

Загальна екологія та радіоекологія

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USE OF NATURAL MINERALS AS SORBENTS OF RADIOCAESIUM IN AGRICULTURAL PRODUCTION

The article elucidates the research of the efficiency of use of natural zeolite and bentonite sorbents and ferrocyanide containing sorbents: ferrocyanide-2 and FWV (ferrocyanide waste of viticulture) for treatment of multicomponent agricultural waste. It is established that all of the studied sorbents have a high sorption capacity regarding ^{137}Cs from the aqueous solution and are characterized by relatively rapid absorption of ^{137}Cs . ^{13}CS is held the strongest by the sorbents ferrocyanide-2 and FWV. The efficiency of sorption of natural sorbents essentially depends more on the presence of K^+ ions in the water solution and is less dependent on pH. The presence of potassium ions in the environment does not affect the effectiveness of sorption of ferrocine drugs.

The high sorption capacity of ferrocyanide waste of viticulture (FVV) is established, which opens prospects for their practical application in agricultural production on the radioactively contaminated territories.

Key words: sorbents, zeolite, bentonite, ferrotsyn, ferrocyanide waste of viticulture, coefficient of sorption, saline solution, ^{137}Cs .

Formulation of the problem

Modern radiological situation on radioactively contaminated areas of Ukraine is mainly caused by the presence of long-lived technogenic radionuclides ^{137}Cs and ^{90}Sr from Chernobyl in a soil-vegetation cover [1, 8].

Once in farmland soil ^{137}Cs is fairly well absorbed by the soil complex, which prevents the movement of ^{137}Cs through the soil profile, its penetration into the ground water and ultimately determines its very long (decades) accumulation in the upper soil horizons and continuous flow into agricultural products [3, 7, 11].

^{90}Sr binds less with the soil complex, but has much higher biological activity for transition into plant; thereby it is also retained in the upper layers of soil due to the biological cycle.

The research has shown that even after 29 years after the fallout in precipitation the main mass of radionuclides (80 %) is concentrated in the zone of roots location of agricultural plants. In natural lands after radioactive fallout, the main activity is in the upper part (10 cm) of soil and in arable soil; radionuclides are distributed evenly

throughout the depth of the processed layer. Calculations show, that in the short term, the self-cleaning process of the contaminated root layer of soil will be negligible due to the vertical migration of radionuclides [2, 4].

Thus if to use radioactively contaminated land and, especially, the land that was earlier withdrawn from agricultural use due to the radiological factor for growing crops and livestock, there is a threat of receiving primary and secondary products (manure, technological liquids) with significant radionuclide contamination. This in turn leads to secondary contamination of soil and creates a number of problems of radiation safety for products transport, storage, processing and recycling. That is, the presence of such products and their use can contribute to improving the radiological situation, due to the additional radiation pollution.

Analysis of recent research and publications

The question of safe use of certain types of waste and by-products of agricultural production on contaminated areas is still topical. For example it is shown in publications of some authors, that the secondary contamination of soil due to using manure as fertilizer for 25 years may reach from 63 to 126 kBk/m² (1,7–3,4 Ci/km²) [9].

One of the most viable solutions to the problem of the purification of products from radionuclides ⁹⁰Sr and ¹³⁷Cs, that got into the environment as a result of the Chernobyl accident, is the use of sorbents. The choice of sorbent is determined by several factors, foremost of which are its absorption characteristics, selectivity towards the radionuclides, chemical and radiation resistance. Certainly, not the last role is played by the cost of the material [5, 7, 8, 10].

Currently, a great amount of mineral, synthetic and organic sorbents are known in the practice of purification of wastes. However, some authors indicate difficulties of assuring relative selectivity of many sorbents. During the purification of multicomponent solutions (chyme of animal digestive tract, liquid manure, technological waste, etc.) the sorbent extracts from them all the components, because it is composed of several types of complexing groups (and thus there are several mechanisms of sorption at the same time). As a result, sorption capacity regarding radioactive components is reduced [7, 10, 13].

In this respect promising is the use of natural mineral sorbents, which have significant sorption-selective properties and the ability to permanently fix radionuclides. It is important when used for purifying low radioactive liquid agricultural waste. Promising is also the use of natural sorbents in animal husbandry. They include a wide range of biophil macro- and microelements that may help improve mineral nutrition of animals. Also because of their sorption properties, they help to reduce the intake of radionuclides to their organism.

Purpose, objects and methods of research

The purpose of the research was a comparative study of sorption-selective properties of natural zeolite and bentonite sorbents and ferrocyanide containing

sorbents, such as: ferrocyanide-2 and FWV (ferrocyanide waste of viticulture) - Russian analogue of HZH-90.

Sorption properties of these sorbents for ^{137}Cs were studied in statistical terms of in vitro depending on the concentration of carrier and lateral ions.

Experimental research was conducted in three stages.

At the first stage of research, the task was to evaluate the effectiveness of ^{137}Cs sorption from water solutions depending on the proportion of solution to sorbent.

Experiments were carried out in two variants with a different volume of ^{137}Cs aqueous solution at pH – 3,18:

First variant - the solution-sorbent proportion was 1:50. The second variant – the solution-sorbent proportion was 1:25. Each variant had 5 parallels (repetition). The solution with the sorbent was stirred intensively for 30 minutes in a magnetic mixer. Next, the mixture of a radioactive solution with the sorbents was left for 24 hours, then filtered through a membrane filter of \varnothing 0,22mkm solution and measured the activity by gamma spectrum.

In this experiment, a solution of ^{137}Cs with its volumetric activity of 6700 ± 67 Bq/l was used for the first variant of experiment and with the activity of 6550 ± 70 Bq/l for the second one.

The objective of the second phase of the research was to evaluate the sorbents absorption rate of ^{137}Cs from an aqueous solution and their retaining capacity towards the given isotope when processing sorbents 1M with the solution of potassium chloride (KCL) and hydrochloric acid (NCl).

In the experiment, the method of consecutive sorption of ^{137}Cs from the aqueous solution and extraction of the absorbed ^{137}Cs from the sorbent was used under the such scheme: sorption from aqueous solution – 30 min, sorption from aqueous solution – 24 hours, extraction with 1M solution of potassium chloride – 24 hours, extraction with 1M solution of hydrochloric acid – 24 hours. After each sorption and extraction, a mixture of radioactive solution with the sorbents was filtered through the membrane filter \varnothing 0,22mkm and ^{137}Cs activity was measured in the filtrate.

At the third stage of research the effectiveness of sorption of ^{137}Cs from 1 % solution of KCL and acidified with 1M NCl was evaluated.

During the experiment, a cup with sorbent was filled with solution containing ^{137}Cs in 1 % KCl, stirred intensively for 30 minutes in a magnetic mixer and left to settle for 24 hours. After that, the solution was filtered through a membrane filter \varnothing 0,22 mm, and the sediment was mixed with a solution of 1M NCl and stirred for 30 minutes ($T \sim 20^\circ \text{C}$). After a day of upholding, the solution was filtered through a membrane filter \varnothing 0,22 mkm.

After a day of settlement, the solution was filtered through a membrane filter \varnothing 0,22mkm. The volume activity of ^{137}Cs was measured in the first and second filtered solution.

As the quantitative characteristics of interaction of sorbents with radionuclide ^{137}Cs there was used a coefficient of sorption (C_s):

$$C_s, \% = 100\% \cdot (C_{\text{beg}} - C_{\text{end}}) / C_{\text{beg}},$$

where C_{beg} and C_{end} – initial and final concentration of ^{137}Cs in the liquid.

In all experiments, the volume activity of ^{137}Cs in solution was determined by γ -spectrometric method on a γ -spectrometer fitted with semiconductor detector type GEM-30185, Ge(Li), GMX-Series ("EG&G ORTEC") with multi-channel analyzer (ADCAM-300 USA, IN-1200, France).

Research results were processed with the help of variation statistics method on the PC using the standard package of statistical programs and applications "Microsoft Excel".

Research results

To succeed in solving the problem of the concentration of radionuclides from water solutions it is necessary to select the proper sorbent and optimal conditions of adsorption of particular isotope.

It is known that the most important parameter, that characterizes the efficiency of sorption of substances from aqueous solutions is adsorption coefficient [3, 12].

The results of grouping the sorption coefficients for ^{137}Cs depending on the type of sorbent and the concentration of isotopes in aqueous solution are shown in Fig. 1–2.

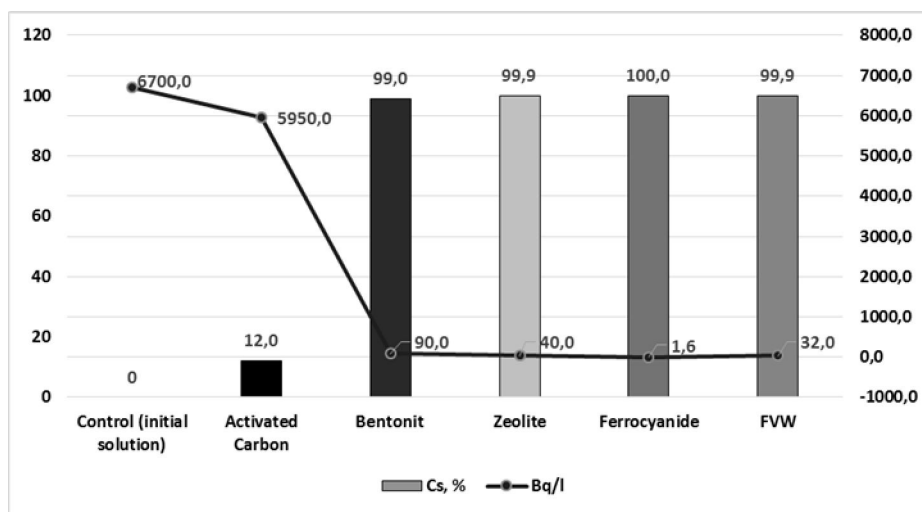


Fig. 1. Coefficients of sorption ^{137}Cs with different sorbents (proportion of sorbent to solution – 1:50)

As can be seen from the figures, the studied sorbents have very high sorption capacity from aqueous solution pertaining to ^{137}Cs . Almost all the sorbents had the

value of Cs of about 100 %. Activated carbon, in this case, was nonspecific sorbent with a rather low efficiency of ^{137}Cs sorption, its Cs was within 12–22 %.

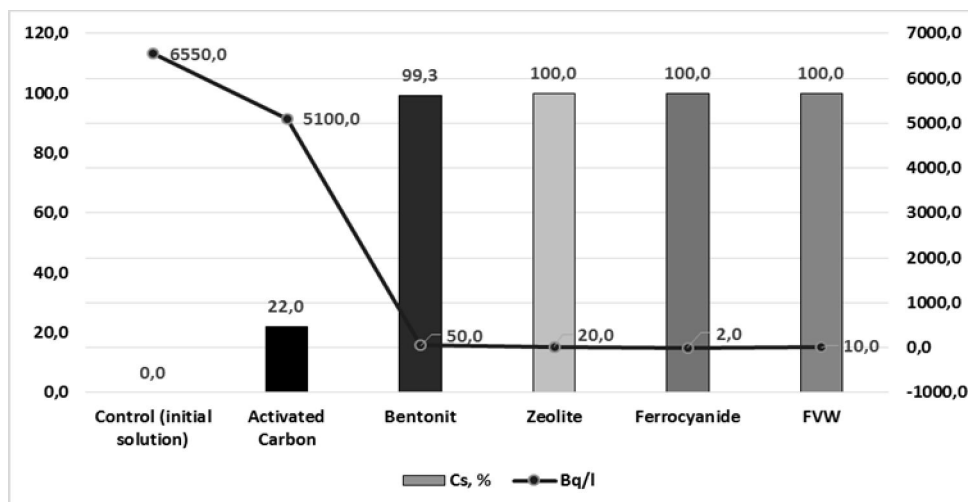


Fig. 2. Coefficients of sorption ^{137}Cs with different sorbents (proportion of sorbent to solution – 1:25)

The proportion of solution-to-sorbent had practically no effect for most sorbents on the efficiency of sorption of ^{137}Cs from water solutions; therefore, in further studies we used solution with the ratio of 1:50.

For the purification of technological liquids and agricultural waste with the multicomponent compound in addition to selectivity, the absorption materials must provide high speed of extraction and high retaining capacity in relation to a particular radionuclide.

It is known that some natural and synthetic sorbents have high selectivity towards strontium and cesium. However, as easily they absorb these elements from solutions, so easily they release them. Therefore, it is important to assess the strength and speed of extraction and absorption of ^{137}Cs or created by him compounds [12].

The results of study of the speed and strength of adsorption of ^{137}Cs by the studied sorbents, based on the environment of solutions are presented in Table 1.

Table 1. ^{137}Cs concentration in solution after sorption and consistent extraction Bq/l (n=5)

Sorbents	Sorbition		Extraction from sorbents	
	Water, 0,5 h.	Water, 24 h.	1M KCL, 24 h.	1M HCL, 24 h.
Control (initial solution)	708,0 ± 70,00			
Zeolite	2,8 ± 1,40	1,0 ± 1,40	514,0 ± 520	32,0 ± 4,00
Ferrocyanide	0,2 ± 0,03	0,6 ± 0,07	2,4 ± 1,30	0,8 ± 0,03
FVW	5,5 ± 1,20	5,9 ± 1,30	31,6 ± 3,30	5,5 ± 1,40

As mentioned above, these properties of sorbents were evaluated by the content of ^{137}Cs in the filtrate obtained by consistent sorption of ^{137}Cs from the aqueous solution and extraction of the absorbed ^{137}Cs from the sorbent under the scheme: sorption from aqueous solution – 30 min, sorption from aqueous solution - 24 hours, extraction with 1M solution of potassium chloride – 24 hours, extraction with 1M solution of hydrochloric acid – 24 hours.

Processing of sorbent KCL enriched by ^{137}Cs shows a tendency of absorbed radionuclides and their compounds to an ion exchange. Hydrochloric acid is extracted by more strongly bounded ^{137}Cs . It should be mentioned, that in the acidic environment the structure of natural sorbents can be ruined, which leads to the withdrawal of radionuclides into the solution.

The experimental results showed that all the studied sorbents are characterized by the relatively rapid absorption of ^{137}Cs . After 0,5 hour of sorption in aqueous solutions was practically no radionuclide left. ^{137}CS is held the strongest by the sorbents ferrocyanide-2 and FWV. When processing ferrocyanide KCL and HCL, less than 0,5% of absorbed radionuclide transfers into the solution, when processing sorbent FVV – less than 5 % of absorbed radionuclides. Similar situation is observed with zeolite. Less than 5 % of absorbed ^{137}Cs transfers into the solution. Only if potassium ions are present in zeolite environment, it is observed a significant desorption of radionuclides – 72,6 % of its concentration in the original solution.

Similar picture can be seen during the sorption ^{137}Cs from 1% KCL solution (Table 2).

Table 2. Concentration of ^{137}Cs in the solutions after contact with sorbents and consistent extraction, Bq/l (n=5)

Sorbents	1% KCL	1M HCL
Control (initial solution)	700,0 ± 70,00	
Bentonite	480,0 ± 50,00	100,0 ± 11,00
Zeolite	250,0 ± 30,00	110,0 ± 10,00
Ferrocyanide	1,2 ± 1,00	0,9 ± 0,80
FWV	12,0 ± 2,00	7,0 ± 3,00

Results presented in Table 2 confirm the allegations of the negative impact of singly charged cations of salt background on the sorption of cesium by the natural sorbents. Sorption capacity of natural bentonite and zeolite sorbents towards ^{137}Cs in the presence of potassium ions is about 30 and 60 % respectively.

The presence of potassium ions in solution does not affect the effectiveness of ferrocine preparations; on the contrary, their sorption capacity was quite high (about 100 %). Their further extraction by 1M solution of NCl does not affect the efficiency of sorption of synthetic sorbents.

With further extraction of natural sorbents with 1M NCl solution, K^+ ions replace Cs^+ and efficiency of natural sorbents increases.

The obtained results correspond with the findings of several authors [6, 9, 13] and justify the low radiological efficiency of the use of natural sorbents for reduction of radionuclides in milk due to the presence of significant concentrations of potassium ions in chyme of cow digestive tract.

Conclusions and prospects of further research

Natural minerals – bentonite, zeolite and synthetic ferrocyanide containing sorbents – ferrocyanide-2 and FWV have very high sorption properties and ability bind radioactive cesium to almost 100 %.

The proportion of the system solution-to-sorbent in 1:25 and 1:50 has almost no effect on the ability of the tested sorbent products.

All the studied sorbents in vitro are characterized by relatively rapid absorption of ^{137}Cs . After 0,5 hour of sorption in aqueous solutions was practically no radionuclide left.

The efficiency of sorption of natural sorbents essentially depends more on the presence of K^+ ions in the water solution and is less dependent on pH of the environment. The presence of potassium ions in the environment does not affect the effectiveness of sorption of ferrocine preparations.

The high sorption capacity of ferrocyanide waste of viticulture (FVV) is established, which opens prospects for their practical application in agricultural production on the radioactively contaminated territories.

It is advisable to concentrate the further research on the sorption properties of natural sorbents in dynamic conditions using the radioactively contaminated multicomponent technological solutions.

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