



# Article Radioiodide Sorption on Natural and Acid-Treated Zeolite

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Abstract: This work is devoted to the study of the effect of acid treatment on the structural and textural properties of natural zeolite and its sorption activity with respect to radioiodide. To carry out the experiments, natural zeolite was treated with nitric acid of various concentrations at 20 and 90 degrees. The following methods were used to study the samples: XRD, SEM, DTA, XRF, FTIR, BET, and CEC analyses. Experiments on the sorption and desorption of radioiodide were carried out. The obtained results indicate that acid treatment results in the gradual leaching of aluminum from the crystal lattice and a significant increase in the specific surface area and microporosity of the zeolite. At the same time, the morphology of clinoptilolite is not significantly changed. Additional studies have shown that acid treatment leads to the hydrophobization of zeolite channels and the formation of an amorphous aluminosilicate phase, which makes a significant contribution to the increase in the specific surface area and microporosity. It was found that, with an increase in the degree of dealumination of the zeolite, there is an increase in the sorption properties with respect to radioiodide. The maximum values of sorption capacity were obtained after treating the zeolite with a 1 M nitric acid solution at 90 °C. With a further increase in the concentration of acid, critical changes in the structure of the zeolite occur, leading to a sharp decrease in the sorption capacity. Iodide sorption is not associated with physical adsorption in the micropores of the zeolite and the newly formed amorphous phase. The main mechanism of the sorption appears to be the interaction with silanol and bridging hydroxyl groups on the surface of the zeolite and the amorphous aluminosilicate phase.

**Keywords:** zeolite; clinoptilolite; acid activation; modification; sorption; radionuclides; iodide

# 1. Introduction

Iodide in the form of <sup>129</sup>I<sup>-</sup> practically does not form poorly soluble compounds in nature, and due to its high organotropy, when it migrates in the environment, it can be integrated into food chains, which poses a direct threat to humans, and in connection with this, the problem of its localization remains relevant today.

Zeolites are a group of minerals related to framework silicates, consisting of siliconoxygen tetrahedrons, penetrated by nanosized channels and possessing specific properties [1]. The isomorphic substitutions of silicon and aluminum in the structure of the



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Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/ licenses/by/4.0/). mineral lead to the formation of an uncompensated negative charge in the zeolite channels, which determines the high sorption properties of zeolites. There are a large number of both natural and synthetic zeolite minerals. The main natural zeolite minerals include clinoptilolite, heulandite, chabazite, mordenite, stilbite, etc. [2]. The main distinguishing features of minerals of the zeolite group from each other are the ratio of silicon to aluminum, the size of the channels and their spatial relationship to each other, as well as the composition of the exchange cations. Zeolites are valuable industrial materials and are used as gas dryers, as sorbents for purifying polluted water in agriculture, construction, medicine, and other industries [3,4].

One of the common methods of changing the properties of both natural and synthetic zeolites is treating them with acid and alkaline solutions. Quite a large number of works are devoted to studying the effect of acid treatment on the properties of zeolites, in particular in relation to the sorption of cations and large organic molecules [5–7]. It is known that acid treatment significantly increases the value of the specific surface area and microporosity of zeolites [8–11]. At the same time, the process of the dealumination of zeolites is associated with changes in the structure of the mineral [12–15]. Depending on the composition of acids, their concentration, and the temperature of treatment, a nonlinear change in the sorption properties of zeolites occurs.

The main mechanism of sorption on minerals of the zeolite group is ion exchange [1,16,17]. This mechanism is responsible for the sorption of positively charged ions. However, after acid activation, additional mechanisms are formed, such as physical adsorption in micropores, and as shown in some works [18,19], as a result of acid treatment, silanol and bridging hydroxyl groups are formed on the surface of particles, which can sorb both cations and anions, depending on the pH of the solution.

The properties of zeolites are affected by the nature of the acids and the degree of exposure. S. Side et al. [11] showed that the improvement of the sorption activity of zeolite when treated with sulfuric and hydrochloric acids occurs only at their low concentrations. M. Silva et al. [8] carried out a comprehensive study comparing various acids on the properties of zeolite. The results suggest that hydrochloric acid modifies the material's pore size, surface area, and surface chemical composition the most. Meanwhile, the zeolite was also significantly, though to a lesser degree, modified by sulfuric and nitric acid treatments; whereas, ice cold acetic acid practically did not change the surface of the samples. V. Tsitsishvili et al. [20] came to the conclusion that the micropores of zeolite treated with acid become more accessible to larger ions and molecules, and its surface area also increases. According to [21,22], acid treatment of zeolites leads to an increase in the degree of hydrophobicity, which was clearly shown using the example of water vapor adsorption.

The main problem in studying the effect of acid treatment on the properties of zeolites is that most of the work mainly considers the sorption of cations or large organic molecules. The study of anion sorption on acid-activated zeolites is rather limited and is mainly devoted to anions of organic dyes [23–26].

The use of zeolites to capture radionuclides released during the operation of nuclear industry enterprises is currently being widely studied, for example the use of zeolites in a special gas purification system at nuclear power plants to trap inert radioactive gases [27]. In addition, the use of zeolites in systems for cleaning volatile radioiodide compounds is being studied [28]. Radioiodide poses a direct threat to human health, especially its isotope <sup>129</sup>I, the half-life of which is 15.7 million years, due to the mobility of iodide in the biosphere, its ability to migrate in food chains, and its high organotropy [29]. Of greatest interest is the capture of radioactive forms of I<sup>-</sup> from aqueous environment due to their higher migration capacity, especially during the long-term isolation of waste containing

<sup>129</sup>I. Research in the direction of removing radioiodide from the aqueous environment mainly involves the impregnation of various materials with increased surface area, which include, among other things, zeolites with silver compounds [30]. The disadvantages of this method are the high cost of raw materials for the production of such sorbents, as well as the probability of silver interaction with sulfide anions, which may be contained in groundwater and, during long-term exposure, is possible during the deep geological disposal of radioactive waste and can reduce the effectiveness of these materials [31]. As a possible alternative, designed to solve the problems of these methods, this paper studies the sorption properties of acid-activated zeolites for the removal of radioactive forms of I<sup>-</sup> at the stages of spent nuclear fuel reprocessing, since maintaining a certain pH level during the disposal of iodide-containing waste in the long term is not possible.

The obtained results in this work show that acid activation can indeed be an effective method for obtaining sorption material for iodide capture. However, an important factor is the selection of the correct acid activation modes. With insufficient or excessive exposure to acid, the sorption characteristics may worsen.

The aim of this work was to trace the relationship between the sorption properties of natural and modified zeolites in relation to radioiodide, as well as a comprehensive study of changes in the structure of the zeolite, including chemical composition, structural and textural features, and thermal properties, depending on the degree of its acid treatment. It is worth noting that only laboratory studies on iodide sorption were conducted, and the fundamental possibilities of using acid activated zeolite were considered. In the future, it is planned to continue this work and conduct experiments with real wastewaters.

#### 2. Materials and Methods

The material for the study is presented by natural volcanic zeolite from the Sokernitskoye deposit. The studied zeolite is represented by a hard, homogeneous rock of grey greenish color with a massive texture and fine-grained structure. The clinoptilolite content in the sample is 71.8%, the specific surface area is  $14 \text{ m}^2/\text{g}$ , and its cation exchange capacity is 161 meq/100 g. Detailed studies of the natural sample were previously published in [16]. The natural sample is indicated by index Z0. Acid-activated samples are indicated as Z1M20-Z8M90. Where "1 M" is the molarity of the nitric acid, and "20" is the processing temperature.

All acid treatment experiments were carried out under static conditions in duplicates. Zeolite samples (2 g each) were placed in 250 mL conical flasks and filled with 200 mL of nitric acid solution (1, 2, 4, 8 M) in a mass ratio of 1:100. The experiments were carried out at room temperature and at 90 °C for 2 h.

In the experiment at 20 °C, the vessels were placed on an LS-210 orbital shaker (LOIP, St. Petersburg, Russia). Experiments with heating were conducted using a magnetic stirrer with a heating function MSH-20A (Witeg Labotechnik GmbH, Wertheim, Germany). After acid treatment, the samples were washed from excess reagent by repeated rinsing (6 cycles were performed) with distilled water, separating the liquid phase using a centrifuge (Eppendorf Centrifuge 5804, Hamburg, Germany) (10 min at 7000 rpm). Then, washing was carried out for two days by the dialysis method. The completeness of washing was controlled by measuring the pH of the supernatant solution. Washing of the zeolite samples was carried out until a pH level of 4.7–5.0 was reached. Experiments at 90 °C were carried out using a reflux condenser on a water bath.

At IGEM RAS by X-ray diffraction (XRD) was used to determine the mineralogical composition of the clay fractions as well as the bulk samples. To obtain XRD patterns, an Ultima-IV X-ray diffractometer (Rigaku, Tokyo, Japan) was used, using semiconductor 1D detector D/Tex-Ultra, CuK $\alpha$  radiation, a scanning range of 3–65° 2 $\theta$ , a scanning speed

of 3°20/min, and a step of 0.02° 20. Moore and Reynolds' recommendations [32] were followed to determine the sample's mineral composition, and the Rietveld method [33] was employed to estimate the quantitive composition, using the BGMN code (Profex software, Version 3.14.3 [34]).

The zeolites' chemical composition was found using X-ray fluorescence spectrometry (XRF) with an Axios mAX XRF spectrometer (PANalytical, Almelo, The Netherlands) on glass beads prepared by fusion with lithium tetraborate at 1200 °C on samples previously dried at 110 °C. The iron content was determined as total Fe<sub>2</sub>O<sub>3</sub>.

The microstructure of the samples was studied with scanning electron microscopy (SEM) using a LEO1450VP SEM (Carl Zeiss, Oberkochen, Germany). Samples in the form of both aggregates and individual particles were prepared for SEM. The samples in powder form were deposited on a double-sided electrically conductive adhesive tape. Compressed air was used to remove excess particles. This resulted in a monolayer of individual particles and aggregates on an adhesive tape. A 5–10 nm thick gold film was applied, under vacuum, to the sample surfaces.

A TGA/DSC 3+ synchronous thermal analyzer (Mettler Toledo, Greifensee, Switzerland) was used to carry out thermal analysis; it was equipped with an o-DTA sensor, which does not require a reference sample. Calibration was carried out using the melting temperature and enthalpy of the following certified materials: zinc, indium, gold, and aluminum. The measurements were taken in a simulated air atmosphere (80% N<sub>2</sub>, 20% O<sub>2</sub>) in the temperature range 40–1000 °C with a gas flow rate of 100 mL/min and heating rate of 10 °C/min, using Al<sub>2</sub>O<sub>3</sub> crucibles with a volume of 70 µL. At a temperature of 110 °C, a long exposure was carried out.

The specific surface area was evaluated using a Quadrasorb SI/Kr analyzer (Quantachrome Instruments, Boynton Beach, FL, USA). Gas adsorption was conducted at the temperature of liquid nitrogen (77.35 K). Nitrogen of 99.999% purity served as an adsorbate. To calibrate the volume of the measuring cells, helium grade 6.0 (99.9999%) was used. The calculation was conducted using the BET multiple-point isotherm in the P/P0 range 0.05–0.30. Before measuring the surface characteristics, the samples were vacuumpumped using the Flo-Vac Degasser installation. This installation is an integral part of the Quadrasorb SI/Kr analyzer, it allows for the pumping of water and gases from the pore space under temperatures in the range of 15–400 °C and system pressures in the range of 101.3 kPa–0.133 Pa. In this work, the samples were pumped at 105 °C (temperature of dehydration) to a residual constant pressure of 0.133 Pa. A higher temperature may damage the aluminosilicates' structure and, thereby, affect the state of the pore space. The pumping was conducted at this temperature for a period of 20 h.

To study the cation exchange capacity (CEC), the method of multiple replacement of exchange cations with ammonium chloride was used. The composition of exchange cations in the solution was determined by the ICP-MS method. Tucker, B.M., Laboratory Procedures for Cation Exchange Measurement on Soils [35].

The leaching of amorphous silica was carried out in fluoroplastic beakers in a 1 M NaOH solution for an hour in a water bath, at a solid: liquid ratio of 1 to 100. Then, the beakers with the samples were cooled in cold water and centrifuged at 2500 rpm for 7 min. The content of  $SiO_2$  in the aqueous phase after treatment was determined spectrophotometrically with the molybdate method [36]. A full description of the technique is given by [37].

The SiO<sub>2</sub> content in the solution was estimated by the optical density after mixing with Euler's reagent ( $[MoO_4^{2-}]$ —0.0707 M;  $[NH_4^+]$ —0.148 M;  $[SO_4^{2-}]$ —0.375 M, pH = 1.2). For this purpose, a selected aliquot of the solution after sample processing was diluted 25 times with 0.1 N HCl, after which 5 mL of the resulting solution was depolymerized

by single boiling with excess KOH and mixed with 25 mL of Euler's reagent. The silicon dioxide content was determined using a calibration graph obtained using a standard silicon solution (1000  $\mu$ g/mL, ICP standard). Optical density was determined at the absorption maximum of the yellow molybdate complex at a wavelength of 400 nm, using an Expert 001 photometer (Econix).

For the sorption experiments,  $Na^{131}I$  was used, 2 MBq, with a half-life period of 8 days (JSC "Izotop", Moscow, Russia). To conduct the sorption experiment, 0.3 g of natural and acid-activated zeolites were prepared in polypropylene centrifuge tubes. A solution with the radioactive tracer iodide-131 in distilled water with a volume of 30 mL was added to the specified samples using an automatic pipette, which, with a sample weight of 0.3 g, corresponded to a ratio of S:L = 1:100. The initial specific activity of the solution was 1000 Bq/mL. The sorption experiment was carried out with continuous stirring on an orbital shaker. The selection of aliquots to determine the concentration of the radionuclide in the liquid phase and to construct kinetic curves (dependence of the degree of sorption, R, on time) was carried out for the following time intervals: 15 min, 30 min, 60 min, 2 h, 3 h, 4 h, 14 h, 20 h, and 38 h.

The interphase distribution coefficient was calculated using Formula (1):

$$K_d = \frac{a_0 - a_p}{a_p} \cdot \frac{V}{m},\tag{1}$$

where  $K_d$  is the interphase distribution coefficient, mL/g;  $a_0$  is the initial volumetric activity of the liquid phase, Bq/mL;  $a_p$  is the volumetric activity of the liquid phase at the moment of reaching sorption equilibrium, Bq/mL; V is the volume of the liquid phase, mL; and m is the mass of the rock sample, g.

The degree of sorption was calculated using Formula (2):

$$R = \frac{a_0 - a_{\rm p}}{a_0} \cdot 100\%,\tag{2}$$

where R is the degree of sorption, %;  $a_0$  is the initial volumetric activity of the liquid phase, Bq/mL; and  $a_p$  is the volumetric activity of the liquid phase at the moment of reaching sorption equilibrium, Bq/mL.

Samples of zeolite from the Sokirnitskoye deposit activated with 1 M nitric acid solution at 90 °C after the sorption of iodide were separated from the liquid phase by centrifugation for 10 min at 8000 rpm. After centrifugation, the solution containing radioactive iodide was decanted and replaced with 30 mL of distilled water to study desorption from the activated zeolite sample, carried out with the constant mixing of the phases on an orbital shaker. To analyze the desorption kinetics, aliquots of the liquid phase were taken after 60, 120, 180, 240, 720, and 1440 min from the start of the experiment to measure the activity. Based on the results obtained, the degree of desorption D was calculated using Formula (3):

$$D = \frac{a}{a_0 - a_p} \cdot 100\%,\tag{3}$$

where a is the specific activity of the liquid phase sample containing desorbed iodide-131, Bq/mL;  $a_0$  is the initial specific activity of the liquid phase before sorption of iodide-131, Bq/mL; and  $a_p$  is the specific activity of the liquid phase after reaching sorption equilibrium, Bq/mL.

## 3. Results and Discussion

#### 3.1. Effect of Acid Treatment on the Composition and Properties of Zeolite

The results of X-ray diffraction showed that the original sample was mainly represented by clinoptilolite (9.0, 7.9, 6.76, 3.98 Å, etc.), as well as impurities of quartz (4.25, 3.34, 2.46, 2.28 Å), feldspars (3.21 Å), and micaceous minerals (9.9 Å) (Figure 1a). The clinoptilolite content is 71.8%. When the sample is treated with nitric acid, a decrease in the intensity of all clinoptilolite reflexes is observed (Figure 1c), indicating the partial destruction of its structure. A particularly distinct decrease in the peak intensity is observed in the samples treated at 90 °C. At the same time, there is an increase in the halo in the region of angles of 15–35° 20, which indicates the formation of an amorphous aluminosilicate phase (Figure 1b)



**Figure 1.** X-ray diffraction patterns of the acid activated samples: (a)—natural and treated samples. Fragments of the XRD patterns: (b)—amorphous phase increase; (c)—decrease in the reflection of the 020.

The acid treatment of zeolite samples resulted in significant changes in chemical composition due to partial dissolution of the crystal lattice and leaching of aluminum from the clinoptilolite tetrahedrons. Increasing the acid concentration from 1 to 8 mol/L at 20 °C resulted in a decrease in the Al<sub>2</sub>O<sub>3</sub> content from 13.14 to 11.25%. On the other hand, the SiO<sub>2</sub> content increased from 68.62 to 74.92% (Table 1). With an increase in temperature to 90 °C, this trend intensified, and critical changes occurred in the clinoptilolite structure. The Al<sub>2</sub>O<sub>3</sub> content decreased to 5.83%, and the SiO<sub>2</sub> content increased to 86.01%. Thus, the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio changed from 5.2 for the natural sample to 14.75 for the sample treated with 8 M acid at 90 °C. The content of potassium, sodium, magnesium, and calcium cations occupying exchange positions in the clinoptilolite channels decreased as a result of

protonation. The magnitude of loss on ignition also decreased, which is associated with an increase in the hydrophobicity and a decrease in the amount of zeolite water in the clinoptilolite channels.

Sample	LOI *	Na <sub>2</sub> O	MgO	$Al_2O_3$	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>
Z0	8.56	1.45	0.75	13.14	68.62	3.35	2.38	0.21	0.04	1.50
Z1M20	7.42	0.47	0.70	11.72	73.59	2.24	2.08	0.17	0.03	1.40
Z2M20	6.49	0.48	0.62	11.73	74.82	2.06	2.10	0.17	0.02	1.34
Z4M20	5.79	0.45	0.65	11.37	75.88	2.03	2.04	0.19	0.02	1.41
Z8M20	7.25	0.41	0.60	11.25	74.92	1.87	1.98	0.18	0.02	1.36
Z1M90	5.25	0.37	0.30	7.15	83.26	1.95	0.55	0.19	0.01	0.94
Z2M90	4.40	0.35	0.26	6.66	84.91	1.88	0.51	0.18	0.01	0.81
Z4M90	4.64	0.37	0.21	6.23	85.41	1.77	0.46	0.18	0.01	0.68
Z8M90	4.58	0.41	0.18	5.83	86.01	1.72	0.43	0.17	0.01	0.60
Z8M90 after alkaline leaching	6.93	0.92	0.16	10.45	78.93	1.5	0.41	0.17	0.01	0.52

Table 1. Chemical composition of natural and modified samples, %.

\* Loss of ignition.

The specific surface area and microporosity were also changed significantly as a result of acid treatment. The initial zeolite sample had a specific surface area of  $14 \text{ m}^2/\text{g}$ , with only meso- and macropores (larger than 2 µm) present. Acid treatment of the samples resulted in a significant increase in the specific surface area and microporosity (Table 2, Figure 2). At 20 °C, the maximum specific surface area was observed in the sample treated with a 1 M acid solution and amounted to  $38.6 \text{ m}^2/\text{g}$ . The total amount of micropores is slightly less than half of the total porosity. When the temperature was increased to 90 °C, the specific surface area increased sharply to  $177.8 \text{ m}^2/\text{g}$ . Moreover, the maximum value was observed in the sample treated with a 2 M acid solution. The main increase in BET occurs due to the growth of microporosity, the area of which reached  $134.4 \text{ m}^2/\text{g}$ .

Table 2. Textural properties of studied samples.

Sampla	Specific Surface	Pore Volume	Mean Pore	T-Method Halsey, SBET, m <sup>2</sup> /g			
Sample	Area SBET, m <sup>2</sup> /g	cm³/g, nm	Diameter, nm	Micropores	Meso/Macropores	Total	
Z0	14.0	0.053	5	-	14.0	14.0	
Z1M20	51.7	0.094	<1	28.2	23.5	51.7	
Z2M20	38.6	0.081	<1	17.1	21.5	38.6	
Z3M20	27.1	0.077	5	6.6	20.5	27.1	
Z8M20	29.7	0.068	<1	12.6	17.1	29.7	
Z1M90	154.8	0.164	<1	115.9	38.9	154.8	
Z2M90	177.8	0.183	<1	134.4	43.4	177.8	
Z4M90	147.0	0.144	1	111.2	35.8	147.0	
Z8M90	154.4	0.151	<1	116.5	37.9	154.4	
Z8M90 after alkaline leaching	21.8	0.066	6	-	21.8	21.8	



Figure 2. Differential distribution of pore sizes of studied samples.

In the course of the work on the acid activation of the samples, a hypothesis was put forward that the sharp increase in the specific surface area, microporosity, and silica content is mainly associated not with the zeolite itself but with the formation of an amorphous aluminosilicate phase, which was also noted in the works of [38–40] the after acid treatment of layered aluminosilicates. To test this idea, the acid-activated sample Z8M90C was treated with a 1 M sodium hydroxide solution.

This alkaline treatment led to the dissolution of the amorphous phase formed as a result of the acid treatment. The  $SiO_2/Al_2O_3$  ratio has increased inversely to values of 7.5, which is close to the natural sample. The specific surface area also decreased to  $24 \text{ m}^2/\text{g}$ . At the same time, the microporosity completely disappeared (Table 2, Figure 2). This effect of alkali may indicate that, after the acid treatment, an amorphous aluminosilicate phase appears in the samples and makes the main contribution to the specific surface area and accounts for the entire volume of the micropores.

As shown by scanning electron microscopy studies, despite the significant effect of acid treatment on the structural and textural features, the morphology of the clinoptilolite particles remained without any significant changes. In the natural sample, sheet-shaped and needle-shaped particles and aggregates with sizes from 0.3 to 2–3  $\mu$ m were observed (Figure 3a). Acid treatment did not lead to a noticeable change in either the shape or size of the particles (Figure 3b).



Figure 3. Micrographs of natural zeolite (a) and sample Z8M90 (b).

The thermal analysis of natural and modified samples allowed us to not only evaluate the effect of acid treatment on the thermal properties of the zeolite but also to quantitatively analyze the ability to sorb ammonium cations in the clinoptilolite structure, depending on the degree of its treatment.

As can be seen in Figure 4a, the main amount of water in the natural sample is released up to 420 °C, which is associated with the release of low-temperature, structurally unbound water and clinoptilolite channels [41]. In acid-activated samples, this temperature decreased to 300 °C, which indicates an easier release of water from the channels and pores of the clinoptilolite. The endothermic effect in the region of 474 °C appeared to be associated with an admixture of micaceous minerals [41]. After the saturation of the samples with NH<sub>4</sub>Cl ammonium (Figure 4b), several distinct endo-effects were observed. The release of the ammonium molecule occurred in three stages, in the range of 100–350, 350–540, and 540–750 °C, which indicates the presence of ammonium both in a weakly bound form (on the surface of clinoptilolite particles and aggregates) and in the pores and channels.



**Figure 4.** Results of thermal analysis of natural and acid-activated samples: (**a**) original samples; (**b**) saturated with ammonium chloride.

It is worth noting that the weight loss of the original zeolite sample saturated with ammonium chloride is significantly higher in comparison with acid-activated saturated samples, which indicates a decrease in the cation exchange capacity of the zeolite after acid activation and an increase in its hydrophobicity.

In Figure 5, a clear correlation was observed between the aluminum content and the loss on ignition in ammonium-saturated samples, which confirms the direct relationship between the hydrophilicity of the zeolite and the degree of its dealumination.



Figure 5. Correlation between the aluminum content and the loss on ignition in ammoniumsaturated samples.

#### 3.1.1. Iodide Sorption

The results of iodide-131 sorption on natural and acid-activated samples are presented in Table 3 and Figure 6.

Table 3. Sorption characteristics of natural and acid-activated samples in relation to iodide-131.



Figure 6. Kinetic curves of sorption of iodide-131 radioisotope on natural and acid-activated samples.

The experiments on radioiodide sorption showed that there is a certain relationship between the degree of acid treatment and the sorption of iodide-131. In general, up to a certain point, the higher the degree of dealumination of clinoptilolite, the greater its sorption properties in relation to iodide. The maximum values of the sorption characteristics were obtained for the sample Z1M90 (R = 97.04%, Kd = 3254 mL/g). However, with a further increase in the degree of exposure to acids, there is a decrease in the sorption. The values of the degree of sorption for samples Z2M90, Z4M90, and Z8M90 were lower than the values obtained for the natural sample. This can be explained by the fact that, when the sample is treated with nitric acid with a concentration of more than 1 M at a temperature of 90  $^\circ$ C, critical changes occur in the clinoptilolite structure and on the surface of the amorphous aluminosilicate phase, which leads to a sharp decrease in the sorption capacity with respect to the iodide radionuclide. An exception is the sample Z2M20, whose sorption indicators are lower than those of the natural sample and do not fit into the general trend. The reasons for such behavior of this sample are not entirely clear and are most likely also associated with structural transitions of the clinoptilolite.

It was found that the sorption equilibrium for almost all acid-activated samples is achieved within 14 h of the experiment. For the natural zeolite sample, the onset of sorption equilibrium was revealed within 20 h of the experiment. The most intensive sorption of iodide-131 occurs on the samples of Z1M20, Z1M90, and Z2M90; the time to achieve sorption equilibrium is 4 h.

#### 3.1.2. pH Dependence of Iodide Sorption

Additional sorption experiments in a wide pH range showed the presence of a pH dependence. The most effective sorption of iodide-131 occurs in a strongly acidic environment (Table 4, Figure 7). The maximum values of the sorption indices for the sample Z1M90 (R = 99.81%,  $K_d$  = 70,700 mL/g) were found at a pH of 2.

R, % Sample Kd, mL/g pH<sub>initial</sub> Z1M90 pH-2 2.26 99.81 52,600 Z1M90 pH-4 4.2499.35 15,337 Z1M90 pH-6.35 97.04 3254 -6 Z1M90 pH-8 8.20 88.48 768 Z1M90 pH-10 10.15 530 84.13 100 95 90 85 Sorption rate R, % 80 75 70 65 60 55 50 500 1000 2500 0 1500 2000 Time, min

Table 4. pH dependence of iodide-131 sorption onto the studied sorbents.

Figure 7. Kinetic curves of sorption of the radioisotope iodide-131 on zeolite sample activated with 1 M nitric acid at 90 °C at different pH values.



Thus, the most suitable conditions for radioiodide capture are solutions with a pH of about 2–3, since in the presence of a large excess of  $OH^-$ , the sorption properties of acid-activated samples are significantly reduced. At pH < 2, there is a risk of aluminum leaching, which can lead to the complete dissolution of the clinoptilolite.

#### 3.1.3. Iodide Desorption

Experiments on the desorption of iodide with distilled water from acid-activated sample Z1M90, after reaching equilibrium during the determination of sorption characteristics, were also conducted. The degree of desorption was about 2.5% (Figure 8), which indicates a physicochemical bond between iodide and the clinoptilolite or the newly formed amorphous aluminosilicate phase.



Figure 8. Kinetic curve of iodide-131 desorption onto the sample Z1M90.

Moreover, there may be several proposed mechanisms for the adsorption of iodide anions. After acid treatment, the zeolite is in the H-form, the interaction of anions with the surface may include electrostatic attraction to protonated silanol groups but may be associated with specific interactions with the formation of van der Waals bonds with certain active centers, including silanol groups and siloxane groups on the surface. This assumption was also noted in other works [18,19], where it was noted that the sorption of both cations and anions on acid-activated zeolites can be associated with the interaction of ions with silanol groups and bridging hydroxyl groups. As the acid treatment results in the formation of a new amorphous aluminosilicate phase, it can be assumed that the iodide partially interacts with it.

### 4. Conclusions

The following conclusions can be drawn from the experiment on natural zeolite treatment with nitric acid of various concentrations. The acid activation of natural zeolite results in the dealumination of the tetrahedrons in the clinoptilolite structure, forming an amorphous aluminosilicate phase, which is characterized by high values of the specific surface area and microporosity. The clinoptilolite structure itself is quite stable and is preserved even under strong acid action. The morphology of the particles also does not undergo significant changes. However, depending on the intensity of acid treatment, the properties of the zeolite change. The cation exchange capacity decreases, and the hydrophobicity increases simultaneously with the degree of the dealumination of the

clinoptilolite. With an increase in the acid concentration and the treatment temperature, the values of the sorption characteristics with respect to radioiodide also increase. The maximum sorption values are typical for the sample treated with 1 M nitric acid solution at 90 °C. However, with more intensive treatment, the sorption value decreases sharply. This is due to the fact that, when aluminum (and partially silicon) is washed out of the clinoptilolite structure, the position of the sorption centers and the charge value change, as well as the formation of silanol groups and bridging hydroxyl groups on the surface of the particles. With an increase in the concentration of nitric acid, at a certain point, critical changes appear to occur in both the clinoptilolite itself and the amorphous phase, which

Considering the features of sorption of the iodide radionuclide, it is worth noting that a strong pH dependence is observed. The best sorption was observed at pH 2. Thus, the most suitable conditions for capturing radioiodide are solutions with a pH value of about 2–3, since in the presence of a large excess of  $OH^-$ , the sorption properties of acid-activated zeolite are significantly reduced. At pH < 2, there is a risk of the complete dissolution of the zeolite.

sharply worsens the sorption properties.

Desorption with distilled water amounted to only 2.5%. The conducted experiments showed that iodide radionuclide has a physicochemical bond with the clinoptilolite. The absence of a correlation between the sorption of the iodide radionuclide and the specific surface area indicates the absence of a connection between I<sup>-</sup> and micropores. It is assumed that the main mechanism of sorption for the iodide radionuclide in an acidic environment is the interaction with silanol and bridging hydroxyl groups, formed as a result of acid treatment on the surface of the clinoptilolite particles and the amorphous aluminosilicate phase.

Thus, the conducted experiments have shown the fundamental possibilities of using acid-activated zeolites for iodide sorption. It is planned to continue this work and conduct experiments using wastewaters from enterprises.

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