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V.V. Kochubei^a, *S.G. Yaholnyk*^a, *S.V. Kniaz*^a, *L.Y. Parashchuk*^b, *M.S. Malovanyy*^a**RESEARCH INTO THE INFLUENCE OF ACTIVATION CONDITIONS OF
TRANSCARPATHIAN CLINOPTILOLITE ON ITS ADSORPTION CAPACITY**^a Lviv Polytechnic National University, Lviv, Ukraine^b Hetman Petro Sahaidachnyi National Army Academy, Lviv, Ukraine

The paper reports the effects of the activation conditions on the adsorption capacity of Transcarpathian clinoptilolite. Naturally occurring clinoptilolite underwent chemical activation by 5% and 25% aqueous solutions of H₂SO₄ at the solid-liquid ratio of 1:10. Thermal activation was performed by the heating of chemically activated clinoptilolite at the temperature of 300°C. Thermal analysis showed that the sample activated by 25% H₂SO₄ solutions demonstrated the highest adsorption capacity with respect to water vapor and the highest content of hydroxyl groups that were lost at the temperatures greater than 500°C. The data obtained can be explained by partial dealumination of zeolite, which is accompanied by an increase in its internal crystalline space and the emergence of additional adsorption active centers. The destruction of Si–O–Al bonds, which gave rise to the Brønsted adsorption active centers, was confirmed by the results of IR spectroscopic and X-ray phase analyses. The IR spectrum of the sample activated by 25% H₂SO₄ solution exhibited a drastic shift of band associated with tetrahedral stretching vibrations to the region of higher frequencies. A significant reduction of reflections in X-ray diffraction pattern of the sample treated by 25% H₂SO₄ solution appeared in the region $2\theta=32-34^\circ$ (CoK_α radiation). This indicated steric strains of crystalline lattice due to decationization and dealumination processes. A comparative analysis of both naturally occurring clinoptilolite and modified by 25% H₂SO₄ solution was performed to characterize the capacity to adsorb direct dye molecules from their aqueous solutions. An increase in the adsorption capacity of activated clinoptilolite was ascribed to the emergence of additional Brønsted acid centers that became available to dye molecules during the activation of clinoptilolite. The constants of the Langmuir monomolecular adsorption isotherm equation were determined.

Keywords: clinoptilolite, thermal analysis, adsorption, direct dyes, activation.**DOI:** 10.32434/0321-4095-2020-131-4-80-87**Introduction**

Naturally occurring zeolites are aluminosilicates exhibiting a strictly regular crystalline structure. The aluminosilicate framework of zeolite has a mature system of cavities, the size of which ranges from 0.4 to 1.1 nm. The negative charge of the mineral framework is compensated by the charge of cations that are in the channels of the structure [1].

Naturally occurring zeolites exhibit the high ion-exchange properties, advanced inner surface of interphase and high adsorption capacity. Due to their chemical and mechanical stability, availability and ability to be regenerated, these minerals are widely used in environmental protection, particularly, in air, soil and water treatment [2].

The water resource potential of Ukraine is at the forefront of the social and environmental well-being and economic growth. Chemical, petroleum and pulp-and-paper industrial waste is the main source of pollution of natural waters with organic substances. The presence of a great amount of organic compounds in water leads to the death of fish, spoils the water's taste and smell and causes eutrophication of waters [3].

Dyes make up a significant part of the waste from the chemical and pulp-and-paper industries. During the dying process, from 20 to 50% of dyes are released into wastewater after the end of the production cycle, depending on its type and the dyeing method used [4]. Such a release significantly

damages the ecological system of the region. A substantial amount of waste is associated with direct dyes. These dyes are widely used due to their affinity for various types of fibers, such as cellulose and amphoteric. Direct dyes ensure the color brightness of fabric, are easy to use and inexpensive.

Over the period of sharpening of water and environmental issues and limited funds for water protection measures, it is important for enterprises to opt for the most optimal wastewater treatment technology. This problem can be solved by employing cheap naturally occurring mineral adsorbents, one of which is zeolite. Deposits of this mineral occur worldwide. In Ukraine, the Sokyrnytske deposit of zeolites is one of the most known.

However, natural zeolite is not able to absorb organic pollutant molecules the size of which is larger than the size of cavities. To improve the adsorption capacity, zeolites undergo the thermal and chemical activation [5]. Exposure to thermal activation leads to the dehydration and release of a space inside the channels. Under the influence of chemical activation, the mineral is decationized, the channels size increases and additional internal cavities appear.

To chemically activate clinoptilolite, solutions of various mineral acids, including HCl, HNO₃, and H₂SO₄, are often employed. In addition, sulfuric acid solutions are used at certain process steps in manufacturing direct dyes. Spent solutions of sulfuric acid with the concentration of ≤25% constitute a significant proportion of waste from dye production. Therefore, it is worthwhile to use H₂SO₄ solutions to receive an adsorbent capable of absorbing direct dyes from their aqueous solutions.

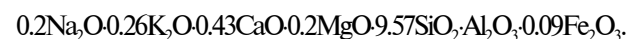
The concentration of acid largely affects the effectiveness of the chemical activation of zeolite. Thus, as reported in ref. [6], when zeolite is treated with 0.3% H₂SO₄ solutions, the mineral can undergo partial decationization without significant dealumination, which does not remarkably influence its structure and ability to participate in adsorption processes. When 3% solutions of H₂SO₄ are used for the treatment, significant decationization and dealumination are accomplished and followed by an increase in the internal crystalline space and adsorption centers. The use of acid solutions of the concentration greater than 25% may cause significant changes in the structure of clinoptilolite: the transition of aluminum into the solution resulting in the formation of a high-silica skeleton.

The purpose of this work was to establish optimal conditions of the activation of naturally occurring zeolite (clinoptilolite) using physical and chemical analysis methods and obtain an adsorbent

with enhanced adsorption characteristics for removing direct dyes from wastewater.

Experimental

Clinoptilolite from the Sokyrnytske deposit (the southwest part of the Transcarpathian internal trough) was used for the research. The mineral rock composition was as follows: clinoptilolite 60–90%, quartz and feldspar 6–7%, clay minerals 2–6%, plagioclase 2%, smectite 7%, the rest was an X-ray amorphous phase. The chemical composition of zeolite included (wt.%): SiO₂ 70.21; Al₂O₃ 12.27; Fe₂O₃ 1.2; FeO 0.55; TiO₂ 0.14; MnO 0.073; P₂O₅ 0.033; K₂O 3.05; Na₂O 1.77; SO₃ 0.10; and (CaO+MgO) 10.604. The composition of clinoptilolite corresponded to the following formula:



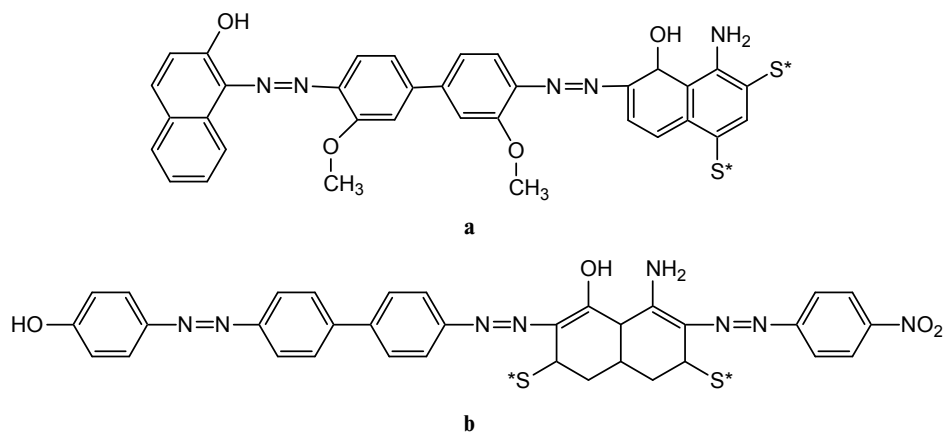
Natural clinoptilolite was activated in the following way. During the day, a fraction of the mineral (0.25 mm sized particles) was treated with 5% and 25% solutions of H₂SO₄ at the 1:10 ratio of solid-to-liquid phases. Activated clinoptilolite was washed out from anion residues. Further, the samples were kept for two hours in air at the temperature of 300°C.

The thermal analysis of clinoptilolite samples was performed using the Q-1500 derivatograph of the Paulik, Paulik and Erdey system at the temperatures from 20 to 1000°C. The samples were analyzed dynamically at the heating rate of 10°C/min in air. The weight of the samples 1 and 2 was equal to 500 mg and that of the samples 3 and 4 amounted to 400 mg. The TG sensitivity was 100 mg, DTG sensitivity was equal to 500 μV and that of DTA was 100 μV. Al₂O₃ was used as a standard. Before conducting thermal studies, the clinoptilolite samples were saturated with water vapor for 2 hours at the room temperature and at the relative pressure of water vapor p/p_s=0.4.

The IR spectra of the dyes and clinoptilolite samples containing adsorbed dyes and being represented in the form of KBr tablets were recorded by using Avatar 320 FT-IR in the range of 4000–400 cm⁻¹.

The adsorption property of clinoptilolite that underwent complex activation was investigated by using the dyes that are shown in Scheme.

To examine the adsorption of direct dyes, clinoptilolite (form 0.2 to 0.62 g) was mixed with the 20 cm³ dye solution with the concentration of 50 g/m³. The resulting suspension was shaken for 12 hours and centrifuged until clinoptilolite was completely detached from the dye solution. The



Scheme. a – direct blue (DB), b – direct green (DG)

liquid phase was filtered off. The equilibrium concentration of dyes in the solution was determined spectrophotometrically using a photoelectric colorimeter KF-77.

The surface tension of dye aqueous solutions was measured by the ring method.

Results and discussion

The thermal analysis is one of the main physical and chemical techniques to examine the properties of substances. Thermal analysis can be used to define the rock's mineral composition. The thermal analysis data can vividly show the nature of mineral-bound water. In addition, the influence of various factors on the structure and chemical composition can be investigated by the nature of the water loss when heated [7].

The results of the complex thermal analysis of clinoptilolite samples are shown as thermograms in Figs. 1–3.

Thermolysis of the clinoptilolite samples includes four stages. At the first stage, the physically adsorbed moisture is released at the temperatures of 20 to 203°C. This process is followed by a rapid mass loss of the samples and a deep endothermic effect that appears on the curve of differential thermal analysis (DTA).

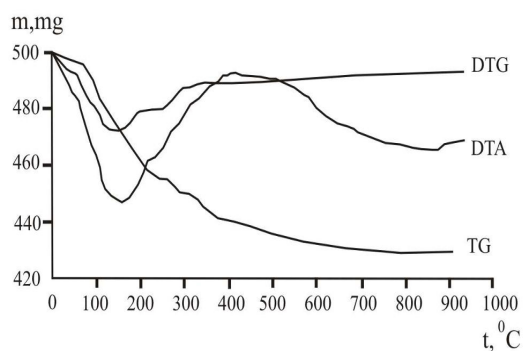


Fig. 1. Thermogram of the sample 1

The second stage of thermolysis in the temperature range from 200 to 410°C fits with the discharge of structured water that is coordinately linked with the mineral exchangeable cations. This process is followed by the gradual mass loss of samples along with a change to the character of a rising region of the DTA curve.

The third stage of thermolysis happens at the temperatures of 400 to 580°C. It demonstrates a release of isolated water molecules being localized

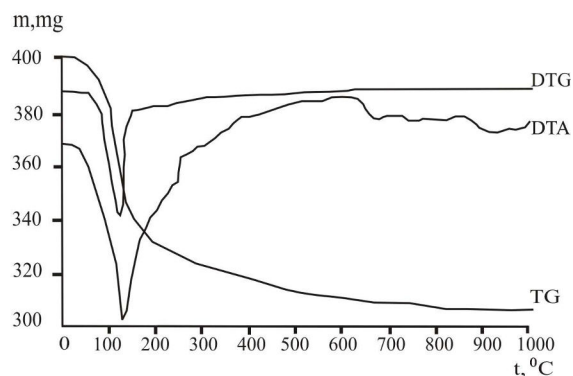


Fig. 2. Thermogram of the sample 2

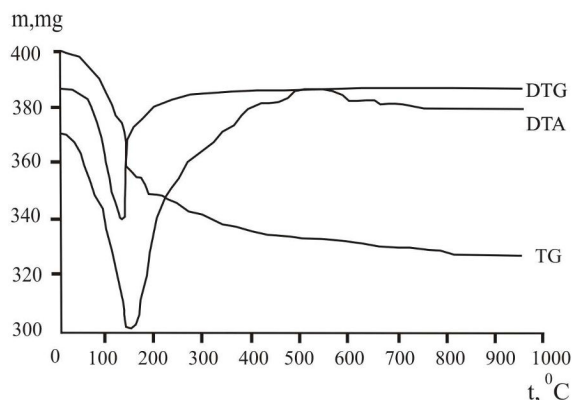


Fig. 3. Thermogram of the sample 3

on the mineral's surface due to water bonds with the OH groups. The process is also accompanied by the appearance of a shallow endothermic effect in the DTA curve.

At the fourth stage in the temperature range of 508–1000°C, one can notice the surface dehydroxylation followed by the liberation of OH groups being chemically bound with the surface. The process ends up with the destruction and amorphization of the clinoptilolite crystalline structure. A strongly manifested endothermic effect appears in the DTA curve.

Considering the mass loss at the first and second stage of thermolysis, the adsorption capability is calculated as to water vapor (Table). The thermogravimetry data demonstrate that the activated samples 2 and 3 exhibit a higher adsorption capacity than the sample 1 of natural clinoptilolite.

An increasing adsorption capacity of activated samples can be adequately explained by the fact that exchangeable cations are removed under the action of H₂SO₄. This is accompanied by liberation of clinoptilolite internal channels. Thermal activation causes diffusion of mobile cations into framework oxygen atoms, followed by an increase in the adsorption space of the mineral [8]. The latter have proved to be filled with water molecules during saturation.

The highest adsorption capacity typical of the sample 3 can be explained by partial dealumination of clinoptilolite under the influence of a 25% H₂SO₄ solution. This results in occurrence of transient pores and macropores in it. Moreover, being exposed to a concentrated acid solution, additional micropores (secondary porosity) that are capable to actively adsorb large-sized water molecules can be formed in the mineral [9].

It should be noted that the activated sample

3 has the largest number of hydroxyl groups that are chemically bound to the surface and detached when the mineral is heated at the temperatures over 500°C. Additional OH groups that appear in the sample are stipulated by the interaction of exchangeable H⁺ ions with atoms of the framework oxygen. This can be followed by the partial destruction of Si–O–Al bonds, the occurrence of additional adsorption-active centers and an increase in the internal effective volume of the mineral. These processes are typically accompanied by an increasing interphase surface of the adsorbent [10].

The results of thermal analysis of clinoptilolite samples fully support the findings of IR-spectroscopic analysis reported in previous publication [11]. An increase in the ligand water content in the activated clinoptilolite samples and their adsorption capacity was confirmed by the changing representation of bands of deformation vibrations of OH groups. The band of the sample of natural clinoptilolite was observed at 1635.40 cm⁻¹ [12]. For the activated samples, it was more intense with an offset to higher frequency, such as 1636.40 cm⁻¹ (sample 2) and 1074.08 cm⁻¹ (sample 3). The existence of a higher number of isolated OH groups on the surface of the activated samples was attributed to that the stretching vibrations of OH groups were deepened and shifted to higher frequencies (2359.82 cm⁻¹ (sample 1), 2361.93 cm⁻¹ (sample 2) and 2362.15 cm⁻¹ (sample 3)). The beginning of the process of partial dealumination of activated clinoptilolite samples corresponds to the destruction of Si–O–Al bonds and is followed by a shift in the absorption band of internal tetrahedral stretching vibrations from 1054.00 cm⁻¹ (sample 1) to 1074.08 cm⁻¹ (sample 2) and 1078.81 cm⁻¹ (sample 3).

The results of thermal and IR spectroscopic analyses of clinoptilolite samples under investigation

The results of thermal analysis of the clinoptilolite samples

Sample	Chemical activation conditions	Sample weight, mg	Temperature range, °C	Mass loss, mg	Adsorption capacity, mmol/g
1	Naturally occurring clinoptilolite	500	20–200	31.0	4.9
			200–400	13.0	
			400–508	4.5	
			508–1000	5.5	
2	5% H ₂ SO ₄ solution	400	20–200	40.1	7.1
			200–410	11.0	
			410–580	4.0	
			580–1000	4.0	
3	25% H ₂ SO ₄ solution	400	20–203	43.0	7.8
			203–410	13.1	
			410–525	2.0	
			525–1000	7.0	

are in good agreement with the data of X-ray diffraction analysis [13]. The diffractograms of activated samples showed changes in the region $2\theta=32-34^\circ$ (CoK_α radiation) which were reflected by a decreasing reflex intensity (-4; 2; 2) and a shift in its interplanar distance from 3.17 Å (the sample of naturally occurring clinoptilolite) to 3.14 Å (the sample of activated 25% H_2SO_4). Such results indicate spatial deformation of the crystal lattice of clinoptilolite caused by decationization and dealumination processes under the influence of activation. This phenomenon led to the display of X-rays from different planes and can cause diffusion of peak diffractograms.

The sample of naturally occurring clinoptilolite and sample 3 were used to examine adsorption. The sample 3 is characterized by the highest adsorption capacity for water molecules and the largest number of adsorption-active centers, as shown by thermal studies.

The adsorption of dyes by the activated clinoptilolite sample was studied in the concentration range below the critical concentration corresponding to the formation of a saturated monomolecular layer on the solution surface and the start of active aggregation of dye molecules. Critical concentrations were found by a curve break σ vs. $\ln c$. The critical concentration is 370 mmol/m^3 and 174 mmol/m^3 for the direct green and blue dye, respectively.

The ability of direct dyes to be adsorbed onto the surface of activated clinoptilolite samples was proved by the IR spectroscopic analysis. In the spectra of the samples that contain adsorbed dyes, additional bands emerge in the region of 1530–1640 cm^{-1} that correspond to the vibrations of $-\text{C}=\text{C}-$ bonds of an aromatic ring of dyes. IR spectra of samples of activated clinoptilolite show an increase in the band intensity in the region of 650–670 cm^{-1} caused by stretching vibrations of $\text{C}-\text{N}$ bonds that are present in the aromatic ring of the adsorbed dyes [14]. A band in the region of 2890–3450 cm^{-1} corresponds to stretching vibrations of proton in NH_3^+ amino groups. This band is shifted to the low-frequency spectrum region as compared to the band of non-proton $-\text{NH}_2$ group (3400–3500 cm^{-1}). The protonation of the amino group can take place during the adsorption of dye molecules as a result of donor-acceptor interaction, which occurs between the lone-pair electrons of the nitrogen atom of the $-\text{NH}_2$ group of the sorbate and the protons of OH groups of activated clinoptilolite (Brønsted acid centers). Thus, it can be argued that adsorption takes place not only under the effect of dispersion forces of interaction between the active fields of the adsorbent

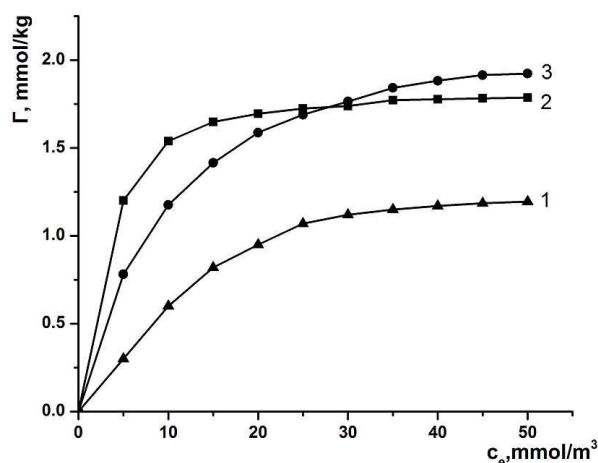


Fig. 4. Adsorption isotherm: 1 – DG dye on surface of the sample 1; 2 – DB dye on surface of the sample 3; 3 – DG dye on surface of the sample 3

and sorbate molecules, but also with the help of chemical forces.

Figure 4 shows the adsorption isotherms of dyes by clinoptilolite treated by the 25% H_2SO_4 solution. In addition, the adsorption isotherm of the DG dye by activated clinoptilolite is illustrated in Figure.

The values of dye adsorption were determined according to the following equation:

$$\Gamma = \frac{C_i - C_e}{m} V,$$

where C_i and C_e are the initial and equilibrium concentration of the dyes in the solution, mmol/m^3 ; V is the volume of dye solution, m^3 ; m is the weight of activated clinoptilolite sample, kg.

Unlike the sample 1, the sample 3 features a higher adsorption capacity in relation to dye molecules. This difference is associated with the fact that not only the external but also a certain part of a near-surface of the pore space of activated clinoptilolite participates in the adsorption of dye molecules. Such near-surfaces contain the adsorption active centers and are available to dye molecules and their associates.

The adsorption isotherms were approximated by the linearized Langmuir equation and the constants of the equation were determined. The limit values of monomolecular adsorption of the DG and DB dyes were equal to 2.32 and 1.86 mmol/kg , respectively. The equilibrium constants of the monomolecular adsorption of the DG and DB amounted to 0.104 and 0.506 m^3/mmol , respectively.

A lower adsorption capacity of the DG dye is due to its molecule that contains methyl groups that

hinder the diffusion of DG molecules into smaller pores of the adsorbent. Additionally, DG dye molecules are able to better associate in the solution, as evidenced by the intensive growth of adsorption in the region of low concentrations and reduction in the region of concentrations greater than 15 mmol/m³.

Conclusions

The adsorbent with enhanced adsorption characteristics were produced via the process of the thermal and chemical activation of naturally occurring clinoptilolite. The use of a 25% solution of H₂SO₄ has proved to be the most optimal conditions to obtain the effective adsorbent. The effect of 25% H₂SO₄ leads to decationization and significant dealumination of clinoptilolite with the preservation of its structure. This process is followed by the emergence of additional adsorption centers and an increase in the volume of internal channels. The increasing number of Brønsted acid centers is confirmed by the occurrence of a large number of OH groups on the adsorbent surface. These groups are lost at temperatures greater than 500°C. Increasing channel sizes are indicated by the better ability of clinoptilolite modified by the 25% H₂SO₄ solution to retain water molecules. During activation, the existence of additional adsorption centers, each becoming more available with increasing pore size, is confirmed by the increased ability of activated clinoptilolite to adsorb dye molecules.

REFERENCES

1. *Structural* and physicochemical properties of natural zeolites: clinoptilolite and mordenite / Korkuna O., Lebeda R., Skubiszewska-Zieba J., Vrublevs'ka T., Gun'ko V.M., Ryczkowski J. // *Microporous Mesoporous Mater.* – 2006. – Vol.87. – P.243-254.
2. *Treatment* of effluents from ions of heavy metals as display of environmentally responsible activity of modern businessman / Malovanyy M., Sakalova H., Vasylynych T., Palamarchuk O., Semchuk J. // *J. Ecol. Eng.* – 2019. – Vol.20. – No. 4. – P.167-176.
3. *Production* of renewable energy resources via complex treatment of cyanobacteria biomass / Malovanyy M., Nikiforov V., Kharlamova O., Synelnikov O. // *Chem. Chem. Technol.* – 2016. – Vol.10. – No. 2. – P.251-254.
4. *Koval M.H., Fomina N.M., Stoliarenko H.S.* Vdoskonalennya tekhnologii ochyshchennya stichnykh vod farbuval'no-ozdobliuvalnogo vyrobnytstva shlyakhom vprovadzhennya protsesiv kavitatsii i elektrokavitatsii ta mozhlyvosti povtornogo vykorystannya stichnykh vod // *Visnyk Cherkaskogo Derzhavnogo Tekhnologichnogo Universytetu.* – 2019. – No. 3. – P.145-152.
5. *Malovanyy M.S., Petrushka I.M.* Wastewater treatment with natural dispersed sorbents. – Lviv: Vydavnytstvo Lvivskoi Politekhniky, 2012. – 180 p.
6. *Wang X., Plackowski C.A., Nguyen A.V.* X-ray photoelectron spectroscopic investigation into the surface effects of sulphuric acid treated natural zeolite // *Powder Technol.* – 2016. – Vol.295. – P.27-34.
7. *Kochubei V.V., Poluizhyn I.P., Yaholnyk S.G.* Research into the kinetics of thermal dehydration of natural glauconite // *Voprosy Khimii i Khimicheskoi Tekhnologii.* – 2012. – No. 4. – P.159-163.
8. *Adsorption* of cadmium on acid-modified Transcarpathian clinoptilolite / Vasylechko V.O., Gryshchouk G.V., Kuz'ma Yu.B., Zakordonskiy V.P., Vasylechko L.O., Lebedynets L.O., Kalytovsky M.B. // *Microporous Mesoporous Mater.* – 2003. – Vol.60. – P.183-196.
9. *Termodesorbtsiya vody i adsorbtsiini vlastyivosti zakarpatskykh tseolitiv* / Zarodonsky V., Vasilechko V., Stashuk P., Grishuk G. // *Visnyk Lvivskogo Universytetu. Seriya Khimichna.* – 2004. – No. 44. – P.247-256.
10. *Adsorption* of water vapor by natural and chemically modified clinoptilolite and modernite samples / Rakytskaya T.L., Kiiose T.A., Truba A.S., Ennan A.A., Dlubobskiy R.M., Volkova V.Ya. // *Chem. Phys. Technol. Surf.* – 2012. – Vol.3. – No. 4. – P.455-462.
11. *Ich-spektroskopichne doslidzhennya zrazkiv khimichno aktyvovanykh zakarpatskykh tseolitiv* / Yaholnyk S.G., Khanik Y.M., Trotskiy V.I., Duleba V.P. // *Visnyk Natsionalnogo Universytetu «Lvivska Politekhnika».* Khimiya, Tekhnologiya Rechovyn ta yikh Zastosuvannya. – 2007. – No. 590. – P.295-298.
12. *Elaipoulos K., Perraki Th., Grigoropoulou E.* Monitoring the effect of hydrothermal treatments on the structure of a natural zeolite through a combined XRD, FTIR, XRF, SEM and N₂-porosimetry analysis // *Microporous Mesoporous Mater.* – 2010. – Vol.134. – P.29-43.
13. *Yaholnyk S.G., Trotskiy V.I., Khanyk Y.M.* Doslidzhennya protsesu khimichnogo modifykuvannya klynoptilolitu z dopomogoyu rentgenofazovogo analizu // *Naukovyi Visnyk NLTU Ukrainy.* – 2006. – No. 16. – P.195-200.
14. *Organic* dye removal from aqueous media by using acid modified Clinoptilolite / Ebrahimi R., Maleki A., Shahmoradi B., Rezaee R., Daraei H., Safari M., Zandsalimi Y., Bahmani P., Puttaiah S.H. // *J. Adv. Environ. Health Res.* – 2018. – Vol.6. – P.118-127.

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ДОСЛІДЖЕННЯ ВПЛИВУ УМОВ АКТИВАЦІЇ ЗАКАРПАТСЬКОГО КЛИНОПТИЛОЛІТУ НА ЙОГО АДСОРБЦІЙНУ ЗДАТНІСТЬ

V.V. Kochubei, S.G. Yaholnyk, S.V. Kniaz, L.Y. Parashchuk, M.S. Malovanyy

Досліджено вплив умов активації на адсорбційну здатність закарпатського клиноптилоліту. Хімічну активацію природного клиноптилоліту проводили 5%-ним та 25%-ним водними розчинами H_2SO_4 при співвідношенні твердої та рідкої фаз 1:10. Термічну активацію здійснювали прогріванням хімічно активованого клиноптилоліту за температури $300^\circ C$. За результатами термічного аналізу зразок, активований 25%-ним водним розчином H_2SO_4 , мав найбільшу адсорбційну здатність відносно парів води та найбільший вміст гідроксильних груп, які втрачались за температур, вищих $500^\circ C$. Отримані результати пояснюються частковим деалюмінванням цеоліту, яке супроводжувалось зростанням його внутрішнього кристалічного простору та появою додаткових адсорбційно-активних центрів. Руйнування зв'язків Si—O—Al, що зумовлює появу адсорбційно-активних центрів Бренстеда, підтверджували результатами ІЧ-спектроскопічного та рентгененофазового аналізів. На ІЧ спектрі зразка, активованого 25%-ним водним розчином H_2SO_4 , спостерігався значний зсув смуги валентних тетраедричних коливань на ділянці вищих частот. На дифрактограмі зразка, активованого 25%-ним водним розчином H_2SO_4 , спостерігалось значне зменшення рефлексів в інтервалі $2\theta=32-34^\circ$ (CoK_α -випромінювання), що свідчило про просторову деформацію кристалічної решітки за рахунок процесів декаціонування та деалюмінвання. Був проведений порівняльний аналіз здатності природного та активованого 25%-ним розчином H_2SO_4 клиноптилоліту адсорбувати молекули прямих барвників з їх водних розчинів. Зростання адсорбційної здатності активованого клиноптилоліту пояснюється появою в ньому додаткових адсорбційних центрів Бренстеда, які стають доступними для молекул барвників в процесі активації клиноптилоліту. Знайдені константи рівняння ізотерми мономолекулярної адсорбції Ленгмюра.

Ключові слова: клиноптилоліт, термічний аналіз, адсорбція, прямі барвники, активація.

RESEARCH INTO THE INFLUENCE OF ACTIVATION CONDITIONS OF TRANSCARPATHIAN CLINOPTILOLITE ON ITS ADSORPTION CAPACITY

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The paper reports the effects of the activation conditions on the adsorption capacity of Transcarpathian clinoptilolite. Naturally occurring clinoptilolite underwent chemical activation by 5% and 25% aqueous solutions of H_2SO_4 at the solid-liquid ratio of 1:10. Thermal activation was performed by the heating of chemically activated clinoptilolite at the temperature of $300^\circ C$. Thermal analysis showed that the sample activated by 25% H_2SO_4 solutions demonstrated the highest adsorption capacity with respect to water vapor and the highest content of hydroxyl groups that were lost at the temperatures greater than $500^\circ C$. The data obtained can be explained by partial dealumination of zeolite, which is accompanied by an increase in its internal crystalline space and the emergence of additional adsorption active centers. The destruction of Si—O—Al bonds, which gave rise to the Brønsted adsorption active centers, was confirmed by the results of IR spectroscopic and X-ray phase analyses. The IR spectrum of the sample activated by 25% H_2SO_4 solution exhibited a drastic shift of band associated with tetrahedral stretching vibrations to the region of higher frequencies. A significant reduction of reflections in X-ray diffraction pattern of the sample treated by 25% H_2SO_4 solution appeared in the region $2\theta=32-34^\circ$ (CoK_α radiation). This indicated steric strains of crystalline lattice due to decationization and dealumination processes. A comparative analysis of both naturally occurring clinoptilolite and modified by 25% H_2SO_4 solution was performed to characterize the capacity to adsorb direct dye molecules from their aqueous solutions. An increase in the adsorption capacity of activated clinoptilolite was ascribed to the emergence of additional Brønsted acid centers that became available to dye molecules during the activation of clinoptilolite. The constants of the Langmuir monomolecular adsorption isotherm equation were determined.

Keywords: clinoptilolite; thermal analysis; adsorption; direct dyes; activation.

REFERENCES

1. Korkuna O., Leboda R., Skubiszewska-Zieba J., Vrublevs'ka T., Gun'ko V.M., Ryczkowski J. Structural and physicochemical properties of natural zeolites: clinoptilolite and mordenite. *Microporous and Mesoporous Materials*, 2006, vol. 87, pp. 243-254.
2. Malovanyy M., Sakalova H., Vasylynych T., Palamarchuk O., Semchuk J. Treatment of effluents from ions of heavy metals as display of environmentally responsible activity of modern businessman. *Journal of Ecological Engineering*, 2019, vol. 20, no. 4, pp. 167-176.
3. Malovanyy M., Nikiforov V., Kharlamova O., Synelnikov O. Production of renewable energy resources via complex treatment of cyanobacteria biomass. *Chemistry & Chemical Technology*, 2016, vol. 10, no. 2, pp. 251-254.

4. Koval M.H., Fomina N.M., Stoliarenko H.S. Vdoskonalennya tekhnologii ochyshchennya stichnykh vod farbuval'no-ozdobliuvalnogo vyrobnytstva shlyakhom vprovadzhennya protsesiv kavitatsii i elektrokavitatsii ta mozhlivosti povtornogo vykorystannya stichnykh vod [Improvement of wastewater treatment technology of dyeing-and-finishing manufacturing by introducing cavitation and electrocavitation processes and the possibility of reuse of wastewater]. *Visnyk Cherkaskogo Derzhavnogo Tekhnologichnogo Universytetu*, 2019, no. 3, pp. 145-152. (in Ukrainian).
5. Malovanyy M.S., Petrushka I.M., *Ochyshchennya stichnykh vod pryrodnyimi dyspersnyimi sorbentamy* [Wastewater treatment with natural dispersed sorbents]. Lvivska Politehnika Publishers, Lviv, 2012. 180 p. (in Ukrainian).
6. Wang X., Plackowski C.A., Nguyen A.V. X-ray photoelectron spectroscopic investigation into the surface effects of sulphuric acid treated natural zeolite. *Powder Technology*, 2016, vol. 295, pp. 27-34.
7. Kochubei V.V., Poluizhyn I.P., Yaholnyk S.G. Doslidzhennya kinetyky termichnoyi degidratatsii pryrodnogo glaukonitu [Research into the kinetics of thermal dehydration of natural glauconite]. *Voprosy Khimii i Khimicheskoi Tekhnologii*, 2012, no. 4, pp. 159-163. (in Ukrainian).
8. Vasylechko V.O., Gryshchouk G.V., Kuz'ma Yu.B., Zakordonskiy V.P., Vasylechko L.O., Lebedynets L.O., Kalytov's'ka M.B. Adsorption of cadmium on acid-modified Transcarpathian clinoptilolite. *Microporous and Mesoporous Materials*, 2003, vol. 60, pp. 183-196.
9. Zarodonsky V., Vasilechko V., Stashuk P., Grishuk G. Termodesorbtsiya vody i adsorbtsiini vlastyvoli zakarpatskykh tseolitiv [Thermal adsorption of water and adsorption properties of Transcarpathian zeolites]. *Visnyk Lvivskogo Universytetu. Seriya Khimichna*, 2004, no. 44, pp. 247-256. (in Ukrainian).
10. Rakytskaya T.L., Kiose T.A., Truba A.S., Ennan A.A., Dlubobskiy R.M., Volkova V.Ya. Adsorption of water vapor by natural and chemically modified clinoptilolite and modernite samples. *Chemistry, Physics and Technology of Surface*, 2012, vol. 3, no. 4, pp. 455-462.
11. Yaholnyk S.G., Khanik Y.M., Trotskiy V.I., Duleba V.P. ICh-spektroskopichne doslidzhennya zrazkiv khimichno aktyvovanykh zakarpatskykh tseolitiv [IR spectroscopic study of samples of chemically activated Transcarpathian zeolites]. *Visnyk Natsionalnogo Universytetu «Lvivska Politehnika». Khimiya, Tekhnologiya Rechovin ta yikh Zastosuvannya*, 2007, no. 590, pp. 295-298. (in Ukrainian).
12. Elaiopoulos K., Perraki Th., Grigoropoulou E. Monitoring the effect of hydrothermal treatments on the structure of a natural zeolite through a combined XRD, FTIR, XRF, SEM and N₂-porosimetry analysis. *Microporous and Mesoporous Materials*, 2010, vol. 134, pp. 29-43.
13. Yaholnyk S.G., Trotskiy V.I., Khanyk Y.M. Doslidzhennya protsesu khimichnogo modyfikuvannya klynoptylolitu z dopomogoyu rentgenofazovogo analizu [Study of the chemical modification process of clinoptilolite using X-ray diffraction analysis]. *Naukovyi Visnyk NLTU Ukrainy*, 2006, no. 16, pp. 195-200. (in Ukrainian).
14. Ebrahimi R., Maleki A., Shahmoradi B., Rezaee R., Daraei H., Safari M., Zandsalimi Y., Bahmani P., Puttaiah S.H. Organic dye removal from aqueous media by using acid modified Clinoptilolite. *Journal of Advances in Environmental Health Research*, 2018, vol. 6, pp. 118-127.