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INCREASING THE SORPTION CAPACITY OF THE NATIVE FORM OF CLINOPTYLOLITE FOR Mn^{2+} IONS TO OBTAIN SORBENTS MODIFIED WITH MANGANESE OXIDES

The object of the research was the process of sorption of Mn^{2+} *ions by natural clinoptilolite (native form) under the influence of ultrasonic (US) radiation for the subsequent production of sorbents modified with manganese oxides, which have additional catalytic and oxidative capacity. Such sorbents with additional functions will be widely used in water purification processes from iron and manganese ions, hydrogen sulphide and a number of organic compounds, as well as highly dispersed and colloidal particles. This will allow combining the processes of purification of dispersed particles and soluble compounds of* Fe^{2+}, Mn^{2+}, *sulphides. The research was carried out with a clinoptilolite fraction of 1.0–1.5 mm, which is used in water purification processes. It was found that the native form of clinoptilolite has a lower sorption capacity for* Mn^{2+} *compared to clinoptilolite previously enriched by washing out impurities. The process of modifying clinoptilolite under the influence of ultrasound made it possible to significantly increase the sorption capacity of the zeolite for* Mn^{2+} *ions, compared not only to the native form of clinoptilolite, but also to the previously enriched one. Thus, at ultrasound powers of 8.0; 10.2 and 12.5 W, the sorption capacity of the native form of clinoptilolite increased by 1.66; 2.14 and 2.41 times, compared to the control experiment (without ultrasound). Compared to the enriched clinoptilolite, an increase in sorption capacity is also observed, although somewhat smaller: at powers of 8.0; 10.2 and 12.5 W it increased by 1.14; 1.47 and 1.65 times. It was found that the increase in temperature has little effect on the value of the sorption capacity of clinoptilolite. The value of the temperature coefficient g close to 1.1 indicates the course of the process in the diffusion region. EDX analysis has shown that the sorption of* Mn^{2+} *ions occurs mainly by the mechanism of selective ion exchange. The sorption capacity of clinoptilolite modified under adiabatic conditions is lower than under isothermal conditions. However, this method of modification has prospects at a higher mass ratio between the modification solution and zeolite. The results obtained have prospects for use in obtaining sorbents based on natural clinoptilolite with additional catalytic properties.*

Keywords: *sorption capacity, manganese(II) ions, manganese oxides, oxidative catalysis, water purification, iron ions, hydrogen sulphide.*

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1. Introduction

The use of modified sorbents of various natures allows to significantly expand and improve their operational properties. In particular, modification provides additional functional properties of such sorbents. For example, along with the main property of such materials, namely, sorption capacity, they acquire magnetic, antibacterial, catalytic, oxidizing and other properties. For example, doping activated carbon with highly dispersed Ni and NiO particles gives it magnetic properties, which ensures almost complete removal of spent sorbent from treated waters [1–3]. Granular filter loading, the surface of which is modified with iron compounds (hematite Fe_3O_4, magnetite Fe_2O_3, goethite a-FeOOH, etc.), which form a porous film, provides an increase in its sorption capacity and gives magnetic properties [3]. Surface modification of porous carbon materials with nickel and iron compounds prevents particle agglomeration, which increases their integral surface area and sorption capacity, and also gives the sorbents magnetic properties [4]. Doping the surface of activated carbon with nanosized particles of cobalt compounds gives the particles additional catalytic properties and ensures high magnetic susceptibility [5].

The modification method is also widely used to improve and expand the properties of a number of natural materials such as clays and zeolites. For example, a promising direction in water purification technologies is the use of materials with an increased specific surface area and additional functional properties. It has been established that the modification of clays with nickel compounds increases the efficiency of removing pollutants of organic origin [6]. The use of natural zeolites, in particular, clinoptilolite, has long been known in various fields [7–9]: first of all, in water purification technologies [10, 11]. It is known that the native form of zeolite has an inherent ion-exchange ability [12], due to which metal ions and ammonium are extracted from water. Doping clinoptilolite with silver in ionic and zero-valent forms gives it additional bactericidal [13] and sorption [14] properties.

Effective removal of iron and manganese ions, hydrogen sulphide from water, especially groundwater, occurs by the method of contact filtration using a filter charge modified with manganese oxides. The surface layer of M_nO_x plays the role of a catalyst for the oxidation of iron compounds [15]. At the same time, manganese(IV) oxide is characterized by greater catalytic activity on the surface of clinoptilolite [16].

It is obvious that the rate of heterogeneous catalytic processes involving manganese oxides will increase with an increase in their content in clinoptilolite and, accordingly, an increase in the active area of M_nO_x particles. It is obvious that the manganese content of oxides is proportional to the content of Mn^{2+} ions in clinoptilolite, which play the role of precursors. One of the methods of modifying clinoptilolite with Mn^{2+} ions is the treatment of zeolite with manganese(II) nitrate solutions [17]. Further formation of highly dispersed M_nO_x particles occurs as a result of the decomposition of sorbed manganese nitrate under the influence of thermal or electromagnetic radiation.

However, as is known, all natural zeolites, including clinoptilolite, are not pure minerals. During their formation, occlusion of various substances, for example, quartz, mica, clays, etc., which are impurities, occurred. They undoubtedly affect the main property of zeolites – sorption capacity. The content of the main component, for example, clinoptilolite in zeolite rock can vary within very wide limits: from 20 %, for example, in deposits in China, to 70–80 % in clinoptilolite of the Sokyrnytskyi deposit. In previous studies, clinoptilolite of the Sokyrnytskyi deposit with a content of the main component of 72–75 % was used. It was previously enriched by washing from clay and other impurities [17]. For this, clinoptilolite of a given dispersion was kept in distilled water for at least 48 hours. This is necessary so that the clay localized in the interlayer space of clinoptilolite is hydrated due to water absorption. This process is long due to the specifics of the localization of clay in clinoptilolite rock. After that, clinoptilolite was separated by filtration, washed with distilled water with stirring and at a ratio of clinoptilolite: water=1:10. After 30 min, clinoptilolite was separated by filtration and the clinoptilolite washing procedure was repeated. The criterion for the end of the washing process was taken to be the value of the optical density of the washing water, which was equal to at least 0.95 % of the optical density of distilled water. That is, until almost transparent washing water was obtained. Depending on the fractional composition, the total water consumption for washing clinoptilolite weighing 10 g ranged from 500–600 cm^3 for the 2.5–3.0 mm fraction to 1200–1400 cm^3 for the 0.063–0.1 mm fraction. It is clear that such a significant water consumption, even if it is used in a countercurrent washing mode or reused after clarification, will significantly increase the cost of the modification process and, accordingly, obtaining a modified sorbent. Based on this, it was interesting to carry out the modification of the sorbent with manganese(II) ions without its preliminary washing from clay.

It is worth noting that natural zeolites of different groups are used to purify different waters without prior enrichment [10, 11].

To intensify the process of sorption of Mn^{2+} ions, it was proposed to carry out this process under the influence of acoustic vibrations of the ultrasonic range. In this case, the positive experience of modifying clinoptilolite with silver ions under the influence of ultrasonic radiation [14] was taken into account due to the acceleration of diffusion processes. In addition, it was expected that ultrasonic radiation would also contribute to the partial purification of zeolite particles from impurities, which would also contribute to an increase in the sorption capacity of clinoptilolite for Mn^{2+} ions. In the existing literature, the effect of ultrasound on the sorption of Mn^{2+} ions by natural clinoptilolite has not been revealed.

The aim of research is to establish the effect of ultrasonic radiation on the sorption capacity of natural clinoptilolite for Mn^{2+} ions. This work is aimed at obtaining cheap sorbents with additional catalytic properties for water purification from iron and manganese ions, as well as hydrogen sulphide.

2. Materials and Methods

The object of research was the process of sorption of Mn^{2+} ions by natural clinoptilolite under the influence of ultrasonic radiation for the subsequent production of sorbents modified with manganese oxides, with additional catalytic and oxidative capacity.

As a starting material with sorption properties, natural clinoptilolite from the Sokyrnytskyi deposit in the Transcarpathian region was used. As in previous studies, the starting clinoptilolite rock with particle sizes of 7–10 mm was ground in a ball mill to obtain a fraction of no more than 3–4 mm [17]. In this case, partial enrichment of clinoptilolite occurred due to the destruction of the rock in places of dislocation of clay and mica layers, the hardness of which is at least half that of clinoptilolite as a mineral. Using a standard set of laboratory sieves, a clinoptilolite fraction of 1.0–1.5 was isolated, which is very often used in bulk filters for water purification.

Clinoptilolite and impurity content was determined using an AERIS Research X-ray diffractometer (Malvern PANalytical) with HighScore Plus software for qualitative and quantitative analysis.

The study of the sorption of manganese(II) ions by the native form of clinoptilolite was carried out in a chemical beaker mounted on a magnetic stirrer at a ratio of zeolite: $Mn(NO_3)_2$ solution 1:2 (the mass of the clinoptilolite sample in all studies was 10±0.01 g) in the intensive stirring mode and under the influence of acoustic radiation of the ultrasonic (US) range under isothermal and adiabatic conditions. In the case of conducting studies under isothermal conditions, the chemical beaker was placed in a thermostatic bath switched with a thermostat, which was mounted on a magnetic stirrer. Ultrasonic radiation was generated using a magnetostrictive type US-emitter "Ultrasonic Disintegrator UD-20" (frequency – 20 kHz; fixed power values 8.0; 9.5; 10.2; 11.8 and 12.5 W). The magnetostrictor concentrator is made of stainless steel Kh18N9T. The scheme of the laboratory setup is shown in Fig. 1. The research was carried out under the following conditions: temperature (in isothermal mode) – 25±0.5, 45±0.5, 65±0.5 °C; ultrasonic radiation power – 8.0; 10.2; 12.5 W. Control experiments in isothermal mode were also carried out with intensive mechanical stirring on a magnetic stirrer, but without the action of ultrasound.

Manganese nitrate solutions with a concentration of 0.5 mol/dm^3 were prepared by dissolving a portion of the crystalline hydrate $Mn(NO_3)_2 \cdot 6H_2O$ in distilled water.

After specified time intervals, a sample of the solution was taken and immediately filtered through a "blue ribbon" paper filter. The solution was analyzed for the content of Mn2+ ions according to the method described in [17]. Based on the results obtained, the average content of manganese(II) ions in clinoptilolite was calculated [17].

After the modification process, clinoptilolite was separated by filtration, washed with distilled water to a pH of the washing water of 6.5±0.25 and dried to a constant weight (±0.001 g) at a temperature of 100±5 °C. The content of manganese(II) ions and exchangeable cations of clinoptilolite was determined by the method of energy-dispersive micro-X-ray spectral analysis (EDX) using an INCA Energy 350 device integrated into the Zeiss EVO-40XVP scanning electron microscope system.

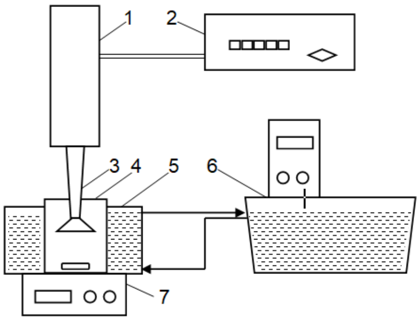

Fig. 1. Laboratory setup for studying the modification of clinoptilolite under the influence of ultrasound radiation: 1 – magnetostrictor; 2 – power supply; 3 – concentrator; 4 – beaker for modification; 5 – thermostatic bath; 6 – thermostat; 7 – magnetic stirrer

To determine the elemental composition of modified clinoptilolite, reference samples with known contents of Mn, Na, K, Ca, Mg, Si, Al, O, Fe were used. Taking into account the anisotropy of the composition of natural clinoptilolite, elemental analysis was performed at least at 5 points and the average value of the ion content, in particular manganese, was calculated.

3. Results and Discussion

It has been established that ultrasound radiation significantly intensifies the sorption of Mn^{2+} ions by the native form of clinoptilolite, as a result of which the sorption capacity of the zeolite increases (Fig. 2).

It was found that the sorption of Mn^{2+} ions mainly occurs by the mechanism of ion exchange. This is evidenced by the decrease in the content of elements such as Mg and Na in the surface layer of clinoptilolite (Fig. 3). At the same time, the content of K and Ca practically does not change. Therefore, it can be stated that the ion exchange in the studied system is selective: first, Mg^{2+} and Na^{+} cations are exchanged for Mn^{2+} ions.

The nature of the change in sorption capacity over time obtained for the 1.0–1.5 mm fraction is very similar to that for clinoptilolite previously washed from impurities (Fig. 4, dependence 5 [17]).

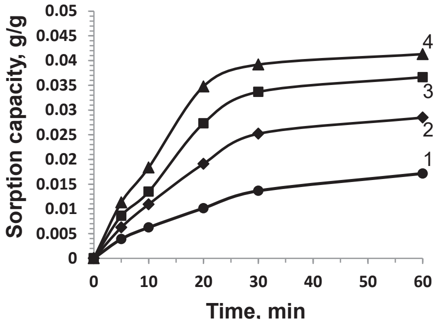

Fig. 2. Dependence of the sorption capacity of the native form of natural clinoptilolite (fraction 1.0–1.5 mm; 25 °C) on time at the power of US radiation, W: 1 – without US; 2 – 8.0; 3 – 10.2; 4 – 12.5

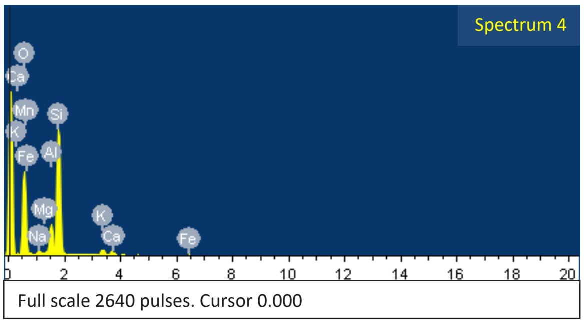

Fig. 3. EDX analysis of the surface of clinoptilolite modified with Mn^{2+} ions under isothermal conditions at 25 °C; ultrasound power 8.0 W

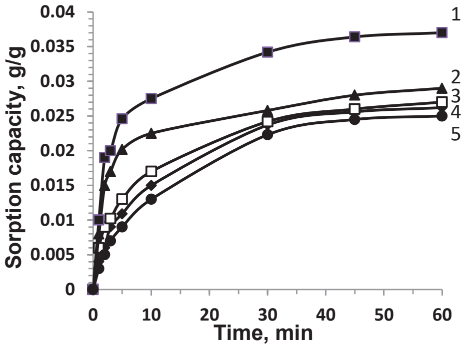

Fig. 4. Dependence of the sorption capacity of natural clinoptilolite on time (20 °C) for the dispersion of clinoptilolite particles, mm: 1 – 0.063–0.1; 2 – 0.1–0.25; 3 – 0.25–0.5; 4 – 0.5–1.0: 5 – 1.0–1.5 [17]

As expected, without the action of US-radiation, the sorption capacity of the native form of clinoptilolite is less than for the previously prepared (washed), namely by 1.44 times. However, under the action of ultrasound radiation, the sorption capacity of clinoptilolite increases (Fig. 2) and, ultimately, significantly increases compared to the washed one. Thus, the ratio of the sorption capacity of the native form of clinoptilolite under the action of ultrasound, achieved 60 min from the beginning of the experiment, to the sorption capacity of the previously washed one (Fig. 4, dependence 5) is equal to: at a power of 8.0 W – 1.14; 10.2 W – 1.47; 12.5 W – 1.65. This undoubtedly confirms the positive effect of ultrasound radiation on the sorption of manganese(II) ions.

If to compare the sorption capacity of the native form of clinoptilolite, achieved under the influence of ultrasound (experiment duration 60 min) with the control experiment (native form, without ultrasound), then at ultrasound radiation powers of 8.0; 10.2 and 12.5 W it increases by 1.66; 2.14 and 2.41 times, respectively.

As can be seen, increasing the power does not provide a proportional increase in the sorption capacity. Thus, when increasing the power from 8.0 to 10.2 (by 1.27 times), the sorption capacity of the native form of clinoptilolite increases by 1.29 times, and when increasing from 10.2 to 12.5 (by 1.23 times) – by 1.13 times. That is, the effectiveness of the action of ultrasonic radiation decreases with increasing power. This can be explained by the fact that ultrasonic radiation causes the effect of cavitation, which is accompanied by the formation of cavitation bubbles in the volume of the medium. In this case, the formation of cavitation bubbles of the second and subsequent generations is possible, which also appear on the surface of clinoptilolite particles. Therefore, they can partially block the surface of zeolite particles, which somewhat neutralizes the effect of ultrasonic radiation.

The phenomenon of cavitation causes an increase in the temperature of the reaction medium. Under isothermal conditions, the heat generated by cavitation is removed by the coolant. However, if the process is carried out under adiabatic conditions, then an increase in temperature can contribute to an increase in the rate of sorption of manganese(II) ions due to both diffusion phenomena and the rate of ion exchange with the participation of exchangeable cations of clinoptilolite. Therefore, to establish the effect of temperature, further studies were carried out under isothermal conditions at temperatures of 45 and 65 °C. The dependence of the sorption capacity of clinoptilolite (native form) on time at temperatures of 45 and 65 °C is shown in Fig. 5 and Fig. 6.

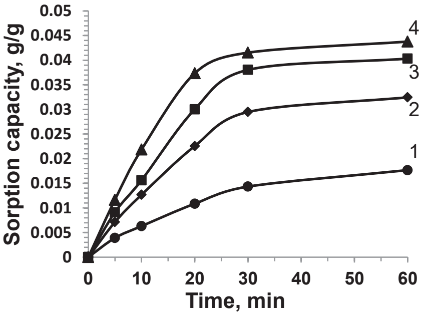

Fig. 5. Dependence of the sorption capacity of the native form of natural clinoptilolite (fraction 1.0–1.5 mm; 45 °C) on time at the power of ultrasound radiation, W: 1 – without US; 2 – 8.0; 3 – 10.2; 4 – 12.5

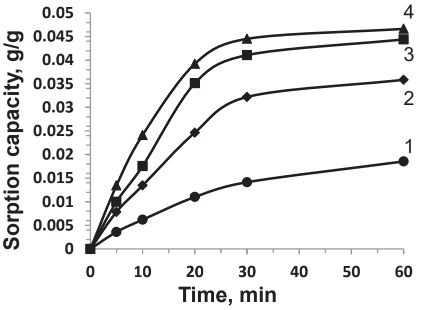

Fig. 6. Dependence of the sorption capacity of the native form of natural clinoptilolite (fraction 1.0–1.5 mm; 65 °C) on time at the power of ultrasound radiation, W: 1 – without US; 2 – 8.0; 3 – 10.2; 4 – 12.5

The dependence of the sorption capacity of clinoptilolite on temperature in the range of 25–65 °C for all values of the power of ultrasonic radiation is practically linear (Fig. 7). Accordingly, the value of the reliability of the approximation of the corresponding linear equations is close to 1; it varies within 0.9969–0.9985.

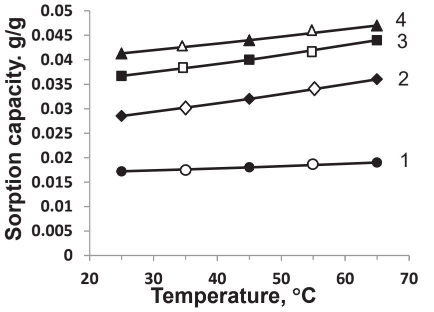

Fig. 7. Dependence of the sorption capacity of the native form of clinoptilolite (fraction 1.0–1.5 mm) on temperature (experiment duration 60 min) at the power of ultrasound radiation, W: 1 – without US; 2 – 8.0; 3 – 10.2; 4 – 12.5 (unshaded marks correspond to calculated values)

Therefore, it made no sense to conduct research at intermediate temperatures (35 °C and 55 °C).

Analysis of the obtained dependences showed that the value of the sorption capacity depends slightly on the temperature. Thus, the increase in sorption capacity (slope tangent) in the range of 25–65 °C was equal to (DSC/DT, (g Mn^{2+}/g)/grad): without the action of ultrasound – $2.5\cdot10^{-6}$; 8.0 – $4.4\cdot10^{-5}$; 10.2 – $3.5\cdot10^{-5}$; 12.5 – $4.3\cdot10^{-5}$. This means that the process of sorption of Mn2+ ions occurs in the diffusion region. A priori, taking into account the intensive mixing of the reaction medium both due to mechanical mixing and the action of ultrasound vibrations, it can be stated that this process occurs precisely in the internal diffusion region. That is, it is limited by the diffusion of ions in the internal channels and pores of the zeolite. The conclusion about the diffusion region of the process is confirmed by the values of the sorption rate of Mn^{2+} ions. In this case, we proceeded from the following assumption. The process involving clinoptilolite belongs to heterogeneous ones, and therefore its rate must be expressed in terms of the contact area of the phases. However, clinoptilolite particles have an irregular shape and are characterized by a very developed surface, which is difficult to take into account. Therefore, the sorption rate, as in previous studies [17], was expressed in relation to the mass of clinoptilolite (Table 1).

Table 1

Values of the sorption rate of Mn^{2+} ions

Temperature, °C	The value of the sorption rate of Mn^{2+} ions (mol/g·s) at the power of ultrasonic radiation (W)			
	without ultrasound	8.0	10.2	12.5
25	$2.36\cdot10^{-7}$	$3.78\cdot10^{-7}$	$5.21\cdot10^{-7}$	$6.85\cdot10^{-7}$
45	$2.42\cdot10^{-7}$	$4.24\cdot10^{-7}$	$5.45\cdot10^{-7}$	$7.27\cdot10^{-7}$
65	$2.42\cdot10^{-7}$	$4.85\cdot10^{-7}$	$6.06\cdot10^{-7}$	$7.88\cdot10^{-7}$

Based on the fact that the dependence of the sorption capacity on temperature is linear (Fig. 7), the values of the sorption capacity were determined at temperatures of 35 and 55 °C. After that, the values of the temperature coefficient (g) were calculated for different powers of ultrasonic radiation. Thus, for powers of 8.0; 10.2 and 12.5 W, the average value of g was equal to 1.07; 1.06; 1.04, respectively. That is, all values of g approach 1.1, which is characteristic of the diffusion region of the heterogeneous process.

Taking into account the fact that under the influence of US the temperature of the reaction medium increases, further modification of clinoptilolite with Mn^{2+} ions was carried out under conditions close to adiabatic. The modification process was carried out until the temperature of the modification solution reached 65 °C. Previously, the reaction medium was thermostated at 25 °C.

It was calculated that a temperature of 65 °C can be reached in about 8 min at a radiation power of 8.0 W, 6 min at 10.2 W, and 4.5 min at 12.5 W. In real conditions, it is practically impossible to ensure truly adiabatic conditions, since there are significant heat losses through the magnetostrictive system. Therefore, the process actually lasted longer: at 8.0 W – ~14 min; 10.2 W – ~11.5 min; 12.5 – ~9 min. At the same time, the following average values of the sorption capacity (g/g) of the native form of clinoptilolite with respect to Mn2+ ions were achieved at the power of ultrasonic radiation (W): 8.0 – 0.014; 10.2 – 0.016; 12.5 – 0.021. As expected, the obtained values of sorption capacity are lower than those obtained under isothermal conditions at a temperature of 65 °C, since the duration of the process is shorter, and the specified temperature is reached only during the modification process. However, if the modification process is carried out at a higher mass ratio of solution to clinoptilolite, for example, 1:50 and more, then the duration of the process will be longer. This should lead to an increase in the sorption capacity of clinoptilolite.

At the same time, the EDX method established that the content of Mn^{2+} ions in the surface layer of clinoptilolite particles is higher than that achieved under isothermal conditions and reaches 2 % by mass. At the same time, exchangeable clinoptilolite cations were not detected in this layer (Fig. 8). This means that they were replaced by Mn^{2+} ions as a result of ion exchange. This phenomenon requires further research.

Several samples of clinoptilolite modified with Mn^{2+} ions were heated at a temperature of 250±5 °C for 60 min. At the same time, clinoptilolite particles acquired a dark brown to almost black color, which indicated the formation of manganese oxides. Analysis of the photo (Fig. 9) of the clinoptilolite surface shows that the entrance windows of the channels in clinoptilolite are not blocked.

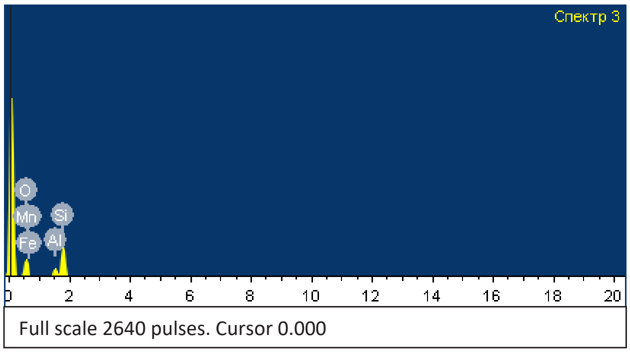

Fig. 8. EDX analysis of the surface of clinoptilolite modified with Mn^{2+} ions under adiabatic conditions; ultrasound power 8.0 W

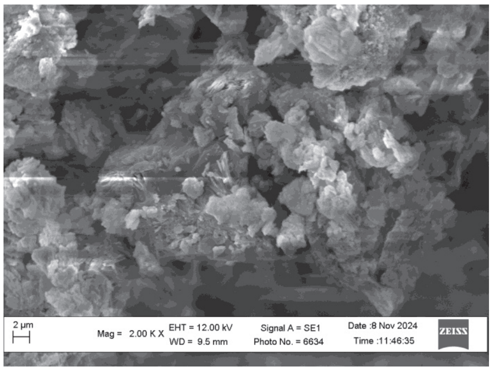

Fig. 9. Image of the surface of clinoptilolite covered with manganese oxide particles

Therefore, it can be expected that the sorption properties of clinoptilolite modified with manganese oxides towards various water pollutants will not deteriorate. However, this will be the subject of further research.

Limitation of the study: to implement the research results into practice, it is necessary to develop an industrial technology for modifying natural clinoptilolite under the influence of ultrasonic radiation. However, it is necessary to take into account that the power of magnetostrictive emitters is limited, and unproductive energy consumption increases with increasing radiation power.

Impact of martial law conditions: The study was also influenced by the conditions of martial law in Ukraine, namely: due to power outages, the operation of the thermostat and ultrasonic emitter may be suspended. In the absence of an uninterrupted power supply, the experiment may be interrupted.

Prospects for further research: in further research it is necessary to focus on the modification of natural clinoptilolite of other fractions used in water purification technologies, and using different concentrations of the precursor – manganese(II) nitrate. In addition, it is necessary to establish rational conditions for the conversion of sorbed manganese(II) nitrate into manganese oxides and to study the sorption and catalytic properties of the obtained sorbents.

4. Conclusions

Modification of natural clinoptilolite with manganese(II) ions under the action of ultrasonic radiation provides a greater sorption capacity compared to pre-enriched clinoptilolite. Under the action of ultrasonic radiation, the sorption capacity of the native form of clinoptilolite at a temperature of 25 °C increases from 1.14 to 1.65 times compared to the enriched zeolite, and reaches 0.041 g/g (at 25 °C) and 0.047 g/g (at 65 °C). This makes it possible to use the native form of clinoptilolite in technologies for obtaining sorbents with additional catalytic properties without its enrichment.

The process of modifying natural clinoptilolite should be carried out in adiabatic conditions, which will simplify the technological process of obtaining the sorbent.

It has been established that the modification process occurs in the internal diffusion region. Therefore, the concentration of the precursor (manganese(II) nitrate) is not decisive. Therefore, to reduce the consumption of the precursor, it is advisable to carry out the modification with solutions with lower concentrations of manganese(II) nitrate.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this study, including financial, personal, authorship, or any other, that could affect the study and its results presented in this article.

Financing

The research was performed without financial support.

Data availability

The manuscript has no associated data.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating this work.

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