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Research into the possibility of using natural sorbents to purify wastewater from heavy metal ions

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ABSTRACT

Despite the availability of a wide range of wastewater treatment methods, the growing level of anthropogenic pressure on surface water bodies necessitates the improvement of existing water treatment technologies and the development of more effective approaches. One promising area is the use of adsorption methods, which are highly effective and technologically simple. Among the variety of sorption materials for removing heavy metal ions from natural and waste waters, natural sorbents, in particular zeolites, attract special attention due to their high adsorption capacity and availability. This study investigated the adsorption capacity of natural (clinoptilolite) zeolites and their modified forms with respect to Cu^{2+}, Mn^{2+} and Zn^{2+} ions with a view to considering their use for the purification of wastewater from heavy metal ions. A periodic method was used with metal ion concentrations in the model solution ranging from 0.05 to 10.0 mg/dm³. The selected concentration levels correspond to the maximum permissible values and are most characteristic of wastewater from metallurgical enterprises. The adsorption capacity of natural and modified forms of zeolite was determined for the adsorption system as a function of sorbate concentration. It has been established that clinoptilolite modified by a combined method demonstrates the maximum sorption capacity. It has been shown that in the range of low concentrations of heavy metal ions (0.05–0.1 mg/dm³) within 24 hours, their complete removal from the solution is observed regardless of the method of sorbent modification. At the same time, with an increase in the concentration of metal ions in the aqueous solution, the efficiency of the adsorption process gradually decreases. The results of the experiments showed that under static conditions, the most intensive removal of heavy metal ions occurs in an acidic environment, which is associated with the effective interaction of Me^{2+} aqua ions with mobile cations of the sorbent. According to research, the sequence of selectivity of heavy metal ions can be represented as as $Cu^{2+} > Zn^{2+} > Mn^{2+}$. The results obtained confirm that zeolites have great potential for removing heavy metal cations from industrial wastewater due to their high adsorption capacity and availability.

Keywords: wastewater, heavy metals, adsorption, zeolite, sorption capacity, sorbent modification.

INTRODUCTION

The problem of removing heavy metal ions from wastewater is quite relevant, as heavy metals are toxic and have a negative impact not only on the environment but also on human health (Yegorova et al., 2025; Kopylov et al., 2024). In addition, military operations in Ukraine exacerbate the problem, as Russian troops are deliberately targeting water collection, treatment and supply infrastructure, as well as sewage treatment plants, increasing the risk of heavy metal contamination (Tsyganenko-Dzyubenko et al., 2024; Zhukova et al., 2025).

The main industrial sources of significant amounts of pollutants are electroplating plants, as well as enterprises in the machine-building and metalworking industries. Technological processes at such facilities are characterised by intensive use of water resources, which leads to the formation of large volumes of wastewater saturated with ions of heavy and non-ferrous metals, in particular copper, zinc, iron, cadmium, chromium, nickel and other elements.

The relevance of this problem determines the need to apply effective and comprehensive technologies for the purification of wastewater from heavy metal ions, among which biosorption (Bashir et al., 2019; Peng et al., 2018), chemical precipitation (Janyasuthiwong et al., 2015), ion exchange (Bashir et al., 2019), membrane methods (Lebron et al., 2021; Marder et al., 2021) and adsorption processes (Bakalár et al., 2019).

Among the existing approaches to removing heavy metal ions from aqueous environments, sorption methods are one of the most effective. Their effectiveness is due to the possibility of achieving a high degree of purification at relatively low economic costs. In addition to traditional adsorbents widely used in such processes, in particular activated carbon, silica gels and synthetic zeolites, in recent years there has been growing interest in the use of natural dispersed minerals as alternative sorption materials (Khochubei et al., 2025; Kovo et al., 2015; Saravanan et al., 2013).

This is confirmed by numerous experimental studies and applied developments (Eprikashvili et al., 2024; Schütz et al., 2016). Due to their porous structure and significant specific surface area, mineral sorbents are characterised by high adsorption, catalytic and ion-exchange properties, which ensures their ability to selectively remove various classes of substances from aqueous solutions (Younas et al., 2021; Chai et al., 2021). The economic efficiency of using natural sorbents in various technological processes is further enhanced by the availability of effective methods for controlling their geometric structure and chemical surface properties, as well as the existence of significant industrial deposits in Ukraine and the relatively low cost of mineral raw materials with adsorption characteristics (Malyovanyi et al., 2013; Ivanenko et al., 2020).

An analysis of scientific publications reveals a wide range of studies devoted to the use of natural zeolites as sorbents for removing heavy metal ions from wastewater (Erdem et al., 2004; Finish et al., 2023). Due to their developed porous structure, high specific surface area and ion exchange properties, zeolites, in particular clinoptilolite, demonstrate an effective ability to bind metal cations in aqueous environments. Analysis of the works has established that the most studied processes are the adsorption of copper ions (Sabadash et al., 2017) and zinc ions (Bakalár et al., 2022), for which the dependence of sorption capacity on pH, initial metal ion concentration, contact time, and sorbent particle size distribution has been established. The study (Ugrina et al., 2025) compared the sorption of Cu^{2+} by natural and modified Fe(III) zeolite and found that pH has the greatest impact on copper ion removal. For zinc ions (Zn^{2+}), a sufficiently high sorption capacity from aqueous solutions by ion exchange on natural zeolite has also been demonstrated, but the efficiency of Zn^{2+} removal is lower than for Pb^{2+} and Cu^{2+} (Perić et al., 2004). Studies (Bakalár et al., 2022) have established that the efficiency of Zn^{2+} ion sorption depends on the properties of zeolite pores and the competitive interaction of zinc ions and other ions with the active centres of zeolite. In the work (Sabadash et al., 2019), the adsorption of Pb^{2+} and Zn^{2+} ions by natural zeolite from single-component solutions under conditions of their simultaneous presence was experimentally investigated. It was shown that the atomic radius significantly affects the selectivity of ion removal, while in multicomponent systems, the determining factors for the selectivity of heavy metal ion adsorption are electronegativity, ion radii, and the pH value of the precipitate of the corresponding metal hydroxides.

The adsorption of manganese ions (Mn^{2+}) by natural zeolites has been studied less systematically, although available data indicate the possibility of their removal from aqueous solutions, mainly through ion exchange and surface complexation (Pyrih et al., 2024).

In order to increase the sorption capacity of natural zeolites, various modification methods are used in many studies, including acid or alkali activation, heat treatment, and chemical surface modification. These methods contribute to changes in pore structure, an increase in the number of active centres, and improved selectivity for certain metal ions. In particular, the work (Oktaviani et al., 2021) analyzed the features of adsorption of nickel, zinc and copper ions in single- and multicomponent systems, as well as the influence of the pH value of the medium on the adsorption capacity and selectivity of metal ion removal by a modified zeolite-g-polyacrylamide adsorbent, successfully synthesized by the authors.

In comparison, synthetic and modified zeolites demonstrate higher sorption properties than natural ones, and their effectiveness depends on the type of modification. The authors of the study (Medykowska et al., 2024) found that synthetic

Na-X zeolite has a well-developed surface area of 728 m^2/g and a pore diameter of 1.73 nm and is quite effective in adsorbing heavy metal ions in both single-component and bimetallic systems.

The largest number of scientific publications is devoted to the acid modification of zeolites with the formation of their H-form. In particular, the authors (Eprikashvili et al., 2022) studied the process of acid treatment of natural zeolite (clinoptilolite) with boiling HCl for its subsequent use in adsorption purification of wastewater. It was found that the formed H-forms of zeolite are characterised by a high concentration of active centres, which was identified on the basis of X-ray diffractograms and IR spectra.

However, most existing studies focus on the adsorption of individual ions in model single-component solutions, whereas real wastewater is characterised by the presence of several metals simultaneously, which leads to competition for the active centres of the sorbent and changes in the adsorption mechanisms. Comparative studies of the adsorption of copper, manganese and zinc ions on natural and modified zeolites under the same conditions remain limited, which complicates the assessment of sorbent selectivity and the prediction of their effectiveness in practical water treatment systems. In this regard, it is relevant to conduct a comparative analysis of the sorption properties of natural and modified zeolite with respect to Cu^{2+}, Mn^{2+} and Zn^{2+} ions under conditions as close as possible to real wastewater. The patterns of influence of the pH value of the environment and the concentration of pollutant ions on the adsorption capacity of natural zeolite from the Sokyrnytskyi deposit (Zakarpattia region, Ukraine) under static conditions have also not been sufficiently studied. The results obtained can serve as a basis for optimising the technological parameters of adsorption purification processes and selecting the most effective sorption materials for the comprehensive removal of heavy metals from wastewater.

Therefore, the aim of this work is to study the influence of solution pH and heavy metal ion concentration on the adsorption capacity of natural zeolite from the Sokyrnytskyi deposit (Zakarpattia region, Ukraine) as well as zeolite modified by physical, chemical and combined methods, on the removal of heavy metal ions from aqueous solutions (Cu^{2+}, Mn^{2+}, Zn^{2+}) under static conditions. Achieving this goal will contribute to the improvement of wastewater treatment technologies at ferrous and non-ferrous metallurgical enterprises and the expansion of the practical application of zeolites.

To achieve this goal, the following tasks were solved:

- study of the kinetics of ion exchange reactions of Cu^{2+}, Mn^{2+} and Zn^{2+} under static conditions;
- determination of the possibility of using natural clinoptilolite from the Sokyrnytskyi deposit (Zakarpattia region, Ukraine) and its modified forms to purify aqueous solutions from heavy metal ions;
- comparative analysis of the adsorption of copper, manganese and zinc ions on natural and modified zeolites under identical conditions.

MATERIAL AND METHODS

Material and its characteristics

A natural mineral of volcanogenic-sedimentary origin of the clinoptilolite type, belonging to the class of microporous framework aluminosilicates, was used as a sorption material – zeolite from the Sokyrnytskyi deposit in the Zakarpattia region, Ukraine (Figure 1).

Natural zeolite from the Sokyrnytskyi deposit is a microporous framework aluminosilicate mineral with exchangeable cations of alkali and alkaline earth metals and water molecules in its intracrystalline space. The basis of zeolite from the Sokyrnytskyi deposit is clinoptilolite, a microporous aluminosilicate mineral.

The crystalline framework of zeolites is constructed from TO_4 tetrahedra (where T denotes the central oxide atom), such that each oxygen atom located at the vertex of a tetrahedron simultaneously serves as a vertex for an adjacent tetrahedron (Figure 2). This specific arrangement of atoms enables the formation of a rigid framework containing internal channels and cavities capable of accommodating ions, atoms, and molecules whose sizes correspond to the dimensions of the available free space. As a result of this unique structure, zeolites are widely used as ion-exchange materials, adsorbents, and molecular sieves, and are also employed as catalysts for chemical reactions.

The main physical-chemical characteristics of the Sokyrnytsky clinoptilolite used in the study met the requirements of technical specifications of Ukraine TU U 08.1-00292540-001:2019 «Natural zeolite from the Sokyrnytsky deposit.

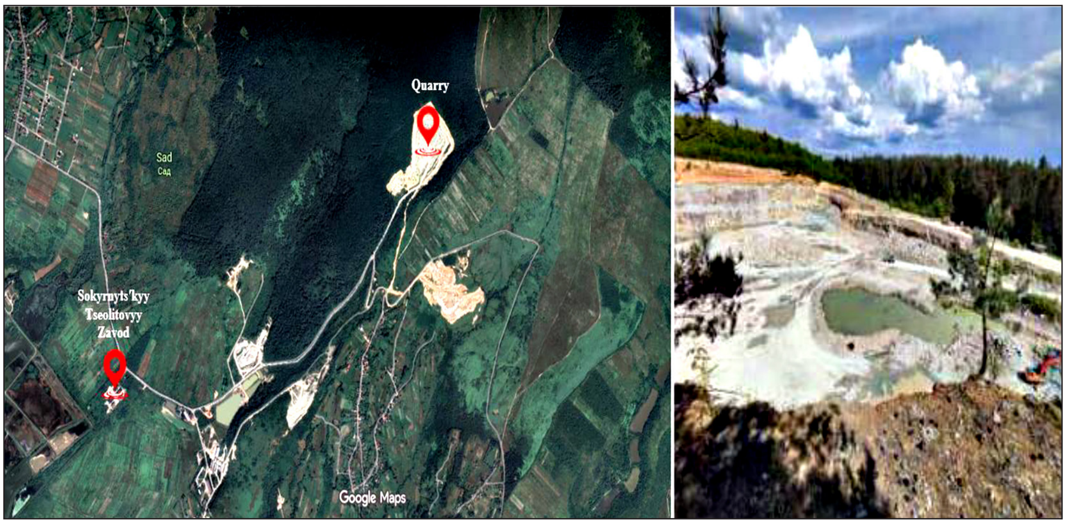

Figure 1. Sokyrnytsky zeolite deposit of PJSC «ZAKARPATNERUDPROM» (general view of the career)

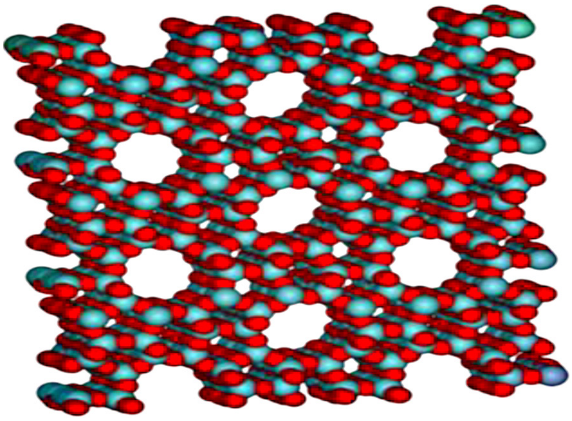

Figure 2. Microporous molecular structure of zeolite (Golomeova et al., 2016)

Technical specifications» developed by specialists of the manufacturing enterprise (internal regulatory document of the manufacturer, provided upon request).

The main physical and chemical properties of zeolites from the deposit are presented in Figure 3.

The studies used natural zeolite without prior modification with a grain size of 1.0–3.0 mm. The average density of the rock ranges from 1740 to 1920 kg/m³, porosity is 20.2–28.1%, moisture content does not exceed 8%, and compressive strength is 40–80 MPa.

The chemical composition of the mineral (%) is characterised by the following content of main components: SiO_2 — 71.5; Al_2O_3 — 13.1; Fe_2O_3 — 0.9; TiO — 0.5; CaO — 0.44; MgO — 0.68; P_2O_5 — 0.014; (K_2O + Na_2O) — 3.03; F — 0.025; As — 0.0015; Pb — 0.002; Cu — 0.02 (according to TU U 08.1-00292540-001:2019).

The mechanism of heavy metal sorption on natural zeolite can be characterised as ion-exchange adsorption. In terms of structure and composition, zeolites are aluminosilicates containing oxides of alkali and alkaline earth metals, i.e. zeolite contains sodium, potassium, magnesium and calcium cations that are weakly bound to the elements of the main structure. Therefore, these cations are replaced by cations from the solution, in particular cations of heavy metals – copper, zinc and manganese, which have a sorption capacity greater than alkali and alkaline earth metals.

An ion exchange reaction takes place: Na^+, K^+ and Ca^{2+} cations are replaced by Cu^{2+}, Zn^{2+} and Mn^{2+} cations, which makes it possible to use zeolite to remove these ions from wastewater:

$$2Na^{+}\text{zeolite} + Cu^{2+} \rightarrow Cu(\text{zeolite})_2 + 2Na^{+} \quad (1)$$

$$2K^{+}\text{zeolite} + Zn^{2+} \rightarrow Zn(\text{zeolite})_2 + 2K^{+} \quad (2)$$

$$Ca^{2+}\text{zeolite} + Mn^{2+} \rightarrow Mn(\text{zeolite})_2 + Ca^{2+} \quad (3)$$

Experimental methods

Preparation of model solutions

The object of the study was samples of aqueous solutions of heavy metals containing individual pollutants in the form of copper, manganese and zinc ions.

To determine the adsorption capacity of sorbents, solutions of Cu^{2+}, Mn^{2+} and Zn^{2+} with concentrations of 0.05 mg/dm³, 0.1 mg/dm³, 1.0 mg/dm³, 5.0 mg/dm³ and 10.0 mg/dm³ were prepared from standard samples. The selected concentration range corresponds to the maximum permissible values for the metal ions under study and is most characteristic of wastewater from metallurgical enterprises containing heavy metals.

Calculations for preparing solutions of the required concentrations were made based on the law of equivalents:

$$C_1V_1 = C_2V_2 \tag{4}$$

where: C_1, C_2 – concentrations of solutions,
V_1, V_2 – volumes of solutions.

Working solutions were prepared by sequential dilution, starting with the solution with the highest concentration. To prepare 2 dm³ of the stock solution with a mass concentration of 10.0 mg/dm³, 20 cm³ of the standard solution was added to a measuring flask, 1 cm³ of which contained 1.0 mg of copper, manganese or zinc ions. From the resulting stock solution, a series of working solutions with mass concentrations of 5.0, 1.0, 0.1 and 0.05 mg/dm³ were prepared. For this purpose, 500, 100, 10 and 5 cm³ of the stock solution were taken with a pipette and transferred to 1 dm³ volumetric flasks. The contents of each flask were brought to the mark with distilled water and thoroughly mixed. As a result, working solutions with mass concentrations of metal ions of 5.0, 1.0, 0.1 and 0.05 mg/dm³ were obtained, which were used for further studies.

Determination of heavy metal ion concentrations

The concentration of heavy metal ions in model wastewater solutions was determined photocolorimetrically using standard methods with the KFK-2MP device, while the pH of the initial solutions and filtrates was measured using a portable pH meter pH-410.

The mass concentration of Cu^{2+}, Zn^{2+} and Mn^{2+} ions in the test sample was determined using a calibration graph based on the results of optical density measurements. To determine the concentration using the calibration graph method, a series of 5–8 standard solutions of different concentrations was prepared and the optical density of each solution was measured, making at least 3 parallel determinations for each point.

The photometric method for determining the mass concentration of zinc ions is based on their interaction with diphenylthiocarbazone (dithizone) dissolved in carbon tetrachloride, which results in the formation of red-coloured zinc dithizone. The optical density was determined at a wavelength of 535 nm. The dithizone-zinc complex is red in colour, and the intensity of the colour is proportional to the zinc concentration. Zinc reacts quantitatively with dithizone in the pH range of 4–7. In this environment, copper, cadmium, lead, nickel, cobalt, bismuth, thallium, indium, mercury, silver, gold and palladium also react with dithizone. To eliminate the influence of these elements, the study was conducted at pH=5 with the addition of sodium thiosulphate.

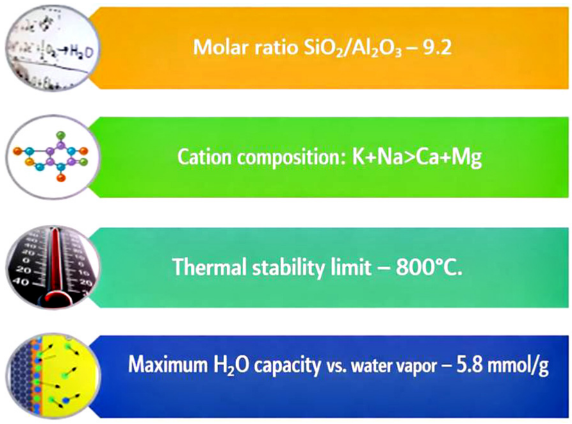

Figure 3. Main physicochemical properties of zeolites from the Sokyrnytsky deposit (according to TU U 08.1-00292540-001:2019 «Natural zeolite from the Sokyryntsi deposit. Technical conditions»)

The determination of the mass concentration of copper ions in an aqueous solution is based on the ability of this metal to form a coloured complex with sodium diethyldithiocarbamate in an alkaline environment of blue-violet colour. The intensity of the solution colour is directly proportional to the concentration of copper in the wastewater. The optical density of the coloured solutions was measured on a KFK-2MP photoelectric concentration-type colorimeter at a wavelength of $\lambda = 490$ nm in a cuvette with a working length of $l = 20$ mm. The sensitivity of the method is 10 µg Cu/dm³.

The mass concentration of manganese ions in aqueous solutions was determined by a photometric method based on the oxidation of Mn^{2+} ions to MnO_4^- permanganate ions by persulphate in an acidic medium, resulting in an intense pink-purple colour. The resulting coloured form of manganese is stable for a period of time sufficient for photometric measurements, and the intensity of the colour is directly proportional to the concentration of Mn^{2+} ions in the solution. The optical density of the solutions was measured on a KFK-2MP photoelectric colorimeter at a wavelength λ = 530 ± 10 nm, which corresponds to the maximum light absorption of permanganate ions, relative to a blank sample. The measurements were carried out in cuvettes with a layer thickness of 10 mm.

Sorption capacity

The sorption capacity of the studied sorbent for heavy metal ions was evaluated in stages with an analysis of the influence of such parameters as pollutant concentration, sorption process duration, and pH of the environment.

Stage I of the study

At the first stage of the research, the adsorption capacity of natural and modified zeolite in three different ways was evaluated on model aqueous solutions prepared from standard samples of copper (II), manganese (II) and zinc (II) sulphates with concentrations of 0.05; 0.1; 1.0; 5.0 and 10.0 mg/dm³. The adsorption capacity of zeolite was studied at a temperature of 20 ± 1 °C under static conditions.

The adsorption capacity of zeolite with respect to heavy metal ions was studied as follows: 1.0 g of sorbent (in terms of dry mass) was placed in a flat-bottomed flask and 250 cm³ of a solution containing one of the contaminant ions in a given concentration range from 0.05 to 10.0 mg/dm³ was added. The resulting system was stirred and kept at rest for 24 hours (Figure 4).

After completion of the sorption process, the suspension was filtered through a "blue" tape filter, and the filtrate was analysed for the residual concentration of contaminant ions using the Equation 5.

$$A = \frac{C_0 - C_e}{m} \cdot V \tag{5}$$

where: C_0 – initial ion concentration in the model wastewater solution, mg/cm³,
$C_{рів}$ – equilibrium concentration of ions in a model wastewater solution, mg/cm³,
V – volume of the studied wastewater, cm³, m – adsorbent mass, g.

The removal ratio (RR) of metal ion was estimated by Equation 6.

$$\varphi = \frac{C_0 - C_e}{C_0} \cdot 100\% \tag{6}$$

where: C_0 and C_e are the initial and final concentration of metal ions respectively (mg/dm³).

Stage II of the study

In the second stage of the research, the effect of sorption duration on the adsorption capacity of natural and modified zeolite (using three methods) with regard to heavy metal ions was evaluated. The duration of contact between the sorbent and the solution varied from 5 minutes to 24 hours at a constant concentration of the ion being determined of 1.0 mg/dm³. The experiments were performed using the same methodology as in the first stage.

Figure 4. Contact time of the studied solutions required to establish adsorption equilibrium (illustrated by the zeolite–Cu^{2+} system; the initial model solution without sorbent is blue on the left)

Stage III of the study

In the third stage of the research, the influence of the pH of the environment on the adsorption activity of zeolite was determined. In the experiments, constant ion concentrations (1.0 mg/dm^3) were maintained, and the pH of the initial solution and filtrate was measured after 24 hours of contact with natural and modified sorbents. The studies were conducted at pH 3.05, 6.90 and 10.5, using a 1N NaOH solution to form an alkaline environment, after which the residual concentration of pollutant ions in the filtrate was determined using Equation 5.

Modification of natural zeolite

To increase the sorption capacity of zeolite, it was modified in three ways. Physical (thermal) activation was carried out by calcining the sorbent in a drying oven at a temperature of 120 °C for 12 hours. Chemical activation was carried out by treating the zeolite with a 7% HCl solution in a ratio of ‘sorbent: acid solution’ of 1:6 for 5 hours. After acid treatment, the sorbent was washed with distilled water until the pH of the wash water reached neutral, after which it was dried first in a water bath to an air-dry state and then in an oven at a temperature of 100–105 °C for 2 hours.

The combined modification involved a combination of heat treatment and acid activation. First, the sorbent was heat treated at 120 °C for 12 hours, after which it was acid treated with hydrochloric acid solution using the method described above and dried.

RESULTS AND DISCUSSION

The sorption capacity of zeolite for heavy metal ions was evaluated for both natural and modified sorbents in aqueous solutions containing only one contaminant agent at concentrations of 0.05, 0.1, 1.0, 5.0, and 10.0 mg/dm^3. The selected concentration levels correspond to the maximum permissible values and are most characteristic of wastewater from metallurgical enterprises.

Analysis of the experimental data showed that zeolite modified by a combined method exhibits the highest sorption activity towards copper, zinc and manganese ions. In the range of low concentrations (0.05–0.1 mg/dm^3) within 24 hours, the sorbent completely adsorbs copper, manganese and zinc ions, regardless of the method of its modification.

The calculated values of the residual concentration of Cu^{2+}, Mn^{2+} and Zn^{2+} ions in the filtrate after completion of the sorption process, calculated using equation (5), are given in Table 1.

A comparative analysis of the results presented in Table 1 showed that at a copper ion concentration of 1.0 mg/dm^3, the degree of purification calculated using Equation 6 is 44.0% for natural zeolite and 80.0% for the sorbent modified by the combined method.

At the same time, it was found that with an increase in the concentration of the pollutant in the solution, the sorption efficiency decreases. In particular, for zeolite modified by a combined method, at a copper ion concentration of 1.0 mg/dm^3, the degree of purification is 80.0%, while at a concentration of 10.0 mg/dm^3 it decreases to 62.5%.

In the case of sorption of manganese and zinc ions by zeolite, other patterns were observed. Analysis of experimental data showed that the adsorption of these ions proceeds more slowly and is less efficient. In particular, the adsorption capacity of the sorbent for manganese and zinc ions was lower compared to the adsorption of copper ions under the same conditions (Table 1).

Thus, at a pollutant concentration of 1.0 mg/dm^3, the degree of purification for natural zeolite was 27.0% for manganese ions and 35.0% for zinc ions, while for the sorbent modified by the combined method, these figures reached 51.0% and 63.0%, respectively. Thus, even after combined modification, the adsorption efficiency for manganese and zinc remained 30% lower than for copper ions. In general, the modification of the sorbent did not provide a significant increase in the amount of absorbed ions of these metals, which remained within the range of 18.0–32.0%.

Analysis of the sorption time of copper ions showed that at low concentrations (0.05–0.1 mg/dm^3), both natural and modified zeolite completely adsorbs copper ions within 1 hour. It is impossible to reduce the contact time, since during intensive stirring, the sorbent is partially destroyed and loses its physical integrity, which leads to clouding of the solution. To obtain a transparent filtrate suitable for further determination of the residual ion concentration, additional sample clarification time is required, which is about 1 hour.

To establish the optimal conditions for Cu^{2+} ion sorption, the dynamics of adsorption over

Table 1. Sorption capacity of heavy metal ions by zeolite in a model solution depending on concentration

Concentration of ions in the initial colution, mg/dm^3	Residual concentration of pollutant ions in model solution, mg/dm^3											
	Sample 1[a]			Sample 2[b]			Sample 3[c]			Sample 4[d]		
	Cu^{2+}	Mn^{2+}	Zn^{2+}	Cu^{2+}	Mn^{2+}	Zn^{2+}	Cu^{2+}	Mn^{2+}	Zn^{2+}	Cu^{2+}	Mn^{2+}	Zn^{2+}
0.05	0.001	0.005	0.005	0.001	0.005	0.005	0.001	0.005	0.005	0.001	0.005	0.005
0.1	0.001	0.005	0.005	0.001	0.005	0.005	0.001	0.005	0.005	0.001	0.005	0.005
1.0	0.56	0.73	0.65	0.41	0.685	0.55	0.25	0.53	0.45	0.20	0.49	0.37
5.0	3.85	4.65	4.15	3.58	4.20	3.85	1.75	3.65	3.15	1.80	3.05	2.85
10.0	8.75	9.65	9.15	8.38	9.15	8.65	3.85	8.75	7.25	3.75	8.55	6.80

Note: [a] Natural zeolite, [b] thermally modified zeolite, [c] chemically modified zeolite, [d] combined method of zeolite modification.

time were studied at a solution concentration of 1.0 mg/dm^3 (Figure 5).

Analysis of the dependence of the degree of ion sorption on time (Figure 5) showed that for copper ions, adsorption by zeolite, both in its natural form and after heat treatment, is most active in the first 40 minutes, reaching the maximum sorption capacity. The sorbent modified by the combined method has the highest absorption capacity. Already during the first 15 minutes, the concentration of the solution decreases from 1.0 mg/dm^3 to 0.45 mg/dm^3, i.e. almost twice. Subsequently, the sorption rate decreases significantly, and after 60 minutes, the concentration of Cu^{2+} ions stabilises at 0.2 mg/dm^3, which corresponds to the maximum degree of absorption.

Studies of the sorption activity of zeolite with regard to zinc ions have shown that its adsorption capacity is lower than that of copper ions (Figue 6).

The maximum sorption rate of zinc (II) ions is observed during the first 25–30 minutes. The maximum sorption capacity is reached after 120 minutes of contact between the solution and the sorbent samples. For natural zeolite, the sorption process lasts about 90 minutes to completion, reaching a purification degree of 0.65 mg/dm^3 (35%) with periodic peaks every 30 minutes. Further exposure of the sorbent to the model wastewater solution does not change the results, so sorption is considered complete.

Thermally modified zeolite demonstrates maximum absorption capacity in the first 60 minutes. The degree of zinc ion adsorption reaches its maximum after 120 minutes and is 45%.

The highest sorption rates are observed for zeolite after chemical and combined modification. Active sorption begins after 10 minutes of the experiment, and maximum sorption properties are achieved within 15–45 minutes. The degree of adsorption reaches its maximum at the 60th minute, amounting to 0.3 mg/dm^3 and 0.2 mg/dm^3, respectively.

In the case of manganese ion sorption, zeolite exhibits other patterns. Analysis of the data

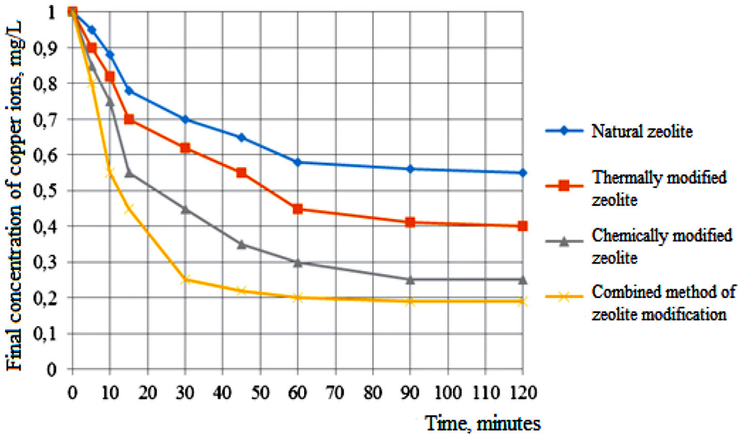

Figure 5. Kinetic curves of the adsorption capacity of zeolite samples with respect to cuprum ions with a concentration of 1.0 mg/dm^3 versus time

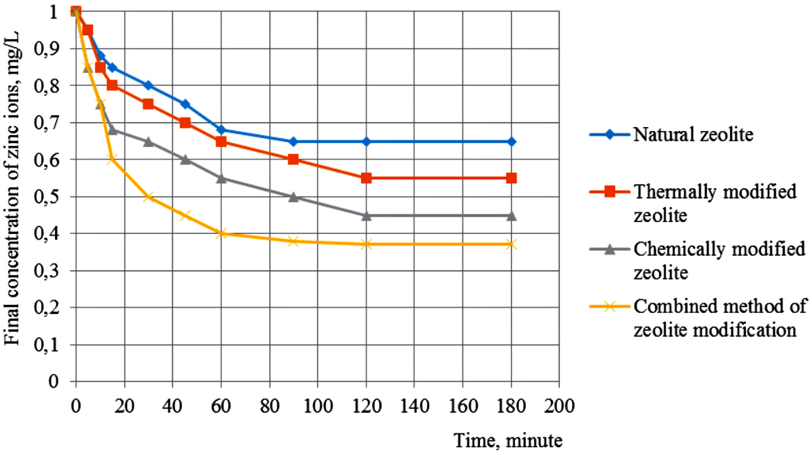

Figure 6. Kinetic curves of the adsorption capacity of zeolite samples with respect to zinc ions with a concentration of 1.0 mg/dm³ versus time

obtained (Figure 7) showed that the adsorption process proceeds much more slowly, and the maximum sorption capacity is reached only after approximately 240 minutes of contact with the sorbent. The prolongation of the sorption time is observed both for natural zeolite and for sorbents modified by various methods.

In the first 30 minutes, the concentration of manganese ions in natural zeolite decreases to only 0.965 mg/dm³, which corresponds to 3.5% adsorption. Similar dynamics are observed until the limit value of 0.78 mg/dm³ is reached. For thermally modified sorbent, adsorption occurs in the same time intervals, but with an increased degree of absorption during the first 120 minutes, reaching 0.75 mg/dm³, which is 25.0%. Zeolite shows the best results after chemical and combined modification.

Active sorption begins within the first hour of the experiment, after which its rate decreases, and the maximum degree of adsorption is reached after 3 hours and amounts to 50.0%.

A comparative analysis of the data obtained showed that the zeolite under study exhibits higher selectivity towards copper ions. This confirms the well-known rule that the degree of adsorption of heavy metal ions depends on their valence. For cations of the same valence, absorption increases with increasing atomic mass and decreasing ion radius. Thus, the atomic mass of Cu^{2+} ions is 63.546 a.m.u., the ion radius is 72 pm; for Mn^{2+} – 54.93855 a.m.u., 80 pm; for Zn^{2+} – 65.382 a.m.u., 138 pm. Thus, copper ions, having a larger atomic mass and a smaller radius, are adsorbed by zeolite more efficiently than manganese and zinc ions.

Since the concentrations of heavy metal ions in model wastewater solutions are approximately 1 mg/dm³, based on the data obtained, the sorption efficiency of heavy metals by zeolite can be formulated in the following order: Cu(II) > Zn(II) > Mn(II).

Analysis of the degree of absorption showed that adsorption occurs mainly by an external diffusion mechanism. Calcium ions probably replace hydrogen ions in the zeolite framework through ion exchange, after which the released calcium precipitates on the surface of the sorbent in the form of calcium sulphate.

The results of experimental studies of the sorption of heavy metal ions from model solutions on natural zeolite and sorbent modified in three ways at different initial pH values are presented in Table 2.

Analysis of the data presented in Table 2 showed that under static conditions, zeolite, both in its natural form and after modification, exhibits the highest sorption activity towards heavy metal ions at low pH values. In our opinion, this is due to the effective interaction of Me^{2+} aqua ions with mobile cations of the sorbent.

As the pH in the solution increases, the proportion of metal hydroxo complexes increases. Since cations in the form of $Me(OH^{)(n-1)+}$ have a significantly larger effective radius compared to hydrated ions, they cannot penetrate the pores of zeolite, which slows down the internal diffusion stage of adsorption.

In a neutral and alkaline environment, with a predominance of hydroxyl forms of metals, the adsorption process is practically absent.

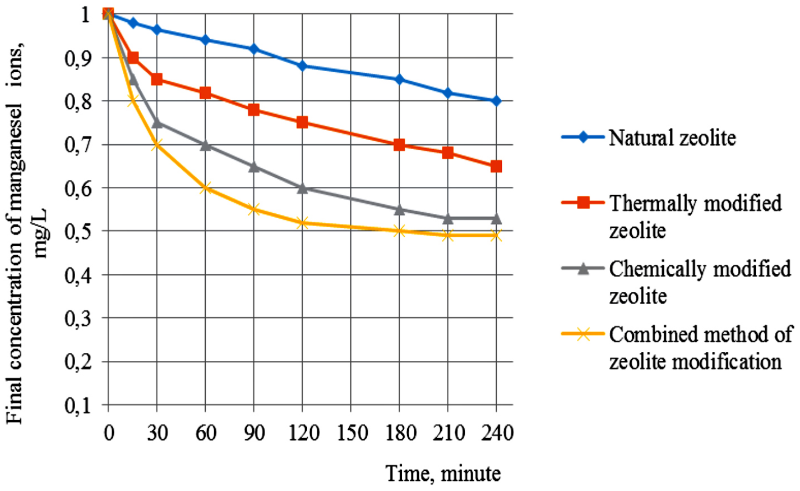

Figure 7. Kinetic curves of the adsorption capacity of zeolite samples with respect to manganese ions with a concentration of 1.0 mg/dm³ versus time

Table 2. The adsorption capacity of zeolite for heavy metal ions depending on the pH of the solutions at a concentration of 1.0 mg/dm³

Ion	pH of the solution	Final concentration of metal ions respectively, mg/dm³			
		Sample 1[a]	Sample 2[b]	Sample 3[c]	Sample 4[d]
Cu^{2+}	3.05	0.05	0.04	0.035	0.025
	6.90	1.0	1.0	1.0	1.0
	10.50	1.0	1.0	1.0	1.0
Mn^{2+}	3.05	0.075	0.07	0.06	0.06
	6.90	1.0	1.0	1.0	1.0
	10.50	1.0	1.0	1.0	1.0
Zn^{2+}	3.05	0.085	0.08	0.075	0.075
	6.90	1.0	1.0	1.0	1.0
	10.50	1.0	1.0	1.0	1.0

CONCLUSIONS

The effectiveness of using zeolite from the Sokyrnytskyi deposit for purifying natural and wastewater from municipal enterprises from copper, manganese and zinc ions has been established. Based on experimental studies using various methods of sorbent modification, it has been determined that zeolite modified by a combined method exhibits the highest sorption capacity.

In the range of low concentrations (0.05–0.1 mg/dm³) within 24 hours, the sorbent completely adsorbs heavy metal ions regardless of the modification method. With an increase in the concentration of metals in the solution, the sorption efficiency decreases.

In addition, zeolite demonstrates higher selectivity for copper ions, which confirms the generally accepted rule: the adsorption of heavy metal ions increases with an increase in their atomic mass and a decrease in their radius. Analysis of the degree of metal absorption allows us to conclude that the adsorption process is predominantly driven by external diffusion.

It has been established that under static conditions, zeolite, both in its natural form and after modification, most effectively adsorbs heavy metal ions at low pH values. In our opinion, this is due to the interaction of Me^{2+} aqua ions with mobile cations of the sorbent. As the pH increases, the proportion of metal hydroxo complexes increases.

Since cations in the form of $Me(OH)^{(n-1)+}$ have a significantly larger effective radius compared to hydrated ions, they cannot penetrate the pores of zeolite, which slows down the internal diffusion stage of adsorption.

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