



Influence of chemical activation on the ability of Transcarpathian clinoptilolite to adsorb direct dyes

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✔ **Abstract.** Significant quantities of wastewater are generated in dyes synthesis processes and in technologies involving their use, which are toxic to living organisms, making the purification of industrial wastewater from organic colouring substances a pressing issue nowadays. The aim of this study was to investigate the prospects of using natural clinoptilolite from the Sokyrnytske deposit and its activated forms in the purification processes of wastewater from direct dyes. Natural clinoptilolite was activated by treatment with 5% H_2SO_4 and HCl aqueous solutions and heating at 300°C for two hours. The impact of activation conditions on the structural adsorption properties of clinoptilolite has been determined using a comprehensive thermal analysis method. The adsorption of the direct violet dye by natural and activated clinoptilolite has been investigated using spectrophotometric methods at pH 7 and a light wavelength of 550 nm, corresponding to the maximum value of light absorption coefficient. According to the results of thermal analysis, activated clinoptilolite samples exhibited a more developed specific surface area and a higher presence of hydroxyl groups, which can serve as active adsorption sites on the surface. The results of the violet dye adsorption have corresponded to the monomolecular Langmuir theory, indicating the energetic homogeneity of the adsorption centres. By linearizing the Langmuir adsorption isotherm equation, adsorption characteristics of natural and activated clinoptilolite with a 5% HCl aqueous solution relative to the direct violet dye have been determined. Activated clinoptilolite has shown increased sorption capacity (9.53 mmol/kg) compared to natural clinoptilolite (2.28 mmol/kg). The improvement in adsorption characteristics of activated clinoptilolite has been explained by its partial dealumination, resulting in the appearance of meso- and macropores capable of retaining dye molecules. The use of a 30% H_2SO_4 aqueous solution in activation processes and heating above 400°C has caused mineral degradation, confirmed by electron images of its surface. Practical value of the study lies in the recommendation to apply activated clinoptilolite in the purification processes of wastewater from organic pollutants

✔ **Keywords:** zeolite; sorbent; colourants; thermal analysis; light wavelength; adsorption characteristics

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Introduction

One of today's problems is the reduction of the world's freshwater reserves. Particularly harmful pollutants in the hydrosphere are organic compounds. Among such pollutants, organic dyes, which are widely used in the technological processes of the light, food, pulp and paper industries, occupy a prominent place. In textile production, direct anionic dyes are widely used. These dyes are characterized by affinity for both cellulose fibres and amphoteric fibres (silk, leather, fur). According to M.G. Koval (2022), depending on the type of dye and the method of dyeing the fabric, from 20 to 50% of dyes enter the wastewater at the end of the production cycle. When washing dyed fabrics, the unfixed dye is washed off the surface of the fibre and enters the wastewater in significant quantities, many times exceeding the norms of maximum permissible concentrations. According to a study by J. Pavlović *et al.* (2022) the presence of dyes in water bodies reduces light transmission, negatively affects photosynthesis, disrupts self-purification processes and causes significant damage to aquatic ecosystems.

There are many technologies for wastewater treatment from organic pollutants. Researchers N.M. Tolstopalova *et al.* (2019) include chemical (coagulation, ozonation, photochemical reactions, electrochemical destruction, electrochemical coagulation), physical (adsorption, membrane separation, ion exchange) and biological treatment to traditional methods of removing dyes from the aqueous phase. In particular, N. Öz *et al.* (2021) investigated membrane microfiltration technology in details. According to spectrophotometric studies, the discoloration effects of dye solutions were 91-95%, 94-98% and 96-99% at light wavelengths of 436 nm, 525 nm and 620 nm. M. Madani (2021) described the technology of electrochemical treatment of effluents from direct dyes, investigated the influence of various factors on the efficiency of dye removal – the duration of purification, the pH of the medium, the presence of sodium chloride in the dye solution. Scientists T.V. Solodovnik *et al.* (2019) investigated the influence of the conditions of coagulation and flocculation processes on the degree of purification of dyed model solutions, similar in composition to wastewater of textile enterprises, using a natural flocculant – chitosan in combination with inorganic coagulants.

During the period of hostilities and limited funds for water protection measures, it is important for enterprises to choose the most optimal wastewater treatment technology. One of the important methods of elimination of hydrosphere pollutants is the technology of adsorption treatment of effluents with the use of mineral sorbents. Scientists S. Matiuk & V. Gribinko (2019) claim that the sorption method allows to remove a trace amounts of contaminants, makes it possible to remove substances of an extremely wide nature from wastewater, regardless of their chemical resistance. Mineral sorbents of natural origin such as zeolites and clay minerals, which are characterized by a sufficiently high sorption capacity, cation exchange properties, availability and low cost, are widely used for wastewater

treatment. Natural sorbents are widespread in Ukrainian deposits and are effectively used in various sectors of the national economy. Significant deposits of zeolite rocks are found in Transcarpathia and the mountainous Crimea. The most significant industrial importance among them belongs to the Sokyrnytske zeolite deposit. O.I. Ivanenko *et al.* (2020) note that the reserves of zeolite deposits of the Sokyrnytske deposit amount to 125.6 million tons, of which 39.5 million tons are high-quality zeolites. Clinoptilolite is one of the varieties of zeolites that belongs to the heulandite group and is widely used in practice.

The specific properties of this adsorbent are caused by the structure of the three-dimensional aluminosilicate framework, the presence of a developed system of cavities and channels, which contain a complex of exchangeable cations and water molecules. However, natural zeolites are not able to absorb molecules of organic pollutants, the size of which is larger than the size of the voids of the mineral. To improve the adsorption properties, zeolites are subjected to various types of activation. It is stated in the work of A. Ivanchenko *et al.* (2021) that under the influence of chemical activation, which proceeds as a result of the action of mineral acids, partial dealumination of the mineral occurs, which is accompanied by a change in the structural and adsorption parameters – specific surface area and pore size. Scientists I. Fediv *et al.* (2022) noted that one of the most common methods of improving the sorption properties of zeolites is thermal treatment at elevated temperatures, which causes water desorption and the release of zeolite channels.

However, the results of research on the adsorption properties of zeolites are still not sufficiently complete and systematized. The method of activation of zeolites, which makes it possible to form a system of channels in the mineral capable of retaining molecules of surface-active substances and dyes in the process of adsorption, requires a more detailed study. The efficiency of mineral modification depends on the nature and concentration of the acid, the contact time of the acid with the sample, the ratio of liquid and solid phases, the temperature at which activation is carried out. It is also necessary to take into account the peculiarities of the structure of adsorbate molecules. In particular, the ability of zeolites to adsorb dye molecules is influenced by the property of dyes to dissociate and, under certain conditions, to form associates. Therefore, the aim of the work was to investigate the effect of complex thermal and chemical activation with the participation of solutions of chloride and sulfate acids on the structural and adsorption characteristics of one of the types of zeolite, Transcarpathian clinoptilolite, for use in the process of wastewater treatment from dyes.

Materials and Methods

In this work, the natural zeolite clinoptilolite of the Sokyrnytske deposit of the Zakarpattia Region (Ukraine) was studied. Chemical composition of the mineral

(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; CaO, MgO – 10.604. The composition of clinoptilolite corresponds to the formula: 0.2Na₂O · 0.26K₂O · 0.43CaO · 0.2MgO · 9.57SiO₂ · Al₂O₃ · 0.09Fe₂O₃.

Natural clinoptilolite with an average grain size of 0.25 mm (sample 1) was activated by treatment with a 5% solution of H₂SO₄ (sample 2) and a 5% solution of HCl (sample 3) at a ratio of solid and liquid phases of 1:10 during the day. After activation, the solid residue was washed with distilled water until a negative reaction to Cl⁻, SO₄²⁻ ions. Samples treated with mineral acids were kept for two hours at a temperature of 300°C.

Thermal analysis of clinoptilolite samples was performed on a Q-1500 derivatograph of the Paulik-Paulik-Erdey system (MOM, Hungary) in the temperature range of 20-1000°C. The samples were analysed in a dynamic mode with a heating rate of 10°C per minute in

an air atmosphere. The mass of the sample of natural clinoptilolite was 500 mg, the mass of activated samples was 400 mg. The sensitivity according to the scale of TG (thermogravimetric curves) was equal to 100 mg, according to the scale of DTG (differential thermogravimetric curves) – 500 μV, and sensitivity according to the scale of DTA (differential thermal analysis curves) – 100 μV. Measurement error of mass loss was ± 0.5%. The reference substance was Al₂O₃. Before conducting thermal studies, clinoptilolite samples were saturated with water vapour for two hours at room temperature. The specific surface area of natural and activated zeolite samples was approximately calculated based on the mass loss during their dehydroxylation. To determine SSA, the area (0.21 · 10⁻¹⁸ m²), which accounted for one chemisorbed water molecule was taken into account (Vasilechko *et al.*, 2000). Direct violet (DV) dye was used to study the adsorption capacity of clinoptilolite samples (Fig. 1).

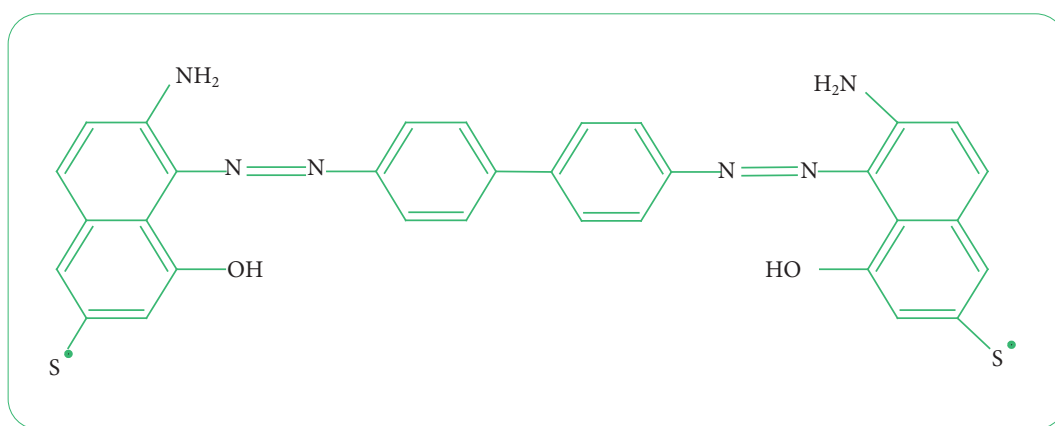


Figure 1. Structural formula of direct violet

Source: created by the authors

The surface tension of aqueous dye solutions and the critical micelle concentration (CMC) were measured by ring tear-off method. To study the adsorption, 0.62 g of clinoptilolite was mixed with 20 ml of DV dye solution of the proper concentration. That suspension was shaken periodically during 12 hours. Next, the suspension was precipitated until the clinoptilolite was completely separated from the dye solution, the liquid phase was filtered out. The adsorption value of the DV dye was determined by the difference in the concentrations of the initial and equilibrium solutions.

Concentrations of dye solutions were found using the Perkin Elmer-402 spectrophotometer (Perten, USA) in the range of light wavelengths of 195-900 nm. The operating range of light wavelengths for adsorption studies was established by determining the dependence of the light absorption coefficient on the light wavelength at different pH values.

To measure pH, an ionometer I-160MI (Tensor, Ukraine) was used, commutated by a system of electrodes ES-10603 and ESr-10103. In the preparation of alkaline solutions (pH 13), 0.5 ml of M NaOH was added to 10 ml of DV dye solution with a concentration of 50 mmol/m³,

and in the preparation of acidic solutions (pH 1-2), 0.2 ml of 1.0 · 10⁻⁴ M HCl and 0.15 ml of 1.0 · 10⁻⁴ M H₂SO₄ were added to 10 ml of dye solution. The adsorption capacity of natural and activated clinoptilolite was evaluated by modelling experimental data with the Langmuir equation (Álvarez-Ayuso & García-Sánchez, 2003):

$$A = \frac{A_{\infty} Kc}{1 + Kc}, \quad (1)$$

where A – the adsorption value; A_∞ – adsorption capacity of the monolayer or the limit value of monomolecular sorption; K – the constant of adsorption-desorption equilibrium; c – the equilibrium concentration. In order to study the effect on the structure of clinoptilolite at high temperatures and acid solutions of higher concentrations, additional studies were carried out. Clinoptilolite was heated at a temperature of 500°C for two hours, in some studies the mineral was activated with a 30% solution of H₂SO₄. Surface images of natural and activated clinoptilolite samples were obtained using an electron microscope JSM T 220 A Scanning microscope (JEOL, Japan).

Results

Thermal analysis is one of the important methods for studying the properties of a substance. On the basis of thermal analysis data, it is possible to get a visual idea of the nature

of water bound by a mineral, and by the nature of its loss when heated, to investigate the influence of various factors on its properties. Figure 2 shows a thermogram of clinoptilolite activated with a 5% H_2SO_4 aqueous solution.

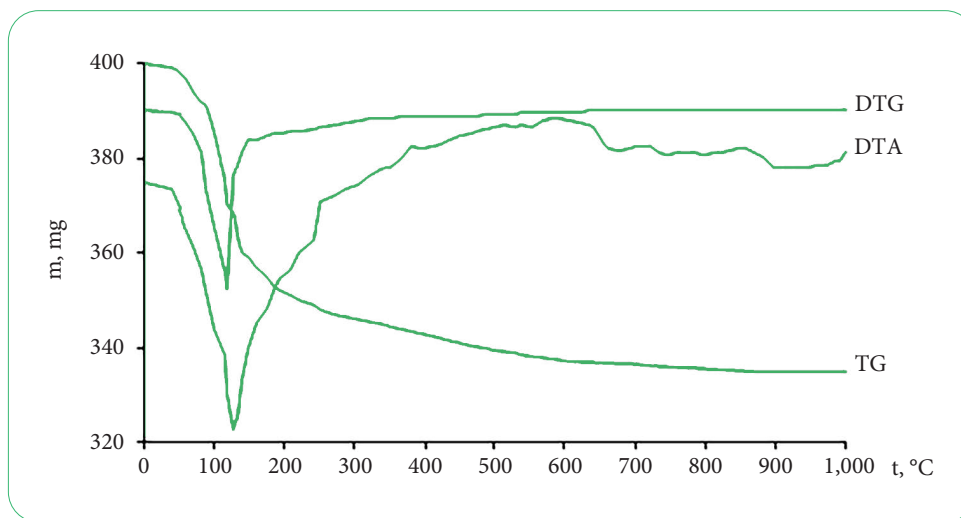


Figure 2. Thermogram of a sample activated with 5% H_2SO_4 aqueous solution (sample 2)

Source: created by the authors

At the first stage of thermolysis of clinoptilolite samples, there was a separation of physically adsorbed, structured water, which is coordinately bound to exchangeable cations, and water, which is localized on the surface of the mineral due to hydrogen bonds with surface OH groups (hydroxyl groups). This process was accompanied by a significant loss of sample mass, the appearance of a clear extremum on the DTG curves and a deep endothermic effect on the DTA curves.

At the second stage of thermolysis of the samples, dehydroxylation of the surface occurred, which was

accompanied by cleavage of OH groups and gradual loss of sample mass. The process culminated in the destruction of the structure of the mineral. A broad endothermic effect appeared on the DTA curve. The loss of samples' mass at the second stage of thermolysis is proportional to the content of surface OH groups, which are able to serve as adsorption-active centres of the mineral.

Figure 3 shows a comparison of the TG curves of natural and activated clinoptilolite samples. Table 1 presents the results of complex thermal analysis of clinoptilolite samples.

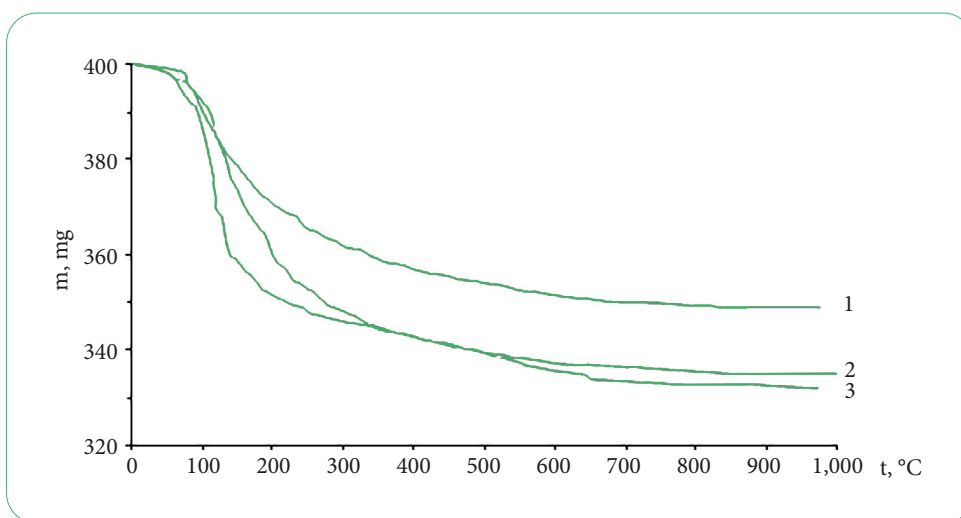


Figure 3. TG curves

Note: 1 – sample 1; 2 – sample 2; 3 – sample 3

Source: created by the authors

Table 1. Results of thermal analysis of natural and activated clinoptilolite samples

Sample	Stage	Sample weight, mg	Temperature interval, °C	Weight loss, mg	Specific surface area, m ² /g
1	I	500	20-508	48.5	77.26
	II		508-1,000	5.5	
2	I	400	20-525	55.1	96.57
	II		525-1,000	5.5	
3	I	400	20-525	57.5	114.13
	II		525-1,000	6.5	

Source: created by the authors

As can be seen from Table 1, activated clinoptilolite samples were characterized by a higher content of hydroxyl groups and a more developed specific surface area. The increase in SSA under the action of mineral acids can be explained by partial dealuminization of clinoptilolite, which was accompanied by an increase in pore volume, the appearance of secondary porosity and, accordingly, the number of additional adsorption-active centres (Vasilechko *et al.*, 2015).

Additional OH groups in the process of chemical activation of clinoptilolite can appear during the interaction of exchangeable H⁺ ions with frame oxygen atoms. The action of temperature can also affect the content of the adsorption centres of the mineral. It is known that an increase in temperature causes the diffusion of exchangeable

cations into the internal channels of the zeolite structure. Additional OH groups can appear due to the interaction of polarized water molecules, which are coordinately bound to mobile cations (Melnyk *et al.*, 2022).

The choice of the optimal temperature for thermal activation of clinoptilolite was established in separate studies. The sample, thermally activated at a temperature of 300°C, had the highest adsorption capacity relative to water vapour. Heating of clinoptilolite to a temperature of 400°C caused deterioration of its structural and adsorption characteristics. The result obtained was explained by the partial destruction and amorphousness of the mineral structure. The beginning of the destruction of the clinoptilolite structure at temperatures above 400°C was confirmed by electron microscope images of its surface (Fig. 4).

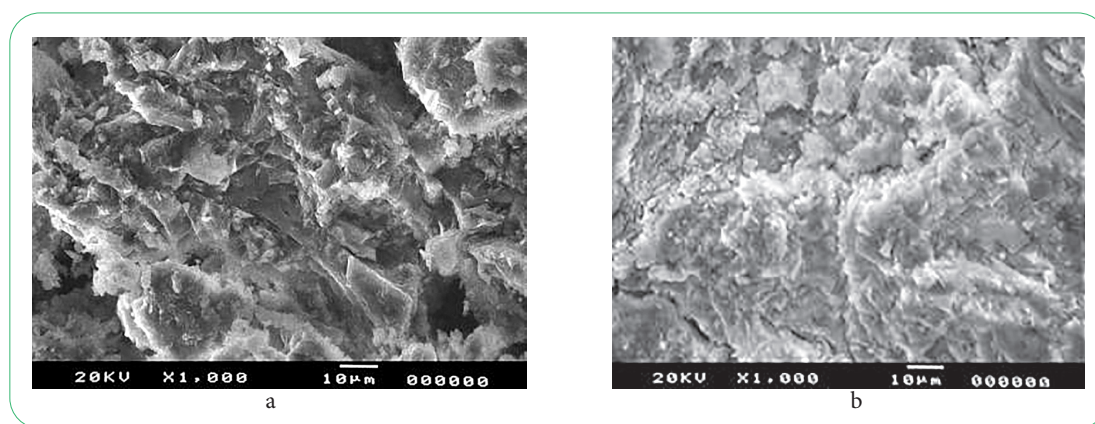


Figure 4. Electronic images of the clinoptilolite surface

Note: a – natural; b – heated at 550°C

Source: created by the authors

Clear crystal faces were observed on the surface of the natural clinoptilolite sample, and there was a system of voids and channels. When the clinoptilolite sample was heated to 550°C, defects and disturbances of the crystal lattice appeared, which were accompanied by a decrease in the size of elementary cells. The faces of the mineral became fuzzy and blurred. Under the influence of high temperatures, the surface of the mineral was “sintered” and its structure was destroyed.

The concentration of the acid greatly influences the chemical activation efficiency of zeolite. According to

the authors X. Chen & W.V. Srubar (2020) found that H₂SO₄ solutions of low concentration (≤ 5%) are capable of causing decation and slight dealuminization of zeolite, which is accompanied by an increase in its internal crystalline space and an increase in the number of adsorption centres. Sulfate acid solutions of higher concentrations (≥ 25%) can cause significant changes in the structure of clinoptilolite and deterioration of its adsorption characteristics. Figure 5 shows a comparison of surface images of clinoptilolite samples activated with 5% and 30% H₂SO₄ solutions.

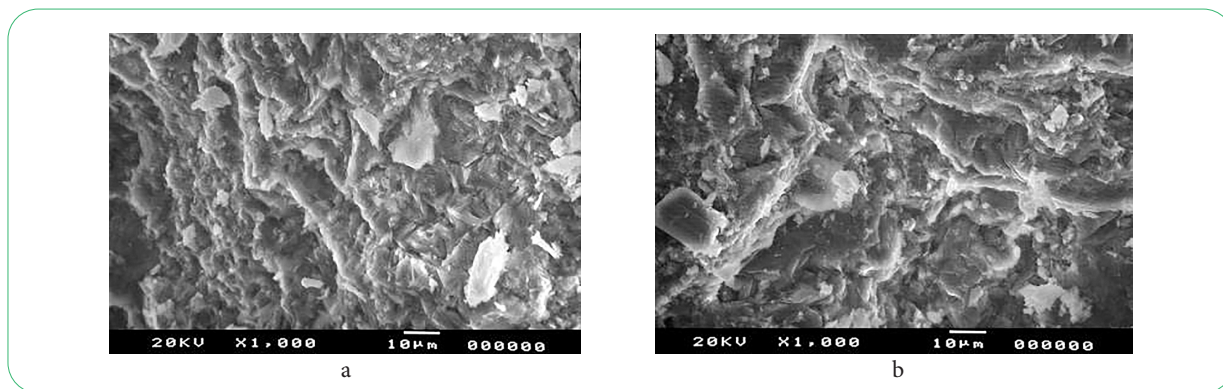


Figure 5. Electronic surface images of activated clinoptilolite

Note: a – activated with 5% H_2SO_4 aqueous solution; b – activated with 30% H_2SO_4 aqueous solution

Source: created by the authors

Treatment with a 30% H_2SO_4 solution caused certain changes in the surface of the sample – the edges of the mineral became less clear, and the appearance of the surface blurred, which indicated the initial destruction of the structure of the mineral. When clinoptilolite was treated with a 5% H_2SO_4 solution, no significant changes were observed in the image of the sample surface. The processes of partial dealuminization of clinoptilolite under the influence of acids of low concentrations (5% H_2SO_4 solution and 5% HCl solution) were confirmed by infrared spectroscopy. Acid solutions caused only a slight dealuminization of clinoptilolite with partial destruction of Si-O-Al bonds, as evidenced by the displacement of the absorption bands of valence intra-tetrahedral oscillations from 1054.00 cm^{-1} (sample 1) to 1074.08 cm^{-1} (sample 2) and 1082.30 cm^{-1} (sample 3). Natural and activated 5% HCl clinoptilolite, which was

appropriate to the highest specific surface area, was studied for its ability to adsorb molecules of DV dye. Adsorption of the dye was carried out below the CMC. Dyes are colloidal surfactants that are able to form associates in solution. The dissolution of dyes in water takes place due to the interaction of polar groups with water. At low concentrations, the dye molecules are adsorbed on the surface of the liquid. This process is accompanied by a decrease in the surface tension of the solution. When a critical concentration is reached, a saturated monomolecular layer formed by dye molecules is formed on the surface of the liquid, and dye associations – micelles – begin to form in the solution. Due to the appropriate orientation of the dye molecules in the micelles, the surface tension of solutions at concentrations higher than CMC ceases to change. The CMC of the DV dye was found by breaking in the curve $\sigma = f(\text{Inc})$ (Fig. 6).

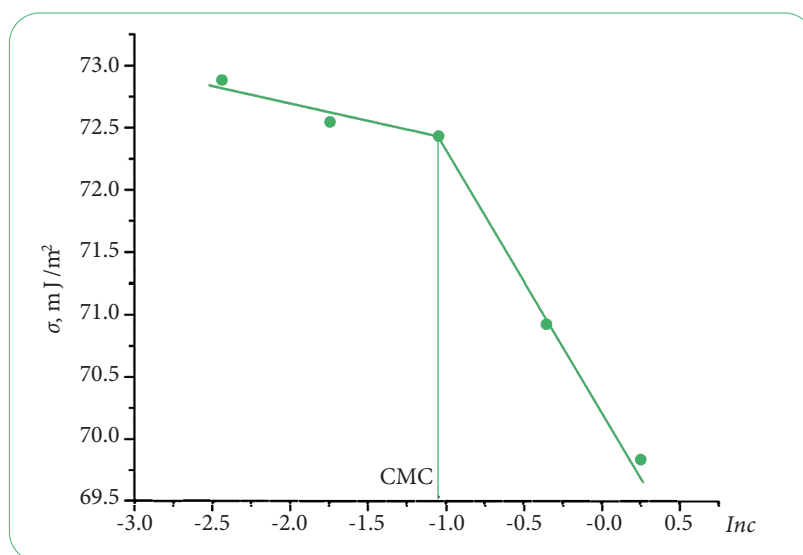


Figure 6. Dependence $\sigma = f(\text{Inc})$ for a DV dye aqueous solution

Source: created by the authors

For a DV dye aqueous solution, the CMC was 0.36 mol/m^3 . The pH of the medium significantly affects

the optical properties of dye solutions. Ionization of the electron-donor amino group of direct dyes occurs with

an increase in the acidity of the medium and consists in the attachment of a proton to a nitrogen atom. In this case, the neutral group is converted into a cation (Yahodynets *et al.*, 2019). As a result of the disappearance of the lone pair of electrons, the amino group ceases to be an electron donor substituent and the dye molecule

interacts with light as if this substituent does not exist. This can lead to a shift in the maximum light absorption to the long-wavelength region and a decrease in the intensity of light absorption. Figure 7 shows the dependence of light absorption coefficients on the wavelength of light at different pH values.

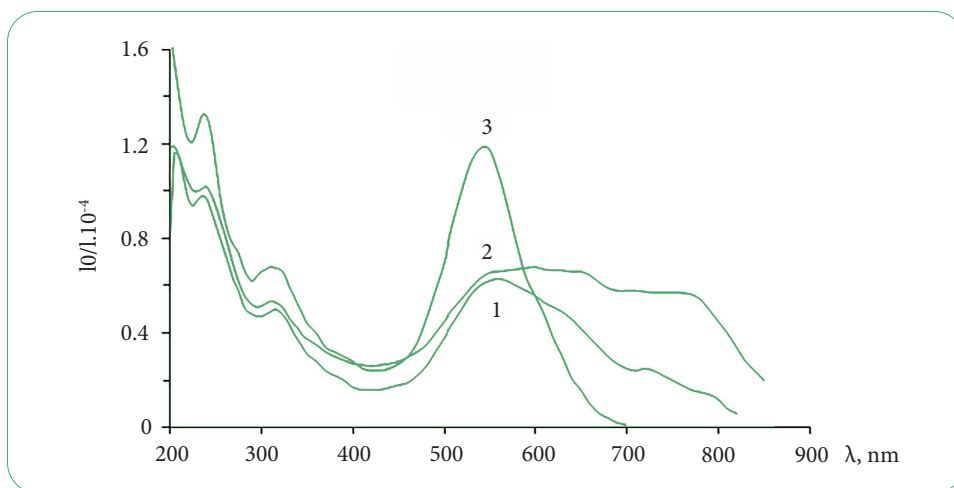


Figure 7. Dependence of light-absorption coefficients of DV solutions on light-wavelength at different pH values
Note: 1 – pH 1-2 when adding $1.0 \cdot 10^{-4}$ M HCl; 2 – pH 1-2 when adding $1.0 \cdot 10^{-4}$ M H_2SO_4 ; 3 – pH 7
Source: created by the authors

As can be seen from Figure 7, the DV aqueous solution at pH 7 (curve 3) was characterized by a symmetrical band of $\pi-\pi^*$ transitions with a maximum light absorption coefficient ($1.18 \cdot 10^4$) at a wavelength of 550 nm. At pH 1-2, when hydrochloric acid dye was added to the solution (curve 1), the absorption band became less intense and asymmetrical, the maximum of the light absorption coefficient ($0.63 \cdot 10^4$) was appropriate to a wavelength of 560 nm. At pH 1-2, when (curve 2) was added to the H_2SO_4 solution, the maximum of the asymmetric band was manifested at a wavelength of 600 nm,

it corresponded to the value of the light absorption coefficient of $0.68 \cdot 10^4$.

The influence of the alkaline environment on the value of the light absorption coefficient was insignificant and the appearance of the spectrum (curve 3) of the DV dye solution practically did not change. Therefore, the adsorption of DV dye by natural and activated clinoptilolite was carried out at pH 7 at a light wavelength of 550 nm. Figure 8 shows the isotherms of adsorption of the DV dye by samples 1 and 3. To depict the dependence $A=f(c)$, the equilibrium concentrations of the DV dye in solution were used.

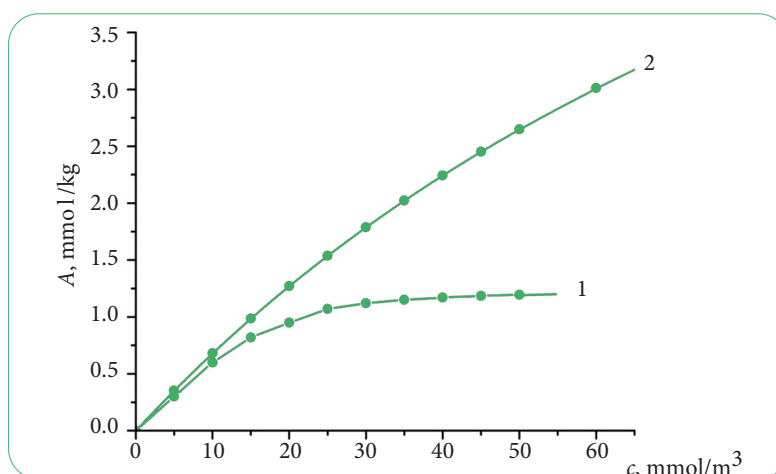


Figure 8. DV dye adsorption isotherms

Note: 1 – sample 1; 2 – sample 3
Source: created by the authors

As can be seen from Figure 8, the adsorption of the DV dye corresponded quite well to the monomolecular adsorption of Langmuir. By linearization of the Langmuir adsorption isotherm equation, its constants were found – the estimated value of the limiting monomolecular adsorption

A_{∞} and the adsorption-desorption equilibrium constant K (Table 2). High values of correlation coefficients (R^2) of experimental and theoretical data evidenced about the possibility of using the Langmuir equation for modelling sorption isotherms.

Table 2. Isotherm parameters of adsorption of DV dye by natural and activated clinoptilolite

Sample	A_{∞} , mmol/kg	K , m ³ /mmol	R^2
Sample 1	2.28	0.031	0.98
Sample 2	9.53	0.008	0.99

Source: created by the authors

As can be seen from the above data, activated sample 3 was characterized by a greater adsorption capacity relative to the DV dye. The result can be explained by the fact that in the shallow dealuminization of clinoptilolite, caused by the action of acid, meso- and macropores appear in its structure, which are able to sorb dye molecules. The effect of temperature (300°C) can cause the migration of exchangeable cations to inaccessible areas of the mineral framework, releasing the volume internal crystalline space, which acquires the ability to be filled with adsorbate molecules. Activated clinoptilolite was characterized by a greater adsorption capacity not only in relative to organic dyes, but also to water vapour. This was evidenced by a greater mass loss of activated samples at the first stage of thermolysis in the temperature range of 20-525°C (Table 1).

Adsorption of the dye on the active sites of clinoptilolite can occur not only under the influence of dispersive forces but also as a result of chemical interactions. Donor-acceptor interactions can occur between the OH groups of clinoptilolite (Brønsted acid sites) and NH₂ groups of the DV dye with the participation of protons of the hydroxyl group and an unshared pair of electrons of the nitrogen amino group. Thus, the results of the physical and chemical studies confirm that the activated clinoptilolite of the Sokyrnytske deposit is an effective absorbent for wastewaters.

Discussion

It is also worth to analyse other works on this topic, which consider types of absorbents other than clinoptilolite. Adsorption materials used in wastewater treatment technologies include activated carbon obtained from various natural materials, solid agricultural waste, clays, silica materials, zeolites, etc.

N. Ahmad *et al.* (2023) stated that activated carbon is one of the best adsorbents for the extraction of direct dyes and anionic surfactants from wastewater. Scientists from India N.M. Andal & K. Thangamani (2016) studied the sorption capacity of activated carbon obtained by heat treatment of the bark of the *Prosopis juliflora* shrub. The sorption capacity of carbon relative to the direct black dye was high and amounted to 500 mg/g. Researchers E. Chasova & O. Demchyshyna (2019) conducted a study of the

ability of activated carbon obtained from various raw materials to adsorb anionic surfactants. The sorption capacity of stone activated carbon relative to sodium dodecyl sulfonate was 0.42 mol/g, and wood activated carbon was 0.37 mol/g. The data above shows that activated carbon can effectively extract direct dyes as a sorbent. However, its high cost and the need for regeneration have limited its widespread use. Much more accessible and cheaper to extract are sorbents of mineral origin, the most important representatives of which are zeolites, including clinoptilolite, which was studied in this study, and clay materials.

Clays are an important class of mineral adsorbents due to their availability and high sorption capacity. Bentonite clays are especially widely used, the main rock-forming mineral of which is montmorillonite (MMT). As stated by the authors of V. Kochubei *et al.* (2022), montmorillonite is a layered aluminosilicate that has a mobile crystal lattice. In the cavities between the layers there are exchangeable cations that can be easily exchanged for other organic and inorganic cations. Ionogenic organic dyes are colloidal compounds, which are divided into anionic (direct, acidic) and cationic (basic) according to the sign of the ion charge. Bentonite clays are able to actively absorb cationic dyes by the interlayer space, the adsorption of which occurs by the mechanism of ion exchange. Direct diazo dyes, which include DV, in water dissociate into an organic anion, which MMT is able to absorb only by the side faces due to active groups = Al – OH, which dissociate in an aqueous medium by the main mechanism. According to Q. Zhang *et al.* (2019) the adsorption capacity of Shandong Yihe Pharmaceutical's Na-montmorillonite with respect to methyl violet cationic dye was 1.35 mmol/g, and 0.08 mmol/g to anionic methyl orange dye.

The effect of the pH of the medium on the adsorption capacity of nanomontmorillonite by Nanosav Company (Iran) relative to the dye direct red 23 was investigated by the authors S.M. Pormazar & A. Dalvand (2020). The maximum extraction of direct dye from synthetic textile waters was achieved at pH 2. According to the authors, under these conditions, protonation of the active groups of the adsorbent surface occurred, which ensured an increase in the electrostatic attraction of dye anions to the positively charged areas of the MMT. The maximum extraction of direct red

23 dye from a solution with a concentration of 0.05 g/l was 2.5 mg/g. According to the results of the research, the sorption capacity of Transcarpathian zeolite (2.28 mmol/kg) is significantly inferior to the adsorption characteristics of bentonite clays. The lower sorption capacity of zeolites is explained by the peculiarities of their structure – the presence of a rigid crystal lattice, which is not able to expand when absorbing large organic compounds and their associates.

However, the ability of zeolites to take part in adsorption processes is largely determined by the conditions of formation of the host rock, the nature of exchangeable cations, and the structural characteristics of the mineral. The adsorption characteristics of zeolite are significantly influenced by the way it is modified. As confirmed in the studies carried out by the authors of this work, the action of a 5% HCl aqueous solution can cause a threefold increase in the adsorption capacity of Transcarpathian clinoptilolite relative to the DV dye (Table 1). Similar results were obtained by the authors of R. Ebrahimi *et al.* (2018), who investigated the effect of acid activation on the adsorption properties of Iranian clinoptilolite relative to the dye direct red 23. The adsorption of the dye was subject to Langmuir's theory. The action of phosphoric acid caused an increase in the adsorption capacity of zeolite from 0.3 mmol/kg (natural zeolite) to 0.6 mmol/kg. Activation with sulfate acid provided an increase in the adsorption capacity of zeolite to 0.9 mmol/kg. The mean free energy of adsorption was 8.2-8.9 kJ/mol and indicated that the adsorption of the dye was able to proceed by the mechanism of weak chemisorptions.

The authors H. Ünlü & N.J.M. Horing (2022) noted that natural zeolites have a three-dimensional rigid framework that has a negative charge and are characterized by low adsorption capacity relative to direct dyes. To improve the adsorption characteristics of zeolites relative to anionic azo dyes, scientists proposed to modify its surface with a quaternary amine – hexadecyltrimethylammonium bromide (CTAB). As a result of this modification, the surface of the zeolite acquired a positive charge, which led to an increase in sorption capacity relative to anionic dyes. Thus, the modification of Turkish zeolite with CTAB caused an increase in its sorption capacity with respect to active black dye 12.93 mg/g (natural zeolite) to 61 mg/g, relative to active red dye 15.94 mg/g (natural zeolite) to 111 mg/g, relative to active yellow dye from 13.15 mg/g to 89 mg/g. Based on the data, it can be confirmed that surface modification with quaternary amines is more effective than the acid modification in this article. However, it is known that CTAB is a cationic surfactant that can pollute the hydrosphere, which makes the method proposed by the authors of the study safer for the environment.

A. Ivanchenko *et al.* (2021) noted that textile dyes cannot be completely removed from wastewater by traditional methods of water treatment, which leads to the introduction of sorption post-treatment into the complex technological scheme. For the final stage of purification, the authors proposed to use zeolite activated with 7% HCl, H₂SO₄ and H₃PO₄ aqueous solutions. It was noted that zeolite activated

by HCl was characterized by the highest efficiency of extraction of anionic dye methylene orange and the best results in the release of elements Al, K, Na, Ca, Mg, Fe, which was accompanied by an increase in the internal crystalline space of the mineral and the number of active sites. Similar results of hydrochloric acid on the structural and adsorption characteristics of Transcarpathian clinoptilolite were confirmed by the thermal analysis data (Table 1) given in this paper.

Like bentonites, zeolites are characterized by a selective ability to adsorb cationic dyes, which is largely determined by the acidity of the medium. M.M. Mahmoudi *et al.* (2019) noted that at pH \geq 8 modified with a 5% H₂SO₄ aqueous solution, Iranian clinoptilolite was characterized by increased sorption capacity against the cationic dye methylene blue. A decrease in pH caused a decrease in the negative charge of the surface, which favoured the adsorption of anionic forms of substances. Adsorption of direct DV dye by Transcarpathian clinoptilolite of the Sokyrnytske deposit was carried out at pH 7. Probably, a decrease in pH can cause an increase in the sorption capacity of clinoptilolite relative to anionic dyes, which may be an interesting object of further research.

Thus, in terms of adsorption characteristics, natural zeolites are inferior to some mineral sorbents. But the surface occurrence, low cost of extraction and large reserves of natural deposits in Ukraine can ensure the widespread use of these minerals in adsorption technologies for wastewater treatment.

✓ Conclusions

According to the results of thermal studies, the chemical activation of the Transcarpathian clinoptilolite of the Sokyrnytske deposit caused an increase in the specific surface area due to the appearance of secondary porosity. According to thermal analysis, the specific surface area of natural clinoptilolite was 77.26 m²/g. The action of a 5% H₂SO₄ aqueous solution led to an increase in the specific surface area of the mineral to 96.57 m²/g, and a 5% HCl aqueous solution up to 114.13 m²/g.

Complex thermal and chemical activation of clinoptilolite caused the appearance of additional adsorption centres, which can serve as hydroxyl groups of the mineral. The appearance of additional OH groups during chemical activation of the mineral with 5% H₂SO₄ and HCl aqueous solutions is due to the interaction of exchangeable H⁺ ions with oxygen frame atoms. Additional hydroxyl groups during heat treatment of clinoptilolite arise as a result of the diffusion of exchange ions into the internal channels of the mineral structure and their interaction with polarized water molecules. The use of mineral acids of higher concentration (\geq 25%) in the process of activation and heating to temperatures above 400°C caused the destruction of the clinoptilolite structure.

Adsorption of DV dye with natural and activated clinoptilolite was carried out at pH 7, which corresponded to the maximum value of the light absorption coefficient. In adsorption studies, the initial concentrations of DV dye

solutions did not exceed the CMC (0.36 mol/m^3), at which the dye is able to exist in solution in the form of associates. Data of adsorption of DV dye by natural and modified 5% HCl aqueous solution clinoptilolite were consisted with the Langmuir's theory, which testified to the monomolecular mechanism of adsorption and the energy homogeneity of the adsorption centres of the mineral.

Clinoptilolite activated by the action of 5% HCl aqueous solution was characterized by a higher adsorption capacity (9.53 mmol/kg) relative to the DV dye, compared to natural clinoptilolite (2.28 mmol/kg). The use of hydrochloric acid in chemical activation processes caused shallow dealuminization of clinoptilolite and an increase in pore size. Activated clinoptilolite acquired the ability to adsorb dye molecules not only on the outer surface but also on the internal space.

The absorption of direct anionic dyes by zeolites can proceed by the mechanism of weak chemisorption, complicated by electrostatic repulsive forces that occur between the negatively charged surface of zeolite and the anions of direct dyes. The protonation of the zeolite surface, caused by a decrease in the pH of the medium, is greatly able to improve the sorption capacity of zeolite. Therefore, the purpose of further research may be to study the effect of the pH of the medium on the efficiency of extraction of anionic dyes from their aqueous solutions.

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✓ Conflict of Interest

None.

✓ References

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Вплив хімічної активації на здатність закарпатського клиноптилоліту адсорбувати прямі барвники

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✔ **Анотація.** У процесах синтезу барвників і технологіях із їх використанням утворюються значні кількості стічних вод, які є токсичними по відношенню до живих організмів, що робить очищення промислових стоків від органічних забарвлюючих речовин актуальною проблемою сьогодення. Метою роботи було дослідити перспективи використання природного клиноптилоліту Сокирницького родовища та його активованих форм у процесах очищення стоків від прямих барвників. Активація природного клиноптилоліту здійснювалась обробкою 5 % водними розчинами H_2SO_4 і HCl та нагріванням впродовж двох годин за температури $300^\circ C$. Вплив умов активації на структурно-адсорбційні характеристики клиноптилоліту встановлювався методом комплексного термічного аналізу. Адсорбція барвника прямого фіолетового природним та активованим клиноптилолітом досліджувалася спектрофотометричним методом за рН 7 за довжини світлової хвилі 550 нм, якій відповідало максимальне значення коефіцієнта світлопоглинання. За результатами термічного аналізу активовані зразки клиноптилоліту відзначалися більш розвиненою питомою поверхнею та наявністю більшої кількості гідроксильних груп, які здатні служити адсорбційно-активними центрами поверхні. Результати адсорбції барвника прямого фіолетового підпорядковувались мономолекулярній теорії Ленгмюра, що свідчило про енергетичну однорідність адсорбційних центрів. Шляхом лінеаризації рівняння ізотерми адсорбції Ленгмюра знаходили адсорбційні характеристики природного й активованого 5 % водним розчином HCl клиноптилоліту відносно барвника прямого фіолетового. Активований клиноптилоліт відзначався підвищеною сорбційною ємністю (9,53 ммоль/кг) у порівнянні з природним клиноптилолітом (2,28 ммоль/кг). Покращення адсорбційних характеристик активованого клиноптилоліту пояснювали його частковим dealюмініванням, появою в структурі мезо- та макропор, здатних утримувати молекули барвника. Застосування в процесах активації 30 % водного розчину H_2SO_4 та нагрівання до температур вищих $400^\circ C$ викликало деградацію мінералу, що підтверджувалось електронними зображеннями його поверхні. Практична цінність дослідження полягає в рекомендації застосовувати активований клиноптилоліт у процесах очищення стічних вод від органічних забруднень

✔ **Ключові слова:** цеоліт; адсорбент; барвники; термічний аналіз; коефіцієнт світлопоглинання; адсорбційні характеристики