

Article

Estimation of ^{137}Cs Distribution and Recovery Using Various Types of Sorbents in the Black Sea Surface Layer

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Abstract: Monitoring ^{137}Cs in seawater is necessary for the timely detection of radioactive contamination. The possibility of sorption and the sorption efficiency of ^{137}Cs from seawater were studied for the first time during several cruises of the R/V (research vessel) Professor Vodyanitsky using various types of sorbents based on transition metal ferrocyanides (Anfezh, Niket, Uniket, FSS, FD-M, FIC, Termoxid 35, NKF-C) and zirconium phosphate (Termoxid 3A). The influence of the seawater flow rate and volume of the sorbent used for the recovery of ^{137}Cs was estimated. The ferrocyanide sorbents Niket, Uniket, Termoxid 35, and FIC showed the best sorption efficiency (60–100%) at a seawater flow rate of 2–4 column volumes per minute. The data obtained during three cruises on the R/V Professor Vodyanitsky were analyzed. A detailed (28 sampling points) spatial distribution of ^{137}Cs in the Black Sea along the southern coast of Crimea was studied using the sorbents that showed the best characteristics. An increase in ^{137}Cs activity in the study area was not found, and the average activity was $9.01 \pm 0.87 \text{ Bq/m}^3$.

Keywords: ^{137}Cs ; seawater; sorbents; sorption; Black Sea; ferrocyanide sorbents



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1. Introduction

The problem of marine ecosystem pollution is given considerable attention all over the world [1].

The constant monitoring of marine areas for technogenic radionuclides and other pollutants is necessary to identify the sources of pollutants in time to prevent negative impacts on living organisms.

One of the consequences of the accident at the Chernobyl nuclear power plant (26 April 1986) is the contamination of the Black Sea with technogenic radionuclides, the main of which is ^{137}Cs , with a half-life of approximately 30 years.

Information about ^{137}Cs content in seawater is needed to determine its accumulation coefficients in hydrobionts. ^{137}Cs , having similar properties to potassium, accumulates in muscle tissue.

The distribution of ^{137}Cs after the Chernobyl disaster was studied in many expeditions. The main works discussing the results of expeditionary studies include the research conducted by K.O. Buesseler et al. [2] and V.N. Egorov et al. [3]. Staneva et al. [4] performed a mathematical modeling of ^{137}Cs distribution, and the current state of the issue was described in several articles by S. Gulín et al. [5,6] and R. Delfanti et al. [7]. Many methods for the radioanalytical determination of ^{137}Cs have been developed [8]. Currently, improved

sorption materials are being developed worldwide. For cesium recovery, many sorbents based on potassium [9,10] and calcium [11] aluminosilicates, as well as ferrocyanides with various supporting materials (polyacrylonitrile fiber [12], zeolite [13,14], silica gel [15], etc.), have been synthesized.

While copper hexacyanoferrate was used in some of the first studies on the recovery of ^{137}Cs from seawater [16], at present, mixed nickel–potassium hexacyanoferrate on an acrylate support KFeNiCN-PAN [17] is more widely used. The fiber impregnated with hexacyanoferrate has a developed specific surface, which increases the speed and efficiency of the extraction of radionuclides from seawater; therefore, this type of material can be considered the most promising. At the same time, the high sorption efficiency of ^{137}Cs from seawater is shown by sorbents based on cellulose support and silica gel, for example, a Russian-made sorbent of the FSS [18].

Sorption materials intended for the recovery, concentration, and isolation of ^{137}Cs from radioactively contaminated seawater are of considerable interest [19], for example, resorcinol–formaldehyde resin [20]. Its advantage is the possibility of repeated use after elution and regeneration. Another option is chitosan–ferrocyanide sorbents [21]. They were successfully tested under expeditionary conditions during radioecological monitoring of the Barents and Kara Seas. These sorbents also show a high sorption efficiency for ^{137}Cs [22].

This paper continues the work performed in a series of articles [18,22–24] devoted to the recovery of cesium, including ^{137}Cs , from seawater by various types of sorbents based on transition metal ferrocyanides (Anfezh, Niket, Uniket, FSS, FD-M, Termoxid 35, NKF-C, FIC), resorcinol–formaldehyde polymer (Axionit RCs), and zirconium phosphate (Termoxid 3A).

In previous articles, we determined the distribution coefficients for cesium and plotted output sorption curves for different seawater flow rates. The dynamic exchange capacity (DEC) and total dynamic exchange capacity (TDEC) of sorbents were determined [22,23]. A study was performed on the physicochemical regularities (isotherm and kinetics) of cesium sorption from seawater. The obtained dependences of the sorption parameters on time were described using the models of intraparticle diffusion; the pseudo-first and pseudo-second orders, the Elovich model, the dependence of sorption parameters on the equilibrium concentration of the metal in the solution; and the Langmuir, Freundlich, and Dubinin–Raduskevich sorption isotherms [24].

The purpose of this study was to evaluate the sorption efficiency of ^{137}Cs by various types of sorbents to select the most effective sorbents and develop a technique for ^{137}Cs recovery from seawater, allowing us to analyze the current radioecological state of the Black Sea, namely its ^{137}Cs contamination after the Chernobyl disaster.

A systematic assessment of the distribution of ^{137}Cs is necessary to identify fresh sources of this radionuclide. In the absence of a fresh source, the distribution of ^{137}Cs in the surface layer is homogeneous [18] because this radionuclide is practically not adsorbed onto suspended matter. Therefore, when assessing the distribution of ^{137}Cs , it is necessary to indicate the time parameters and number of research cruises. This will make it possible to compare the results of ^{137}Cs distribution obtained in different time intervals and identify possible changes.

This paper presents the results of three expedition studies: the 113 (4–29 June 2020), 116 (22 April–17 May 2021), and 121 (19 April–14 May 2022) cruises of the R/V Professor Vodyanitsky. Sorbents that showed the best characteristics for cesium recovery, including ^{137}Cs , from seawater under laboratory conditions were selected for expeditionary studies [18,22–24].

2. Materials and Methods

2.1. Sorbents

Commercially available sorbents based on transition metal ferrocyanides (Anfezh, Niket, Uniket, FSS, FD-M, FIC, Termoxid 35, NKF-C), and zirconium phosphate (Termoxid 3A) were used to recover ^{137}Cs from seawater. Table 1 provides their characteristics.

Table 1. Characteristics of sorbents used to recover ^{137}Cs from seawater.

| Sorbent; Technical Conditions (TC) ¹ | Manufacturer | View | Granulation, mm | Bulk Density, g/mL | Sorbent Composition | | Reference |
|---|--|--------------------------------------|--------------------|-----------------------|------------------------|---|-----------|
| | | | | | Support | Sorption-Active Phase: Content, Mass % | |
| Anfezh; TC 2165-003-26301393-99 | SPE Eksorb Ltd. (Yekaterinburg, Russia) | blue irregular granules | 0.1–1.0 | 0.25–0.4 | cellulose | ferric potassium ferrocyanide; not less than 10 | [25–27] |
| Niket; TC 2165-008-26301393-2005 | | green irregular granules | 0.1–2.5 | 0.5–0.7 | cellulose | nickel potassium ferrocyanide; not less than 10 | [23,28] |
| Uniket; TC 2165-012-26301393-2010 | | dark-blue irregular granules | 0.1–2.5 | 0.8–1.2 | cellulose | ferric potassium ferrocyanide; not less than 10 | [23,29] |
| FSS; TC 2641-012-57989206-2012 | Frumkin IPCE RAS (Moscow, Russia) | green irregular granules | 0.2–3.0 | 0.5–0.6 | silica gel | nickel potassium ferrocyanide; 8–10 | [18] |
| FD-M; TC 2641-019-57983206-2012 | | brown irregular granules | 0.5–1.0 | 0.1–0.2 | phosphorylated wood | copper potassium ferrocyanide; 5.0–5.5 | [23,30] |
| FIC; laboratory sample | | blue irregular granules | 0.1–1.0 | 0.25–0.4 | activated carbon | iron ferrocyanide; not less than 10 | – |
| Termoxid 35; TC 2641-006-12342266-2004 | JSC “Inorganic Sorbents” (Zarechny, Sverdlovsk region, Russia) | dark-green spherical granules | 0.4–1.5 | 1.1–1.2 | zirconium hydroxide | nickel potassium ferrocyanide; 30–35 | [31–33] |
| Termoxid 3A; TC 2641-004-12342266-2004 | | white spherical granules | 0.4–1.0 | 1.05–1.10 | – | zirconium phosphate | [33] |
| NKF-C | UrFU (Yekaterinburg, Russia) | light-brown irregular granules | 0.2–0.6 | 0.25–0.4 | cellulose | nickel potassium ferrocyanide; not less than 10 | [6] |

¹ Technical conditions (TC) are issued as a document establishing technical requirements that a specific product, material, substance, or group must conform with. They also specify the procedures to determine whether those requirements have been met.

2.2. Seawater Sampling

Water samples from the sea surface layer (up to 3 m) were taken at various stations during cruises 113 (4–29 June 2020), 116 (22 April–17 May 2021), and 121 (19 April–14 May 2022) of the R/V Professor Vodyanitsky along the southern coast of Crimea in the Black and Azov Seas.

Samples were taken using a Unipump Bavlenets BV 0.12-40-U5 submersible vibration pump (Subline Service LLC, Moscow, Russia), pumped through a polypropylene filter with a pore size of 1 μm FCPS1M series (Aquafilter Europe Ltd., Lodz, Poland), which served to remove suspended particles from the water, after which the samples filled plastic containers with a volume of 250 L located on board the vessel.

2.3. Sorption of ^{137}Cs

Sorption of ^{137}Cs was carried out by a single-column method by passing 250 L of seawater from a tank using a LongerPump WT600-2J peristaltic pump (Longer Precision Pump Co., Baoding, China) through a column filled with 50 or 100 mL of the sorbent (Figure 1).

To evaluate the yield in the seawater sample, stable cesium was added as a tracer at a concentration of 2.5 mg/L. In the process of sorption, every 10–20 L, samples of the passed seawater were taken into plastic test tubes for further evaluation of the yield.

After elution, the sorbent was squeezed out to remove excess seawater and dried in a SNOL-3.5.5.3.5/3.5-I2 oven (LLC “NPF TermIKS”, Moscow, Russia) at a temperature of 70–80 °C.



Figure 1. Sorption of ^{137}Cs from seawater: (a) sampling barrels; (b) columns with sorbents.

2.4. Determination of ^{137}Cs Activity in Sorbent Samples

Measurement of the specific activity of ^{137}Cs in sorbent samples was carried out in Petri dishes on a low-background spectrometric setup MKS-01A “MULTIRAD” (LLC “NTC Amplitude”, Zelenograd, Russia) with a gamma spectrometric tract “MULTIRAD-gamma” with a NaI(Tl) scintillation detector (diameter 63 mm, height 63 mm, resolution 7% for ^{137}Cs peak, MDA (Minimum Detectable Activity) was 0.47 Bq/m^3). Spectrometric data were registered and processed using the Progress software on the operational system Windows 10. The time for recording the activity of a single sample averaged 24 h. The efficiency of recording ^{137}Cs activity in the samples was calibrated using a certified source with a known specific activity. The error in measuring the activity of each sample (σ) usually did not exceed 10%. The spectra of sorbents after cesium recovery are shown in Figure S1 in the supplementary materials.

2.5. Determination of Cesium Concentration

The concentration of stable cesium to evaluate output was determined on a KVANT-2 atomic absorption spectrophotometer (LLC “Kortek”, Moscow, Russia) in an air–acetylene flame in the emission mode at a wavelength of 852.1 nm. The sorption efficiency (E , %) of ^{137}Cs from seawater was calculated from stable cesium using the formula [34,35]:

$$E = \frac{V \cdot C_0 - \sum V_p \cdot C_p}{V \cdot C_0} \cdot 100\%, \quad (1)$$

where C_0 is the initial cesium concentration, mg/L; V is the total volume of seawater passed through the sorbent, L; C_p is the cesium concentration in a portion of seawater passed through the sorbent, mg/L; and V_p is the volume of a portion of seawater passed through the sorbent, L.

3. Results and Discussion

3.1. Evaluation of the Sorption Efficiency of ^{137}Cs by Various Sorbents

The possibility and efficiency of ^{137}Cs sorption from seawater by various types of sorbents were studied during cruises 113 (4–29 June 2020) and 116 (22 April–17 May 2021) of the R/V Professor Vodyanitsky.

Table 2 shows the results of our study on the influence of the sorbent volume on the sorption efficiency of ^{137}Cs . We found that the sorption efficiency of ^{137}Cs increased with an increase in the volume of the sorbent, which is associated with an increase in the contact area of the phases. So, for example, when using 50 mL of the FIC sorbent, the sorption efficiency is 60%, and when using 100 mL, it is 91.6%.

Table 2. Dependence of sorption efficiency (E , %) of ^{137}Cs on volume (mass) of sorbent (seawater flow rate 4 CV/min (column volumes per minute)).

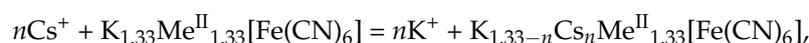
| Sorbent | Niket | Uniket | Termoxid 35 | FIC | FSS | Anfezh | NKF-C | FD-M | Termoxid 3A |
|-----------------------------|-------|--------|-------------|------|------|--------|-------|------|-------------|
| Sorbent volume V , mL | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 |
| Mass of sorbent m , g | 46.5 | 34.5 | 60.0 | 17.5 | 28.6 | 15.0 | 13.0 | 13.0 | 56.5 |
| Sorption efficiency E , % | 93.0 | 78.9 | 67.4 | 60.0 | 27.3 | 26.0 | 16.3 | 16.1 | 5.44 |
| Sorbent volume V , mL | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Mass of sorbent m , g | 93.0 | 69.0 | 120 | 35.0 | 57.2 | 30.0 | 26.0 | 26.0 | 113 |
| Sorption efficiency E , % | 99.3 | 94.8 | 96.5 | 91.6 | 42.1 | 41.7 | 23.2 | 22.5 | 8.07 |

The same volumes of sorbents were compared; however, the studied sorbents have different bulk densities and, accordingly, different masses. Tables 1 and 2 show that sorbents with a lower bulk density (Anfezh, FD-M, FSS, NKF-C) have a lower cesium sorption efficiency due to their lower mass and, accordingly, a smaller phase contact area.

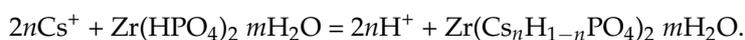
The exceptions are the Termoxid 3A sorbent, which, despite its high bulk density, shows a low cesium sorption efficiency, and the FIC sorbent, which, despite its low bulk density, shows a high cesium sorption efficiency. This can be explained by the high availability of sorption centers due to the developed porous structure of activated carbon, which supports the FIC sorbent.

Cesium sorption mechanisms are as follows:

- Sorbents based on transition metal ferrocyanides (Anfezh, Niket, Uniket, FSS, FD-M, FIC, Termoxid 35, NKF-C) [22,36]:



- Sorbents based on zirconium phosphate (Termoxid 3A) [22,37]:



There is no direct relationship between the mechanisms and sorption efficiency. The sorption efficiency is determined by the sorbents' capacities up to breakthrough and saturation, which depend on the sorption kinetics. The parameters for the studied sorbents were determined in our previous articles [23,24].

Figure 2 shows the effect of the seawater flow rate on the sorption efficiency of ^{137}Cs with 50 mL of sorbents.

The sorption efficiency of ^{137}Cs decreases with an increase in the flow rate due to a decrease in the contact time between seawater and the sorbent. Therefore, at a speed of 2 CV/min, 100 mL of seawater is passed through 50 mL of sorbent in 1 min, and at a speed of 8 CV/min, 400 mL of seawater is passed; therefore, the sorption efficiency decreases.

The optimum flow rate of seawater for the studied sorbents is 2–4 CV/min. For this range of rates, the ferrocyanide sorbents Niket, Uniket, Termoxid 35, and FIC have the best

sorption efficiency (60–100%), while the sorption efficiency of ^{137}Cs by other sorbents is less than 30%.

A considerable technical task under expeditionary conditions is to achieve high-speed seawater percolation through a fixed sorbent bed to reduce the analysis time. This requirement is best met by the Uniket, FSS, and FIC sorbents with coarse grains. The use of highly dispersed sorbents, such as Anfezh, becomes difficult with an increase in the percolation speed [23,24].

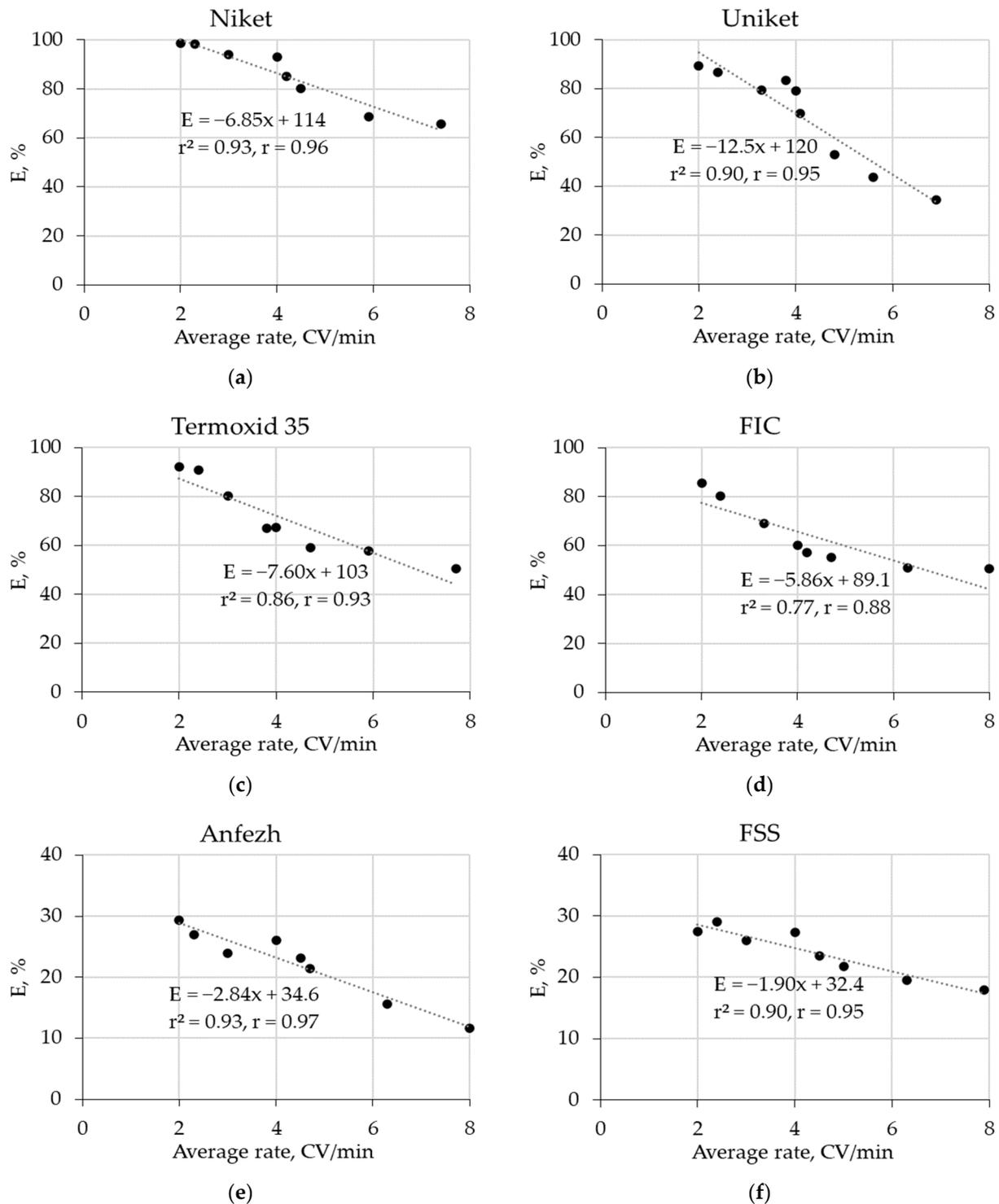


Figure 2. Cont.

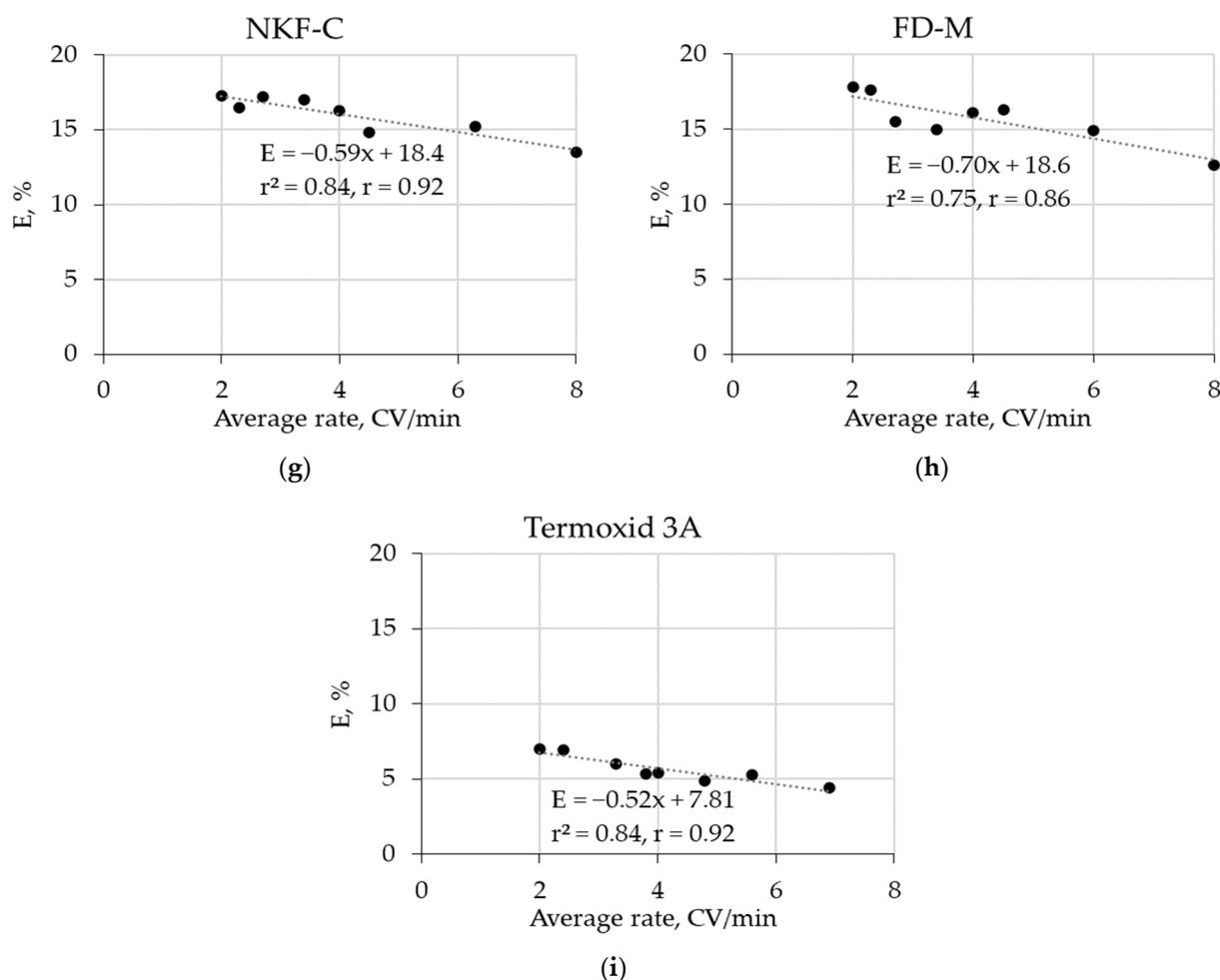


Figure 2. Dependence of sorption efficiency (E, %) of ^{137}Cs on average rate of passage of seawater by sorbents: (a) Niket; (b) Uniket; (c) Termoxid 35; (d) FIC; (e) Anfezh; (f) FSS; (g) NKF-C; (h) FD-M; (i) Termoxid 3A (volume of sorbents—50 mL; the volume of seawater—250 L).

Based on the results obtained, we developed a procedure for recovering ^{137}Cs from seawater using commercially available ferrocyanide sorbents (Figure 3):

1. Pump 250 L of seawater into a container on board the vessel while simultaneously filtering seawater through a polypropylene filter with a pore diameter of $1\ \mu\text{m}$;
2. Add a sample of cesium nitrate to the seawater in the container to a concentration of 2–3 mg/L of cesium to assess the sorption efficiency, then leave for 5–6 h to equalize the concentration of cesium in the entire volume of the container;
3. Load 50 mL of Niket, Uniket, Termoxid 35, FIC sorbent, or 100 mL of FSS or Anfezh sorbent into the column;
4. Pass 250 L of prepared seawater through the column with the sorbent at a speed of 2–4 CV/min;
5. Periodically (every 10–20 L), take a sample of seawater passed through the sorbent to assess the sorption efficiency of stable cesium;
6. After sorption, dry the sorbent in an oven at a temperature of 70–80 °C and place it in a Petri dish;
7. Determine the activity of ^{137}Cs in the sorbent on a scintillation gamma spectrometer with an exposure of at least 24 h to achieve a measurement error of no more than 10%.

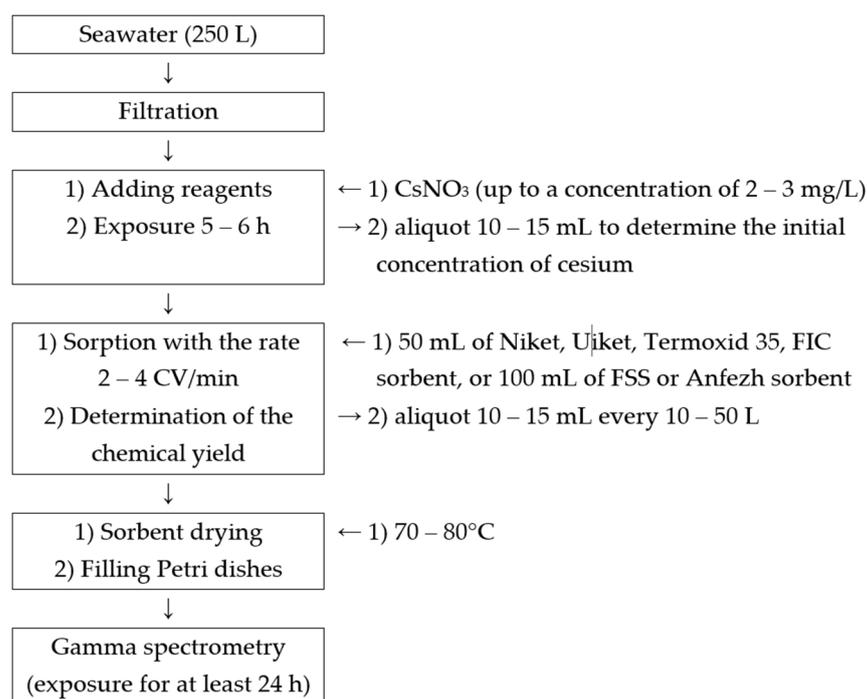


Figure 3. Scheme of method developed for ¹³⁷Cs sorption.

This technique is applied in further studies on the concentration of ¹³⁷Cs from seawater.

Figure 4 shows the values of the specific activity of ¹³⁷Cs in the surface layer of the Black and Azov Seas, which were obtained by studying the sorption efficiency during cruises 113 and 116 of the R/V Professor Vodyanitsky. Increased values of ¹³⁷Cs activity are observed in the western part of the study area due to the proximity of the source of entry—the Dnieper River (Ukraine) [38].

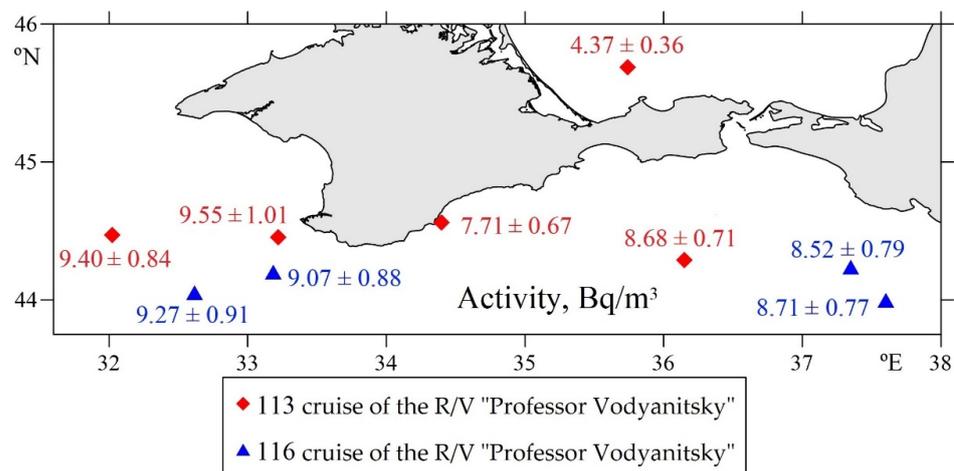


Figure 4. Specific activity values of ¹³⁷Cs (Bq/m³) in surface layer of Black and Azov Seas (along the southern coast of Crimea), obtained during cruises 113 (4–29 June 2020) and 116 (22 April–17 May 2021) of R/V Professor Vodyanitsky.

3.2. Surface Distribution of ¹³⁷Cs in the Black Sea in Spring 2022

To analyze the current radioecological state of the Black Sea, including its contamination with ¹³⁷Cs after the Chernobyl accident, an analysis of ¹³⁷Cs concentration was carried out by the developed method presented above. The sorbents that showed the best parameters of sorption efficiency of ¹³⁷Cs during cruises 113 and 116 of the R/V Professor Vodyanitsky were used. During cruise 121 of the R/V Professor Vodyanitsky

(19 April–14 May 2022), 28 seawater samples were taken and processed at 28 stations. The layout of the stations is shown in Figure 5.

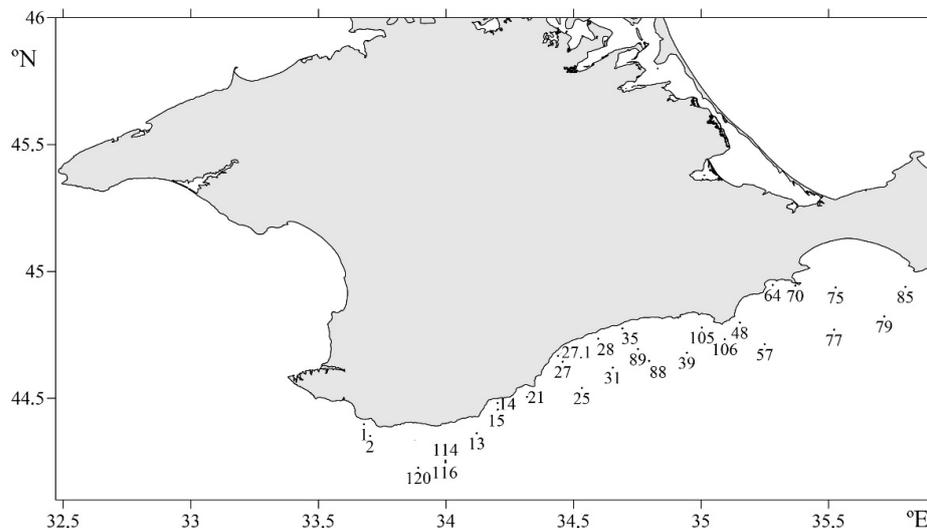


Figure 5. Location of sampling stations during cruise 121 (19 April–14 May 2022) of R/V Professor Vodyanitsky (along the southern coast of Crimea, stations numbering during the cruise retained).

Table 3 shows the results obtained.

Table 3. Parameters of samples and stations during study of the distribution of ¹³⁷Cs in cruise 121 (19 April–14 May 2022) of R/V Professor Vodyanitsky.

| Station Number | Coordinates of Sampling Points | | Sorbent | E, % | A _{sp} ¹³⁷ Cs, Bq/m ³ |
|----------------|--------------------------------|-------------------|-------------|------|--|
| | Northern Latitude | Eastern Longitude | | | |
| 1 | 44.39808 | 33.67864 | Termoxid 35 | 67.3 | 8.73 ± 0.89 |
| 2 | 44.35120 | 33.70265 | Uniket | 69.8 | 8.73 ± 0.88 |
| 13 | 44.36246 | 34.12065 | Termoxid 35 | 82.1 | 9.75 ± 0.79 |
| 14 | 44.48178 | 34.20170 | Uniket | 78.7 | 10.0 ± 0.98 |
| 15 | 44.45617 | 34.20333 | FIC | 64.4 | 9.50 ± 0.95 |
| 21 | 44.50590 | 34.31795 | FIC | 69.2 | 9.62 ± 1.27 |
| 25 | 44.54041 | 34.53309 | Termoxid 35 | 79.9 | 9.04 ± 1.07 |
| 27 | 44.64467 | 34.45784 | FIC | 64.0 | 9.06 ± 0.94 |
| 27.1 | 44.66783 | 34.43950 | Niket | 95.0 | 8.41 ± 0.79 |
| 28 | 44.73593 | 34.59710 | FIC | 56.5 | 8.57 ± 0.83 |
| 31 | 44.62115 | 34.65419 | Termoxid 35 | 79.8 | 9.13 ± 0.75 |
| 35 | 44.77496 | 34.69233 | FIC | 63.5 | 7.60 ± 0.86 |
| 39 | 44.67979 | 34.94443 | Niket | 93.8 | 9.12 ± 0.96 |
| 48 | 44.79867 | 35.15200 | Termoxid 35 | 80.1 | 8.85 ± 0.75 |
| 57 | 44.71315 | 35.24935 | FIC | 66.5 | 7.33 ± 0.68 |
| 64 | 44.94662 | 35.28064 | Uniket | 75.0 | 8.62 ± 0.81 |
| 70 | 44.94445 | 35.36925 | FIC | 66.9 | 9.21 ± 1.01 |
| 75 | 44.93706 | 35.52754 | Termoxid 35 | 78.1 | 9.03 ± 0.75 |
| 77 | 44.77019 | 35.52102 | FIC | 64.8 | 9.03 ± 0.92 |
| 79 | 44.82319 | 35.71791 | Niket | 92.7 | 8.62 ± 0.83 |
| 85 | 44.93957 | 35.80088 | FIC | 59.3 | 9.66 ± 0.90 |
| 88 | 44.64783 | 34.79639 | Termoxid 35 | 80.3 | 9.09 ± 0.80 |
| 89 | 44.69392 | 34.75217 | FIC | 64.3 | 10.4 ± 0.91 |
| 105 | 44.77917 | 35.00317 | Termoxid 35 | 76.2 | 9.69 ± 0.84 |
| 106 | 44.73351 | 35.09265 | Termoxid 35 | 73.5 | 9.09 ± 0.85 |
| 114 | 44.25389 | 33.99746 | FIC | 55.7 | 9.07 ± 0.76 |
| 116 | 44.24846 | 33.99762 | Termoxid 35 | 78.4 | 9.07 ± 0.82 |
| 120 | 44.22626 | 33.89136 | FIC | 59.5 | 8.28 ± 0.78 |

Figure 6 shows the distribution of ¹³⁷Cs in the surface layer of the Black Sea along the southern coast of Crimea. The value of ¹³⁷Cs activity varied over space in the range of 7.33–10.4 Bq/m³ and averaged 9.01 ± 0.87 Bq/m³. Thus, the spatial variability of the

cesium concentration field in the study area was within the error range of the method for determining this parameter.

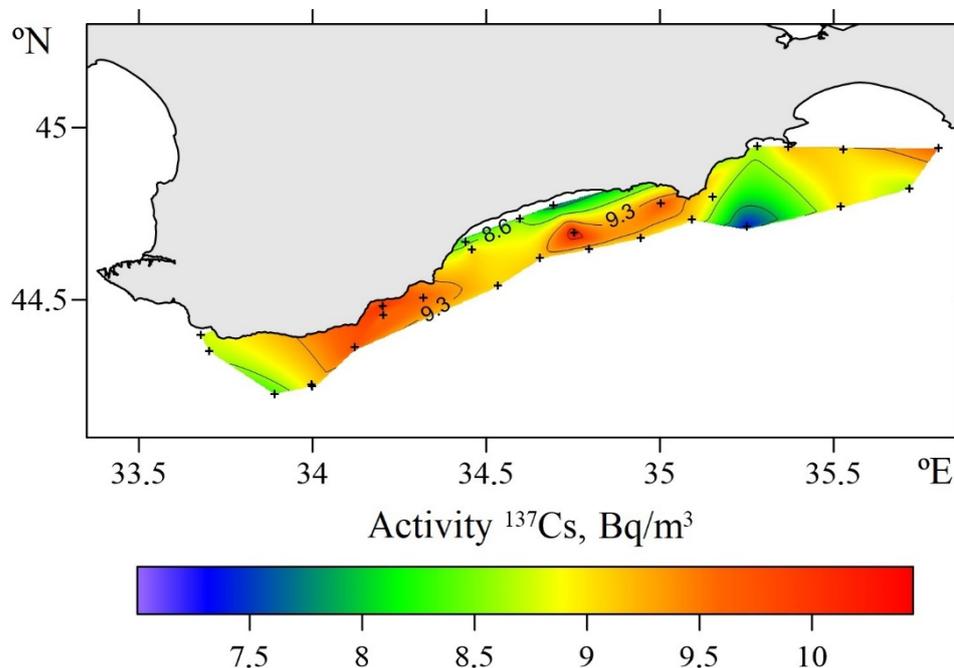


Figure 6. Distribution of ^{137}Cs in surface layer of Black Sea (along the southern coast of Crimea), obtained during cruise 121 (19 April–14 May 2022) of R/V Professor Vodyanitsky.

According to the literature data, ^{137}Cs activity in the Black Sea was $20.0 \pm 1.1 \text{ Bq/m}^3$ in 2007 [7], $17.1 \pm 0.9 \text{ Bq/m}^3$ in 2013 [6], and $14.4 \pm 1.3 \text{ Bq/m}^3$ in 2015 [39]. The data obtained are consistent with the published data [6,7,39], taking into account the half-life for the decrease in ^{137}Cs inventory, which, according to [38], is 8.6 years for the period 1987–2011. The decrease in ^{137}Cs activity in the surface layer of the Black Sea is associated with its radioactive decay and penetration into the underlying layers [38]. Thus, an increase in ^{137}Cs activity in the study area was not determined.

During cruise 121, a limited area of the Black Sea along the southern coast of Crimea was available for study; the sampling and measurement of samples were not carried out at the western part of the Black Sea, where elevated values of ^{137}Cs activity are usually observed due to the proximity of the source of cesium, the Dnieper River (Ukraine) [38].

According to the Radiation Safety Norms–99/2009 [40] of Russia, the allowable concentrations (intervention levels) of ^{137}Cs in seawater are 11 Bq/L; therefore, the current levels of ^{137}Cs in the surface water of the Black Sea are below the maximum allowable.

4. Conclusions

Systematic monitoring of ^{137}Cs content in seawater is necessary for the timely detection of sources of radioactive contamination entering the environment, allowing for decision makers to take measures to prevent negative impacts on living organisms.

The possibility of ^{137}Cs recovery from seawater and its sorption efficiency were studied using various types of sorbents based on transition metal ferrocyanides (Anfezh, Niket, Uniket, FSS, FD-M, Termoxid 35, NKF-C, FIC) and zirconium phosphate (Termoxid 3A). We found that the sorption efficiency of ^{137}Cs decreased with an increase in the flow rate due to a decrease in the contact time of seawater with the sorbent. The optimum flow rate of seawater for the studied sorbents is 2–4 CV/min. The ferrocyanide sorbents Niket, Uniket, Termoxid 35, and FIC showed the best sorption efficiency (60–100%). Based on the results obtained, a procedure was developed for recovering ^{137}Cs from seawater.

To analyze the current radioecological state of the Black Sea, namely its contamination with ^{137}Cs after the Chernobyl accident, in the spring of 2022, the spatial distribution of ^{137}Cs in the Black Sea along the southern coast of Crimea was studied using the developed methodology and sorbents that showed the best characteristics. The value of ^{137}Cs activity varied over space in the range of 7.33–10.4 Bq/m³ and averaged 9.01 ± 0.87 Bq/m³. The data obtained are consistent with the literature data, taking into account the half-life for the decrease in ^{137}Cs inventory; an increase in ^{137}Cs activity in the study area was not found. The current levels of ^{137}Cs in the surface water of the Black Sea are below the maximum allowable level.

Further research is needed in the coastal ecosystems of the Black Sea, which are accumulators of anthropogenic radionuclides.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr11020603/s1>, Figure S1: Spectra of sorbents after cesium recovery.

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References

1. Kotelyanets, E.A.; Gurov, K.I.; Tikhonova, E.A.; Kondratev, S.I. Pollutants in Bottom Sediments in the Balaklava Bay (the Black Sea). *Phys. Oceanogr.* **2019**, *26*, 414–424. [\[CrossRef\]](#)
2. Buesseler, K.O.; Livingston, H.D. Time-Series Profiles of ^{134}CS , ^{137}CS and ^{90}SR in the Black Sea. In *Sensitivity to Change: Black Sea, Baltic Sea and North Sea. NATO ASI Series (Series 2: Environment)*; Özsoy, E., Mikaelyan, A., Eds.; Springer: Dordrecht, The Netherlands, 1997; Volume 27, pp. 239–251. [\[CrossRef\]](#)
3. Egorov, V.N.; Povinec, P.P.; Polikarpov, G.G.; Stokozov, N.A.; Gulin, S.B.; Kulebakina, L.G.; Osvath, I. ^{90}Sr and ^{137}Cs in the Black Sea after the Chernobyl NPP accident: Inventories, balance and tracer applications. *J. Environ. Radioact.* **1999**, *43*, 137–155. [\[CrossRef\]](#)
4. Staneva, J.V.; Buesseler, K.O.; Stanev, E.V.; Livingston, H.D. The application of radiotracers to a study of Black Sea circulation: Validation of numerical simulations against observed weapons testing and Chernobyl ^{137}Cs data. *J. Geophys. Res.* **1999**, *104*, 11099–11114. [\[CrossRef\]](#)
5. Gulin, S.B.; Mirzoyeva, N.Y.; Egorov, V.N.; Polikarpov, G.G.; Sidorov, I.G.; Proskurnin, V.Y. Secondary radioactive contamination of the Black Sea after Chernobyl accident: Recent levels, pathways and trends. *J. Environ. Radioact.* **2013**, *124*, 50–56. [\[CrossRef\]](#) [\[PubMed\]](#)
6. Gulin, S.B.; Egorov, V.N.; Duka, M.S.; Sidorov, I.G.; Proskurnin, V.Y.; Mirzoyeva, N.Y.; Bey, O.N.; Gulina, L.V. Deep-water profiling of ^{137}Cs and ^{90}Sr in the Black Sea. A further insight into dynamics of the post-Chernobyl radioactive contamination. *J. Radioanal. Nucl. Chem.* **2015**, *304*, 779–783. [\[CrossRef\]](#)
7. Delfanti, R.; Özsoy, E.; Kaberi, H.; Schirone, A.; Salvi, S.; Conte, F.; Tsabaris, C.; Papucci, C. Evolution and fluxes of ^{137}Cs in the Black Sea/Turkish Straits System/North Aegean Sea. *J. Mar. Syst.* **2014**, *135*, 117–123. [\[CrossRef\]](#)

8. Lehto, J.; Hou, X. *Chemistry and Analysis of Radionuclides. Laboratory Techniques and Methodology*; Wiley-VCH: Weinheim, Germany, 2011; 426p.
9. Yarusova, S.B.; Shichalin, O.O.; Belov, A.A.; Azon, S.A.; Buravlev, I.Y.; Golub, A.V.; Mayorov, V.Y.; Gerasimenko, A.V.; Papynov, E.K.; Ivanets, A.I.; et al. Synthesis of amorphous KAlSi_3O_8 for cesium radionuclide immobilization into solid matrices using spark plasma sintering technique. *Ceram. Int.* **2021**, *48*, 3808–3817. [[CrossRef](#)]
10. Ohara, E.; Soejima, T.; Ito, S. Removal of low concentration Cs(I) from water using Prussian blue. *Inorg. Chim. Acta* **2021**, *514*, 120029. [[CrossRef](#)]
11. Le, Q.T.N.; Cho, K. Caesium adsorption on a zeolitic imidazolate framework (ZIF-8) functionalized by ferrocyanide. *J. Colloid Interface Sci.* **2021**, *581*, 741–750. [[CrossRef](#)]
12. El-Shazly, E.A.A.; Dakroury, G.A.; Someda, H.H. Sorption of ^{134}Cs radionuclide onto insoluble ferrocyanide loaded silica-gel. *J. Radioanal. Nucl. Chem.* **2021**, *329*, 437–449. [[CrossRef](#)]
13. Bondar, Y.; Olkhovyk, Y.; Kuzenko, S. Nanocomposite adsorbent based on polyacrylonitrile fibers for rapid and selective removal of Cs radionuclides. *J. Radioanal. Nucl. Chem.* **2021**, *330*, 1221–1231. [[CrossRef](#)]
14. Gordienko, P.S.; Yarusova, S.B.; Shabalin, I.A.; Slobodyuk, A.B.; Nekhlyudova, E.A.; Shichalin, O.O.; Papynov, E.K.; Kuryavyi, V.G.; Polyakova, N.V.; Parot'kina, Y.A. Synthesis of Calcium Aluminosilicates from Nanostructured Synthetic Na Zeolites and Study of Their Sorption Properties. *Russ. J. Inorg. Chem.* **2022**, *67*, 1393–1399. [[CrossRef](#)]
15. Panasenko, A.E.; Shichalin, O.O.; Yarusova, S.B.; Ivanets, A.I.; Belov, A.A.; Dran'kov, A.N.; Azon, S.A.; Fedorets, A.N.; Buravlev, I.Y.; Mayorov, V.Y.; et al. A novel approach for rice straw agricultural waste utilization: Synthesis of solid aluminosilicate matrices for cesium immobilization. *Nucl. Eng. Technol.* **2022**, *54*, 3250–3259. [[CrossRef](#)]
16. Mann, D.R.; Casso, S.A. In situ chemisorption of radiocesium from seawater. *Mar. Chem.* **1984**, *14*, 307–318. [[CrossRef](#)]
17. Breier, C.F.; Pike, S.M.; Sebesta, F.; Tradd, K.; Breier, J.A.; Buesseler, K.O. New applications of KNiFC-PAN resin for broad scale monitoring of radiocesium following the Fukushima Dai-ichi nuclear disaster. *J. Radioanal. Nucl. Chem.* **2016**, *307*, 2193–2200. [[CrossRef](#)]
18. Dovhyi, I.I.; Kremenchutskii, D.A.; Bezhin, N.A.; Kozlovskaya, O.N.; Milyutin, V.V.; Kozlitsin, E.A. Distribution of ^{137}Cs in the Surface Mixed Layer of the Black Sea in summer 2017. *Phys. Oceanol.* **2020**, *36*, 387–396. [[CrossRef](#)]
19. Avramenko, V.A.; Egorin, A.M.; Papynov, E.K.; Sokol'nitskaya, T.A.; Tananaev, I.G.; Sergienko, V.I. Processes for treatment of liquid radioactive waste containing seawater. *Radiochemistry* **2017**, *59*, 407–413. [[CrossRef](#)]
20. Egorin, A.M.; Palamarchuk, M.S.; Tokar', E.A.; Tutov, M.V.; Azarova, Y.A.; Tananaev, I.G.; Avramenko, V.A. Sorption of ^{137}Cs from seawater onto resorcinol-formaldehyde resin. *Radiochemistry* **2017**, *59*, 160–165. [[CrossRef](#)]
21. Egorin, A.; Tokar, E.; Zemsikova, L.; Didenko, N.; Portnyagin, A.; Azarova, Y.; Palamarchuk, M.; Tananaev, I.; Avramenko, V. Chitosan-ferrocyanide sorbents for concentrating Cs-137 from seawater. *Sep. Sci. Technol.* **2017**, *52*, 1983–1991. [[CrossRef](#)]
22. Dovhyi, I.I.; Bezhin, N.A.; Tananaev, I.G. Sorption methods in marine radiochemistry. *Russ. Chem. Rev.* **2021**, *90*, 1544–1565. [[CrossRef](#)]
23. Bezhin, N.A.; Dovhyi, I.I.; Milyutin, V.V.; Kaptakov, V.O.; Kozlitsin, E.A.; Egorin, A.M.; Tokar', E.A.; Tananaev, I.G. Study of sorbents for analysis of radiocesium in seawater samples by one-column method. *J. Radioanal. Nucl. Chem.* **2021**, *327*, 1095–1103. [[CrossRef](#)]
24. Bezhin, N.A.; Dovhyi, I.I.; Tokar, E.A.; Tananaev, I.G. Physical and chemical regularities of cesium and strontium recovery from the seawater by sorbents of various types. *J. Radioanal. Nucl. Chem.* **2021**, *330*, 1101–1111. [[CrossRef](#)]
25. Leppänen, A.-P.; Kasatkina, N.; Vaaramaa, K.; Matishov, G.G.; Solatie, D. Selected anthropogenic and natural radioisotopes in the Barents Sea and off the western coast of Svalbard. *J. Environ. Radioact.* **2013**, *126*, 196–208. [[CrossRef](#)] [[PubMed](#)]
26. Remez, V.P.; Sapozhnikov, Y.A. The rapid determination of caesium radionuclides in water systems using composite sorbents. *Appl. Radiat. Isot.* **1996**, *47*, 885–886. [[CrossRef](#)]
27. Remez, V.P.; Zheltonozhko, E.V.; Sapozhnikov, Y.A. The Experience of Using ANFEZH Sorbent for Recovery of Radioactive Caesium from Sea Water. *Radiat. Prot. Dosim.* **1998**, *75*, 77–78. [[CrossRef](#)]
28. Semenishchev, V.S.; Pyankov, A.A.; Remez, V.P.; Afonin, Y.D.; Nikiforov, A.F. Study of physicochemical and sorption properties of nickel and iron hexacyanoferrates to cesium. *Sorpt. Chromatogr. Process* **2020**, *20*, 54–63. (In Russian) [[CrossRef](#)]
29. Matel, L.; Dulanska, S.; Silikova, V. Composite sorbents for radionuclide separation. In *XXXIX Days of Radiation Protection. Proceedings of Presentations and Posters*; Slovenska Zdravotnicka Univerzita: Bratislava, Slovakia, 2018; p. 578.
30. Nada, A.M.A.; Moussa, W.M.; El-Mongy, S.A.; El-Sayed, E.S.A. Physicochemical Studies of Cation Ion Exchange Wood Pulp. *Aust. J. Basic Appl. Sci.* **2009**, *3*, 9–16.
31. Sharygin, L.M.; Muromskii, A.Y. Inorganic Sorbent for Ion-Selective Purification of Liquid Radioactive Wastes. *At. Energy* **2000**, *89*, 658–662. [[CrossRef](#)]
32. Sharygin, L.M.; Muromskii, A.Y. Inorganic Sorbent for Selective Treatment of Liquid Radioactive Wastes. *Radiochemistry* **2004**, *46*, 185–189. [[CrossRef](#)]
33. Voronina, A.V.; Noskova, A.Y.; Semenishchev, V.S.; Gupta, D.K. Decontamination of seawater from ^{137}Cs and ^{90}Sr radionuclides using inorganic sorbents. *J. Environ. Radioact.* **2020**, *217*, 106210. [[CrossRef](#)]
34. Pincam, T.; Jampeetong, A. Treatment of Anaerobic Digester Effluent Using Typha angustifolia L.: Growth Responses and Treatment Efficiency. *J. Water Environ. Technol.* **2020**, *18*, 105–116. [[CrossRef](#)]

35. Kadko, D. Upwelling and primary production during the U.S. GEOTRACES East Pacific Zonal Transect. *Glob. Biogeochem. Cycles* **2017**, *31*, 218–232. [[CrossRef](#)]
36. Tananaev, I.V.; Seifer, G.B.; Kharitonov, Y.Y.; Kuznetsov, V.G.; Korolkov, A.P. *Chemistry of ferrocyanides*; Nauka: Moscow, Russia, 1971; 320p. (In Russian)
37. Lokshin, E.P.; Ivanenko, V.I.; Avsaragov, H.-M.B.; Melnik, N.A.; Vladimirova, V.V.; Kalinnikov, V.T. Purification of water-salt solutions with Ti(IV) and Zr(IV) phosphates. *At. Energy* **2002**, *92*, 118–123. (In Russian) [[CrossRef](#)]
38. Gulin, S.B.; Egorov, V.N. Radioactive Tracers in the Black Sea: A Tool for Environmental Assessment and Ecological Regulation. In *Genetics, Evolution and Radiation*; Korogodina, V., Mothersill, C., Inge-Vechtomov, S., Seymour, C., Eds.; Springer: Cham, Germany, 2016; pp. 303–313.
39. Mirzoeva, N.Y.; Gulin, S.B.; Miroshnichenko, O.N. Radionuclides of strontium and cesium. In *Black Sea System*; Lisitsyn, A.P., Ed.; Scientific World: Moscow, Russia, 2018; Volume 7.2, pp. 605–624. (In Russian)
40. *Radiation Safety Standards (RSS-99/2009)*; Sanitary Rules and Norms 2.6.1.2523-09. Federal Center for Hygiene and Epidemiology of Rospotrebnadzor: Moscow, Russia, 2009; 88p. (In Russian)

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