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Modelling of Cs^+ uptake by natural clinoptilolite from water media

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Natural zeolite clinoptilolite from Beli Plast deposit (Bulgaria) was studied and characterized as ion-exchanger for cesium removal from waste water. Batch procedure was applied to investigate the influence of pH, time and Cs concentration on the sorption effectiveness. The studied system was best described by a pseudo-second-order rate model with a rate constant k_2 of 37.03 and 0.103 g meq^{-1} min^{-1} for cesium concentrations of 64.9 and 649 mg L^{-1}, respectively. The equilibrium data were fitted to the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models. The best correlation was found with the Langmuir model and the estimated maximum exchange capacity was 1.044 meq/g. The reaction energy, calculated from the D-R model is 13.4 kJ mol^{-1}.

Key words: clinoptilolite, Cs+ ion exchange, kinetics, equilibrium.

INTRODUCTION

Nuclear energetic and other industrial and medical activities lead to generation and deposition of radioactive and other wastes. The most abundant radionuclides in these wastes are the radioactive isotopes of Cs and Sr. Due to their long half lives these elements are hazardous nuclear contaminants. The radioactive forms of cesium Cs^{135} and Cs^{137} have fission yields of 6.54 and 6.18%, respectively [1]. The leaching of cesium isotopes in hydrological cycles, combined with their high solubility and mobility in water media and chemical similarity to potassium make them bioavailable and dangerous for all living systems

The management of radioactive wastes aims to remove the contaminating cations and to make their disposal more efficient and safety. It should be taken into account that the radioactive ions are presented in very low concentrations (ppm and lower) in strong acidic or alkaline solutions with high contents of sodium ions. Different separation techniques and materials are tested for radionuclide removal, which must be chosen to conform to the properties of the liquid phase and the specificity of the solid phase. One appropriate chemical method that achieved this aim is ion exchange and natural zeolites appear to be suitable materials due to their selectivity for Cs isotopes and radiation and mechanical stability. In addition, they are found in nature in high amounts and are relatively cheap.

The ion exchange characteristics of a lot of natural zeolites have been studied with respect to their potential utilization in nuclear wastewater treatment. The research interest is generally centered on clinoptilolite as a member of this group that exhibits good exchange characteristics to metal cations and is widely distributed in nature [2–12].

The published studies describe different aspects of clinoptilolite application as ion exchanger. Cesium removal from aqueous solution by natural clinoptilolite from different localities and countries has been reported by Cortes-Martinez et al. [4] and Rajec and Domianová [5]. Results from investigation of samples containing clinoptilolite and mordenite [6] or clinoptilolite, mordenite and habazite [7] have been reported. Studies of mixtures of zeolites and other alumosilicate materials as bentonites [8] or kaolinite [9] are also presented. Physicochemical characteristics of the uptake, distribution coefficients and maximal capacities are compared and discussed with respect to the mineralogical and chemical composition of ion exchangers. The effect of zeolite modification in different cationic forms on its physicochemical properties for Cs uptake has been discussed as well [10, 11]. The selectivity of natural clinoptilolite towards the main radioactive elements Cs, Sr, and Co in the wastes has been studied by Smičiklas et al. [12].

In the above cited papers the studies aimed to describe different characteristics of the Cs^+ uptake by clinoptilolite applying a variety of techniques. The objective was to find effective and reliable method for removal of cesium from radioactive wastes.

In the present study we continue the characterization of Bulgarian clinoptilolite from Beli Plast deposit as ion exchanger for heavy metals and ions of radinuclides [13, 14, 15]. The aim is to study the Cs^+ behavior as a function of interaction time, pH, temperature and initial concentrations under batch conditions and to apply

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the obtained data to different kinetics and thermodynamic models in order to receive equations, describing mathematically the run of the processes. The parameters of models give possibility to make conclusions about the uptake mechanism and the rate controlling interactions.

EXPERIMENTAL

The used clinoptilolite rich tuff is from the Beli Plast deposit (East Rhodopes, Bulgaria). After grinding and sieving a portion with a grain size <75 µm was separated for the experiments. The mineralogical composition of the sample was determined by powder XRD analysis and revealed that the zeolitized tuff consists mainly of about 85 wt.% clinoptilolite and minor content of opal-CT ~15 wt.%. The chemical analysis of the adsorbent is described in [15].

The clinoptilolite sample was used in the ion exchange experiments without any pretreatment. All used chemicals were of analytical grade. The cesium stock solution was prepared from CsCl (Merck). The working solutions were prepared by appropriate dilution. Cesium uptake was studied by agitated batch experiments. In general, the procedure for kinetic, equilibrium and pH studies was as follows: to an amount of 0.1 g of material in a screw capped polypropylene bottles there were added 20 ml of cesium solution with pH, adjusted by addition of diluted HCl or NaOH. The bottles were placed on a horizontal shaker, shaken during necessary contact time and the suspensions were separated by centrifugation at 4000 rpm. The recovered supernatant solutions were appropriately diluted if necessary and cesium concentration was determined by atomic absorption spectrometry (Perkin-Elmer 30-30 spectrophotometer). The cesium content in the solid phase was calculated using the equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where, q_e (mg g^{-1}) is the concentration of cesium in the solid phase, C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentrations of the cesium solutions, respectively, V (L) is the volume, and m (g) is the natural clinoptilolite mass. The experiments were carried out in duplicate.

RESULTS AND DISCUSSION

Effect of pH on the Cs uptake

The effect of the initial pH of the solution on the cesium uptake onto clinoptilolite was investigated by the batch procedure as described above using Cs solution with concentration of 664.5 mg L^{-1}, contact time 450 min and pH range from 0.7 to 10.8. As an alkaline element cesium is in the form of monovalent cation in the entire pH interval. The relationships between the initial pH and the final pH and the amount of the retained Cs are presented in Figure 1. It can be seen from the graph that the changes in pH are small for the initial pH <4.0 and pH$_{fin}$ increases in acidic solutions and decreases for pH$_{in}$ in the alkaline range. This fact demonstrates that clinoptilolite has amphoteric properties – it accepts protons at low pH and is deprotonated at high pH. The uptake of Cs is effective even at low pH$_{in}$ = 2 (effectiveness E = 64.48%) and then increases and remains nearly constant (E ~ 69%) at the range of pH$_{in}$ 3 up to 10.8. The corresponding capacities q_e of Cs$^+$ uptake for these conditions of the pH experiment at equilibrium are q about 0.7 meq g^{-1}.

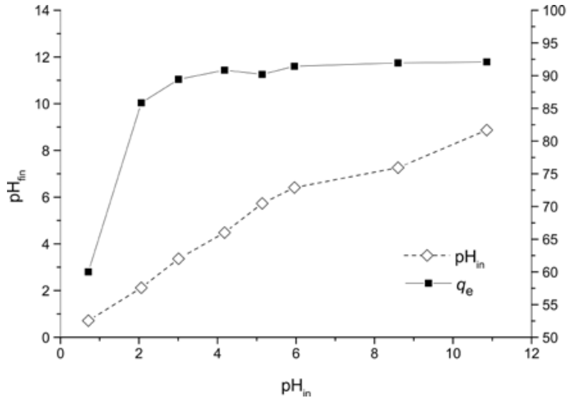

Fig. 1. Effect of pH$_{in}$ on cesium uptake by natural clinoptilolite (0.1 g + 20 ml 664.5 mg L^{-1} Cs, contact time 450 min)

These changes in pH$_{fin}$ and the extent of Cs removal with pH might be explained as follows: at low pH$_{in}$ the H$^+$ ions are in high concentration and compete with the Cs$^+$ ions in the interaction with clinoptilolite making ion-exchange with the extra-framework cations This results in low cesium uptake and in increasing of pH. At higher pH more cesium ions can be exchanged and q increases.

Kinetic studies

The kinetic of the Cs$^+$ uptake by clinoptilolite was studied by bath procedure as described above, using a set of solutions for two concentrations of 649 and 64.9 mg L^{-1} Cs$^+$ at pH$_{init}$ of 5.4 and contact times of 15, 18. 60, 120, 360, 600, 850 and 1490 min. The rate and extent of removal of Cs$^+$ are shown on Fig. 2 a.

As seen from the run of the plot of the lower concentration 64.9 mg L^{-1} and the calculated value of q_e, the loaded amount of cesium increases very quickly, reaches equilibrium in the first 25 min and then remains constant. The removal efficiency (E%) of clinoptilolite for Cs^+ changes from 91.3 to 99.5%, i.e. almost all of the Cs^+ ions were removed within 25 min of reaction. The initial pH of the solutions rose slowly from 5.4 to near neutral value of 6.7 within 120 min and remained at this value to the end of the interaction. For the higher studied concentration the results indicate that q_e increase quickly in the first 25 min then the changes are small until equilibrium is reached after 360–600 min. By this time the removal efficiency increases from 52.1 to 80.8% and pH_{fin} increases to 6.8. These changes of pH are result of exchange of extra framework cations from the clinoptilolite structure for Cs^+ cations from solution.

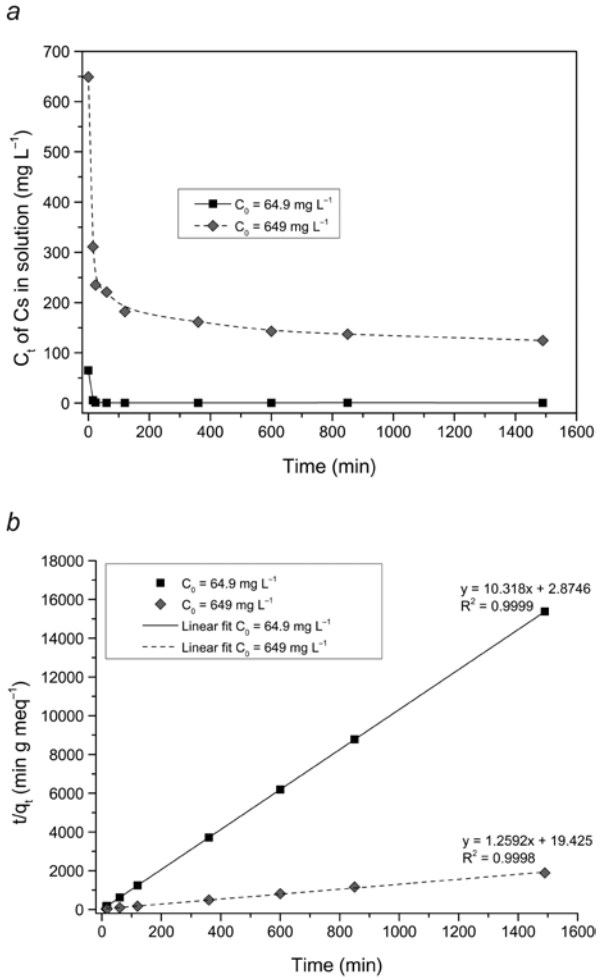

Fig. 2. a) Cesium ion-exchange kinetic for two different concentrations as a function of interaction time (0.1 g material, 20 ml Cs^+ 649 and 64.9 mg L^{-1}, pH_{init} 5.4); b) Pseudo-second-order kinetic model fitted to experimental data for the Cs-uptake by clinoptilolite

To investigate the mechanism and to determine the process that governs the rate of the reaction, three different models describing the kinetics have been applied. They were pseudo-first-order, pseudo-second-order, and intraparticle diffusion models.

The pseudo-first-order rate model was applied in its linear integrated form [16]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad (2),$$

where q_e and q_t in meq g^{-1} are the concentrations of Cs^+ in the studied natural clinoptilolite sample at equilibrium and at any time t (min), k_1 in min^{-1} is the pseudo-first-order rate constant.

When the relationship between ln ($q_e - q_t$) and t is linear, k_1 is estimated from the gradient of the plot.

The pseudo-second-order kinetics is represented by the linear equation [17]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (3)$$

where k_2 (in g meq^{-1} min^{-1}) is the apparent pseudo-second-order rate constant. The values of k_2 and q_e may be calculated from the gradient and the intercept of the linear plot, respectively.

The data from the kinetic measurements were interpreted by the method of regression analysis. The relationship between the experimental results and the theoretically fitted lines for the pseudo-second-order model is shown in Fig. 2b. The obtained equations for the two models with the corresponding squares of regression coefficients R^2 and the apparent pseudo-rate constants k_1 and k_2 are listed in Table 1.

The high values of correlation coefficients R^2 (0.9999) for the fitting of pseudo-second-order kinetic model and experimental data are indicative for the validity of this model for both studied concentrations. In addition, the calculated equilibrium values of uptake capacities q_e are very close to the experimentally observed data. The R^2 values obtained by fitting the Cs^+ uptake data to the pseudo-first-order model are also statistically significant (about 0.9) but lower and indicate that this model is less adequate. Moreover, the q_e values obtained from the first–order kinetic model and the experimental q_e values differ from 39.83% to 73.87%. A similar result for kinetics modeling was described previously in [4, 9, 12].

Table 1. Parameters of model kinetics equations for the removal of Cs^+ by natural clinoptilolite.

Cs^+ concentration, mg L^{-1}	First-order-rate model			Second-order-rate model			$q_{e,\ exp}$, (meq g^{-1})
	R^2	k_1 (min^{-1})	$q_{e\ calc}$ (meq g^{-1})	R^2	k_2 (g meq^{-1} min^{-1})	$q_{e\ calc}$ (meq g^{-1})	
64.9	0.9054	0.0014	0.0583	0.9999	37.03	0.097	0.097±0.0001
649	0.8986	0.0039	0.202	0.9999	0.103	0.774	0.773±0.014

As it is known, the simple kinetic models and the calculated equations are mathematical expressions and description of the kinetic process and give only a possibility to predict the results of interaction between the sample and the cations and to compare different systems. The actual chemical reactions and processes that represent the mechanism and determine the rate of uptake include interaction phenomena that are fast and transport phenomena as film diffusion and diffusion of the solute cations into the interior of the pores.

The estimation of the film and the intraparticle diffusion by applying the model equations and a discussion of their role in the uptake is presented in [18]. Our attempt to apply these equations for treating the experimental results gives plots that involve two phases and did not have a zero intercept, i.e. do not correspond to the requirements of the models and do not give exact answer for the rate controlling process. Both mechanisms contribute to the rate of uptake, but no one determines the overall rate.

Isotherms studies

The equilibrium isotherms give a possibility to describe and to design the uptake systems. The equilibrium data for cesium uptake by natural clinoptilolite was collected from agitated batch experiment, varying Cs^+ concentration in the interval 64.9–2596 mg L^{-1}, at pH_{init} ~5.40 and time of interaction of 24 h.

Several isotherm models are known and applied for characterization of uptake equilibrium as relation between the equilibrium concentration of exchanged cation in the liquid and solid phases. Three most often used ones are selected in this study – those of Langmuir [19] and Freundlich [20] and Dubinin–Radushkevich (D-R) [21].

The linear forms of Langmuir and Freundlich isotherm models can be represented by equations (4) and (5), respectively:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (4)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where C_e (meq L^{-1}) and q_e (meq g^{-1}) are respectively the equilibrium cesium concentrations in the aqueous phase and in the solid phase, q_m (meq g^{-1}) represents the maximum uptake capacity, b (L meq^{-1}) is the site energy factor, connecting to the equilibrium constant (affinity term). K_F (meq g^{-1})/(meq $L^{-1})^{1/n}$ and n (dimensionless) are Freundlich parameters.

The nature of the sorption process was investigated by the application of the D-R isotherm model equation (6):

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (6)$$

where, q_e, q_m and C_e (in eq g^{-1}) are as described above, β is a constant related to the sorption energy, R is the gas constant (kJ mol^{-1} K^{-1}), T is the absolute temperature (K), and ε is a Polanyi potential:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (7)$$

The constant β is related to the energy of interaction E by:

$$E = (-2\beta)^{-1/2} \quad (8)$$

The isotherm of Cs uptake by natural clinoptilolite is plotted as a function of concentration of cesium onto clinoptilolite versus the corresponding equilibrium concentration in the solution (Fig. 3a). The initial pH of the solutions increased from the values of 5.4 to between 6.6 and 6.7 units for all concentrations of experiment. The experimental data were fitted by the method of least squares regression analysis to the three models. The corresponding linear fits are presented on Fig. 3b, c, d and the parameters of the three models are presented in Table 2.

Table 2. Langmuir, Freundlich, and D-R isotherm parameters for Cs^+ uptake by natural clinoptilolite

Model	Linear form of equation	R^2	b (L meq^{-1})	$q_{m\ calc}$ (meq g^{-1})	$q_{m\ calc}$ (mg g^{-1})	$q_{m\ exp}$ (meq g^{-1})
Langmuir	$C_e/q_e = 0.957C_e + 0.129$	0.9996	7,384	1.044	138,75	1,031 ±0.006
Model	Linear form of equation	R^2	K_F ($meq^{1-1/n}$ $L^{3/n}$ g^{-1})	$1/n$	n	
Freundlich	$\log q_e = 0.279 \log C_e + 0.172$	0.9410	0,672	0.172	3,57	
Model	Linear form of equation	R^2	$q_{m\ calc}$ (meq g^{-1})	β (eq^2 kJ^{-2})	E (kJ mol^{-1})	
Dubinin – Radush-kevich	$\ln q_e = -6.405 + 0.0028\ \varepsilon^2$	0.9850	1.650	0.1726	13.4	

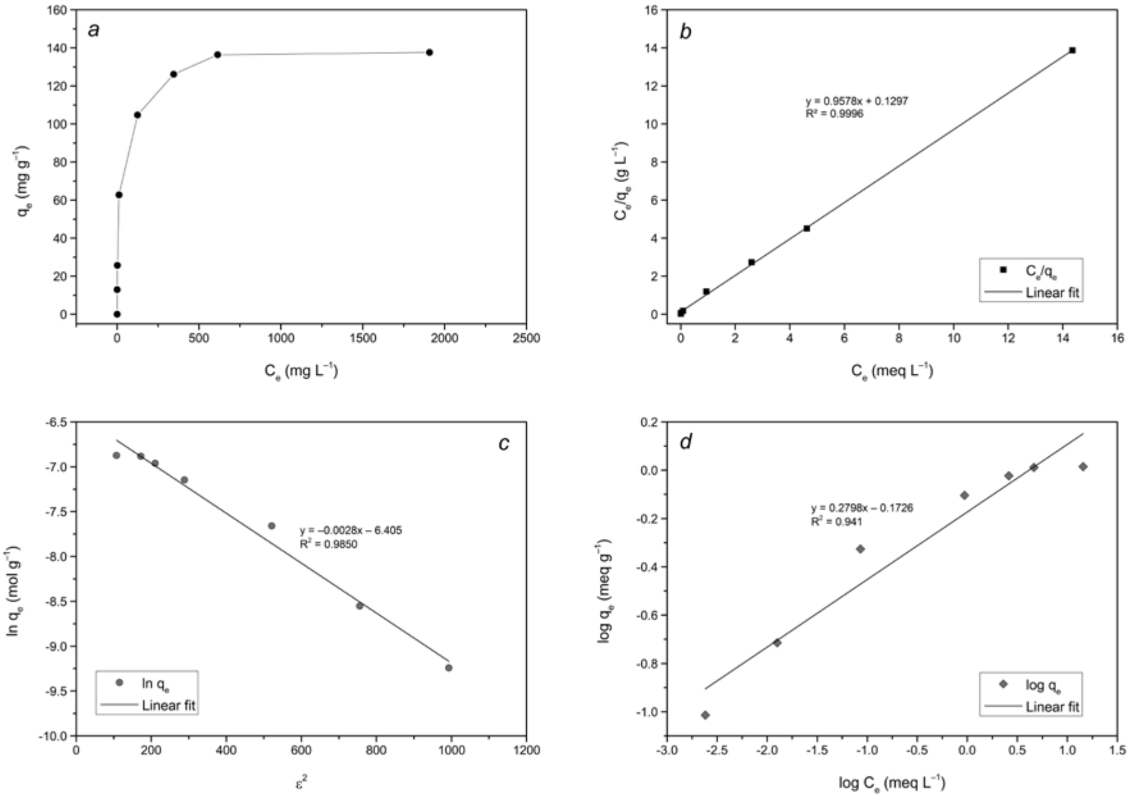

Fig. 3. Isotherm of Cs$^+$ uptake by natural clinoptilolite (*a*); Isotherm models fitted to experimental data – Langmuir (*b*); Freundlich (*c*); D-R (*d*)

According to the square regression coefficients R^2 the best correlation is obtained with the Langmuir isotherm model. The Freundlich and D-R models were found to correlate a little less although there is a good correlation for the lower initial concentrations in the initial part of the plots. The calculated equilibrium uptake of Cs$^+$ by the Langmuir isotherm model was 1.044 meq g^{-1} (138.75 mg g^{-1}) and is quite close to the experimentally found value of 1.031 meq g^{-1} − the difference being 1.27%. The results, obtained for equilibrium modeling of Cs$^+$ uptake by clinoptilolite differ in different studies. Cortés-Martinéz et al [4] observed that the Langmuir-Freundlich model describes the isotherms, Shahwan et al [9] found that isotherm data for Cs$^+$ uptake by clinoptilolite can be fitted by both Freundlich and D-R models, while in [12] the Langmuir model is in good agreement with the experimental data as are our observations. This result indicates the monolayer uptake and assumes structurally homogeneous material with the energetically identical exchange sites.

The D-R isotherm model gives information about the nature of interaction between clinoptilolite and the cesium cations. The parameter β was applied to calculate the mean energy of interaction, E (eq. 8), related to the mechanism of the uptake reaction [22]. The obtained value of E = 13.4 kJ mol^{-1} is in the range 8–16 kJ mol^{-1} and indicates an ion exchange mechanism.

A lot of papers were found in the literature concerning the study of Cs$^+$ uptake by clinoptilolite and determination of maximum exchange capacity. In order to make a reasonable comparison, we present only the results obtained using non modified clinoptilolite, the same technique of interaction and similar conditions with those in our investigation. Smičiklas et al. [12] reported for natural clinoptilolite from Serbia a maximal capacity of 45.53 mg g^{-1}. Cortes-Martinez et al [4] have found for two natural clinoptilolite tuffs from Mexico values of q_m 170.35 and 236.31 mg g^{-1}, respectively. Close to them are the results obtained from Boraj et al. [7] for natural clinoptilolite from Japan, Futatsui deposit – 169.8 mg g^{-1}, whereas Schahwan et al. [9] found 7.72 Cs$^+$ mg g^{-1} for clinoptilolite rich tuffs from Anatolia, Turkey.

An other parameter that characterize the selectivity, capacity and affinity of ion exchange and allows to compare different systems, is the distribution coefficient K_d (in mL g^{-1}), defined by the following equation:

$$K_d = \frac{1000 q_e}{C_e} \qquad (9)$$

K_d is determined using 132.91 mg L^{-1} Cs$^+$ (1×10^{-3} M) in the above described conditions and its value is 17 000±1600. This value is very close to distribution coefficient K_d = 15 360 for cesium uptake by sodium titanosilicates [23].

CONCLUSIONS

The natural clinoptilolite from Beli Plast deposit was studied as a potential material for removing Cs^+ from contaminated solutions.

The used clinoptilolite removes Cs^+ with relatively high effectiveness E = 41,3% even from strong acidic solutions with pH = 0.7. At low concentration about 69 mg L^{-1} the cesium retention is about 97–98%. For the studied Cs^+ concentrations >500 mg L^{-1} the effectiveness E reaches 69%.

The exchange kinetics of the process is relatively fast for low cation concentrations. The obtained pseudo-second-order model equations provide a necessary tool for prediction and comparison when such process is carried out.

The modeling of the equilibrium of the process and the respective Langmuir model equations could be used for calculation and estimation of the degree of Cs removal.

On the basis of the obtained results the used natural zeolite material could serve as well-performing and economically effective material for treatment of Cs^+ contaminated wastes.

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МОДЕЛИРАНЕ НА ЙОНЕН ОБМЕН НА Cs^+ С ПРИРОДЕН КЛИНОПТИЛОЛИТ ВЪВ ВОДНИ РАЗТВОРИ

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(Резюме)

В тази статия се представят резултатите от изучаването на природен зеолит клиноптилолит от находище Бели Пласт (България) като йонообменен материал за отстраняване на цезий от замърсени води. Изследването е проведено по метода на сорбция в съд с разбъркване за установяване на влиянието на pH, времето на контакт и концентрацията на Cs върху ефективността на извличането му. Кинетиката на тази система се описва с най-висока степен на корелация на експерименталните данни с уравнението на модела на реакция от втори порядък със скоростна константа k_2 37.03 и 0.103 g meq^{-1} min^{-1} за двете концентрации на Cs – респективно 64.9 и 649 mg L^{-1}.

Експерименталните данни от изследване на равновесието бяха съпоставени с моделите на изотерми на Лангмюир, Фройндлих и Дубинин–Радушкевич. Най-добра корелация беше намерена с модела на Лангмюир като изчисленият максимален обменен капацитет беше 1.044 meq/g. Енергията на реакцията беше изчислена по модела на Дубинин–Радушкевич е E = 13.4 kJ mol^{-1}.