of ^{134}Cs, ^{137}Cs, and ^{90}Sr from high-salt solutions similar in composition to seawater [30]. However, the distribution coefficients of Cs and Sr are low: 530 and 840 mL/g, respectively.

In the work [31], Kuznetsov A. Yu. et al. presented porous, highly filled composite materials in the form of films. Ultrahigh-molecular-weight polyethylene was used as a matrix; solid paraffin (number of carbon atoms from 24 to 40) was used as a solvent; and Na-A zeolite, strontium ferrite, and nickel ferrocyanide served as fillers. High selectivity of the sorbent containing nickel ferrocyanide particles toward ^{137}Cs and ^{90}Sr was shown.

Thus, for a sample containing 70% nickel ferrocyanide, the distribution coefficient of ^{90}Sr reached 3.2 × 10^4 mL/g, and it reached 5.2 × 10^4 mL/g for ^{137}Cs.

One of the natural sorbents for recovering various radionuclides is bentonite clays, the main feature of which is a high sorption capacity. Thus, in the work [32], a study was conducted on the sorption of ^{90}Sr and ^{137}Cs by natural and mono-cationic (Na, Mg, and Ca) forms of bentonite clay from the Taganskoye deposit (Kazakhstan). To obtain the studied sorbents of the Na, Mg, and Ca forms, bentonite was treated four times with chlorides, after which it was washed with distilled water to remove excess salt. Bentonite and its Na and Mg forms showed a high degree of recovery of ^{90}Sr and ^{137}Cs of more than 95 and 73%, respectively; the Ca form showed lower values of the degree of recovery of ^{90}Sr up to 84%, but it had higher ^{137}Cs—90%. The distribution coefficient of ^{90}Sr on bentonite and its Na and Mg forms was more than 2.1 × 10^3 mL/g, and for ^{137}Cs, the highest result was shown by the Ca form—9.1 × 10^2 mL/g.

In addition, sorbents have been developed that allow for the simultaneous sorption of Co [33,34] or U and Pu [35] isotopes, along with Cs and Sr isotopes. Thus, in the work [33], Efimova et al. conducted a study on the sorption of radionuclides ^{60}Co, ^{137}Cs, and ^{85}Sr with iron oxides α-Fe_2O_3 and Fe_3O_4. The proposed materials recovered ^{60}Co from drinking water best of all (for α-Fe_2O_3, the degree of recovery reached 51.4%; for Fe_3O_4—71.6%) and slightly worse for ^{90}Sr (for α-Fe_2O_3 the degree of recovery was 19.8%, for Fe_3O_4—34.8%); and ^{137}Cs was practically not recovered (the degree of recovery for α-Fe_2O_3 and Fe_3O_4 did not exceed 8.7 and 18.7%, respectively). It was also shown that the sorption efficiency increases with an increasing pH value, with the highest degree of recovery established at pH 9. For ^{60}Co, ^{90}Sr, and ^{137}Cs it is 93, 73, and 26%, respectively (for Fe_3O_4), and 85, 41, and 18%, respectively (for α-Fe_2O_3). It should also be noted that at any pH value, the sorption efficiency of the studied radionuclides fits into the following series: $^{60}\text{Co} > {}^{90}\text{Sr} > {}^{137}\text{Cs}$.

In the work [34], Kitikova et al. investigated phosphate sorbents FD-1, FD-2, and FD-3 based on natural dolomite, obtained by acidic and acid-free phosphating of the original sample using the phosphating agents H_3PO_4 (C = 20%), $H_3PO_4 + NH_4OH$ (pH = 10), and NaH_2PO_4, respectively, while the FD-2 sample was pre-dissolved in HNO_3. Of the obtained samples, FD-2 showed the best sorption characteristics: the distribution coefficients of ^{60}Co and ^{85}Sr were 2.4 × 10^4 mL/g and 2.7 × 10^3 mL/g, respectively. In high-salt solutions (35 g/L), the FD-2 sorbent retains its selective sorption properties toward ^{60}Co, while the distribution coefficient of ^{85}Sr decreased to 0.2 × 10^3 mL/g. The high selective sorption properties of this sorbent are also preserved when recovering ^{60}Co and ^{85}Sr radionuclides from a multi-component solution.

Avrorin et al. [35] proposed a composite inorganic sorbent in the form of a non-magnetic fraction of product of a metallurgical slag processing for the removal of ^{235}U, ^{239}Pu, ^{137}Cs, and ^{90}Sr from aqueous solutions in the pH range of 3–11 under dynamic conditions. The composition of the material was calcium silicate Ca_2SiO_4, lithium iron oxide $Li_{9.28}Fe_{21.34}O_{32}$, coesite SiO_2, ferrous grossular $Ca3Al_{1.332}Fe_{0.668}Si_3O_{12}$, ringwoodite Fe_2SiO_4, and sodium aluminosilicate $Na_{14.88}Al_{15.26}Si_{32.74}O_{96}$. The distribution coefficient for ^{235}U was 3.1 × 10^5 mL/g, while that of other radionuclides was several orders of magnitude less: ^{239}Pu—5.6 × 10^3 mL/g, ^{137}Cs—1.3 × 10^2 mL/g, and ^{90}Sr—1.4 × 10^2 mL/g.

It is also necessary to identify sorbents for the extraction of ^{152}Eu, ^{241}Am, and ^{85}Sr [36], which are silica gel KSK-1 or ion-exchange resin KU-2–8 modified with micro-amounts of fullerenes ($C_{60} - C_{70}$) in the presence of crown ether for stabilization. The selectivity of sorption by the obtained samples decreased in the series: $^{241}\text{Am} > {}^{152}\text{Eu} > {}^{85}\text{Sr}$.

Sorbents for the complex recovery of natural radionuclides are less commonly reported. Among the sorbents that allow for the comprehensive recovery of natural radionuclides, the most important are sorbents based on manganese dioxide. They demonstrate high sorption characteristics when recovering isotopes of radium [37–39], thorium [39–41], ^{210}Pb, ^{210}Po [42,43], and ^{7}Be [43].

Several articles [44–47] discuss the use of these sorbents for the recovery of ^{90}Sr from natural media under static conditions. High distribution coefficients (exceeding 10^3 mg/L) have been reported [46], indicating the possibility of utilizing these sorbents for the recovery of ^{90}Sr from radioactive waste containing seawater. However, under dynamic conditions, these sorbents have not been effectively applied for the sorption of ^{90}Sr from natural environments, because they actively sorb macro-components: calcium ions; and transition metals, including both dissolved and hydrolyzed forms. In addition, as indicated above, many radionuclides (^{7}Be, isotopes of Th, Ra, Pb, and Po) are effectively sorbed.

Sorbents based on iron(III) hydroxide show high sorption efficiency of thorium [48,49], ^{210}Pb, and ^{210}Po [49,50] isotopes, along with cosmogenic ^{7}Be [49,51,52], ^{32}P, and ^{33}P [49,53] isotopes.

In our previous review [54], we discussed the removal of radionuclides from seawater using various sorption materials, including those designed for the simultaneous extraction of multiple radionuclides. The paper also demonstrates the effectiveness of different sorbents under real conditions. However, there is a notable deficit of research focused on the production of sorbents for the complex extraction of both artificial and natural radionuclides from liquid media of natural origin.

Therefore, earlier [55], we developed new material based on sorbents made of polyacrylonitrile (PAN) fiber combined with manganese dioxide (PAN-MnO_2) [39] and iron(III) hydroxide (Fe-H) [49], which also contained transition metal ferrocyanides. We assessed the influence of the synthesis temperature of the sorbents, the concentration and pH of the potassium ferrocyanide solution, and the concentrations of the transition metal salts used in production. Optimal formulations and conditions for the synthesis of sorbents have been established: CoFe-PAN, Con-PAN, and FeMn-PAN. The structure of the obtained sorbents was studied using infrared spectroscopy, thermogravimetric analysis, and scanning electron microscopy. Research on sorbents was carried out for the recovery of microquantities of ^{137}Cs [55]. The physicochemical patterns of sorption and desorption of Cs by the obtained sorbents were also described [56].

This study is a logical continuation of the works [55,56], aimed at describing the structure of the obtained sorbents, assessing their selectivity toward radionuclides and the influence of the salt content of natural waters on their sorption efficiency, and researching the obtained sorbents on large volumes of natural waters to assess the possibility of recovering artificial ^{137}Cs and natural radionuclides.

2. Materials and Methods

2.1. Materials

CRMs (Certified Reference Materials of solutions of metal ions) [57] produced by Ormet LLC (Yekaterinburg, Russia) were used to prepare calibration solutions and solutions for studying the sorption selectivity: Li CRM 0138:2000, Na CRM 0143:2000, K CRM 0134:2000, Rb CRM 1058:2004, Cs CRM 0160:2004, Mg CRM 0139:2000, Ca CRM 0135:2000, Sr CRM 0148:2000, Ba CRM 0351:2002, Al CRM 0306:2002, Pb CRM 0525:2003, Bi CRM 0541:2003, Cr CRM 0293:2002, Mn CRM 0300:2002, Fe CRM 0518:2003, Co CRM 0305:2002, Ni CRM 0144:2000, Cu CRM 0523:2003, Zn CRM 0032:1998, and Cd CRM 0136:2000.

Cesium nitrate, strontium nitrate, potassium dihydrogen orthophosphate, and beryllium sulfate, chemically pure for analysis, produced by ReaKhim JSC LLC (Moscow, Russia), were used as additives for studying the sorption of elements from various natural solutions.

To obtain sorbents, we used sodium hydroxide, iron(III) chloride, ammonia, potassium ferrocyanide, cobalt(II) chloride (ReaKhim LLC, Moscow, Russia), and potassium permanganate (NevaReaktiv LLC, St. Petersburg, Russia) Pro Analysis qualifications, along with PAN fiber (Moscow Wool Spinning Factory, Moscow, Russia).

2.2. Methods for Preparing the Support and Obtaining Sorbents

The methods of preliminary preparation of the support are described in detail in [39,49], and the preparation of sorbents is described in [55].

Preliminary preparation of the initial PAN fiber was performed by two methods: by treatment with potassium permanganate (conversion of PAN to the form of PAN-MnO_2) [39] and by precipitation of iron(III) hydroxide with ammonia on pre-hydrolyzed PAN (conversion of PAN to the form of PAN-$Fe(OH)_3$) [49]. During the process of preliminary preparation of PAN fiber, additional ion-exchange groups (carboxyl, carbonyl, etc.) are formed, increasing the amount of ferrocyanide grafted to the carrier at the following stages of obtaining sorbents.

The sorbents were obtained by treating prepared PAN fiber in a weakly acidic solution of potassium ferrocyanide, followed by treatment in a solution of a transition metal salt, washing, and drying [55].

2.3. Study of the Sorbent's Structure

X-ray diffraction analysis before and after annealing of sorbent samples at 800 °C was performed on a D8 ADVANCE diffractometer (Bruker, Billerica, MA, USA). X-ray patterns of the samples were recorded in the angle range of $3° < 2\theta < 85°$, with a step of 0.02° with a count at a point of 0.6 s. The phase composition was identified using the MATCH! Program version 4.1 and Crystallography Open Database (COD).

Energy-dispersive analysis was performed on a Carl Zeiss CrossBeam the XB 1540 (Zeiss Int., Oberkochen, Germany) with an attachment for energy-dispersive analysis.

2.4. Study of Sorbent Selectivity Under Static Conditions

The study of sorption selectivity was carried out by mixing 0.1 g of the sorbent with 10 mL of a solution with a concentration of each element (Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Pb^{2+}, Bi^{3+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}) of 10 mg/L at pH ≈ 6. Each experiment was repeated at least three times.

The concentrations of elements in solutions were determined by inductively coupled plasma–mass spectrometry on an Agilent 8800 spectrometer (Agilent Technologies, Santa Clara, CA, USA) and by inductively coupled plasma–atomic emission spectrometry on an iCAP 7600 Duo spectrometer (Thermo Scientific, Waltham, MA, USA).

The distribution coefficient (K_d, mL/g) was calculated using the equation given in [58,59].

2.5. Study of Elements' Sorption from Various Natural Solutions Under Static Conditions

To evaluate the efficiency of the obtained sorption materials to artificial and natural radionuclides, we conducted a series of laboratory tests using solutions of natural waters with the addition of a stable element (Cs, P, Be, and Ba as an analog of Ra). The approximate composition of the river water and seawater used in these tests is given in Table 1.

The sorption study under static conditions was carried out by mixing 0.1 g of the sorbent with 20 mL of the studied natural solution for 48 h. Afterward, the sorbent and solution were separated by filtration. Each experiment was repeated at least three times.

Table 1. Approximate composition of natural waters.

Ion	**Concentration, mg/L**		
	Black River [60]	**Black Sea** [61,62]	**Pacific Ocean** [63,64]
Cl^-	5.1–6.2	8790–10,600	19,350–25,160
HCO_3^-	157–186	139–202	36–147
CO_3^{2-}	0.2–20	73.2–88.2	10–96
SO_4^{2-}	8.6–9.3	1290–2140	2700–5580
MoO_4^{2-}	$(0.01–0.97) \times 10^{-3}$	$(1–3.4) \times 10^{-3}$	$(1–4.8) \times 10^{-3}$
K^+	0.54–0.82	139–287	298–586
Na^+	4–4.5	4990–6900	10,700–14,100
Ca^{2+}	51–58.3	217–269	408–754
Mg^{2+}	3.2–7.9	592–756	1290–3070
Sr^{2+}	0.13–0.15	4.46–6.05	6–14
Co^{2+}	$(0.02–0.23) \times 10^{-3}$	$(0.2–1.6) \times 10^{-3}$	$(0.1–6.4) \times 10^{-3}$
Cu^{2+}	$(0.55–1.14) \times 10^{-3}$	$(1–7) \times 10^{-3}$	$(0.6–18) \times 10^{-3}$
Hg^{2+}	$(0–0.04) \times 10^{-3}$	$(0.3–0.4) \times 10^{-3}$	$(0.01–1.42) \times 10^{-3}$
$Fe^{2+} + Fe^{3+}$	$(42.7–90) \times 10^{-3}$	$(5–40) \times 10^{-3}$	$(3–164) \times 10^{-3}$
Mn^{2+}	$(4.7–170) \times 10^{-3}$	$(4–40) \times 10^{-3}$	$(0.1–111) \times 10^{-3}$
Ni^{2+}	$(0.23–0.64) \times 10^{-3}$	$(0.5–3) \times 10^{-3}$	$(0.3–5.4) \times 10^{-3}$
Average salinity, ‰	0.4	18.4	33.8

The concentration of Cs and Ba in solutions was determined on a KVANT-2 atomic absorption spectrophotometer (Kortek LLC, Moscow, Russia) in an air–acetylene flame using the method described in [65]: Cs—in emission mode at a wavelength of 852.1 nm; and Ba—in absorption mode at a wavelength of 553.6 nm.

The concentration of P was determined using a KFK-3-01 photocolorimeter (JSC ZOMZ, Sergiev Posad, Russia) at a wavelength of 880 nm, using the method described in [66]; and that of Be was determined using a KFK-3-01 photocolorimeter (JSC ZOMZ, Sergiev Posad, Russia) at a wavelength of 536 nm, using the method described in [67].

2.6. Evaluation of the Sorption Efficiency for Large Volumes of Natural Waters Under Dynamic Conditions

Surface samples of seawater were collected during coastal expeditions in the waters of the Heraclean Peninsula, as well as partially during the 126th cruise of the collective use center "RV Professor Vodyanitsky" (15 March–7 April 2023) and the 71st cruise of the collective use center "RV Akademik Oparin" (4 June–15 July 2024) using a UNIPUMP BAVLENETS BV 0.12-40-U5 vibration pump (Sabline Service LLC, Moscow, Russia) and a UNIPUMP BCP 3.5-0.5-65 borehole pump (Sabline Service LLC, Moscow, Russia).

The sorption efficiency of ^{137}Cs, ^{7}Be, ^{210}Pb, ^{210}Po, ^{226}Ra, ^{228}Ra, and ^{234}Th by the obtained sorbents was determined using a two-column method by passing 250 L of filtered seawater through two columns filled with 100 mL of sorbent each, at different speeds (1–7.5 C.V./min (column volumes per minute)), using a LongerPump WT600-2J peristaltic pump (Longer Precision Pump Co., Baoding, China). The sorption efficiency (E, %) of the studied radionuclides was determined using the equation for the two-column method given in [68].

The sorption efficiency of ^{32}P and ^{33}P by the obtained sorbents was determined by a single-column method by passing 250 L of filtered seawater with the addition of potassium dihydrogen phosphate to a concentration of 0.5 μmol/L as a tracer of sorption efficiency through one column filled with 100 mL of the sorbent at different speeds (1–7.5 C.V./min) using a LongerPump WT600-2J peristaltic pump (Longer Precision Pump Co., Baoding, China). The sorption efficiency (E, %) of ^{32}P and ^{33}P was determined using the equation for the single-column method given in [52,69].

2.7. Determination of Radionuclide Activity in Sorbent Samples

To determine the activity of ^{137}Cs, ^{7}Be, ^{226}Ra, ^{228}Ra, and ^{234}Th after passing seawater, the sorbents were ashed in an LOIP LF-15/11-G2 muffle furnace (JSC LOIP, St. Petersburg, Russia) to reduce the volume and, accordingly, the self-absorption coefficient when measured on a gamma spectrometer. The resulting ash was sealed in Petri dishes and kept for 3 weeks (to achieve an equilibrium of ^{226}Ra with ^{214}Pb). For the CoFe-PAN sorbent, it is not necessary to keep it for 3 weeks, since it does not sorb radium isotopes. The activity of ^{137}Cs, ^{7}Be, ^{226}Ra, ^{228}Ra, and ^{234}Th was determined on a CANBERRA gamma spectrometer with a BE3825 high-purity germanium detector (Canberra Industries, Meriden, CT, USA). Detection efficiency was estimated using ISOCS/LabSOCS software version 4.0 (Canberra Industries, Meriden, CT, USA).

To further determine the activity of ^{210}Pb and ^{210}Po, radiochemical preparation was carried out, which consisted of dissolving the ash, followed by joint electrochemical deposition of ^{210}Bi and ^{210}Po. The activity of ^{210}Po was determined by alpha spectrometry using the UMF-Spectrum spectrometric complex (LLC NPP Doza, Zelenograd, Russia), and that of ^{210}Pb was determined by ^{210}Bi beta radiometry on the UMF-2000 alpha-beta radiometer (LLC NPP Doza, Zelenograd, Russia).

The determination of the activity of ^{32}P and ^{33}P was not performed in this work due to the low activity of the isotopes ^{32}P and ^{33}P in seawater—0.02–0.1 Bq/m^3—as well as short half-lives of 14.3 and 24.3 days, respectively. Therefore, to determine the activity of ^{32}P and ^{33}P, the volume of seawater samples had to be at least 1000 L, which significantly increases the labor intensity of the work. In addition, the time between concentration and measurement of samples must be minimal, which is often difficult in marine expeditions.

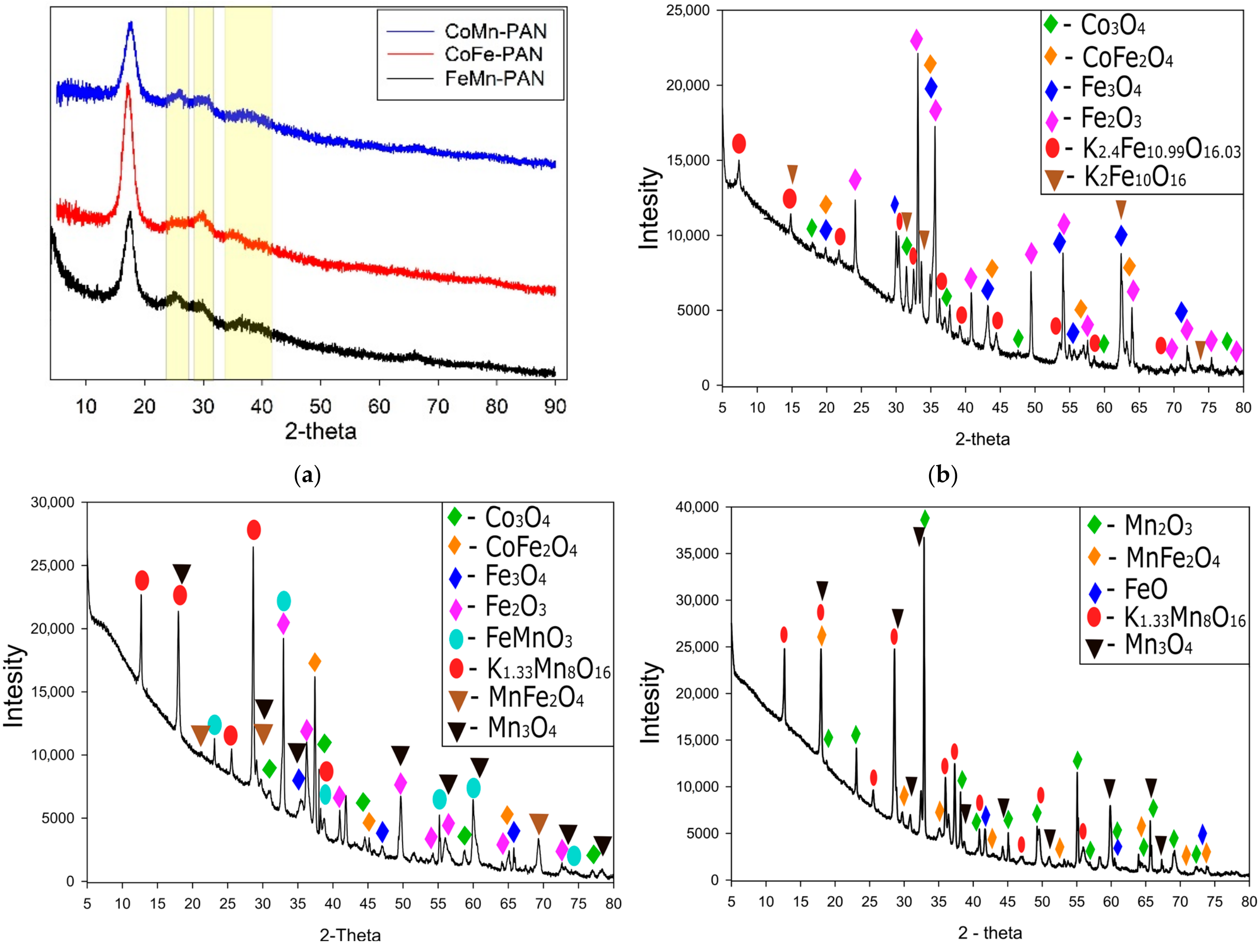
The activity of radionuclides was determined using the equation given in [68].

3. Results and Discussion

3.1. X-Ray Diffraction Analysis

The results of X-ray diffraction analysis before and after annealing of sorbent samples at 800 °C are shown in Figure 1. The X-ray diffraction pattern of the initial composites before annealing contains a characteristic peak of $2\theta = 17°$ corresponding to the rhombic structure of PAN. Weak reflexes corresponding to amorphous transition metal oxides are also observed in the composites. Moreover, depending on the degree and type of heating of the finished fiber, the composition of the metal oxide component can vary from $M_xO_y \cdot MO(OH) \cdot H_2O$ to M_xO_y. The characteristic signals corresponding to M_xO_y, $Mn_xFe_y[Fe(CN)6]_z$ (Figure 1a, $2\theta = 17°, 29°$), $Mn_xCo_y[Fe(CN)6]_z$ (Figure 1a, $2\theta = 17°, 26°, 36°$), and $Co_xFe_y[Fe(CN)6]_z$ (Figure 1a, $2\theta = 17°, 29°, 36°$) have low intensity, which may be associated with the overlap of this phases, the wide amorphous peak of PAN, and the formation of ultradispersed particles with coherent scattering domain sizes of ~2 nm.

The presence of oxides formed during the destruction of transition metal ferrocyanides in the structure of the annealed samples is visible. Also, the annealed samples contain manganese oxides and $K_{1.33}Mn_8O_{16}$ (CoMn-PAN and FeMn-PAN) or iron(III) oxide (CoFe-PAN). This finding indicates that these sorbents will extract not only ^{137}Cs, which was confirmed earlier [55,56], but also natural radionuclides, as confirmed by the results of the studies presented later in this article.



(**a**) (**b**)

(**c**) (**d**)

Figure 1. X-ray diffractograms of sorbents: (**a**) before annealing, (**b**–**d**) after annealing, (**b**) CoFe-PAN, (**c**) CoMn-PAN, and (**d**) FeMn-PAN.

Based on the established structures, the following sorption mechanisms can be assumed for the obtained sorbents, which will be largely based on ion exchange:

- Sorption of ^{137}Cs:

$$2nCs^{+} + Me^{II}Me^{II}[Fe(CN)_{6}] = nMe^{2+} + Me^{II}{}_{1-n}Cs_{2n}Me^{II}[Fe(CN)_{6}], \quad (1)$$

$$3nCs^{+} + Me^{III}{}_{0.8}Me^{II}{}_{0.8}[Fe(CN)_{6}] = nMe^{3+} + Me^{III}{}_{0.8-n}Cs_{3n}Me^{II}[Fe(CN)_{6}], \quad (2)$$

- Sorption of radium isotopes (for CoMn-PAN, FeMn-PAN sorbents):

$$nRa^{2+} + K_{1.33}Mn_{8}O_{16} = 2nK^{+} + K_{1.33-2n}Ra_{n}Mn_{8}O_{16}, \quad (3)$$

- Sorption of phosphorus isotopes (for CoFe-PAN sorbent):

$$nPO_{4}^{3-} + Fe(OH)_{3} = 3nOH^{-} + Fe(OH)_{3-3n}\, nPO_{4} \quad (4)$$

Dissolved forms of thorium isotopes, ^{7}Be, ^{210}Pb, and ^{210}Pb in seawater are represented mainly by neutral hydrolyzed forms, which are concentrated by the physical adsorption mechanism. A small portion of the positively charged forms of these isotopes is concentrated by the ion exchange mechanism.

3.2. Energy-Dispersive Analysis

Using energy-dispersive analysis (Figure 2), an assessment of the distribution of elements on the surface of the obtained composite materials was performed. The established results are presented in Table 2. It is shown that during the formation of the ferrocyanide layer, the distribution of all components of the mixture occurs uniformly, regardless of the synthesis conditions. In addition, the obtained data on the distribution of elements on the sorbents' surface confirm the above assumption that these sorbents will extract not only ^{137}Cs but also natural radionuclides.

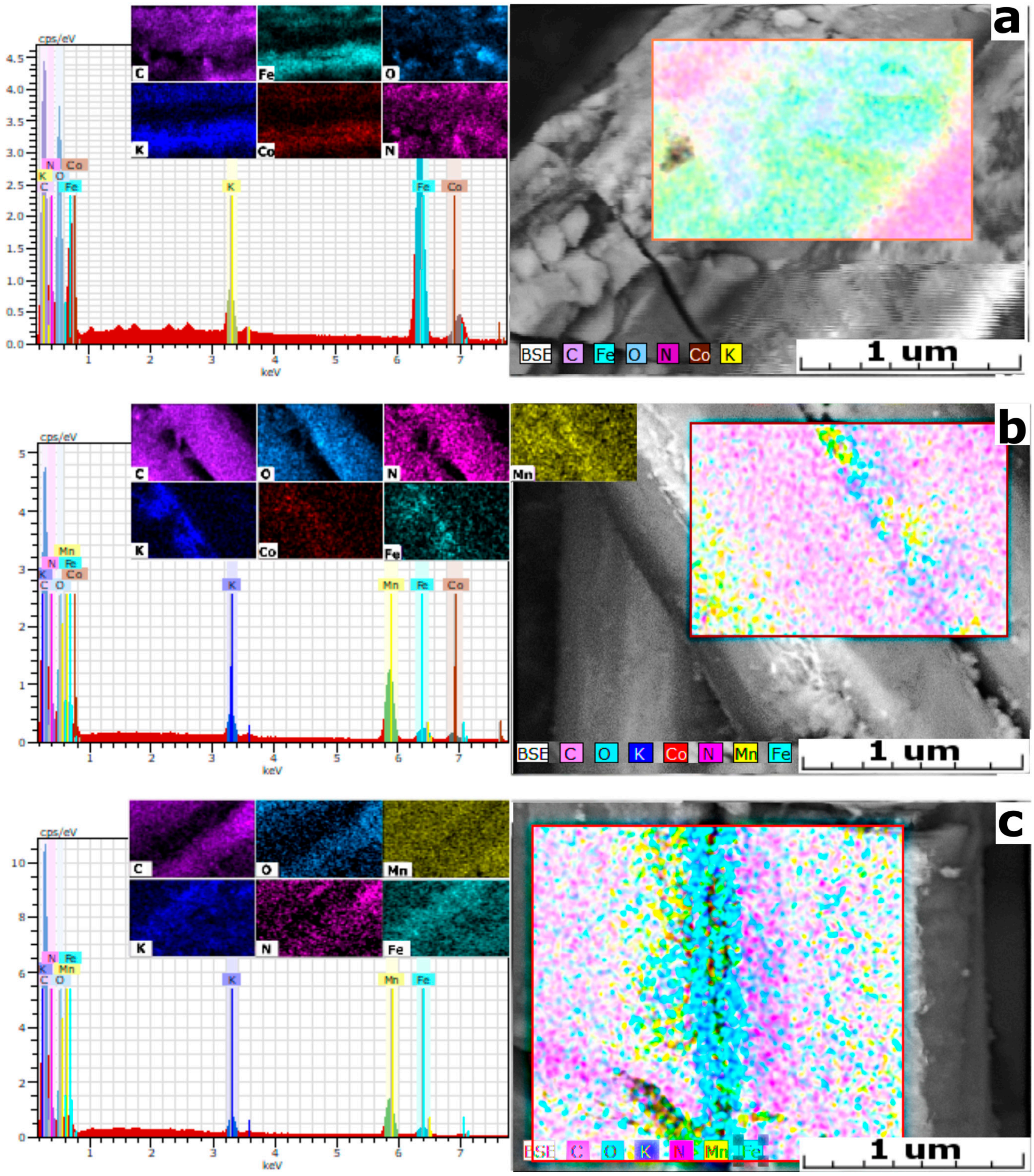


Figure 2. EDS analysis: (**a**) CoFe-PAN, (**b**) CoMn-PAN, and (**c**) FeMn-PAN.

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

Sorbent	Fe, %	Mn, %	Co, %	K, %	C, %	O, %	N, %
CoFe-PAN	26.75 ± 4.20	–	5.44 ± 0.88	3.54 ± 0.47	28.86 ± 5.13	17.24 ± 3.92	18.17 ± 3.05
CoMn-PAN	7.55 ± 1.21	15.23 ± 2.44	4.89 ± 0.65	4.01 ± 0.68	32.97 ± 5.34	15.32 ± 2.63	20.03 ± 2.91
FeMn-PAN	9.68 ± 1.17	33.37 ± 6.02	–	4.41 ± 0.47	32.38 ± 5.46	8.63 ± 1.37	11.53 ± 1.41

3.3. Sorption Selectivity

The results of the assessment of the sorption-selective properties of the adsorbents obtained, for solutions with pH6 and a concentration of each studied element of 10 mg/L, are presented in Table 3.

Table 3. Distribution coefficient (K_d, mL/g) values for the obtained sorbents in the study of sorption selectivity.

Elements		CoFe-PAN	CoMn-PAN	FeMn-PAN
alkaline	Li	<1	<1	<1
	Na	<1	<1	<1
	K	<1	<1	<1
	Rb	13.1 ± 2.7	3.11 ± 0.96	3.12 ± 0.87
	Cs	(1.8 ± 0.4) × 10^5	(1.3 ± 0.3) × 10^5	(9.5 ± 0.7) × 10^4
alkaline earth	Mg	<1	<1	<1
	Ca	<1	<1	<1
	Sr	<1	163 ± 24	159 ± 18
	Ba	23.0 ± 4.5	592 ± 45	561 ± 62
p-elements	Al	<1	18.2 ± 3.6	4.46 ±1.22
	Pb	(6.4 ± 0.9) × 10^3	(9.4 ± 0.3) × 10^3	(9.1 ± 0.4) × 10^3
	Bi	(7.9 ± 0.8) × 10^3	(9.2 ± 0.4) × 10^3	(9.3 ± 0.2) × 10^3
d-elements	Cr	16.6 ± 3.1	18.4 ± 0.9	25.6 ± 4.3
	Mn	<1	<1	<1
	Fe	82.8 ± 7.9	189 ± 7	353 ± 38
	Co	<1	<1	19.6 ± 1.0
	Ni	2.50 ± 0.51	13.8 ± 1.5	26.0 ± 1.5
	Cu	76.7 ± 9.6	124 ± 26	210 ± 22
	Zn	4.09 ± 1.12	6.65 ± 0.88	6.07 ± 1.96
	Cd	2.65 ± 0.73	4.35 ± 1.02	6.48 ± 2.32

The data presented (Table 3) indicate that the obtained sorbents effectively remove Cs: the distribution coefficients' values exceed 10^5 mg/L. This is due to the correspondence between the sizes of the input windows of transition metal ferrocyanides and Cs^+ [45]. Also, the sorbents CoMn-PAN and FeMn-PAN, which contain manganese oxides, exhibit high efficiency in Ba^{2+} recovery. Considering the patterns of change in the properties of elements, we can assume that the distribution coefficient of Ra^{2+} will be higher than that of Ba^{2+}: $Ca^{2+} < Sr^{2+} < Ba^{2+} < Ra^{2+}$.

It was shown that the obtained materials containing manganese and iron(III) oxides exhibit high selectivity for Pb^{2+}, Bi^{3+}, Fe^{3+}, and Cu^{2+}, which is comparable with the literature data for sorbents based on manganese oxides [70–72] and iron(III) oxides [71,73]. This suggests that the materials can also be used for the sorption of ^{210}Pb and ^{210}Po.

3.4. Study of Sorption from Various Natural Solutions

The results of the assessment of the influence of salt content on the distribution coefficients of the studied elements are presented in Table 4. The studies were conducted using natural solutions with additives of natural isotopes of Cs, Be, P, and Ba as an analog of Ra.

Table 4. Dependence of the distribution coefficients (K_d, mL/g) of Cs, Be, P, and Ba on the salt content of natural waters.

Sorbent	Recovered Element	Natural Solutions (Salinity, ‰)		
		Black River (0.4)	**Black Sea (18.4)**	**Pacific Ocean (33.8)**
CoFe-PAN	Cs	$(2.4 \pm 0.5) \times 10^5$	$(5.6 \pm 0.7) \times 10^5$	$(2.8 \pm 0.2) \times 10^5$
	Be	$(1.0 \pm 0.2) \times 10^3$	$(1.2 \pm 0.2) \times 10^3$	950 ± 79
	P	$(5.3 \pm 0.6) \times 10^3$	$(1.1 \pm 0.2) \times 10^4$	$(8.1 \pm 0.4) \times 10^3$
	Ba	31.0 ± 3.8	10.1 ± 2.4	<1
CoMn-PAN	Cs	$(1.8 \pm 0.4) \times 10^5$	$(1.8 \pm 0.3) \times 10^4$	$(1.5 \pm 0.1) \times 10^4$
	Be	916 ± 98	$(1.4 \pm 0.1) \times 10^3$	$(1.1 \pm 0.2) \times 10^3$
	P	<1	<1	<1
	Ba	745 ± 80	521 ± 57	479 ± 52
FeMn-PAN	Cs	$(1.3 \pm 0.2) \times 10^5$	$(1.5 \pm 0.2) \times 10^5$	$(1.2 \pm 0.2) \times 10^5$
	Be	853 ± 57	$(1.3 \pm 0.2) \times 10^3$	982 ± 48
	P	<1	<1	<1
	Ba	684 ± 75	507 ± 64	452 ± 47

It was observed that with an increase in the salinity of the studied natural solution, the distribution coefficients of Cs decrease slightly, which is associated with the high selectivity of the ferrocyanide phase toward cesium ions [45].

The distribution coefficients for beryllium, phosphorus, and barium also decrease slightly with increasing salinity. Moreover, the distribution coefficients for phosphorus and beryllium in river water are lower than the value of these parameters in seawater, which is probably associated with some features of sorption process in seawater, the components of which can act as a salting-out agent, increasing the sorption efficiency of phosphorus and beryllium. In addition, due to the lower pH of river water, the protonation reaction can have an additional competing effect on the sorption of radionuclides [74].

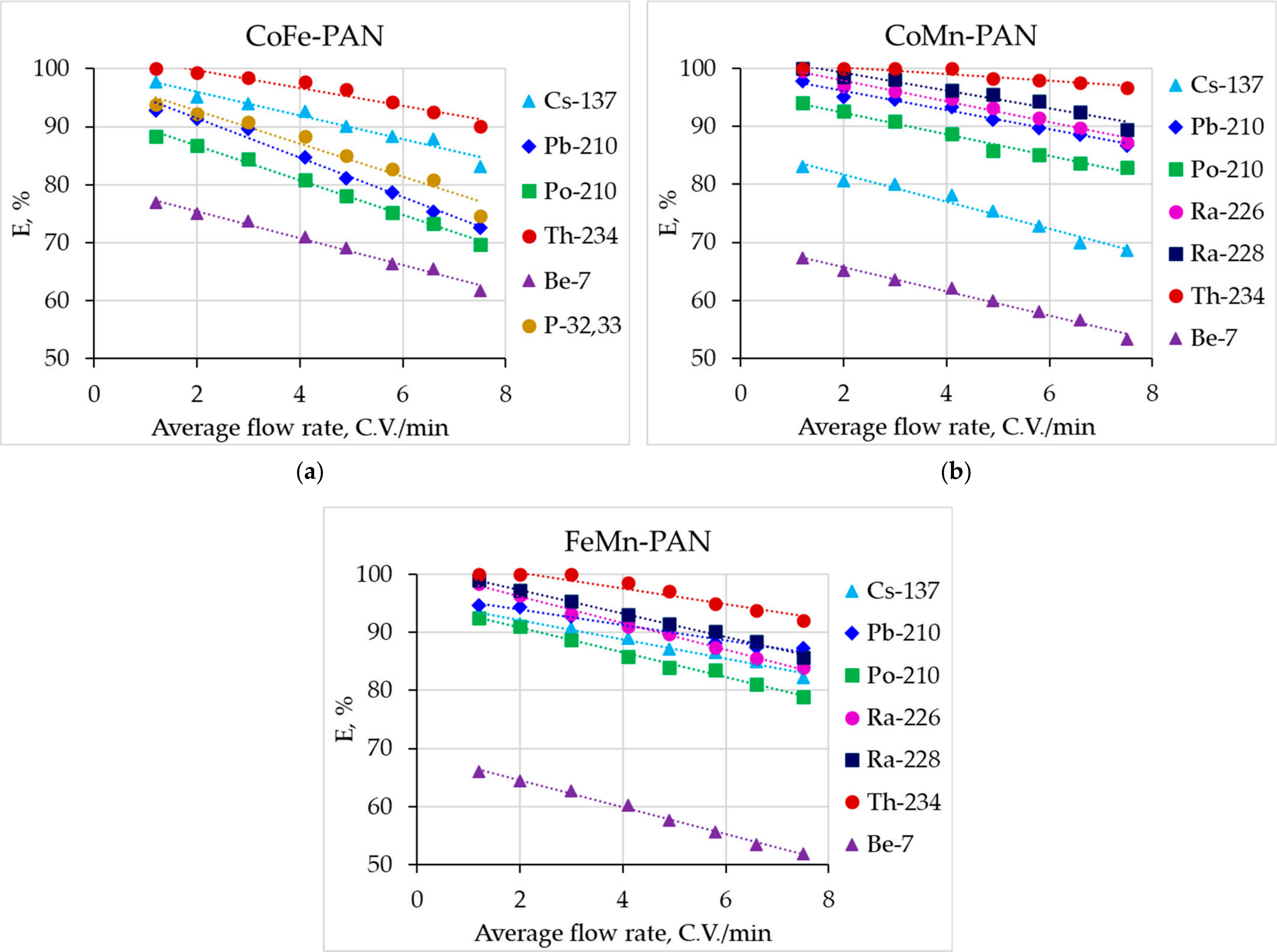
It should be noted that the distribution coefficients for phosphorus, beryllium, barium, and strontium for the sorbents CoFe-PAN, CoMn-PAN, and FeMn-PAN are lower than those of the original sorbents based on polyacrylonitrile fiber and manganese dioxide (PAN-MnO2) and iron(III) hydroxide (Fe-H). This is due to the fact that during the synthesis process, the sorption-active phases of manganese and iron(III) oxides are partially replaced by the phases of transition metal ferrocyanides. As a result, the new sorbent effectively sorbs Cs, but the sorption efficiency for other elements is slightly reduced.

3.5. Testing of the Obtained Sorbents on Large Volumes of Natural Media

To assess the possibility of practical application of materials in expeditionary conditions, a study was conducted on the radionuclides' sorption from large volumes of seawater in the Black Sea and the Pacific Ocean.

Studies using seawater from the Black Sea (average salinity 18.4 ‰) were conducted during coastal expeditions in the waters of the Heraclean Peninsula, and also partially during the 126th cruise of the collective use center "RV Professor Vodyanitsky" (15 March–7 April 2023) at different seawater flow rates. The results obtained are presented in Figure 3.

It is seen that the obtained sorbents CoMn-PAN and FeMn-PAN effectively recover ^{137}Cs, ^{226}Ra, ^{228}Ra, ^{210}Pb, ^{210}Po, ^{234}Th, and the sorbent CoFe-PAN: ^{137}Cs, ^{210}Pb, ^{210}Po, $^{234\mathrm{Th}}$, and cosmogenic ^{32}P and ^{33}P at seawater flow rates of 1–4 C.V./min. The cosmogenic radionuclide 7Be is recovered somewhat worse by the obtained sorbents. However, this allows for a more accurate determination of its activity on the second adsorber when using the two-column method. In addition, it should be noted that ^{137}Cs is recovered with an efficiency exceeding 90% by the CoFe-PAN sorbent at a seawater flow rate of 1–5 C.V./min and by the FeMn-PAN sorbent at a seawater flow rate of 1–3 C.V./min.



(**a**) (**b**)

(**c**)

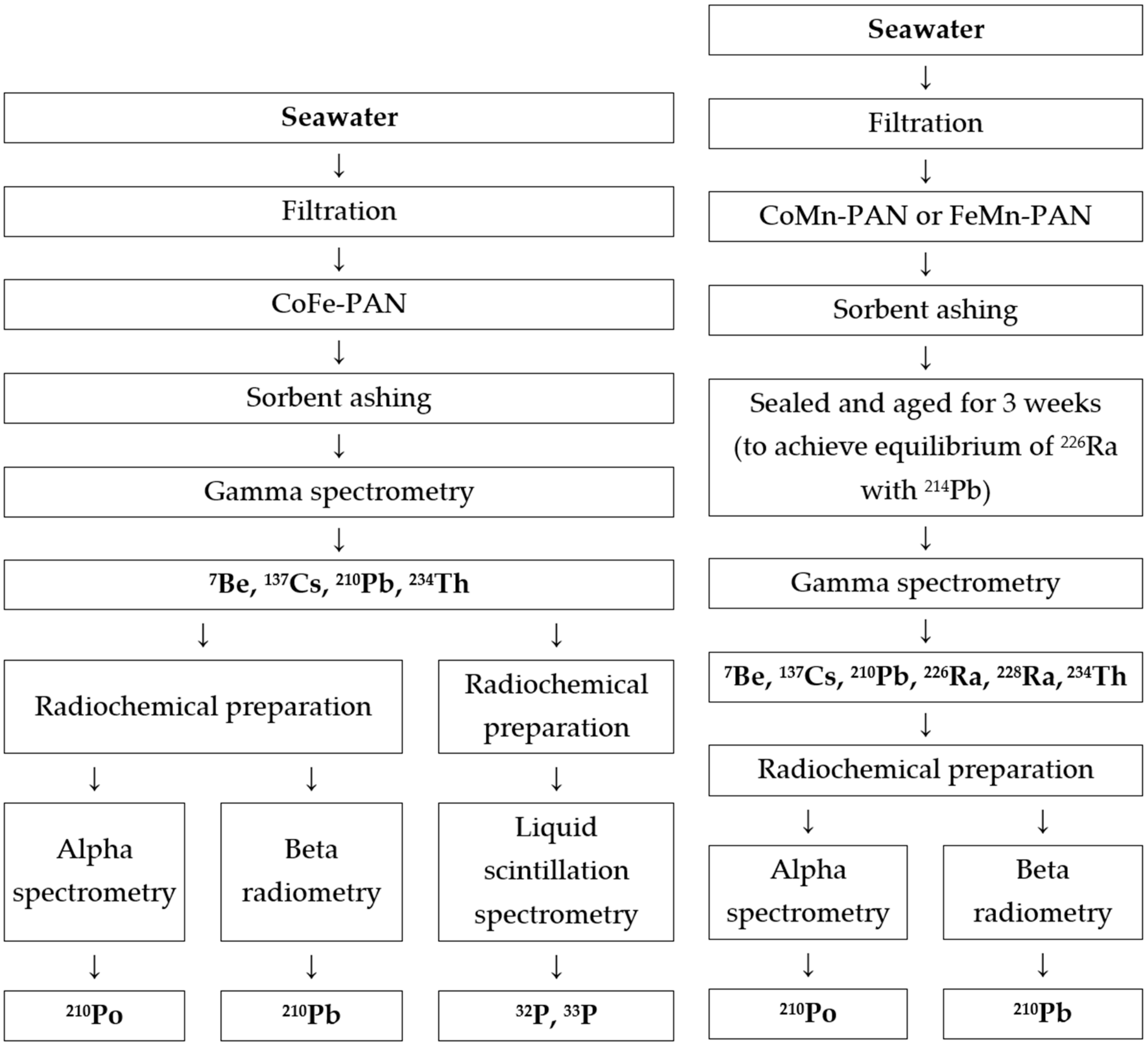
Figure 3. Sorption efficiency of radionuclide from the Black Sea water by the obtained sorbents: (**a**) CoFe-PAN, (**b**) CoMn-PAN, and (**c**) FeMn-PAN (average salinity of 18.4 ‰, 250 L of seawater, and 100 mL of sorbent).

Comparison of the sorption efficiency obtained during studies on the Black Sea water (average salinity of 18.4 ‰) and the sorption efficiency obtained during research in the Northwestern Pacific Ocean (average salinity of 33.8 ‰) during the 71st cruise of the collective use center “RV Akademik Oparin” (4 June–15 July 2024), at a seawater flow rate of 3 C.V./min, are presented in Table 5. It is seen that an increase in the total salt content in seawater has little effect on the sorption efficiency of radionuclides from seawater, thus allowing us to recommend the adsorbent for large-scale use, regardless of the geography of seawater.

Based on the obtained results, methods for the comprehensive determination of artificial ^{137}Cs and natural radionuclides for the obtained sorbents were developed. Step-by-step schemes for each method are shown in Figure 4.

Table 5. Sorption efficiency of radionuclide by the obtained sorbents (250 L of seawater, 100 mL of sorbent, and flow rate of 3 C.V./min).

Seawater (Salinity, ‰)	**Sorbent**	**Sorption Efficiency, %**						
		^{137}Cs	**^{7}Be**	**^{210}Pb**	**^{210}Po**	**^{226}Ra**	**^{228}Ra**	**^{234}Th**
Black Sea (18.4)	CoFe-PAN	94.0 ± 2.1	73.7 ± 1.6	89.7 ± 2.0	84.4 ± 1.9	–	–	98.5 ± 2.2
	CoMn-PAN	80.1 ± 1.8	63.6 ± 1.4	94.7 ± 2.1	90.9 ± 2.0	96.1 ± 2.1	98.1 ± 2.2	100
	FeMn-PAN	90.8 ± 2.0	62.7 ± 1.4	92.8 ± 2.0	87.7 ± 1.9	93.2 ± 2.1	95.3 ± 2.1	100
Pacific Ocean (33.8)	CoFe-PAN	93.5 ± 2.1	70.9 ± 1.6	85.3 ± 1.9	82.1 ± 1.8	–	–	95.5 ± 2.1
	CoMn-PAN	77.4 ± 1.7	58.4 ± 1.3	95.0 ± 2.1	88.9 ± 2.0	95.4 ± 2.1	97.1 ± 2.1	100
	FeMn-PAN	85.5 ± 1.9	63.2 ± 1.4	90.1 ± 2.0	84.2 ± 1.9	92.3 ± 2.0	94.2 ± 2.1	97.2 ± 2.1



(**a**) (**b**)

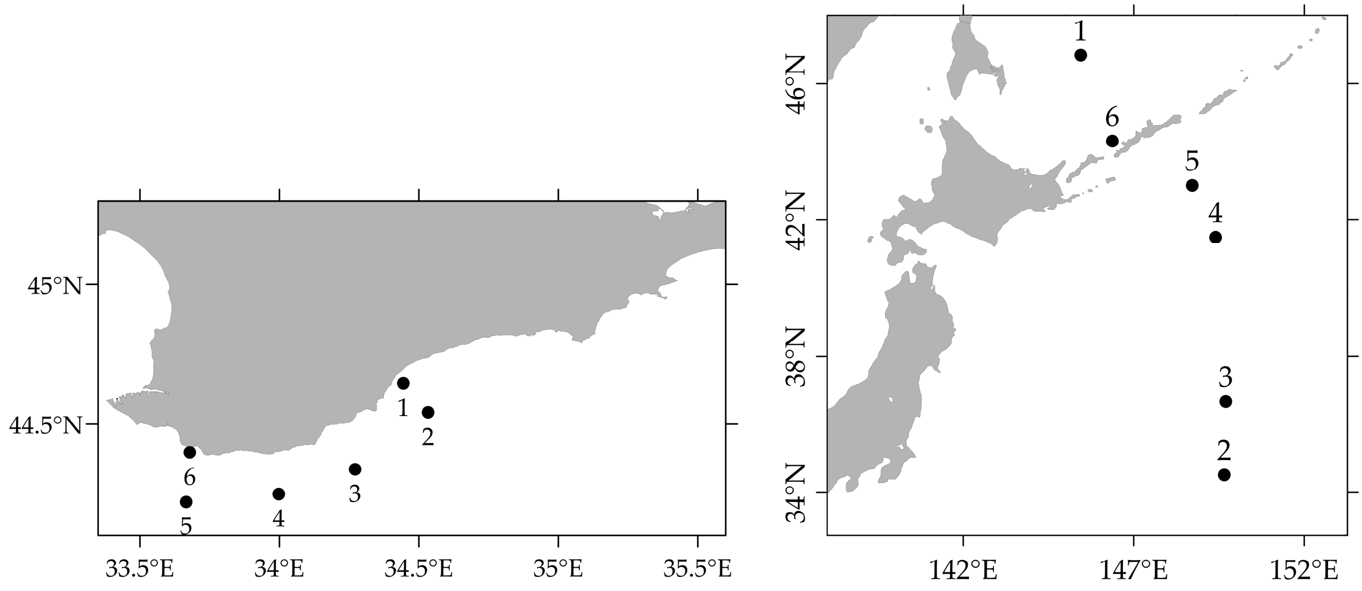
Figure 4. Proposed methods for the comprehensive determination of artificial ^{137}Cs and natural radionuclides using developed sorbents: (**a**) CoFe-PAN; and (**b**) CoMn-PAN or FeMn-PAN.

According to the proposed methods, the activity of ^{210}Pb can be determined by γ-spectrometry [75], but the probability of emitting γ-quanta during its decay is only 4.5%, and the energy of γ-quanta is also low (46.5 keV). As a result, for the γ-spectrometric determination of low activities of ^{210}Pb, special detectors are required to register low-energy γ-quanta and a long exposure time (up to several days) [76]. Therefore, the methods propose an alternative method of β-spectrometric determination by daughter ^{210}Bi [18] after radiochemical preparation.

Also, among the features of the proposed method for CoMn-PAN and FeMn-PAN sorbents, it is necessary to note the requirement for a hermetically sealed sample in a specified geometry (usually Petri dishes of a certain diameter and height for planar detectors or test tubes of a certain volume for detectors with a well) and a 3-week holding period to achieve equilibrium of ^{226}Ra with ^{214}Pb. The sample volume for this method is from 200 L depending on the time interval between sampling and measurement of samples due to the short half-lives of ^{7}Be ($T_{1/2}$ = 53.3 days [77]) and ^{234}Th ($T_{1/2}$ = 24.1 days [77]).

Among the features of the proposed method for the CoFe-PAN sorbent, it should be noted that after gamma-spectrometric determination of ^{7}Be, ^{137}Cs, ^{210}Pb, and ^{234}Th, it is possible to determine either ^{210}Po and ^{210}Pb or ^{32}P and ^{33}P. Simultaneous determination of these radionuclides in one sorbent sample is not possible due to differences in sample preparation. In this case, when determining ^{32}P and ^{33}P, the sample volume should be more than 1000 L, which is associated not only with their short half-lives of 14.3 and 25.3 days, respectively [77], but also with their low activities in seawater—only 0.02–0.1 Bq/m^3 [53].

The developed methods were studied during expeditionary research in the Black Sea and the Pacific Ocean. The sampling points are shown in Figure 5. The established values of radionuclide activity during the expeditionary research are presented in Table 6.



(**a**) (**b**)

Figure 5. Sampling stations in the (**a**) Black Sea and (**b**) Pacific Ocean.

The obtained values of activities coincide with the literature data for the Black Sea (^{137}Cs [10,69], ^{7}Be [12,20], ^{210}Pb and ^{210}Po [49], ^{226}Ra and ^{228}Ra [39], and ^{234}Th [39,78]) and the Pacific Ocean (^{137}Cs [79,80], ^{7}Be [81], ^{210}Pb and ^{210}Po [82,83], ^{226}Ra and ^{228}Ra [80,84,85], and ^{234}Th [86]), indicating the efficiency of the obtained sorption materials and the reliability of the results.

The activities of ^{210}Pb, ^{210}Po, ^{226}Ra, and ^{234}Th in the Pacific Ocean are higher than in the Black Sea, which is associated with a higher concentration of their parent isotope, ^{238}U, in the Pacific Ocean, which directly depends on the salinity of seawater [78]. Isotopes of ^{7}Be, ^{210}Pb, ^{210}Po, and ^{234}Th are adsorbed on suspended matter. For the studied water areas, the activity of ^{7}Be, ^{210}Pb, ^{210}Po, and ^{234}Th increases with distance from the coast and residential areas due to a decrease in suspended matter [39].

Table 6. Parameters of stations and activities of radionuclides in selected samples.

Station Number		**1**	**2**	**3**	**4**	**5**	**6**
Black Sea (spring 2023)							
Sorbent		FeMn-PAN	CoFe-PAN	CoMn-PAN	FeMn-PAN	CoFe-PAN	CoMn-PAN
Coordinates	North Latitude	44.64538	44.54168	44.33689	44.24846	44.22053	44.39808
	East Longitude	34.44425	34.53295	34.27128	33.99762	33.66563	33.67864
Activity, Bq/m^3	^{137}Cs	8.54 ± 0.80	9.34 ± 0.87	9.23 ± 0.91	9.20 ± 0.95	9.04 ± 0.85	8.68 ± 0.87
	^{7}Be	– *	– *	4.81 ± 0.75	6.02 ± 0.83	5.64 ± 0.71	4.05 ± 0.64
	^{210}Pb	1.22 ± 0.12	1.51 ± 0.15	1.18 ± 0.12	1.39 ± 0.14	1.54 ± 0.15	1.87 ± 0.19
	^{210}Po	0.37 ± 0.04	0.62 ± 0.06	0.40 ± 0.04	0.58 ± 0.06	0.72 ± 0.07	0.87 ± 0.09
	^{226}Ra	1.14 ± 0.11	–	0.75 ± 0.08	1.10 ± 0.11	–	0.88 ± 0.09
	^{228}Ra	0.75 ± 0.08	–	0.52 ± 0.05	0.75 ± 0.08	–	0.67 ± 0.07
	^{234}Th	– *	– *	12.4 ± 1.3	12.6 ± 1.1	13.2 ± 1.0	10.1 ± 1.1
Pacific Ocean (summer 2024)							
Sorbent		CoMn-PAN	FeMn-PAN	CoFe-PAN	CoFe-PAN	CoMn-PAN	FeMn-PAN
Coordinates	North Latitude	145.51447	149.73365	149.77839	149.47866	148.79276	146.44370
	East Longitude	46.84548	34.50422	36.66245	41.49080	43.01880	44.32272
Activity, Bq/m^3	^{137}Cs	1.05 ± 0.14	1.61 ± 0.16	1.53 ± 0.16	1.13 ± 0.13	1.18 ± 0.15	1.40 ± 0.14
	^{7}Be	– *	– *	– *	4.32 ± 0.68	3.85 ± 0.81	3.32 ± 0.74
	^{210}Pb	0.72 ± 0.07	2.52 ± 0.25	2.21 ± 0.22	1.87 ± 0.19	1.66 ± 0.17	1.02 ± 0.10
	^{210}Po	0.33 ± 0.03	1.16 ± 0.11	1.05 ± 0.08	0.84 ± 0.08	0.80 ± 0.08	0.45 ± 0.05
	^{226}Ra	1.46 ± 0.15	1.82 ± 0.18	–	–	2.02 ± 0.20	2.14 ± 0.21
	^{228}Ra	0.54 ± 0.05	0.24 ± 0.03	–	–	0.31 ± 0.03	0.68 ± 0.07
	234Th	– *	– *	– *	21.1 ± 3.2	20.2 ± 2.5	17.0 ± 1.8

Note: * Measurement of the activity of ^{7}Be and ^{234}Th at these points was not performed due to their short half-life and the large time interval between the time of sampling and the measurement of the sample.

The activity of ^{137}Cs in the Black Sea reached the values before the Chornobyl accident in 1986, but the activity of ^{137}Cs in the Black Sea is still higher compared to other waters of the World Ocean, due to the isolation of the water area and the presence of a secondary source of influx—the waters of the Dnieper River [87]. Although the studied area of the Pacific Ocean experienced unprecedented artificial impacts from the 2011 Fukushima nuclear power plant accident and ongoing radioactive water discharges, mixing and dilution reduced the activity of ^{137}Cs to pre-accident levels. Radionuclides from the coastal area adjacent to the nuclear power plant were drawn into the Kuroshio Current and then followed in the current flow in an easterly direction toward the open ocean [88].

4. Conclusions

Thus, according to the results of X-ray diffraction and energy-dispersive analyses, new sorbents based on transition metal ferrocyanides and manganese (CoMn-PAN and FeMn-PAN) or iron(III) (CoFe-PAN) oxides were synthesized. These sorbents have a high potential for application to the recovery of artificial ^{137}Cs and natural radionuclides from natural media, as confirmed by the results of a laboratory investigation of the sorbents' selectivity, research on solutions with different salt contents, and expeditionary studies. The possible mechanisms of radionuclide sorption were described based on the established structures of the obtained sorbents.

The selectivity studying results indicate that the obtained sorbents are selective for Cs, as well as Pb and Bi. The distribution coefficients for Cs are exceed 10^5 mg/L, while those for Pb and Bi exceed 10^3 mg/L. Additionally, the sorbents CoMn-PAN and FeMn-PAN, which contain manganese oxides, are effective in Ba^{2+} (the analog of Ra) recovery. Therefore, considering the patterns of change in the properties of elements, we can assume that the distribution coefficient of Ra will be higher than that of Ba·

It was shown that with an increase in the salinity of the studied natural solution, the distribution coefficients decrease slightly. Similar results are observed when comparing the sorption efficiency of radionuclides in large volumes of water from the Black Sea (average salinity, 18.4 ‰) and the northwestern Pacific Ocean (average salinity, 33.8 ‰).

Studies of the obtained sorbents during marine expeditions showed that the obtained materials based on transition metal ferrocyanides and manganese oxides CoMn-PAN and FeMn-PAN effectively recover ^{137}Cs, ^{226}Ra, ^{228}Ra, ^{210}Pb, ^{210}Po, and ^{234}Th at a seawater flow rate of 1–4 C.V./min. The sorbent based on transition metal ferrocyanide and iron(III) oxide CoFe-PAN effectively recovers ^{137}Cs, ^{210}Pb, ^{210}Po, and ^{234}Th, as well as ^{32}P and ^{33}P, at a seawater flow rate of 1–4 C.V./min.

Based on the obtained results, methods for the comprehensive determination of artificial ^{137}Cs and natural radionuclides for the developed sorbents were proposed. The results of researching the developed methods during expeditionary research in the Black Sea and the Pacific Ocean indicate the effectiveness of the obtained sorption materials and the possibility of their use in real expeditionary conditions.

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