

Sorption of Cs⁺ by nano-sized microporous titanium silicates with pharmacosiderite structure

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The uptake of Cs⁺ on as-synthesized pure sodium and potassium nano-sized end-members of a titanosilicate framework with pharmacosiderite structure is investigated. Batch sorption studies are carried out in order to find the optimal conditions for Cs⁺ uptake and to study the kinetics and equilibrium of the process. Kinetic sorption data are analyzed using pseudo-first and pseudo-second order rate models. The adsorption isotherms are described by means of the Langmuir and Freundlich isotherm models. It is found that a simple pseudo-second-order rate model and Langmuir isotherm model provide a good accordance with the experimental data of the Cs⁺ uptake. The maximum adsorption capacity of Cs⁺ is 3.877 and 1.870 meq/g for the Na- and the K-form, respectively. The pseudo-second order rate constants k_2 calculated at different initial Cs⁺ concentrations are presented. The experimental results are indicative that the sorption mechanism is an equivalent ion exchange of Cs⁺ for K⁺ and Na⁺, respectively.

Keywords: titanosilicate framework, ion exchange, Cs⁺ uptake

INTRODUCTION

Microporous titanosilicates and their analogues have attracted attention for more than two decades, because of their structural and functional similarities to the framework of aluminosilicate-based zeolites. Numerous data have been published on radioactive wastewaters purification using titanosilicate materials [1] and the references therein. In this regard, Clearfield [2] paid attention to two compounds with tunnel structures and great affinity for Cs⁺ and Sr²⁺. The first one is a tetragonal titanosilicate of the general formula, Na₂Ti₂SiO₇·2H₂O [3]. It is a synthetic analogue of the mineral sitinakite. The other one was firstly synthesized by Chapman and Roe in 1990 [4] under the name GTS. It has the general formula M₃H(TiO)₄(SiO₄)₃·4H₂O (M is alkali metal cation) and structure identical to that of the mineral pharmacosiderite.

We were able to hydrothermally synthesize nano-sized pure sodium and potassium end-members of the GTS material, as well as intermediate members of the (Na, K) series [5,6]. In the course of the preliminary characterization excess of Si vs. deficiency of Ti in the structures of all run-products was established, being more pronounced for the potassium-rich forms [7]. Based on the ²⁹Si MAS-NMR spectroscopy data a structural model was proposed illustrating the

deficiency of Ti in the framework of all phases being located towards the crystallites periphery [7]. Similarly to the pore size and degree of crystallinity, the controlled surface Ti deficiency appears to be a key-factor for the acid-base properties of such materials and may have a considerable impact on the mechanisms for uptake of radioactive pollutants. The previous investigations on the sorption capability of the GTS materials have mainly been focused on the structural characterization and the crystal-chemical aspects of the process.

In this study nano-sized synthetic pure sodium and potassium end-members of the GTS material were selected and their sorption capacity towards Cs⁺ was investigated. The effects of experimental conditions, kinetics and equilibrium were examined in details and to our knowledge, for the first time different models describing the sorption of Cs⁺ by this material were tested and determined.

EXPERIMENTAL

Adsorption studies

Materials and methods

Cesium stock solution of 0.1N concentration was prepared from CsCl (Merck). The working solutions were prepared by dilution. The cesium uptake was studied using batch experiments with 0.05 g of titanosilicate and 10 ml of cesium solutions. The initial pH was adjusted by addition of dilute HCl or NaOH. The suspension was shaken on a horizontal shaker and was separated by

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centrifugation at 4000 rpm. The cesium concentration in the recovered solutions was measured by atomic absorption spectrometry (Perkin-Elmer 30-30 apparatus). The cesium concentration in the solid phase was calculated using the mass-balance equation:

$$q_e = [(C_0 - C_e) V] / m, \quad (1)$$

where q_e (mg/g) is the concentration of cesium in the solid phase, C_0 and C_e (mg/L) are the initial and the equilibrium concentrations in the sample solution, respectively, V (L) is the volume, and m (g) is the adsorbent mass.

The sorption effectiveness (E %) was calculated using Eq. 2:

$$E\% = 100m_s / (VC_0), \quad (2)$$

where C_0 (mg/L) is the initial concentration of Cs⁺, m_s (mg) is the mass of sorbed metal, V (L) is the volume.

Effect of the experimental conditions on the Cs⁺ uptake

The effect of pH on cesium adsorption was investigated as described above using solutions with initial concentration of 500 mg Cs /L in the pH range from 1.18 to 5.8, shaken for 360 min. Each adsorption experiment was carried out twice. The effect of contact time was determined by the batch sorption experiments described above at $pH_{initial} = 5.6$ and Cs⁺ concentrations of 100, 500, and 2500 mg/L for the Na-form, and 500 and 2500 mg/L for the K-form. The contact time for both titanosilicates varied between 15 and 480 min.

The relation between initial concentration and sorbed amount was studied by equilibrium isotherm experiments (optimal $pH = 5.6$, contact time 360 min) by varying the Cs⁺ concentrations in the range from 0 to 2500 mg/L.

The distribution coefficient K_d (ml/g) was determined from the equilibrium experiments with 1×10^{-3} M Cs⁺ (132.91 mg/L) by the equation:

$$K_d = 1000 q_e / C_e \quad (3)$$

where C_e (mg/L) and q_e (mg/g) are the concentrations of Cs⁺ in the solution and in the solid, respectively.

The interference of sodium – the major macro component present in radioactive wastes, on Cs⁺ uptake was studied in two types of model solutions. The first type contained NaNO₃ with concentrations of 0, 0.25, 0.5, 1.0, and 4.5 M at $pH_{initial} = 6$. The second type solutions contained 3.5 or 5 M Na⁺ (NaNO₃+NaOH) with $pH = 13.5$.

Modeling of sorption kinetics and equilibrium data

The kinetics of Cs⁺ uptake was studied applying the pseudo-first- and the pseudo-second-order

kinetic models expressed in terms of Eqs. (4) and (5), respectively [8-10]:

$$\log (q_e - q_t) = \log q_e - (k_1 / 2.303) t, \quad (4)$$

$$t / q_t = 1 / (k_2 q_e^2) + (1 / q_e) t, \quad (5)$$

where k_1 (min⁻¹) and k_2 (g/(meq min)) are the apparent pseudo-first and pseudo-second-order rate constants, q_t and q_e are the contents of sorbed cesium (meq/g), at time t and at equilibrium.

The apparent rate constants are complex quantities determined by the processes underlying uptake mechanisms. In general, it is assumed that k_1 is a linear function of the initial ion concentration, whereas k_2 is a complex function of this parameter. However, it should be noted that the actual mechanism of a sorption process also depends on other factors such as sorbent inhomogeneity, transport phenomena (surface and intraparticle diffusion), chemical phenomena (hydrolysis, precipitation), sorbed ion species. Nevertheless, both simple kinetic models are widely used as a base for estimation and comparison of the ion uptake efficiency of sorbents and for prediction of process performance [11].

Adsorption isotherms describe the equilibrium between the ion concentration in solution and the sorbed amount for different initial concentrations. The Langmuir isotherm model (Eq. 6) is based on the assumption that the adsorption for all sites is constant and does not depend on the degree of surface coverage.

$$C_e / q_e = 1 / q_m b + C_e / q_m, \quad (6)$$

where C_e (meq/L) and q_e (meq/g) are the equilibrium cesium concentrations in the liquid and in the solid phase, respectively. The Langmuir parameter q_m (meq/g), represents the maximum sorption capacity and b (L/meq) is the site energy factor describing the equilibrium constant.

The Freundlich isotherm is expressed by equation (8):

$$\log q_e = \log K_F + 1/n \log C_e, \quad (7)$$

where K_F (meq/g)/(meq/L)^{1/n} and n (dimensionless) are Freundlich parameters.

This model is an empirical equation based on the assumption that sorption is a function of the degree of surface coverage. The surface sites have different energy and are not equally available. This model supposes formation of multi-layers of sorbed ions.

The kinetic and equilibrium data were fitted by regression analysis to the kinetic and isotherm models.

RESULTS AND DISCUSSION

Effect of pH

The pH of a suspension is an important parameter that determines the sorbed ions forms and their behavior and affects the sorbent surface sites. On the other hand, the final pH is a result of the processes of ion uptake and gives information about the nature and mechanisms of reactions.

Fig. 1 shows the change in Cs⁺ uptake at different initial pH values. It is indicative that unlike other sorbents, the Na- and K- end-members of the GTS titanosilicates are effective even in highly acidic solution (pH = 1.2), with the efficiency of Cs⁺ removal of 67 and 42%, respectively. The adsorption capacity of both materials significantly increases upon pH increase up to 2.0, then changes very slowly up to pH 2.5 and stays stable at higher pH values.

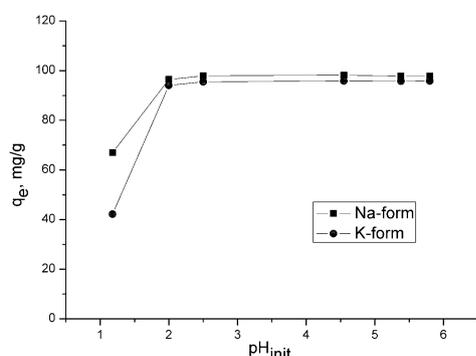


Fig. 1. Changes in the sorbed amount of Cs⁺ as a function of pH.

The final pH values of the solutions after 360 min of shaking are shown in Fig. 3.

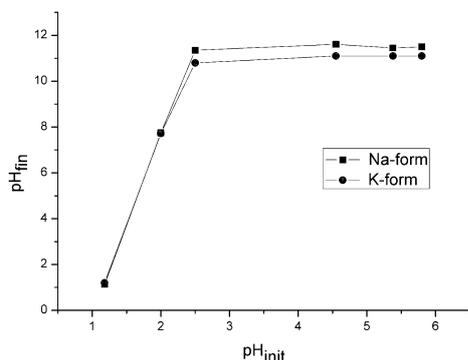


Fig. 2. Changes of pH after the experiments.

From Figs. 1 and 2 it is evident that at pH > 2.5 the q_e, as well as the pH final values remain relatively constant. This is indicative that at pH > 2.5 optimal conditions for Cs⁺ uptake are achieved. This is the reason to choose an initial pH = 5.6 for the subsequent kinetic and isotherm investigations.

The elevated final pH values (~11.5) are due to hydrolysis of the sorbents and exchange of Cs⁺ for Na⁺ and K⁺, as described earlier [12, 13].

Kinetic studies

The rate and degree of sorption of Cs⁺ from solutions by both titanosilicates are shown in Figs. 3 and 4.

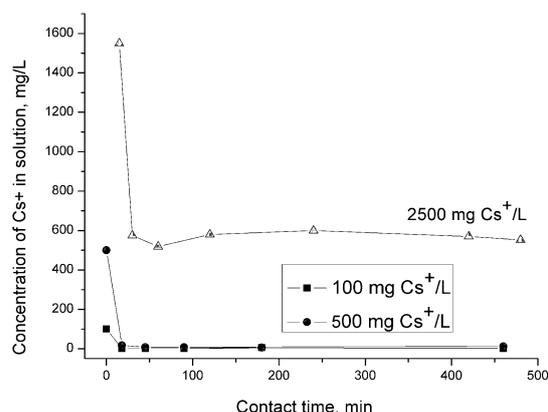


Fig. 3. Cesium uptake kinetics for Na-titanosilicate at three different initial cesium concentrations.

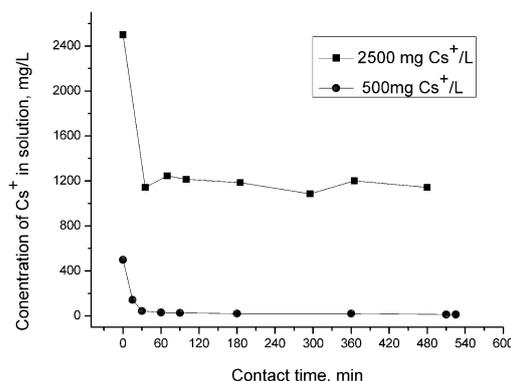


Fig. 4. Cesium uptake kinetics for K-titanosilicate at two different initial cesium concentrations.

Both figures show that the effect of contact time on the uptake of cesium has three different stages. Regarding Na-titanosilicate at 100 mg/L Cs⁺ the first stage is almost instantaneous and the effectiveness of removal *E* is about 99 % within the first 15 min. For the 500 mg/L concentration the effectiveness is >96 % within the first 15 min of treatment, then continues to increase slowly and reaches a value of 99 % after 45 min, after that remaining constant. For the higher initial concentration of 2500 mg/L the effectiveness is 38% after 15 min, 77 % after 30 min, reaching about 80% at the equilibrium measured after 360 min. The pH_{final} increases and falls within the range of 11.0 - 11.3 and 11.0 - 11.5 for the 100 and 500

Table 1. Kinetic data for the uptake of Cs⁺ by Na and K titanosilicates - pseudo-second order model

Sample	Equation	R ²	k ₂ (g meq ⁻¹ . min ⁻¹)	q _{e,calc} (meq/g)	q _{e,exp} (meq/g)
Na-titanosilicate - 100 mg/L	t/q _t = 1.339t + 0.3318	0.9999	5.410	0.747	0.747±0.005
- 500 mg/L	t/q _t = 1.3493t + 0.4275	0.9999	4.258	0.741	0.736 ± 0.004
- 2500 mg/L	t/q _t = 0.3467 + 0.0.0703	0.9998	1.710	2.884	2.89 ± 0.05
K-titanosilicate					
500 mg/L	t/q _t = 1.3648t + 5.6655	0.9999	0.3287	0.732	0.714 ± 0.013
2500 mg/L	t/q _t = 0.5153t + 1.1651	0.9974	0.2297	1.940	1.926 ± 0.070

mg Cs⁺/L, respectively, the lowest values being measured for the first contact time point.

The K-titanosilicate demonstrates a similar sorption behavior. During the first, very fast stage of 15 min the uptake efficiency is 71 % (for 500 mg/L Cs⁺). During the second stage the Cs⁺ uptake slowly increases with contact time up to >90% after 30 min, and as the equilibrium state approaches, the removal efficiency reaches 97 %. The final pH increases, reaching values in the range of 11.0 - 11.2. The uptake profile for a concentration of 2500 mg/L has a similar run. The effectiveness reaches >50 % after the first 30 min, and approaches about 54 % at equilibrium.

Figs. 3 and 4 show that whatever the character of the phenomena governing the interactions between the sorbent and the sorbed ions the uptake is so rapid that almost maximal effectiveness of removal is achieved within the first 15 to 30 minutes of contact time. No doubt, particle size and structural imperfections play a certain role in shortening the diffusion path to the active sites of the sorbent.

Contact time of 360 min was found to be sufficient to reach equilibrium for the batch experiments and thus it was chosen for the subsequent studies.

The data were fitted by regression analysis to the kinetic models. For the pseudo-first order model the values of the correlation coefficient R² were low (0.5002 < R² < 0.9243) indicating that this model is less appropriate.

Strong correlation with the experimental data was obtained for the pseudo-second-order rate model (Table 1) indicated by high R² values and good agreement between theoretical values of q_e and the experimentally obtained data (difference < 2.5 %).

Adsorption isotherms

The isotherms of the adsorbed amount of Cs⁺ as a function of equilibrium concentration (initial ion concentrations were varied in the range from 0 to 2500 mg/L) are plotted in Fig. 5. The profiles of the curves indicate that both titanosilicates have high affinity for Cs⁺ ions. In order to study the mechanism of the adsorption process the equilibrium isotherm data were fitted by least square regression analysis to the Langmuir and the Freundlich models (see Section 2.2.). The experimental data correlate well with the Langmuir isotherm model, whereas the Freundlich model is comparatively less applicable (Table 2.). This means that the sorption sites are homogenous and the adsorption is monolayer.

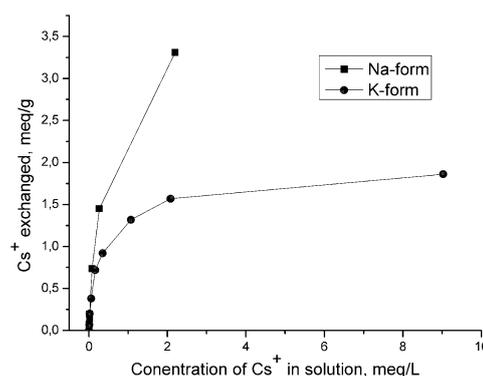


Fig. 5. Cs-exchange isotherms for both pharmacosiderite titanosilicates.

Under the selected experimental conditions, the values of maximum uptake capacity (q_m), calculated from the Langmuir model, are 3.877 and 1.870 meq/g for Na- and K-titanosilicate, respectively. These results are indicative for the higher selectivity of the Na-form for Cs⁺, as

Table 2. Freundlich and Langmuir isotherm parameters for sorption of Cs+ by the Na and K forms of pharmacosiderite titanossilicate

Sample/model	Equation	R ²	b (L/meq)	q _m (meq/g)	q _m (mg/g)
Langmuir					
Na-titanossilicate	$C_e/q_e = 0.2579C_e + 0.0951$	0.9971	2.712	3.877	515.35
K-titanossilicate	$C_e/q_e = 0.5246C_e + 0.1549$	0.9979	3.451	1.870	248.62
Sample/Model	Equation	R ²	K _F	1/n	n
Freundlich					
Na-titanossilicate	$\log q_e = 0.6695 \log C_e + 0.4366$	0.9629	2.732	0.6695	1.493
K-titanossilicate	$\log q_e = 0.4317 \log C_e + 0.0504$	0.9259	0.123	0.4317	2.316

compared to that of the K-form. The sorption capacity of the as-synthesized Na-form is somewhat greater than the reported value of 3.12 meq Cs⁺/g for the Na-exchanged titanossilicate [12]. No data for the sorption capacity of K-titanossilicate were reported in the same work

The distribution coefficients K_d (ml/g) of Na- and K- titanossilicate for Cs⁺ determined under the above described conditions and 0.001M Cs⁺ are 11 300 ± 1700 and 12 700 ± 980, respectively (errors are ± one standard deviation). These results differ from those reported previously for the same concentration distribution coefficients - 15 360 ml/g for the Na-form and 3500 ml/g for the K-titanossilicate, respectively [12].

Adsorption studies for Cs+ in model solutions

The effectiveness of Cs⁺ uptake in NaNO₃ solutions with different molarity is presented in Fig. 6. At low concentrations (up to 0.5M), the effectiveness of Cs⁺ uptake for the Na-titanossilicate is >90% whereas in 4.5 M NaNO₃ the effectiveness drops to about 40 %. These values are even lower for the effectiveness of Cs⁺ uptake by the K-titanossilicate, which is less than 80% in 0.25 M NaNO₃. It is also important to note that in 4.5 M NaNO₃ the effectiveness of both samples is almost the same.

At high alkalinity both the K_d values and the effectiveness of Cs⁺ uptake drop substantially, as compared to those obtained in solutions containing only NaNO₃ (Table 3). The detrimental effect of high alkalinity on cesium uptake by similar materials was previously reported by Möller *et al.* [14].

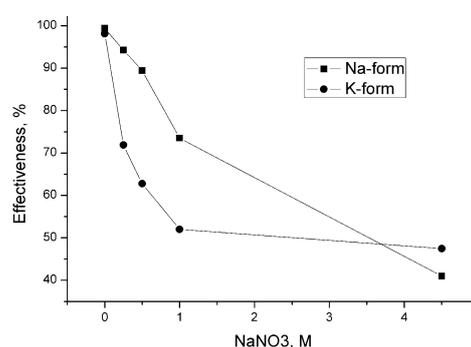


Fig. 6. Effectiveness of Cs⁺ removal as a function of NaNO₃ concentration.

Table 3. Cs+ distribution coefficient and effectiveness in NaNO₃ solutions with pH 13.5

Sample	K _d (ml/g)	E, %
Na- titanossilicate		
3.5 M Na ⁺	86	30.2
5M Na ⁺	49	19.6
K- titanossilicate		
3.5 M Na ⁺	58	23.1
5M Na ⁺	37	14.5

Mechanism of the Cs+ uptake

In order to elucidate the mechanism of Cs⁺ uptake, for each Cs⁺ concentration on the isotherm curves we measured the concentrations of Na⁺ and K⁺ (meq/L) released during the sorption, then we subtracted from these values the concentrations of Na and K released from each titanossilicate in distilled water. The obtained data were compared with the sorbed Cs⁺ (meq/L) by regression analysis. The experimental data correlate well with the linear regression equations with slopes 0.97 (R²=0.9764) for the K- and 1.15 (R²=0.9970) for the Na-form. The obtained results show that cesium uptake by both titanossilicates is due to equivalent cation exchange over the studied concentration range from 0 to 2500 mg Cs⁺/L. The deviation from the ideal value of 1 could be due to errors of measurement.

Another confirmation of this result came from processing of the Cs⁺ uptake data for the Na-form in the high Na⁺ concentration experiments the way Möller *et al.* did [14]. According to these authors the mechanism of uptake in a binary ion system can be estimated from the relation of K_d of the tracer ion (Cs⁺) and the solution concentration of Na⁺. Plotting $\log K_d$ for Cs⁺ as a function of $\log [Na^+]$ (meq/L) gives a straight line with slope $-z_{Cs}/z_{Na}$, (z_{Cs} and z_{Na} being the respective ion charges). When the sorption mechanism is an equivalent ion exchange of Cs⁺ for Na⁺ the theoretical value $-(z_{Cs}/z_{Na})$ is -1. In our case the regression analysis of the relation $\log K_d$ for Cs⁺ as a function of $\log [Na^+]$ for the Na-form gives a value of -1.11 ($R^2=0.9882$) which shows that the Cs⁺ uptake is an equivalent ion exchange for Na⁺ (Fig. 7). In contrast, Möller *et al.* [14] showed for their Na-exchanged titanosilicate samples TSi1 and TAM1 slope values of -1.69 and -1.32, respectively, which were indicative that the situation was no longer of ideal binary ¹³⁴Cs/Na⁺ exchange and other chemical phenomena affected the ideal situation.

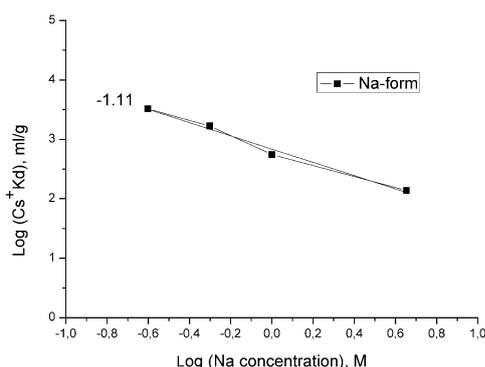


Fig. 7. Effect of the macro component Na⁺ on the distribution coefficients of Cs⁺ K_d , (ml/g) for Na-titanosilicate.

CONCLUSION

Pure sodium and potassium nano-sized end-members of the titanosilicate framework with pharmacosiderite structure – GTS, were hydrothermally synthesized at 100 and 200 °C, respectively. They were tested as potential sorbents in the nuclear wastes treatment. The removal of Cs⁺ ions was investigated under various conditions and it was found that the maximum uptake is reached between pH 2.5 and 5.8 with contact time of 360 min. The samples were effective in the Cs⁺ uptake in slightly acidic (even in acidic liquors at pH about 1) and neutral solutions. Kinetic experiments have shown that both titanosilicates display rapid

kinetics, as particle size and compositional imperfections were found to be important factors in shortening the diffusion path to the active sites of the sorbents. The data from batch adsorption kinetic experiments are well described by the pseudo-second order kinetic model. The Langmuir isotherm model adequately represents the adsorption process and the maximum uptake capacities of the sodium and potassium forms were estimated to be 3.87 and 1.87 meq Cs⁺/g, respectively. Additionally, the sorption of Cs⁺ ions from model solutions with high content of NaNO₃ was examined. It is concluded that the strong interference from the competing Na⁺ cations substantially lowers the Cs⁺ removal effectiveness within the studied pH range. The experimental results are indicative that the sorption mechanism is an equivalent ion exchange of Cs⁺ for K⁺ and Na⁺.

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СОРБЦИЯ НА Cs⁺ ОТ НАНОРАЗМЕРНИ МИКРОПОРЪОЗНИ ТИТАНОВИ СИЛИКАТИ СЪС СТРУКТУРА НА ФАРМАКОСИДЕРИТ

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(Резюме)

Изследвано е задържането на Cs⁺ на титаносиликати със структура на фармакосидерит със синтезирани чисти наноразмерни частици, съдържащи калий и натрий. Изследванията са проведени за намиране на оптималните условия за задържането на Cs⁺ и изучаването на кинетиката и равновесието на процеса. Кинетичните данни са анализирани с помощта на кинетика от псевдо-първи и псевдо-втори порядък. Равновесието се описва от адсорбционните изотерми на Langmuir и Freundlich. Установено е, че простият кинетичен модел на реакция от псевдо-втори порядък и изотермата на Langmuir дават добро съгласие с опитните данни. Максималният адсорбционният капацитет по Cs⁺ е съответно 3.877 и 1.870 meq/g за натриевата и калиевата форма. Представени са скоростните константи k₂, изчислени за различни начални концентрации на Cs⁺. Опитните резултати са показателни за това, че сорбционният механизъм е еквивалентен на йонообмен на Cs⁺ съответно с K⁺ и Na⁺.