

## ТЕХНОЛОГІЯ НЕОРГАНІЧНИХ РЕЧОВИН ТА СИЛІКАТНИХ МАТЕРІАЛІВ

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### INFLUENCE OF ACOUSTIC RADIATION OF ULTRASONIC RANGE ON MODIFICATION OF NATURAL CLINOPTILOLITE BY IONS OF ARGENTUM

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**It was found that under the action of acoustic vibrations of the ultrasonic (US) range, the rate of sorption of Argentum ions and the static capacity of clinoptilolite are much higher than for the original natural zeolite. Pre-activation of the zeolite at 350 °C allows to increase the content of Argentum ions. An increase in both the power of the US-radiation and the modification temperature makes it possible to increase the static capacity of the zeolite. It is shown that the process of modification of clinoptilolite occurs mainly in the transition region. It is established that the modification occurs by a mixed ion-sorption mechanism.**

**Key words: clinoptilolite, Argentum ions, modification, ultrasonic radiation, sorption capacity.**

#### Introduction

Natural zeolites, in particular clinoptilolite, are increasingly used in various industries. This is primarily due to the high sorption and ion exchange capacity, low cost and large volumes of deposits. Most often, zeolites are used as sorbents in technologies for the preparation of natural and wastewater conditioning, for the purification of gas emissions from harmful components. Promising is the use of zeolites in the construction industry because they allow you to reduce the duration of hardening cement, improves the mechanical properties of concrete products [1]. Natural clinoptilolite began to be actively used in medicine [2–4].

In recent years, natural zeolites have been increasingly used, which are pre-activated by physical factors (thermal, electromagnetic, acoustic radiation), the action of chemical reagents [5], and are also subjected to combined physical and chemical effects.

Under the influence of physical factors mainly occurs zeolite dehydration, which leads to the formation of surface hydroxyl groups, which, in turn,

enhance the sorption capacity of natural minerals. Chemical modification in most cases results in the replacement of calcium, magnesium, sodium and potassium ions by the proton of hydrogen, which also allows to increase the sorption capacity of the zeolite. Now with modification of clinoptilolite by metal ions, receive materials that, while maintaining high sorption capacity, acquire new functional properties. For example, zeolites with high catalytic activity, fillers of compositions with anticorrosive properties, materials with pronounced antibacterial action [6–8].

The natural materials with antibacterial properties are zeolites, in particular modified by silver ions. Depending on their dispersion, such materials can be used to solve many problems. For example, modified clinoptilolite by ions of argentum with a dispersion of 1...4 mm is used as filter loading in filters for the preparation of natural water [6, 9], as catalysts in organic synthesis and the like [10]. Silver-modified zeolite with greater dispersion (less than 500 microns) is used as feed additives to increase survival and weight gain of young animals,

for the production of antiseptic dressings for the treatment of purulent wounds and ulcers. Fine particles of silver-modified zeolite have the ability to absorb electromagnetic radiation in the radio frequency range.

Therefore, the preparation of natural sorbents modified with silver ions due to their increasing use is of considerable practical interest. Previous studies have shown that activation of clinoptilolite by electromagnetic radiation of the ultra-high frequency range allows to slightly increase the sorption capacity of clinoptilolite with respect to Argentum ions [11]. It is also shown that this capacity also depends on the dispersion of the zeolite [12]. However, such a very effective method of intensifying the sorption process on clinoptilolite as acoustic has not been investigated.

**The aim of the study** was to investigate the modification of natural clinoptilolite by silver ions under the action of ultrasonic radiation.

#### Materials and methods of research

The studies used natural clinoptilolite of the Sokyrnytsia deposit in the Transcarpathian region (TUU 20.5-43073742-002: 2019). Natural clinoptilolite is not a pure mineral; it contains impurities, in particular, clay – up to 14 %. For clay separation, the zeolite fraction of 2–3 mm in a ball mill was crushed to sizes < 2.0 mm (mill drum volume – 3 dm<sup>3</sup>; its rotation frequency – 1 s<sup>-1</sup>; drum fill degree – 40±5 %; duration grinding – 10 minutes). The zeolite fraction of less than 0.25 mm size, in which the clay content is highest, was discarded, and the clinoptilolite fraction > 0.25 mm was ground again and further classified. All modification studies were performed using a very narrow fraction of zeolite – 0.056 ... 0.063 mm.

The thermal activation of the zeolite was carried out in an electric furnace until reaching a constant mass. The “Ultrasonic disintegrator UD-20” magnetostrictive emitter with a steel concentrator with a working diameter of 15 mm was used to generate ultrasonic oscillations. The power of ultrasonic radiation was changed discretely in the range of 8.0... 12.5 W (frequency 22 kHz).

Modification of zeolite (10 g) by Argentum ions carried out in 0,1 N AgNO<sub>3</sub> solution (100 cm<sup>3</sup>) under constant mixing in the turbulent regime at the facility, in the previous work [13].

The concentration of Argentum ions in the solution was determined potentiometrically using an Ag-selective electrode ELIS-131Agas a measuring electrode paired with a chloride silver reference electrode EVL-1M3.1-100, which was switched to millivoltmeter F-30. Before each study, the Ag-selective electrode was calibrated in AgNO<sub>3</sub> solutions.

The sorption capacity of clinoptilolite relative to Argentum ions (mEq/g) was determined by the formula

$$S_{Ag} = \frac{(N_0 - N_i) \cdot V}{m},$$

where  $N_0$ ,  $N_i$  – initial and current concentration of Argentum ions in solution, mEq/dm<sup>3</sup>(mmol/dm<sup>3</sup>);  $V$  – volume of solution, dm<sup>3</sup>;  $m$  – mass of clinoptilolite, g.

#### Results of the studies and their discussion

Under the influence of acoustic radiation of the ultrasonic range with a power of 10.2 W at the temperature of the 20 °C modification process, the capacity of the original clinoptilolite relative to Argentum ions increased by 1.6 times – from 0.189 [13] to 0.303 mEq/g (Fig. 1, curve 1). An increase in the capacity of the zeolite with respect to Ag ions without any (thermal or chemical) modification can be caused by two factors: the crushing of the zeolite particles, which leads to an increase in the total their surface area, and an increase in the diffusion rate of Ag ions in the boundary layer near the solid surface. However, a sedimentation analysis of the significant change in the dispersion of the zeolite particles under the action of ultrasonic radiation for 15 min was not recorded (the difference did not exceed the measurement errors). Therefore, the main factor that led to an increase in the capacity of the zeolite is, first of all, the acceleration of diffusion phenomena.

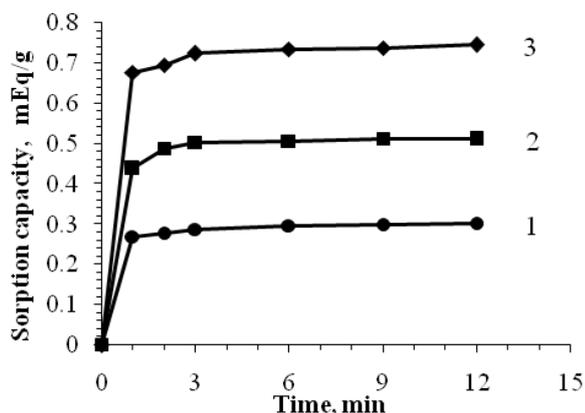
The inflection on the dependence of the sorption capacity on time was observed after 1–2 min. During this time, almost 90 % of the Argentum ions were absorbed from the total absorbed. The equilibrium state, which was recorded to achieve a constant value of the potential of the Ag-selective electrode (a constant concentration of Ag<sup>+</sup> ions) in the modification solution, was reached within 12–15 minutes. Instead under a mechanical mixing inflection observed mostly between 4–8 minutes (depending on the conditions of activation of zeolite) and

advancing the state of equilibrium after the 25th minute [13]. The initial rate of sorption of Ag ions under the action of ultrasound oscillations was  $4.48 \cdot 10^{-3}$  mmol/g·s (when mixing was an order of magnitude less than  $5.83 \cdot 10^{-4}$ ).

As was shown previously [13], due to thermal activation, it is possible to significantly increase the sorption capacity of zeolite by Ag<sup>+</sup> ions. Thus, activation at temperatures of 200–350 °C makes it possible to increase this figure by almost 4 times, compared to the original mineral. Under the influence of ultrasonic radiation with a power of 10.2 W, the sorption capacity of the zeolite, which was previously activated at 350 °C, reached 0.511 mEq/g (Fig. 1, curve 2).

This is 1.7 times higher than for thermally activated (over 350 °C) and 2.7 times higher than in the case of initial (inactive) samples of zeolite modified by mechanical stirring. The initial rate of sorption of Ag<sup>+</sup> ions activated at 350 °C by clinoptilolite in the ultrasonic field increased to  $7.30 \cdot 10^{-3}$  mmol/g·s.

Increasing the modification temperature of clinoptilolite (activated at 350 °C) from 20 to 30 °C contributes to increasing the static sorption capacity to 0.746 mEq/g. The initial speed of the process was  $1.13 \cdot 10^{-2}$  mEq/g·s. The temperature coefficient of the process, calculated at the initial velocities at the modification temperatures of 20 and 30 °C and considering that the ion exchange is described by the first-order equation, was 1.55. This means that the modification of Argentum ions by thermally activated zeolite, which is a typical heterogeneous process, occurs in the transition – diffusion-kinetic region.

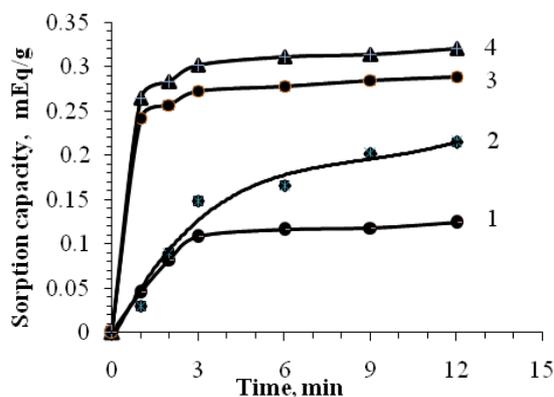


*Fig. 1. The dependence of the sorption capacity of the original clinoptilolite on time at the power of ultrasonic radiation of 10.2 W;*

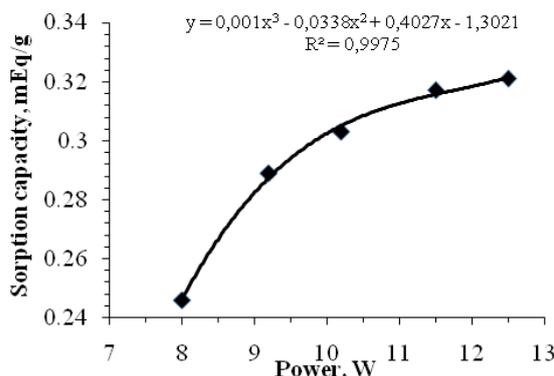
*zeolite (modification temperature, °C): 1 – initial (20); 2 – activated at 350 °C (20); 3 – activated at 350 °C (30)*

It could be predicted that the rate of diffusion of Argentum ions in the boundary layer and the pores of clinoptilolite depends on the intensity of the cavitation processes, which are determined by the power of the acoustic radiation. Therefore, further investigated the sorption of Ag<sup>+</sup> ions original clinoptilolite for different power ultrasonic radiation at 20 °C.

As expected, the decrease in radiation power leads to a decrease in both the initial velocity and the static sorption capacity of the zeolite. Thus, at 8.0 and 9.2 W (differ by 15 %), the initial process speeds differ slightly (1.25 times) and are equal to  $6.00 \cdot 10^{-4}$  and  $7.50 \cdot 10^{-4}$  mmol/g·s, accordingly. However, the static capacity of the zeolite at a power of 9.2 W is equal to 0.215 mEq/g, which is 1.7 times more than 8.0 W (0.124 mEq/g) (Fig. 2).



*Fig. 2. The dependence of the sorption capacity of the original clinoptilolite on time in power of ultrasonic radiation, W: 1 – 8.0; 2 – 9.2; 3 – 10.2; 4 – 12.5*



*Fig. 3. Dependence of the static sorption capacity of the original clinoptilolite on the power of ultrasonic radiation, W (20 °C modification temperature)*

An increase in power from 10.2 to 12.5 W (1.23 times) does not provide a significant increase in the sorption capacity of clinoptilolite – only 1.1

times (0.2889 and 0.3209 mEq/g, respectively). In this case, the initial process velocities also differ 1.1 times –  $4.03 \cdot 10^{-3}$  and  $4.42 \cdot 10^{-3}$  mmol/g·s (Fig. 3).

The energy introduced into the environment by acoustic radiation and proportional to its power can be considered equivalent to the thermal energy introduced into the environment, which is determined by its temperature. For example, at a radiation power of 10.2 W for 7 min, an amount of released energy is equivalent to the amount of thermal energy required to heat 100 g of water at 10 degrees. Therefore, the increase in the rate of sorption of  $\text{Ag}^+$  ions from 1.1 to 1.7 times with an increase in the power of ultrasound radiation by about 1 W indicates that the process is largely limited by diffusion phenomena.

The decrease in the sorption capacity of clinoptilolite with the increase in the power of ultrasound radiation can also be explained by the peculiarities of the flow of sorption of Argentum ions by such highly porous mineral as clinoptilolite. The pores of this zeolite (their volume is 45... 50 % of the volume of the particle) contain air. After immersion in an aqueous solution, the air bubbles are partially desorbed, which is why the name of the mineral – “zeolite”. Under the influence of ultrasonic vibrations, degassing accelerates. An increase in the power of ultrasonic radiation causes an increase in the acoustic pressure acting on the clinoptilolite particles. The bubble of gas that has diffused from the inner region of the zeolite particle to the surface is simultaneously subjected to such multidirectional forces as surface tension, wetting force, ejection force, fluid pressure and acoustic pressure:

$$F_{s,t} + \sigma_w \leftrightarrow F_e + F_l + F_{a,p},$$

where  $F_{s,t}$  – force of surface tension;  $\sigma_w$  – wetting force;  $F_e$  – ejection force;  $F_l$  – the force of the fluid pressure;  $F_{a,p}$  – acoustic pressure force.

Increasing the acoustic pressure shifts the equilibrium in this system of forces to the left, making the desorption of bubbles from the surface of the clinoptilolite particle more difficult. These considerations are confirmed by the observation of air desorption from 3...4 mm size clinoptilolite particles under the action of ultrasound. After separation of the vast majority of air from the zeolite cavities, some of them cover the surface of the zeolite in the form of small bubbles (Fig. 4a).

However, immediately after switching off the ultrasonic emitter, these bubbles virtually simultaneously desorb from the surface of the clinoptilolite particles and rise to the liquid surface (Fig. 4b). Similar processes occur with the participation of highly dispersed zeolite particles, although the size of the gas bubbles that are desorbed are much smaller. Based on the results obtained, it can be argued that an increase in acoustic radiation power causes an increase in the sorption capacity of clinoptilolite, in particular due to its degassing; however, the gas desorption efficiency decreases.

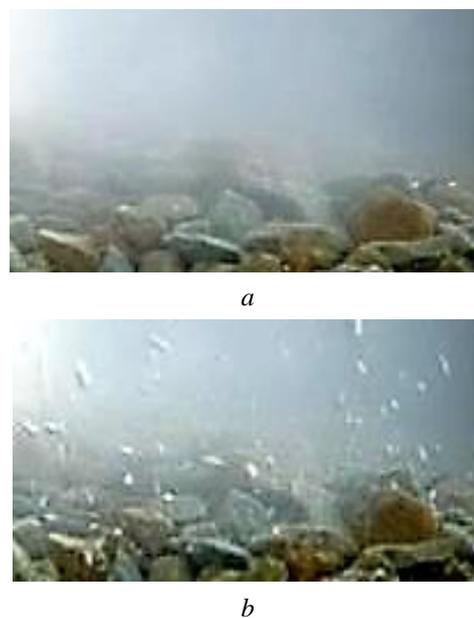


Fig. 4. Photo of particles of clinoptilolite 3... 4 mm: a – bubbles on the surface of the zeolite under the action of ultrasound; b – allocation of air bubbles after the termination of the ultrasound

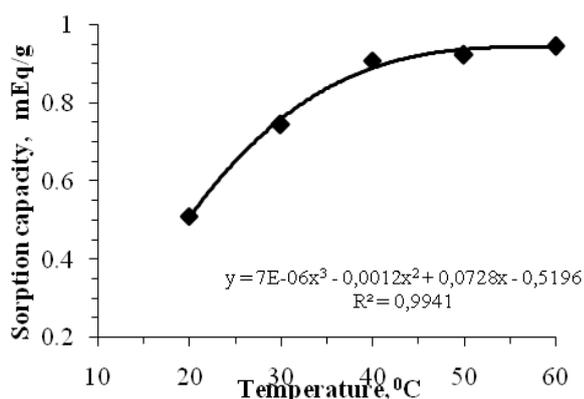
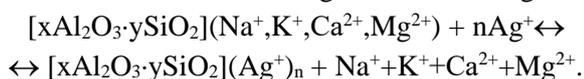
An increase in power exceeding 11.5 watts (under specific conditions the specific power is  $0.115 \text{ J/cm}^3$ ) is not feasible as the sorption capacity increase becomes smaller (Fig. 5). Therefore, the specific energy consumption will increase and the economic efficiency of the process will decrease.

Due to the modification of Argentum ions of clinoptilolite, previously activated at 350 °C and under the influence of ultrasonic radiation with a power of 10.2 W, the sorption capacity increased almost twice – from 0.511 (at 20 °C) to 0.946 (at 60 °C) mEq/g (Fig. 5).

At temperatures above 40 °C, the increase of sorption capacity sharply decreases (at increase to 50

°C equals only 0,014 mEq/g), and in the future it practically does not change (taking into account the error of measurement of the electrode potential of Ag-selective electrode), whereas in the range temperatures of 20... 30 °C, this increase was equal to 0.235 mEq/g, and in the range of 30... 40 °C – 0.164. Thus, modification of clinoptilolite by Argentum ions should be performed at a temperature of no more than 40 °C.

The cation exchange capacity of natural clinoptilolite is 0.15...0.20 mEq/g. Studies have shown that the sorption of Argentum ions reaches much higher values – more than 0.9 mEq/g, that is, a phenomenon known as the “superequivalent ion exchange” of Ag<sup>+</sup> ions. Based on this, it can be argued that the absorption of Argentum ions by highly dispersed clinoptilolite occurs by two mechanisms. The first is the gross-ion exchange



*Fig. 5. Dependence of the static sorption capacity of clinoptilolite activated at 350 °C on the temperature at the power of ultrasonic radiation 10,2 W*

Obviously, the number of Argentum equivalents that replaced the exchange ions (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) by the ion exchange mechanism alone cannot be greater than their content in clinoptilolite. Therefore, it can be assumed that the remaining ions of Argentum are absorbed by zeolite due to sorption. After the sorption process of Ag<sup>+</sup> ions, the zeolite was separated from the AgNO<sub>3</sub> solution by filtration and washed with distilled water until no Ag<sup>+</sup> ions were present in the filtrate. The content of Ag<sup>+</sup> in the wash water did not exceed 1·10<sup>-3</sup> mEq/dm<sup>3</sup>. That is, the Ag<sup>+</sup> ions (and therefore the counterions – NO<sub>3</sub><sup>-</sup>) were retained in the pores of the clinoptilolite rather firmly.

It was found that over time, samples modified with Ag<sup>+</sup> ions and washed with distilled water clinoptilolite in the air changed color – acquired a gray shade of varying intensity depending on the content of Argentum ions. This is due to the conversion of Argentum ions into dispersed silver particles under the action of light. This fact also confirms the assumption that part of the Ag ions is present in the clinoptilolite particles not due to the ion exchange but due to sorption of the nitrate argentum solution. It has been shown that changes in the coloration of clinoptilolite particles by Ag ions no greater than the magnitude of the static sorption capacity are observed.

### Conclusions

Pre-thermal activation promotes increasing the sorption capacity of clinoptilolite with respect to Argentum ions.

Modification of clinoptilolite by Argentum ions under the action of ultrasound radiation leads to an increase in its static sorption capacity.

The process of modification of clinoptilolite by Argentum ions occurs in the transition (diffusion-kinetic) region.

It was found that the sorption of Argentum ions is impeded by the air contained in the pores of clinoptilolite and which partially desorbs under the influence of acoustic vibrations.

The static capacity of clinoptilolite relative to Argentum ions increases with the modification temperature; the largest increase of this value was observed in the temperature range of 30... 40 °C.

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### **ВПЛИВ АКУСТИЧНИХ ВИПРОМІНЮВАНЬ УЛЬТРАЗВУКОВОГО ДІАПАЗОНУ НА МОДИФІКУВАННЯ ПРИРОДНОГО КЛИНОПТИЛОЛІТУ ЙОНАМИ АРГЕНТУМУ**

Встановлено, що під дією акустичних коливань ультразвукового (УЗ) діапазону швидкість сорбції йонів Аргентуму та статична ємність клиноптилоліту значно вищі, ніж для вихідного природного цеоліту. Попереднє активування цеоліту за температури 350 °С дає змогу збільшити вміст йонів Аргентуму. Збільшення потужності УЗ-випромінювання, і температури модифікування дає змоги досягнути збільшення статичної ємності цеоліту. Показано, що процес модифікування клиноптилоліту відбувається здебільшого у перехідній області. Встановлено, що модифікування відбувається за змішаним йонно-сорбційним механізмом.

**Ключові слова:** клиноптилоліт, йони Аргентуму, модифікування, ультразвукове випромінювання, сорбційна ємність.