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DECONTAMINATION OF RADIOACTIVE LIQUID SYSTEMS BY MODIFIED CLAY MINERALS

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Abstract. The process mechanism for sorption of strontium and cesium from liquid radioactive waste using modified bentonites from Yaziv sulfur deposit was investigated. The technique for predicting the intensity of the sorption process based on the comparison of experimental and calculated values of mass transfer coefficients was proposed. It was detected that the process of sorption extraction of strontium and cesium from liquid medium using modified clay minerals may be best described by a three-parameter model of the adsorption isotherms.

Key words: modified bentonite, adsorbent, liquid radioactive waste (LRW), diffusion.

1. Introduction

Steady growth in human economic activity leads to a considerable increase in polluted water volumes. Although a large number of sewage treatment plants have been put into operation at the enterprises of this country in recent decades, the technologies used today mostly are outdated and ineffective. As a result the insufficiently treated waste water, its falling into the hydrosphere creates a significant environmental hazard. Therefore, researchers have faced an urgent need to develop modern highly effective technologies for integrated wastewater treatment from hazardous environmental contaminants with minimum cost and with maximum purification degree. In full, it concerns wastewater contaminated with dyes, radionuclides and organic solvents, which belong to the most dangerous ones for the hydrosphere.

Radioactive materials and ionizing radiation sources are widely used in nuclear power engineering, in medicine, in many industries and in scientific research. The emergence of liquid radioactive waste (LRW) is possible in any of these areas. The LRW can be formed as a result of rules violation while handling radioactive materials, as a result of depressurization of containers with ionizing radiation sources during decontamination or decommissioning of nuclear installations.

An effective method for the LRW decontamination is the flotation and coagulation process. In water decontamination it is difficult to separate flotation and coagulation, because the scheme implements the consequent application of the both methods – coagulation followed by flotation of sludge with foaming [1].

In case of applying iron hydroxide paired with flotation reagent at pH=7 the degree of extraction of Sr-90 was 35–40 %, whereas at pH = 11 it increased to 98 % [2], this can be explained by chemical deposition of Sr-90 in the form of hydroxide. Removal of Sr-90 with the use of iron and manganese hydroxides does not exceed 50 % in acidic medium, while 70 % – in neutral and 98 % – in alkaline medium. In contrast, the removal of Cs-134 with manganese hydroxide does not occur throughout the pH range. Overall, the removal of Sr-90 and Cs-137 by coagulation cannot achieve the high levels of exclusion.

Swedish scientists [3] found that coagulation and flotation methods may remove virtually all radionuclides, except Sr and Cs, in the case of aluminum and iron salts application with subsequent filtering through sand filters. The disadvantage of this method is formation of large amounts of radioactive sludge.

At present considerable attention of leading domestic and foreign scientists is paid to adsorption methods, including obtaining the effective adsorbents based on natural minerals. Besides, the mineral resources of Ukraine are represented by many minerals (natural zeolites, glauconites, bentonites, palygorskites) which have a developed porous structure and possess the adsorption and ion exchange properties, they can be successfully used in environment protection technologies for the sorption treatment of wastewater.

2. Research goals

The aim of the work is to explore kinetic characteristics of the process of adsorption of Sr-90 and

Cs-134 by modified clay minerals from liquid radioactive waste, and to develop a technique for predicting the intensity of sorption processes on the basis of comparative analysis of experimental and calculated data as well as their compliance with the adsorption isotherm.

3. Results and theoretical interpretation

The form of the adsorption isotherm curve allows characterizing the intensity of sorption processes. For most of the adsorption systems, this curve has a peculiar form of the Langmuir isotherm. A specific feature of this type of adsorption isotherms is that the value of a particular component concentration in solution is such that in the solid phase the equilibrium concentration reaches the value which can be considered almost constant.

In order to increase the sorption capacity of bentonite minerals we performed their modification using ferrocyanides of iron (III) and copper (II), hydroxide of titanium (IV), a solution of titanium (IV), chloride of stannum (IV) in an organic solvent and hydroxide of antimony (V).

The infrared spectra of the samples of modified bentonite clay in the area of 2800-3800 cm^{-1} are shown in Figure 1, a. The presence of identical bands in the spectra of all samples at 3697 cm^{-1} and 3620 cm^{-1} (curves 1 – 6) indicates the equivalence of surface and internal hydroxyl groups associated with structural silicon and aluminum both in natural clay and in its modifications.

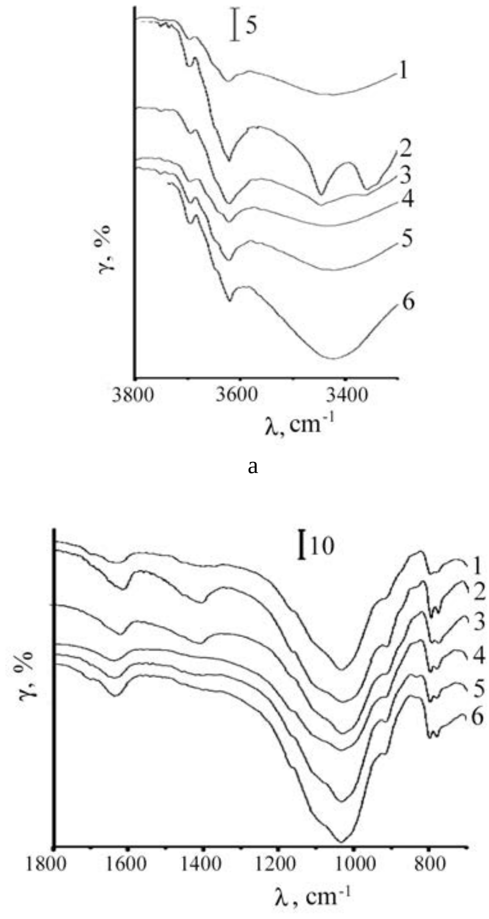
For the samples of the clay matrix with ferrocyanide of iron, with hydroxides of titanium, stannum and antimony (curves 1, 4, 5, 6) the band in 3430 cm^{-1} is identical, while for the samples with ferrocyanide of copper and ferrocyanide of copper and potassium (curves 2, 3) a split of peak is observed which forms two absorption bands in 3440 cm^{-1} and 3356 cm^{-1}. Such character of peaks is observed in the infrared spectra of Cu-form montmorillonite belonging to the vibrations of hydroxyl groups associated with dimerized copper molecules. It should be noted that the partial replacement of copper ions for potassium ions (ferrocyanide of copper-potassium on clay matrix sample) decreases the number of hydroxyl groups involved in the formation of hydrogen bonds with water molecules, which is manifested by the reduction of peak intensity after 3356 cm^{-1} (Fig. 1, *a* – curve 3).

Figure 1, *b* shows the absorption spectra of samples in the area 700–1800 cm^{-1}. All spectra (curves 1–6) are present a band in 1630 cm^{-1}, that is characteristic of the deformation vibrations of water adsorbed on the surface of the mineral. It should be noted that its position for the sample modified with ferrocyanide of iron (curve 1) remains unchanged as compared to the natural mineral, whereas for the samples with hydroxides of antimony, titanium, and stannum (curves 4, 5, 6) the band bias is observed in the region of higher frequencies (1636 cm^{-1}). This indicates the formation of additional hydrogen bonds between the adsorbed water and coordinating metal centres present in the modified clay mineral. The band shift into the area of lower frequencies (1616 cm^{-1}) for the samples with ferrocyanides of copper and copper-potassium (curves 4, 5) is associated with structural changes in clay mineral that occur due to formation of these ferrocyanides.

In the process of modification the destruction of calcium and magnesium carbonates takes place. This is confirmed by the disappearance of the characteristic peaks of carbonate component after 874 cm^{-1} and 710 cm^{-1} (Fig. 1, *b*, curves 1–6).

The undertaken investigations of chemical modification prove that the destruction of carbonate component occurs on the surface of montmorillonite and the phases of ferrocyanides of iron (III), copper (II), copper-potassium, as well as hydroxides of titanium (IV), stannum (IV) and antimony (V) are formed. The modified samples have a well-developed surface that allows to predict the external-diffusion mechanism of sorption.

Taking into account the character and properties of pollutants we can choose the optimal method of modifying natural sorbents for intensification of sorption processes during the treatment of contaminated liquid media.



a

b

Fig. 1. Infrared spectra of the samples of modified bentonite clay (where λ- wavelength, γ – bandwidth)

The isotherm of strontium sorption by the natural clay (taken from Yaziv sulfur deposit and modified by ferrocyanide of iron at the temperature of 20 °C) is presented in Figure 2. The process kinetics for Langmuir isotherms in the area of component high concentrations in the solution has internal-diffusive character. In the area of low concentrations corresponding with the linear part of adsorption isotherms the limiting stage of the process is external-diffusive kinetics ($C = 5 \cdot 10^{-4}$ mol/dm^3). In the transient interval of concentrations the kinetics is mixed.

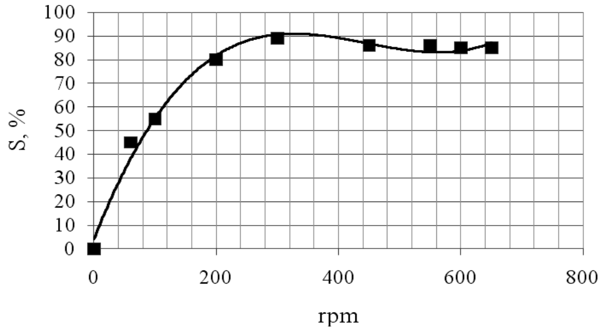


Fig. 2. The isotherm of strontium sorption by bentonite clay (taken from Yaziv sulfur deposit and modified by ferrocyanide of iron). The ratio “liquid: solid phase” equals 100 cm^3/mg, pH=7

We investigated the process of absorption of strontium at the concentration of $C = 1 \cdot 10^{-4} - 5 \cdot 10^{-4}$ mol / dm^3, corresponding to pollution of real water bodies and lies in the intermediate area.

Natural clay of Yaziv sulfur deposit has a capacity of 0,14 mEq Sr per 1 g of clay. Relatively high sorption capacity in respect to Sr is explained by the content of carbonates [4]. The increase of sorption capacity is determined by the ion-exchange character of sorption when Ca^{2+} ions being present in the structure of the clay matrix are replaced by Sr^{2+} ions.

Modifying natural clay by ferrocyanides of transition metals significantly increases the sorption capacity regarding Sr to 0,19; 0,20 and 0,25 mEq Sr per 1 g of ferrocyanide of iron, ferrocyanide of copper, and ferrocyanide of copper-potassium, respectively. However, for such modified sorbents as hydroxide of titanium, hydroxide of stannum, and hydroxide of antimony the sorption capacity increases to the values of 0,35; 0,25 and 0, 23 mEq Sr per 1 g of sorbent respectively [6].

Therefore, we investigated the mechanism of external diffusion on the example of sorbent modified by titanium oxide, which has the highest ability to absorb strontium from a solution. For this purpose, we have studied the process of Sr^{2+} sorption by modified sorbent (hydroxide of titanium on clay matrix) in dynamic conditions. To examine the sorption of Sr using the method of weighed portions, we prepared the working solutions with 0,01 mol / dm^3 concentration, which were diluted with distilled water to the required concentration. Thus, the model solutions that simulate active water were created.

To carry out the sorption experiments in static conditions, a weighted portion of clay sorbent was placed in a container, then the appropriate volume of Sr solution was added, observing optimum ratio of "solid phase: liquid" = 1:100 [5, 6]. Constant process temperature of 20 °C in a water bath was maintained. After the experiments a suspension was separated by centrifugation (400 rpm, time of separation – 15 min) then the aliquot of solution was collected and the content of $Sr^{2+}$was analyzed.

The study was conducted on a device with paddle stirrer, the frequency of revolutions of which was varied in the range of 50–650 rpm. Samples were taken at the certain time intervals and were analyzed regarding the content of Sr^{2+} in solution.

The data shown in Figure 3 indicate that the increase in the number of revolutions over 300 rpm does not enlarge the rate of sorption process that allows to assert that adsorption process goes into internal diffusion area in which the external parameters do not affect the kinetics of sorption.

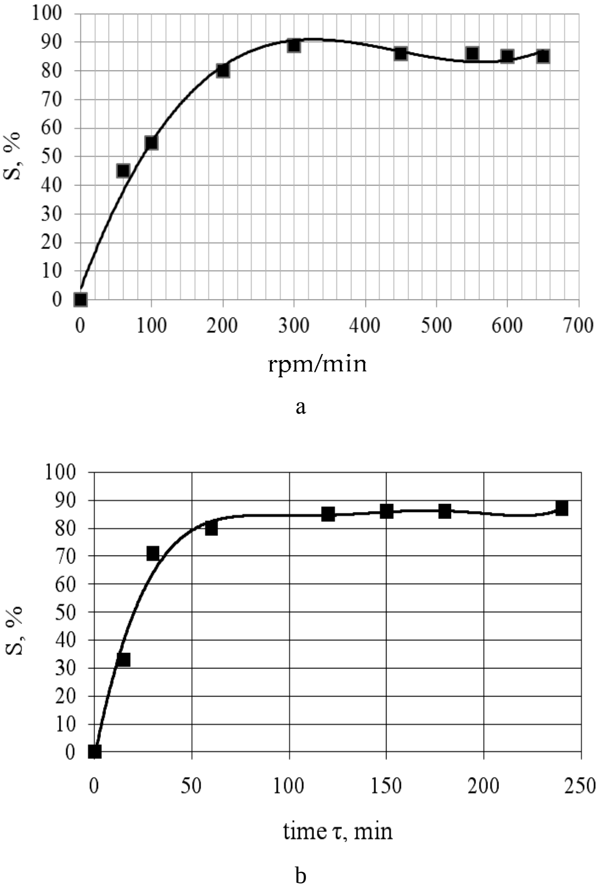


Fig. 3. The dependence of degree of strontium sorption by bentonite clays on:
a – the number of revolutions per minute n (rpm);
b – time τ (min).
The bentonite clays were taken from Yaziv sulfur deposit and were modified by titanium oxide.
The ratio “liquid: solid phase” equals 100 cm^3/mg, initial concentration of strontium is $5 \cdot 10^{-4}$ mol/dm^3, pH=7

The duration of stirring at the maximum level of sorption is within 40-50 minutes. Efficiency of sorption of cesium by ferrocyanide of iron on clay matrix correlates straightly to the amount of the added sorbent. The increase in the ratio of "liquid: solid phase" from 500 to 100 dm^3 / kg sorption enlarges the sorption by 40 %, while a further increase up to 50 dm^3 / kg leads only to 9 % growth. The dependence of the sorption of cesium on the amount of another added sorbent – ferrocyanide of copper-potassium on clay matrix – is similar as for the removal of strontium.

Thus, the most effective ratio of "liquid: solid phase" which provides a maximum area of contact of sorbent with the liquid and maximum degree of purification, should be considered as 100 dm^3 / kg.

To confirm the sorption kinetics we performed mathematical calculations of internally-diffusive process of sorption. The results of calculations are presented in Table 1.

Assessing the process kinetics on the whole it should be noted that the effective time to achieve the highest possible degree of strontium sorption for all sorbents investigated does not exceed 1 hour.

The primary source of information on the progress of the adsorption process is the adsorption isotherm. In order to determine optimal parameters and type of adsorption isotherm we conducted the interpretation of experimental data within the known theoretical models.

The established types of isotherms which best describe the sorption process of removal by modified clay minerals (on the example of Cs) are given in the Table 2.

The sorption process of Cs removal on natural clay is described best of all using three-parametric models and Langmuir isotherm. In other cases, the process of sorption removal of Cs is best described by isotherms of Redlich – Peterson (for clay materials modified with ferrocyanide of iron, with ferrocyanide of copper, with hydroxide of titanium), Langmuir ((for clay materials modified with ferrocyanide of copper-potassium), Tosh (for clay materials modified with hydroxide of stannum), and Langmuir – Freundlich (for clay materials modified with hydroxide of stibium). In all cases, the three-parametric isotherms give high values of the determination coefficient indicating the chemical heterogeneity of sorbents surface and the presence of sorption groups of different chemical nature, which differ in chemical activity. During the sorption process the filling of the most active centers of sorption is observed primarily. The surface is continuously filled until all the centers with the lowest energy are be occupied. Data compliance with three-parametric isotherms shows that the sorption proceeds with formation of a monomolecular layer. This is especially true for the removal of cesium in clay materials modified with ferrocyanide of iron and modified with ferrocyanide of copper-potassium for which a constant value is approaching 1, thus the sorption proceeds according to Langmuir mechanism.

Introduction into the structure of the clay mineral hydroxides of transition metals (clay minerals modified by hydroxides of titanium, stannum, stibium) slightly increases sorption capacity. Minor differences in sorption capacity as compared to the natural clay mineral, are probably caused by acid activation of clay mineral surface, that occurs in the process of modification under the influence of free hydrochloric acid.

The process of sorption removal of Sr can be described by Redlich-Peterson isotherms (for natural clay, for clay materials modified with ferrocyanides of iron and copper-potassium), Langmuir isotherms (for clay materials modified with ferrocyanides of copper), Freundlich isotherms (clay minerals modified by hydroxides of titanium, stannum, stibium) (see Figure 4). The three-parameter isotherms in the case of sorbents of the ferrocyanides and natural clay group give high values of determination coefficient whereas in the case of hydroxides on clay matrix $K_{LF} \rightarrow 0$, that is why the Langmuir-Freundlich isotherm cannot describe the process correctly, and the data are interpreted according Freundlich model.

Table 1

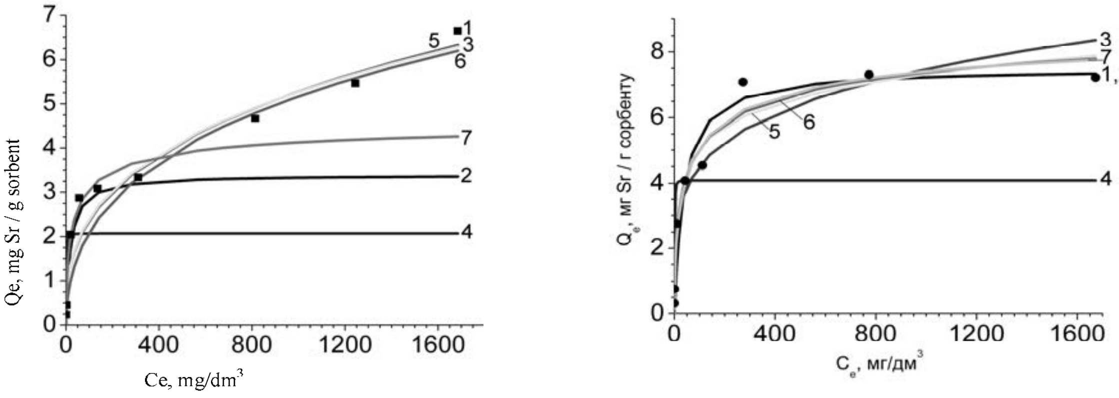
Calculation results of internally-diffusive process of sorption

Modified sorbent based on the clay matrix	μ_n	tgα	Coefficient of internal diffusion D_{in}, m^2/s	Mass transfer coefficient at internal diffusion, *m/s*
Ferrocyanide of copper-potassium on clay matrix	4,471	$2{,}23\cdot10^{-4}$	$7{,}748\cdot10^{-12}$	$1{,}068\cdot10^{-2}$
Ferrocyanide of copper on clay matrix	10,791	$4{,}92\cdot10^{-4}$	$6{,}445\cdot10^{-12}$	$0{,}921\cdot10^{-2}$
Hydroxide of titanium on clay matrix	7,693	$2{,}72\cdot10^{-4}$	$3{,}892\cdot10^{-12}$	$0{,}556\cdot10^{-2}$
Hydroxide of antimony (stibium) on clay matrix	10,795	$5{,}15\cdot10^{-4}$	$3{,}748\cdot10^{-12}$	$0{,}535\cdot10^{-2}$
Hydroxide of tin (stannum) on clay matrix	11,991	$5{,}83\cdot10^{-4}$	$3{,}485\cdot10^{-12}$	$0{,}497\cdot10^{-2}$
Ferrocyanide of iron on clay matrix	17,091	$4{,}10\cdot10^{-4}$	$1{,}784\cdot10^{-12}$	$0{,}254\cdot10^{-2}$
Natural clay	6,993	$7{,}69\cdot10^{-4}$	$0{,}877\cdot10^{-12}$	$0{,}125\cdot10^{-2}$

Table 2

Parameters of adsorption isotherms and criteria for statistical evaluation of the process of sorption removal of cesium on the modified clay minerals

	Natural clay	Ferrocyanide of iron on clay matrix	Ferrocyanide of copper on clay matrix	Ferrocyanide of copper-potassium on clay matrix	Hydroxide of titanium on clay matrix	Hydroxide of tin (stannum) on clay matrix	Hydroxide of antimony (stibium) on clay matrix
1	2	3	4	5	6	7	8
Langmuir isotherm							
q_m	6,59	14,53	24,14	**43,82**	10,26	6,52	6,41
K_L	0,03	0,76	0,20	**0,11**	0,01	0,02	0,02
R^2	0,9937	0,8838	0,7724	**0,9404**	0,9548	0,9658	0,9700
SNE	3,91	3,57	3,99	**3,32**	3,74	4,07	4,01
Freundlich isotherm							
K_f	1,22	1,06	1,30	2,14	0,25	0,24	0,22
n	0,15	2,26	1,98	1,99	1,48	1,52	1,66
R^2	0,8474	0,8086	0,8804	0,8668	0,9740	0,9869	0,9556
SNE	3,81	3,66	3,51	3,99	3,53	3,84	3,82
Dubinin-Radushkevych isotherm							
q_m	0,21	14,27	24,88	41,31	3,54	3,08	2,18
E	0,22	1,29	1,86	0,26	9,70	0,22	0,21
R^2	0,3738	0,8685	0,7545	0,9087	0,7448	0,7800	0,6632
SNE	3,90	3,62	3,76	3,80	3,93	3,86	3,84
Redlich-Peterson isotherm							
K_{RP}	1,75	**3,04**	**5,91**	5,39	**1,01**	0,67	0,65
a_{RP}	0,00	**0,17**	**1,04**	0,17	**13,95**	1,85	1,85
$в$	0,14	**0,97**	**0,73**	0,95	**0,001**	0,45	0,51
R^2	0,9996	**0,9115**	**0,8907**	0,9430	**0,9885**	0,9347	0,9232
SNE	3,80	**3,27**	**3,31**	3,44	**3,36**	3,65	3,67
Tosh isotherm							
q_m	**2,73**	27,65	25,67	46,41	3,88	3,10	**3,73**
b_T	**0,01**	1,50	0,60	0,06	0,10	0,40	**0,54**
n_T	**1,50**	0,49	0,22	1,01	0,07	0,21	**0,21**
R^2	**0,9956**	0,9524	0,8955	0,9387	0,9904	0,9010	**0,8762**
SNE	**3,67**	3,63	3,33	3,81	3,96	3,61	**3,54**
Langmuir-Freundlich isotherm							
q_m	4,76	18,22	24,56	44,32	–	**6,43**	8,19
K_{LF}	0,06	0,35	0,74	0,07	–	**0,01**	0,01
n_{LF}	1,48	0,62	1,08	1,04	–	**0,75**	0,90
R^2	0,9993	0,9547	0,8917	0,9383	–	**0,8408**	0,9789
SNE	3,92	3,36	4,10	3,53	–	**3,53**	3,78



a b

Fig. 4. Strontium sorption isotherms:
a – ferrocyanide of iron on clay matrix; b – ferrocyanide of copper on clay matrix
(1 – experimental data, 2 – Langmuir isotherm; 3 – Freundlich isotherm; 4 – Dubinin-Radushkevych isotherm;
5 – Redlich-Peterson isotherm; 6 – Tosh isotherm; 7 – Langmuir-Freundlich isotherm).
The ratio “liquid: solid phase” equals 100 cm^3/mg, pH=7

Describing the affinity of strontium to sorption materials based on modified minerals, it should be mentioned that it is rational to build a kinship series only for the materials where sorption is satisfactorily described by Freundlich equation (all the materials except sorbents modified by ferrocyanides of copper and copper-potassium). By affinity the sorbents are placed as follows: natural clay > sorbent modified by hydroxide of antimony > sorbent modified by hydroxide of titanium > sorbent modified by hydroxide of stannum. Characteristically, the materials based on hydroxides have better absorption characteristics than natural minerals (see Figure 4).

The obtained data and its interpretation for different types of adsorption isotherms allows to describe and to predict the process of LRW sorption cleaning on modified clay minerals as well as to choose the materials with the best sorption properties regarding Cs and Sr (clay sorbents modified by ferrocyanides of iron, copper and copper-potassium for Cs sorption, and bentonite clay sorbents modified by ferrocyanide of copper-potassium, by hydroxides of titanium and antimony for Sr sorption).

4. Conclusion

It was revealed that the process of sorption removal of Cs and Sr with the modified clay minerals is best described by the three-parameter models of Redlich – Peterson and Langmuir – Freundlich. This testifies the presence of active centers of different chemical nature in the sorbents. It was shown that surface modification of bentonite clay with ferrocyanides of iron and copper significantly increases mineral sorption capacity regarding cesium, as well as modification with hydroxides of titanium, tin and antimony – regarding strontium.

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