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Synthesis of Nanostructured Sodium Aluminosilicate from Rice Straw and Its Sorption Properties

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Abstract—We have demonstrated the possibility of preparing nanostructured, X-ray amorphous sodium aluminosilicate with a specific surface area of 364 m^2/g using an alkaline rice straw hydrolysate. Its Cs^+ sorption properties have been studied under static conditions in solutions with various salt compositions (seawater and nitrate solutions).

Keywords: nanostructured sodium aluminosilicate, synthesis, rice straw, sorption properties

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INTRODUCTION

Plant processing waste is being considered more and more often as an attractive raw material for producing a number of functional materials, including zeolites with various compositions and structures and various composite sorbents. In this area of research, extensive studies have been concerned with autoclave synthesis of zeolites from rice husk ash [1–6]. At the same time, there is a large amount of rice production waste in the form of silicon-containing straw—several times greater than the amount of rice husk. However, only a limited number of studies have dealt with the synthesis of aluminosilicates from rice straw, modification of such materials, and their properties [7, 8].

In a number of studies [9–11], sorbents for extracting heavy metal ions were produced by thermal and chemical modification of rice straw. Ali et al. [7] investigated the autoclave synthesis of zeolite ZSM-5 (below 160°C) using a silicon-containing component prepared from rice straw and also lignin and tetrapropylammonium bromide ($C_{12}H_{28}NBr$) as templates. A zeolite sample with a specific surface area of 397 m^2/g prepared using lignin at a temperature of 160°C was further modified with various amounts of tetrapropylammonium bromide, and Cr(VI) extraction from aqueous potassium chromate solutions was studied at room temperature, solid : liquid = 500 and pH 5. The modified zeolite was shown to have better sorption characteristics in comparison with the unmodified material.

Later, Ali et al. [8] proposed that zeolite ZSM-5 produced using rice straw be modified with ferrocyanide complexes in the synthesis step to give Prussian blue (Berlin blue).

Previously, researchers at the Institute of Chemistry, Far East Branch, Russian Academy of Sciences, demonstrated the possibility of preparing calcium silicates [12] and sodium and calcium aluminosilicates [13] using alkaline solutions that resulted from alkaline hydrolysis of rice straw. They studied the Cs^+ sorption properties of sodium aluminosilicates with a specific surface area from 69 to 134 m^2/g prepared from rice straw. Their sorption capacity was shown to reach $A_{max} = 1.3$ mmol/g. Evaluation of Cs^+ sorption kinetics at sorption times from 1 to 60 min showed that the kinetic curve plateaued after just 5–10 min, following which the amount of sorption remained unchanged. Analysis of the temperature effect on Cs^+ extraction kinetics shows that raising the temperature from 20 to 60°C has no effect on the sorption capacity of sodium aluminosilicates and that the degree of Cs^+ extraction at 20°C is 82.6–88.6% [14]. In preparing practical recommendations as to the use of sorbents, it is important to have data on the effect of the ionic composition of the salt background on the extraction of the corresponding ions from aqueous solutions, in particular on the kinetic parameters of the process.

The objectives of this work were to synthesize nanostructured sodium aluminosilicate from an alkaline rice straw hydrolysate and study its Cs^+ sorption properties in solutions with various salt compositions (seawater and nitrates).

EXPERIMENTAL

Sodium aluminosilicate synthesis. As a silicon-containing raw material, we used Lugovoi (Far East selection) rice (*Oryza sativa*) straw collected in 2008–2017 in settlement Timiryazevskii, Primorskii krai. The straw was cut into parts 5–10 mm in length, washed with water, and dried in air. A weighed amount of the straw was treated with a 1 M NaOH solution at 90°C for 1 h (solid : liquid = 1 : 13). The undissolved solid residue had the form of a fibrous cellulose material suitable for use as a raw material in the pulp and paper industry. The silicate-ion-containing solution was separated by filtration. Next, a saturated aluminum sulfate solution was added to it with vigorous stirring at room temperature until pH 7 was reached. The precipitate was given time to completely settle (at least 5 h), collected on a filter, and washed with water until the water washings were sulfate free ($BaCl_2$ test). The precipitate thus obtained was dried at 105°C. The solids yield was 12.2% relative to the weight of the starting material.

Cs^+ sorption experiments. Sorption experiments were carried out under static conditions at a solid : liquid ratio of 1 : 400 and a temperature of 20°C in aqueous cesium chloride solutions in distilled water or seawater with different initial Cs^+ concentrations, from 0.16 to 3.2 mmol/L, with stirring on a magnetic stirrer for 3 h. The distribution coefficient K_d for Cs^+ sorption from distilled water and seawater was determined at solid : liquid ratios of 1 : 100, 1 : 400, 1 : 1000, and 1 : 2000.

In a control experiment, weighed amounts of the sorbent were placed in test tubes containing distilled water and seawater and stirred in parallel with the samples. Next, the solutions were separated from the sorbent by filtration (blue ribbon filter paper) and analyzed for Cs^+ and Na^+ ions.

Seawater for the preparation of solutions with different Cs^+ concentrations was taken in the Sea of Japan in the water area of Amur Bay (Vladivostok) and passed through white ribbon filter paper. The ion concentrations in the seawater were as follows (μg/mL): Na+, 9443.8, K^+, 364.0; Ca^{2+}, 357.3; and Mg^{2+}, 1246.2.

Sorption kinetics were assessed under static conditions at a solid : liquid ratio of 1 : 400 and a temperature of 20°C in aqueous cesium chloride solutions in distilled water or seawater and 0.01 M pure-grade $NaNO_3$, KNO_3, and NH_4NO_3 at sorption times from 1 to 60 min. The initial Cs^+ concentration and initial solution pH are listed in Table 1. The distribution coefficient K_d for Cs^+ sorption from solutions of the above nitrates with concentrations of 0.01, 0.1, and 0.5 M was determined at a solid : liquid ratio of 1 : 400 (sorption time of 3 h).

Table 1. Characteristics of the starting solutions for assessing Cs^+ extraction kinetics

Solution type	Solution pH	Initial Cs^+ concentration, mmol/L
Seawater	8.1	0.76
Distilled water	6.2	0.78
0.01 M $NaNO_3$	7.8	0.95
0.01 M KNO_3	7.7	0.8
0.01 M NH_4NO_3	7.7	0.78

Characterization techniques. Elemental compositions were determined by energy dispersive X-ray fluorescence spectroscopy using a Shimadzu EDX 800 HS spectrometer system (Japan). Analysis was carried out with no allowance for light elements, using software supplied with the spectrometer. The relative error of determination was within ±2%. X-ray diffraction patterns were collected on a Bruker D8 Advance diffractometer (Germany) with CuK_α radiation. The specific surface area of our samples was determined by low-temperature nitrogen adsorption measurements with a Sorbtometr-M instrument (Russia). Thermal analysis was carried out using an MOM Q-1000 thermoanalytical system (heating rate of 5 K/min). The particle size distribution was measured by a Fritsch Analysette 22 Micro Tec plus laser particle sizer (Germany).

The concentrations of cesium and sodium ions in solution were determined by atomic absorption spectroscopy (AAS) on a Solaar M6 double-beam spectrometer (Thermo Scientific, the United States) using the 852.1 and 586.6 nm analytical lines, respectively. The detection limit for cesium ions in aqueous solutions was 0.01 μg/mL and that for sodium ions was 0.0002 μg/mL. The relative error of determination of these ions by AAS was 15%.

In all of our experiments, the concentration of hydrogen ions was monitored by a Sartorius PB-11 pH meter with a PY-P11 electrode (Germany).

The sorption capacity (A_s, mmol/g) of the samples was evaluated as

$$A_s = \frac{(C_0 - C_{eq})}{m}V, \quad (1)$$

where C_0 (mmol/L) is the initial Cs^+ concentration in solution, C_{eq} (mmol/L) is the equilibrium Cs^+ concentration in solution, V(L) is the volume of the solution, and m (g) is the mass of the sorbent.

The degree of Cs^+ extraction (α, %) was evaluated as

$$\alpha = \frac{(C_0 - C_{eq})}{C_0} \times 100\%. \quad (2)$$

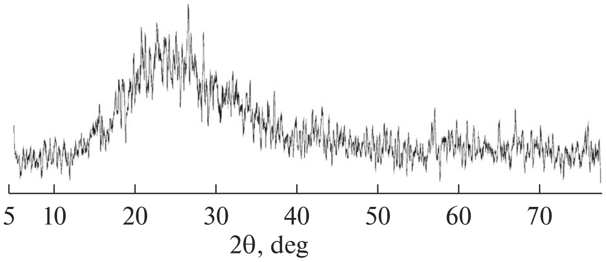

Fig. 1. X-ray diffraction pattern of the sodium aluminosilicate sample studied.

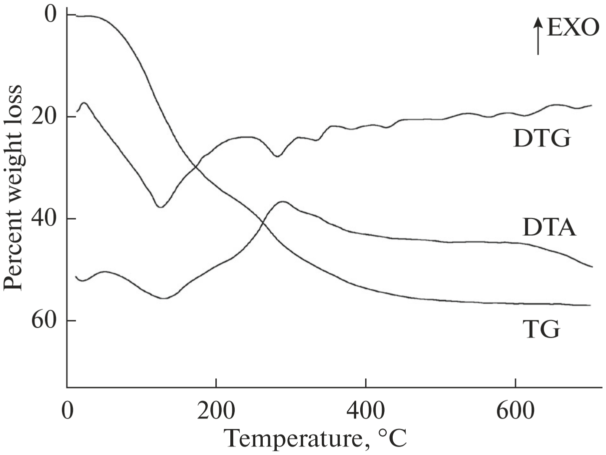

Fig. 2. Thermal analysis data for the sodium aluminosilicate.

The distribution coefficient (K_d, mL/g) was calculated as

$$K_d = \frac{(C_0 - C_{eq})V}{C_{eq}m}. \quad (3)$$

RESULTS AND DISCUSSION

The quantitative elemental composition of the sample obtained was determined to be (wt %) Si, 49.6; Al, 30.7; Na, 17.1; and K, 2.1. This composition corresponds to the molar ratio M : Si : Al = 0.45 : 1 : 0.64.

According to X-ray diffraction results, the sample was X-ray amorphous. Its X-ray diffraction pattern (Fig. 1) shows a halo peaking at an interplanar spacing of 3.21–3.28 Å.

The specific surface area of the sodium aluminosilicate is 364 m^2/g.

According to the thermogravimetry (TG) data in Fig. 2, water removal begins at about 40°C and reaches completion near 220°C. The associated weight loss is 15.3%. Above 220°C, oxidation of the organic component begins, accompanied by an exotherm in the differential thermal analysis (DTA) curve, with a peak at 280°C, which corresponds to the oxidation of noncrystalline or weakly crystallized cellulose. The small peak in the DTA curve between 600 and 620°C is due to the oxidation of the carbonized residue. The loss on ignition during heating to 1000°C is 31.7%.

The particle size of the sample ranges from 0.2 to 50 μm, with a peak in the size distribution at 10 μm (Fig. 3).

The experimental data on Cs^+ sorption by the sorbent under study were used to construct sorption isotherms (Fig. 4).

It is seen in Fig. 4 that Cs^+ sorption from seawater is accompanied by a considerable reduction in the sorption capacity of the sodium aluminosilicate. The degree of Cs^+ extraction from solutions with no salt background reaches 96.2%, whereas that from seawater does not exceed 25.7%.

To evaluate the sorption properties of the sample, the isotherms were analyzed in terms of the Langmuir equation:

$$\frac{C_{eq}}{A_s} = \frac{1}{A_{max}k} + \frac{C_{eq}}{A_{max}},$$

where C_{eq} is the equilibrium Cs^+ concentration in solution, A_{max} is the maximum sorption capacity, and k is the Langmuir constant.

The constants in this equation were calculated from the slope and vertical intercept of the plot of C_{eq}/A_s against C_{eq} (Fig. 5).

The Freundlich equation in its logarithmic form was used to obtain a linear plot of ln A_s against ln C_{eq} and graphically determine the parameters K_F and n:

$$\ln a = \ln K_F + \frac{1}{n}\ln C_{eq},$$

where a (mmol/g) is the amount of adsorption; K_F is the equilibrium constant of the Freundlich equation, related to the sorption capacity; and the parameter $1/n$ quantifies the sorbent–sorbate interaction strength.

The graphically determined parameters of the Langmuir and Freundlich equations are listed in Table 2. It is seen from Table 2 that the Langmuir model is better suited for describing Cs^+ sorption by the synthetic sodium aluminosilicate, as evidenced by the corresponding correlation coefficients. The maximum sorption capacity A_{max} for Cs^+ sorption from solutions with no salt background and from seawater is 1.2 and 0.16 mmol/g, respectively.

Table 3 presents distribution coefficients for cesium sorption on sodium aluminosilicate from seawater and a solution with no salt background (distilled water). It is seen that large distribution coefficients are observed in the case of cesium sorption from the solutions with no salt background at any solid : liquid ratio.

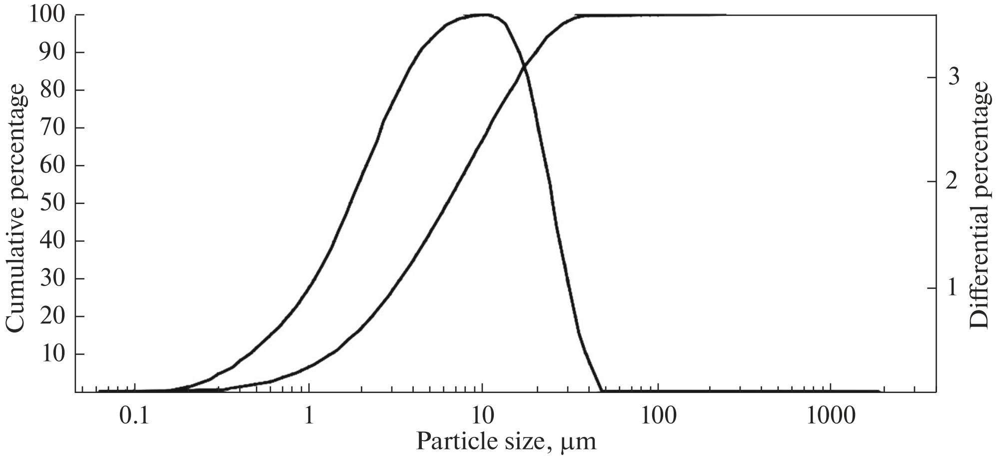

Fig. 3. Particle size distribution of the sodium aluminosilicate.

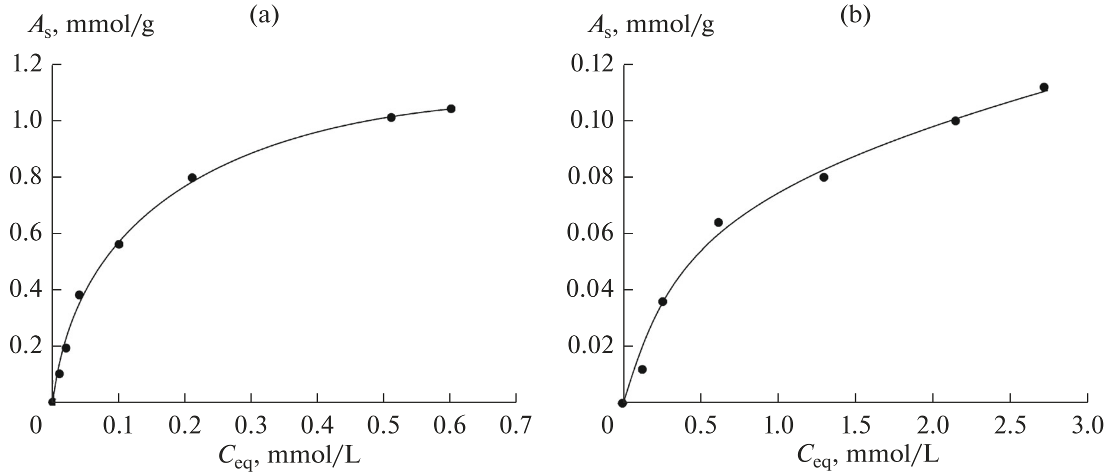

Fig. 4. Cs^+ sorption isotherms for the sodium aluminosilicate in solutions in (a) distilled water and (b) seawater.

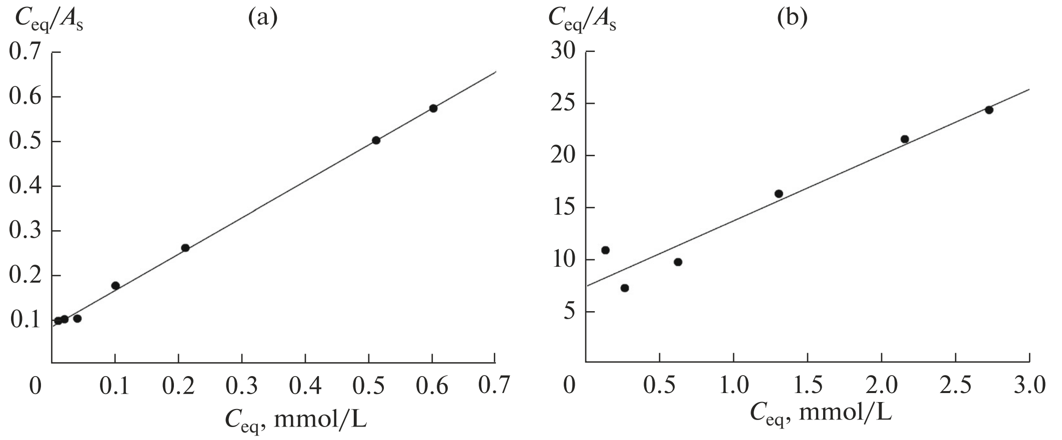

Fig. 5. Cs^+ sorption isotherms represented as Langmuir plots for the synthetic sodium aluminosilicate in solutions in (a) distilled water and (b) seawater.

Table 2. Parameters of the Langmuir and Freundlich equations obtained by analyzing Cs^+ sorption isotherms for the synthetic sodium aluminosilicate

Solvent	Distilled water	Seawater
Langmuir equation		
k, L/mmol	9.5	0.875
$A_{\max}$, mmol/g	1.2	0.16
R^2	0.9985	0.9427
Freundlich equation		
K_F, (mmol/g)(L/mmol)$^{1/n}$	1.7	0.9427
$1/n$	0.5521	14.9
R^2	0.9452	0.6589

Table 3. Distribution coefficient K_d for cesium sorption on sodium aluminosilicate from seawater and a solution with no salt background

Solid : liquid	K_d, mL/g	
	distilled water (pH 6.2)	seawater (pH 8.1)
1 : 100	8567	111
1 : 400	7400	107
1 : 1000	8750	86
1 : 2000	11000	82

Note that the highest value of K_d (11000 mL/g) is observed at a solid : liquid ratio of 2000. The amount of cesium sorption from seawater is considerably smaller throughout the range of solid : liquid ratios examined.

Figure 6 shows integral kinetic curves for Cs^+ sorption from solutions with different salt compositions by the sorbent under study. All of the kinetic curves are seen to plateau after just 5 min, with no changes in the amount of sorption thereafter. After this time, the degree of Cs^+ extraction is 96.4% from distilled water, 19.7% from seawater, 87.4% from the $NaNO_3$ solution, 70.0% from the KNO_3 solution, and 69.2% from the NH_4NO_3 solution. Thus, the amount of cesium sorption from seawater is considerably smaller in comparison with the other solutions under investigation. In the case of Cs^+ sorption from the 0.01 M nitrate solutions, the highest degree of cesium extraction is observed for sorption from the 0.01 M $NaNO_3$ solution. Similar data were obtained by Gordienko et al. [15], who studied the ^{137}Cs sorption properties of synthetic nanostructured potassium aluminosilicate in sodium, potassium, and ammonium nitrate solutions.

Table 4 illustrates the effect of nitrate salt concentration on the cesium distribution coefficient on sodium aluminosilicate. It is seen that the largest distribution coefficient is observed for cesium sorption from the sodium nitrate solutions. In the case of Cs^+ sorption from the potassium and ammonium nitrate solutions, the distribution coefficient is smaller. With increasing nitrate concentration in solution, the amount of Cs^+ sorption decreases in all cases.

CONCLUSIONS

Nanostructured, X-ray amorphous sodium aluminosilicate with a specific surface area of 364 m^2/g has been synthesized using an alkaline rice straw hydrolysate and its Cs^+ sorption properties have been studied in solutions with various salt compositions (seawater and nitrate solutions).

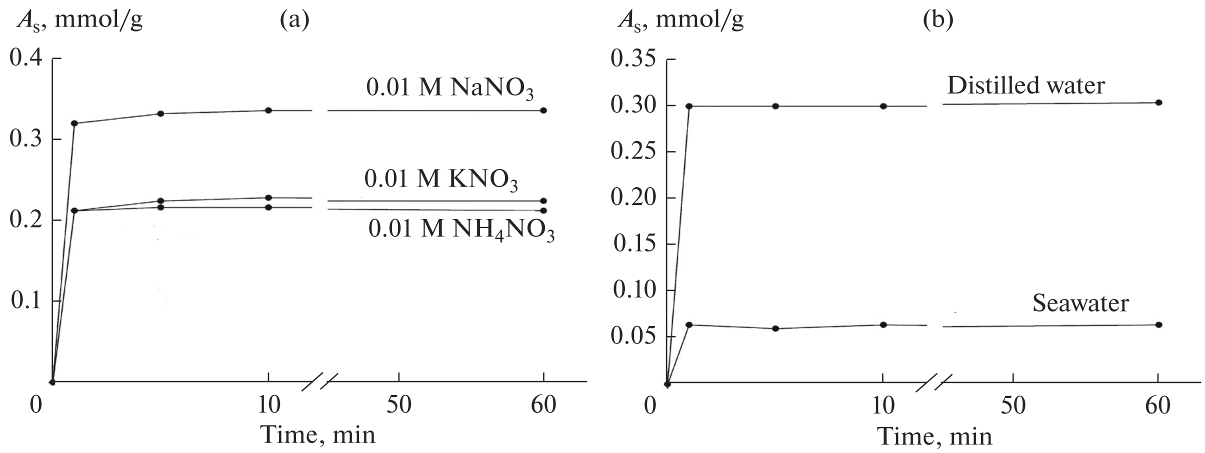

Fig. 6. Integral kinetic curves for cesium sorption on the sodium aluminosilicate from solutions with different salt compositions: (a) 0.01 M sodium, potassium, and ammonium nitrates; (b) distilled water and seawater.

Table 4. Effect of nitrate salt concentration (solid : liquid = 1 : 400) on the cesium distribution coefficient on sodium aluminosilicate

Salt concentration, mol/L	K_d, mL/g (solution pH)		
	$NaNO_3$	KNO_3	NH_4NO_3
0.5	81 (7.7)	13 (7.3)	11 (6.4)
0.1	360 (7.5)	97 (7.5)	230 (7.0)
0.01	3055 (7.8)	933 (7.7.)	917 (7.7)

The sorption capacity of the compound studied has been shown to be considerably lower in the case of cesium sorption from seawater. The degree of Cs^+ extraction from the solutions with no salt background reaches 96.2%, whereas that from seawater does not exceed 25.7%. The Langmuir model has been shown to be best suited for describing Cs^+ sorption by synthetic sodium aluminosilicate from seawater and solutions with no salt background, as evidenced by the corresponding correlation coefficients. The maximum Cs^+ sorption capacity A_{max} in solutions with no salt background and in seawater is 1.2 and 0.16 mmol/g, respectively. Large distribution coefficients are observed in the case of cesium sorption from the solutions with no salt background at any solid : liquid ratio. The highest value of the distribution coefficient K_d (11000 mL/g) is observed at a solid : liquid ratio of 2000. The distribution coefficient for cesium sorption from seawater is considerably smaller throughout the range of solid : liquid ratios examined.

Analysis of sorption kinetics in the solutions studied demonstrates that the corresponding kinetic curves plateau after just 5 min, with no changes in the amount of sorption thereafter. After this time, the degree of Cs^+ extraction is 96.4% from distilled water, 19.7% from seawater, 87.4% from the $NaNO_3$ solution, 70.0% from the KNO_3 solution, and 69.2% from the NH_4NO_3 solution. In the case of Cs^+ sorption from the 0.01 M nitrate solutions, the highest degree of Cs^+ extraction is observed for sorption from the $NaNO_3$ solution. The largest distribution coefficient is observed for cesium sorption from the sodium nitrate solutions. In the case of Cs^+ sorption from the potassium and ammonium nitrate solutions, the distribution coefficient is substantially smaller. With increasing nitrate concentration in solution, the amount of Cs^+ sorption decreases in all cases.

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