Study of the Sorption Properties of Natural Zeolite in Relation to Indium(III) and Gallium(III) Cations on the Model Systems

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Abstract: This paper presents the systematic studies of the sorption capacity of natural zeolite with respect to In^{3+} and Ga^{3+} cations in the model systems "natural zeolite–In^{3+}–H_2O" and "natural zeolite–In^{3+}–Ga^{3+}–H_2O", while varying a number of the main process factors. The patterns of sorption of In^{3+} and Ga^{3+} cations by the natural zeolite of the Shankanai deposit are revealed, depending on the zeolite vs. solution ratio, temperature, and time. It is shown that the sorption of In^{3+} cations by natural zeolite can be controlled by the process duration. The longer the process, the less the sorption by natural zeolite. It has been found that the sorption of In^{3+} cations in the "natural zeolite–In^{3+}–Ga^{3+}–H_2O" model system depends on the amount of zeolite and temperature, and the sorption of Ga^{3+} cations depends on the temperature and time. The physicochemical characteristics of the spent sorbents confirm the sorption of the cations, present in the systems under study.

Keywords: sorption; natural zeolite; indium cations; gallium cations; degree of sorption; sorption capacity

1. Introduction

The production of elemental phosphorus by electrothermal processing of phosphates is associated with the formation of various phosphorus-containing industrial wastes, including the HPV cottrel "milk", which is a hard-to-destroy emulsion of variable composition, stabilized by highly active pollutants [1]. Its processing is difficult for a number of reasons. As a result, liquid phosphorus wastes are stored in settling tanks, and significant amounts of commercial phosphorus are lost. The presence of cottrel "milk" in phosphorus plants, operating on sintering raw materials, along with phosphorus and Ag, In, Ga and cyan-containing components, makes it possible to consider it as a cheap raw material source for obtaining rare and precious metals and ferrocyanides from a number of metals, which are not produced in the Republic of Kazakhstan, but are widely used [2,3]. Gallium and indium (Ga, In) are used in the electronic industry as conductors, superconductors, optical and magnetic materials, etc. There is practically no production of the above metals in Kazakhstan, they are purchased from abroad. From the analysis of the scientific and patent literature, it has been revealed that, firstly, the production of indium and gallium is a laborious, multi-stage process, often carried out at elevated temperatures and pressures, using expensive organic reagents. Secondly, there is a very limited number of published works on the extraction of these metals from mineral phosphorus-containing raw materials, including phosphorus production waste.

Taking into account the significant reserves of phosphorus production waste in Kazakhstan, the development of new methods for extracting a number of precious metals on the basis of domestic raw materials is very relevant.

In recent years, sorption methods have been widely used to purify the aqueous media, industrial effluents, and industrial wastes, where natural materials with high sorption properties, in particular zeolites, are used as sorbents [4].

The efficiency of the practical use of zeolite as a sorption raw material is stipulated by the peculiarities of the crystal structure, which consists of a three-dimensional structure

of SiO_4 and AlO_4 tetrahedrons with channels, ranging in size from 3 to 20 Å, and has a negative charge [5]. A feature of the structure of the silicon–aluminum–oxygen frameworks of zeolites is the presence of a system of regular channels and communicating cavities, capable of holding ions, atoms and molecules of the substances, whose size corresponds to that of free space. Alkaline and alkaline-earth cations, which compensate for the negative charges of the aluminum–oxygen tetrahedrons of the framework, are located in these voids of the crystal lattice, occupying only a relatively small part of their volume. Depending on the temperature, zeolites are able to absorb water and many harmful substances (radionuclides, heavy metals, pesticides, nitrates). The results of a comparative study of copper ion extraction from aqueous solutions, using a natural zeolite of the Honguruu deposit (Yakutia), are presented in the work [6]. The high selectivity in ion exchange is associated with the ratio of the sizes of the exchanged ions, and the sizes of the cavities in the structure of zeolites [7].

The sorption capacity of zeolites from the Shankanai deposit (the Republic of Kazakhstan, the Almaty region) with respect to NH^{4+} ions, heavy and nonferrous metals has been shown in a number of works [8–10]. Natural zeolite from the Shankanai deposit is promising for the purification of aqueous media from iron ions [11,12], zinc, copper, and lead [13]. The possibility of groundwater purification from the ions of heavy and nonferrous metals with natural zeolite from the Shankanai deposit has been experimentally confirmed [13]. It has been established that, under static conditions, the degree of purification from zinc, copper, and lead cations is 3.75–4.0 times higher than that under dynamic ones. Indium is quite effectively extracted by the sorption method from the industrial wastes of mining and metallurgical enterprises [14]. According to information in the scientific literature, it can be assumed that the natural zeolite, during the purification of cottrel "milk"(CM) filtrate, will sorb the In^{3+} and Ga^{3+} cations present in the liquid phase of the CM. In this regard, systematic studies of the sorption capacity of natural zeolite with respect to the In^{3+} and Ga^{3+} cations have been carried out depending on a number of main process factors (temperature, time, and component ratio) in the "natural zeolite–In^{3+}–H_2O"and "natural zeolite–In^{3+}–Ga^{3+}–H_2O" model systems.

Moreover, the purpose of this work describes the extraction of rare metals (In^{3+} and Ga^{3+}) from phosphorus production wastes (cottrel"milk"), using natural zeolite from the Shankanai deposit.

2. Materials and Methods

For the experiment in this work, we used zeolite from the Shankanai deposit, with the content of the main components, wt.%: K_2O—1.38; Na_2O—0.95; Fe_2O_3—0.16; Al_2O_3—10.81; CaO—2.32; MgO—0.93; SiO_2—65.28, and losses upon ignition—18.15. Natural zeolites of the Shankanai deposit (the Republic of Kazakhstan, the Almaty region) are composed of up to 80% geylandite-clinoptilolite [15]. The main properties of the porous structure of natural zeolite: sorption exchange capacity (SEC) for iodine—3.67 mg-eq/g, EC of the cation exchanger—0.997 mg-eq/g, SEC of the anion exchanger—0.4985 mg-eq/g, total pore volume—0.07 g/cm^3 [16,17].

The specified concentration of cations was created by introducing the calculated amount of $In(NO_3)_3·3H_2O$ and $Ga(NO_3)_3·3H_2O$ salts into the solution. The initial and residual concentration of metals in the filtrate after their sorption was determined on a Perkin ElmerA Analyst 400 atomic absorption spectrometer (AAS) (PerkinElmer, Waltham, MA, USA). To quantify the multifactorial experiment, we used the method of mathematical planning (orthogonal rotatable 3-factor experiment of the 2nd order) [18–20].

The variable factors of the process in this study were: X_1–the consumption rate of natural zeolite, i.e., the "natural zeolite (T): indium-, gallium-containing solution(L)"ratio, from 0.5 to 3 g per 100 g; X_2—temperature, from 25 to 60 °C, andX_3—time, which varied from 5 to 60 min (Table 1).

Table 1. Plan center coordinates, variation levels.

Coded Value	Natural Value		
	X_1, S:L, g	X_2, T (°C)	X_3, τ (min)
Upper level (+1)	2.5	53	49
Plan center-Level Zero (z_i^0)	1.75	42.5	32.5
Lower level (−1)	1.0	32	16
Axis spacing (Δz_i)	1.5	21	33
Axial distance (+1682)	3.0	60	60
Axial distance (−1682)	0.5	25	5

The constant factors were the concentrations of the In^{3+} and Ga^{3+} cations (100 mg/L), pH 4.

Sorption extraction of Ga(III) and In(III) cations by zeolite was carried out in a thermostat upon stirring. The sample was weighed on an analytical balance to the exactness of the fourth decimal place, quantitatively transferred into a 250 ml volumetric flask, and filtered. In the resulting filtrate, the content of the In^{3+} and Ga^{3+} cations was determined. The degree of sorption (*R*, %) was calculated by Formula (1):

$$R = \frac{Co - Cp}{Co} \cdot 100\% \tag{1}$$

where *Co* is the initial concentration of metal ions in the solution, mg/L; *Cp* is the concentration of metal ions in the solution after the interaction with the sorbent, mg/L.

The determined parameter was the residual content of In^{3+}/Ga^{3+} (mg/L) in the systems under study after the sorption—$Y_{In3+/Ga3+}$.

The experiment planning area was set, using the inequality:

$$-1 < x_i < +1 \tag{2}$$

where i = 1, 2, ... n. Here x = −1 is the minimum value of the variable factor; x = +1 is the maximum value of the variable factor, i.e., $x_{mid} = (x_{min} + x_{max})/2$.

The values of variables from the natural form to the encoded one were transformed according to the formula:

$$X_i = z_i - z_i^0 / \Delta z_i \tag{3}$$

where z_i—the value of the factors in natural terms at the lower or upper levels; z_i^0—the value of the factors at zero level (in the plan center); Δz_i—an interval of variation along the axis.

The specific values of the planning factors and the results of the experiments are shown in Table 2.

Using computer processing of the experimental data, the following regression analysis was carried out. The accuracy of the results (dispersion of reproducibility) was determined by the formula:

$$S_{res}^2 = \frac{\sum_{i=1}^{m} (y_i - y_i)^2}{m - 1} \tag{4}$$

To identify the zeolitesamples (before and after the sorption) the following physical research methods were used: scanning electron microscopy (SEM) JEOL brand "JXA-8230" (JEOL, Tokyo, Japan), IR spectroscopic analysis on a SpecordM-80 spectrophotometer in the spectral region 400–4000 cm^{-1}, thermal analysis (DTA) was filmed with a Shimadzu DTG-60 (Shimadzu Scientific Instruments, Inc., Columbia, SC, USA), Philips FW 1700 X-ray diffraction analysis (XRD) (Amsterdam, The Netherlands).

Table 2. The output parameters of the experiment on the sorption of the In(III) cations in the "natural zeolite-In^{3+}-H$_2$O" system.

#	Coded Value			Parameters			Results	
							In(III)	
	Z_1, S:L (g)	Z_2, T (°C)	Z_3, τ (min)	X_1, S:L (g)	X_2, T (°C)	X_3, τ(min)	Residual Content In^{3+} (mg/L)	Degree of Sorption (%)
1	−1	−1	−1	1:100	32	16	69.0	31.0
2	+1	−1	−1	2.5:100	32	16	48.0	52.0
3	−1	+1	−1	1:100	53	16	36.0	64.0
4	+1	+1	−1	2.5:100	53	16	54.0	46.0
5	−1	−1	+1	1:100	32	49	62.0	38.0
6	+1	+1	+1	2.5:100	32	49	76.0	24.0
7	−1	+1	+1	1:100	53	49	71.0	29.0
8	+1	0	+1	2.5:100	53	49	79.0	21.0
9	−1.682	0	0	0.5:100	43	33	86.0	14.0
10	+1.682	0	0	3:100	43	33	48.0	52.0
11	0	−1.682	0	1.75:100	25	33	75.0	25.0
12	0	+1.682	0	1.75:100	60	33	67.0	33.0
13	0	0	−1.682	1.75:100	43	5	58.0	42.0
14	0	0	+1.682	1.75:100	43	60	38.0	62.0
15	0	0	0	1.75:100	43	33	50.0	50.0
16	0	0	0	1.75:100	43	33	52.0	48.0
17	0	0	0	1.75:100	43	3	58.0	42.0
18	0	0	0	1.75:100	43	33	73.0	27.0
19	0	0	0	1.75:100	43	33	55.0	45.0
20	0	0	0	1.75:100	43	33	59.0	41.0

3. Results and Discussion

3.1. Study of the Sorption Process in the "Zeolite–In^{3+}–H$_2$O" Model System

The study of the sorption capacity of natural zeolite with respect to indium (III)ions was carried out on the "natural zeolite–In^{3+}–H$_2$O"model system according to the planning matrix (Table 1).

The results obtained are presented in Table 2, the processing of which has made it possible to obtain the regression Equation (5), describing the effect of the (S:L) ratio, temperature, and time on the residual content of the In^{3+} cations (Y_{In}, mg/L), as well as the degree of their sorption in the system under study at the end of the process.

As a result of processing the experimental data, the regression Equation (5) wasobtained, which makes it possible to calculate the residual content of the In(III) cations (Y_{In}, mg/L) in the solution at the end of the sorption process by the zeolite, with various combinations of the main factors:

$$Y_{In} = 62.811 + 12.704X_3 \tag{5}$$

The adequacy of the regression equation has been checked by the Fisher criterion by the ratio of variances:

$$F = \frac{S_{res}^2}{S_{repr}} \tag{6}$$

In this case, the residual variance is equal to:

$$S_{res}^2 = \frac{\sum_{i=1}^{N} (y_i - y_i)^2}{N - 1} \tag{7}$$

where l is the number of significant coefficients in the regression equation, equal to 5.

It has been found that F < F1-p(f_1,f_2) = Y_{In} 4.294 < 4.699, i.e., the equation adequately describes the experiment.

An analysis of the regression Equation (5), which describes the sorption of the In^{3+} cations by natural zeolite, has shown that the process is determined by only one factor:time. As time increases, the residual content of the In^{3+} cations in the liquid phase of the system increases; the sorption degree decreases due to the desorption of the absorbed indium from zeolite into the liquid phase of the system (Figure 1c).
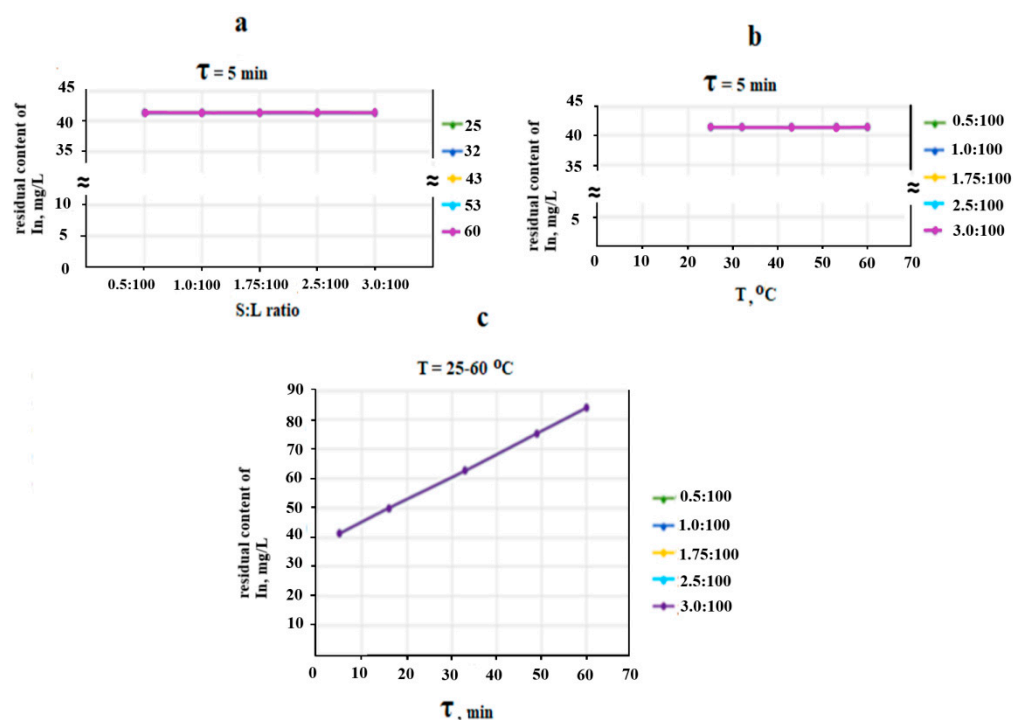
Figure 1. Influence of the studied factors on the residual content of In^{3+} in the liquid phase of the "natural zeolite–In^{3+}–H_2O"system.(**a**) S:L ratio; (**b**) temperature, °C; (**c**) time, min.

The sorption curves of indium on the amount (the S:L ratio) of the sorbent and temperature have a rectilinear form, and are located parallel to the abscissa axis (Figure 1a,b). Both factors under study do not affect the process of sorption of the In^{3+} cations by natural zeolite. A high degree of sorption of theIn^{3+} ions, which practically remains constant with an increase in time, is achieved already within 5–10 min and approaches 58.6% at any zeolite:solution ratio.

An analysis of the obtained data regarding the sorption of the In^{3+} cations by natural zeolite has shown that the sorption of indium can be controlled by the process time; the longer the process, the less it is sorbed by natural zeolite.

3.2. Study of the Sorption Process in the "Zeolite–In^{3+}–Ga^{3+}–H_2O" Model System

Since the In^{3+} and Ga^{3+} cations are simultaneously present in the liquid phase of the CM, the study of a natural zeolite sorption capacity with respect to these ions under the conditions of their simultaneous presence has been carried out on the "natural zeolite–In^{3+}–Ga^{3+}–H_2O"model system according to the planning matrix (Table 2), with the same values of variables (S:L; T, °C; τ, min). The process of sorption of the cations has been carried out under the conditions of constant and equal concentrations of the In^{3+} and Ga^{3+} cations (100 mg/L) at pH 4.

The results are presented in Table 3, the processing of which made it possible to obtain the regression Equations (3) and (4), describing the effect of the zeolite amount, temperature, and time on the residual content of the In^{3+} (Y_{In} mg/L) and Ga^{3+} (Y_{Ga} mg/L) cations, as well as on the degree of their sorption in the examined system at the end of the process.

The sorption of the In^{3+} cations in the presence of the Ga^{3+} ions, depending on the (zeolite:solution) ratio, temperature and time of the process, is described by an adequate (F < F1-p($f_1.f_2$) = Y_{In} 4.471 < 4.699) equation:

$$Y_{In} = 73.851 - 13.986X_1 - 9.594X_2^2 \tag{8}$$

Table 3. Planning matrix and results of the experiment of the cation sorption in the "natural zeolite–In^{3+}–Ga^{3+}–H$_2$O" system.

№	Parameters			Results			
				In(III)		Ga(III)	
	X_1, S:L	X_2, T (°C)	X_3, τ(min)	Residual Content In^{3+} (mg/L)	Degree of Sorption (%)	Residual Content Ga^{3+} (mg/L)	Degree of Sorption (%)
1	1:100	32	16	76	24	63	37
2	2.5:100	32	16	49	51	53	47
3	1:100	53	16	81	19	41	59
4	2.5:100	53	16	51	49	50	50
5	1:100	32	49	87	13	59	41
6	2.5:100	32	49	58	42	53	47
7	1:100	53	49	82	18	56	44
8	2.5:100	53	49	61	39	57	43
9	0.5:100	43	33	80	20	52	48
10	3:100	43	33	28	72	54	46
11	1.75:100	25	33	36	64	61	39
12	1.75:100	60	33	51	49	43	57
13	1.75:100	43	5	60	40	63	37
14	1.75:100	43	60	62	38	50	50
15	1.75:100	43	33	73	27	75	25
16	1.75:100	43	33	70	30	70	30
17	1.75:100	43	33	58	42	58	42
18	1.75:100	43	33	71	29	78	22
19	1.75:100	43	33	72	28	74	26
20	1.75:100	43	33	73	27	71	29

An analysis of the regression Equation (8) has shown that only the coefficients b_0, b_1 and b_2 (S:L, T °C) were significant. The residual content of the In(III) cations after the sorption by natural zeolite is a function of the sorbent rate (X_1) and temperature (X_2). The numerical value of the X_1 coefficient is higher than that of the X_2 coefficient, which indicates its greater influence on the output parameter. At the same time, the negative value at the X_1 coefficient in the regression Equation (8) shows that an increase in the consumption of zeolite will increase the sorption of the indium cations.

An analysis of the sorption curves of the In^{3+} cations in the presence of the Ga^{3+} cations has shown that the sorption curves in the block for each of the studied factors, regardless of the other two factors, are similar to each other. We present a graphical representation for each factor in one Figure 2.
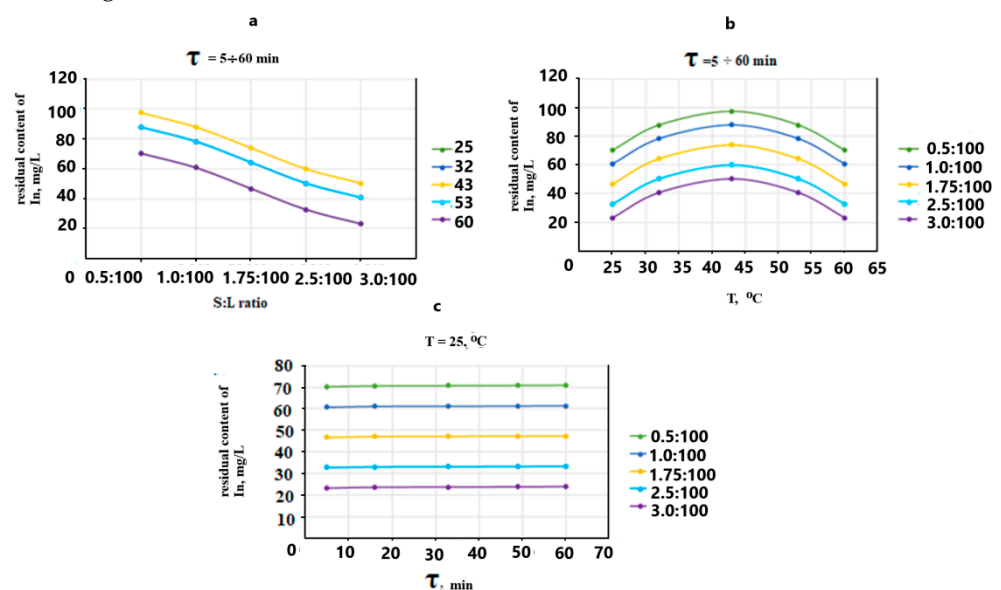

Figure 2. Influence of the studied factors on the residual content of In^{3+} in the liquid phase of the "natural zeolite–In^{3+}–Ga^{3+}" system. (**a**) zeolite norm (S:L); (**b**) temperature, °C; (**c**) time, min.

Figure 2a shows that, in the entire time interval under study for all temperatures, the residual content of the In^{3+} cations in the liquid phase of the system under study decreases with an increase in the zeolite amount, and, accordingly, the sorption degree increases. For example, at 43 °C and the sorbent consumption of 0.5 g per 100 g of the solution, the degree of sorption of the In^{3+} cations is 0.6%, at a consumption of 1 g of the sorbent per 100 g of the solution, the sorption degree increases up to 11%, and at a rate of 3 g per 100 g of the solution, up to 50%.

The second significant factor affecting the sorption of the In^{3+} cations is temperature (X_2). In the regression Equation (2), the effect of temperature is represented by the negative quadratic term. The sorption curves of indium (III) in the entire studied time interval for all S:L ratios are extreme in nature, with a pronounced maximum in the region of 43 °C (Figure 2b). The residual content of the In^{3+} cations increases with an increase in the temperature up to 43 °C, and decreases above this temperature; the degree of their sorption decreases and then increases. So, at S:L = 0.5:100 at 25 °C, the sorption degree is 30%, at 32 °C-11%, at 43 °C-0.05%, and at 60 °C-29.5%. The appearance of a maximum in the indium sorption curves may be due to the physical adsorption of a part of the In^{3+} cations, and may also be a consequence of the competing effect between the cations for the vacant exchange centers in the zeolite structure, or the tendency of the system to equilibrium.

The sorption curves of the indium (III) cations, from time to time, have a rectilinear character and are located parallel to the abscissa axis (Figure 2c). The time factor does not affect the process of sorption of the In^{3+} cations by natural zeolite. Thus, a high degree of their sorption is already achieved in 5 min and remains almost constant.

The least of the In^{3+} cations in the presence of the Ga^{3+} ions, regardless of time, is sorbed in the range of 40–45 °C at the S:L ratio = 0.5:100 (Ks = 0.8%), and the most of all is sorbed at 25 and 60 °C, at S:L = 3:100 (Ks = 71%).

As for the sorption of the Ga^{3+} cations in the presence of the In^{3+} ions, the process is described by the Equation (9):

$$Y_{Ga} = 72.649 - 9.218X_2{}^2 - 12.709X_3{}^2 \qquad (9)$$

The adequacy of the resulting regression equation is confirmed by the inequality $F < F_{1-p}(f_1, f_2) = Y_{Ga}$ 4.642 < 4.699.

From the resulting regression Equation (9) it can be seen that, as in the case of the indium (III) sorption, three coefficients b_0, $b_2{}^2$ and $b_3{}^2$ (T, °C and time) have turned out to be significant.

The comparison of the coefficient values of the regression Equation (9) has shown that the process time has the greatest influence on the output parameter, but the negative sign at the X_3 coefficient shows that an increase or decrease in the value of this factor will not increase the sorption capacity of natural zeolite with respect to the Ga^{3+} ions. The same will be the case for the coefficient relating to the process temperature, which has a negative sign ($X_2{}^2$).

An analysis of the sorption curves of the Ga^{3+} cations in the presence of the In^{3+} cations has shown that, as in the case of the sorption of the In^{3+} cations, in each block of the studied factor, regardless of the other two factors, the sorption curves have the same character. Therefore, as an example, one Figure is given for each process factor (Figure 3).

The kinetic curves of the sorption of the Ga(III) cations on the sorbent amount for all temperatures and in the entire studied time interval are rectilinear (Figure 2a). As seen in this Figure, the norm of the sorbent has no effect on the process of sorption of the Ga^{3+} cations by natural zeolite. For example, in 5 min process at S:L = (0.5–3):100 and 25 °C, 63.3% is sorbed.
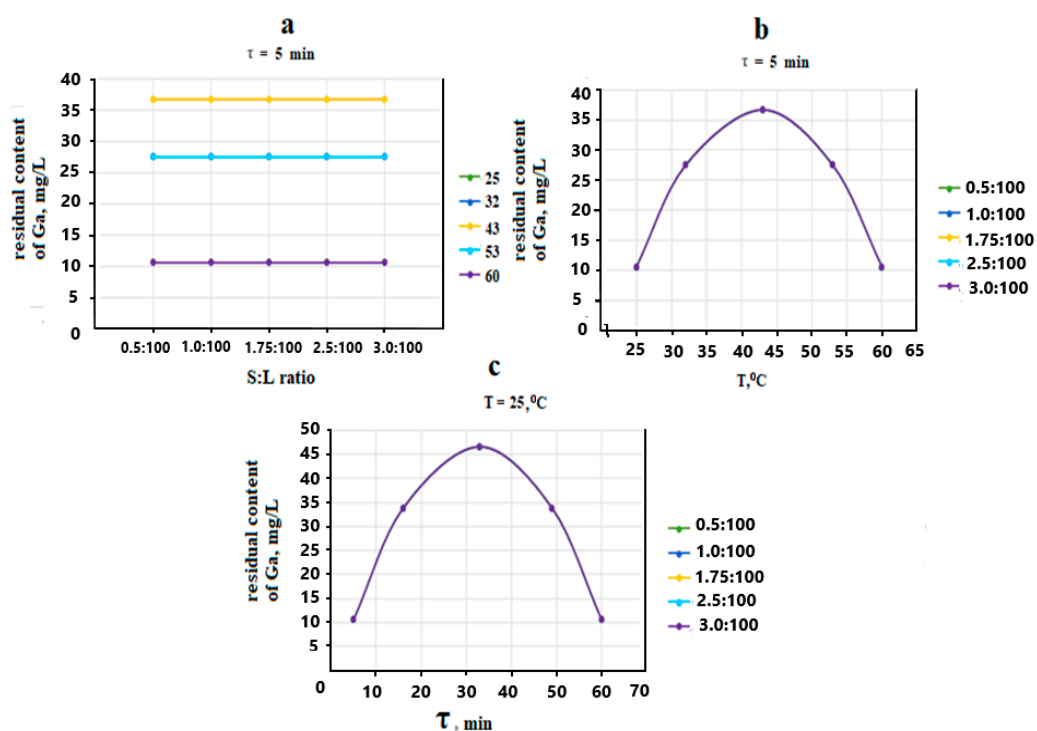
Figure 3. The influence of the studied factors on the residual content of Ga^{3+} in the liquid phase of the "natural zeolite–In^{3+}–Ga^{3+}" system. (**a**) the S:L ratio; (**b**) temperature, $°C$; (**c**) time, min.

The temperature has a significant effect on the sorption capacity of natural zeolite with respect to the gallium (III) cations. As seen in Figure 3b, the sorption curves are extreme in nature with a maximum in the temperature region of 43 $°C$, similar to the In^{3+} sorption curves (Figure 2b). As the temperature rises to the specified value, the residual content of gallium in the solution increases and then decreases. Accordingly, the degree of sorption decreases, then increases. For example, 90% Ga^{3+} is sorbed at 25 $°C$, 63.5% Ga^{3+} at 43 $°C$, and 90% Ga^{3+} at 60 $°C$, over the entire time interval and the S:L ratios under study.

The sorption curves of the Ga(III) cations versus time, as well as temperature, are extremal in nature, with a maximum at 33 min (Figure 3c). Accordingly, with an increase in time up to the specified value, the degree of sorption decreases and then increases. So, for all S:L ratios at 25 $°C$ for 5 min 90.5% Ga^{3+} is sorbed, in 33 min—51.9% and in 60 min—90.5%.

The minimum degree of sorption of the Ga^{3+} cations, regardless of the S:L ratio, can be obtained at 43 $°C$ in 33 min (K_s = 53%), and the highest degree of sorption for all S:L ratios at 25 $°C$ for the 10 and 60 min process (K_s = 90%). The influence of the nature of the cations present in the system affects the sorption of the In^{3+} ions. At a consumption rate of zeolite of 3 g per 100 g of the indium-and gallium-containing solution and 60 $°C$ for 60 min, the maximum amount of the In^{3+} (K_s = 80%) and Ga^{3+} (K_s = 90%) cations is sorbed, and at S:L equal to 0.5:100 and 43 $°C$ (1–2)% In^{3+} and (48–50)% Ga^{3+}.

Based on the fact that in this work, natural zeolite is used to concentrate the In^{3+} and Ga^{3+} cations in the liquid phase of the cottrel "milk" by purifying it from all other impurity ions, for example, such as Ca, Mg, Si, K, as well as PO_4^{3-} anions-, SO_4^{2-}, etc., located in the CM filtrate, the optimal conditions are those that correspond to the minimum absorption of all cations present in the system.

3.3. Physicochemical Study of Zeolite, Isolated after the Sorption of the Trivalent Cations

To elucidate the structural changes in zeolite occurring during the sorption of the In^{3+} and Ga^{3+} cations, a physicochemical analysis of zeolites, isolated from the studied systems under the conditions of their maximum and minimum absorption, has been carried out.

A comparative analysis of the IR spectrum of natural zeolite (Figure 4a) with the IR spectra of zeolites, isolated from the "natural zeolite–In^{3+}–H_2O" and "natural zeolite–In^{3+}–Ga^{3+}–H_2O"systems under the conditions of the most complete absorption of the cations (Figure 4b–d) has shown that, after the sorption of cations in the IR spectra, the frequency, characterizing the region of stretching vibrations of water 3444.7 cm^{-1}, broadens and its intensity decreases, and the maximum shifts: 3444.7 $cm^{-1} \rightarrow$ 3433.2 $cm^{-1} \rightarrow$ 3437.1 $cm^{-1} \rightarrow$ 3438.2 cm^{-1}.
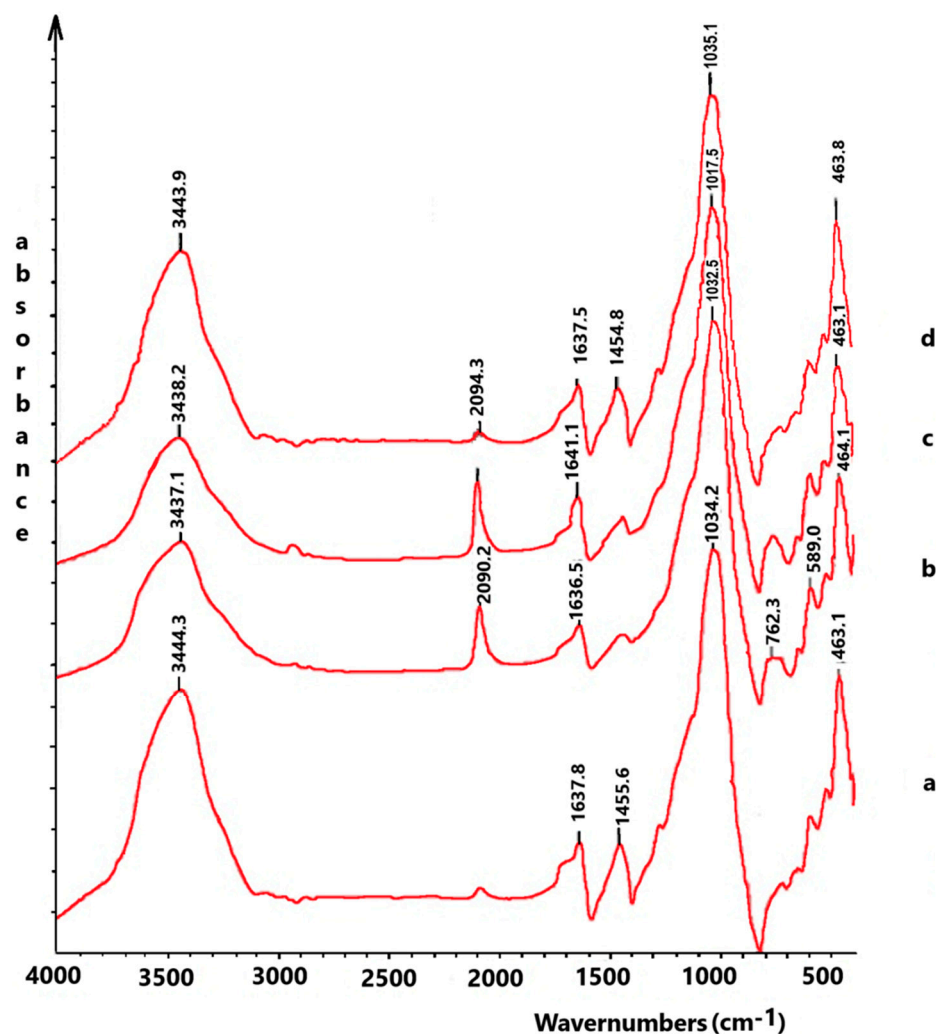

Figure 4. TheIR spectra of zeolites. Zeolites: a—natural; with the maximum content of cations: b and c—In^{3+} and Ga^{3+}; d—with the minimum content of the In^{3+} and Ga^{3+} cations.

In the water deformation vibrations, the transition of the absorption bands presents in the spectrum of natural zeolite 1637.8 cm^{-1} and 1455 cm^{-1} (Figure 4a) into one frequency in the region of 1641.1 . . . 1636.6 cm^{-1} and this is observed in the spectrum of metal-containing zeolites (curves b−d), indicating the sorption of the cations present in the systems. The strengthening of its intensity and the shift to the high-frequency region 1637.8 $cm^{-1} \rightarrow$ 1638.4 $cm^{-1} \rightarrow$ 1636.5 $cm^{-1} \rightarrow$ 1641.1 cm^{-1} is due to the sorption of the In^{3+} and then the sorption of the In^{3+} and Ga^{3+} cations in the "natural zeolite–In^{3+}–Ga^{3+}–H_2O" system.

In the IR spectra of the metal-containing zeolites, a new frequency appears in the high-wave region 2094.3–2090.2 cm^{-1}, and the new low-frequency components in the region 760 . . . 762.3 cm^{-1} and 589 . . . 590 cm^{-1}, the intensity of which increases with increasing diversity types of the sorbed cations in the system, which indicates an increase in the vibrations of the Me–O bonds [21], and is a consequence of the formation of the In–O bond in zeolite, and also the Ga–O bond in the indium-gallium-containing zeolite.

As for the IR spectrum of zeolite isolated from the "natural zeolite–In^{3+}–Ga^{3+}" system under the conditions of the lowest absorption of cations (Figure 4d), its spectrum practically approaches the IR spectrum of natural zeolite (Figure 4a). This suggests that, under these conditions, natural zeolite practically does not adsorb cations.

An X-ray phase analysis has shown a number of intense diffraction maxima: 6.71 Å (22.3%); 4.0 Å (15.4%); 3.4 Å (20.4%); 3.3 Å (100%); 2.9 Å (38.2%); 2.8 Å (26.1%); 2.7 Å (14.2%); 1.8 Å (12.8%) and 1.7 Å (6.5%), which are registered on the X-ray pattern of natural zeolite (Figure 5a).
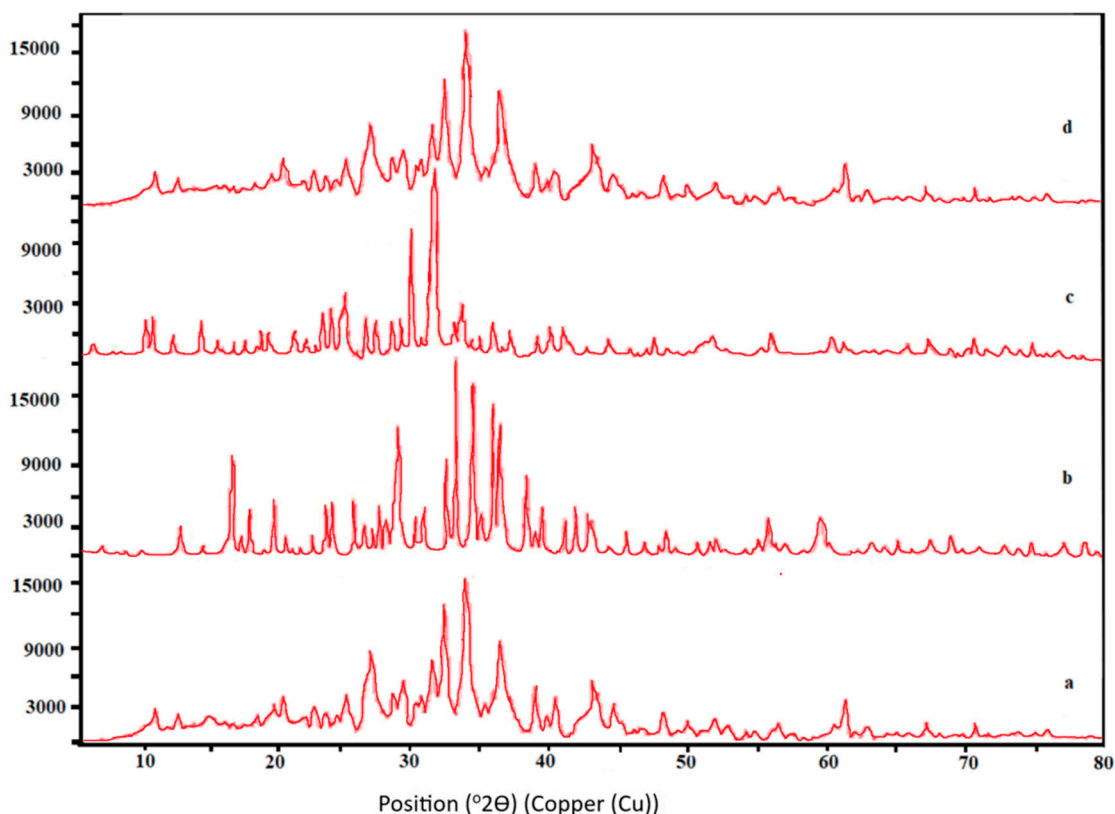

Figure 5. TheX-ray patterns of zeolites. Zeolites: a—natural; zeolite with the maximum content of the cations: b—In^{3+}; c—In^{3+} and Ga^{3+}; d—zeolite with the minimum content of the In^{3+} and Ga^{3+} cations.

In the X-ray pattern of the zeolite, isolated from the "natural zeolite–In^{3+}–H_2O" system (Figure 4b), the diffraction maxima with dα = 4.1 Å (23.5%); 4.0 Å (18%); 3.3 Å (100%); 2.9 Å (1%); 2.8 Å (25.3%); 1.8 Å (11%) and 1.7 Å (8%) are identical to the similar reflections fixed on the X-ray diffraction pattern of natural zeolite (Figure 5a). It is necessary to note the coincidence in the positions of such diffraction maxima as 5.1 Å (18.9%); 4.66 Å (20%); 3.9 Å (58%); 3.8 Å (29.3%); 3.6 Å (16.1%); 3.4 Å (46.3%) and 3.0 Å (54.3%) in the studied and natural zeolites, but in this case, their intensities are redistributed. Thus, for these reflections, the intensity of the diffraction pattern of zeolite after the sorption of the In^{3+} cations increases by 8.9%, respectively; 9.2%; 6.3%; 19.2%; 4.8% and 18.6%. At the same time, the diffraction maxima with dα = 3.7; 2.7; 2.3; 2.0; 1.89 Å are not recorded on the X-ray pattern of the studied zeolite, fixed on the X-ray pattern of natural zeolite, but a new intense diffraction maximum appears with dα = 3.2 Å (73.7%). Moreover, the X-ray diffraction pattern of the zeolite, isolated from the "natural zeolite–In^{3+}–H_2O" system (Figure 5b) becomes more complicated compared to the X-ray diffraction pattern of the natural one (Figure 5a). The revealed changes in the X-ray diffraction pattern of the indium-containing zeolite are due to the sorption of trivalent In.

In the X-ray pattern of the zeolite, isolated from the "natural zeolite–In^{3+}–H$_2$O" system (Figure 5b), the diffraction maxima with dα = 4.1 Å (23.5%); 4.0 Å (18%); 3.3 Å (100%); 2.9 Å (1%); 2.8 Å (25.3%); 1.8 Å (11%) and 1.7 Å (8%) are identical to the similar reflections fixed in the X-ray diffraction pattern of natural zeolite (Figure 5a). It is necessary to note the coincidence in the positions of such diffraction maxima as 5.1 Å (18.9%); 4.66708 Å (20%); 3.9 Å (58%); 3.8 Å (29.3%); 3.6 Å (16.1%); 3.4 Å (46.3%) and 3.0 Å (54.3%) in the investigated and natural zeolites, but in this case, their intensities are redistributed. Thus, for these reflections, the intensity of the diffraction pattern of zeolite after the sorption of the In^{3+} cations, increases by 8.9%, respectively; 9.2%; 6.3%; 19.2%; 4.8% and 18.6%. Moreover, the X-ray pattern of the zeolite, isolated from the "natural zeolite–In^{3+}–H$_2$O" system (Figure 5b) becomes more complicated in comparison with the X-ray pattern of the natural one (Figure 5a). The revealed changes in the X-ray diffraction pattern of the indium-containing zeolite are due to the sorption of the trivalent In cations.

An analysis of the X-ray diffraction pattern of the zeolite, isolated from the "natural zeolite–In^{3+}–Ga^{3+}" system (Figure 5c), has shown that the height of the most intense diffraction maximum with dα = 3.3 Å (100%), fixed on the diffraction patterns of natural and two previous zeolites, decreases by 31.8%. New intense peaks with dα = 4.2 Å (17.5%) are registered in the X-ray pattern of the indium-gallium-containing zeolite; 3.7 Å (14%); 2.7 Å (7.2%) and a very strong diffraction maximum of 3.1 Å (100%). The reflections with dα = 4.0 Å (1.9%); 3.80 Å (29.3%) and 3.0 Å (54.3%), fixed in the diffraction pattern of the indium-containing zeolite, are not prescribed. Coinciding with the diffraction patterns of the investigated indium-containing zeolites the positions of a number of the diffraction maxima, such as 4.6 Å; 4.1 Å; 3.9 Å; 3.6 Å; 3.4 Å; 3.2 Å; 2.9 Å; 2.8 Å and 2.5 Å after the simultaneous sorption of the In^{3+} and Ga^{3+} cations decreases by 12%, respectively; 4.8%; 28.6%; 5.0%; 33.8%; 54.6%; 18.9%; 12.6% and 6%. These changes in the X-ray diffraction pattern of the zeolite, isolated from the "natural zeolite–In^{3+}–H$_2$O" system, are due to the sorption of the In^{3+} and Ga^{3+} cations.

The comparison of the X-ray diffraction pattern of the zeolite, isolated from the "natural zeolite–In^{3+}–H$_2$O" system under the conditions of the highest residual content of all cations (Figure 5d) has shown that almost all reflections on it coincide with the diffraction maxima of natural zeolite (Figure 5a). The noted slight decrease in the intensity of the diffraction peaks dα = 6.71 Å by 0.4%; 4.0 Å by 0.7%; 3.9 Å by 0.8% and 1.8 Å by 0.5% and the appearance of a very low intensity of reflections with dα = 4.3 Å (1.5%) and 3.1 Å (0.9%) indicates a very slight sorption of cations, present in the system. An X-ray phase analysis has confirmed the data of IR spectroscopy.

A derivatographic analysis of the zeolite, isolated from the "natural zeolite–In^{3+}–H$_2$O" system under the conditions of the most complete adsorption of cations has shown that the DTA curve shows a weak exoeffect at 238.8 °C and a narrow endothermic effect at 623.55 °C (Figure 6b), but less intensive. The revealed changes in the derivatogram of the studied zeolite indicate the sorption of the In^{3+} cations.

The total weight loss for the zeolite, isolated after the sorption of the indium (III) cations is 3.692%.

The derivatogram of a zeolite with the minimum content of cations from the "natural zeolite–In^{3+}–Ga^{3+}" system (Figure 6c) approaches the derivatogram of natural zeolite (Figure 6a) by the nature of the DTA curve and by the total weight loss of the sample. The obtained results of the derivatographic analysis confirm the data of IRS and X-ray.

The micrographs of the natural and obtained samples after the sorption are presented in Figure 6. The surface of the indium-containing zeolite (Figure 7b) becomes less crystalline and more homogeneous; the number of pores decreases because there is a greater filling of the exchange centers, channels, and pores with the sorbed In^{3+} cations. After simultaneous sorption of the In^{3+} and Ga^{3+} cations, the sorbent surface morphology (Figure 7c) changes. Its surface becomes even more homogeneous, but still composed of various very small particles, held together quite tightly and evenly distributed throughout the structure (Figure 7c).
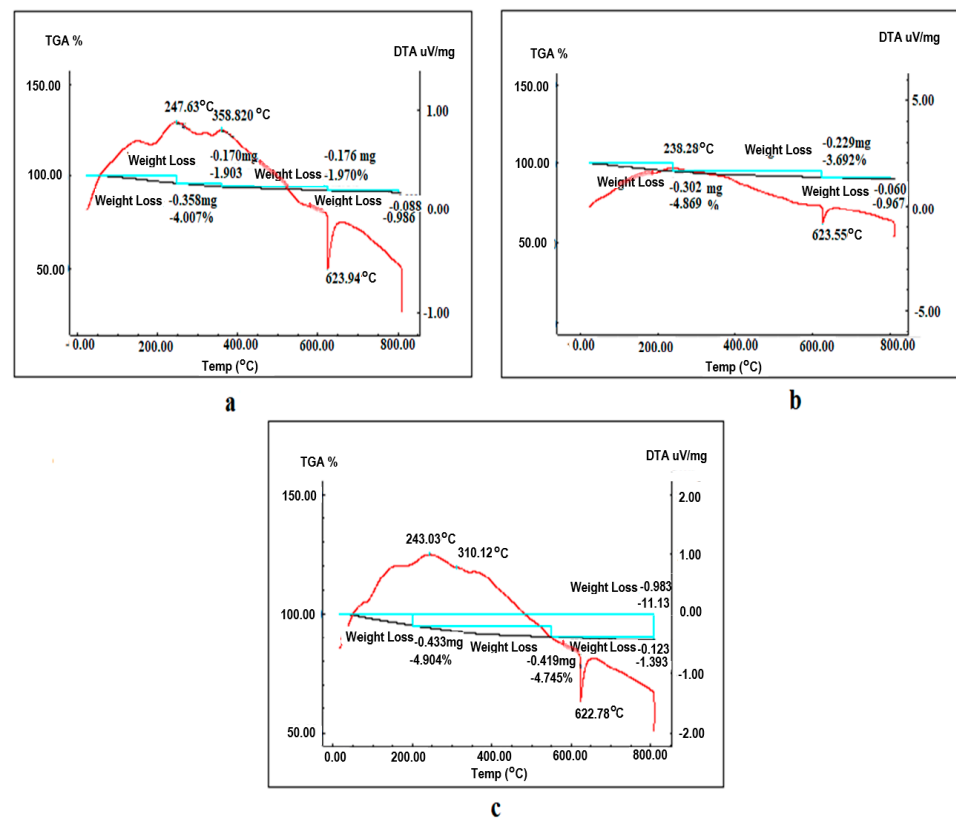
Figure 6. The derivatograms of zeolites. Zeolites: (**a**) natural; with the maximum content of cations: (**b**) In^{3+}; (**c**) with a minimum content of the In^{3+} cations.
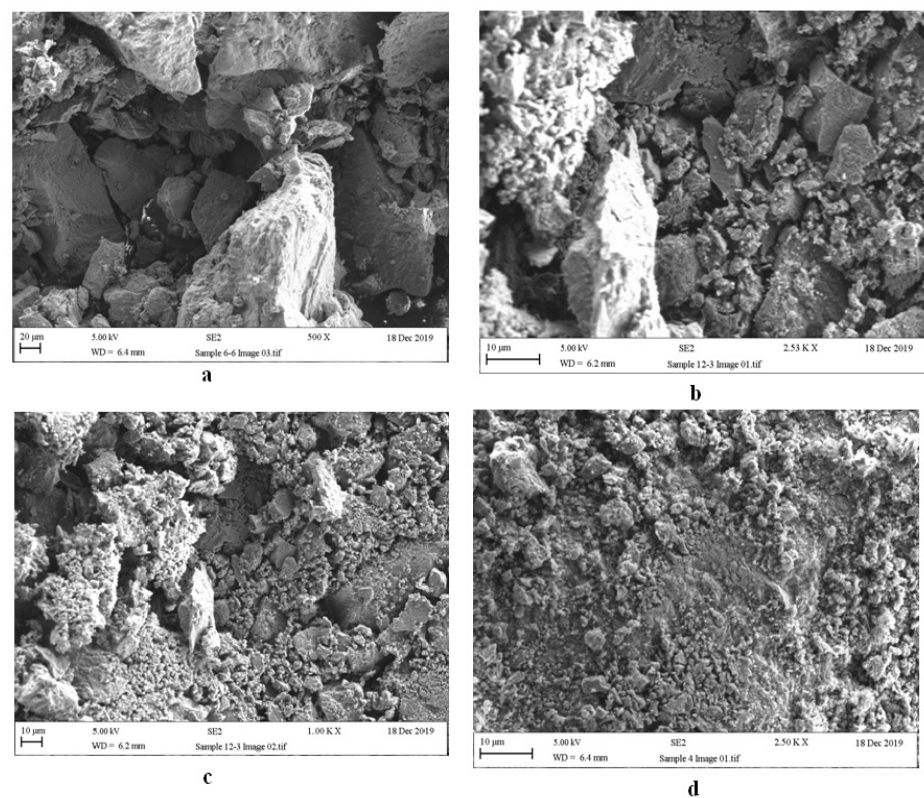

Figure 7. The micrograph of zeolites. Zeolites: (**a**) natural; with the maximum cation content: (**b**) In^{3+}; (**c**) In^{3+} and Ga^{3+}; (**d**) with the minimum content of the In^{3+} and Ga^{3+} cations.

As seen from the SEM data, as the presence of cations in the system that differ in nature (valency, charge) increases, the number of free and active centers in the sorption processes, as well as voids and channels in the zeolite structure after the sorption, noticeably decreases, and the surface becomes more and more homogeneous.

As for the zeolite, isolated from the "natural zeolite–In^{3+}–Ga^{3+}" system with the minimum content of the sorbed cations (Figure 7d), its surface approaches the surface of natural zeolite (Figure 7a), i.e., in this case, there is no sorption of the In^{3+} and Ga^{3+} cations present in the system, which confirms the above methods of analysis.

4. Conclusions

The patterns of sorption of the In^{3+} and Ga^{3+} cations by the natural zeolite of the Shankanai deposit depending onthe S:L ratio (zeolite:solution), temperature, and time have been revealed.

In a system that simultaneously contains the In^{3+} and Ga^{3+} cations in equal concentrations, the sorption of the In^{3+} cations depends on the zeolite amount and temperature, and the Ga^{3+} cations depend on the temperature and time.

A physicochemical analysis (IR, XPA, DTA, SEM) of the zeolites, isolated from the "natural zeolite–In^{3+}–H_2O" and "natural zeolite–In^{3+}–Ga^{3+}"systems under the conditions of the most complete adsorption of cations, has shown that, as the diversity of types of the sorbed cations increases, the physicochemical characteristics of the spent sorbents change noticeably, which confirms the sorption of the cations, present in the systems under study. It has been shown that the physicochemical characteristics of the zeolite, isolated from the "natural zeolite–In^{3+}–Ga^{3+}"system under the conditions of their lowest sorption, are almost identical to the characteristics of natural zeolite, which indicates the absence of cation sorption by the sorbent.

Taking into account the cationic composition of the solution and selecting the conditions of the sorption process, it is possible to use natural zeolite for the purposeful purification of the filtrate of cottrel "milk" from the In and Ga impurities.

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