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Sorption of cesium by aluminosilicate sorbents from rice straw

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Abstract. Using rice straw of various varieties of the Far Eastern selection as a source of silicon, a number of samples of sodium aluminosilicates with a Si:Al ratio from 1.02 to 1.56 were synthesized. For the obtained samples, the elemental and phase composition was found, the thermal properties were investigated. The morphology of aluminosilicates was studied: the particle size varies from 0.2 to 50 μm with a maximum distribution of about 10 μm , the specific surface area is 364 m^2/g . The acid-base properties of the surface of aluminosilicates are characterized by pH-metry methods and the Hammett indicator method, the nature of the distribution of adsorption centers on the surface is established. The sorption capacity of the obtained samples, determined with respect to methylene blue (MB), is from 31.9 to 103.9 mg/g . By varying the synthesis conditions, it was shown that the greatest sorption capacity with respect to MB is achieved at the time of hydrolysis of the original rice straw for 60 minutes. It is shown that the sorption of Cs^+ ions in the obtained samples is described by the Langmuir model. The sorption properties with respect to Cs^+ ions from aqueous solutions with different salt background were studied.

1. Introduction

The spectrum of the chemical composition of silicates and aluminosilicates is quite wide [1]. They are mainly used as fillers for construction materials, sorbents, catalyst carriers and ion exchange materials [2]. An important characteristic of its surface is the acid-base properties [3], which make it possible to predict the reactivity and sorption capacity of a surface with respect to pollutants of various nature (metal cations and organic dyes).

Synthetic aluminosilicates surpass natural analogues in a number of indicators. The most significant advantages of synthetic aluminosilicates are their constant composition and the absence of impurities. The chemical and phase composition of synthetic aluminosilicates is largely determined by the method of preparation and the feedstock [4].

In addition to traditional mineral raw materials and wastes from their processing, silicophilous plants, in particular, rice, are an alternative source of silicon for the chemical industry. The by-products of rice cereal production – straw and fruit casings – are renewable raw materials, each year around 800 million tons are produced around the world. It is known to use rice husk ash as a source of silicon in the synthesis of zeolites [5–10]. Works on the synthesis and study of the functional properties of aluminosilicates from rice straw are much less [11–13]. A promising area of application



of synthetic aluminosilicates is their use for the purification of aqueous solutions from cesium ions, which is confirmed by a number of studies [14–16].

Earlier, sodium and potassium aluminosilicates with a specific surface area of 69–134 m²/g and a sorption capacity relative to Cs⁺ ions up to 1.3 mmol/g were obtained from alkaline rice straw hydrolysates at the Institute of Chemistry of the Far East Branch of the Russian Academy of Sciences [17]. During the sorption of Cs⁺ ions, the kinetic curve reaches a plateau already after 5 – 10 minutes and with an increase in temperature from 20 to 60 °C, the sorption capacity does not change, the degree of extraction of Cs⁺ ions is 82.6–88.6% [18]. When choosing sorbents, it is also necessary to have some data on the effect of the ionic composition of the salt background on the degree of extraction of the corresponding ions from aqueous solutions. Of practical interest are the values of the sorption parameters in the sorption of cesium ions from natural sea water containing Cs⁺ ions in various concentrations.

The purpose of this work is to obtain aluminosilicates from rice straw (RS), to study the acid-base properties of their surface, to study the sorption capacity of samples with respect to methylene blue and cesium ions, including sorption from solutions of complex salt composition.

2. Experimental

Rice straw (*Oryza sativa*) of the Far Eastern selection varieties harvested in 2017 was used as a source of silicon. Straw was ground into pieces 5–10 mm long, washed with water and air-dried. For the extraction of silicon, the straw was subjected to alkaline hydrolysis in a 1M solution of NaOH with a ratio solid-to-liquid 1:13 at a temperature of 90°C for a fixed time. A saturated aqueous solution of aluminum sulfate Al₂(SO₄)₃·18H₂O, taken in a molar ratio of Al₂(SO₄)₃·18H₂O : Si = 1 : 3, was added to the hydrolyzate obtained at room temperature, then the reaction mixture was neutralized with HCl solution. The precipitation was kept for at least 5 hours, separated with a filter and washed with water. The precipitate was dried at 105 °C [17].

An elemental analysis of aluminosilicate samples was performed by the method of energy dispersive X-ray fluorescence spectroscopy on a Shimadzu EDX 800 HS spectrometer (Japan). X-ray diffractograms were recorded on a Bruker D8 Advance diffractometer (Germany) in Cu K_α-radiation. The specific surface of the samples was found by the method of low-temperature nitrogen adsorption using a Sorbtometer-M device (Russia). A thermal analysis was performed on an MOM Q-1000 derivatograph (heating rate 5 K/min). Particle size distribution was determined on a Fritsch ANALYSETTE 22 MicroTec plus laser particle size analyzer.

The acid-base properties of the surface of sorbents were studied by the method of adsorption of indicators (Hammett's method) using 13 indicators with pK_a values in the range from –0.29 to +16.80 [19]. According to the obtained values, the distribution curves of the centers of adsorption of indicators on the surface of aluminosilicates were constructed.

The sorption properties of the obtained aluminosilicates were studied on model solutions of methylene blue (MB) [20, 21] and solutions of cesium chloride. A study of the sorption of methylene blue from aqueous solutions was carried out under static conditions at a temperature of 20°C, with a sorbent : solution ratio of 1:200, with MB concentration of 80.8–841.6 mg/L. After stirring for 40 min, the suspension was centrifuged, the optical density of the solution was measured with a ZOMZ KFK-3-01 spectrophotometer (Russia) at a wavelength of 657 nm. Experiments on cesium sorption were carried out under static conditions at a ratio of sorbent : solution 1: 400 and temperature of 20 °C with stirring from 1 to 60 minutes. Aqueous solutions of CsCl with different initial concentrations of Cs⁺ ions in the range from 0.16 to 3.2 mmol/L based on distilled sea water and 0.01 M of NaNO₃, KNO₃, NH₄NO₃ were used. The solutions were separated from the sorbent by filtration. Sea water, on the basis of which solutions with different contents of Cs⁺ ions were prepared, was collected in the Sea of Japan, Amursky Bay (Vladivostok), filtered through a “white ribbon” filter.

The content of Cs⁺ and Na⁺ ions in solutions was determined by atomic absorption spectrometry (AAS) with a Solaar M6 spectrometer (Thermo Scientific, USA).

The sorption capacity (A_c , mmol/g) of the samples was calculated by the formula (1)

$$A_c = \frac{(C_{ini} - C_e)}{m} \cdot V, \quad (1)$$

where C_{ini} is the initial concentration of Cs^+ ions in the solution, mmol/L; C_e is the equilibrium concentration of Cs^+ ions in the solution, mmol/L; V is the volume of solution, L; m is the mass of sorbent, g.

The degree of extraction of Cs^+ ions (α , %) was calculated by the formula (2).

$$\alpha = \frac{(C_{ini} - C_e)}{C_{ini}} \cdot 100\%, \quad (2)$$

3. Results and Discussion

3.1. Characteristics of the samples

The samples synthesized in this work are X-ray amorphous, and a halo with a maximum corresponding to an interplanar distance of 3.21–3.28 Å is observed in the diffraction pattern. The composition of the samples corresponds to sodium aluminosilicate (Table 1).

Table 1. Characteristics of the samples.

Sample	Straw strain	Content of elements according to EDX, mass. %				M:Al:Si ^a	LI ^b , %
		K	Na	Al	Si		
1	Khankaiskiy-429	3.16	16.36	39.05	41.43	0.21:1:1.02	24.98
2	Dariy	2.94	18.76	33.82	44.46	0.28:1:1.26	30.68
3	Lugovoy	2.15	17.66	31.08	50.22	0.27:1:1.56	31.74
4	Dubrava	3.11	17.28	31.08	47.94	0.30:1:1.47	43.35

^a – molar ratio

^b LI – loss on ignition, 1000 °C

The influence of the processing conditions of rice straw on the sorption properties of samples depending on the time of alkaline hydrolysis was studied. From straw strain *Lugovoy*, samples were obtained with a duration of hydrolysis of 60, 40 and 20 minutes (Table 2). As one can see, all samples have a similar composition.

Table 2. Characteristics of samples obtained at different times of hydrolysis.

Sample	Hydrolysis time	Content of elements according to EDX, mass. %				M:Al:Si	LI, %
		K	Na	Al	Si		
3	60 minutes	2.15	17.66	31.08	50.22	0.27:1:1.56	31.74
5	40 minutes	3.49	4.65	35.05	50.75	0.22:1:1.39	23.50
6	20 minutes	2.14	8.88	33.52	35.86	0.35:1:1.03	29.18

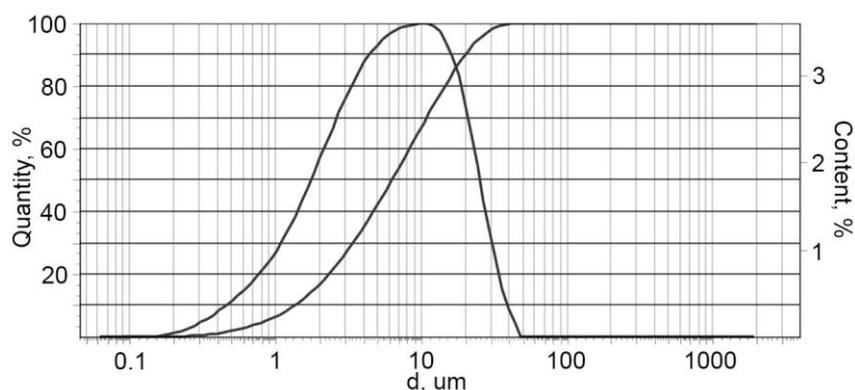


Figure 1. Size distribution of sodium aluminosilicate (sample 3) particles.

The specific surface of sample 3 is $364 \text{ m}^2/\text{g}$, and the particle size has a distribution maximum of about $10 \mu\text{m}$ (figure 1). A thermogravimetric analysis of sample 3 (figure 2) showed that the removal of water begins at about $40 \text{ }^\circ\text{C}$ and ends at $220 \text{ }^\circ\text{C}$. Above $220 \text{ }^\circ\text{C}$, oxidation of the organic component begins, followed by an exoeffect on the DTA curve with a maximum at $280 \text{ }^\circ\text{C}$, which corresponds to the oxidation of non-crystalline or slightly crystallized cellulose. A small maximum on the DTA curve at about $600\text{--}620 \text{ }^\circ\text{C}$ is associated with the oxidation of the carbonated residue. The total mass loss on ignition is 31.7% .

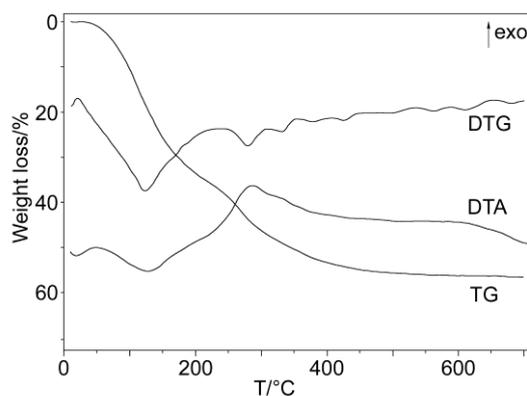


Figure 2. Thermogravigram of sodium aluminosilicate (sample 3).

The study of the acid-base properties of the surface of samples and the distribution of active centers by the indicator method showed that on the surface there is a set of Lewis and Brønsted sites of both acidic and basic types [19]. In the spectra of the distribution of adsorption centers, there are 3 main bands describing active sites (figure 3): Brønsted acidic ($\text{pK}_a +2.5$), weakly acidic ($\text{pK}_a +6.4$), and Lewis acidic ($\text{pK}_a +16.8$) sites.

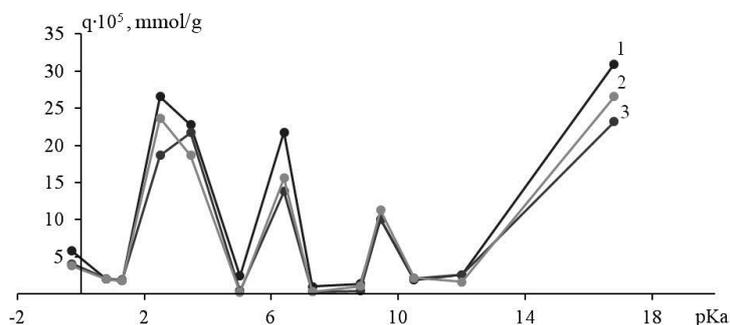


Figure 3. Distribution of adsorption centers of indicators on the surface of aluminosilicates (numbering as per table 2).

Brønsted acid sites with a pKa of +2.5 most likely correspond to the silanol groups $\equiv\text{Si}-\text{OH}$ [22]. The centers of adsorption with pKa +6.4 are characterized by the fact that they show neither basic nor acidic properties, due to the equality of E–O and O–H bonds [23]. The presence of weak Brønsted sites on the surface corresponds to OH groups of a different nature (for example, $=\text{Si}(\text{OH})_2$, $-\text{Al}(\text{OH})_2$) [22]. Lewis acid sites with pKa +16.8 are coordinatively unsaturated surface aluminum atoms with a localized positive charge.

3.2. Sorption characteristics

The methylene blue (MB) sorption on the obtained aluminosilicate samples occurs via a monolayer mechanism, as evidenced by the isotherm type (figure 4). The values of the sorption capacity for MB are shown in table 3.

Table 3. Value of the sorption capacity of aluminosilicates.

Raw materials and conditions for obtaining aluminosilicate	Sorption capacity with respect to MB, mg/g
Khankaiskiy-429, 60 minutes	32.9
Dariy, 60 minutes	31.9
Lugovoy, 60 minutes	103.9
Dubrava, 60 minutes	46.6
Lugovoy, 40 minutes	47.1
Lugovoy, 20 minutes	43.6

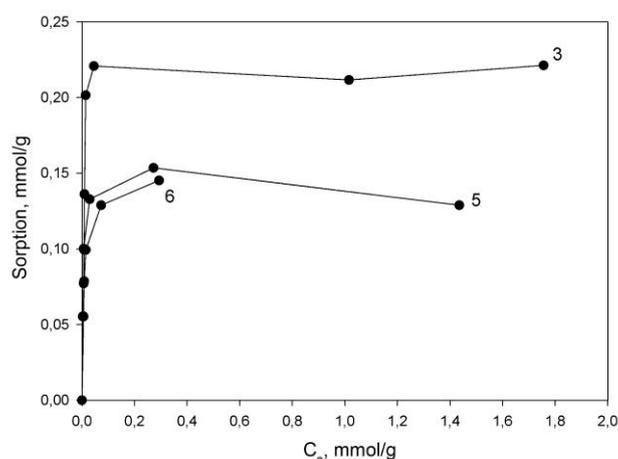


Figure 4. Sorption isotherms of methylene blue by samples of aluminosilicates (numbering as per table 2).

From table 3 it can be seen that the sorption capacity of the samples depends both on the rice variety, the straw of which was used as a raw material, and on the time of alkaline hydrolysis of the straw. Of all the varieties of rice, the use of RS of *Lugovoy* variety as a source of silicon allows obtaining aluminosilicate with the highest sorption capacity. In this case, the best result is achieved with an alkaline hydrolysis time of 60 minutes. Reducing the time of hydrolysis to 40 or 20 minutes dramatically reduces the sorption properties of the product.

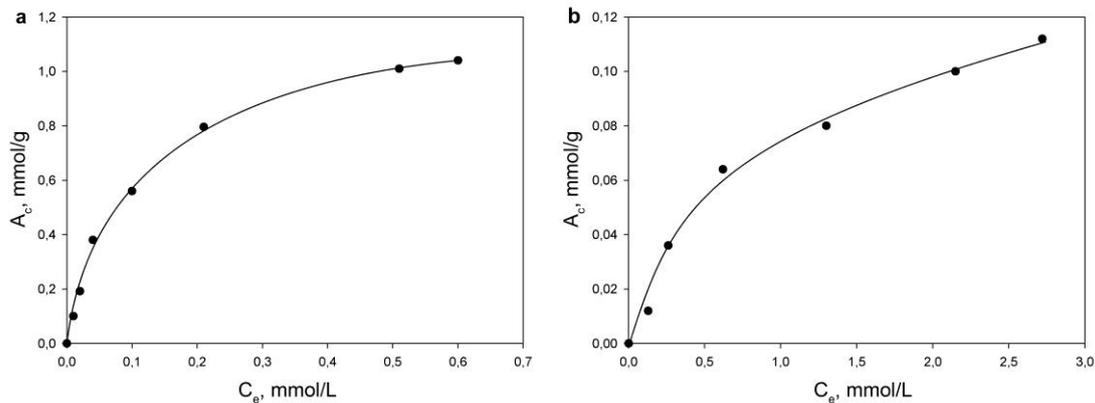


Figure 5. Sorption isotherms of Cs⁺ ions with sodium aluminosilicate from solutions based on distilled (a) and sea (b) water.

Based on the obtained experimental data on the sorption of Cs⁺ ions, sorption isotherms were built (figure 5). As can be seen from the figure, during the sorption of Cs⁺ ions from sea water, a significant decrease in the sorption capacity is observed. The degree of extraction of Cs⁺ ions from solutions without salt background reaches 96.2%, and from sea water it does not exceed 25.7%.

To assess the sorption properties, the isotherms obtained were analyzed in the coordinates of the Langmuir equation and the Freundlich empirical equation. Langmuir equation:

$$\frac{C_p}{A_c} = \frac{1}{A_m \cdot k} + \frac{C_p}{A_m},$$

where C_e is the equilibrium concentration of Cs⁺ ions in the solution, A_m is the maximum sorption capacity, k is the Langmuir constant.

The constants of the equation were calculated from the slope and intersection of the lines on the graph in the corresponding coordinates of the linear C_e/A_c equation from C_e (figure 6).

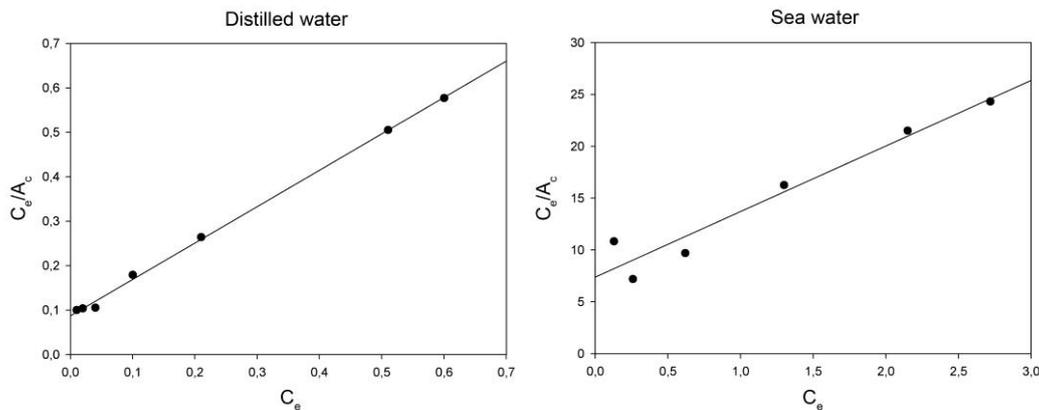


Figure 6. Sorption isotherms of Cs⁺ ions with synthetic sodium aluminosilicate in the respective coordinates of the Langmuir linear equation.

The logarithmic form of the Freundlich equation was used to construct a linear dependence and $\ln A_c - \ln C_e$ and a graphic definition of the parameters K_F and n :

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

where K_F is the equilibrium constant of the Freundlich equation relating to the sorption capacity; $1/n$ is a parameter indicating the intensity of the sorbent-sorbate interaction. The parameters of the Langmuir and Freundlich equations found graphically are presented in table 4.

Table 4. Parameters of the Langmuir and Freundlich equations obtained by analyzing the isotherms of sorption of Cs^+ ions with synthetic sodium aluminosilicate.

Parameters of equation	Type of solution containing Cs^+ ions	
	Distilled water	Sea water
<i>Langmuir equation</i>		
$k, L/mmol$	9.5	0.88
$A_m, mmol/g$	1.2	0.16
R^2	0.9985	0.94
<i>Freundlich equation</i>		
$K_F, (mmol/g) \cdot (L/mmol)^{1/n}$	1.7	14.90
$1/n$	0.5521	0.66
R^2	0.9452	0.90

The table shows that for describing the sorption of Cs^+ ions with synthetic sodium aluminosilicate, the Langmuir model is most suitable, as evidenced by the corresponding correlation coefficients. The maximum sorption capacity of A_m during the sorption of Cs^+ ions from solutions without salt background and from sea water is 1.2 and 0.16 mmol/g, respectively.

Figure 7 (a, b) displays the integral kinetic curves of the sorption of Cs^+ ions from solutions of different salt composition with the studied sorbent.

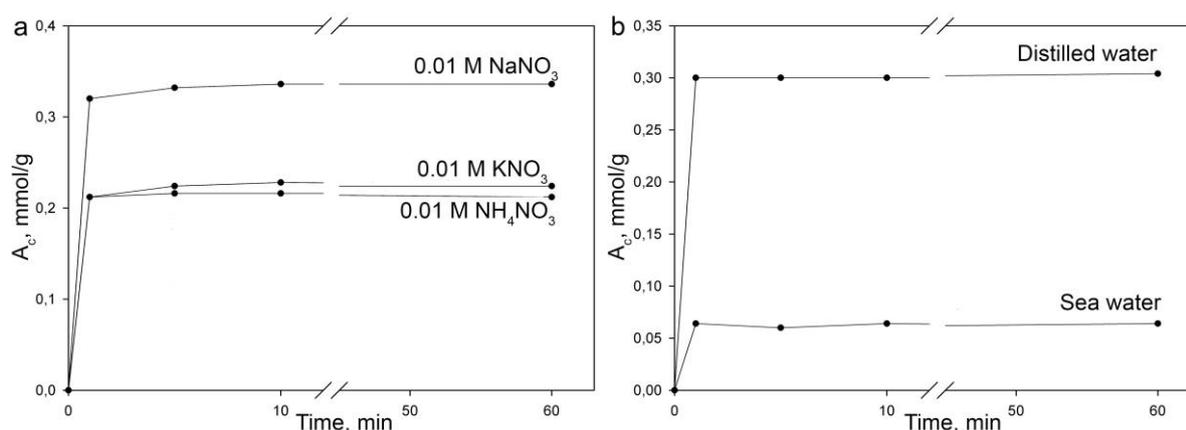


Figure 7. Integral kinetic curves of sorption of cesium by sodium aluminosilicate from solutions of different salt composition: a – 0.01 M solutions of nitrates; b – distilled and sea water.

In all the cases under consideration, the kinetic curves have already reached the plateau within 5 minutes, while the degree of extraction of Cs^+ ions in the case of distilled water is 96.4%; sea water – 19.7%; $NaNO_3$ – 87.4%; KNO_3 – 70.0%; NH_4NO_3 – 69.2%. Thus, the sorption of cesium in sea water

is significantly reduced compared with all the studied types of solutions. During sorption of Cs⁺ ions from 0.01 M solutions of nitrates, the highest values of the degree of extraction of Cs⁺ ions are observed during sorption from a 0.01 M solution of NaNO₃. Similar data were obtained by the authors [24] in the study of the sorption properties of synthetic potassium aluminosilicate in the extraction of ¹³⁷Cs from solutions of nitrates-containing salts.

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