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# Comparative characterization of biosorbents by thermodynamic and kinetic functions in processes of radionuclides adsorption

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The current concept of handling low-level liquid radioactive waste (LRW) consists of development of technological schemes providing efficient and cheap LRW treatment. In addition, such technologies ought to lead to compacting of radioactive waste in combination with long-term, reliable and safe isolation from the biosphere. Unfortunately, some types of waste from the nuclear industry still stay in uncontrolled storage condition and represent a serious environmental hazard. All of this often leads to the fact that technically occurred radionuclides come into the environment, changing the natural radioactivity of soils, natural waters and sediments 1. Processing of any type of LRW and environmental rehabilitation based on the extraction and concentration of long-lived and highly toxic radionuclides from solutions which contain complex chemical and radionuclide compounds. In order to solve the problem of safe handling of waste from radiochemical plants, it is necessary to involve fractional isolation of radioactive components before storage. It is also important to have reliable analytical methods for determining the ultra low level of radionuclides in environment. To implement these processes, various types of sorbents may be widely used. A special feature of inorganic sorbents (IS) is high selectivity with respect to cesium and strontium ions, high chemical, thermal and radiation resistance. However, their usage is limited by the mechanical parameters of these materials. The efficiency of organic sorbents (OS) depends to a large extent on the composition and concentration of salts in solutions, surfactants and types of ligands. But small compaction of used types of IS and OS leads to a growth of in the volume of solid secondary waste and the cost of their disposal [2].

In recent years, development of a new class of sorbents consisting or involving substances of biogenic origin (biosorbents) has been widely applied. The most widespread are polymeric materials based on chitin (CT) and chitosan (CTS), which have a wide raw material base e.g. marine crustaceans shells, fungi, bee and other insects, etc. This supply base is constantly expanding due to the involvement of new alternative sources[3]. The unique properties of CT and CTS are high sorption ability, low ash content, biodegradability to substances that are safe for living matter, the possibility of obtaining sorbents with optimal geometry and a large surface of particles. The presence of amino group in CTS chain allows making functionalization of the biopolymer and producing sorbents with high selectivity and improved capacitance characteristics. Thus, the study of interaction of radionuclides with polymeric materials based on CT and CTS is an actual scientific and practical task [4–7].

Now it is well known the large number of sources containing data on the thermodynamic properties and kinetic characteristics of CT and CTS in the processes of interaction with radionuclides[8]. However, the comparative analysis of sorbents with combination of a complex of physicochemical characteristics in literature has been rarely given.

Mass transfer laws in adsorption processes have been shown how the interaction between radionuclides and sorbent surfaces take place. The mass transfer process is a complex phenomenon, which is the result of internal and external diffusion [9].

Various polymeric sorbents were used in this work to analyze their properties by thermodynamic and kinetic laws. A natural complex of chitin and melanin Mycoton (NCTM-Mycoton) [10] and its modifications by inorganic substances have been used for adsorption of An, Eu and Sr (MDM-15 contains 15% w. $MnO_2$ or MSB-15 contains 15% w. $BaSO_4$)[11], Cs (Mycoton-Cs contains 30% w. $K_2Cu[Fe(CN)_6]$)[10] respectively. Spherical granulated chitosan (SGCTS)[12], chitosan cryogel (CCTS) and chitosan cryogel crosslinked by pyridoxal

phosphate (CCTS-PP)[13,14] also have been investigated in radionuclides adsorption.

To determine the rate of the process, experimental data have been used to calculate the diffusion coefficients (D) and Bio number (Bi). Both of them reflects the similarity of the distributed substance transfer through the boundary of the solid and liquid phases, and includes the ratio of the mass transfer coefficient and the coefficient of internal diffusion characterizing the rates of external and internal diffusion.

To evaluate the interaction of sorbate with a sorbent, adsorption isotherm were obtained and maximal capacity ($A_\infty$) were calculated. The interaction of the sorbate with the sorbent was estimated from the value of the Gibbs energy.

Table. Comparative characterization by thermodynamic and kinetic functions of different types of biosorbents and radionuclides

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- by Freundlich equation

The table shows that the calculated values of Bi, for all types of sorbent, are less than 10. This fact allows to conclude that the mechanism of sorption by CT and CTS-containing polymers is rather complicated and it takes place both in the external and internal diffusion zones[9]. However, the main part of the process is the external diffusion. For inorganic modifications, it has been noted the displacement of the mechanism toward the external diffusion region, as a result of preferential sorption on a fine crystalline inorganic modifier.

As it has been shown in the table, for all the sorbents studied, the values of $\Delta G_0$ have been reached the value less than –40 kJ/mol. Due to this fact the process can be attributed as weak interactions. The increase in $\Delta G_0$ in case of cesium adsorption on Mycoton-Cs has been shown the decisive contribution of inorganic material in interaction with radionuclides.
Investigations of the sorption processes with using CT and CTS-containing sorbents have been described by Langmuir adsorption model. Only one exception has been obtained. The freshly formed HCTS adsorbs uranium and in this case the sorption processes can be described by Freundlich equation. It was established that the highest values of the capacity (A) for uranium were obtained on CCTS-PP.

Comparison of $A_\infty$ for Cs obtained with Mycoton-Cs and SGCTS-Cs (contains 60% w. $K_2Cu_3[Fe(CN)_6]_2$ [15] showed that the use of chitosan with a higher modifier content allows to achieve higher values of the capacities. Capacity of modifier is an important factor in the future of its application in decontamination technology of $^{137}Cs$-containing solutions and analytical practice. Under dynamic conditions in fixed bed column experiments Mycoton-Cs loses the modifier on the surface, in contrast to the SGCTS-Cs where the ferrocyanide is firmly fixed in the volume of the adsorbent. Nevertheless, the equilibrium in Cs sorption has been established faster with usage Mycoton-Cs than applying SGCTS-Cs.

Comparative analysis of thermodynamic data and kinetic characteristics allowed to reveal the factors influencing on interaction efficiency of radionuclides with biosorbents.
1. The addition of highly disperse inorganic matters leads to increase in selectivity, process speed, sorbent capacity when biosorbents interact with strontium and cesium.
2. Changing the structure of chitosan by reducing the degree of crystallinity gives an improvement of sorption characteristics.
3. Forming cryogels from chitosan leads to increament in the capacity and speed of the sorption process and expands the number of the adsorbed radionuclides.
4. Modification of spherical granulated chitosan by inorganic materials allows the creation of strong and efficient sorbents for cesium adsorption from sea water and high salted technology solution

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**Primary authors:** Dr VELESHKO, Alexander (National Research Centre "Kurchatov Institute"); Dr RUMYANTSEVA, Ekaterina (NRC "Kurchatov institute"); Prof. KIL'DEEVA, Natalia (Moscow state university of design and technology); Mr PAL, Nikolay (NRC "Kurchatov institute"); Dr OZHOGINA, Vera (NRC "Kurchatov institute")

**Presenter:** Dr VELESHKO, Alexander (National Research Centre "Kurchatov Institute")

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