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Volodymyr Vasylechko
Analytical Chemistry Department Ivan Franko National University of Lviv
Oksana Kostiv
Analytical Chemistry Department Ivan Franko National University of Lviv
Volodymyr Sydorchuk
Institute for Sorption and Problems of Endoecology National Science of Ukraine, Department of Heterogeneous Catalytic Processes Oxidation
Olexandr Gromyko
Microbial Culture Collect ion of Antibiotic Producers, Ivan Franko National University of Lviv
Viktor Fedorenko
Department of Genetics and Biotechnology, Ivan Franko National University of Lviv
Svitlana Khalameida
svkhal@ukr.net

Institute for Sorption and Problems of Endoecology National Academy of Sciences of Ukraine, Department of Heteregeneous Catalytic Processes Oxidation Mudraka Oleg, 13 Kyiv, 03164 UKRAINE
Svitlana Bagday
Analytical Chemistry Department Ivan Franko National University of Lviv

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Volodymyr Vasylechko[1,2], Oksana Kostiv[1], Volodymyr Sydorchuk[3], Olexandr Gromyko[4], Viktor Fedorenko[5], Svitlana Khalameida[3*], Svitlana Bagday[1]

[1]*Analytical Chemistry Department Ivan Franko National University of Lviv, Lviv, Ukraine*

[2]*Department of Food Technology Lviv University of Trade and Economics Lviv, Ukraine*

[3]*Institute for Sorption and Problems of Endoecology National Science of Ukraine, Department of Heterogeneous Catalytic Processes Oxidation, Kyiv, Ukraine; e-mail: svkhal@ukr.net*

[4]*Microbial Culture Collect ion of Antibiotic Producers, Ivan Franko National University of Lviv, Lviv, Ukraine*

[5]*Department of Genetics and Biotechnology, Ivan Franko National University of Lviv Lviv, Ukraine*

Volodymyr Vasylechko: vasylechko@ukr.net

Oksana Kostiv: oksana.kostiw@lnu.edu.ua

Volodymyr Sydorchuk: bilychi@ukr.net

Olexandr Gromyko: smu62@ukr.net

Viktor Fedorenko: v.fedorenko.1951@gmail.com

Svitlana Khalameida: svkhal@ukr.net

Svitlana Bagday: svitlana.bahday@lnu.edu.ua

Abstract

This study proposes an integrated approach in which clinoptilolite-based preconcentration of Bi(III) from water is coupled with valorization of the Bi-loaded sorbent for subsequent water remediation. The sorption behavior of Transcarpathian clinoptilolite toward Bi(III) was investigated under dynamic conditions and was strongly influenced by solution acidity and thermal pretreatment of clinoptilolite. Selective Bi(III) uptake was achieved at pH 2.5, with a maximum sorption capacity of 14.1 mg g^{-1}. Bi(III) was quantitatively recovered from the sorbent using 1 M HNO_3, enabling its determination by spectrophotometry after solid-phase extraction over the concentration range of 0.5–200 ng mL^{-1}. The proposed method allows for the detection of bismuth at the level of 0.2 ng mL^{-1} wth an enrichment factor of 200. XRD, FTIR and UV-Vis spectroscopy, low-temperature nitrogen adsorption–desorption were used to assess the structural, surface, and optical properties of the Bi-loaded clinoptilolite produced during the preconcentration process. Under visible irradiation, it promoted 90–97% removal of safranin T from aqueous solution, accompanied by mineralization. The material also demonstrates activity against such microbes as *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans*. These results demonstrate that an analytical sorbent can simultaneously serve as a platform for trace-metal recovery and as a precursor to a value-added remediation material. The proposed strategy links environmental monitoring with resource recovery and pollutant remediation, offering a route to reduce analytical waste while generating a multifunctional material for water treatment.

Keywords: Clinoptilolite; Bismuth(III); Solid-phase extraction; Trace determination; Spectrophotometry; Preconcentration; Photocatalysis; Antimicrobial activity

Introduction

Bismuth belongs to the category of rare but, from an applied perspective, important elements. Its content is $0.48 \cdot 10^{-5}$ % w/w in the Earth's crust (Emsley 1998). Although bismuth forms its own minerals, it is a by-product of the processing of polymetallic ores (lead-zinc, copper, molybdenum-cobalt), mainly by extraction from concentrates containing tenths and hundredths of a percent of this metal (Emsley 1998; Norman 1998). Bismuth is used as a component of alloys, a semiconductor material for thermoelectric generators and oxidation or photocatalysts, as well as for the manufacture of photoelectrochemical detectors and bismuth nanotubes (Li et al. 2001; Fang et al. 2001; Wang et al. 2021). Compounds of b ismuth are also used in medicine as an antiseptic and astringent in the treatment of the gastrointestinal tract. Bismuth drugs are used externally in the form of powders and ointments for dermatitis, eczema, and trophic ulcers (Chekman et al. 2010). Sources of bismuth

entering natural waters are wastewater from metallurgical, chemical-pharmaceutical, galvanic, and cosmetic industries, as well as leaching processes of bismuth-containing minerals. Prolonged exposure to high doses of bismuth salts in humans can damage the kidneys, liver, central nervous system, skin, and mucous membranes (Chekman et al. 2010). Therefore, monitoring the bismuth content in natural and wastewater is necessary.

Analytical control of environmental objects and biosubstrates for bismuth content is most often carried out using spectrophotometric methods (Amin and Zaafarany 2015; Madrakian et al. 2003; Smanova et al. 2025), atomic absorption spectrometry (Arpadjan et al. 1997; Bakircioglu et al. 2003; Giacomelli et al. 2000; Haruta et al. 1989; Naghizadeh et al. 2015; Parodi et al. 2015; Şahan et al. 2010; Tokman and Akman 2004; Yıldız et al. 2025; Zhang 2011), voltammetry (Bhalotra and Prui 2001), hydride generation atomic fluorescence spectrometry (Chen 2011; Lu et al. 2023) and inductively coupled plasma ICP (Chen et al. 2011; El-Shahawi et al. 2011; Rao et al. 2006). However, it is very often necessary to perform pre-concentration, extraction and/or the separation of residual amounts of bismuth during sample analysis, even with using highly sensitive and selective modern methods such as ICP, atomic absorption spectroscopy, atomic fluorescence spectrometry involving hydride formation (Arpadjan et al. 1997; Bakircioglu et al. 2003; Chen et al. 2011; El-Shahawi et al. 2011; Giacomelli et al. 2000; Haruta et al. 1989; Lu et al. 2023; Naghizadeh et al. 2015; Parodi et al. 2015; Rao et al. 2006; Şahan et al. 2010; Tokman and Akman 2004; Yıldız et al. 2025; Zhang 2011). The extraction of this rare metal from technological solutions is another important task. The solid-phase extraction (SPE) method is gaining increasing popularity for the concentration and separation of metals, as well as for their isolation from the matrix (Maya et al. 2018; Velarde et al. 2023). This method offers several advantages compared to other concentration and separation techniques: high values of extraction factor and enrichment, quick phase separation, the near-total absence of toxic organic solvents, and the possibility of integration with various detection methods, low cost, possibility of automation of sample preparation, ease of operation. Furthermore, the SPE method provides significant environmental advantages over traditional liquid-liquid extraction, directly aligning it with the main green approaches in analytical chemistry.

The solid-phase extraction method uses a variety of sorbents. Known sorbents for bismuth (III) ions are silica gels modified with organic reagents (Chebotarev et al. 2021; Haruta et al. 1989; Naghizadeh et al. 2015), immobilized polyurethanes (Arpadjan et al. 1997; El-Shahawi et al. 2011; Moawed et al.2017), chelate resins (Amin and Zaafarany 2015; Belkhouche and Didi 2010; Rao et al. 2006; Şahan et al. 2010; Tereshatov et al. 2023; Tokman and Akman 2004), activated carbon (Giacomelli et al. 2000; Madrakian et al. 2003), immobilized carbon nanotubes (Parodi et al. 2015), bamboo carbon (Chen et al. 2011), rice husk ash (Bakircioglu et al. 2003), chelating polymers (Asadi-Ojaee et al. 2019; Maharramov et al. 2017; Smanova et al. 2025), nickel hydroxide nanoflower (Yıldız et al.

2025), dithizone-coated barium strontium titanate nanopowder (Zhang 2011), microcrystalline naphthalene (Bhalotra and Prui 2001), metal organic frameworks based on Zr(UiO-66) (Lu et al. 2023). In most cases, the synthesis, modification and use of these sorbents require complex organic substances and toxic solvents (Amin and Zaafarany 2015; Arpadjan et al. 1997; Belkhouche and Didi 2010; Chebotarev et al 2021; El-Shahawi et al. 2011; Haruta et al. 1989; Maharramov et al. 2017; Moawed et al. 2017; Naghizadeh et al. 2015; Parodi et al. 2015; Rao et al. 2006; Şahan et al. 2010; Tereshatov et al. 2023; Tokman and Akman 2004).

Natural zeolites, including the most widespread of them, clinoptilolite, are considered as promising sorbents in the SPE method (Maya et al. 2018; Velarde et al. 2023). These natural aluminosilicates have a number of advantages over other sorbents (Baile et al. 2019; Davis 2002). Natural zeolites exhibit both high sorption capacity at low concentrations and total sorption capacity for different substances, resistance to aggressive media, selectivity. In addition, they are quite available and cheap materials. In particular, Transcarpathian clinoptilolite relates to the low-silicon calcium clinoptilolites and and contains no clay impurities (Tarasevich et al. 1991). It is known (Zhou et al. 2024) that zeolites with low Si content exhibit increased cation exchange capacity and, accordingly, have advantages in the extraction of ions of heavy metal from aqueous solutions.

From the perspective of sustainability, circular economy, and waste valorization, an important challenge in solid-phase extraction is the possible secondary environmental liability generated by spent sorbent containing of hazardous transition metals (Fouda-Mbanga et al. 2024; Ma et al. 2023; Rial and Ferreira 2022). Re-using of such spent sorbents within the framework of the "adsorbent-to-photocatalyst" conversion strategy is one option to solve this problem (Chen et al. 2020). In other words, this is non-conventional way to create materials with necessary characteristics (Rodríguez-Iznaga et al. 2022). Zeolites, being insulators like all aluminosilicates, do not exhibit photocatalytic activity. Nevertheless, clinoptilolite natural zeolites are used as supports of effective photocatalysts for the adsorptiob abd neutralization of dyes, antibiotics, pesticides and other new organic water pollutants. The high catalytic activity of such composite photocatalysts is due to the synergistic effect of combining natural zeolite as a sorbent with semiconductors, in particular based on bismuth compounds (Tan et al. 2020; Zhang et al. 2017; Zhou et al. 2024). Moreover, natural clinoptilolite itself can demonstrate activity due to the presence of impurity oxides of transition metals - TiO_2, Fe_2O_3 (Alvarez-Aguiñaga et al. 2020). In addition, clinoptilolite with sorbed cations (including spent adsorbents) also shows photocatalytic activity under action of visible irradiation (Sydorchuk et al. 2025). In this work, it was shown that the adsorption of metal ions from aqueous solutions for analytical purposes is, in fact, a simply method for preparation visible-driven photocatalysts with controllable metal content.

Another option for reusing the spent sorbent is based on the fact that the framework of clinoptilolite is recognized as biologically inert and safe (Auerbach et al. 2003; Kraljević Pavelić et al. 2018). Among natural zeolites, only clinoptilolite is authorized for medical and food industry applications (Auerbach et al 2003; EFSA Panel 2013; Flowers et al. 2009; Grifasi et al. 2025; Izmirova et al. 2001; Kahramanova 2010; Kraljević Pavelić et al. 2018; Sydorchuk et al. 2025). Moreover, drugs based on bismuth nanoparticles, contained in zeolite pores, exhibit high antibactericidal activity, in particular against *Pseudomonas aeruginosa* (Chekman et al. 2010; Satya et al. 2025).

The principal objective of this study was to evaluate the dynamic sorption behavior of Bi(III) ions on natural Transcarpathian clinoptilolite, aiming to design a solid-phase extraction method for preconcentrating and spectrophotometrically determining trace bismuth in aqueous matrices. Based on the obtained results, the Bi-loaded clinoptilolite after the preconcentration process was evaluated as a value-added material for environmental remediation. The photocatalytic degradation of Safranin T under visible illuminastion and the antimicrobial activity against selected microorganisms were studied in order to assess the possibility of converting the spent sorbent into a multifunctional material. Thus, the work integrates environmental monitoring of trace bismuth with adsorption-based separation and subsequent valorization of the Bi-loaded sorbent for water purification applications.

Experimental

Materials and Reagents

Natural clinoptilolite investigated in this work was obtained from the Sokirnytsia deposit (Transcarpathian region, Ukraine). Characterization data indicated a zeolite purity of 85–90% and a specific surface area of 62 $m^2\ g^{-1}$ determined via water adsorption (Vasylechko et al. 2013). The following components are present in clinoptilolite. (in wt %): SiO_2, 67.29; Al_2O_3, 12.32; TiO_2, 0.26; Fe_2O_3, 1.26; FeO, 0.25; MgO, 0.99; CaO, 3.01; Na_2O, 0.66; K_2O, 2.76; H_2O, 10.90 (Tarasevich et al. 1991). Its porous structure consists of a collection of pores ranging in size from 1 to 18 nm, with a maximum observed in the 2.2–2.4 nm range on the pore size distribution curve (Zakordonski et al. 2004). The zeolite samples were comminuted using a mortar and pestle to obtain the desired particle size fraction. The resulting grains were washed with distilled water, dried at room temperature, and subsequently calcined at the designated temperatures for 2.5 h in a drying oven WSU 200 (Germany) and muffle furnace SNOL 7.2/1100 (Lithuania). The zeolite samples were cooled in a desiccator after calcination.

Analytical grade reagents were used throughout. A standard bismuth(III) aqueous solution (1 mg mL^{-1}) was prepared by dissolving metallic bismuth (99.99% purity, Johnson Matthey) in 7 M HNO_3. A bismuth(III) initial solution (100 μg mL^{-1}) was prepared via appropriate dilution of the standard solution with distilled water. The pH of this solution was less than 0.5. The initial solution of bismuth

(III) nitrate was stored for no longer than a day. Lower-concentration working solution (0.5 μg mL^{-1}) was prepared by further diluting the initial solution with distilled water.

Adsorption measurements and techniques for determining bismuth content in solution

The sorption abilities of clinoptilolite were investigated under dynamic conditions using SPE method as described in detail in the paper (Slota et al. 2022). For preconcentration, the Bi(III) salt solution was pumped through a cartridge containing 0.6 g of sorbent at a flow rate of 5 mL min^{-1}. The breakthrough of Bi(III) ions was photometrically monitored via their reaction with potassium iodide in the presence of thiourea. Among other photometric methods (Upor et al. 1985), this procedure is highly sensitive and sufficiently selective. Photometric determination of Bi^{3+} with KI in the presence of thiourea is based on an orange-yellow complex $[BiI_4]^-$ formation in an acidic medium with a maximum light absorption at λ = 460 nm. However, it was found that the sensitivity of the method increases several-fold (LDL = 100 ng/mL) compared to the visible region of the spectrum when optical density is measured in the UV range at λ = 345 nm (Figs. 1, 2). Thiourea is added to eliminate the influence of Fe^{3+}, $Cr_2O_7^{2-}$, Cu^{2+}, which can oxidize iodide ions (I^-) to free iodine (I_2), which distorts the results. Thus, thiourea additionally acts as a masking agent for a number of ions, in particular Fe^{3+}, which increases the selectivity of the method. In addition to the main exchangeble cations (Ca^{2+}, Na^+, K^+, Mg^{2+}) of Transcarpathian clinoptilolite, the exchange complex of this zeolite also contains Fe^{3+} cations (Vasylechko et al. 2003; 2013).

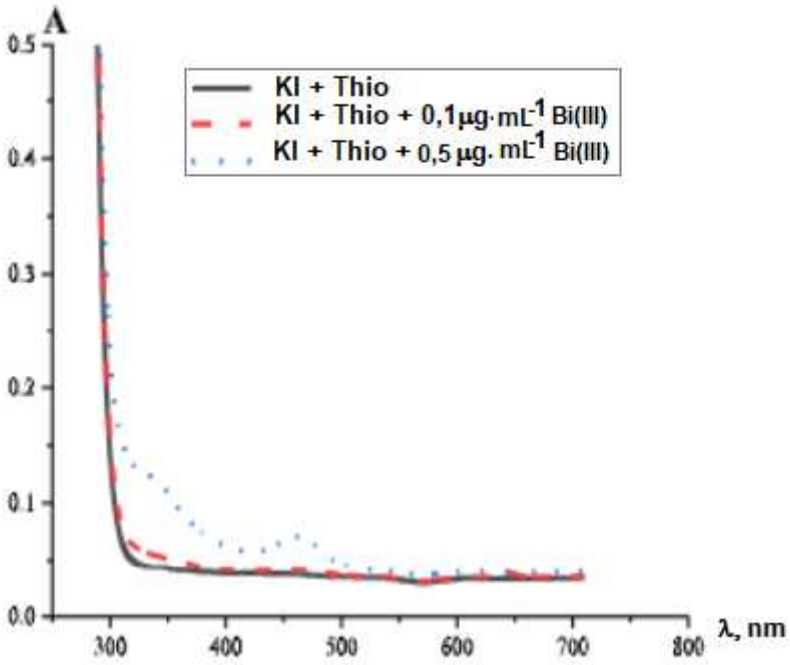


Fig. 1 Light absorption spectra of KI and thiourea solutions and products of their interaction with

Bi(III)

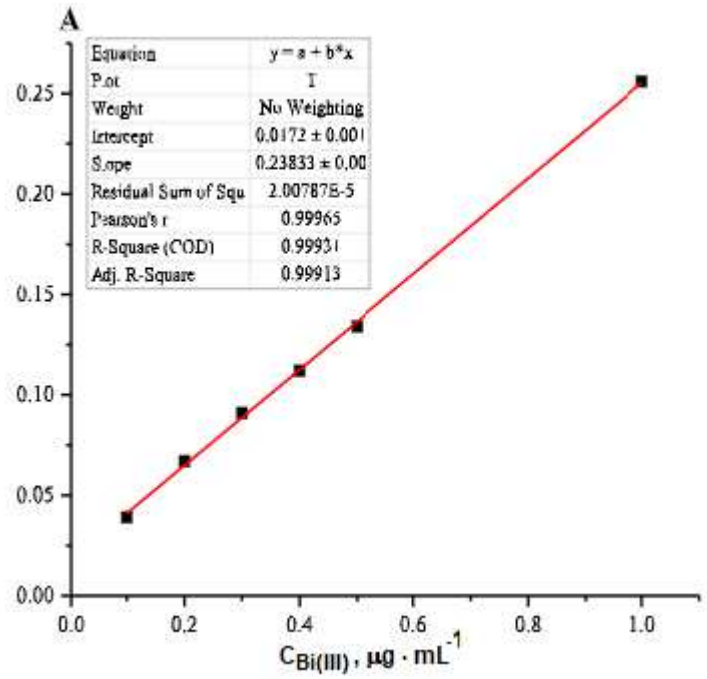


Fig. 2 Calibration graph for spectrophotometric determination of Bi(III) and its parameters

Fe3+ cations enter the mother liquors and eluates from the zeolite matrix when the sorption of ions of heavy metal on Transcarpathian clinoptilolite occurs (Vasylechko et al. 2003; 2013). Therefore, eliminating the interfering effect of Fe^{3+} ions on the results of determining the Bi^{3+} content, in particular when recording the passing moment of this cation, is a necessary condition.

Method of spectrophotometric determination of Bi(III)

2.5 mL of HNO_3 (1:3), an aliquot of the test solution containing Bi^{3+} ions, 1.0 mL of 10% KI solution, 1.0 ml of 10 % thiourea solution as well as distilled water to the mark were added in a 25 mL volumetric flask. The resulting solution is kept for 5 min and photometered at 345 nm. The values of optical densities were obtained from the absorption spectra recorded using a ULAB-102 spectrophotometer (China) and quartz cuvettes with a light-absorbing layer thickness of 3 cm. 10 mL of the various eluents (aqueous solutions of alkali metal salts and acid) were passed through the sorption cartridge at a flow rate of 0.5 mL min^{-1} for desorption of Bi(III) from the zeolite bed. The Bi(III) content in the eluates was determined spectrophotometrically using the same metal as used to detect the breakthrough point.

Physicochemical characteristics of clinoptilolites with adsorbed Bi^{3+}

X-ray diffraction (XRD) patterns and structural characteristics of the materials were obtained on a modernized DRON-3M diffractometer using CuK_α radiation (λ= 0.154185 nm).). Fourier-transform infrared (FTIR) spectra of Bi(III)-loaded clinoptilolites were recorded in the 4000–400 cm^{-1} range at a resolution of 2 cm^{-1} using a Shimadzu IRTracer-100 spectrophotometer equipped with a DRS-8000A diffuse reflectance accessory; samples were prepared as KBr mixtures (1:10 mass ratio). Diffuse reflectance spectra (DRS) of the clinoptilolite powders were acquired over a wavelength range of 200–800 nm using a Shimadzu UV-2450 spectrophotometer, and optical bandgap E_g values were subsequently determined via Tauc plots. Textural properties and pore structure parameters were derived from low-temperature N_2 adsorption–desorption isotherms measured on a Micromeritics ASAP 2405N analyzer. The specific surface area (SSA) was calculated using the Brunauer–Emmett–Teller (BET) method.

Photocatalytic properties

The photocatalytic activity of the materials under visible light illumination was evaluated through the degradation of safranin T (ST, $1 \cdot 10^{-5}$ mol L^{-1} solution aqueous solution), which serves as both a persistent model dye and a real-world organic pollutant. Photocatalytic experiments were conducted in a glass reactor using a 100 W LED Cool Daylight lamp (Philips) with a power density of 3 W cm^{-2}; this light source emits exclusively in the visible region, featuring a broad spectral band spanning 500–700 nm with a maximum emission at 565 nm. Due to the pronounced dark adsorption of ST on clinoptilolite, a catalyst-to-dye solution ratio of 10 mg/80 mL was selected as optimal. Concentration profiles were monitored spectrophotometrically by measuring the absorbance intensity at 520 nm at specific intervals between 30 and 600 min, with the overall degradation efficiency calculated at the 600-min mark. To evaluate ST mineralization into inorganic products, total organic carbon (TOC) analysis was performed using a Shimadzu TOC-L Analyzer with 20 mL sample aliquots, and the degree of mineralization was determined based on the net TOC reduction over the 600-min irradiation period.

Measurement of antimicrobial activity

The gram-positive bacterium *Staphylococcus aureus* ATCC 25923, the gram-negative bacterium *Escherichia coli* ATCC 25922, and the yeast fungus *Candida albicans* ATCC 885-653 were used as test cultures for evaluating the antimicrobial activity of zeolite compositions with metals. 1 mg of clinoptilolite and clinoptilolite compositions with Bi(III) and Ag(I) ions were added to 3 ml of isotonic NaCl solution. After that, 1 ml of a suspension of test culture cells of *E. coli, S. aureus*, and *C. albicans* with a concentration of about 108 cells mL^{-1} was added. The mixture was incubated in 50 ml flasks, shaking at 200 rpm for 60 min. After that, 0.1 ml of suspensions were taken and 10-fold dilutions were made. Suspensions of *S. aureus* and *E. coli* were inculated onto LB-agar plate containing 10 g tryptone, 5 g yeast extract, 10 g NaCl, 15 g agar-agar per liter deionized water, and suspensions of *C. albicans* – on Sabouraud medium consisting of 10 g peptone, 40 g dextrose, and 15 g agar-agar per liter of deionized H_2O and the number of colonies formed was counted. Antimicrobial activity was assessed by determining the percentage of cells that survived after incubation with clinoptilolite compositions with Bi(III) and Ag(I)B ions and were able to form colonies. For control, test culture cells were incubated under the same conditions in isotonic NaCl solution without the addition of zeolite compositions with metals.

Results and Discussion

Sorption characterization

It is known that Bi(III) salts are prone to hydrolysis with the formation of insoluble compounds, which usually makes it difficult, and often impossible, to study of Bi(III) ions sorption. With this in mind, we found conditions (Bi(III) concentration, pH, and storage time of working solutions) under which hydrolysis of trace amounts of Bi(III) does not occur. For the determination of Bi(III) in aqueous solutions, we used a spectrophotometric method using KI in the presence of thiourea. It is also known that the colored complex anion $[BiI_4]^-$ can be formed only by unhydrolyzed forms of Bi(III). Therefore, if even partial hydrolysis of Bi(III) occurs in the working solutions, the yield of the complex $[BiI_4]^-$ and the optical density at $\lambda = 345$ nm will be lower. During these studies, the following experiment was conducted: two series of working solutions of Bi(III) were prepared in the pH range from 4 to 10 with a metal concentration of 1 μg mL^{-1} and 0.5 μg mL^{-1}. The change in the optical density of the solutions depending on the storage time of the working solutions of Bi(III) at different pH was studied. The results of the studies are presented in Tables 1, 2, from which it can be seen that in neutral, weakly acidic, and weakly alkaline solutions ($pH \leq 9.0$) with a lower

concentration of Bi(III) ions (0.5 μg mL^{-1}), the hydrolysis process occurs more slowly than in solutions of similar acidity with a higher concentration of ions of this metal.

The optical density of the solutions, and accordingly the concentration of Bi(III) ions, remains unchanged for almost 5 h (Table 2).

Table 1 The optical density of the complex ion $[BiI_4]^-$ as function of the contact time for a 1 μg mL^{-1} Bi(III) working solution at various pH values.

Contact time of Bi(III) solutions, min	pH						
	4.0	5.0	6.0	7.0	8.0	9.0	10.0
	The value of the optical density of solutions of the complex ion $[BiI_4]^-$ [a]						
0	0.086	0.086	0.087	0.087	0.089	0.088	0.089
30	0.083	0.083	0.084	0.086	0.083	0.081	0.086
60	0.081	0.080	0.081	0.080	0.088	0.080	0.080
180	0.077	0.078	0.076	0.075	0.076	0.073	0.074
290	0.038	0.04	0.04	0.039	0.039	0.039	0.04
300	0.010	0.009	0.010	0.008	0.010	0.009	0.008

[a] For analysis, 7.5 mL of the test solution was transferred to a 25 mL volumetric flask, followed by the addition of the required reagents.

Table 2 Dependence of the optical density of solutions of the complex ion $[BiI_4]^-$ on the contact time for 0.5 μg mL^{-1} solution Bi(III) solution at different pH

Contact time of Bi(III) solutions, min	pH						
	4.0	5.0	6.0	7.0	8.0	9.0	10.0
	The value of the optical density of solutions of the complex ion $[BiI_4]^-$ [a]						
0	0.086	0.087	0.085	0.087	0.088	0.087	0.038
30	0.085	0.087	0.084	0.085	0.083	0.085	0.036
60	0.084	0.088	0.082	0.085	0.088	0.084	0.035
180	0.087	0.086	0.081	0.084	0.086	0.085	0.034
290	0.082	0.085	0.085	0.082	0.083	0.084	0.035
300	0.070	0.079	0.078	0.079	0.078	0.078	0.028

[a] To prepare the photometric solution, in addition to the necessary reagents for the spectrophotometric determination of Bi(III), 15 mL of the test solution was added to a 25 mL volumetric flask.

Therefore, it can be stated that such solutions are true. At the same time, solutions with a higher concentration of Bi(III) ions (1 μg mL^{-1}) are noticeably hydrolyzed after a three-hour exposure

(Table 1). Subsequent Bi(III) sorption studies on Transcarpathian clinoptilolite were performed using freshly prepared 0.5 μg mL^{-1} working solutions (pH ≤ 9.0) stored for no longer than 5 h.

Effect of Grain Fraction

The relationship between the grain size of clinoptilolite and its dynamic sorption capacity for Bi(III) was systematically evaluated. (Table 3). The results of Table 3 show that clinoptilolite's Bi(III) ions sorption capacity increases significantly with decreasing grain size of the sorbent.

Table 3 Effect of sorbent grain size on the Bi(III) sorption capacity of clinoptilolite (initial Bi(III) concentration: 0.5 μg mL^{-1}, pH 2.5).

Particle fraction size, mm	Sorption capacity, μg g^{-1}
0.20 – 0.31	13875
0.31 – 0.35	1595
0.35 – 0.50	850
0.50 – 0.70	175

Consequently, using clinoptilolite with the smallest grain size is recommended for dynamic regimes. However, granules smaller than 0.20–0.31 mm introduce operational challenges because highly dispersed sorbents significantly restrict solution flow. Therefore, a clinoptilolite grain size of 0.20–0.31 mm was selected as the optimum for subsequent experiments.

Effect of pH

The effect of medium acidity on Bi(III) sorption onto clinoptilolite was investigated (Fig. 3). The required pH value of the Bi(III) salt solution was created by adding diluted HNO_3 or NaOH solutions. The results obtained indicate that clinoptilolite effectively sorbs Bi(III) from acidic solutions. As can be seen, clinoptilolite demonstrated high sorption efficiency for Bi(III) in acidic media.

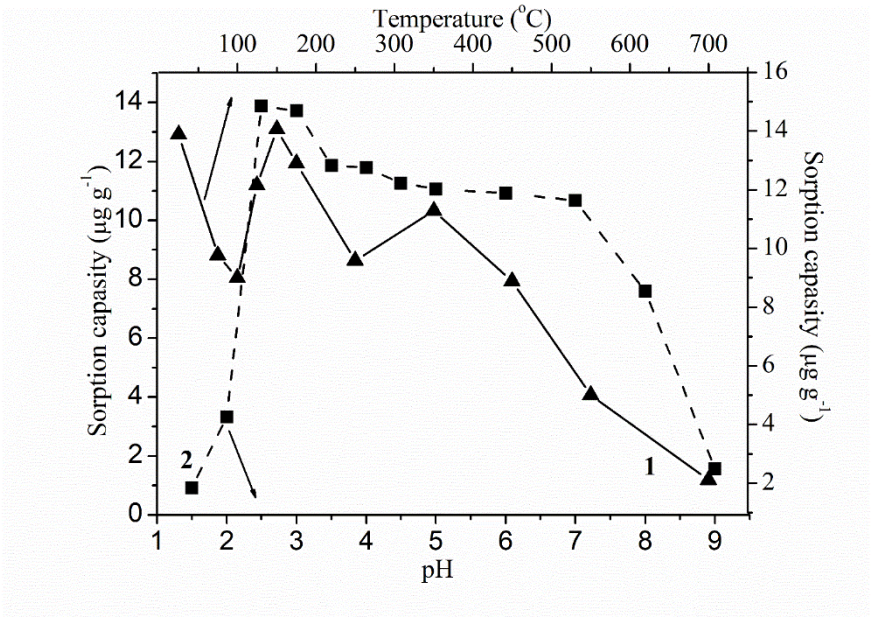


Fig. 3 Effect of solution pH (1) and heat treatment temperature of clinoptilolite (2) on its Bi(III) sorption capacity (initial Bi(III) concentration: 0.5 μg mL^{-1}; pH 2.5 for curve 2).

Maximum in sorption capacity is observed when using a Bi(III) solution with a pH of 2.5. In solutions with pH < 2. This nature of the Bi(III) sorption may be attributed to the peculiarities of surface structure of Transcarpathian clinoptilolite, because even when the acidity of the medium increases to pH 2 zeta potential of this zeolite remains negative (Slota et al. 2022), as well as due to the forms of existence of Bi(III) in aqueous solutions at different pH values. Under acidic conditions at low concentrations, Bi(III) forms cationic hydroxo complexes of various compositions. In strongly acidic solutions (pH 1-3), the cationic hydroxo complex $[Bi(OH)]^{2+}$ pre-dominates, while in weakly acidic solutions (pH 4-6), the polynuclear hydroxo complex $[Bi_9(OH)_{22}]^{5+}$ is dominant. The proportion of other cationic hydroxo complexes of Bi(III) in acidic solutions, namely $[Bi(OH)]^{2+}$, $[Bi_6(OH)_{12}]^{6+}$, $[Bi_9(OH)_{20}]^{7+}$ and $[Bi_9(OH)_{21}]^{6+}$, is insignificant. In weakly alkaline solutions, dissolved Bi(III) at trace levels is predominantly present as the neutral hydrolyzed species $Bi(OH)_3$ (Fig. 4, taken from (Baes and Mesmer 1976)). From Fig. 3, it is seen that the sorption capacity of clinoptilolite increases noticeably in Bi(III) solution with pH < 3.5 and reaches its maximum value at pH 2.5. With further acidification of the solution to pH 1.5, the sorption capacity of clinoptilolite decreases sharply. The profile of Bi(III) sorption capacity on clinoptilolite correlates strongly with the abundance of the $[Bi(OH)]^{2+}$ cationic hydroxo complex between pH 1.5 and 3.5.

Figure 4 illustrates that the formation of the $[Bi(OH)]^{2+}$ hydroxo complex initiates at pH < 3.5 and the highest content of this hydroxo complex (> 80 %) is recorded in solutions with pH 2.5. With further acidification of the solution, the proportion of the hydroxo complex $[Bi(OH)]^{2+}$ decreases, while the proportion of unhydrolyzed Bi^{3+} increases. These data indicate that the Transcarpathian clinoptilolite most effectively sorbs the cationic hydroxo complex $[Bi(OH)]^{2+}$.

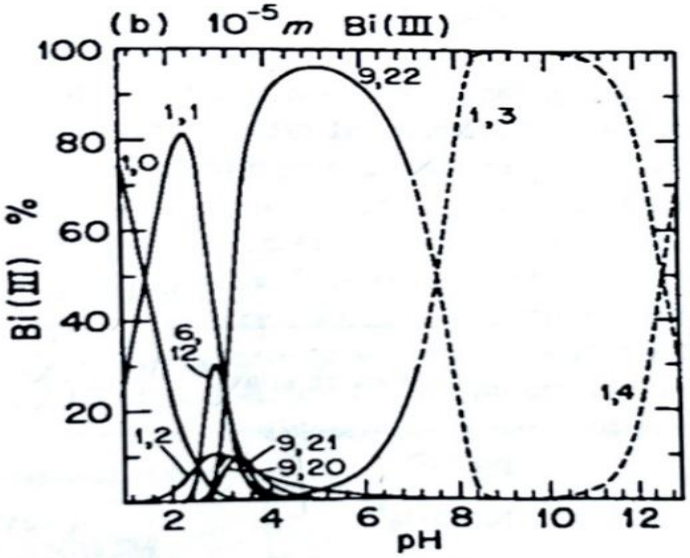


Fig. 4 Distribution of Bi(III) species as a function of pH for a given total bismuth concentration: $1.0 \cdot 10^{-5}$ M (1.0 – Bi^{3+}; 1.1 – $BiOH^{2+}$; 1.2 – $Bi(OH)_2^{+}$; 1.3 – $Bi(OH)_3$; 1.4 – $Bi(OH)_4^{-}$; 6.12 – $Bi_6(OH)_{12}^{6+}$; 9.20 – $Bi_9(OH)_{20}^{7+}$; 9.21 – $Bi_9(OH)_{21}^{6+}$; 9.22 – $Bi_9(OH)_{22}^{5+}$). Taken from (Baes and Mesmer 1976).

Within the weakly acidic and neutral pH range (4–7), where the polynuclear hydroxo complex $[Bi_9(OH)_{22}]^{5+}$ is dominant, high sorption efficiency of clinoptilolite is also manifested. In contrast, in weakly alkaline solutions, where the predominant bismuth species is the neutral, soluble hydrolyzed form $Bi(OH)_3$, clinoptilolite exhibits poor sorption efficiency. At pH 9, where $Bi(OH)_3$ is 100 %, the the sorption capacity of clinoptilolite is minimal (Fig. 3). Therefore, Transcarpathian clinoptilolite effectively sorbs partially hydrolyzed cationic forms of Bi(III), which contain hydroxyl groups OH^-. The adsorption activity cannot be attributed to the whole sorbent surface, but only to its certain areas – active centers. The uncompensated chemical bonds – defects of the crystal lattice, groups of atoms with uneven electronic density distribution or groups capable of ion exchange are gathered in active centers. The active sorption centers toward heavy metals in Transcarpathian clinoptilolite are predominantly surface OH groups (Slota et al. 2022; Vasylechko et al. 2003; 2013; Zakordonski et al. 2004). Partially hydrolyzed cationic forms of Bi(III), in particular $[Bi(OH)]^{2+}$ and $[Bi_9(OH)_{22}]^{5+}$ and surface OH groups of clinoptilolite at the initial stage of adsorption can form an intermediate product with H-bonds with subsequent formation of a heteronuclear structure with hydroxo-bridges. The adsorption of hydrolyzed forms of heavy metal ions, in particular, their cationic hydrolyzed forms, on the surface of clinoptilolite is described by the authors of the article (Godelitsas and Armbruster 2003).

Therefore, the highest Bi(III) sorption capacity of Transcarpathian clinoptilolite is achieved under acidic conditions at pH 2.5. At the same time, other heavy metals are effectively sorbed on this zeolite only from weakly alkaline or neutral solutions (Slota et al. 2022; Vasylechko et al. 2003; 2013). Such a difference in the optimal pH values for Bi(III) and the remaining heavy metals allows for selective concentration of Bi(III) and its separation from other heavy metals.

Effect of temperature of clinoptilolite the pre-calcination

Sorption ability of Transcarpathian clinoptilolite is also determined by its pre-calcination (Vasylechko et al. 2003; 2013). To evaluate how pre-calcination affects bismuth sorption, the clinoptilolite samples were heated at various temperatures for 2.5 hours, cooled in a desiccator, and then tested for their Bi(III) capacity (Fig. 3). The highest value of the sorption capacity is exhibited by clinoptilolite samples pre-calcined at 150 °C, as well as uncalcined samples of this zeolite. More detailed, temperature increasing to 100 °C leads to a reduction of sorption capacity. In Transcarpathian clinoptilolite, the water condensed in pores is removed at temperatures < 100 °C. This temperature stage corresponds to the external diffusion region of the desorption process. In this region, the zeolite releases only a minimal fraction (1–2%) of its bound water (Zakordonski et al. 2004). It is likely that these processes cause a reduction of the ability ability of clinoptilolite to sorption of Bi(III) (Fig. 3).

The increase in the capacity of the sorbent to the maximum value of 14055 μg g^{-1} was observed in the range of 100-150 °C. These temperature range corresponds to the second stage of desorbing water bound to the Transcarpathian clinoptilolite surface. This stage makes a decisive contribution to thermal desorption of water and is characterized by a high activation energy, indicating a distinct activation mechanism. During the second stage of thermal desorption, capillary-bound water is removed from the mesopores (Zakordonski et al. 2004). It probably influences on the subsequent sorption of Bi(III).

We associate the maximum at 350 °C on this dependence with structural changes in the zeolite. In particular, the number of surface sinalol groups (Si-OH), which are sorption active towards heavy metals, increases after clinoptilolite calcination at 300-350°C due to dealumination process (Tomazović et al. 1996). Transcarpathian clinoptilolite treated at 350°C have the highest value of specific surface area of 86 m^2 g^{-1} measured using water as adsorbate (Vasylechko et al. 2013). The latter also contributes to the sorption of Bi(III). The decreased sorption capacity of clinoptilolite calcined above 350 °C is attributed to partial amorphization of the zeolite structure. In work (Vasylechko et al. 2003), it was found that the amorphization of the natural form of Transcarpathian clinoptilolite is already clearly visible at such temperatures.

Desorption

In order to find efficient Bi(III) desorbing agents, the solutions of HNO_3, HCl as well as alkali metal nitrates and chlorides were studied. The ubtained results (Table 4) show that HNO_3 is the efficient desorbing agent. 1.5 M and 1 M HNO3 solutions provide total desorption of pre-sorbed bismuth.

Table 4 Efficiency of bismuth (III) desorption[a]

Desorbent	Desorption (%)
1.5 M HNO_3	100
1 M HNO_3	100
0.5 M HNO_3	90
1 M HCl	75
1 M KNO_3 (adjusted to pH 1 with HNO_3)	90
1 M KNO_3 (adjusted to pH 2.5 with HNO_3)	60
1 M KCl (adjusted to pH 2.5 with HCl)	40
1 M NaCl (adjusted to pH 2.5 with HCl)	20
1 M $NaNO_3$ (adjusted to pH 2.5 with HNO_3)	15

[a]Experimental conditions: eluent flow rate = 0.5 mL min^{-1}; total eluent volume = 10 mL.

Acid solutions presumably provide preliminary dissolution of sorbed bismuth hydrolyzed and their subsequent desorption under dynamic conditions. The Bi(III) concentration in the eluates was evaluated spectrophotometrically under the same conditions as for recording the “breakthrough” moment.

Influence of foreign ions on Bi(III) sorption

The effect of common co-existing water ions on the preconcentration of Bi(III) by clinoptilolite was investigated at pH 2.5. The permissible ion concentration ratio ($C_{ion}/C_{Bi(III)}$) was determined based on a maximum 5% deviation in breakthrough capacity. Table 5 demonstrates that a 10–500-fold excess of these foreign components does not interfere with the quantitative sorption of trace Bi(III).

Table 5 Effect of co-existing Ions and Tolerance Limits on Bi(III) Sorption
(Bi(III) concentration =0.5 μg mL^{-1} at pH 2.5)

Admixture	Tolerance limit ($C_{ion}/C_{Bi(III)}$)
Na^+	500
K^+, Mg^{2+}	40
Ca^{2+}, NH_4^+	10

The maximum for Bi(III) sorption capacity of clinoptilolite is significantly influenced by Ca^{2+} and NH_4^+ ions, the permissible multiple of which is 10. Consequently, even when water macro-components exceed allowable limits and reduce sorption efficiency, the residual breakthrough capacity remains high enough to ensure successful Bi(III) concentration.

Analytical performance

The high sorption capacity of Transcarpathian clinoptilolite for Bi(III)—even at low concentrations and in the presence of other water constituents—combined with the availability of effective desorbing agents, makes it suitable for the preconcentration of Bi(III) during the preparation of water samples for analysis. A method for the preconcentration of trace Bi(III) via solid-phase extraction is proposed for use in the spectrophotometric analysis of water.

Sample preconcentration procedure

An HNO_3 solution was added to 0.5–2.0 L of the water sample until a pH of ~1 was reached, after which the mixture was heated on a sand bath for 1 hour. Following filtration through a dense paper filter, the pH of the solution was adjusted to 2.5 using an NaOH solution. The solution was then passed through a pre-concentration cartridge packed with 0.6 g of clinoptilolite (grain size fraction 0.20–0.31 mm, pre-calcined at 150 °C). The flow was maintained using a peristaltic pump at a rate of 5 mL/min. Subsequently, the cartridge was rinsed with 50 mL of distilled water under identical flow conditions. Bi(III) desorption was achieved using 10 mL of 1 M HNO_3 under a flow rate of 0.5 mL min^{-1}. The resulting eluate was quantitatively collected into a 10.0 mL volumetric flask. The Bi(III) concentration in the eluate was determined spectrophotometrically using KI in the presence of thiourea, following the procedure described in the experimental section.

Overall, the proposed method for the Bi(III) ions determination shows linearity in the range of 0.5 to 200 ng/mL. The detection limit is 0.2 ng/mL. The use of the proposed pre-concentration method for Bi(III) allows for an enrichment factor of 200.

Photocatalytic properties of clinoptilolites with adsorbed Bi^{3+}

A selective environmental analytical procedure for Bi(III) monitoring using SPE on clinoptilolite can be base for followed valorization of the Bi-loaded material into a multifunctional environmental material with second-life utilization of the spent sorbent. Particularly, the Bi-loaded clinoptilolite, generated during the preconcentration procedure, can be subsequently used as an adsorbent for purification of water from pollutants or visible-light-active photocatalyst. It well known that adsorption and photocatalytic ability of such spent materials is determined by their physicochemical characteristics.

As mentioned above (in experimental part), tested Bi-containing clinoptilolites possess high adsorption ability respect to safranin T (ST) as one of the such typical pollutants. The obtained sorption capacity exceeds that for the initial clinoptilolite by almost 1.5 times (Table 6). Obviously, this is not related to a change in the porous structure of clinoptilolite due to adsorption Bi^{3+} cations. The latter is evidenced by the isotherms of N_2 low-temperature adsorption-desorption shown in Fig. 5a, as well as parameters calculated from them. Thus, the specific surface area (SSA) practically does not change after adsorption of Bi^{3+}: its value is 15 m^2 g^{-1} for initial clinoptilolite and is within 14-17 m^2 g^{-1} for Bi-clinoptilolite samples which is close to the measurement error for such low SSA values (Fig. 5a, Table 7). Moreover, total pore volume decreases after Bi^{3+} adsorption although mesoporous fraction is almost retained (Table 7). The similar trends were previously found for clinoptilolites with other adsorbed cations (Sydorchuk et al. 2025). The crystal structure of clinoptilolite also remains practically unchanged after Bi^{3+} cation adsorption (Fig. 5b). This is explained by the very low content of Bi-oxygen species (0.96-1.41 % w/w), which cannot form either a separate oxide phase or affect the structure of clinoptilolite: Rietveld refinement analysis showed only minor variations in certain lattice parameters relative to the initial matrix, all of which fall within experimental error limits, consistent with previous literature (Prieto-Laria et al. 2025; Sydorchuk et al. 2025).

FTIR spectra recorded (Fig. 5c) also confirm absence of bands related to Bi_2O_3 phase in the region 400-600 cm^{-1} (Hobosyan et al. 2016) as well as visible change in the range 600-700 cm^{-1} which is associated with ring vibrations influenced by the extra-framework cations (Mozgawa 2000; Prieto-Laria et al. 2025). But a shift of the main clinoptilolite band, corresponding to internal ν_{as} (O–T–O) stretching, from ~1055 to ~1030 cm^{-1} after Bi^{3+} sorption is observed. This indicates the introduction of Bi^{3+} cations into aluminosilicate framework (Doula 2007; Mozgawa 2000). In addition, a band with a maximum centered at 1145 cm^{-1}, which is not observed in the spectrum of the initial clinoptilolite, appears in the spectra of Bi-containing samples. It can be attributed to Bi-OH vibration in CPT-O^-−Bi^{3+}, CPT-O^-−$Bi(OH)^{2+}$ or CPT-O^-−$Bi(OH)_2^+$ groups (Hobosyan et al. 2016) as well as to the sorbed Bi polynuclear hydroxo complexes $[Bi_6O_x(OH)_{8-x}]^{(10-x)+}$.

Table 6 Adsorption and photocatalytic results for Bi-containing samples respect to safranin T ($1 \cdot 10^{-5}$ mol L^{-1})

N	Samples, content of Bi and conditions of preparation	$k_d \cdot 10^5$ (s^{-1})	% adsorption	% photocatalysis/mineralization
1	Initial natural clinoptilolite	3.2	39	29/14
2	Bi (9.6 mg g^{-1}) / clinoptilolite 250°C pH=2.5	4.2	46	36/24

3	Bi (11.1 mg g^{-1}) / clinoptilolite pH=5	6.3	50	47/40
4	Bi (11.3 mg g^{-1}) / clinoptilolite 350°C pH=2.5	5.4	56	41/32
5	Bi (13.7 mg g^{-1}) / clinoptilolite pH=3	5.1	59	36/27
6	Bi (14.1 mg g^{-1}) / clinoptilolite150°C pH=2.5	4.9	57	35/29

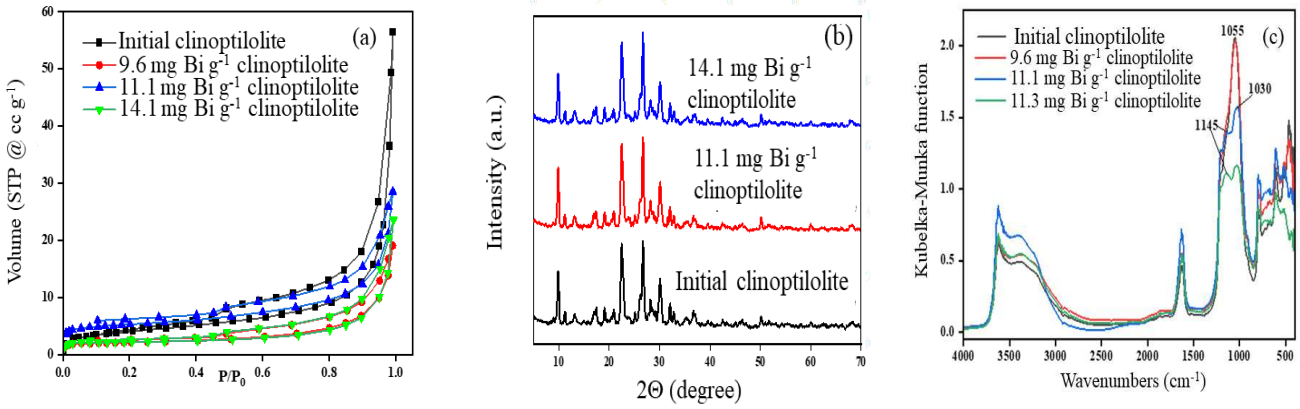


Fig. 5 The N_2 adsorption-desorption isotherms (a), the XRD patterns (b), the FTIR spectra (c) of some clinoptilolite based samples

Table 7 Some physicochemical characteristics of clinoptilolites with sorbed Bi^{3+}

N	Samples, content of Bi and conditions of preparation	SSA (m^2 g^{-1})	V/V_{me} (cm^3 g^{-1})	$E_{g.app}$ (eV)
1	Initial natural clinoptilolite	15	0.10/0.05	3.17
2	Bi (9.6 mg g^{-1}) / clinoptilolite 250°C pH=2.5	14	0.05/0.04	2.78
3	Bi (11.1 mg g^{-1}) / clinoptilolite pH=5	17	0.06/0.05	2.41
4	Bi (11.3 mg g^{-1}) / clinoptilolite 350°C pH=2.5	16	0.06/0.05	2.41
5	Bi (13.7 mg g^{-1}) / clinoptilolite pH=3	15	0.05/0.04	2.45
6	Bi (14.1 mg g^{-1}) / clinoptilolite150°C pH=2.5	14	0.05/0.05	2.40

Therefore, the significant increase in dark adsorption of ST Bi-clinoptilolite samples (Table 6) may be a result of the complexation of safranin T molecules with bismuth cations (Eltaboni et al. 2022; Saad et al. 2007; Tan et al. 2022; Satya et al. 2025) as well as through OH groups which bound with cations (band 1146 cm^{-1} in Fig. 5 c). This is confirmed by similar results previously obtained for clinoptilolites with other adsorbed cations (Sydorchuk et al. 2025). Indeed, the nitrogen-containing groups of ST act as electron donors (Lewis bases) that readily form coordinate bonds with the electron-deficient Bi^{3+} active sites acting as a Lewis acid. The formation of such surface complex

species is the critical first step for next degradation of ST under irradiation. Thus, clinoptilolite samples with sorbed Bi^{3+} cations show significantly higher activity compared to initial clinoptilolite under the same conditions. Fig. 6. demonstrates a representative example of the temporal spectral variations for the ST solution.

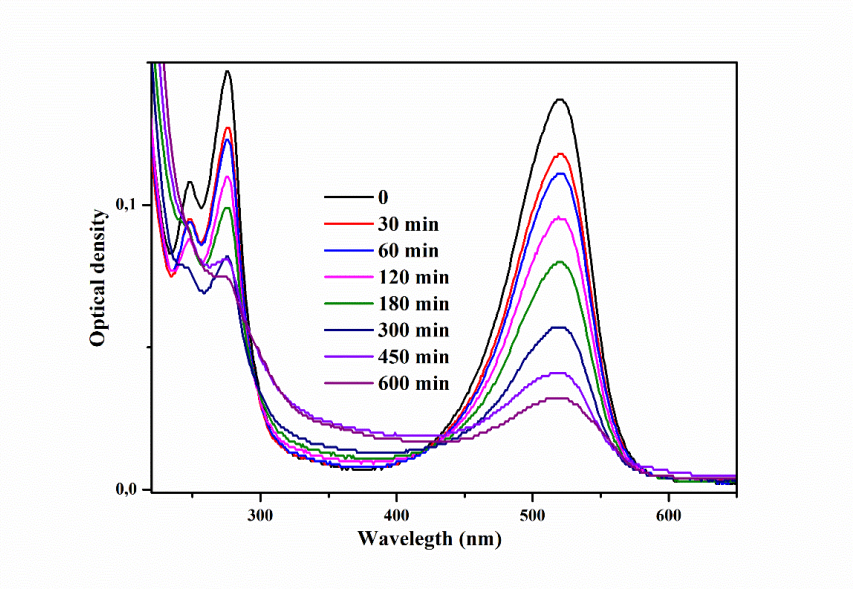


Fig. 6 Time-dependent spectra of safranin T solution during irradiation using sample Bi (9.6 mg g^{-1}) /clinoptilolite 250°C pH=2.5 as photocatalyst

Comparative degradation kinetics of ST under visible light catalyzed by initial and Bi-clinoptilolite samples are shown in Fig. 7. The degradation rate constants k_d, calculated from these data, are summarized in Table 6. The degradation process obeys pseudo-first-order kinetics, showing satisfactory linearity (R^2 = 0.98-0.99).

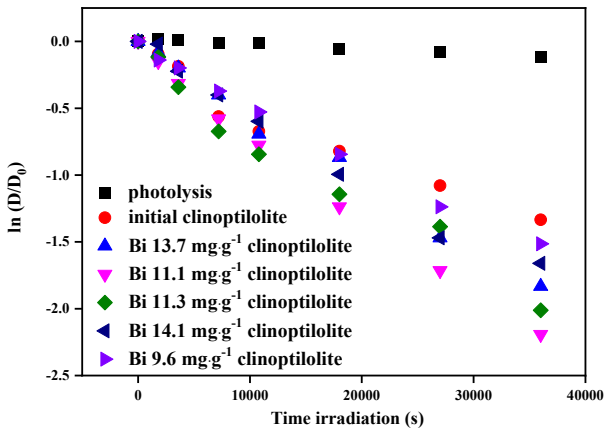


Fig. 7 Kinetic curves of safranin T photocatalytic degradation using initial clinoptilolite and different Bi-containing samples

The initial sample demonstrates activity in the degradation of safranin under the influence of visible irradiation due to impurities of iron species as mentioned above. As can be seen, the overall degree of Safranin T removal from an aqueous solution via adsorption and photocatalytic degradation reaches 95–97% for10 hours. Particularly, the sample 3 from Table 6 (Bi (11.1 mg g^{-1}) pH=5) has the best photocatalytic activity (maximal value of rate constant degradation k_d) i.e maximum photocatalytic contribution to the overall ST removal effect.

Interestingly, almost the same k_d value was obtained for clinoptilolite with approximately the same content of silver cations, as reported in the work (Sydorchuk et al. 2025). Also, it is noteworthy that sample 3 does not contain the largest amount of adsorbed Bi^{3+}cations (11.1 mg g^{-1}). Further increase in bismuth content to 14.1 mg g^{-1} leads to a decrease in activity. This may be, in particular, due to the increase in dark adsorption of ST (Table 6) i.e increasing surface coverage and blocking of Bi-oxygen species by Safranin T molecules which decreases the efficiency of the photoinduced processes. From an applied point of view, a more critical indicator is the mineralization degree of safranin T, which reflects its complete conversion into benign inorganic substances. The calculations, based on the determination of the total organic carbon content (TOC), shows that its value reaches 40% for the most active sample 3 (Table 6).

It is obvious that the activity of the tested compositions depends not only on the bismuth content, but also on its state in the clinoptilolite structure and, accordingly, its effect on the electronic characteristics of the composition, which can be assessed using UV-Vis spectroscopy. It is known that natural clinoptilolite exhibited a weak broad absorption extending into the visible region, attributable to Fe-containing impurities (Alvarez-Aguiñaga et al. 2020; Rodríguez-Iznaga et al. 2022; Wang et al. 2022). After Bi incorporation, the intensity of this absorption increased substantially and new UV absorption features appeared. Representative UV-Vis spectra displayed in Fig. 8a can indicate different states of Bi^{3+} cations in the clinoptilolite matrix. These absorption bands observed are attributed to $O^{2-} \rightarrow Bi^{3+}$ charge-transfer transitions characteristic of highly dispersed Bi(III) species. Thus, the sample containing 9.6 mg g^{-1} Bi displays a band at 208 nm (these band is also present in spectra of other samples prepared at pH 2.5-3), whereas the spectrum of sample containing 11.1 mg g^{-1} Bi exhibits bands at 228 nm. The difference in its position is directly related to the pH at which the adsorption of Bi^{3+} ions occurred, namely 2.5 and 5, respectively. Obviously, the shift from 208 to 228 nm can be considered as potential evidence of changing Bi speciation, rather than simply a loading effect from 9.6 mg to 11.1 mg g^{-1}. As mentioned above, the hydroxocomplex $[Bi(OH)]^{2+}$ exists predominantly in the solution in the first case, while the polynuclear hydroxocomplex $[Bi_9(OH)_{22}]^{5+}$ dominants in the second case (Fig. 4). Therefore, the appearance of multiple absorption bands in UV-Vis spectra suggests the presence of Bi(III) ions in different local coordination environments in clinoptilolite matrix, likely corresponding to isolated framework-associated

(possibly at ion-exchange positions) and partially hydrolyzed Bi(III) species. The latter is fully consistent with mentioned above observation that partially hydrolyzed forms are preferentially adsorbed. At pH 5, where $Bi_9(OH)_{22}^{5+}$ is predicted to be an important aqueous Bi(III) hydrolysis species, incorporation of Bi into clinoptilolite may involve retention of polynuclear Bi hydroxo species rather than exclusively mononuclear Bi^{3+} exchange ions. Nevertheless, the absence of diffraction peaks in XRD diffractograms attributable to Bi_2O_3 (Fig. 5a) also indicates that bismuth is highly dispersed within the clinoptilolite matrix and does not form separate crystalline oxide phases as in work (Wang et al. 2022). Finally, the absorption bands at 240 and 370 nm are attributed to impurities of iron: octahedral Fe^{3+} ions integrated directly into the zeolite frsamework and extra-framework isolated Fe^{3+} ions in octahedral coordination (Alvarez-Aguiñaga et al. 2020). These spectra confirm the formation of Bi-modified clinoptilolite composite, which is often designed for enhanced visible light absorption and improved photocatalytic performance.

Therefore, the enhanced visible absorption can be interpreted as resulting from Bi-induced modification of the electronic structure of the Fe-containing clinoptilolite rather than from the appearance of visible absorption in an otherwise optically inactive matrix. At the same time, the Tauc plots, plotted according to indirect transition (Fig. 8b) as in work (Prieto-Laria et al. 2025), namely region of 2–3 eV, indicate one of the factors for the improvement of photocatalytic performance of clinoptilolite after the introduction of Bi^{3+} cations: it is likely associated with additional Bi-related localized states. The formation of these new sub-levels that correspond to the apparent band gap (more correctly, apparent optical transition energies) 2.4-2.8 eV is observed. It should be noted that spectrum of bulk Bi_2O_3 contains broad band in the range 275-310 nm and band gap for this sample is 2.85 nm. Indicated changes may reflect modification of the distribution of Bi-/Fe-related localized states and/or charge-transfer transitions associated with the different Bi hydrolysis/speciation conditions during its sorption from solutions.

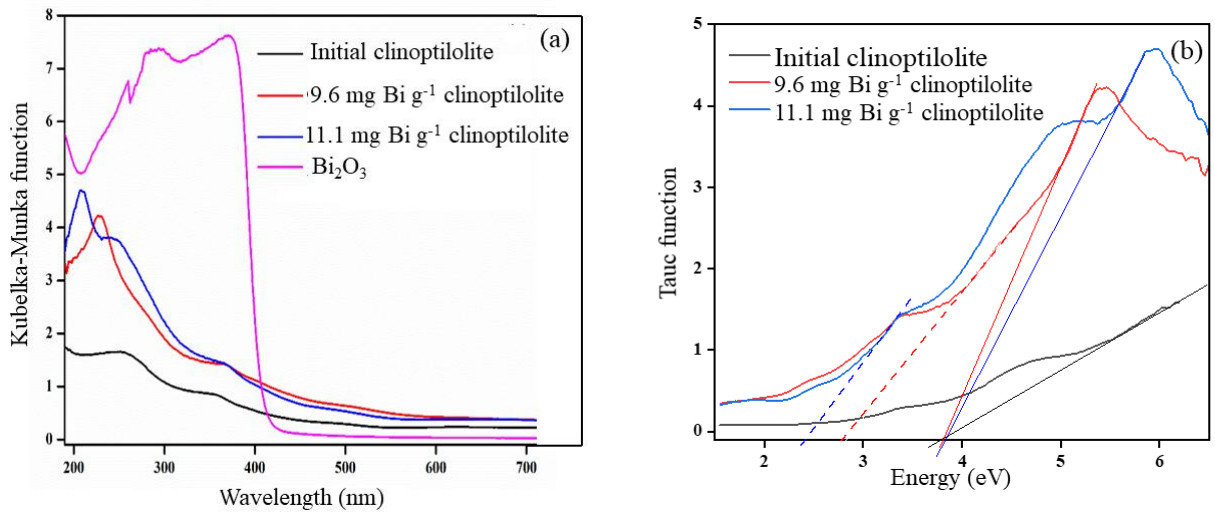


Fig. 8 DRS UV-Vis spectra of initial clinoptilolite, Bi_2O_3 and two Bi-containing samples (a) and Tauc plots (indirect transition) for initial and two Bi-clinoptilolites (b).

Establishing above mentioned dependencies makes it possible to optimize the process conditions not only for the sorption and concentration of bismuth, but also for the preparation of compositions with adjustable bismuth content, its state in the clinoptilolite matrix, and photocatalytic and antimicrobial activity. Therefore, the clinoptilolite framework acts as a rigid, stable host during sorption of Bi (III). It retains its porosity and crystallinity. The atomic content and dispersion of bismuth as well as its state in clinoptilolite matrix can be regulated depending on conditions of Bi^{3+} adsorption. This creates intra-band gap states (sublevels) that shift light absorption from UV to visible light. As a result, the guest bismuth ions generate the reactive oxygen species (ROS) under visible light to destroy of safranin T molecules. Apparently, the optimal photocatalytic activity reflects the balance between the formation of photoactive centers associated with Bi and the overfilling/blocking of adsorption sites, rather than simply the magnitude of visible light absorption.

Biological activity

It is known that the photocatalytic and antibacterial activities of bismuth-clinoptilolite compositions are highly similar because they are driven by the same fundamental chemical mechanism: the processes involves generating reactive oxygen species (ROS), which subsequently react with the organic pollutants (Ma et al. 2025). When bismuth species are embedded into a clinoptilolite matrix, light exposure can trigger parallel pathways that simultaneously degrade organic pollutants and destroy bacterial cells. Therefore, the antimicrobial performance of the composition of silver-containing Transcarpathian clinoptilolite, as well as in combination with bismuth ions at different concentrations of inhibitory factors were investigated. Gram-positive bacteria *S. aureus* ATCC 25923, gram-negative bacteria *E. coli* ATCC 25922, and yeast fungi *C. albicans* ATCC 885-653 used as test cultures. The following compositions were tested: zeolite - zeolite, zeolite-Ag 2.1 - zeolite with Ag^+ at a content of 2.1 mg g^{-1}; zeolite-Bi 2.1 - zeolite with Bi^{3+} at a content of 2.1 mg g^{-1}; zeolite-Ag 2.1+ Bi 2.1 - zeolite with Ag^+ at a content of 2.1 mg g^{-1}; and Bi at a content of 2.1 mg g^{-1}, zeolite-Ag 2.1+ Bi 2.1 - zeolite with Ag^+ at a content of 2.1 mg g^{-1} and Bi at a content of 12.0 mg/g. All studied compositions were used at a content of 5 mg mL^{-1} (Fig. 9).

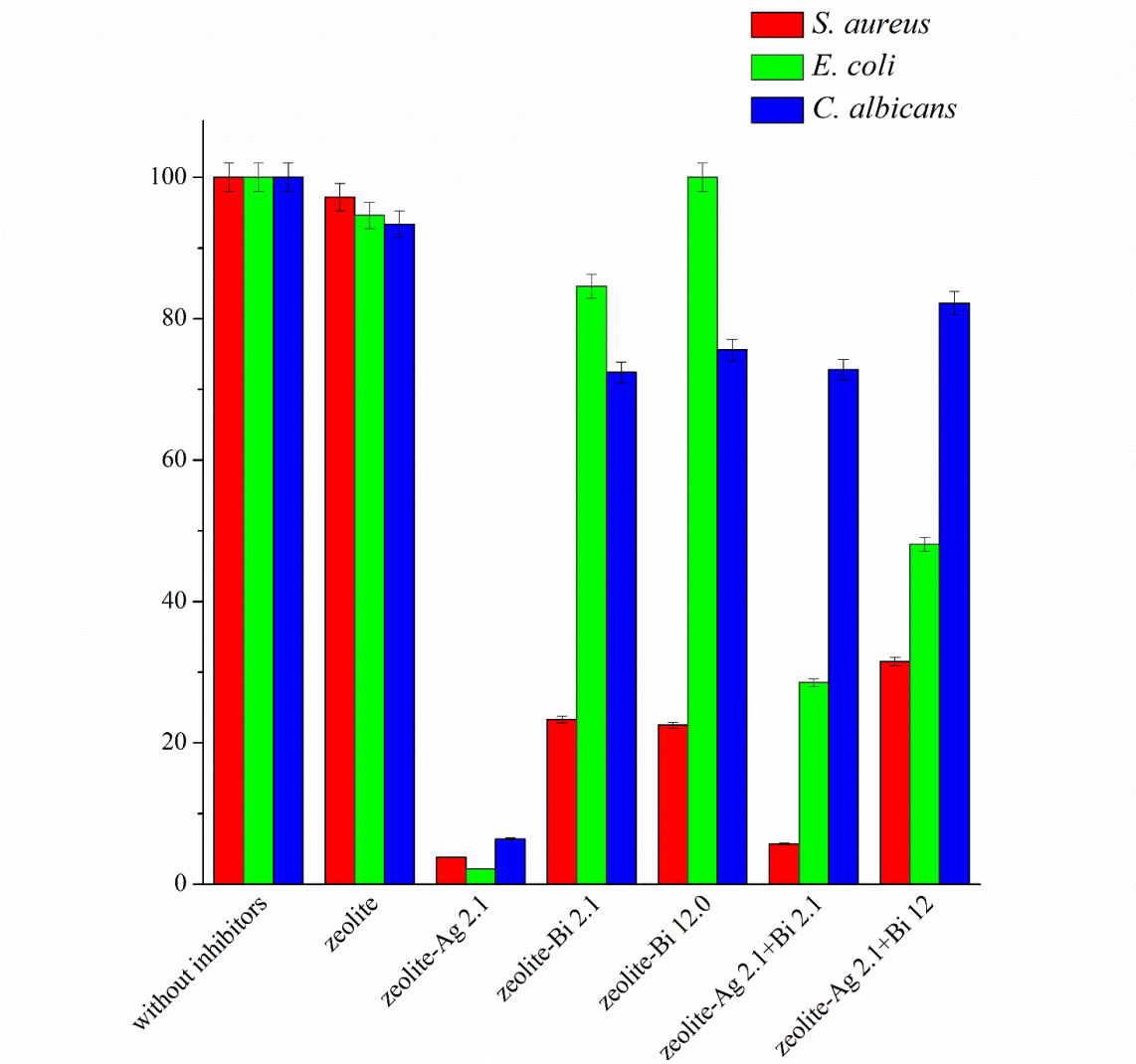


Fig. 9. Survival (%) of *Staphylococcus aureus* ATCC 25923 cells, gram-negative bacteria *Escherichia coli* ATCC 25922, and yeast fungi *Candida albicans* ATCC 885-653 using clinoptilolite compositions with silver and bismuth ions

In the presence of clinoptilolite microparticles, the survival of the studied test cultures of bacteria and fungi almost did not decrease and ranged within 93-97 %, compared to samples cultured without the addition of zeolites. Cultivation of test cultures in the presence of a composition with Ag^{+}, as in previous studies, reduced survival to 6.4 % of *C.albicans*. 3.8 % of *S.aureus* and 2.2 % of *E.coli*. Compositions with different concentrations of bismuth also showed antimicrobial activity against the test cultures used. For example, in the presence of clinoptilolite with Bi^{3+} at a concentration of 2.1 mg g^{-1}, slightly more than 23% of *S.aureus*, almost 85% of *E.coli* and 72.4% of *C. albicans* survived. Increasing the bismuth concentration in the composition to 12 mg g^{-1} did not cause a decrease in the survival of the tested cultures. The combination of bismuth ions at a concentration of 2.1 mg g^{-1} with silver in a composition with clinoptilolite reduced the survival of *S.aureus* to 5.7 %, *E.coli* to 28.5 %, and *C.albicans* to 72.4 %. Increasing the concentration of Bi^{3+} in

the composition with silver and clinoptilolite to 12 mg g^{-1} did not contribute to an increase in the antimicrobial effect, but rather inhibited it. Therefore, Bi-clinoptilolite samples demonstrate sufficient antimicrobial activity against *S. aureus*, although lower compared to silver-containing compositions, being significantly cheaper, including due to use of spent adsorbents.

Discussions

The obtained results of sorption of Bi(III) from an acidic environment are based on the study of the state of both clinoptilolite surface and Bi-cations ions in solution. The first of them depends on the conditions of clinoptilolite pre-treatment, and the second is determined by the solution pH and concentration of Bi(III) ions. Thus, it is possible to regulate the nature and number of active centers of clinoptilolite and, as a result, the capacity towards Bi(III) cations by changing the temperature of the pre-calcination of clinoptilolite (Fig. 3). In addition, the low pH value – about 2.5 – ensures selective sorption of Bi(III) cations, which is necessary for their preliminary concentration and separation. The most significant analytical results are the following: systematic study of dynamic solid-phase extraction of Bi(III) using clinoptilolite and optimization of sorption parameters; enrichment factor value is 200, detection limit - 0.2 ng mL^{-1} and linear range 0.5–200 ng mL^{-1}.

Although complete desorption of Bi(III) cations is achieved using 1-1.5 M HNO_3 (Table 4), ultimately the regenerated clinoptilolite accumulates bismuth after recycling. Therefore, the challenge of disposal, as with any spent adsorbent, arises (Fouda-Mbanga et al. 2024). A selective analytical procedure for Bi(III) monitoring, concentrating and separating which is based on clinoptilolite SPE, followed by valorization of the Bi-loaded sorbent into a multifunctional environmental material without additional treating is a logical step from the perspective of a green chemistry approach. By modifying the electronic structure of clinoptilolite, the introduction of Bi^{3+} provides strong absorption in the visible light spectrum and creates a material with potential functional properties beyond adsorption, namely photocatalytic and antimicrobial activity.

The high efficiency of both activities is dictated by how bismuth and the clinoptilolite matrix interact: /i/ porous structure of clinoptilolite facilitates maximal contact between the photocatalyst, light, and adsorbed ST as well as capturing and concentrating bacterial cells close to the active ROS generation zones; /ii/ exchanged Bi^{3+} cations prevent particle aggregation and formation of new sub-levels corresponding to visible region and, as a result, promote triggering of photocatalytic process under visible irradiation. For these Bi(III) ions exchanged-clinoptilolite compositions as for described earlier other cations (Matsuoka and Anpo, 2003a; 2003b), the optimum of metal is achieved at surprisingly low loadings compared to the range of 5–10 wt% and higher, which has often been reported previously for Bi_2O_3- or BiOCl-zeolite composites (Di et al. 2021; Pavlovi´c and Raji´c, 2024). This interpretation is strongly supported by the general clinoptilolite-photocatalyst literature, even though

direct precedents for Bi^{3+}-exchanged clinoptilolite are scarce. Obviously, isolated Bi^{3+} ions exchanged into clinoptilolite (nano-dots) generate localized Bi–O charge-transfer states absorbing in the visible region. These atomically dispersed Bi species function as photocatalytically active sites. The zeolite framework spatially isolates the Bi centers, suppressing recombination. Above ~1.1 wt% Bi, increasing surface coverage (shielding) by Safranin T (Table 6) decreases the efficiency of the photoinduced processes due to the greater number of sites for its coordination binding and/or local association of Bi species. As mentioned above, the similar trend is observed for antimicrobial activity (Fig. 9). This is essentially the same conceptual approach that was used to explain Ag^{+} and Cu^{+} zeolite photocatalysts, except that the relevant excitation would be Bi–O charge transfer in the visible region rather than *via* UV excitation (Matsuoka and Anpo 2003a; 2003b). Enhanced visible-light photocatalytic/antimicrobial activity of Bi-clinoptilolite compositions correlates with UV-Vis and Tauc analysis which indicate a reduction of apparent optical transition energies after Bi sorption. Therefore, incorporation of Bi(III) modifies the physicochemical and optical characteristics of clinoptilolite while largely preserving its native crystalline and porous framework. These changes are associated with enhanced visible-light activity toward safranin T removal, while the Bi-containing materials additionally exhibit antimicrobial activity.

A possible mechanistic model of the photocatalytic process for Bi^{3+}-exchanged clinoptilolite could be as follows:

1. Safranin T adsorbs inside pores and on external surfaces.
2. Bi^{3+} centers absorb visible photons through Bi–O charge-transfer transitions.
3. Excited electrons are transferred to adsorbed oxygen:
4. Superoxide and subsequent reactive oxygen species attack the dye molecules.
5. Bi^{3+}-related centers also act as electron traps, suppressing recombination.

Therefore, it is proposed the loop on a zero-waste analytical and environmental application by merging SPE method with the adsorbent-to-photocatalyst conversion: Bi(III) monitoring → Bi(III) capture on clinoptilolite → Bi-doped clinoptilolite formation → visible-light photocatalysis → antimicrobial remediation.

5. Conclusions

The sorption performance of Transcarpathian clinoptilolite with respect to bismuth ions from aqueous media under dynamic mode were studied depending on the conditions of pretreatment of clinoptilolite and the pH of the solution. It has been established that clinoptilolite most effectively sorbs partially hydrolyzed cationic forms of Bi(III) from acidic solutions. The optimal conditions for Bi(III) sorption

were established as follows: a 0.5 μg mL^{-1} Bi(III) solution passed through the sorbent at a flow rate of 5 mL min^{-1}, a zeolite grain size of 0.2–0.31 mm, a clinoptilolite pre-heating temperature of 150 °C, and a solution pH of 2.5. The clinoptilolite exhibited a maximum Bi(III) sorption capacity of 14.1 mg g^{-1}. While other heavy metals are effectively sorbed on this zeolite only from weakly alkaline or neutral solutions. Such a difference in the optimal pH values for Bi(III) and the other heavy metals allows for selective concentration of Bi(III) and its separation from these metals.

A solid-phase extraction (SPE) preconcentration method has been developed for the spectrophotometric determination of trace Bi(III) in water samples. Under optimal conditions, an enrichment factor of 200 was obtained. The method exhibits a wide linear range of 0.5–200 ng mL^{-1} with a detection limit of 0.2 ng mL^{-1}.

The sorbed Bi^{3+} cations, which essentially play the role of dopants, modify the electronic structure of the prepared compositions, likely create additional active sites that enhance the adsorption of the nitrogen-containing Safranin T molecules and promote its degradation in visible light due to decrease in apparent optical transition energies. Taking into account the high dark adsorption capacity for safranin T, the use of the Bi-clinoptilolite compositions provides a synergistic adsorption-photocatalytic effect for its removal from water: the overall degree of dye removal from solution achieves 90-97% and the degree of mineralization – 40%. Also, the samples of clinoptilolite-based compositions with different Bi(III) contents also exhibit antimicrobial activity. In particular, the composition, even with such a low content of 2.1 mg/g, reduces survival of *S. aureus* to 23.3 %, *E. Coli* - to 84,6 %, and *C. albicans* - to 72.4 %.

Therefore, the dynamic adsorption of Bi(III) ions onto Transcarpathian clinoptilolite simultaneously enables trace analytical determination of bismuth as well as produces Bi-containing clinoptilolite materials. This opens the way from analytical monitoring of trace Bi(III) to the formation of Bi-containing clinoptilolite materials exhibiting photocatalytic and antimicrobial activity.This study bridges environmental monitoring and waste valorization through an integrated 'adsorbent-to-photocatalyst' approach. This dual-functionality combines analytical studies with using a post-analytical waste product into a highly effective agent for solar-driven photocatalytic dye degradation and antimicrobial disinfection.

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Author contributions

Volodymyr Vasylechko: Conceptualization, Methodology, Investigation, Writing – original draft

Oksana Kostiv: Performed the experiments.

Volodymyr Sydorchuk: Data curation, Formal analysis, Visualization.

Olexandr Gromyko: Performed the experiments; Analyzed the obtained data.

Viktor Fedorenko: Performed the experiments.

Svitlana Khalameida: Performed the experiments; Data analysis and interpretation, Manuscript preparation, Approval.

Svitlana Bagday: Data analysis and interpretation, Manuscript preparation

All authors discussed the results and approved the final version of the manuscript.

Data availability All data generated or analyzed during this study are included in this article.

Declarations

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