11th Serbian-Croatian-Slovenian Symposium on Zeolites

May 20-22, 2026
Faculty of Technology and Metallurgy,
Belgrade, Serbia

BOOK OF PAPERS

ZDS

CROZA

SiZA

BOOK OF PAPERS
11th Serbian-Croatian-Slovenian Symposium on Zeolites

Faculty of Technology and Metallurgy, Belgrade, Serbia

May 20-22, 2026

Editors
Danina Krajišnik
Ana Palčić
Alenka Ristić

Publisher
Serbian Zeolite Association (SZA), Belgrade, Serbia, May 2026.

ISBN-978-86-916637-3-5

Organizers

Serbian Zeolite Association (SZA)
Croatian Zeolite Association (CROZA)
Slovenian Zeolite Association (SiZA)

Hosting institutions

Faculty of Technology and Metallurgy, University of Belgrade (Belgrade, Serbia)
Institute for Technology of Nuclear and Other Mineral Raw Materials – ITNMS (Belgrade, Serbia)
Faculty of Physical Chemistry, University of Belgrade (Belgrade, Serbia)

Under the auspices of

Ministry of Science, Technological Development and Innovation, Republic of Serbia
Federation of European Zeolite Associations (FEZA)

All articles in the Book of papers were reviewed.

Organizers

Organizing Committee

Dr **Aleksandra Daković**, Institute for Technology of Nuclear and Other Mineral Raw Materials, Serbia
Dr **Jelena Dikić**, Innovation Centre of the Faculty of Technology and Metallurgy, Serbia
Dr **Milena Obradović**, Institute for Technology of Nuclear and Other Mineral Raw Materials, Serbia
Dr **Srna Stojanović**, University of Belgrade, Faculty of Physical Chemistry, Serbia
Dr **Ana Palčić**, Ruđer Bošković Institute, Croatia
Prof. Dr **Nediljka Vukojević Medvidović**, University of Split, Faculty of Chemistry and Technology, Croatia
Dr **Sanja Bosnar**, Ruđer Bošković Institute, Croatia
Doc. Dr **Darko Vušak**, University of Zagreb, Faculty of Science, Croatia
Dr **Alenka Ristić**, National Institute of Chemistry, Slovenia
Marjana Gantar Albreht, National Institute of Chemistry, Slovenia
Prof. Dr **Nataša Novak Tušar**, National Institute of Chemistry, Slovenia, and University of Nova Gorica, Slovenia

Scientific Committee

Prof. Emerita Dr **Vesna Rakić**, University of Belgrade, Faculty of Agriculture, Serbia
Prof. Dr **Ljiljana Damjanović-Vasilić**, University of Belgrade, Faculty of Physical Chemistry, Serbia
Prof. Dr **Sanja Jevtić**, University of Belgrade, Faculty of Technology and Metallurgy, Serbia
Prof. Dr **Danina Krajišnik**, University of Belgrade, Faculty of Pharmacy, Serbia
Prof. Dr **Jasna Hrenović**, University of Zagreb, Faculty of Science, Croatia
Assoc. Prof**. Ivona Nuić**, University of Split, Faculty of Chemistry and Technology, Croatia
Assoc. Prof. **Marin Ugrina**, University of Split, Faculty of Chemistry and Technology, Croatia
Dr **Andraž Krajnc**, National Institute of Chemistry, Slovenia
Prof. Dr **Petar Djinović**, National Institute of Chemistry, Slovenia, and University of Nova Gorica, Slovenia
Dr **Matjaž Mazaj**, National Institute of Chemistry, Slovenia

Time	Wednesday, 20.05.2026.	Thursday, 21.05.2026.	Friday, 22.05.2026.
9:30		Plenary lecture 2 Vladimir Paunović	Keynote speaker 2 Jasna Hrenović
9:45			
10:00			Oral lecture 10: Milena Pantić
10:15		Oral lecture 5: Ana Palčić	Oral lecture 11: Katarina Rondović
10:30		Oral lecture 6: Majda Potkonjak	Coffee break
10:45		Coffee break	
11:00	Registration		Oral lecture 12: Dragana Radovanović
11:15		Invited lecture 2 Marija Marković	Short oral presentations (6): Stevan Stupar, Srna Stojanović, Katarina Sokić, Marija Simić, Bojana Rajičić, Ana Radosavljević-Mihajlović
11:30			
11:45		Sponsor talk (2) Altium	
12:00		Sponsor talk (3) AstrineXLab	Closing remarks
12:15		Lunch	Lunch
12:30			
12:45			
13:00	Opening		
13:15	Plenary lecture 1 George E. Christidis	Keynote speaker 1 Aljaž Škrjanc	
13:30			
13:45		Oral lecture 7: Ljiljana Matović	
14:00	Lunch	Oral lecture 8: Darko Vušak	
14:15		Coffee break	
14:30			
14:45		Oral lecture 9: Miloš Čenić	
15:00	Invited lecture 1 Mario Nikola Mužek	Short oral presentations (6): Jasna Hrenović, Miljan Radošević, Alenka Ristić, Ana Palčić, Nediljka Vukojević Medvidović, Marin Ugrina	
15:15			
15:30	Oral lecture 1: Sunčica Mileta		
15:45	Oral lecture 2: Tiana Milović	Free time	
16:00	Oral lecture 3: Aleksandra Popović		
16:15	Coffee break		
16:30			
16:45	Sponsor talk (1) MC Labor		
17:00	Oral lecture 4: Blanka Dadić		
17:15	Short oral presentations (6): Ivona Nuić, Milena Obradović, Danina Krajišnik, Marina Trgo, Nevena Rističević, Natalija Petronijević		
17:30		Guided tour	
17:45			
18:00			
18:15			
18:30			
18:45			
19:00		Conference dinner	

CONTENTS

PLENARY LECTURES

INVATED LECTURES

KEYNOTE LECTURES

ORAL PRESENTATIONS

SHORT ORAL PRESENTATIONS

PLENARY LECTURES

SYNTHESIS OF HIGH ADDED VALUE ZEOLITES FROM WASTE MATERIALS: ONE LINK IN THE VIRTHOUS CIRCLE OF CIRCULAR ECONOMY

Georgios E. Christidis
Technical University of Crete, School of Mineral Resources Engineering. 73100 Chania, Greece.
E-mail: gchristidis@tuc.gr

ABSTRACT

Zeolites have been synthesized from a variety of volcanic glasses consisting of waste materials from extraction of natural and expanded perlite and pumice among others. The synthesis experiments simulate alteration of volcanic glasses to zeolite in nature. The main disadvantage of the end products is the formation of zeolitic materials with variable purity, similar to the natural environments. Yet, the formation of zeolites from volcanic glasses provides the opportunity for an investigation of the upgrading of mineral resources which are either not exploited or are waste materials of mining activity, thus supplying the chain of circular economy. There are two pathways of synthesis of high added value zeolites from Si-rich glass waste materials. The first pathway is a two-step process, producing zeolite Na-Pc, zeolite V, and hydroxysodalite in the first step pure zeolite A and/or zeolite X in the second step. The latter 2 zeolites are used in detergents and as molecular sieves. The second pathway resembles the hydrogel process and yields zeolite Y, used as catalyst in petroleum cracking.

The first pathway includes direct hydrothermal treatment of the Si-rich glass with a caustic solution (usually NaOH). The end products are low grade materials and their composition depends on the composition of the caustic solution, temperature and the parent glass. Typical end products are zeolite Na-Pc, zeolite V, hydroxysodalite and at temperature higher than 140°C analcime and albite. Zeolitization removes Si and K to the solution acquiring a steady state, thus producing a Si-rich liquid. Under the specific experimental conditions, it is not possible to obtain zeolite A, because solid products with SiO_2:Al_2O_3 ratios ~2:1 have high Na_2O:Al_2O_3 ratios. Hence, hydroxysodalite is the stable product. In contrast zeolite X (SiO_2:Al_2O_3 ratios ~3:1) may be a by-product of zeolitization at $T<100°C$. Pure zeolite A can be synthesized from polymerization of the Si-rich solution after addition of Na-aluminate. Zeolite A is favoured by lower SiO_2:Al_2O_3 ratios of the starting gel and its crystal order increases with increasing reaction time. Zeolite X formed from mixtures with SiO_2:Al_2O_3 ratios ≥ 3. Mass balance calculations showed that the integrated two-step process yields 112 kg zeolite A and 61 kg zeolite NaPc, from 100 kg perlite waste after addition of 80 kg 2N NaOH solution.

Yet, zeolite Y was not synthesized in these experiments, due to constraints of the preparation method. During mixing of liquids only one major chemical parameter was controlled, usually the SiO_2:Al_2O_3 ratio. The SiO_2:Na_2O and the Na_2O:Al_2O_3 ratios and the amount of water cannot be controlled simultaneously. A new method was employed, which involves dissolution of the glass and precipitation of a SiO_2 gel. Then Na-aluminate solution was added to the SiO_2 gel, the mixture was homogenized and heated at 90°C for 1h to >120h. The critical parameters for synthesis are the SiO_2:Al_2O_3:Na_2O:H_2O ratios. However, opposite to the previous synthesis, these ratios can be controlled. A Si-sinter, perlite, and pumice glasses were used. Hence the method can be extended to other Si-rich glasses, provided that they are not devitrified. Zeolite Y was synthesized after 3 h and its yield and crystal order increased with reaction time. Minor zeolite Na-Pc by-product was crystallized after 9 h. Hence synthesis of a pure zeolite Y product was quantitative with the final product containing >90% of the zeolite.

Therefore, synthesis of pure high added value zeolites A, X and Y can be synthesized from waste materials of the mining industry, thus contributing to rational utilization of raw materials and thus to the virtuous circle of circular economy.

ADVANCING ZEOLITE-CATALYZED PROCESSES FOR SUSTAINABLE CHEMICALS AND FUELS PRODUCTION

Vladimir Paunović
Paul Scherrer Institute, Villigen 5232, Switzerland
E-mail: vladimir.paunovic@psi.ch

ABSTRACT

Heterogeneous catalysis plays a central role in producing fuels and chemicals, yet most current processes still rely on fossil feedstock. Methanol-to-hydrocarbons (MTH) conversion over zeolite-based catalysts offers a promising pathway to generate essential hydrocarbons, such as light olefins and aromatics from renewable methanol. However, broader implementation is limited by insufficient selectivity and rapid deactivation of zeolite-based catalysts.

This research addresses these challenges by combining advanced kinetic, spectroscopic, and diffraction methods available at PSI to clarify key reaction pathways and deactivation mechanisms. The recent findings that reveal the role of critical intermediates and the spatial distribution of coke species, supported by synchrotron and neutron-based techniques are highlighted. These insights have guided the development of more selective and stable MTH catalysts, enabling significant improvements in olefin productivity and resulting in a recent PSI patent application.

How data-driven approaches and machine-learning tools help uncover structure–performance relationships and predict catalytic behavior are also shown. Finally, future directions that integrate catalyst synthesis, kinetic studies, and operando spectroscopy to advance catalyst design for MTH and related processes such as ammonia synthesis and plastics upcycling are outlined.

INVITED LECTURES

HEAVY METAL REMOVAL ON SELECTED SORBENTS IN BATCH REACTORS

Mario Nikola Mužek, Anita Bašić, Sandra Svilović
Faculty of Chemistry and Technology, University of Split, Ruđera Boškovića 35, 21000 Split
E-mail: muky@ktf-split.hr

ABSTRACT

The removal of heavy metals from wastewater is essential due to their toxicity, persistence, and bioaccumulation. Sorption using aluminosilicate materials such as zeolite NaX and geopolymers has proven to be an efficient and economically viable approach. This study represents a mini-review of the various effects of copper and cobalt sorption kinetics in both, single and binary systems. Sorption kinetics are predominantly described by pseudo-second-order models with high correlation coefficients ($R^2 > 0.99$), indicating reaction-controlled mechanisms. Batch reactor design, mixing speed, initial concentrations of heavy metals and temperature significantly influence on sorbent performance, with optimal operation near just-suspended impeller speed, reducing energy consumption while maintaining high efficiency. In binary Cu^{2+}-Co^{2+} systems, competitive ion exchange reduces removal efficiency, with performance strongly dependent on initial concentration ratios. The study highlights the importance of integrating kinetics, reactor design, operating conditions, and multi-component interactions for efficient wastewater treatment.

Keywords: zeolite NaX, geopolymer, copper, cobalt, binary system, sorption kinetics, reactor design.

INTRODUCTION

Industrial development has resulted in significant water pollution, with heavy metals like copper (Cu^{2+}), cobalt (Co^{2+}), and lead (Pb^{2+}) posing severe risks to aquatic ecosystems and human health. Unlike organic pollutants, heavy metals do not degrade and tend to accumulate through the food chain. Conventional methods of heavy metal removal including chemical precipitation, coagulation, membrane filtration, solvent extraction, oxidation, and reduction often require substantial energy and chemical inputs. Among various methods that have been proposed for wastewater treatment, sorption has emerged as a preferred and effective method due to its simplicity, effectiveness, high efficiency, and ability to remove a wide range of pollutants [1-5].

Zeolites have proven to be promising sorbents due to their high sorption capacity, selectivity, and structural resilience. They possess a well-defined pore structure, large surface area, and favourable sorption properties, making them particularly effective in removing a variety of pollutants from aqueous solutions, including heavy metals and organic compounds. Additionally, geopolymers, amorphous analogues to synthetic zeolites synthesized from industrial by-products like fly ash, offer a sustainable, low-cost alternative for heavy metal removal with performance comparable to synthetic zeolites.

Despite extensive research on sorption capacity and kinetics, limited attention has been given to the optimization of reactor design and their impact on process efficiency and energy consumption. Most studies focus on material properties and operating conditions, such as pH, temperature, initial concentration dependence while neglecting the crucial role of reactor geometry and hydrodynamics [6].

Additionally, real wastewater systems often contain multiple metal ions, making competitive sorption effects highly relevant.

This paper presents an overview of the selected authors works on kinetic modelling, reactor design, and binary system behaviour to provide a comprehensive understanding of sorption processes.

EXPERIMENTAL

The following section outlines the experimental methodology common to all studies discussed in this mini-review. Although individual works may differ in specific parameters or conditions, the general approach remained consistent throughout all selected studies [1–9]. The experimental scheme is presented in Figure 1. The analysis is based on experimental sorption studies involving zeolite NaX and fly ash-based geopolymers as sorbents for heavy metal removal. Zeolite NaX particles typically fall within a size range less than 0.090 mm, while geopolymer particles fall within a size range of 0.071–0.090 mm, ensuring sufficient surface area and minimizing intraparticle diffusion limitations [10,11].

Batch experiments were conducted in reactors containing a specified amount of heavy metal solution and sorbent material (the amount ratio depends on whether an equilibrium or kinetic experiment was conducted).

Kinetic analysis was performed using the Lagergren pseudo-first-order, pseudo-second-order models (Ho, Ritchie and Blanchard; mathematically equivalent forms), Elovich model, Mixed surface reaction and diffusion-controlled sorption kinetic model, and Weber-Morris model to identify the rate-controlling step.

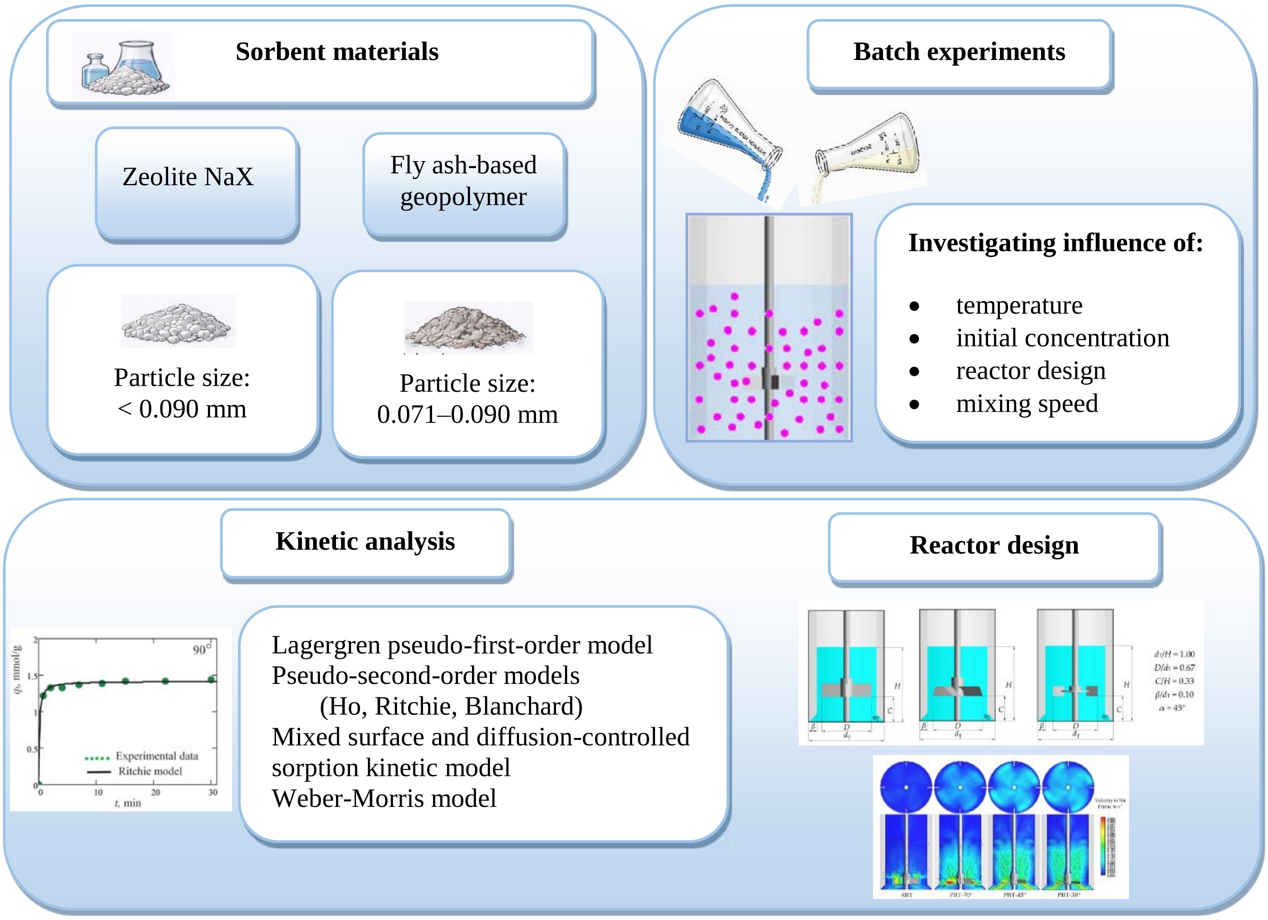


Figure 1. Experimental set-up.

RESULTS AND DISCUSSION

Sorption of copper ions on both zeolite NaX and geopolymer sorbents shows rapid initial uptake, with equilibrium achieved within 30–60 minutes depending on conditions [1-4]. The pseudo-second-order models generally provide an excellent fit indicating that surface reaction dominates the process for applied reaction conditions [5,6]. Zeolite NaX exhibits higher capacities and faster kinetics, while geopolymers provide cost-effective and sustainable alternatives.

Increasing the initial metal concentration leads to higher sorption capacity due to increased driving force, while removal efficiency decreases at higher concentrations due to saturation of active sites. An increase in temperature results in enhanced sorption rates and a slight increase in equilibrium capacity, indicating an endothermic process, for both heavy metals.

Table 1. Sorption and thermodynamic characteristics of zeolite NaX and geopolymer

Parameter	Zeolite NaX	Geopolymer
Particle size (mm)	< 0.090 mm	0.071–0.090
Maximum experimental capacity for Cu 298K, q_e (mmol g^{-1})	1.652	1.136
Maximum experimental capacity for Co at 298K, q_e (mmol g^{-1})	1.102	0.857
Equilibrium time	≈ 30 min	≈ 50 min
Effect of initial concentration, c_0 (mmol dm^{-3})	Increase in q_e values with increasing c_0, slight decrease in removal efficiency at high c_0	Increase in q_e values with increasing c_0, more pronounced decrease in efficiency due to earlier saturation
Effect of temperature for Cu, T (K)	Increase in q_e values: 1.714(308), 1.750(318)	Increase in q_e values: 1.183(308), 1.217(318)
Effect of temperature for Co, T (K)	Increase in q_e values: 1.184(308), 1.225(318)	Increase in q_e values: 0.980(308), 1.102(318)
Gibbs free energy, ΔG^0 (kJmol^{-1})	Negative, becomes more negative with the increase of T indicating spontaneous process, becomes more positive with the increase of c_0	Slightly less negative than zeolite NaX, becomes more negative with the increase of T indicating spontaneous process, becomes more positive with the increase of c_0
Enthalpy change, ΔH^0 (kJmol^{-1})	Positive indicating endothermic process	Positive indicating endothermic process
Entropy change, ΔS^0 (kJmol^{-1}K^{-1})	Positive, increased randomness at interface	Positive but mostly lower than zeolite NaX, less structural reorganization
Thermodynamic nature	Spontaneous and endothermic	Spontaneous and endothermic
Overall performance	High efficiency, strong selectivity, stable behaviour at higher c_0 and T	Lower cost, sustainable, but slightly lower capacity

Hydrodynamic conditions significantly influence sorption efficiency. At mixing speeds below the just-suspended impeller speed (N_{JS}), incomplete particle suspension limits the available surface area. At speeds equal to or slightly below N_{JS}, nearly complete removal efficiency is achieved while minimizing energy consumption. Increasing mixing speed beyond N_{JS} does not significantly improve sorption efficiency but increases power consumption [1,6]. Reactor design affects flow patterns and suspension behaviour. Baffles eliminate vortex formation but increase energy consumption. Experimental results indicate that unbaffled reactors can achieve similar sorption efficiency as baffled ones but with significantly lower power consumption due to reduced resistance to fluid flow [1,6].

In binary systems, competition between copper and cobalt ions significantly affects sorption performance. Experimental studies show that removal efficiency decreases compared to single systems and depends strongly on initial concentration ratios. The removal rate of copper ions from solution was faster than the removal of cobalt ions, both in monometallic solutions and the mixture. Increasing cobalt concentration reduces copper uptake due to competition for active sites, confirming that sorption is governed by ion-exchange selectivity. Nevertheless, the process remains reaction-controlled, and Ritchie kinetic model provides a good agreement with the results obtained [8].

CONCLUSION

The results show that sorption efficiency depends on initial concentration, temperature, reactor design, and mixing speed. Zeolite NaX exhibits superior sorption capacity and faster kinetics, while geopolymer offers a sustainable alternative with slightly lower capacity. Sorption processes are reaction-controlled and are generally well described by pseudo-second order models at selected reaction conditions.

The integration of kinetic modelling, reactor design, and multi-component system behaviour is essential for designing efficient wastewater treatment processes.

ACKNOWLEDGMENT

This work was fully supported by the European Union through the NextGenerationEU program (Project: Advanced Technologies for Wastewater Treatment and Material Corrosion Resistance in Aggressive Media—ANTARES; No. IP-UNIST-28; Project leader: L. Vrsalović).

REFERENCES

[1] A. Bašić, M. N. Mužek, Ž. Penga, S. Svilović, *Processes*, 2025, **13**, 712.

[2] M. N. Mužek, S. Svilović, J. Zelić, *Desalin. Water Treat.*, 2014, **52**, 2519-2526.

[3] M. N. Mužek, S. Svilović, M. Ugrina, J. Zelić, *Desalin. Water Treat.*, 2016, **57**, 10689-10699.

[4] S. Svilović, M. N. Mužek, I. Nuić, P. Vučenović, *Water Sci. Technol.*, 2019, **80(1)**, (2019) 98-108.

[5] M. N. Mužek, S. Svilović, J. Zelić, *Sep. Sci. Technol.*, 2016, **51**, 2868-2875.

[6] A. Bašić, Ž. Penga, M. N. Mužek, S. Svilović, *Results Eng.*, 2022, **16**, 100554.

[7] A. Bašić, M. N. Mužek, S. Svilović, *Appl. Surf. Sci. Adv.*, 2023, **18**, 100507.

[8] A. Bašić, M. N. Mužek, L. Kukoč-Modun, S. Svilović, *Kem. Ind.*, 2020, **69(9-10)**, 465-471.

[9] S. Svilović, D. Rušić, R. Žanetić, *Chem. Biochem. Eng. Q.*, 2008, **22(3)**, 299-305.

[10] P. Rajandran, N. Masngut, N. H. A. Manas, N. I. Wan Azelee, S. F. Z. M. Fuzi, M. A. H. Bunyamin, *Int. J. Environ. Sci. Technol.*, 2025, **22**, 3943-3964.

[11] J. Aguila-Rosas, F. J. Cano, A. Nagaya, C. T. Quirino-Barreda, M. de Jesús Martínez Ortiz, A. Guzmán Vargas, I. A. Ibarra, E. Lima, *Chem. Commun.*, 2025, **61**, 11706.

NATURAL AND MODIFIED ZEOLITES AS ADSORBENTS OF MYCOTOXINS

Marija Marković, Milica Ožegović, Milena Obradović, Aleksandra Daković
Institute for Technology of Nuclear and Other Mineral Raw Materials, Franše d' Epere 86, 11000 Belgrade, Serbia
E-mail: m.markovic@itnms.ac.rs

ABSTRACT

Mycotoxins are secondary metabolites of fungi that commonly contaminate cereals and other food and feed crops worldwide. They pose significant health risks to animals and humans due to their acute and chronic toxicity, teratogenic, mutagenic, and carcinogenic effects [1]. The most practical and cost-effective method for reducing mycotoxin exposure in livestock is the use of adsorbents in animal feed. The role of these materials is to bind mycotoxins in the gastrointestinal tract, preventing their absorption and toxicity. Natural minerals, like zeolites, effectively adsorb aflatoxin B_1 (AFB1), but adsorbing less polar, hydrophobic mycotoxins such as zearalenone (ZEN) and ochratoxin A (OCHRA) typically requires surface modification with long-chain organic cations (surfactants) [2]. Adsorption of mycotoxins by the natural zeolites and organo-zeolites differs between zeolite types (clinoptilolite vs phillipsite) but is also dependent on the pH of the solution (pH 3 - stomach conditions and pH 7 - intestinal conditions). For organo-zeolites, adsorption of mycotoxins is additionally dependent on the type of surfactant used for the modification of specific zeolites and on the amount of the organic phase present at the zeolitic surface.

This study presents how the type of natural zeolite and the type of surfactant affect the adsorption of the mycotoxins: ZEN, OCHRA and AFB1. Adsorption behavior of the two natural zeolites - phillipsite (Neapolitan Yellow Tuff, Campania, Italy) and clinoptilolite (Zlatokop deposit, Vranje, Serbia) toward mycotoxins was compared. Both natural zeolites were modified with cetylpyridinium chloride (CP) at 50% and 100% of their external cation exchange capacity. Additionally, phillipsite was modified with hexadecyltrimethylammonium bromide (HB) at the same levels for comparison [3]. Organo-zeolites showed significantly higher adsorption of OCHRA and ZEN compared to unmodified zeolites, confirming that the organic cations on the surface are primarily responsible for binding these mycotoxins, but mechanism of their adsorption differs between zeolites. AFB1 adsorption was high on unmodified zeolites, and modification with CP and HB ions did not change its adsorption capacity. Since inorganic cations (calcium) at the surface of natural zeolites are active sites relevant for AFB1 adsorption, for efficient AFB1 adsorption, modification of zeolite surfaces with surfactant is not necessary. However, adsorption of AFB1 was dependent on the type of natural zeolite as well as on the pH of the solution.

Keywords: mycotoxins, adsorption, phillipsite, clinoptilolite, surfactant.

REFERENCES

[1] M. Buszewska-Forajta, *Toxicon.*, 2020, **182**, 34–53.

[2] M. Marković, A. Daković, G.E. Rottinghaus, A. Petković, M. Kragović, D. Krajišnik, J. Milić, *Colloids Surfaces A Physicochem. Eng. Asp.*, 2017, **529**, 7–17.

[3] M. Marković, A. Daković, G.E. Rottinghaus, M. Kragović, A. Petković, D. Krajišnik, J. Milić, M. Mercurio, B. de Gennaro, *Colloids Surfaces B Biointerfaces.*, 2017, **151**, 324–332.

KEYNOTE LECTURES

GREEN SYNTHESIS APPROACHES IN THE SYNTHESIS OF ZEOLITIC IMIDAZOLATE FRAMEWORKS

Aljaž Škrjanc[1,2]
[1]National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenian
[2]University of Nova Gorica, Vipavska 11c, SI-5270 Ajdovščina, Slovenia
E-mail:aljaz.skrjanc@ki.si

ABSTRACT

With rising interest in different sorption applications of zeolitic imidazolate frameworks (ZIFs), a subgroup of metal–organic frameworks (MOFs), the environmental impact of the synthesis of these materials has to be reduced as much as possible. Most synthesis procedures for materials still heavily rely on formamide-based solvents such as DMF and DEF coupled with a large excess of either metal precursors (MPs) or linkers (L).

To that end, different remediation strategies have thus far been implemented. The fastest and easiest is the exchange of solvent for environmentally less problematic bio-based organic solvents, simple alcohols or even water wherever possible. While this has proven to be effective in a lot of MOF syntheses, general approaches towards DMF replacement still need to be further developed. Most common issues with this approach are lowered solubility of linkers as well as shifted acid-base equilibria, which crucially affect the crystallization of MOFs and ZIFs.

Another alternative to green solvent-based solvothermal methods is mechanochemical synthesis. In mechanochemical synthesis, three main approaches are utilised: neat-grinding, liquid-assisted grinding, and liquid-assisted grinding followed by solvent vapour aging. While often being the fastest and greenest syntheses, they are still limited in scaling up and by the lower crystallinity of the obtained products, if compared to solvothermal methods. This can be further improved by aging or by incorporating other energy sources, like heating.

The ideal synthesis would have the least amount of solvent possible, or none at all, would be done with stoichiometric ratios of metal to linker, with short synthesis times leading to phase pure products with high yields. If this is not possible, the solvents should ideally be easy to recycle or reuse. While single reuse of mother liquors is already reported, multiple reuses are still not published to date.

In the presentation, an overview of recent green synthesis methods used in the synthesis of known and new ZIFs will be presented, including solvothermal and mechanochemical syntheses as well as the feasibility of solvent reuse will be commented.

Keywords: green synthesis, zeolitic imidazolate frameworks, mechanochemistry, metal–organic frameworks

ACKNOWLEDGEMENTS

I would like to thank prof. dr. Nataša Zabukovec Logar for the support with the work, dr. Matjaž Mazaj, prof. dr. Anton Meden and izr. prof. dr. Amalija Golobič for their help with crystallography, Mojca Opresnik for her help with SEM, and Edi Kranjc for PXRD measurements. I would like to thank ARIS programme P1-0021 for funding.

TWO FACES OF ZEOLITES: FRIENDS AND FOES OF *ACINETOBACTER SPP.*

Jasna Hrenović
University of Zagreb, Faculty of Science, Zagreb, Croatia
E-mail: jasna.hrenovic@biol.pmf.hr

ABSTRACT

Zeolites are widely investigated as functional materials in environmental biotechnology due to their high surface area, porosity, and ion-exchange capacity. Depending on their origin and modification, zeolites may exert contrasting effects on microorganisms, acting either as efficient carriers for beneficial bacteria or as antimicrobial agents against pathogenic species. This study presents a comprehensive overview of the "two faces" of zeolites through their interactions with bacteria of the genus *Acinetobacter*, focusing on environmentally relevant and clinically significant species.

Natural zeolites from different geographical origins, as well as other natural minerals such as perlite [1] and sepiolite [2,3], proved to be excellent carriers, hosting up to billions of viable bacterial cells per gram of material. The extent of immobilization was strongly influenced by surface area and macroporosity, whereas mineralogical composition, cation exchange capacity, and zeta potential alone were not reliable predictors [4]. Natural clinoptilolite-rich zeolitized tuffs (NZ) were evaluated as carriers for phosphate-accumulating bacteria, primarily *Acinetobacter junii*, which plays an important role in biological phosphorus removal from wastewater. Orthophosphate removal prior to discharge is essential to prevent eutrophication of natural water bodies. Due to their rough surface morphology and large specific surface area, NZ particles enable rapid and intensive bacterial immobilization [4]. Scanning electron microscopy revealed biofilm formation on NZ surfaces within 24 h of contact, both in nutrient-poor and nutrient-rich aquatic environments [5]. The capacity of NZ for bacterial attachment was found to be occupied during the first 24 h, while further increases in immobilized cell numbers resulted from bacterial growth within the formed biofilm. Furthermore, bacterial surface hydrophobicity was shown not to be a crucial factor governing immobilization onto hydrophilic NZ surfaces [6].

In contrast to their supportive role for beneficial bacteria, zeolites can also function as effective antagonists of pathogenic *Acinetobacter* spp., particularly *Acinetobacter baumannii*, an emerging multidrug-resistant pathogen with high environmental persistence. Natural zeolites modified with antimicrobial agents, including copper, silver, and cationic surfactants, exhibited pronounced dose-dependent antibacterial to bactericidal effects against *A. baumannii* [7,8]. The bactericidal activity of Cu- and Ag-modified zeolites was attributed to the presence and release of metal cations, while surfactant-modified zeolites showed strong antimicrobial effects depending on surfactant loading and surface configuration [9]. These materials demonstrated high efficiency in water systems as well as in contaminated soils, where Ag-modified zeolites enabled rapid elimination of viable *A. baumannii* with minimal impact on native microbial communities, highlighting their potential for environmental remediation [10].

Additionally, the effects of commercially produced synthetic zeolite A (LTA) on *A. junii* were investigated [11]. Unlike natural zeolites, synthetic zeolite A exhibited concentration-dependent inhibitory to bactericidal effects. Chemical analysis revealed the leaching of aluminum and silicon in the form of low-molecular-weight aluminosilicate species, resulting from hydrolysis and partial dissolution of the zeolite structure in water. These leached species were identified as the primary cause of toxicity to bacterial cells,

raising concerns about the unintended antibacterial effects of synthetic zeolites in biological wastewater treatment systems.

Overall, this work demonstrates that zeolites possess dual and contrasting biological roles. Natural clinoptilolite-rich tuffs serve as highly efficient carriers for beneficial bacteria, while appropriately modified zeolites can act as powerful tools for controlling pathogenic microorganisms. At the same time, synthetic zeolites may pose ecological risks due to their potential toxicity. Understanding these two faces of zeolites is essential for their safe and effective application in environmental and biotechnological systems.

Keywords: *Acinetobacter junii*, *Acinetobacter baumannii*, clinoptilolite, disinfection, wastewater treatment.

REFERENCES

[1] T. Ivanković, J. Hrenović, L. Sekovanić, Influence of the degree of perlite expansion on immobilization of *Acinetobacter junii*. *Biochemical Engineering Journal*, 2010, 51, 117-123.

[2] J. Hrenović, T. Ivanković, D. Tibljaš, D. Kovačević, L. Sekovanić, Sepiolite as carrier of the phosphate-accumulating bacteria *Acinetobacter junii*. *Applied Clay Science*, 2010, 50, 582-587.

[3] J. Hrenović, Ž. Žigovečki Gobac, V. Bermanec, Occurrence of sepiolite in Croatia and its application in phosphate removal from wastewater. *Applied Clay Science*, 2012, 59-60, 64-68.

[4] J. Hrenović, T. Ivanković, D. Tibljaš, The effect of mineral carrier composition on phosphate-accumulating bacteria immobilization. *Journal of Hazardous Materials*, 2009, 166, 1377-1382.

[5] J. Hrenović, D. Tibljaš, S. Dekić, C. Venter, Mode of *Acinetobacter baumannii* immobilization onto natural zeolite in nutrient-poor and nutrient–rich water. *8th Serbian-Croatian-Slovenian Symposium on Zeolites*, 2019, Belgrade, Serbia, 93-96.

[6] J. Hrenović, D. Tibljaš, S. Dekić Rozman, T. Ivanković, Does bacterial surface hydrophobicity level influence their immobilization onto natural zeolite? *9th Croatian-Slovenian-Serbian Symposium on Zeolites*, 2012, Split, Croatia, 72-74.

[7] S. Jevtić, S. Grujić, J. Hrenović, N. Rajić, Surfactant-modified clinoptilolite as a salicylate carrier, salicylate kinetic release and its antibacterial activity. *Microporous & Mesoporous Materials*, 2012, 159, 30-35.

[8] J. Hrenović, J. Milenković, I. Goić-Barišić, Nevenka Rajić, Antibacterial activity of modified natural clinoptilolite against clinical isolates of *Acinetobacter baumannii. Microporous & Mesoporous Materials*, 2013, 169, 148-152

[9] J. Hrenović, M. Rožić, L. Sekovanić, Aleksandra Anić-Vučinić, Interaction of surfactant-modified zeolites and phosphate accumulating bacteria. *Journal of Hazardous Materials*, 2008, 156, 576-582.

[10] J. Hrenović, S. Dekić, J. Dikić, S. Kazazić, G. Durn, N. Rajić, Metal-loaded zeolite remediation of soils contaminated with pandrug-resistant *Acinetobacter baumannii*. *Archives of Industrial Hygiene and Toxicology*, 2020, 71, 146-151.

[11] J. Hrenović, D. Željezić, N. Kopjar, A. Sarpola, J. Bronić, L. Sekovanić, Antimicrobial activity of commercial zeolite A on *Acinetobacter junii* and *Saccharomyces cerevisiae*. *Journal of Hazardous Materials*, 2010, 183, 655-663.

ORAL PRESENTATIONS

ISOTHERM MODELING OF Zn(II) SORPTION ONTO FRUIT PIT-DERIVED SORBENTS AS SUSTAINABLE ALTERNATIVES TO NATURAL ZEOLITE

Sunčica Mileta[1,2]*, Ivona Nuić*[2]*, Marin Ugrina*[2]
[1]Ivanal d.o.o., Gorička 19, Industrijska zona Podi, 22000 Šibenik, Croatia
[2]Faculty of Chemistry and Technology, University of Split, Ruđera Boškovića 35, 21000 Split, Croatia
E-mail:suncica.mileta@gmail.com

ABSTRACT

In this study, Zn(II) sorption was investigated using three fruit pit-derived sorbents and compared with natural zeolite and Na-modified zeolites prepared by 24 h and 72 h sodium treatments. The fruit pit-derived sorbents exhibited sorption capacities of 0.049 – 0.061 mmol/g, while natural zeolite reached 0.088 mmol/g. Na-modified zeolites showed the highest capacities (0.302 mmol/g and 0.322 mmol/g), but only a modest improvement was observed after prolonged sodium modification, indicating that extended treatment increases processing costs without providing proportionally higher performance. The tested materials also displayed distinct Zn(II) removal efficiencies, with Na-modified zeolites showing the highest performance (up to 98 %), followed by natural zeolite (up to 84%) and fruit pit-derived sorbents (up to 54%). Evaluation using four two-parameter isotherm models, showed that the Langmuir model best described Zn(II) sorption for all materials, suggesting monolayer sorption on relatively homogeneous surfaces and a strong affinity of Na-modified zeolites for Zn(II). Although less efficient, fruit pit-derived sorbents represent renewable and low-cost materials with potential as sustainable alternatives for Zn(II) removal.

Key words: Zn(II) sorption, biosorbents, fruit pits, natural zeolite, Na-modified zeolite, adsorption isotherms

INTRODUCTION

Heavy metal contamination, including Zn(II) has become increasingly prevalent in aquatic environments due to industrial activities, technological development and intensive agriculture. Because of their toxicity and persistence, efficient and sustainable water treatment methods are essential. Adsorption is widely recognized as a simple and economically viable technique for the removal of metal ions from aqueous systems. Natural zeolites are widely used as effective sorbents, while increasing attention has recently been directed toward renewable biomass-derived materials, such as fruit pits, as low-cost and sustainable alternatives [1–4]. However, their adsorption performance is still less frequently evaluated in direct comparison with conventional mineral sorbents such as natural zeolites. Therefore, this study investigates Zn(II) sorption on fruit pit–derived biosorbents and compares their performance with natural and Na-modified zeolites. Equilibrium data were analysed using four two-parameter isotherm models [5] to elucidate sorption behaviour and enable a reliable comparison with a conventional sorbent under identical conditions, thereby assessing the potential of fruit pit materials as sustainable alternatives for Zn(II) removal.

EXPERIMENTAL

Materials

Fruit pit-derived sorbents were prepared from olive (OP), cherry (CP) and sour-cherry pits (SCP) collected from a local fruit-processing plants. The pits were thoroughly washed with distilled water to remove impurities, dried at 40 ºC to constant mass, mechanically ground, milled and sieved to obtain particle-size fractions of 0.56 − 1.00 mm selected for sorption experiments.

Natural zeolite (NZ) with the same particle size used in this study originates from the Zlatokop deposit in Serbia (≤ 80% clinoptilolite, Si/Al = 4.08, CEC = 1.42 meq/g). To improve the sorption efficiency, sodium-rich zeolites (Na-NZ) were prepared by treating NZ with 1 mol/L NaCl solution for 24 hours (Na-NZ-24) or 72 hours (Na-NZ-72), respectively.

Sorption experiments

Four Zn(II) aqueous solutions of different initial concentrations ($c_o \approx 0.5 - 5$ mmol/L) were prepared by dissolving $Zn(NO_3)_2 \cdot 6H_2O$ salt in ultrapure water. Sorption was performed in a batch mode at room temperature (23 ± 2 °C), solid/liquid ratio of 1 g/100 mL, at mixing speed of 230 rpm, for 24 h. Each experiment was conducted in triplicate to ensure reproducibility and reliability of the results. After the contact time elapsed, the suspensions were filtered, and the filtrates were analyzed for residual Zn(II) concentration (c_r). The initial and residual Zn(II) concentrations were determined by flame atomic absorption spectrometry (AAS) using a PinAAcle 900F instrument. Also, the initial (pH_o) and equilibrium pH_e values were measured as supporting parameters. The capacity of each sorbent, i.e. the amount of Zn(II) sorbed at equilibrium (q_e, mmol/g) and removal efficiency (α, %) were calculated using following equations:

$$q_e = (c_o - c_r)\cdot V/m \qquad (1)$$

$$\alpha = (c_o - c_r)/c_o \cdot 100 \qquad (2)$$

where c_o and c_r are the initial and the residual Zn(II) concentrations (mmol/L), V is volume of treated Zn(II)-contaminated water (L) and m is mass of the sorbent (g).

RESULTS AND DISCUSSION

The calculated sorption capacities and removal efficiencies of the tested materials are presented in Figure 1a and 1b.

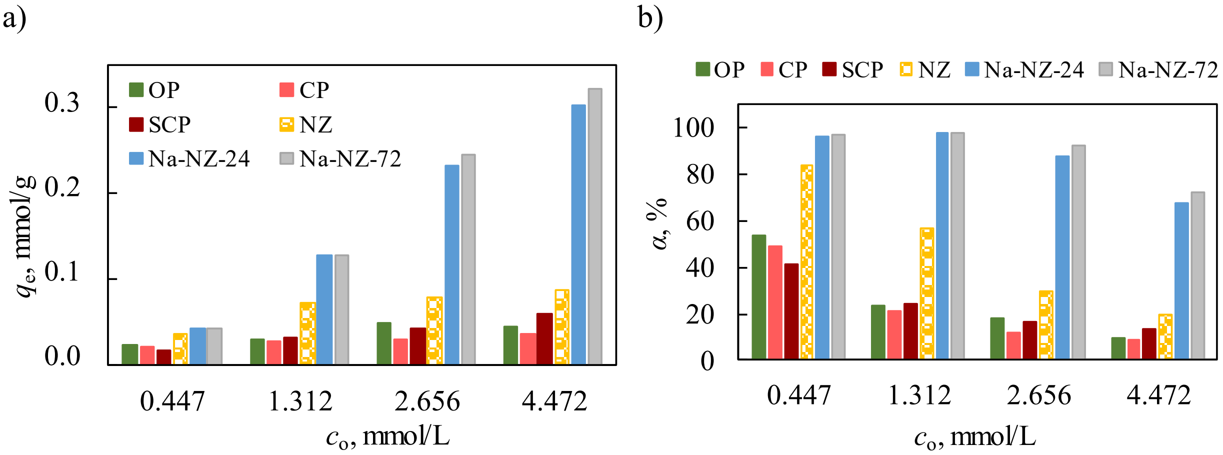


Figure 1. a) capacities and b) removal efficiencies of different sorbents within 24 h

The results show that the sorption capacity of all investigated materials increases with increasing initial Zn(II) concentration (Fig. 1a). Higher capacities at elevated concentrations reflect the greater availability of Zn(II) ions in solution and the stronger concentration gradient that promotes mass transfer toward the sorbent surface. At lower concentrations, only the most accessible and energetically favorable sorption sites are occupied. The maximum sorption capacities reveal clear differences among the investigated materials. Fruit pit–derived sorbents showed maximum capacities in the range 0.038 – 0.061 mmol/g (CP < OP < SCP), while natural zeolite reached maximum value of 0.088 mmol/g. Significantly higher maximum capacities were obtained for Na-modified zeolites (0.302 mmol/g for Na-NZ-24 and 0.322 mmol/g for Na-NZ-72), confirming that sodium modification markedly enhances Zn(II) sorption. The slightly lower sorption capacity of fruit pit-derived sorbents may reflect structural differences affecting the availability of active sites for metal binding, which remains to be clarified in future investigations.

In line with these observations, Zn(II) removal efficiency (α, %) decreased with increasing initial Zn(II) concentration (Fig. 1b). High removal efficiencies at low initial concentrations are associated with the abundance of available sorption sites, whereas their progressive saturation leads to lower relative removal at higher concentrations. At the lowest Zn(II) concentration, removal efficiencies ranged from 41 – 54 % for the biosorbents, compared with 84 % for natural zeolite. In contrast, Na-modified zeolites achieved near-quantitative Zn(II) removal (96 – 98 %) and maintained relatively high efficiencies even at elevated Zn(II) concentrations (67 – 72 %), confirming their superior affinity and accessibility of sorption sites. This performance can be attributed to the enhanced ion-exchange capacity resulting from Na-modification.

Equilibrium sorption data were fitted using the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm models [5]. The model parameters were obtained from the linearized forms of the respective equations using linear regression, and the resulting values are summarized in Table 1. The goodness of fit was evaluated using the correlation coefficient (R^2) and by comparing the experimental and calculated sorption capacities. In addition, the Langmuir separation factor (R_L) was calculated to assess the favorability of sorption, where values between 0 and 1 indicate favorable sorption.

Table 1. Isotherm parameters obtained for Zn(II) sorption onto investigated sorbents.

Model	Parameter	Sorbent					
		OP	CP	SCP	NZ	Na-NZ-24	Na-NZ-72
	$q_{e,exp.}$ mmol/g	0.049	0.038	0.061	0.088	0.302	0.322
Langmuir	q_m. mmol/g	0.049	0.040	0.063	0.090	0.318	0.340
	K_L. L/mmol	3.265	2.712	0.857	6.906	11.734	14.159
	R_L	0.191	0.217	0.427	0.107	0.068	0.057
	R^2	0.978	0.982	0.951	0.997	0.998	0.999
Freundlich	$1/n_F$	0.241	0.177	2.009	0.220	0.370	0.396
	K_F	0.035	0.028	0.418	0.071	0.306	0.363
	n_F	4.151	5.556	0.498	4.552	2.702	2.525
	R^2	0.867	0.962	0.931	0.917	0.823	0.839
Temkin	B	0.082	0.0051	0.0152	0.0128	0.0528	0.0589
	K_T L/g	80.66	277.95	10.47	314.19	233.37	235.12
	b_T kJ/mol	302.29	486.04	163.08	193.66	46.95	42.08
	R^2	0.815	0.924	0.943	0.948	0.967	0.977
Dubinin - Radushkevich	K_D mol^2/kJ^2	0.0028	0.0020	0.0052	0.0024	0.0035	0.0037
	q_m mmol/g	0.080	0.052	0.153	0.146	0.848	1.055
	E kJ/mol	13.36	15.81	9.81	14.43	11.95	11.62
	R^2	0.865	0.943	0.988	0.949	0.852	0.878

Among the tested isotherm models, the Langmuir model showed the best agreement with the experimental data, as reflected by the highest correlation coefficients (R^2 = 0.951 – 0.999), suggesting that Zn(II) sorption occurs predominantly as monolayer adsorption on relatively homogeneous active sites. Olive and cherry pit-derived sorbents exhibited the closest fit to the Langmuir model, whereas sour cherry pits showed a slightly smaller difference between Langmuir and Freundlich fits, indicating somewhat greater surface heterogeneity ($n_F = 0.498$). Sorption capacities obtained from the Langmuir model ranged from 0.040 to 0.063 mmol/g for the fruit pit–derived sorbents, with natural zeolite showing a higher capacity of 0.090 mmol/g. The highest capacities were observed for Na-modified zeolites (0.318 mmol/g and 0.340 mmol/g), demonstrating that Na-modification substantially enhances Zn(II) uptake, while extending the modification time from 24 to 72 h resulted in only a marginal increase. The calculated Langmuir separation factor values ($R_L = 0.057 – 0.427$) fell between 0 and 1 for all sorbents, confirming favourable Zn(II) sorption. Although fruit pit-derived sorbents exhibited lower sorption capacities than zeolitic materials, their favourable sorption behaviour and renewable origin highlight their potential as sustainable, low-cost alternatives for Zn(II) removal.

CONCLUSION

Zn(II) sorption on all investigated materials was best described by the Langmuir isotherm, indicating predominantly monolayer adsorption on relatively homogeneous sorption sites, although sour cherry pits exhibited slightly greater surface heterogeneity. Na-modified zeolites, prepared through a simple and low-cost NaCl treatment, exhibited the highest sorption capacities and strongest affinity for Zn(II), while natural zeolite showed moderate performance. Fruit pit–derived sorbents, used in their unmodified form, displayed lower sorption capacities but remained favourable. Despite their lower capacity compared to zeolitic materials, these results highlight fruit pit waste as promising low-cost sorbents for sustainable metal ion removal.

Acknowledgment

This research was funded by the European Union through the “NextGenerationEU” (project ANTARES, IP-UNIST-28).

REFERENCES

[1] I. Michalak, K. Chojnacka, A. Witek-Krowiak, State of the Art for the Biosorption Process-a Review, **170** (2013) 1389-1416, https://doi:org/10.1007/s12010-013-0269-0

[2] H. Bamdad, K. Hawboldt, S. MacQuarrie, A review on common adsorbents for acid gases removal: Focus on biochar, Renewable and Sustainable Energy Reviews **81** (2018) 1705-1720, doi: https://doi:org/10.1016/j.rser.2017.05.261

[3] P. Payra, P. K. Dutta, Zeolites: A Primer, Handbook of Zeolite Science and Technology, S. M. Auerbach, K. A. Carrado, P. K. Dutta, M. Dekker, Inc., New York, Basel, (2003) 1-24.

[4] B. Subotić, J. Bronić, A. Čizmek, T. Antonić, C. Kosanović, Zeoliti: Svojstva, uporaba, istraživanje, Kemija u Industriji **43** (1994) 457-489.

[5] J.Wang, X. Guo, Adsorption kinetic and isotherm models of heavy metals by various adsorbents An overview, Critical Reviews in Environmental Science and Technology **53** (2023) 1837-1865, doi: https://doi.org/10.1080/10643389.2023.2221157

COMPRESSIVE STRENGTH OF REPAIR CEMENT-BASED MORTARS CONTAINING ZEOLITIC TUFF AND LIMESTONE

Tiana Milović
University of Novi Sad, Faculty of Technical Sciences, Department of Civil Engineering and Geodesy,
Trg Dositeja Obradovića 6, Novi Sad, Serbia, Research Associate
E-mail: tiana.milovic@uns.ac.rs

ABSTRACT

The aim of this paper was to evaluate the effect of cement replacement with 0 %, 10 %, 15 % and 20 % of zeolitic tuff as supplementary cementitious material, as well as with combination of 10 % zeolitic tuff and 10 % ground limestone, on the compressive strength of repair cement/cement-based mortars, prepared with water-to-binder ratio of 0.5. Applied zeolitic tuff was obtained from the quarry "Igroš-Vidojevići" (Brus, Serbia), while ground limestone was taken from quarry "Jelen Do" (Požega, Serbia). Following the performance requirements given in the standard SRPS EN 1504-3:2010, the 28-day compressive strength of the tested mortars was determined in accordance with standards SRPS EN 12190:2010. Based on the obtained results, it was concluded that all investigated mortars met the requirement for structural repair mortar class R4 according to SRPS EN 1504-3:2010 in a term of compressive strength, while the optimal compressive strength was obtained with combination of zeolitic tuff and ground limestone.

Keywords: natural zeolite, ground limestone, supplementary cementitious material, filler, repair mortar compressive strength.

INTRODUCTION

The growing number of reinforced concrete structures and infrastructure approaching the end of their service life requires innovative sustainable solutions for preservation and retrofitting [1]. In order to restore damaged concrete to its original condition, various types of repair mortars can be used. The usage of repair cement-based mortars containing mineral additions, besides environmental benefits, can also have mechanical, physical and durability advantages. Therefore, this paper deals with the effect of zeolitic tuff (ZT) as type II mineral addition, and combination of ZT and ground limestone (GL) as type I mineral addition, on 28-day compressive strength of repair cement-based mortars. Natural zeolites as volcanic or volcano-sediment materials have a honeycomb-like structure with extremely small pores and channels that offers large total specific surface, which represents the base of their high pozzolanic reactivity [2], while limestone powder is widely used in cement-based materials and reportedly, can influence their properties by filler, nucleation, dilution and chemical effects [3].

MATERIALS, MIXTURES AND METHODS

In order to examine the effect of ZT as supplementary cementitious material (SCM), as well as mixture of ZT and GL on the 28-day compressive strength of the repair cement-based mortars, the following component materials were used for the mixtures preparation: (i) Ordinary Portland cement CEM I 42.5R (Lafarge-BFC Serbia), (ii) ZT with particle diameter size less than 125 μm, from the quarry "Igroš-Vidojevići“ (Brus, Serbia), (iii) GL from "Jelen Do" quarry (Požega, Serbia), (iv) CEN standard sand, in accordance with SRPS EN 196-1:2017, and (v) deionized water. Used ordinary Portland cement (OPC), GL and ZT had density of 3.126 g/cm^3, 2.587 g/cm^3 and 2.386 g/cm^3 (determined in accordance with SRPS EN 1097-7:2023), and Blaine specific surface area of 4188.6 cm^2/g, 3182.21 cm^2/g and

8292.97 cm^2/g (determined in accordance with SRPS EN 196-6:2019, respectively. The ZT activity index was determined in accordance with the standard SRPS EN 450-1:2014, and after 28 and 90 days ZT activity indexes were 93 % and 103 %, respectively.

Mineralogical analysis of ZT was performed by XRD analysis (Philips PW1710 device) under the following experimental conditions: monochromatic Cu Kα radiation with 1.5418 Å wavelength in the 5–55° of 2θ range, scan rate 0.02° and 0.5s per step, at a voltage of 40 kV and a current of 30 mA. According to the XRD diffractogram presented in Fig. 1, the main mineral phase of the ZT is clinoptilolite, one of the most common, widespread and abundant natural zeolite [4]. Other phases determined in the clinoptilolite-rich ZT are mica group minerals, feldspar, smectite ("swelling" clay mineral), quartz, analcime (a form of natural zeolite with irregular channels) and amphibole.

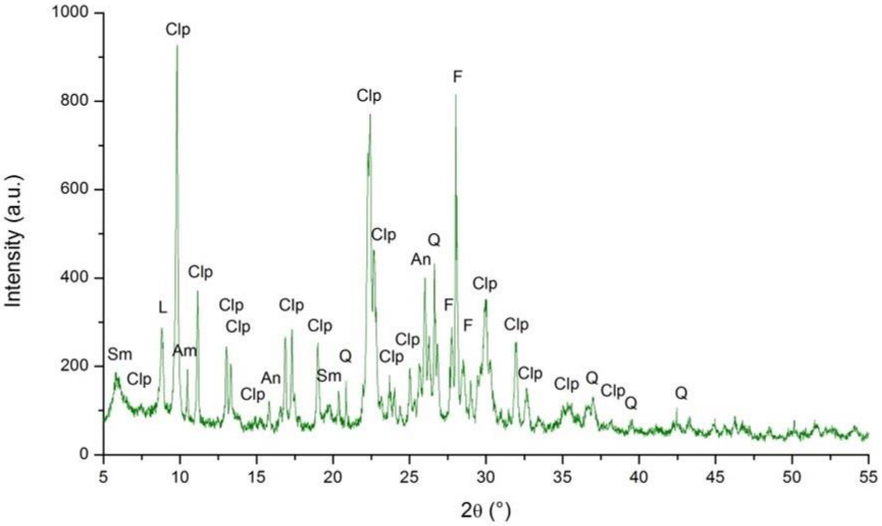


Figure 1. XRD diffractogram of ZT (Clp – clinoptilolite, L – mica group minerals, F – feldspar, Sm – smectite, Q – quartz, An – analcime, Am – amphibole).

Five different cement/cement-based repair mortars (Tab. 1) were made with 0 %, 10 %, 15 % and 20 % of ZT as SCM by mass, and one combination of 10 % ZT and 10 % GL, to determine the compressive strength. All mortar mixtures were prepared with water-to-binder ratio of 0.5 according to SRPS EN 12190:2010.

Table 1. Composition of the repair mortar mixtures.

Component materials	C	ZT10	ZT15	ZT20	ZT10GL10
CEM I 42.5 R (g)	450	405	382.5	360	360
ZT (g)	-	45	67.5	90	45
GL (g)	-	-	-	-	45
CEN standard sand (g)	1350	1350	1350	1350	1350
Deionized water (g)	225	225	225	225	225

The compressive strength of the mortars was determined according to the standard SRPS EN 12190:2010 using prism-shaped specimens with dimension of 40 × 40 × 160 mm^3, at the age of 28 days, after recommended curing resume (covered in film for 24 h, demoulded after 24 h and cured under water at (21 ± 2)°C for 27 days). The mean strength values were obtained by testing the six prism halves per mortar mixture. The load at failure was determined using a hydraulic press with a capacity of 150 kN.

RESULTS AND DISCUSSION

The 28-day compressive strengths of mortars, prepared with water-to-binder ratio of 0.5, containing 0 %, 10 %, 15 % and 20 % of ZT as SCM, and combination of 10 % ZT and 10 % GL, by cement mass, are shown in Fig. 2. Considering that obtained results were higher than 45 MPa, all examined mortars fulfilled the requirement for class R4 (the highest one) of structural repair mortar according to the standard SRPS EN 1504-3:2010 in term of compressive strength.

The highest value of compressive strength had mortar containing 10 % ZT (55.52 MPa), the lowest one had mortar contating 20 % ZT as SCM (48.96 MPa), while control (C) mortar had compressive strength of 51.72 MPa. Replacing OPC with 10 % ZT led to an increase in strength by 7 %, which is in accordance with the results obtained by Milović et al. [5]. A further increase in the OPC substitution, with 15 % and 20 % ZT, led to a slight increase in strength by 4 %, and a decrease by 5 %, respectively. This decrease in compressive strength with increasing levels of OPC replacement with ZT (especially at the 20 % OPC replacement level) may be attributed to the dilution effect [6]. Although the compressive strengths were determined at the mortars age of 28 days, which is in accordance with the standard requirement for repair mortars, the mortars with 10 % as well as with 20 % ZT already had higher strengths compared to the control, even though they contain pozzolan, which takes up to 90 days to react to a greater extent. Moreover, the mortar containing a mixture of 10 % ZT and 10 % GL had almost the same strength as the control (only 1 % increase), but had a higher strength by about 7 % compared to the mortar ZT20 (both mortars, ZT20 and ZT10GL10, contain the same amount of OPC, i.e. 80 %, while 20 % is replaced).

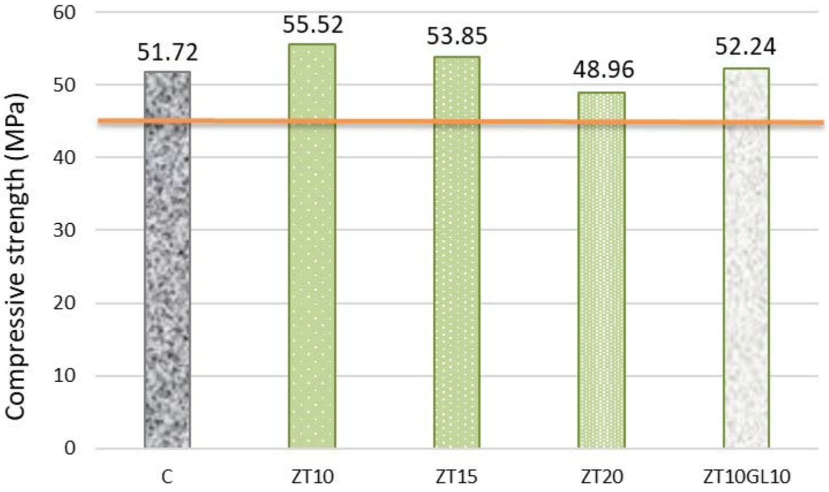


Figure 2. The 28-day compressive strengths of control and cement-based repair mortars.

Based on the results of the relevant literature review conducted by Wang et al. [3], when it is used in cement-based materials, GL can influence their properties by filler, nucleation, dilution and chemical effects, depending on its particle size and amount. Therefore, a higher 28-day compressive strength of mortar containing 20 % blended ZT and GL in comparison to the mortar containing 20 % ZT, can be explained due to GL influence on early hydration rates, filler effect, while it acts as a nucleating site for hydration and pozzolanic reaction products.

CONCLUSION

Based on the obtained experimental results, in a term of the compressive strength of the repair cement-based mortars, prepared with water-to-binder ratio of 0.5, that contain 0 %, 10 %, 15 % and 20 % ZT as SCM by cement mass, and combination of 10 % ZT and 10 % GL, the following can be concluded:

- With 28-day compressive strengths higher than 45 MPa, all tested mortars fulfilled the requirement for structural repair mortars of class R4 in a term of compressive strength, according to the standard SRPS EN 1504-3:2010;
- Repair mortar containing 10 % ZT had the highest compressive strength (higher by 7 % compared to the control one). With increasing OPC replacement up to 20 %, the strengths decreased, but they were still in the control range (the difference was ±5 %);
- Since OPC was used to prepare the repair mortar, based on the obtained compressive strength value 20 % of the clinker can be replaced with a combination of ZT and GL (as well as with ZT alone);
- Repair mortar containing combination of 10 % ZT and 10 % GL had the compressive strength in range of control one (but a slightly higher than mortar with 20 % ZT) and therefore, in term of compressive strength and sustainable development it represents the optimal solution.

In order for any of these tested mortars to be used for the repair of concrete structures, it is necessary to test all the necessary properties and check whether these mortars meet the requirements for structural repair mortar of class R4 (or R3) according to SRPS EN 1504-3:2010 in terms of modulus of elasticity, capillary absorption, adhesive bond, restrained shrinkage/expansion, thermal compatibility (freeze-thaw), resistance to carbonation, etc. Once the mortar class for the required properties has been determined, the mortar can be prepared and used on site by mixing of already blended dry powder ingredients with deionized water, and adding CEN standard sand. Prepared fresh mortar can be manually applied to the previously adequately prepared concrete surface, in places where restoration is needed.

ACKNOWLEDGMENT

This research has been supported by the Ministry of Science, Technological Development and Innovation (Contract No. 451-03-34/2026-03/200156) and the Faculty of Technical Sciences, University of Novi Sad through project “Scientific and Artistic Research Work of Researchers in Teaching and Associate Positions at the Faculty of Technical Sciences, University of Novi Sad 2026” (No. 01-3609/1).

REFERENCES

[1] C.R. Rusnak, *Infrastructures*, 2025, **10(4)**, 99.

[2] A. Babak, M. Shekarchi, *Cement and Concrete Composites*, 2010, **32(2)**, 134–141.

[3] D. Wang, C. Shi, N. Farzadnia, Z. Shi, H. Jia, Z. Ou, *Construction and Building Materials,* 2018, **181**, 659–672.

[4] I. Rodríguez-Iznaga, M. G. Shelyapina, V. Petranovskii, *Minerals*, 2022, **12**, 1628.

[5] T. Milović, O.Rudić, S.O. Furgan, M. Radeka, M. Malešev, V. Radonjanin, S. Baloš, M. Laban, *Chem. Ind. Chem. Eng. Q.*, 2021, **27(4)**, 403−415.

[6] T. Milović, S. Šupić, M. Malešev, V. Radonjanin, *Sustainability*, 2022, **14**, 2736.

CHARACTERIZATION AND ADSORPTION PERFORMANCE OF ZEOLITE-BASED GEOPOLYMERS

Dušan Trajković[1,2], Aleksandra Popović[2], Jelena Dikić[1], Dragana Živojonović[2]
[1] Innovation Centre of Faculty of Technology and Metallurgy, 11120, Belgrade, Serbia
[2] University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11120, Belgrade, Serbia
E-mail: dtrajkovic@tmf.bg.ac.rs

ABSTRACT

Geopolymers are inorganic materials formed through the alkaline activation of aluminosilicate precursors. The synthesis of these materials is carried out at room temperature, which favorably contributes to the reduction of energy resources required for their production. Various natural materials can be used as precursors for their synthesis, including zeolites, diatomaceous earth, and clays, as well as different types of waste materials rich in aluminum and silicon, such as fly ash, blast furnace slag, slag, red mud, and others. These materials have attracted particular attention due to their high mechanical strength and high adsorption capacity. In this context, the use of zeolites as precursors for the synthesis of these inorganic materials represents a potential solution for overcoming the main limitations of their wider industrial application. The synthesis of geopolymers was carried out using a NaOH and Na_2SiO_3 solution in a 1:1 ratio, after which the obtained paste was shaped into spherical beads. The adsorption performance was evaluated using model cationic dyes, namely methylene blue, crystal violet, brilliant green, and basic fuchsin. Adsorption experiments were carried out by contacting 0.2 g of the synthesized adsorbent with 20 cm^3 of dye solution at an initial concentration of 25 mg dm^{-3}, over a contact time of 3 h at 25 °C. The obtained materials, both before and after the adsorption process, were characterized by optical microscopy, scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and powder X-ray diffraction (XRD). The results showed that the removal efficiency reached 76.7% for methylene blue, 95.7% for crystal violet, 98.8% for basic fuchsin, and 99.6% for brilliant green. These findings indicate a strong potential for the application of the synthesized materials in industrial wastewater treatment processes.

Keywords: Zeolite, geopolymer, cationic dyes, efficiency

Acknowledgements: The authors of this study are grateful for the support from the Ministry of Science, Technological Development and Innovations of the Republic of Serbia, which provided the funds for this work (Contract No. 451-03-33/2026-03/200135 and 451-03-33/2026-03/200287).

BACTERIAL IMMOBILIZATION ON NATURAL ZEOLITE: ROLE OF SPECIES PROPERTIES AND CONTACT TIME

Blanka Dadić, Jasna Hrenović, Tomislav Ivanković
University of Zagreb, Faculty of Science, Zagreb, Croatia
E-mail: blanka.dadic@biol.pmf.hr

ABSTRACT

Natural zeolites were widely investigated as biocarriers for bacteria due to their porous structure and rough surface area, which promote bacterial immobilization and persistence. However, the efficiency of bacterial immobilization can vary significantly depending on the properties of the bacterial species involved as well as immobilization time.

In this study, the immobilization on natural zeolite of two bacterial species, *Pseudomonas putida* and *Klebsiella pneumoniae*, was investigated at two contact times (5h and 24h), representing early and prolonged immobilization period. Zeolite used in this study was Aqualite^{TM} (Josab International AB, Sweden), a natural clinoptilolite tuff composed of clinoptilolite (60%), sanidine (15%), opal-CT (15%), quartz (5%), and smectite (5%), with a grain size of 595 µm. For *P. putida*, the number of immobilized bacteria significantly increased after 24h (7.3±0.1 log CFU/g) compared to 5h (6.9±0.1 log CFU/g), indicating that longer contact time enhanced the immobilization process for this species. In contrast, *K. pneumoniae* did not exhibit a significant difference in immobilization between the two incubation periods (5h - 5.3±0.1 log CFU/g; 24h - 5.4±0.2 log CFU/g). *P. putida* showed significantly higher numbers of immobilized bacteria on zeolite compared to *K. pneumoniae* at both observed time points. The observed differences were likely associated with the structural characteristics of the bacteria, namely active motility. *P. putida* has flagella on the cell surface, which may facilitate more efficient contact with the zeolite surface and increased the probability of immobilization. On the other hand, *K. pneumoniae* is a non-motile bacterium characterized by a thick capsule that may reduce direct contact between the bacteria and the zeolite surface, potentially leading to lower immobilization.

These findings indicated that both bacterial characteristics and immobilization time influenced the efficiency of bacterial immobilization on natural zeolite. Understanding these interactions could contribute to improved application of natural zeolite as a biocarrier in wastewater treatment and bioremediation systems.

STUDY OF CATALYTIC POTENTIAL OF ZEOLITES FOR OXIDATION OF VOLATILE ORGANIC COMPOUNDS

Filip Car[1]*, Ana Palčić*[2]*, Vesna Tomašić*[1]
[1]University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19, Zagreb, Croatia
[2]Ruđer Bošković Institute, Bijenička cesta 54, Zagreb, Croatia
E-mail: fcar@fkit.unizg.hr

ABSTRACT

The catalytic oxidation of volatile organic compounds (VOCs) is one of the key application areas for zeolites. In such systems, zeolites may serve as standalone catalysts, but they are more commonly used as supports for catalytically active components such as noble metals or transition metal oxides. In this context, zeolites provide a flexible and efficient support for developing catalysts for VOC oxidation in various gas purification applications. Aromatic compounds from the BTEX group (benzene, toluene, ethylbenzene and xylene isomers) are frequently used for this purpose, with benzene being a particularly relevant model compound due to its high chemical stability and resistance to oxidation.

In this study, a series of powdered MFI- and FAU-type zeolites was investigated for the catalytic oxidation of benzene as a representative VOC. The tested zeolites were compared in terms of catalytic activity, and those showing the best performance were selected as supports for the deposition of mixed manganese oxides as catalytically active components. Aqueous 1 M nitrate solutions of transition metal salts were used as precursors, mixed in a molar ratio of Mn/X (X = Fe, Cu, Ni, Co, Cr, and Zn) = 1:1, and deposited onto zeolite supports by the wet impregnation method. Characterization of the prepared catalysts included determination of their physicochemical and morphological properties using multiple instrumental techniques. After calcination at 500 °C, the prepared catalysts were tested in the fixed-bed reactor, and catalytic activity was monitored by *on-line* analysis using gas chromatography.

Significant improvements in the catalytic performance of zeolites modified with mixed manganese-based metal oxides were achieved compared to the parent zeolites, with the best results observed for the CBV760 zeolite-supported mixed manganese–iron oxide catalyst ($MnFeO_x$), which achieved benzene conversion above 95% at temperatures as low as 250 °C.

Keywords: zeolites, catalytic oxidation, volatile organic compounds, mixed Mn oxides.

ACKNOWLEDGEMENT

This research was conducted within the framework of the project HEMCAT, financed by the European Union’s NextGenerationEU fund from source 581–The recovery and resilience mechanism in the framework of programme financing of public higher education institutions and public scientific institutes.

DURABILITY OF LIME BASED MORTARS CONTAINING NATURAL ZEOLITE IN THE PRESENCE OF SODIUM SULFATE

Majda Potkonjak[1], *Marina Škondrić*[2*], *Vladana Rajaković-Ognjanović*[2], *Zorana Naunović*[2]
[1]Highway Institute, Boulevard Peka Dapčevića 45, 11000 Belgrade, Serbia
[2]Faculty of Civil Engineering, University of Belgrade, Bulevar kralja Aleksandra 73, 11000 Belgrade, Serbia
E-mail:amarina@grf.bg.ac.rs

Keywords: lime based mortars, historical buildings, renders, durability, soluble salts

INTRODUCTION

Lime based rendering mortars were used as an outer coating of many historical buildings during ancient times and middle ages, and up to the beginning of the twentieth century. In order to improve their properties in humid conditions, addition of natural pozzolanic materials was applied. Natural zeolites were used as a pozzolanic material in the countries that are not rich in other pozzolana. When cured in humid conditions, addition of natural zeolites to lime mortars has the similar impact as addition of pozzolanic materials. Nevertheless, when the environmental conditions change to relative humidity around 50%, the reduction of compressive and flexural strenghts are observed. This paper investigates the behavior of composite specimens composed of porous stone base, with two layers of lime based rendering mortars containig natural zeolite. These specimens were exposed to the influence of two sodium sulfate solutions, with concentration of 5 and 10%.

EXPERIMENTAL

Preparation of composite specimens analyzed in this research was explained in detail previously [1]. The specimens were 5 years old at the beginning of the test. One group of samples was prepared using pure lime mortars (designated with letter A), while the other group was prepared using natural zeolite from Igroš, Brus, as a partial replacement of lime in the amount of 20 and 40% (designated with letter B). The analysis of the behaviour of these specimens in the presence of sodium sulfate was done in accordance with the recommendation of the RILEM Technical Comitee 271-ASC [2]. What has been observed was that in the first phase of the analysis, salt was accumulated near the surface of the specimens. In the following stages, the specimens were exposed to changes in the relative humidity. The instrument used for secure curing conditions was climatic chamber (produced by Memmert). Mass of the specimens was measured during each stage of the test. At the end of the test the loose material from the specimen's surface was brushed away, while the first layer of mortar under the brushed part was crushed and sieved through the 2 mm sieve. After described preparation, the X-ray fluoresence (XRF) measurements were performed in order to define the amount of the sulphur in the specimens exposed to soluble salt. Leaching test was also performed, in order to define the amount of released sulphate ions. Mixtures containing 10 g of the specimens and 100 mL of deionized water were prepared, and after intense mixing, filltered through 45 μm. The concentration of sulphate ions was detected using ion chromatography (instrument used was Metrohm 861).

RESULTS AND DISCUSSION

Photographs of the samples at the beginning and at the end of the test, are presented in Fig. 1. The sulphur content of the layers beneath the brushed part of the specimens, obtained by XRF measurements, toghether with the amount of dissolved ions measured using ion chromatography are presented in Table 1.

As it can be noticed from the photos, there were no great visual differences between the different groups of samples nor there were visual differences from the influence of different salt concentrations. The change observed visually by deterioration of samples is present in all of the samples at the end of the analysis. After the analysis of the layer beneath the brushed material, it can be observed that the samples with less deterioration are samples marked as A-2 and B-1 which retained higher amount of salt in the tested layer. This could possibly lead to further deterioration of these samples, if the exposition was contined. These conclusions were not confirmed through XRF measurements, where lower percent of sulphur was found in both samples signed as type B.

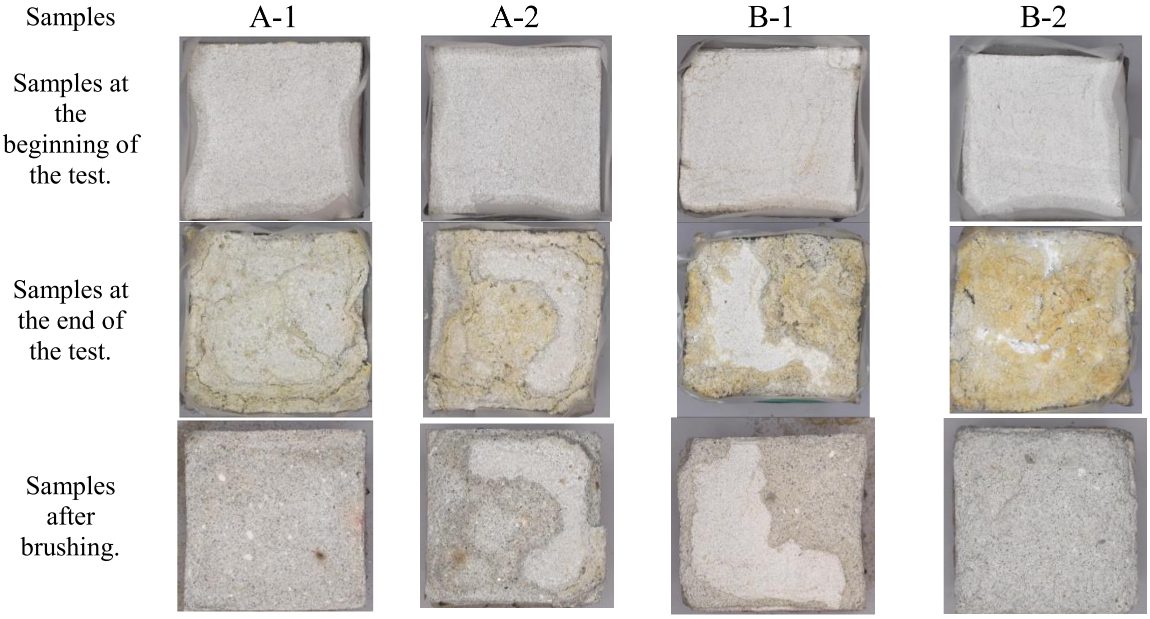


Figure 1. Photographs of the samples before (first raw), after the finalization (second raw) of the test and after brushing (third raw)

Table 1. The results of the sulphate concentration in the top layer remaining on the sample after brushing

	Concentration of sodium sulfate solution applied	Mass of the brushed debris (g)	S content obtained through XRF measurement (ppm)	SO_4^{2-} dissolved ions (mg/L)
A-1	5%	13.67	3092.39	338
A-2	10%	12.85	9746.90	1300
B-1	5%	9.38	2641.14	896
B-2	10%	20.02	2563.53	470

The obtained results are promissing due to the similar level of damaged structure developed in analyzed groups of specimens, as well as lower amount of sulphur available for reaction and further deterioration. Still, it would be of interest to detect the different reaction products that induce the damage mechanism and path observed on the specimens.

REFERENCES

[1] M. Aškrabić, M.Vyšvařil, T. Žižlavský, Contribution to the durability testing of the lime-based render, in Proceedings of XXVII Congress DIMK and IX Congress SIGP, 2022, 363-369

[2] B. Lubelli et al. Recommendation of RILEM TC 271-ASC: New accelerated test procedure for the assessment of resistance of natural stone and fired-clay brick units against salt crystallization, *Mater.Struct.*, 2023, 56

GAMMA-IRRADIATION-MOFIDIED UIO-66 FOR EFFICIENT HEXAVALENT CHROMIUM REMOVAL FROM AQUEOUS SOLUTIONS

Radojka Vujasin[1]*, Djordje Petrović*[1]*, Srboljub Stanković*[1]*, Marija Egerić*[1]*, Yi-nan Wu*[2]*,*
Aleksandar Devečerski[1]*, Ljiljana Matović*[1,2,3]
[1]Vinča Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, Mike Petrovića Alasa 12-14, Vinča, Belgrade, Serbia
[2]State Key Laboratory of Water Pollution Control and Green Resource Recycling, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China
[3]Center of Excellence "CEXTREME LAB", Vinča Institute of Nuclear Sciences – National Institute of the Republic of Serbia, University of Belgrade, Mike Petrovića Alasa 12-14, Vinča, Belgrade, Serbia
E-mail: ljiljam@vin.bg.ac.rs

ABSTRACT

Hexavalent chromium (Cr(VI)) is a carcinogenic, highly toxic, and mobile pollutant frequently detected in industrial wastewater, posing a major environmental concern due to its high solubility and persistence. In this work, γ-irradiation was employed to modify the structural and adsorption properties of the zirconium metal–organic framework UiO-66 for improved Cr(VI) removal from aqueous solutions.

Irradiation was performed using a Cobalt-60 source at absorbed doses from 5 Gy to 2000 kGy (dose rates 113 Gy/h–31 kGy/h). X-ray diffraction revealed dose-dependent microstructural changes, indicating decreased crystallinity and defect formation even at low doses. At higher doses, the peak shifted toward lower 2θ, suggesting increased lattice strain, while partial crystallinity was retained. Nitrogen sorption analysis showed an increase in specific surface area from 915 to 1140 m²/g after irradiation at 2000 kGy. FTIR analysis confirmed the preservation of functional groups, including the oxyanion-binding region (~900 cm⁻¹).

Adsorption experiments conducted at initial Cr(VI) concentrations of 10 and 50 mg/dm³ showed that removal efficiency increased with sorbent dosage (0.1–2 g/dm³), reaching ~100% at the highest dose. At 10 mg/dm³, removal at 0.1 g/dm³ increased from 32.9% (non-irradiated) to 41.8% (2000 kGy), while at 0.3 g/dm³ it increased from 68.6% to 72.7%. At 50 mg/dm³, the effect was more pronounced: removal at 0.1 g/dm³ increased from 9.0% to 10.6%, and at 0.3 g/dm³ from 24.6% to 38.0%. Low irradiation doses (5–50 Gy) had a negligible effect, whereas high-dose irradiation significantly improved performance, particularly at higher pollutant concentrations and lower sorbent dosages.

The enhanced adsorption is attributed to irradiation-induced defect formation and increased specific surface area from 915 m²/g to 926 m²/g. The micro–mesopore distribution changed, with the mesopore fraction increasing from 55% in the non-irradiated sample to 66% after irradiation. These findings demonstrate that γ-irradiation by modifying the porous structure of the MOF is an effective approach to improve MOF-based materials for Cr(VI) remediation.

Keywords: Cr(VI) removal, UiO-66, gamma irradiation.

ACKNOWLEDGEMENTS

We acknowledge the support to this work provided by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia under registration number: 451-03-33/2026-03/ 200017.

METAL–ORGANIC FRAMEWORKS WITH COPPER(II), *N*-ALKYLATED GLYCINE AND 3,3’-BIPYRIDINE: TWO FORMS OF THE SAME FAMILY

Darko Vušak[1], *Katarina Ležaić*[1], *Mia Jurković*[1], *David-Kučera Čavara*[2], *Željka Soldin*[1], *Dijana Žilić*[2], *Biserka Prugovečki*[1]
[1]University of Zagreb, Faculty of Science, Department of Chemistry, Horvatovac 102a, HR-10000 Zagreb, Croatia
[2]Ruđer Bošković Institute, Division of Physical Chemistry, Bijenička cesta 54, HR-10000 Zagreb, Croatia
E-mail:dvusak@chem.pmf.hr

ABSTRACT

Metal–organic frameworks (MOFs) have been intensively investigated over the last 30 years. MOFs are easily modified to perform certain functionality, hence the versatility of MOFs was widely demonstrated across a broad range of applications, including: catalysis, sensing, enantiomeric separation, gas adsorption and separation, and production of liquid water by harvesting vapour from the air [1-3]. Rapid expansion of research generated over 100,000 MOF datasets in the Cambridge Structural Database [4]. Some aspects of these materials are still scarcely researched, such as predictive understanding of the influence of synthetic pathways on structural features and their functionality [1].

Metal–organic frameworks containing *N*-alkylated amino acids have not yet been structurally characterised in the literature, nor have copper(II) MOFs incorporating 3,3'-bipyridine together with an additional chelating ligand [3]. In this work, we present the investigated synthetic pathways and four crystal structures of copper(II) MOFs with a general formula $\{[\mathrm{Cu(AA)(NO_3)(3,3'\text{-}bpy)}]\cdot\mathrm{solvents}\}_n$ (AA = *N*-methyl- or *N*-ethlyglycinate; 3,3’-bpy = 3,3’-bipyridine). X-ray structural analysis was performed to elucidate how the alkyl chain length of the *N*-alkylglycine, the crystallisation solvent, and other experimental parameters affect the crystal packing of the obtained frameworks (Figure 1). Thermal and magnetic behaviour of compounds were investigated.

Keywords: crystal structures; metal–organic frameworks; solvatomorphism, synthesis.

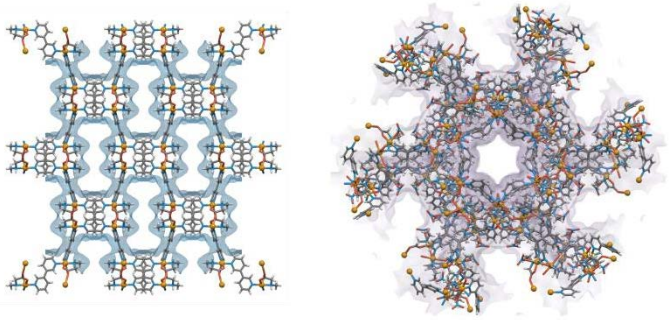


Figure 1. Crystal packing of orthorhombic (left) and cubic (right) forms of MOFs $\{[\mathrm{Cu(AA)(NO_3)(3,3'\text{-}bpy)}]\cdot\mathrm{solvents}\}_n$.

REFERENCES

[1] M.L. Barsoum, K. M. Fahy, W. Morris, V. P. Dravid, B. Hernandez, O. K. Farha, *ACS Nano*, 2025, **19**(1), 13–20
[2] X. Niu, M. Yuan, X. Yang, H. Li, R. Zhao, Y. Liu, H. Zhao, K. Wang, *ACS Appl. Nano Mater.*, 2024, **7**(16), 19175–19183
[3] W. Xu, O. M. Yaghi, *ACS Cent. Sci*. 2020, **6**(8), 1348–1354.
[4] C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, *Acta Cryst.*, 2016, **B72**, 171–179

SCREENING OF Cu AND/OR Mn CONTAINING ZEOLITES AS CATALYSTS FOR TOTAL OXIDATION OF VOLATILE ORGANIC COMPOUNDS

Miloš Čenić[1], *Matej Bubaš*[1], *Magdalena Jabłońska*[2] *Nataša Novak Tušar*[1,3]
[1]National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia
[2]University of Łódź, Faculty of Chemistry, Tamka 12, 91-403 Łódź, Poland
[3]University of Nova Gorica, Vipavska 13, 5000 Nova Gorica, Slovenia
E-mail: milos.cenic@ki.si

ABSTRACT

Volatile organic compounds (VOCs) are classified as organic compounds with boiling points lower than 250 °C at atmospheric pressure. They are a major class of pollutants and can negatively impact both human health and the environment. Several approaches are being used for lowering the emissions and removal of VOCs, with catalytic oxidation being among the most common and efficient.

Zeolites are a group of microporous, crystalline aluminosilicate minerals which possess properties such as high surface area, uniform micropore structure, hydrophobicity, and thermal stability. Due to these properties, they are commonly employed as adsorbents and catalysts for air purification. Among the transition metals, Mn and Cu are promising candidates for the abatement of VOCs due to their excellent redox properties, high activity and resistance to poisoning, with some indications of a synergistic effect between these two metals [1].

In this work, we investigated the catalytic activity of four different zeolite types (SSZ-13, Y, ZSM-5, and ERI) for total catalytic oxidation of toluene as a model VOC. The parameter used for comparing the catalytic activity of measured samples was T_{90}, which represents the temperature at which 90 % of the reactants are converted into products. Each zeolite was first loaded with a relatively high amount of Mn (10 wt.%), after which the first group of catalytic tests was conducted. The best-performing catalyst was Mn-doped Y, showing a T_{90} of around 387 °C. For the next group of catalytic tests, each zeolite was first loaded with the same amount of Mn (10 wt.%) and subsequently loaded with 3 wt.% Cu. It was observed that the introduction of Cu significantly increased the toluene conversion in a large part of the measured temperature range.

Through these measurements, we have identified several promising zeolites for the removal of VOCs, and have shown that the addition of Mn and Cu can further improve their catalytic activity. These findings provide a promising starting point for the design and optimization of more efficient zeolite-based catalysts for the oxidative degradation of VOCs.

Keywords: Cu-Mn, zeolites, catalytic oxidation, toluene.

REFERENCES

[1] Jiang, Y., Cheng, S., Su, C., Jiang, Y., Sun, X., Zhang, G., Liu, Y., Dou, X., & Yang, Z. (2024). Bimetallic Mn-Cu oxide catalysts for toluene oxidation: Synergistic effect and catalytic mechanism. Applied Surface Science, 670, 160629.

ORGANOZEOLITES AS DUAL ANTIOXIDANT AND ANTIMICROBIAL AGENTS WITH HIGH EFFICIENCY FOR REMOVAL OF DICLOFENAC SODIUM

Milena Pantić[1], Maja Kozarski[1], Vesna Lazić[1], Milena Obradović[2], Milica Ožegović[2], Aleksandra Daković[2]
[1]Faculty of Agriculture, Institute for Food Technology and Biochemistry, University of Belgrade, Nemanjina 6, 10080 Belgrade, Serbia
[2]Institute for Technology of Nuclear and Other Mineral Raw Materials, Franše d' Epere 86, 11000 Belgrade, Serbia
E-mail: milenas@agrif.bg.ac.rs

ABSTRACT

This study investigates multifunctional properties of organozeolites obtained from natural zeolite clinoptilolite from Vranjska Banja deposit (Serbia), modified with three cationic surfactants in amount of 100% of zeolite external cation exchange capacity (ECEC). The starting material was modified using three different surfactants - octadecyldimethylbenzylammonium chloride (sample OZ-100), cetylpyridinium chloride (sample ZCP-100), and benzalkonium chloride (sample ZBC-100). Organozeolites were evaluated in terms of antioxidant (Fe^{2+} chelating) and antimicrobial properties. Adsorption kinetics of non-steroidal anti-inflammatory drug diclofenac sodium (DS) was also determined. All materials exhibited high Fe^{2+} chelating ability and pronounced as broad-spectrum antimicrobial activity. Drug adsorption kinetics revealed that the pseudo-second-order model best describes DS removal, with differences in rate and capacity among samples. The results highlight the potential of organozeolites as multifunctional materials for environmental applications.

Keywords: natural zeolite, surfactants, antioxidant and antimicrobial activity, drug adsorption kinetics.

INTRODUCTION

Natural zeolites have an infinite three-dimensional cage-like structure, ion-exchange, and adsorption properties. Their hydrophilic nature limits their affinity toward organic molecules, especially those with non-polar or moderately polar character. To overcome these limitations, surface modification with organic cations, such as quaternary ammonium salts − surfactants, has been widely investigated. This modification transforms the zeolite surface to hydrophobic, enhancing its affinity towards organic compounds. The resulting materials, known as organozeolites, exhibit improved adsorption performance toward mycotoxins and drugs compared to unmodified zeolite [1,2].

Besides high adsorption efficacy to adsorb organic compounds, antibacterial and antioxidant activities of organozeolites are very important for their potential practical applications. It was documented that surfactant modified minerals have antimicrobial properties. Study of Schulze-Makuch et al. [3] showed that that zeolite - clinoptilolite modified with hexadecyltrimethyl ammonim ions was bactericidal, and removed *Escherichia coli* (100%) and viruses (about 99%) from contaminated water.

This study investigates the multifunctional properties of the three organozeolites obtained by modification of the natural clinoptilolite from Vranjska Banja deposit with different cationic surfactants in amounts equal to 100% of zeolite ECEC. The aim of this study was to evaluate the antioxidative and antimicrobial activity as well as to investigate adsorption kinetics for DS, of studied organozeolites.

EXPERIMENTAL

The natural zeolite (Z) from Vranjska Banja deposit (Serbia) mainly consisting of clinoptilolite was used in experiments. The cation exchange capacity (CEC) of Z was 139 meq/100g, while ECEC of Z was 10 meq/100g [1]. The Z was modified in amount equal to 100% ECEC with three cationic surfactants: octadecyl dimethyl benzyl ammonium (ODMBA) chloride, cetylpyridinium (CP) chloride, and benzalkonium (BC) chloride. The resulting samples were labelled as OZ-100, ZCP-100, and ZBC-100. The procedure for preparation and characterization of organozeolites was described elsewhere [1,2].

Fe^{2+} chelating ability was determined *in vitro* according to the method given by Todorov et al. with slight modifications [4]. Analyzed solutions of organozeolites (0.03125 – 4.0 mg/mL, 1.0 mL) were prepared in 1M phosphate buffer (pH 7). The absorbance of the examined samples was measured on a UV–VIS 1800 spectrophotometer (Shimadzu, Kyoto, Japan) at 562 nm. Citric acid and ethylene diamine tetra acetic acid (EDTA) were used as positive controls.

Antimicrobial activity of organozeolites was tested against Gram-positive *Bacillus cereus* ATCC 11778, Gram-negative *Pseudomonas aeruginosa* ATCC 35032, yeast *Candida albicans* ATCC 10231, and the mycotoxigenic mold *Fusarium graminearum* (isolate 4606, Maize Institute *Zemun Polje*), adjusted to 10^6 CFU/mL. Broth dilution method at oganozeolites concentrations of 25, 50, and 100 mg/mL following UV treatment in laminar flow chamber for sterilization of the samples was applied [4]. The results were expressed as $\log_{10}$ CFU/mL. A CFU reduction of $\geq 3 \log_{10}$ is defined as microbicidal activity.

For the kinetic experiments, diclofenac sodium (DS) solutions with an initial concentration of 20 mg/L were agitated for different time intervals (0-90 min). The experiments involved addition of 25 mg of each organozeolite to the 25 mL of DS solution. Kinetic experiments were performed at pH 7 in phosphate buffer solution. After predetermined time intervals, solutions were filtered and concentrations of non-adsorbed drug were determined using UV-Visible Spectrophotometry (UV-VIS 1800, Shimadzu). The amounts of adsorbed DS were calculated from the difference between the initial drug concentration and its concentration in the supernatant after the equilibrium.

RESULTS AND DISCUSSION

The ability to chelate iron ions was used to assess antioxidant potential. Iron is an essential micronutrient but it becomes toxic at higher concentrations, as it generates free radicals by interconverting between ferrous (Fe^{2+}) and ferric (Fe^{3+}) forms. Fe^{2+}chelators/antioxidants possess ability to mobilize tissue iron by forming soluble stable complexes that are then excreted from the body. In our study all organozeolites showed extremely high Fe^{2+} chelating ability (Figure 1). It is important to note that chelating ability for all tested samples decreased with increasing initial sample concentration. In the tested concentration range of 0.03125-4.0 mg/mL the chelating ability for OZ-100 decreased from 96.02-87.96%, for ZCP-100 from 97.46-76.88%, and for ZBC-100 from 98.28-76.95%. The citric acid control sample showed negligible chelating ability while EDTA proved to be an excellent chelating agent.

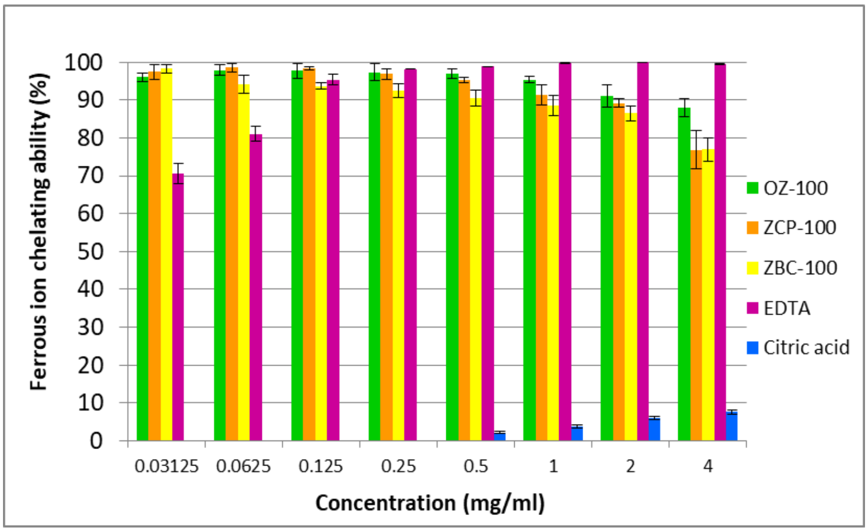


Figure 1. Fe^{2+} chelating ability of organozeolites. Data represent means ± standard deviation (n = 3)

Results of the antimicrobial assay demonstrated concentration-dependent antimicrobial effects of ZCP-100 and ZBC-100. At lower concentrations, the antimicrobial efficiency of the modified zeolites decreased in the following order: OZ-100 > ZBC-100 > ZCP-100. Organozeolite OZ-100 completely reduced growth of all microbial strains (25-100 mg/mL), except *P. aeruginosa* which showed resistance to all organozeolites even at 100 mg/mL. *C. albicans* was the most susceptible, exhibiting complete inhibition at all tested materials in the range 25-100 mg/mL. Antifungal activity against mycotoxigenic *F. graminearum* was generally effective, although ZCP-100 did not demonstrate inhibitory activity at the lowest concentration. Same sample was less effective against *B. cereus*, but still possesses strong microbial reduction (≥3 $\log_{10}$ CFU/mL). Concentration of 100 mg/mL completely reduced microbial growth with all organozeolites, except resistant Gram-negative bacteria.

Adsorption of DS by organozeolites was followed by determination of adsorption kinetics. The results of influence of contact time on the adsorption of DS on organozeolites are shown in Figure 2.

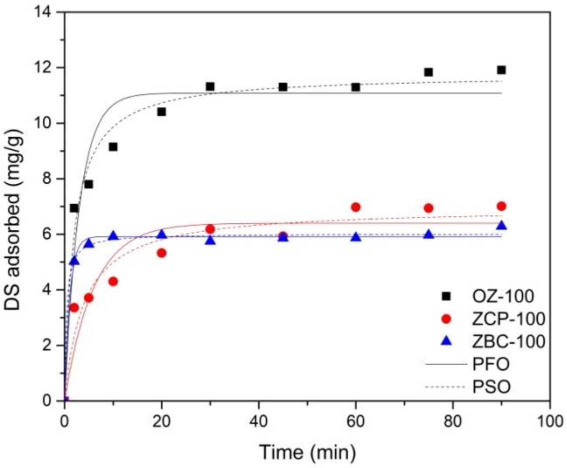


Figure 2. The effect of contact time on the adsorption of DS on organozeolites

Kinetics data were fitted according to commonly used kinetic models for the analysis of the data on adsorption of organic contaminants by organominerals: pseudo-first-order (PFO) and pseudo-second-order (PSO) models. The fitting parameters are presented in Table 1.

Table 1. Kinetic parameters for the adsorption of DS on organozeolites

Model	**Parameter**	**OZ-100**	**ZCP-100**	**ZBC-100**
Experimental data	$q_{e(exp)}$(mg/g)	11.9	7.0	6.3
PFO	k_1 (1/min)	0.33	0.17	0.93
	q_{e1} (mg/g)	11.1	6.4	5.9
	r^2	0.925	0.868	0.992
PSO	k_2 (g/(mg·min))	0.04	0.04	0.43
	q_{e2} (mg/g)	11.8	7.0	6.0
	r^2	0.978	0.938	0.994

Kinetic analysis of DS adsorption revealed differences among organozeolites. The results of kinetic data fitting indicated that the PSO model best describes the experimental data. Higher coefficients of determination (r^2) and better agreement between the experimental values $q_{e(exp)}$ and the q_e values calculated from the models suggest that PSO model better describes DS adsorption. Organozeolites OZ-100 and ZCP-100 reached adsorption equilibrium in approximately 60 min, while ZBC-100 achieved equilibrium in 20 min. Since the starting zeolite showed practically no adsorption of DS, for all studied organozeolites, adsorption of DS significantly increased. This means that surfactant ions are active sites at which DS molecules are adsorbed. Organozeolite OZ-100 exhibited the highest DS maximum adsorbed amount (11.9 mg/g), followed by ZCP-100 (7.0 mg/g) and ZBC-100 (6.3 mg/g). Kinetic parameters showed that DS adsorption on ZBC-100 is the fastest initially, although with lower adsorption efficiency, whereas OZ-100 has slower initial adsorption but higher overall maximum adsorbed amount while ZCP-100 showed the moderate rate and efficacy.

CONCLUSION

Organozeolites demonstrated significant multifunctional properties. All samples showed high Fe^{2+} chelating ability and notable antimicrobial activity, depending on surfactant type in organozeolite and microbial concentration (25−100 mg/mL). Adsorption of DS was fast with reaching adsorption equilibrium in 60 min for OZ-100 and ZCP-100, and 20 min for ZBC-100. Among the samples, OZ-100 showed the highest DS maximum adsorbed amount, while ZBC-100 exhibited the fastest adsorption kinetics. The results obtained in this study suggest the potential of organozeolites for environmental applications, e.g. removal of organic pollutants from contaminated water.

ACKNOWLEDGMENT

This research was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia, grant numbers 451-03-34/2026-03/200116 and 451-03-33/2026-03/200023.

REFERENCES

[1] A. Daković, M. Tomašević-Čanović, V. Dondur, G.E. Rottinghaus, V. Medaković, S. Zarić, Colloids Surf. B Biointerfaces 46 (2005) 20–25.

[2] M. Obradović, A. Daković, D. Smiljanić, M. Ožegović, M. Marković, G.E. Rottinghaus, J. Krstić, Microporous Mesoporous Mater. 335 (2022) 111795.

[3] D. Schulze-Makuch, S.D. Pillai, H. Guan, R. Bowman, E. Couroux, F. Hielscher, J. Totten, I.Y. Espinosa, T. Kretzschmar, EOS, Trans. Am. Geophys. Union 83 (2002) 193–201.

[4] J. Todorov, M. Pantić, M. Kozarski, V. Lazić, N. Todorović, M. Obradović, A. Daković, D. Krajišnik, N. Milašinović, M. Mirković, Processes 13 (2025) 1–21.

Eu-MODIFIED MORDENITE AS A LUMINESCENT SENSOR AND ADSORBENT OF FLUOROQUINOLONE ANTIBIOTICS

Katarina Rondović[1], Srna Stojanović[1], Kristina Mojsilović[2], Marko Dević[2], Rastko Vasilić[2], Vladislav Rac[3], Ljiljana Damjanović-Vasilić[1]
[1]University of Belgrade, Faculty of Physical Chemistry, Studentski trg 12-16, 11000 Belgrade, Serbia
[2] University of Belgrade, Faculty of Physics, Studentski trg 12-16, 11000 Belgrade, Serbia
[3] University of Belgrade - Faculty of Agriculture, Belgrade, Serbia
E-mail:katarina.rondovic@ffh.bg.ac.rs

Lanthanide-containing zeolites have a wide range of applications, particularly as light-emitting phosphors and luminescent sensors [1]. Combining long-lived Ln^{3+} emission with zeolite morphology yields materials with unique optical properties. The aim of this work was to investigate the potential applications of Eu^{3+}-exchanged natural zeolite mordenite (MOR) as an adsorbent for a fluoroquinolone (FQ) antibiotic norfloxacin (NOR), and as a fluorescent sensor for its detection. Due to its ecotoxicity and chemical stability, the occurrence of NOR in surface waters and wastewater has been recognized as a significant threat to human health and aquatic ecosystems [2]. Eu^{3+}-MOR was prepared by an aqueous ion-exchange procedure at ambient temperature using a europium(III) nitrate hydrate, followed by calcination at 500 ^{o}C. Characterization of the obtained material was performed using X-ray powder diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), diffuse reflectance spectroscopy, photoluminescence (PL) spectroscopy, low temperature N_2 adsorption and zeta potential measurements. The europium content of Eu^{3+}-MOR was determined to be 3.6 ± 0.5 wt% by EDS analysis. Batch experiments were performed at $C_0 = 10$ g L^{-1} NOR, with a solid-liquid ratio of 1 g L^{-1}, at (20 ± 1) °C. The influence of pH on the adsorption and emission characteristics of Eu^{3+}-MOR was investigated. The highest NOR adsorption was achieved at pH = 4. At acidic conditions, Eu^{3+}-MOR displayed negative values of zeta potential therefore NOR ($pKa_1 \sim 6.2$) in its cationic form can be attracted by the negatively charged surface. Under alkaline conditions the carboxylic groups of NOR are predominantly ionized ($pKa_2 \sim 8.5$). The PL spectrum of Eu^{3+}-MOR at pH= 9 exhibited an increase in the intensity of $^5D_0 \rightarrow {}^7F_n$ (n = 0-4) transitions detected at approximately 587, 598, 619, 651 and 701 nm respectively, characteristic of Eu^{3+}, with increasing NOR concentrations. This enhancement is primarily attributed to the ability of the anionic form of FQs to form complexes with metal cations, facilitating energy transfer between NOR and Eu^{3+} [3]. These findings highlight the potential of Eu^{3+}-MOR as a multifunctional material capable of identifying and eliminating FQ antibiotic NOR.

Keywords: Eu^{3+}-exchanged mordenite, luminescent sensor, norfloxacin

ACKNOWLEDGEMENT

This research was funded by the Science Fund of the Republic of Serbia, grant number 7309 ZEOCOAT and the Ministry of Science, Innovation, and Technological Development of the Republic of Serbia (451-03-137/2025-03/200146, 451-03-136/2025-03/200162 and 451-03-65/2024-03/200116).

REFERENCES

[1] Y. Wang, H. Li, *CrystEngComm*, 2014, **16**, 9764

[2] M. Patel, R. Kumar, K. Kishor, T. Mlsna, C. U. Pittman, Jr., D. Mohan, *Chem. Rev.*, 2019, **119**, 3510

[3] E. A. Serna-Galvis, J. Arboleda-Echavarria, A. Echavarria-Isaza, R. A. Torres-Palma, *Environ. Sci. Pollut. Res.*, 2024, **31**, 63427

ADSORPTION BEHAVIOR OF Cd^{2+}, Pb^{2+}, AND Hg^{2+} IONS ON NATURAL AND SYNTHETIC ZEOLITES IN A MODEL SYSTEM OF CONDENSATE FROM VACUUM PYROLYSIS OF BATTERIES

Marija Štulović[1], *Jelena Dikić*[1], *Dragana Radovanović*[1], *Nataša Gajić*[1], *Katarina Sokić*[2], *Željko Kamberović*[2], *Sanja Jevtić*[2]
[1] Innovation Centre of the Faculty of Technology and Metallurgy in Belgrade, Ltd., 11000 Belgrade, Serbia,
[2] Faculty of Technology and Metallurgy, University of Belgrade, 11000 Belgrade, Serbia,
E-mail: mstulovic@tmf.bg.ac.rs

ABSTRACT

Heavy metal contamination originating from spent battery processing represents a significant environmental challenge due to the toxicity and persistence of Pb^{2+}, Cd^{2+}, and Hg^{2+} ions [1-3]. Among available treatment methods, adsorption using zeolites has attracted considerable attention because of their ion-exchange capacity, developed porosity, and low cost [2, 4-7].

In this study, the adsorption behavior of Cd^{2+}, Pb^{2+}, and Hg^{2+} ions were investigated using natural clinoptilolite zeolite from Vranjska Banja and synthetic zeolite 4A. A multicomponent aqueous solution was prepared to simulate condensate generated after vacuum pyrolysis of spent batteries. Adsorption experiments were carried out under ambient conditions at mixing speeds of 300 and 600 rpm.

The zeolites were characterized by X-ray powder diffraction (XRPD), thermogravimetric analysis (TG/DTG), scanning electron microscopy (SEM), and Brunauer–Emmett–Teller (BET) surface area analysis, while metal ion concentrations before and after adsorption were determined by atomic absorption spectroscopy (AAS).

The obtained results showed that natural clinoptilolite exhibited the highest affinity toward Cd^{2+} ions, achieving 98% removal efficiency, followed by Pb^{2+} (65%) and Hg^{2+} (45%). Synthetic zeolite 4A achieved complete removal of Cd^{2+} and Pb^{2+} ions under the investigated conditions. Adsorption kinetics in all systems were best fitted by the pseudo-second-order kinetic model, indicating that chemisorption is the dominant adsorption mechanism [2, 6].

ACKNOWLEDGEMENT:

This work was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (451-03-33/2026-03/200287 and 451-03-34/2026-03/200135)

REFERENCES:

[1] E. Kuldeyev, M. Seitzhanova, S. Tanirbergenova, K. Tazhu, E. Doszhanov, Z. Mansurov, S. Azat, R. Nurlybaev, R. Berndtsson, *Water*, 2023, 15(12), 2215.
[2] G. M. P. Kumara, K. Kawamoto, *Water Air Soil Pollut*., 2021, 232(11), 463.
[3] P. Ramos, E. J. Borojovich, O. Zeiri, Y. Amar, M. Gottlieb, *J. Hazard. Mater*., 2023, 457, 131784.
[4] S. S. Alotaibi, H. M. Ibrahim, A. G. Alghamdi, *Applied Sciences,* 2024, 14(23), 10864.
[5] V. J. Inglezakis, A. Kudarova, A. Guney et al., *Sustain. Chem. Pharm*., 2023, 32, 101017.
[6] Y. Zhang, H. Li, M. Chen, X. Zhao, *ACS Omega*, 2023, 8(12), 11021–11032.
[7] I. Nuić, M. Gosar, M. Ugrina, M. Trgo, *Processes*, 2022, 10(4), 639.

SHORT ORAL PRESENTATIONS

COMPARATIVE ASSESSMENT OF IBUPROFEN SORPTION ONTO FRUIT PIT-DERIVED SORBENTS AND NATURAL AND MODIFIED ZEOLITES: A PRELIMINARY STUDY

Ivona Nuić, Lucija Matuzić, Jelena Grubeša, Marin Ugrina, Marina Trgo, Franko Burčul, Ana Vučak
Faculty of Chemistry and Technology, University of Split, Ruđera Boškovića 35, 21000 Split, Croatia
E-mail: ivona@ktf-split.hr

ABSTRACT

The removal of ibuprofen (≈ 1 mg/L) from simulated wastewater was investigated using natural clinoptilolite and its Na-, Fe-, and S-enriched forms, as well as fruit-processing by-products (olive, cherry, and sour cherry pits) at initial pH_o values of 3.06, 4.03, and 5.57. Sorption was strongly pH-dependent, with the highest removal observed at pH_o 3.06 for all sorbents. Among zeolites, Na-enriched clinoptilolite showed the best performance (41%), while fruit pits achieved higher removal efficiencies, reaching up to 81% for sour cherry pits.

Keywords: ibuprofen, fruit pit-derived sorbents, zeolites, wastewater treatment

INTRODUCTION

Ibuprofen, a non-steroidal anti-inflammatory drug, is frequently detected in aquatic environments due to its extensive global consumption and incomplete removal in conventional wastewater treatment processes. Although even low concentrations can affect non-target aquatic organisms and potentially disrupt ecosystem stability [1–3], the regulatory framework for pharmaceuticals in drinking water remains limited. Maximum concentrations are not legally established, and their occurrence is primarily assessed through risk-based evaluations. Moreover, efforts are ongoing to include these compounds on priority substance lists [4]. This highlights the need for effective and reliable removal strategies. Adsorption is a promising approach for the removal of ibuprofen due to its simplicity and efficiency. While conventional adsorbents such as activated carbon and synthetic resins exhibit high performance, their cost and regeneration requirements limit their wider application [1,5]. Consequently, attention has shifted toward low-cost and sustainable alternatives, including zeolites and biosorbents derived from agricultural waste [1,2,6]. In this context, fruit pits and zeolitic materials as abundant, inexpensive, and environmentally friendly sorbents, were evaluated for the removal of ibuprofen from water.

EXPERIMENTAL

Preparation of the ibuprofen-contaminated water

Contaminated water containing ≈ 1 mg/L of ibuprofen was prepared by dissolving ibuprofen (Ibuprofen Anti-inflammatory, Sigma-Aldrich, purity ≥ 98.0%) in methanol (LC-MS grade, Chromasolv, Honeywell), followed by dilution with ultrapure water (Purelab Flex 3, Elga). To optimize sorption, the effect of the initial pH (pH_o) of ibuprofen-contaminated water was evaluated at pH_o values of 5.57 (natural, unadjusted), 4.03, and 3.06, with the latter two adjusted using glacial acetic acid (99.8–100.5%, AnalaR NORMAPUR).

Preparation of sorbent materials

Natural zeolite (NZ) from the Zlatokop deposit (Serbia), containing ≈ 80% clinoptilolite with calcium as the dominant exchangeable cation, was washed and dried, milled, sieved, and chemically modified to enhance its sorption properties. Sodium-enriched zeolite (Na-Z) was obtained by NaCl treatment, iron-enriched zeolite (Fe-Z) by sequential treatment with

$Fe(NO_3)_3·9H_2O$, NaOH, and $NaNO_3$, and sulphur-enriched zeolite (S-Z) by Na_2S at 150 °C [7]. Olive pits (OP), cherry pits (CP), and sour cherry pits (SCP) were collected from local fruit processing plants, washed with distilled water, dried at 40 °C to constant mass, milled, and sieved without separating the shell and kernel to facilitate recycling. A particle size fraction of 0.56–1.00 mm was used for all tested sorbents.

Batch sorption experiments

The 0.5 g of each sorbent was mixed with 50 mL of ibuprofen-contaminated water at 25 ± 2 °C and 230 rpm for 24 h in an orbital shaker. After filtration, equilibrium pH_e was determined. After additional filtration through a 0.20 µm microfilter, the residual ibuprofen concentration (c_r) was analysed by UHPLC–MS/MS (UltiMate 3000RS – TSQ Quantis) equipped with an Accucore™ C18 column (150 × 2.1 mm, 2.6 µm; Thermo Fisher Scientific, Waltham, MA, USA). All experiments were performed in triplicate, and results are reported as mean values.

Zeta potential measurement

Zeta potential of olive, cherry, and sour cherry pits in aqueous ibuprofen solution (pH_o = 5.57) was measured by means of Malvern Zetasizer Ultra device, by dispersing ≈ 1 mg of each sample in 2 mL of solution, followed by ultrasonication for 1–2 min. Measurements were performed in triplicate and reported as mean values.

RESULTS AND DISCUSSION

Sorption capacity (q_e, mg/g)) and removal efficiency (α, %) of ibuprofen were determined from batch experiments and calculated as follows:

$$q = [(c_o - c_r) \cdot V] / m \qquad (1)$$

$$\alpha = [(c_o - c_r)/c_o] \cdot 100 \qquad (2)$$

where c_o and c_r are the initial and residual ibuprofen concentrations (mg/L), m is the sorbent mass (g), and V is the solution volume (L). Figure 1 presents sorption capacity and removal efficiency of the tested sorbents versus the initial pH_o of ibuprofen-contaminated water.

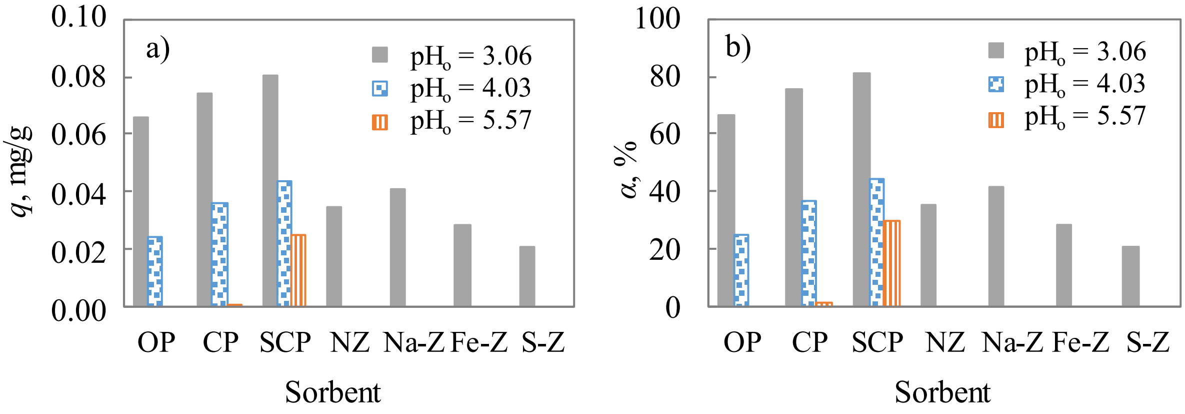


Figure 1. a) Sorption capacity and b) removal efficiency of different sorbent materials for ibuprofen.

The results show marked differences in sorption behaviour depending on both the sorbent type and the initial pH_o. At pH_o 5.57, only two (cherry and sour cherry pits) of the seven sorbents demonstrated measurable sorption, with capacities of 0.001 mg/g and 0.025 mg/g and removal efficiencies of 1.2% and 30.2%, respectively. Decreasing the pH_o to 4.03

increased the capacities of all pits, with sour cherry pits again showing the highest values (0.044 mg/g and 44.6%). Only at the lowest pH$_o$ of 3.06 zeolite samples exhibited ibuprofen removal, with Na-Z achieving the best result of 0.041 mg/g and 41.3%. It is worth mentioning that its modification was done with low-cost and environmentally safe agent. Fruit pit-derived sorbents consistently outperformed zeolites across all tested pH$_o$ values, reaching a maximum removal efficiency of 81.3% for sour cherry pits. This is unsurprising, since zeolites were originally modified for the sorption of heavy metals, yet their effectiveness for ibuprofen was evaluated.

Sorption efficiency is governed by sorbent properties, contaminant speciation, and pH [8,9]. All tested materials had negatively charged surfaces, as indicated by zeta potentials of OP (-36.86 mV), CP (-32.17 mV), SCP (-28.41 mV), and clinoptilolite-based materials (NZ -22.8 mV; Na-NZ -25.7 mV; Fe-NZ -29.7 mV; S-NZ -39.9 mV) [7]. At pH > pK_a (4.91), ibuprofen is mostly anionic ($-\mathrm{COO}^-$) and electrostatically repelled by the negatively charged sorbent surface, resulting in limited sorption at pH$_o$ 5.57, likely via cation-mediated bridging and surface complexation, along with minor contributions from hydrogen bonding and London dispersion forces [6,7,10,11]. At pH < pK_a, ibuprofen, as a weak acid, is largely neutral and more lipophilic minimizing electrostatic repulsion and enhancing sorption. Maximum removal occurred at pH$_o$ 3.06, where partial protonation of surface functional groups further reduces surface negativity. Under these conditions, sorption is dominated by hydrophobic interactions and hydrogen bonding, particularly for sour cherry pits, whose lignin-rich aromatic structure provides abundant binding sites, and for the Na-enriched clinoptilolite, which offers the most accessible cation-mediated sorption sites among the tested zeolites [6,7,10,11]. Literature reports similar maximum sorption of pharmaceutical compounds under strongly acidic conditions (pH ≈ 2) with marked decreases at alkaline pH (> 7), especially for zeolites [11,12]. Equilibrium pH$_e$ values (Figure 2) further support these observations.

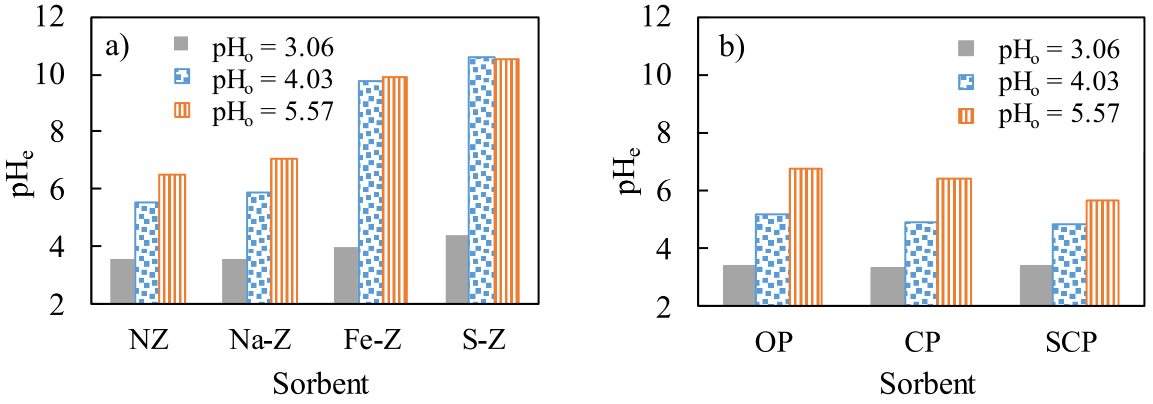


Figure 2. Equilibrium pH$_e$ values after 24 h sorption onto: a) fruit-pit derived sorbents and b) natural and modified zeolites

Zeolites showed higher pH$_e$ after sorption (Fe-Z 9.87 and S-Z 10.52 at pH$_o$ = 5.57), corresponding to lower performance, whereas fruit pits had lower pH$_e$ and higher efficiencies. The lowest pH$_e$ was observed at pH$_o$ = 3.06, corresponding to the most effective conditions. Although lower pH could further enhance removal, highly acidic conditions are not recommended in practical applications due to potential equipment damage and material degradation.

CONCLUSION

These preliminary results demonstrate that ibuprofen removal from contaminated water is highly challenging, with solution pH playing a key role. Although significantly higher removal was achieved at pH_o 3.06, further lowering of pH, while potentially increasing removal efficiency, is neither operationally justified nor practical for water treatment applications. Therefore, efficient removal of pharmaceuticals requires the use of combined or advanced treatment processes. Given their emerging contaminant status, pharmaceuticals should be included in routine water quality monitoring, with maximum allowable concentrations urgently defined. Additionally, readily available and environmentally friendly materials show promising potential (41% removal on Na-enriched clinoptilolite and 81% on sour cherry pits) for use in combined treatment processes or, with further appropriate modification, as standalone sorbents.

Acknowledgment

This research was funded by the EU through the “NextGenerationEU” (project ANTARES, IP-UNIST-28). Part of the equipment used in this research was financed by the EU project KK. 01.1.1.02.0018.

REFERENCES

[1] A.S. Mestre, J. Pires, J.M.F. Nogueira, J.B. Parra, A.P. Carvalho, C.O. Ania, *Bioresour Technol.* 2009, **100**(5), 1720-1726.

[2] M. Patel, A.K. Chaubey, C.U. Pittman Jr., D. Mohan, *Environ. Sci. Adv.*, 2022, **1**, 530-545.

[3] S.D. Kayode-Afolayan, E.F. Ahuekwe, O.C. Nwinyi, *Sci. Afr.*, 2022, **17**, e01288.

[4] S. Han, K. Choi, J. Kim, K. Ji, S. Kim, B. Ahn, X. Zhang, *Aquat. Toxicol.*, 2010, **98**(3), 256-264.

[5] A. Ayati, B. Tanhaei, H. Beiki, P. Krivoshapkin, E. Krivoshapkina, C. Tracey, *Chemosphere*, 2023, **323**, 138241.

[6] D. Smiljanić, B. de Gennaro B, A. Daković, B. Galzerano, C. Germinario, F. Izzo, G.E. Rottinghaus, A. Langella, *J Environ Manage.*, 2021, **15**, 286:112168.

[7] I. Nuić, K. Galov, M. Ugrina, F. Burčul, A. Vučak, *Kem. Ind.*, **75** (3-4), 173-181, 2026.

[8] G. Duman, C. Okutucu, S. Ucar, R. Stahl, J. Yanik, *Bioresource Technol*, 2011, **102**(2), 1869-1878.

[9] S. Farhadi, M. Javanmard, M. Safavi, *Nutr. Food Sci. Res.*, 2022, **9**(1), 19-29.

[10] M. Yamin, Z. K. Ghouri, N. Rohman, J. A. Syed, A. Skelton, K. Ahmed, *J. Mol. Graph. Model.*, 2024, **128**, 108720.

[11] P. Iovino, S. Canzano, S. Capasso, A. Erto, D. Musmarra, *Chem. Eng. J.*, 2015, **277**, 360-367.

[12] P. Szabová, D. Varjúová, M. Kováčová, J. Prousek, I. Bodík, *Pol. J. Environ. Stud.*, 2022, **31**, 10.15244/pjoes/142580.

COMPARATIVE EVALUATION OF KETOPROFEN ADSORPTION ON CETYLPYRIDINIUM – MODIFIED ZEOLITE AND KAOLIN

Milena Obradović[1]*, Milica Ožegović*[1]*, Marija Marković*[1]*, Aleksandra Daković*[1]*, Danina Krajišnik*[2]
[1]Institute for Technology of Nuclear and Other Mineral Raw Materials, Franše d' Epere 86, 11000 Belgrade, Serbia
[2]Department of Pharmaceutical Technology and Cosmetology, Faculty of Pharmacy, University of Belgrade, 11221 Belgrade, Serbia
E-mail:m.obradovic@itnms.ac.rs

ABSTRACT

Natural minerals, such as zeolite and kaolin, possess hydrophilic surfaces that limit their affinity for hydrophobic or anionic molecules such as ketoprofen (KET), a nonsteroidal anti-inflammatory drug (NSAID), commonly found as pollutants in the aquatic ecosystems [1,2]. To overcome this limitation, mineral surfaces are often modified with cationic surfactants, enhancing their adsorption capacities [3]. Surfactant cetylpyridinium (CP) chloride was used to modify the surface of natural zeolite (Z) from Vranjska Banja (Serbia), primarily composed of the mineral clinoptilolite and kaolin (K) from Rgotina (Serbia), mainly composed of the mineral kaolinite. Both Z and K were treated with two levels of CP − 50% and 100% of the external cation exchange capacity of Z and the cation exchange capacity of K. The resulting samples, denoted as ZCP-50, ZCP-100, KCP-50, and KCP-100, were characterized using Fourier transform infrared spectroscopy (FTIR) and determination of zeta potential. In the comparative study, obtained materials were tested for KET adsorption with particular focus on the effects of surfactant loading, mineral type, and solid phase content. The adsorption of KET on the organominerals was studied using different concentrations of suspensions (0.4, 1.0, 2.0, and 4.0 g/L), while the drug concentration was kept constant at 20 mg/L in phosphate buffer at pH 7. Unmodified Z and K did not adsorb KET, however modification with surfactant led to its pronounced increased adsorption. For CP−modified minerals, KET adsorption increased with increasing of the amount of solid phase in the suspension and with increase of the surfactant amount at surfaces of clinoptilolite and kaolinite. For Z and K with the highest amount of CP, the maximum adsorbed amounts of KET under the applied experimental conditions were 4.1 mg/g for KCP-100 and 4.6 mg/g for ZCP-100, indicating that both materials are effective adsorbents for KET.

Keywords: ketoprofen, zeolite, kaolin, adsorption, cetylpyridinium chloride.

ACKNOWLEDGMENT

This research was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia through grant agreements: 451-03-33/2026-03/200023 (Institute for Technology of Nuclear and Other Mineral Raw Materials); and 451-03-33/2026-03/200161 and 451-03-34/2026-03/200161 (University of Belgrade – Faculty of Pharmacy).

REFERENCES

[1] F. Mansouri, K. Chouchene, A. Wali, J. Labille, N. Roche, M. Ksibi, *Chemosphere*, 2024, **353**, 141469.

[2] M. Ožegović, M. Obradović, A. Daković, M. Marković, D. Smiljanić, *Metall. Mater. Data*, 2025, **3**, 69–73.

[3] M. Obradović, A. Daković, D. Smiljanić, M. Ožegović, M. Marković, G. E. Rottinghaus, J. Krstić, *Microporous Mesoporous Mater.*, 2022, **335**, 111795.

CHITOSAN/TETRACYCLINE/ZEOLITE COMPOSITE FILMS: INVESTIGATION OF FUNCTIONAL AND BIOPHARMACEUTICAL PROPERTIES

Danina Krajišnik[1], *Snežana Uskoković-Marković*[2], *Aleksandra Daković*[3], *Marija Marković*[3]
[1]Department of Pharmaceutical Technology and Cosmetology, University of Belgrade – Faculty of Pharmacy, Serbia
[2]Department of Analytical Chemistry, University of Belgrade – Faculty of Pharmacy, Serbia
[3]Institute for Technology of Nuclear and Other Mineral Raw Materials (ITNMS), Belgrade, Serbia
E-mail: danina.krajisnik@pharmacy.bg.ac.rs

ABSTRACT

Zeolite-based biopolymer composites have attracted significant attention for drug delivery, tissue engineering, and wound healing applications due to their inherent biocompatibility, biodegradability, and non-toxicity [1]. The potential use of biocomposites with antibacterial activity is particularly noteworthy [2]. In this study, biopolymeric composite films were prepared using chitosan, a natural cationic polysaccharide polymer [3], and a zeolite-tetracycline (ZTCl) composite. The preparation of ZTCl composite by adsorption of tetracycline (TCl) onto natural zeolite-clinoptiloite from Vranjska Banja deposit has been previously described [4]. Commercial low molecular weight chitosan, glycerol as a plasticizer, and a 1% acetic acid solution were used to prepare the composite film (denoted as FZTCl) by casting and solvent evaporation, maintaining a polymer/ZTCl mass ratio of 1.5:1.0. For comparison, a control film (F0) without the ZTCl was also prepared. The functional properties (mass, thickness, and swelling) of both FZTCl and F0 were evaluated, as well as the drug release profile from FZTCl in pH 7.4 phosphate buffer at 37 °C over 6 h. The average mass and thickness of FZTCl (110 ± 4 mg, 146 ± 9 μm) were higher than those of F0 (70 ± 2 mg, 85 ± 8 μm). The swelling capacities of the films after 6 h (in pH 7.4 phosphate buffer at 37 °C) were up to 270% for F0 and up to 370% for FZTCl. During the testing period approximately 48% of TCl was released in a sustained manner. The physical integrity of the film was maintained and no cracks or splitting were observed during swelling and drug release testing. Further investigations of the antibacterial activity and mechanical properties of zeolite-based polymer composite films will reveal their potential for drug delivery application.

Keywords: natural zeolite; clinoptilolite; tetracycline; functional properties; drug release

ACKNOWLEDGEMENT

This research was funded by the Ministry of Science, Technological Development and Innovation, Republic of Serbia through following Grant Agreements: (No. 451-03-33/2026-03/200161 and 451-03-34/2026-03/200161) (University of Belgrade-Faculty of Pharmacy) and 451-03-33/2026-03/200023 (ITNMS).

REFERENCES

[1] M. Shahjahan, Y. Iqbal, S. Javed, S. Shahid Chatha, T. Tahir, K. Shahzad, T. Salman, M. Qamar, S. Ullah, S. *Rev. Inorg. Chem.*, 2025, https://doi.org/10.1515/revic-2025-0081

[2] M. Haghbin, R. E. Malekshah, M. Sobhani, Z. Izadi, B. Haghshenas, M. Ghasemi, B. S. Kalani, H. Samadian, *Int. J. Biol. Macromol.,* 2023, **235**, 123766.

[3] S. Jagdale, A. Dixit, S. Gaware, B. Agarwal. *Int. J. Biol. Macromol.,* 2023, **257**, 128697

[4] D. Krajišnik, S. Uskoković-Marković, A. Daković, M. Marković, Proc. 10th Slovenian-Serbian-Croatian Symposium on Zeolites, Slovenia, 2024, 83-86.

REMOVAL OF LEAD IONS ONTO NATURAL ZEOLITE IN PRESENCE OF FULVIC AND HUMIC ACIDS

Marina Trgo, Ivona Nuić, Marin Ugrina
Faculty of Chemistry and Technology, University of Split, Rudjera Boskovica 35, 21000 Split, Croatia
marina.trgo@ktf-split.hr

ABSTRACT

Examination of lead ions removal onto natural zeolite is performed in suspensions with presence of organic matter through the addition of commercial liquids Fertireg® and Humistar® commonly used for fertilization of the plants in agriculture. Prepared concentrations of Fertireg® in suspensions were 0.12% and 3% and Humistar® 0.06% and 3% which are recommended for the soil additions. Experiments have shown that Fertireg® has no effect on removal efficiency of lead ions onto zeolite, within the examined range of additions. The presence of the humic acids in the Humistar® has shown increased removal efficiency for lead ions in the suspension with 3% of organic matter and at pH=7-8. From the obtained results the organic matter has no competitive effect in sorption of lead ions onto zeolite. Moreover, there is observed synergy of organic humic acid in lead ions removal. These results could be important for application of natural zeolite in the soil remediation.

Keywords: lead ions, zeolite, fulvic acids, humic acids, soil remediation.

INTRODUCTION

The application of natural zeolites in environmental remediation processes is becoming increasingly significant, particularly for the removal of harmful substances toward which zeolites exhibit a high affinity. These include heavy metal ions, primarily Pb, Zn, Cu, and Cd [1].

However, under real conditions in contaminated soil, organic matter is present in amount greater than 70%, originating mostly from the decomposition of non-living organic matter. Approximately 80–90% of this consists of humic substances formed through natural degradation processes, i.e., humification. Humic substances include both fulvic and humic acids, which play a role in the transport of nutrients to plant roots. These acids are added as commercial products into soils in agriculture to improve plant growth. Therefore, it is important to investigate the influence of the presence of humic and fulvic acids on the efficiency of heavy metal ion removal from soil/aquatic media using natural zeolite as a remediation agent. Fulvic and humic acids are macromolecules with a complex structure possessing multiple functional groups such a phenolic (–OH) and carboxylic (–COOH) that can interact with heavy metals through complex formation or chelation [2,3]. A large number of hydrophilic –OH groups shows different behavior depending on pH, where deprotonation leads to formation of negative sorption sites. Specifically, the presence of organic matter may affect bioavailability of nutrients and enhance the sorption of heavy metal ions into plant body. But it may also reduce heavy metal bioavailability [4] and improve soil remediation increasing their removal efficiency onto zeolite.

Recent studies show that there are different interpretations of the mechanisms of metal ions binding to zeolites in the presence of organic acids. They can adsorb to silica particles in sandy soils, probably through hydrophobic interactions, creating aggregates which improve both, better drainage and water holding capacity. The fate, bioavailability and migration of metal ions in soils are closely linked to the presence of adsorbed humic substances. This research aims to provide insight into the sorption capacity of zeolites as a function of pH, as well as the concentration of fulvic and humic acids and concentration of lead ions.

EXPERIMENTAL

The lead ions solutions with a concentrations of 2 and 4 mmol/L were prepared by dissolving $Pb(NO_3)_2$ salt in ultrapure water and the exact concentration was determined by complexometric analysis and flame atomic absorption spectrometry (FAAS).

The natural zeolite sample originated from the Vranjska Banja deposit (Republic of Serbia) and contains a high content of clinoptilolite. It was sieved to a particle size of 0.09–0.56 mm, dried at 40°C, and stored in sealed glass containers. Experiments were carried out in 100 mL of aqueous Pb^{2+} solution with different initial concentrations, by mixing with 1 g of zeolite (control samples) and repeated in the presence of a defined concentration of fulvic and humic acids.

Fertireg® and Humistar® are commercial products used for plant nutrition. Fertireg® contains a high concentration of fulvic acids, while Humistar® contains a high concentration of humic acids. Their addition to the zeolite/aqueous Pb^{2+} system resulted in a content of organic acids, corresponding to the additions recommended for agricultural use.

Experiments with fulvic acids were performed in mentioned suspensions at solution/zeolite ratio 100 mL/1g and different Fertireg® volume content of 0.12% and 3%. After 24 hours in shaker at room temperature (20–22°C) suspension is filtrated and lead content in filtrate is determined using FAAS. All measured pH values after equilibration where on range 3.5–3.8.

Experiments with humic acids were performed in same suspensions at different Humistar® volume content of 0.06% and 3% and two pH solutions from 5–6 and 7–8. After 24 hours in shaker at room temperature (20–22°C) suspension is filtrated and lead content in filtrate is determined using FAAS. All pH values after equilibration where on range 4.56–5.83.

The removal efficiency in all experiments is calculated using equation:

$$\alpha = ((c_o - c_e)/c_e) \cdot 100 \quad (1)$$

where:

α – removal efficiency, %

c_o – initial lead concentration, mmol/L

c_e – equilibrium lead concentration, mmol/L.

RESULTS AND DISCUSSION

The graphical comparison of the Pb^{2+}removal efficiency onto natural zeolite in presence of different Fertireg® content at two examined lead concentrations are presented in Figure 1. In control suspensions, without organic matter – fulvic acids the removal efficiency is in accordance with our previous investigations, increases with increasing of initial concentration of lead ions.

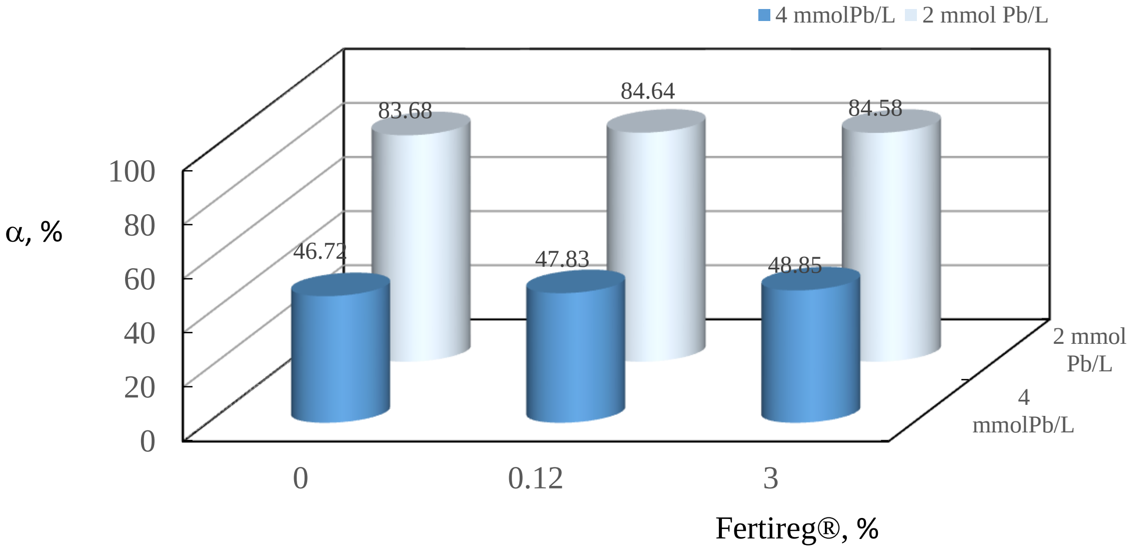


Figure 1. Comparison of the removal efficiency of lead ions onto zeolite in solutions with different content of organic matter-fulvic acids.

Removal of lead ions in presence of humic acids at different content of organic matter-humic acids and pH values are presented on the Figure 2.

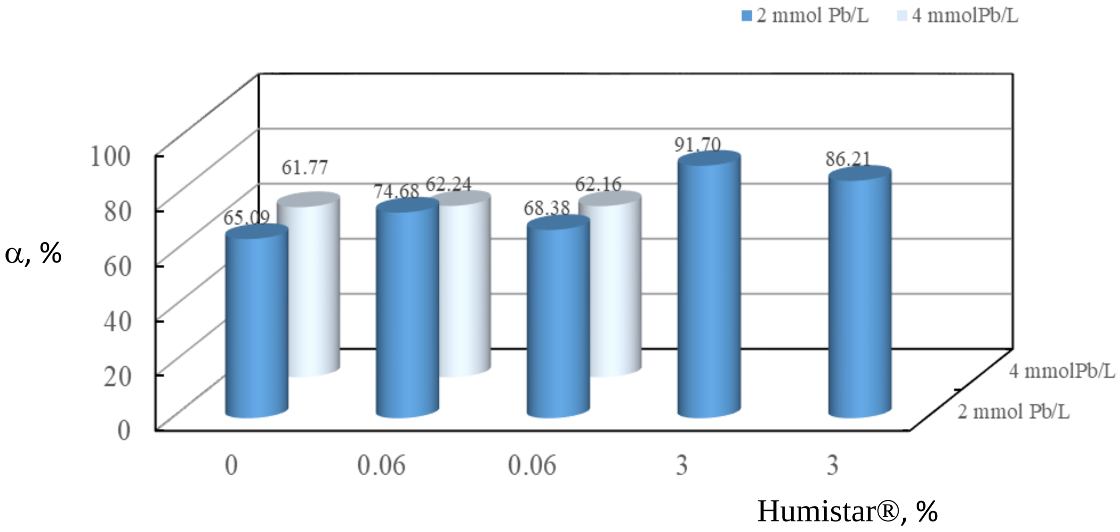


Figure 2. Comparison of the removal efficiency of lead ions onto zeolite in solutions with different content of organic matter-humic acids, at different pH values.

According to the Figure 1, addition of organic matter doesn't affect removal efficiency of lead ions onto natural zeolite. Namely, molecule of the fulvic acid has many –OH and –COOH groups which are not dissociated in acidic medium and in this experiment their sorption affinity toward positive ions are not recorded. Values of pH=3.5–3.8 in equilibrium confirms that precipitation does not occur and removal of Pb(II) is ion exchange and sorption onto natural zeolite.

From the Figure 2 is visible that addition of Humistar® increases removal efficiency compared to control suspensions without organic matter. In suspensions with 0.06% of Humistar® removal efficiency increases compared to control solutions, for both initial Pb(II) concentrations, where at pH=7–8 equals 74.68% what is higher compared to result 68.38% obtained for the pH=5–6. In suspensions with 3% of Humistar® removal efficiencies are highest, particularly at pH=7–8, where is obtained the highest value of 91.70%. This can be explained with deprotonation of the humic acid molecule in weak alkaline medium, where releasing the H^+ the humic acid molecule becomes negative sorption site for the lead ions [5]. This big molecule behaves as carrier of the metal ions and due to its sorption to the zeolite particle, combined with ion exchange as a main mechanism, contributes to the higher overall removal efficiency. Also the equilibrium pH=4.56–5.83 confirms that precipitation doesn't occur. Many authors tried to explain the mechanism of mass transfer of metal ions in the presence of the big organic molecules. Some of them means that competition of the organic matter can decrease cation sorption, while others present organic molecule as a sorbent for nutrients enabling their assimilation by plants [6]. This mechanism is very important for successful fertilization of the soil. This research aims to explain effect of the organic matter on the remediation of the polluted soil using natural zeolite.

CONCLUSION

It can be concluded that organic matter as the Fertireg® and Humistar® additions into suspensions do not affect natural zeolite as established remediation agent in removal of the lead ions from the aqueous solutions e.g. wastewaters. Moreover, there is a positive contribution without competitive effect as has been presumed in the literature. Application of the remediation using zeolites can be carried out simultaneously with soil fertilization.

Acknowledgment

This research was funded by the EU through the "NextGenerationEU" (project ANTARES, IP-UNIST-28).

REFERENCES

[1] N. Vukojević Medvidović, I. Nuić, M. Ugrina, M. Trgo, *Water Air Soil Pollut.*, 2018 **229**, 367.

[2] S. Wang, T. Terdkiatburana, M. O. Tad´e, *Separ. Purif. Technol.*, 2008, **62**, 64.

[3] Alnasra, F.I. Khalili, F.A. Alhnafat, *Desalin. Water Treat.*, 2024, **320**, 100604.

[4] J. An, E. Hea Jho, K. Nam, *J. Hazard. Mater.*, 2015, **286**, 236.

[5] L. Dai, W. Zhao, G. Wang, B. Wei, K. Zhang, T. Han, G. Ma, *Desalin. Water Treat.*, 2021, **235**, 221.

[6] M. Aminul Islam, D. W. Morton, B. B. Johnson, M. J. Angove, *Separ. Purif. Technol.*, 2020, **247**, 116949.

INFLUENCE OF SYNTHETIC ZEOLITES ON THE LEAF-TO-STEM RATIO IN FORAGE PEA

Nevena Rističević, Igor Đurđić, Branka Govedarica,Tanja Jakišić, Vesna Milić
University of East Sarajevo, Faculty of Agriculture, 30 Vuka Karadžića Street, East Sarajevo, Republic of Srpska, Bosnia and Herzegovina, e - mail: *nevena.risticevic@pof.ues.rs.ba.*

ABSTRACT

An experiment was conducted in the greenhouse of the Faculty of Agriculture, University of East Sarajevo, in the spring of 2025 to examine the effects of a control treatment and ten types of synthetic zeolites, as well as their application rates, on the leaf-to-stem ratio in forage pea. The experiment used 20 L containers filled with soil, with treatments including different amounts of zeolite. Forage pea seeds were sown in the prepared containers, harvesting was done at the beginning of the pod formation stage.. Naturally dried leaves and stems were weighed, and the leaf-to-stem ratio was determined. Based on the obtained data, the percentage proportions of leaves and stems were calculated, and the results were statistically analyzed using analysis of variance (ANOVA). The analysis of variance indicated a statistically significant effect of zeolite type on the proportions of leaves and stems, while the amount of zeolite had no significant effect. Additionally, a significant interaction between zeolite type and application rate was observed for leaf proportion. The application of certain zeolite types resulted in an increased proportion of leaves compared to the control treatment. The highest leaf proportion was recorded in the Purmol 10ST (65.13%) and ZEOflair 6010 (63.39%) treatments, while the highest stem proportion was observed in the control treatment, what suggests that the application of appropriate zeolite types can improve the leaf-to-stem ratio and, consequently, the forage quality of forage pea.

Keywords: forage pea, zeolites, leaf, stem, forage quality

INTRODUCTION

The cultivation of annual forage legumes under production conditions in the Republic of Srpska and Bosnia and Herzegovina does not have a long tradition, where forage pea (*Pisum sativum* var. *arvense* L.) is significant in haylage production, less frequently in silage, and is one of commonly grown crops in the cropping structure, most often cultivated in mixtures with cereals such as oats, rye, or triticale (Đurđić, 2020).

The leaf-to-stem ratio is one of the key indicators of forage crop quality, as it directly affects the chemical composition and digestibility of biomass. A decrease in the leaf-to-stem ratio is associated with increased fiber content, particularly cellulose and lignin, which reducesthe nutritional value of forage (Kara and Sürmen, 2023). During plant growth, the content of structural carbohydrates increases, while protein content decreases, further reducing the digestibility and nutritional value of biomass (Kara and Sürmen, 2023). Forage pea is an important source of protein in animal nutrition, and its feeding value largely depends on the morphological characteristics of the plant (Uzun et al., 2005).

Zeolites affect soil porosity and pore size distribution based on soil structure, quality, zeolite type, and reaction conditions. They influence water infiltration rate, hydraulic conductivity, water content, water retention capacity, andreduce fertilizer leaching (Comegna et al., 2023; Prisa et al., 2023).

This study aimed to determine the effect of different zeolite application rates, mixed with soil, on the stem-to-leaf ratio, and consequently on forage quality.

EXPERIMENTAL

This experiment was conducted as a factorial experiment based on a randomized complete block design with three replications in 20-liter pots filled with 15.31 kg of soil. Five seeds of spring pea (*Pisum sativum* L.) variety 'Saša' were sown in each pot. The research was conducted in the greenhouse of the Faculty of Agriculture, University of East Sarajevo, on spring forage pea (*Pisum sativum* var. *arvense* L.) during 2025.

A two-factor experiment was established with three replications. Factor A was the application of different zeolites: a control treatment (A0) and ten synthetic zeolites produced by Zeochem in Zvornik. Seven zeolites (denoted as ZEOflair) are hydrophobic and organophilic since they have a high content of SiO_2: ZEOflair 100 (A1), ZEOflair 350 (A2), ZEOflair 800 (A3), ZEOflair 810 (A4), ZEOflair 6010 (A5), ZEOflair 6034 (A6), and ZEOflair 6035 (A7). ZEOflair 100, ZEOflair 350, ZEOflair 800, and ZEOflair 810 belong to the MFI structural type, while ZEOflair 6010, ZEOflair 6034, and ZEOflair 6035 represent a mixture of zeolite and silica gel.

Three zeolites were from the Purmol group of alkaline aluminosilicates, belonging to the LTA structural zeolite type. Since LTA zeolites are well know for their hudrophilicity and high cation exchange capacities, and having in mind that they are fine powders (3–10 μm diameter) it is expected here that they absorb water and prevent its rapid evaporation or leaching into deeper soil layers, (crucial during dry periods) and to bind fertilizer ions (such as K^+ and NH_4^+), preventing them from being washed away by rain, and then gradually release them directly to plant roots (slow-release fertilizer effect). These zeoites are: potassium type with 3 Å pores, denoted Purmol 3ST (A8), recommended for use in applications where co-adsorption of molecules other than water may be a concern; sodium type with 4 Å pores, denoted as Purmol 4ST (A9), which combines a high water adsorption capacity and is characterized by a lower pH value; and sodium type with 10 Å pores, Purmol 10ST (A10), a non-standard formulation with broader pores. In addition to water, it can adsorb larger molecules and impurities such as certain hydrocarbons.

Factor B was the different zeolite application rate mixed with soil: 30.625 g (B_1), 61.25 g (B_2), and 122.5 g (B_3), i.e., zero, 2, 4, and 6 g kg^{-1} of soil. The soil used in the experiment was previously utilized as a disposal site for waste materials, including deposited soil from construction sites and spent compost used in mushroom (*Agaricus bisporus*) production. The soil used in the experiment had a neutral reaction (pH_{KCl} 7.11), high nitrogen content (0.44%) and humus content (2.83%).

A random sample for analysis was taken from five pots and three replications, with one plant selected at the stage of first pod maturity. The leaves were then separated from the stem and naturally dried, after which they were weighed to determine the total sample mass. Based on these values, the percentage share of leaves and stems in the total biomass was calculated.

Statistical analysis was performed using the SPSS software package (Statistical Package for the Social Sciences), applying analysis of variance (ANOVA). The significance of differences between means was determined using the LSD test.

RESULTS AND DISCUSSION

The stem-to-leaf ratio results are presented in Table 1. Leaf and stem proportions varied depending on the zeolite type and application rate. On average, stems accounted for 44.94% and leaves for 55.06%. Zeolite type significantly affected both stem and leaf proportions. The highest leaf proportion was recorded for Purmol 10ST (65.13%), while the lowest values were observed for ZEOflair 350 (41.28%) and ZEOflair 800 (41.93%). High leaf proportions were also found for ZEOflair 6010, Purmol 4ST, ZEOflair 6034, ZEOflair 6035, and Purmol 3ST. In the control treatment, stem proportion (51.90%) was higher than leaf proportion (48.10%). The highest stem proportions were recorded for ZEOflair 350 (58.72%) and ZEOflair 800

(58.07%), while the lowest were found for Purmol 10ST (34.87%), ZEOflair 6010 (36.61%), and Purmol 4ST (38.35%). All observed differences were statistically significant.

Table 1. Effects of different types and application rates of synthetic zeolites on the stem to leaf ratio in forage pea

Zeolite	Zeolite application rate (g)	Stem (%)	Leaf (%)
Control	0	51.90^{B}	48.10^{CDbc}
ZEOflair100	1	45.93	54.07^{asc}
	2	64.74	35.26^{de}
	3	37.98	62.02^{ab}
	Average	49.55^{B}	50.45^{BC}
ZEOflair 350	1	77.51	22.49^{ef}
	2	54.16	45.84^{cd}
	3	44.50	55.50^{abc}
	Average	58.72^{A}	41.28^{D}
ZEOflair 800	1	87.41	12.59^{f}
	2	40.48	59.52^{abc}
	3	46.32	53.68^{abc}
	Average	58.07^{A}	41.93^{D}
ZEOflair 810	1	49.98	50.02^{bc}
	2	47.73	52.27^{abc}
	3	46.51	53.49^{abc}
	Average	48.07^{B}	51.93^{BC}
ZEOflair 6010	1	42.12	57.88^{abc}
	2	34.31	65.69^{a}
	3	33.39	66.61^{a}
	Average	36.61^{CD}	63.39^{A}
ZEOflair 6034	1	40.14	59.86^{abc}
	2	37.62	62.38^{ab}
	3	46.33	53.67^{abc}
	Average	41.36^{C}	58.64^{A}
ZEOflair 6035	1	42.26	57.74^{abc}
	2	46.35	53.65^{abc}
	3	39.20	60.80^{abc}
	Average	42.60^{C}	57.40^{AB}
Purmol 3ST	1	41.02	58.98^{abc}
	2	46.59	53.41^{abc}
	3	36.12	63.88^{ab}
	Average	41.24^{C}	58.76^{A}
Purmol 4ST	1	39.76	60.24^{abc}
	2	37.25	62.75^{ab}
	3	38.05	61.95^{ab}
	Average	38.35^{CD}	61.65^{A}
Purmol 10ST	1	35.6	64.40^{ab}
	2	34.39	65.61^{a}
	3	34.61	65.39^{a}
	Average	34.87^{D}	65.13^{A}
Mean		44.94	55.06
Maximum		87.41	66.61
Minimum		33.39	12.59

Considering the effect of zeolite application rates, no clear trend of increase or decrease in leaf and stem proportions was observed, indicating that the applied zeolite amounts did not significantly affect these parameters.

The interaction between zeolite type and application rate was not significant for stem proportion, but a significant interaction effect was observed for leaf proportion.

The results indicate that zeolite type plays a more important role in determining the plant's morphological composition than the application rate. Similar findings were reported by Kara and Sürmen (2023), who emphasized the importance of plant structure for forage quality, while Uzun et al. (2005) highlighted that morphological differences among plants significantly affect the nutritional value of forage.

Table 2. ANOVA parameters: zeolite type and application rate

Parameters	**F test/ LSD**	**Type of zeolite (A)**	**Zeolite application rate (B)**	**AB**
Stem (%)	F exp	2.585^{*}	1.549^{ns}	0.713^{ns}
	0.05	5.70	3.12	9.87
	0.01	7.58	4.15	13.13
Leaf (%)	F exp	21.096^{**}	$0,696^{ns}$	5.198^{**}
	0.05	6.38	3.5	11.06
	0.01	8.49	4.65	14.70

CONCLUSION

Based on the conducted research, it can be concluded that zeolite application affects the leaf-to-stem ratio in forage pea. Zeolite type had a statistically significant effect, while the application rate showed no significant influence. The highest leaf proportion, indicating better forage quality, was recorded with Purmol 10ST and ZEOflair 6010, whereas the highest stem proportion was observed with ZEOflair 350 and ZEOflair 800. These results suggest that selecting an appropriate zeolite type is important for improving forage pea quality, while the applied amount is less decisive. Further research should investigate the mechanisms of zeolite action and their effects on other quality parameters in forage pea and other forage crops.

REFERENCES

1. A. Comegna, C. Belviso, A.R. Rivelli, A. Coppola, G. Dragonetti, A. Sobhani, S.Lovelli, Analysis of critical water flow and solute transport parameters in different soils mixed with a synthetic zeolite. *Catena* 2023, **228**, 107150.
2. I. Đurđić, 2020. Qualitative and Quantitative Traits of Selected Spring Field Pea Genotypes Depending on Top Dressing and Agroecological Growing Conditions. *Doctoral dissertation. Faculty of Agriculture East Sarajevo*, 1-144. In Bosnian.
3. E. Kara, M. Sürmen, Yield and Quality Characteristics of Forage Pea Varieties at Different Phenological Stages. *ADÜ Ziraat Dergisi*, 2023, 20(2), 295–301.
4. D. Prisa, Zeolites: A potential strategy for the solution of current environmental problems and a sustainable application for crop improvement and plant protection. GSC Advanced Research and Reviews 2023, **17(1)**, 011–022.
5. A. Uzun, U. Bilgili, M. Sincik, I. Filya, E. Acikgoz, Yield and quality of forage type pea lines of contrasting leaf types. *European Journal of Agronomy*, 2005, **22(1)**, 85–94.

EFFICIENCY OF ORGANOZEOLITE AND ORGANOBENTONITE IN THE REMOVAL OF DIESEL FROM CONTAMINATED WATER

Natalija Petronijević[1], Aleksandra Daković[2], Milena Obradović[2], Jelena Avdalović[3], Jelena Milić[3], Kristina Joksimović[3], Vladimir Beškoski[1]

[1]University of Belgrade – Faculty of Chemistry, Studentski trg 12-16, 11000 Belgrade, Serbia

[2]Institute for Technology of Nuclear and Other Mineral Raw Materials, Bulevar Franše d' Epere 86, 11000 Belgrade, Serbia

[3]University of Belgrade – Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia

npetronijevic@chem.bg.ac.rs

ABSTRACT

Contamination of groundwater and surface waters with diesel fuel represents a significant environmental challenge. The water–soluble fraction of diesel (WSFD) is of particular interest because of its toxic effects on aquatic ecosystems and human health. Among remediation techniques, adsorption methods stand out as they are efficient, inexpensive, simple to apply, and require little energy.

In this study, the possibility of using organozeolite (OZ) and organobentonite (OB) for the removal of WSFD was investigated. The raw material for obtaining OZ was a natural zeolite clinoptilolite from the Zlatokop deposit (Vranje, Serbia). The zeolitic surface was modified with the cationic quaternary ammonium salt hexadecyltrimethylammonium bromide (HDTMA-Br) at 100% of the zeolite's external cation exchange capacity [1]. Similarly, for preparation of OB, a natural clay bentonite from the Šipovo deposit (Bosnia and Herzegovina) was modified with the same quaternary ammonium salt at 100% of its cation exchange capacity. The starting raw materials, OZ and OB were characterized by differential scanning calorimetry with thermogravimetry and Fourier transform infrared spectroscopy prior to use.

The adsorption kinetics was performed by mixing 50 mg of each organomineral with 50 mL of WSFD at the initial concentration of 20 mg/L at time interval 0–1440 min. The success of the adsorption process was estimated by analyzing the WSFD concentration in test OZ and OB flasks before and after adsorption in the liquid phase according to ISO 9377-2, by Agilent 7890A gas chromatograph with a flame ionization detector. Both adsorbents bound more than 90% of diesel, with the difference that equilibrium for OZ was reached after 60 min, while for OB after 120 min. Pseudo-second-order kinetic model best described the kinetics data. Isotherm study was investigated by mixing of 50 mg of OZ or OB with 50 mL of various concentrations of WSFD (2–20 mg/L) for 60 min. The equilibrium data for both adsorbents were best described by a linear isotherm model. Maximum adsorbed amounts of WSF, under applied experimental conditions were 17.7 mg/g for OZ and 17.0 mg/g for OB. Since OB contains much higher amount of HDTMA (328 mg/g) compared to OZ (36 mg/g), the similar WSFD maximum adsorbed amounts and faster kinetics make OZ more economically suitable material for treatment of water contaminated with WSFD.

Keywords: organozeolite, organobentonite, the water–soluble fraction of diesel.

Acknowledgements: This work was financially supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (grant numbers 451-03-33/2026-03/200023, 451-03-33/2026-03/200026, and 451-03-33/2026-03/200168).

REFERENCES

[1] M. Lukić, A. Daković, K. Joksimović, J. Milić, M. Obradović,V. Beškoski, J. Avdalović, *Minerals* **2024**, 14, 1287.

LEACHATE TREATMENT THROUGH A NATURAL ZEOLITE COLUMN

Jasna Hrenović[1], *Tomislav Ivanković*[1], *Blanka Dadić*[1], *Ivan Jukić*[2], *Aleksandra Anić Vučinić*[3]

[1] University of Zagreb, Faculty of Science, Zagreb, Croatia
[2] Bikarac d.o.o., Šibenik, Croatia
[3] University of Zagreb, Faculty of Geotechnical Engineering, Varaždin, Croatia
E-mail: jasna.hrenovic@biol.pmf.hr

ABSTRACT

Leachate from the old municipal landfill Bikarac (Šibenik, Croatia) is characterized by high concentrations of biologically non-degradable substances, intense brown colour caused by humic compounds, and a significant bacterial load. Bacteria originating from municipal waste may pose a public health risk and should be effectively removed during leachate treatment. In this study, purification of raw leachate was tested in a fixed-bed column filled with commercially available natural zeolitized tuff (NZ). During 48 h of continuous filtration (63.3 bed volumes), NZ demonstrated efficient removal of heterotrophic bacteria (up to 93.7%) and suspended solids (up to 61.3%). Bacterial breakthrough occurred at 59 bed volumes, likely due to biofilm saturation on the NZ surface. Outlet pH initially decreased due to cation exchange of NZ, but returned to inlet values by the end of the experiment. The intense brown colour of the leachate remained unchanged. These results confirmed that NZ can serve as a low-cost adsorbent for removal of bacteria and particles, although it was ineffective for colour removal from raw leachate.

Keywords: bacteria, filtration, immobilization, zeolitized tuff.

INTRODUCTION

Bikarac d.o.o. is a regional municipal company and the waste management centre for Šibenik-Knin County in Croatia. It is responsible for the reception, treatment and disposal of municipal waste generated within the county. The waste management centre comprises a mechanical-biological treatment facility and a composting plant for the treatment of separately collected biodegradable waste. The Bikarac site also includes a landfill that has been in operation since the 1980s and has been gradually modernised in line with the development of the waste management system. Over the past seven years, only pre-treated waste resulting from the mechanical-biological treatment process, with a significantly reduced biodegradable content, has been landfilled. This has contributed to reducing environmental risks, greenhouse gas emissions and pressure on landfill capacity. It is estimated that approximately 1.7 to 2 million tonnes of waste have been landfilled at the Bikarac site from the start of operations to date.

The composition of landfill leachate depends on numerous factors and varies over time and between locations, making its treatment particularly challenging. The municipal landfill Bikarac generates stabilized leachate rich in biologically nondegradable substances [1]. Leachate contains high concentrations of diverse bacterial species. Bacteria originating from municipal waste may pose a potential risk to mammalian health and should therefore be effectively removed from leachate [2].

Natural zeolitized tuff (NZ), rich in clinoptilolite, is a nontoxic material that lacks antibacterial activity. However, NZ particles provide a rough surface suitable for the attachment of various bacteria, enabling the formation of stable bacterial biofilms [3]. Consequently, NZ particles are capable of capturing up to 10^9 bacteria per gram [4].

The aim of this study was to evaluate the feasibility of leachate purification, with particular emphasis on bacteria removal, using a column filled with NZ.

EXPERIMENTAL

The leachate was sampled in June 2025 at the Bikarac LLC municipal landfill near City of Šibenik in Croatia. The commercially available NZ ZeoSand® (Velebit Agro, Croatia), containing a minimum of 80% clinoptilolite, of particle size 0.5 - 1 mm was used for experiment. The NZ was washed with deionised water to remove dust and dried prior to filling the column. The glass liquid chromatography column of 10 mm inner diameter, 15 mm outer diameter and 200 mm in length (GE Healthcare Ltd, London, UK) was filled with NZ and flow rate of 19.79 mL/h was ensured by peristaltic pump (Gilson minipuls3). The filtration of leachate through the fixed-bed column was flowed for 63.3 bed volumes (BV) that lasted 48h.

In inlet and outlet water the bacteriological and physico-chemical parameters were followed. Total heterotrophic bacteria were cultivated on nutrient agar at 22°C/3 days after decimal dilution of water in sterile phosphate buffered saline. The number of heterotrophic bacteria counted in technical triplicate was expressed as colony forming units (CFU) per one mL of water. Colour (PtCo scale) and suspended solids (mg/L) were measured spectrophotometrically (Hach DR2500). The pH value of water was measured by WTW SenTix81 electrode. The purification of leachate was expressed as a percent of reduction in outlet as compared to inlet water.

RESULTS AND DISCUSSION

Total heterotrophic bacteria were successfully removed (up to 93.7%) in the outlet as compared to the inlet water (Table 1) up to 33 BV, when a decrease of removal was evidenced. According to the polynomial fitting, the breakthrough for bacteria removal occurred at 59 BV (Figure 1).

Table 1. Performance of column filled with ZeoSand®. Inlet water: pH 8.37; suspended solids 403 mg/L; total heterotrophic bacteria 7.32±0.06 log CFU/mL.

Bed volume	**Heterotrophic bacteria removal (%)**	**Suspended solids removal (%)**	**pH**
1.3	82.8±0.9	29.0	7.32
2.6	83.1±0.4	30.5	7.60
4.0	84.6±1.2	36.0	7.60
26.4	93.6±0.8	61.3	8.19
33.0	93.7±0.3	56.3	8.22
35.6	69.6±2.5	57.1	8.22
59.4	-21.2±14.7	39.7	8.30
63.3	-3.1±9.2	35.5	8.38

The successful removal of bacteria during the first part of experiment followed by failure of removal is consistent with the previously described model of biofilm formation on NZ [3]. Bacteria were quickly attached onto the surface of NZ particles, start to excrete the extracellular polymeric substances and formed a stable biofilm. No further incorporation of bacteria present in water occurred in the formed biofilm. If nutrients are available in water, only multiplication of bacteria inside the initially formed biofilm can occur. Similar purification pattern was described in a column filled with NZ from Vranjska Banja in Serbia [5]. Numbers of bacterium *Acinetobacter baumannii* suspended in natural spring water were reduced up to 99% during the first 8 h of the run, while after 24 h numbers were even higher in the outlet as compared to inlet water. The column breakthrough was also reported for removal of total heterotrophic bacteria present in effluent from the municipal wastewater treatment plant [5].

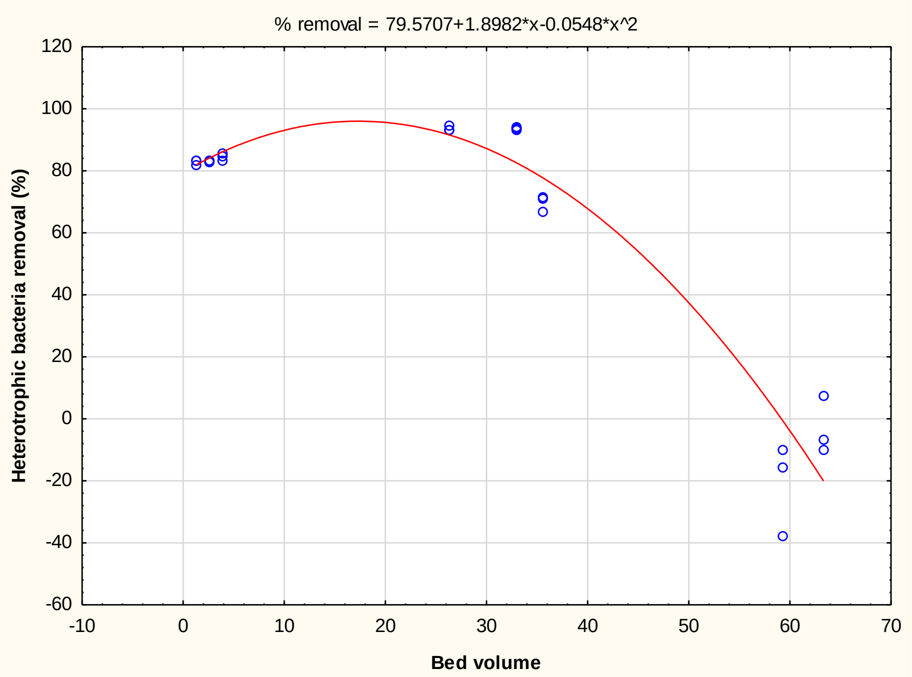


Figure 1. Removal of total heterotrophic bacteria in outlet as compared to inlet water during the filtration of leachate through the fixed-bed column filled with NZ.

Removal of suspended solids followed the similar polynomial fit (Table 1), but complete breakthrough did not occur up to the end of experiment. Suspended solids in leachate were attributed to the microorganisms and nondegradable organic flocks. Drop of suspended solids removal during the experiment, but without breakthrough, suggested the retention of larger flocs inside pores of column filling, while bacteria were not retained in column due to the biofilm formed on the surface of NZ particles.

Passage of leachate through the NZ column resulted in a decrease in outlet pH up to one pH unit, with the effect becoming progressively weaker over time (Table 1). After the passage of 63.3 BV, the pH of the outlet water equilibrated with that of the inlet water. The observed pH shift toward neutrality after passage through the column is attributed to cation exchange processes occurring at exchangeable sites within the structure of Na/Ca-clinoptilolite. Ammonium ions (NH_4^+), abundant in the leachate, replaced exchangeable Na^+ and Ca^{2+} ions within the clinoptilolite framework [1]. Due to the weakly acidic nature of ammonium, its partial hydrolysis in the aqueous phase contributed to a slight increase in H^+ concentration, resulting in moderate outlet water acidification. By the end of the experiment, the return of outlet pH to inlet values indicates exhaustion of the zeolite's exchangeable cation capacity and its buffering effect.

The inlet water was highly brown, exceeding 500 PtCo units, and this intense colour persisted in the outlet water throughout the experiment (data not shown). The brown colour of the leachate was attributed to dissolved organic compounds, particularly humic substances, which are negatively charged under neutral to slightly alkaline conditions. This behaviour reflects the limited capacity of NZ to remove humic substances [6].

The examination of total bacteria removal, without focus on single bacterial species, from raw leachate by the use of nonsterilized commercial NZ offers the valuable results for the application in real scale.

CONCLUSION

Filtration of landfill leachate through a column filled with NZ resulted in significant removal of total heterotrophic bacteria and suspended solids during the initial phase of operation. However, bacterial removal was time-limited due to saturation of the biofilm layer on NZ particles, with breakthrough occurring at approximately 59 BV. Outlet pH initially shifted toward neutrality, but returned to the inlet value by the end of the experiment, indicating the exhaustion of zeolite's buffering capacity. The intense brown colour of the leachate was not removed by passage of leachate through the NZ column.

The commercially available NZ ZeoSand® proved to be a low-cost and environmentally friendly material for removal of bacteria from landfill leachate. While long-term operation is limited, NZ column filtration may be suitable as a post-treatment polishing step in leachate treatment technology.

REFERENCES

[1] M. Ugrina, L. Tomić, A. Buzdovačić, M. Petrić, M. Trgo, N. Vukojević Medvidović, I. Nuić, S. Matešić, Landfill leachate treatment by batch multi-stage process using natural zeolite, *Proceedings of the 8th Serbian-Croatian-Slovenian Symposium on Zeolites*, Belgrade, Serbia, 2019, 109-112.

[2] S. Renou, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: Review and opportunity. *J. Hazard. Mat.,* 2008,150, 468-493.

[3] J. Pavlović, J. Hrenović, D. Povrenović, N. Rajić, Advances in the applications of clinoptilolite-rich tuffs. *Materials*, 2024, 17, 1306.

[4] J. Hrenović, Interaction of zeolites and phosphate accumulating bacteria, Wong, T.W. (ed.): *Handbook of Zeolites: Structure, Properties and Applications*, Nova Science Publishers, Inc, Hauppauge NY, SAD, 2009, 439-467.

[5] T. Ivanković, J. Dikić, S. Rolland du Roscoat, S. Dekić, J. Hrenović, M. Ganjto, Removal of emerging pathogenic bacteria using metal-exchanged natural zeolite bead filter. *Water Sci. Technol.*, 2019, 80, 1085-1098.

[6] Y. Zhan, Z. Zhu, J. Lin, Y. Qiu, J. Zhao, Removal of humic acid from aqueous solution by cetylpyridinium bromide modified zeolite. *J. Environ. Sci. (China)*, 2010, 22, 1327-34.

OPTIMIZATION OF THE SYNTHESIS OF ANIONIC ZIRCONIUM ELLAGATE FRAMEWORKS

Miljan Radošević[1,2], Ciara Byrne[1,2], Aljaž Škrjanc[1,2], Nataša Zabukovec Logar[1,2]
[1]National Institute of Chemistry, Hajdrihova 19,1000 Ljubljana, Slovenia
[2]University of Nova Gorica, Vipavska 11c, SI-5270 Ajdovščina, Slovenia
E-mail: miljan.radosevic@ki.si

ABSTRACT

Over the past few decades, a wide range of new materials and approaches, for the removal of pollutants from water, has been developed. One of these approaches has been the use of metal-organic frameworks (MOFs). Neutral frameworks MOFs have already been successfully tested for their efficiency with dyes, metals and even some pharmaceutical pollutants. Recently, the preparation of an anionic zirconium ellagate MOF, SU-102, was reported[1] and its stability as well as efficiency in the adsorption of cationic pollutants were tested. SU-102 uses DMF as an organic structure directing agent (OSDA), which later can be exchanged for alkali metal ions. Other OSDAs were also tested and other formed structures were reported.[2]

Our work focuses on the expansion of the OSDA used in zirconium ellagate framework synthesis, and the consequent evaluation of the stability of both as-prepared and ion-exchanged frameworks. The idea is to explore different parameters such as: impact of different OSDAs, various times and temperatures have on phase formation, crystallinity and morphology. The prepared crystalline frameworks will then be ion-exchanged, and the OSDA evaluated based on ease of exchange and framework retention. XRD confirmed that all the SU-102 samples are phase pure. Further textural and structural properties was examined and compared using SEM, Nitrogen physisorption and TG.

Keywords: metal-organic frameworks, environmental remediation, charged frameworks

ACKNOWLEDGEMENTS:

We would like to express our gratitude to Mojca Opresnik for her help with SEM and Edi Kranjc for PXRD measurements. We would like to thank the Slovenian Research and Innovations agency programme P1-0021 for funding.

REFERENCES

[1] E. Svensson Grape, A. J. Chacón-García, S. Rojas, Y. Pérez, A. Jaworski, M. Nero, M. Åhlén, E. Martínez-Ahumada, A. E. Galetsa Feindt, M. Pepillo, M. Narongin-Fujikawa, I. A. Ibarra, O. Cheung, C. Baresel, T. Willhammar, P. Horcajada and A. K. Inge, *Nat. Water 2023 15*, 2023, **1**, 433–442.

[2] E. Svennson Grape, A. Lopez-Olvera, Y. Zheng,Y. Xia, T. Willhammar and A. K. Inge, *ChemRxiv*, 2025, [Preprint], https://doi.org/10.26434/chemrxiv-2024-n90rn-v2

SIMULTANEOUS THERMAL ANALYSIS OF COMPOSITE SORBENTS FOR THERMOCHEMICAL ENERGY STORAGE

Jan Marčec[1,2], *Nataša Zabukovec Logar*[1,2], *Alenka Ristić*[1*]
[1]National Institutue of Chemistry, Department of Inorganic Chemistry and Technology, Laboratory for Adsorbents, Hajdrihova 19, Ljubljana, Slovenia
[2]University of Nova Gorica, School of Science, Vipavska 13, Ajdovščina, Slovenia
E-mail:alenka.ristic@ki.si

ABSTRACT

Thermochemical energy storage (TCES) is an emerging technology under investigation for harvesting waste heat and promoting the integration of renewable energy to combat climate change. Heat released during the adsorption of a working fluid, most commonly water, onto an adsorbent can be used for space heating or domestic hot water [1]. Recent research has focused on developing thermochemical materials with high water adsorption capacity, high energy storage capacity, suitable kinetics, and structural stability for the efficient utilization of waste or renewable heat.

Here, we present an experimental determination of the heat released after adsorption of water on ZIF-90 and 94 (Zeolitic Imidazolate Framework)-derived nanoporous carbons (NPC) and their composites with 10, 15, and 20 wt.% LiCl under operating conditions of Tads/Tdes/Tcond = 30/120/10 °C, using a simultaneous thermal analyser (accuracy ±0.1 μg) (STA 449 F1, Netzsch, Germany). This STA consists of a thermobalance connected to a water vapour generator (ProUmid MHG 100), which is linked to the gas supply of the STA device. The samples were placed in an open aluminium crucibles with a maximum volume of 85 μL

Due to relatively low water uptake at 30 %RH (0.15 g/g for NPC-90 and 0.14g/g for NPC-94), the heats of adsorption for pure NPCs are 506.3 and 466.0 kJ/kg for NPC-90 and NPC-94, respectively. In contrast, the LiCl-containing composites exhibit significantly increased water adsorption capacity (0.69 g/g) and heats of adsorption, up to four times higher: composites containing 20 wt.% LiCl achieved 2086.9 and 2091.9 kJ/kg.

The study demonstrates the potential of NCP-LiCl composites for TCES applications.

KEYWORDS: composites, NPC-LiCl, STA TG-DSC, heat of adsorption, thermochemical energy storage

ACKNOWLEDGMENT

We would like to thank the Slovenian Research and Innovation Agency for funding the Nanoporous materials research programme (P1-0021). We thank Dr. Daniel Lager (AIT Wien) for measurements using STA 449 F1 (Netzch, Germany), which was carried out within the RISEnergy project (GA. No. 101131793).

REFERENCES

[1] A. Ristić, Chapter: “Sorption Material Developments for TES Applications” in Advances in Energy Storage, A. Hauer (ed), Wiley, 2022, 631–653.

INSIGHTS INTO STRUCTURE DIRECTION DURING ZEOLITE SYNTHESIS

Ana Palčić, Sanja Bosnar
Laboratory for Synthesis of New Materials, Division of Materials Chemistry, Ruđer Bošković Institute,
Bijenička cesta 54, Zagreb, Croatia.
E-mail:ana.palcic@irb.hr

ABSTRACT

Zeolite synthesis is governed by a complex interplay of chemical parameters that control nucleation, crystal growth, and framework topology [1]. Structure directing effect in this reaction arises from the ability of (in)organic species (structure-directing agents – SDAs) to govern the organization/assembly of (alumino)silicate species into distinct framework types due to their specific interactions with soluble silicate species, stabilizing particular building units and intermediates that favor the formation of a certain zeolite array [2].

In this work, the structure directing roles of aluminium sources and alkali cations were systematically investigated in dense hydrogel systems at 150 and 180 °C with or without milling. Complementary analytical techniques were employed to characterize the obtained samples: PXRD, SEM, AAS, NMR, TG, LLS and ATR-IR. The collected set of experimental data offered a comprehensive understanding of structural, morphological and chemical properties of the materials, allowing insight into the processes occurring in the course of the zeolite formation process. The results reveal that both the availability of aluminium species and the presence of inorganic cations critically direct the formation pathways toward BEA- and/or MFI-type zeolite materials. Aluminium acts as a primary structure-directing factor for zeolite beta formation. In the absence of aluminium, only amorphous silica phases form, confirming its indispensable role in initiating zeolite beta crystallization. Temperature introduces a secondary structure-directing effect by shifting the kinetic balance between competing BEA and MFI frameworks. Alkali cations introduce an additional level of structure direction independent of aluminium. The consistent appearance of MFI phase in alkali cation containing systems confirms that cation–silicate interactions play a decisive role in directing MFI framework formation. These findings provide important insights into rational control of zeolite synthesis by tuning both organic and inorganic structure-directing factors.

Keywords: zeolites, structure directing, phase selection, milling

ACKNOWLEDGMENT

A.P. gratefully acknowledges the financial support from the Ruđer Bošković Institute through the internal program KP-2023a, funded within the framework of the National Recovery and Resilience Plan 2021–2026 (NPOO).

REFERENCES

[1] J. Mallette, K. Shilpa, J. D. Rimer, *Chem. Rev.*, 2024, **124**, 3416-3493.
[2] L. Gómez-Hortigüela, M. Á. Camblor, Chapter "Introduction to the Zeolite Structure-Directing Phenomenon by Organic Species: General Aspects" in: Insights into the Chemistry of Organic Structure-Directing Agents in the Synthesis of Zeolitic Materials, L. Gómez-Hortigüela (Ed.), Structure and Bonding, Vol. 175, Springer Cham, 2018.

COMPARATIVE ASSESSMENT OF ZEOLITE-ASSISTED MAGNETIC ELECTROCOAGULATION FOR THE TREATMENT LAUNDRY GREYWATER AND COMPOST WASTEWATER

Nediljka Vukojević Medvidović, Ladislav Vrsalović, Sandra Svilović, Senka Gudić, Elena Pedišić*
Faculty of Chemistry and Technology, University of Split, Ruđera Boškovića 35, 21000 Split, Croatia
E-mail*: nvukojev@ktf-split.hr

ABSTRACT

Electrocoagulation (EC) combined with synthetic zeolite addition (EC-SZ) and static magnetic field assistance (EC-SZ-SMF) was applied for the treatment of synthetic laundry greywater and compost wastewater. The results showed that all EC-hybrid systems effectively reduced turbidity (>95 %) and chemical oxygen demand - COD (54–84 %), with iron electrodes showing higher overall performance for both wastewaters. Based on the total operating cost calculation, Fe-based systems with zeolite and magnetic assistance were the most economical.

Keywords: zeolite-based hybrid process, electrocoagulation, magnet, operating cost

INTRODUCTION

In recent decades, wastewater treatment has become crucial for environmental protection and sustainable resource use, and although classical EC processes efficiently remove suspended and dissolved organic and inorganic solids, their performance can be limited in complex and highly loaded waters, prompting the development of hybrid approaches [1]. This work examines the combined approach of EC and sorption on synthetic zeolite (SZ) with static magnetic field (SMF) assistance for the treatment of compost wastewater and laundry greywater.

EXPERIMENTAL

***Wastewaters* -** Two different wastewaters with similar chemical oxygen demand (COD) values were used: compost wastewater prepared from Agro-compost (with pH 6.57, electrical conductivity 2.09 mS/cm, turbidity 94.07 NTU, and COD 414.72 mg O_2/L) [2], and synthetic laundry greywater prepared from commercial laundry detergent Persil Active Gel (with pH 7.80, electrical conductivity 1494 μS/cm, turbidity 380 NTU, and COD 454.72 mg O_2/L).

Electrodes - Two alloys were used as electrode materials: carbon steel (Fe=98.27%, Cu=1.17%) and Al AA2007 alloy (Al=92.58%, Cu=3.84%). The detailed elemental composition has been reported previously [3].

***Zeolite* -** Synthetic zeolite SZ (particle size of 40 μm, purchased from Alfa Aesar), was used in the EC hybrid process in the amount of 15 g/L. PXRD and SEM-EDS analysis, as well as cation exchange capacity (CEC) of 6.22 meq/g, and density of 2.0605 g/cm^3, were previously reported [1].

***EC-Hybrid processes* -** EC-hybrid processes were conducted in an electrochemical cell filled with 500 mL of solution and a pair of electrodes. Three types of processes were tested: electrocoagulation alone (EC), EC combined with SZ addition (EC-SZ), and EC combined with both SZ addition and ~~a~~ static magnetic field assistance (EC-SZ-SMF). SMF assistance was provided by placing the EC reactor directly on a 0.55 T NdFeB magnet positioned beneath the electrode region. All treatments were carried out under constant conditions of current density of 0.0182 A/cm^2, NaCl electrolyte concentration of 0.5 g/L, electrode spacing of 3 cm, stirring at 250 rpm, and a contact time of 30 min. The pH, turbidity, and COD were recorded and compared, as well as total operational costs, including energy and electrode costs, in order to assess the cost-effectiveness of the EC-hybrid process for treatment of laundry greywater and compost wastewater with two different electrode materials.

RESULTS AND DISCUSSION

Figure 1 compares the pH change during different EC-hybrid processes (EC, EC-SZ, and EC-SZ-SMF) with Al and Fe alloy electrodes for the treatment of compost wastewater and laundry greywater. All EC-hybrid processes showed a gradual increase in pH over reaction time, which is typical for EC due to cathodic water reduction and formation of hydroxide ions (OH^-) [3]. Iron electrodes led to a slightly higher pH increase compared to Al electrodes, which can be related to differences in hydrolysis behaviour of Fe and Al species formed during the process. Al^{3+} tends to form aluminate species (AlO_2^- / $[Al(OH)_4]^-$) that consume OH^-, whereas Fe^{2+} and Fe^{3+} form hydroxo species with lower net OH^- consumption. Although such trends are sometimes interpreted using Pourbaix diagrams, it should be noted that EC operates under non-equilibrium conditions, and these diagrams provide only a general indication of possible species. The addition of SZ further enhanced the pH increase through ion exchange and interactions with ionic species and water, shifting the balance of ions and leading to a higher pH. Magnetic assistance had a mostly minor effect on pH, which is consistent with our previous study on compost wastewater [1]. However, a deviation was observed for the EC-SZ-SMF system with Fe electrodes in laundry greywater, and is in agreement with literature data [4]. Final pH values reached strongly alkaline conditions (≈10–11) for Fe systems and moderately alkaline conditions (≈8–9.5) for Al systems, indicating the influence of electrode material and wastewater composition.

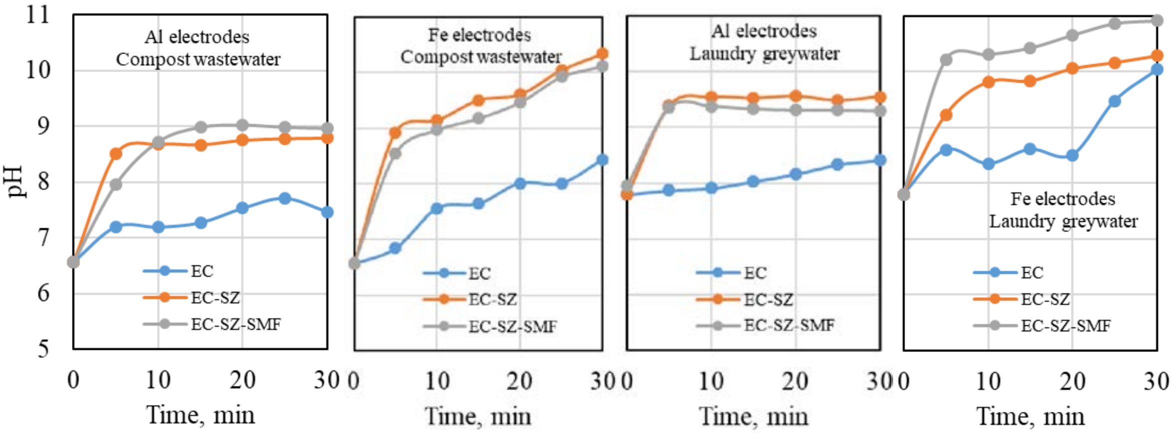


Fig. 1. Comparison of pH values change during different hybrid processes (EC, EC-SZ and EC-SZ-MAG) with Al and Fe electrodes for treatment of compost wastewater and laundry greywater.

Figures 2 and 3 present COD and turbidity reductions for different EC-hybrid configurations. COD removal ranged from 54 % to 84 % for both wastewater types, with the EC process generally achieving the highest removal. Turbidity removal was remarkably high in all cases, exceeding 95 %, despite the large difference in initial turbidity (94.07 NTU for compost wastewater and 380 NTU for laundry greywater). The addition of SZ and SMF assistance did not significantly improve removal efficiency. Differences between EC-SZ and EC-SZ-SMF were small and depended on the electrode material, with slightly higher removal observed for Al electrodes and slightly lower for Fe electrodes in the presence of SMF. Given the small differences, these variations cannot be clearly attributed to magnetic effects alone. Based on COD and turbidity reduction results, effective removal was achieved using the standalone EC process with Fe electrodes for both wastewater types, while Al electrodes also showed comparable removal efficiency in compost wastewater.

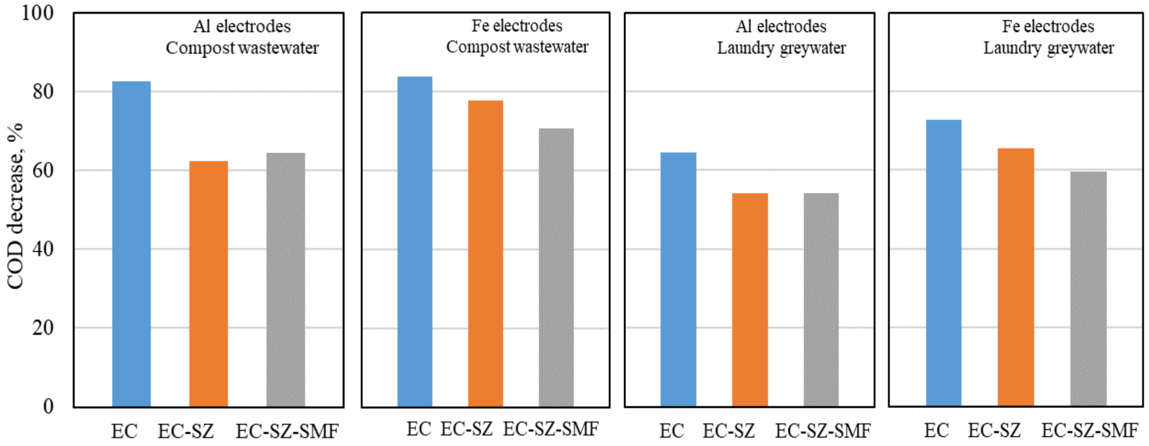


Fig. 2. Comparison of percentage of COD decrease after different EC-hybrid processes (EC, EC-SZ and EC-SZ-SMF) with Al and Fe electrodes for treatment of compost wastewater and laundry greywater.

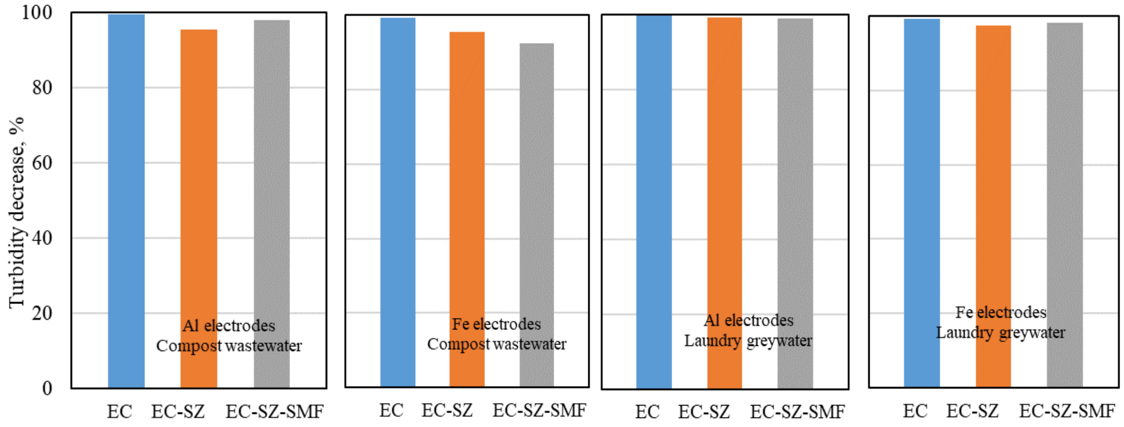


Fig. 3. Comparison of percentage of turbidity decrease after different EC-hybrid processes (EC, EC-SZ and EC-SZ-SMF) with Al and Fe electrodes for treatment of compost wastewater and laundry greywater.

In addition to electrochemical efficiency, material and energy costs must be considered. Material costs include the cost of the electrode, zeolite, magnet, and electrolyte. Here, we will focus only on electrode cost as a part of material cost. Electrode costs were estimated by weighing the electrodes before and after treatment to obtain actual consumption, and multiplying by representative European market prices (Fe ≈ €1/kg; Al ≈ €3/kg) [5].

Table 1. Comparison of electrode, energy and total operating cost.

Hybrid type	Electrode material	Electrode cost, €/m³	Electricity cost, €/m³	Total operating cost, €/m³
Compost wastewater				
EC	Al	1.09	5.13	6.22
EC-SZ	Al	0.89	4.78	5.67
EC-SZ-SMF	Al	1.31	6.97	8.27
EC	Fe	0.44	1.48	1.92
EC-SZ	Fe	0.44	1.29	1.73
EC-SZ-SMF	Fe	0.41	1.30	1.71
Laundry greywater				
EC	Al	0.98	5.79	6.77
EC-SZ	Al	1.11	6.72	7.83
EC-SZ-SMF	Al	0.89	6.17	7.06

EC	Fe	0.41	2.20	2.60
EC-SZ	Fe	0.43	1.78	2.22
EC-SZ-SMF	Fe	0.39	1.61	2.00

Energy costs were calculated based on the electricity consumption per unit volume of treated wastewater, determined as $E=U\cdot I\cdot t/V$, where U is the applied voltage (V), I is the current (A), t is the operation time (h), and V is the reactor solution volume (m^3) [2,3]. The resulting energy consumption was multiplied by the average EU electricity price of 0.22 €/kWh, for non-household consumers [5]. Total operating costs (TOC) were then calculated as the sum of electrode and energy costs (see Table 1).

Results in Table 1 showed that Fe electrodes resulted in significantly lower costs compared to Al electrodes for both wastewaters. The addition of SZ and SMF assistance increases the total operating cost for Al-based systems, while the cost of Fe-based hybrid systems decreases and becomes more stable. The lowest TOC was observed for EC-SZ-SMF with Fe electrodes for both wastewaters (1.71 €/m^3 for compost wastewater and 2.00 €/m^3 for laundry greywater). Electricity costs dominate the TOC for Al electrodes, whereas for Fe electrodes the contributions of electrode and energy costs are more balanced, resulting in lower overall TOC.

CONCLUSION

EC-hybrid processes using Fe and Al electrodes were effective for treatment of both wastewaters. The highest COD and turbidity removal was achieved with the standalone EC process. Differences between EC-SZ and EC-SZ-SMF were small and depended on the electrode material. Although COD and turbidity removal were lower with the addition of zeolite and the presence of SMF, these configurations resulted in lower total operating costs when Fe electrodes were used.

Acknowledgment: This work was supported by the EU NextGenerationEU program under the ANTARES project (No. IP-UNIST-28).

REFERENCES

[1] N. Vukojević Medvidović, L. Vrsalović, S. Svilović, S. Gudić, L. Peran, Hybrid Electrocoagulation with Al Electrodes Assisted by Magnet and Zeolite: How Effective Is It for Compost Wastewater Treatment? *Appl. Sci.*, 2025, **15**, 8194. https://doi.org/10.3390/app15158194.

[2] N. Vukojević Medvidović, M. Brnadić, S. Svilović, S. Gudić, L. Vrsalović, Electrocoagulation, Zeolite and Magnetic Assistance for Wastewater Treatment: Assessing the Role of Electrode Material. *Kem. Ind.*, 2026, **75** (3-4 (special issue)), 191-200. https://doi.org/10.15255/KUI.2025.043.

[3] S. Svilović, N. Vukojević Medvidović, L. Vrsalović, A. Kulić, Combining natural zeolite and electrocoagulation with different electrode materials–electrode surface analysis and Taguchi optimization. *Appl. Surf. Sci. Adv.*, 2022, **12**, 100330, https://doi.org/10.1016/j.apsadv.2022.100330.

[4] M. Ni'am, F. Othman, J. Sohaili, Z. Fauzia, Combined Magnetic Field and Electrocoagulation Process for Suspended Solid Removal from Wastewater, Proceedings of the 1st International Conference on Natural Resources Engineering & Technology, Putrajaya, Malaysia, 2006, 384-393. doi: 10.13140/2.1.5161.4082.

[5] European Commission. Raw Materials Information System (RMIS): Metal Prices and Supply Data. Available online: https://rmis.jrc.ec.europa.eu (accessed on 15 March 2026).

SORPTION-ORIENTED EVALUATION OF THE SELECTIVITY OF IRON SULFIDE-FUNCTIONALIZED NATURAL ZEOLITE CLINOPTILOLITE FOR Hg(II) IN THE PRESENCE OF COMPETING DIVALENT HEAVY METAL IONS

Marin Ugrina[1], *Ivona Barišić*[1], *Antonija Jurič*[2], *Ivona Nuić*[1], *Ana Kokeza*[3], *Marina Trgo*[1], *Martin Gaberšek*[4], *Teja Čeru*[4], *Mateja Gosar*[4]
[1]University of Split, Faculty of Chemistry and Technology, Ruđera Boškovića 35, 21000 Split, Croatia
[2]Regional Veterinary Institute Split, Croatian Veterinary Institute, Poljička cesta 33, 21000 Split, Croatia
[3]Public Health Institute of Split, Vukovarska 46, 21000 Split, Croatia
[4]Geological Survey of Slovenia, Dimičeva ulica 14, 1000 Ljubljana, Slovenia
E-mail: mugrin@ktf-split.hr

ABSTRACT

The sorption-oriented selectivity of iron sulfide-functionalized natural zeolite clinoptilolite (FeSZ) for Hg(II) in the presence of competing divalent heavy metal ions was investigated. The following selectivity order for FeSZ was observed: Hg > Pb > Cd > Cu > Zn > Ni > Co > Mn, with no competitive effect from other ions on Hg uptake, demonstrating the superiority of FeSZ as a material for the remediation of mercury-contaminated sites.

Keywords: iron sulfide-functionalized natural zeolite clinoptilolite, heavy metals, selectivity.

INTRODUCTION

The remediation of soils in the vicinity of the Idrija mine in Slovenia is of considerable importance for preventing mercury dispersion and mitigating adverse effects on the broader ecosystem. Moreover, the contaminated area of Idrija does not represent exclusively a local environmental issue, as it directly affects the occurrence of methylmercury in the northern Adriatic Sea. Specifically, the Idrijca and Soča-Isonzo rivers constitute the primary pathways for the transport of mercury to the Gulf of Trieste [1]. Accordingly, remediation of this area is imperative to limit or prevent the formation of methylmercury. To achieve this objective, various *in situ* and *ex situ* remediation strategies can be considered, among which *in situ* approaches, especially those based on sorption processes, are generally more readily implementable [2]. Consequently, the choice of sorbent plays a pivotal role in determining the success of the sorption process. The selection of a suitable material for *in situ* soil remediation depends on sorption capacity and mercury selectivity, as well as biocompatibility and cost-effectiveness. Natural zeolite minerals exhibit all of the aforementioned characteristics, with the exception of high mercury selectivity. Since iron oxides and sulfides naturally act as mercury scavengers in the hydrogeological layer, simple surface modification of natural zeolites with iron sulfide species can markedly enhance their selectivity for mercury. Therefore, this study aims to assess the selectivity of iron sulfide-functionalized natural zeolite clinoptilolite toward Hg(II) in the presence of competing divalent heavy metal ions.

EXPERIMENTAL

Sample preparation

The natural zeolite clinoptilolite (NZ) collected from the Zlatokop deposit (Vranjska Banja, Serbia) was ground and sieved to a particle size of 0.6–0.8 mm and used as a support for the stabilization of iron sulfide particles. The chemical modification of NZ was performed in two stages, following procedures described by Schwartzman and Cornell [3] and Liu et al. [4]. In the first stage, 1 g of NZ was refluxed at 90 °C with 50 mL of 1 mol/L $Fe(NO_3)_3 \cdot 9H_2O$ solution at pH 8.5 for 48 h, followed by treatment at 150 °C for 4 h with 10 mL of 1 mol/L $Na_2S \cdot 9H_2O$ solution. The obtained iron sulfide-functionalized natural zeolite clinoptilolite

(FeSZ) was washed with ultrapure water until neutral pH and a negative sulfide test were achieved, and then dried in an oven at 40 °C.

The selectivity of FeSZ toward Hg(II) over other selected divalent heavy metal ions (Pb, Cd, Cu, Zn, Ni, Co, Mn) was investigated through sorption-oriented experiments using single-, binary-, and multi-component solutions at $\text{pH} \approx 2$, since mercury starts to precipitate at $\text{pH} > 2.45$. Nitrate salts [$(Hg(NO_3)_2 \cdot H_2O$, $PbNO_3$, $Cd(NO_3)_2 \cdot 4H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$] were used to prepare the solutions in ultrapure water, and the pH of the solutions ($\text{pH} \approx 2$) was adjusted with 1 mol/L HNO_3. The initial concentrations of the single-component solutions were 2 mmol/L. In binary equimolar systems (Hg-Pb, Hg-Cd, Hg-Cu, Hg-Zn, Hg-Ni, Hg-Co, Hg-Mn) the individual heavy metal concentrations were 2 mmol/L, i.e. 4 mmol/L total concentration. In the multi-component equimolar system (8-component) the individual heavy metal concentrations were 2 mmol/L, giving a total concentration of 16 mmol/L. All experiments were conducted in batch mode with a solid-to-liquid ratio of 10 g/L for 24 h at 230 rpm and ambient temperature. The initial and equilibrium concentrations of the heavy metals were measured using flame atomic absorption spectrometry (FAAS) on a PinAAcle 900F spectrometer. The equilibrium amount of heavy metals sorbed on FeSZ, q_e (mmol/g), and the corresponding removal efficiency at equilibrium, α_e (%), were calculated using Equations (1) and (2):

$$q_\text{e} = (c_\text{o} - c_\text{e}) \cdot \frac{V}{m} \qquad (1) \qquad\qquad \alpha_\text{e} = \frac{(c_\text{o} - c_\text{e})}{c_\text{o}} \cdot 100 \qquad (2)$$

where c_o and c_e represent the initial and equilibrium heavy metal concentrations (mmol/L), V is the solution volume (L), and m is the mass of FeSZ (g).

RESULTS AND DISCUSSION

The sorption selectivity of FeSZ for divalent heavy metal ions (Hg, Pb, Cu, Cd, Zn, Co, Ni, Mn) in single-component aqueous solutions is presented in Figure 1.

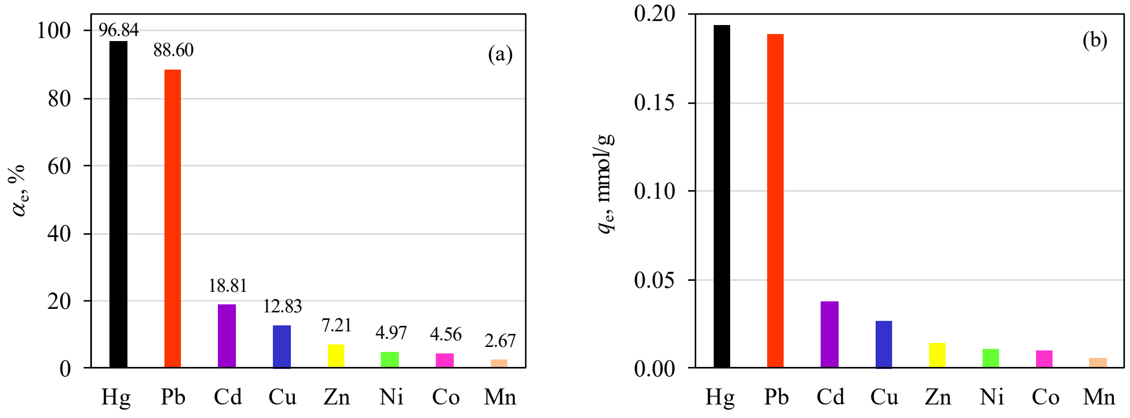


Figure 1. Selectivity of FeSZ toward various divalent heavy metal cations in single-component solutions, expressed in terms of α_e (a) and q_e (b).

The results shown in Figure 1a indicate that Hg and Pb were removed in the highest percentage, reaching 96.84% and 88.60%, respectively. Then follow Cd (18.81%), Cu (12.83%), Zn (7.21%), Ni (4.97%), Co (4.56%), and Mn (2.67%). The highest sorption capacities were achieved for Hg (0.194 mmol/g) and Pb (0.189 mmol/g), while those of the other metal cations were below 0.050 mmol/g (Figure 1b). Based on these results, the selectivity sequence for single-component solutions is as follows: Hg > Pb > Cd > Cu > Zn > Ni > Co > Mn.

Since the selectivity of sorbents toward heavy metal cations is concentration-dependent, the effect of concentration in binary systems was eliminated by using equimolar solutions. The removal efficiency and sorption capacity of FeSZ for heavy metals in binary equimolar systems are shown in Figure 2.

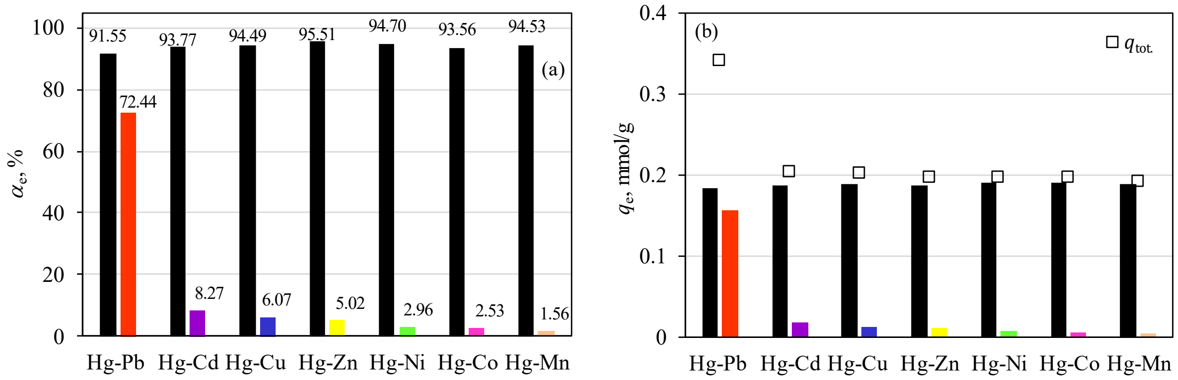


Figure 2. Selectivity of FeSZ towards Hg in the presence of different divalent heavy metal cations in binary equimolar systems, expressed in terms of α_e (a) and q_e (b).

In all tested equimolar binary systems, Hg removal efficiency ranged from 91% to 95% (Figure 2a), confirming the exceptional selectivity of FeSZ toward Hg. Compared to single-component systems, the presence of Hg in binary systems most strongly inhibits the sorption of Mn and least affects Pb, indicating that FeSZ exhibits high selectivity toward Hg and Pb. Furthermore, the sorption capacity of FeSZ for Hg in binary systems decreased slightly compared to that in single-component systems (Figure 2b). A similar trend was observed for Pb, while the sorption capacities of the other heavy metals decreased by nearly twofold. Figure 2b also shows an increase in the total sorption capacity ($q_{tot.}$) in binary systems compared to single-component systems, with the highest value observed in the Hg–Pb system. This is attributed to the higher total concentration of heavy metals in the binary system (4 mmol/L), which increases the concentration gradient and serves as the driving force for overcoming the resistance to mass transfer into the pores and cavities of FeSZ. The results from binary systems exhibit the same selectivity order as observed in single-component solutions.

The removal efficiency of divalent heavy metal cations and the sorption capacity of FeSZ in the multi-component system are shown in Figures 3.

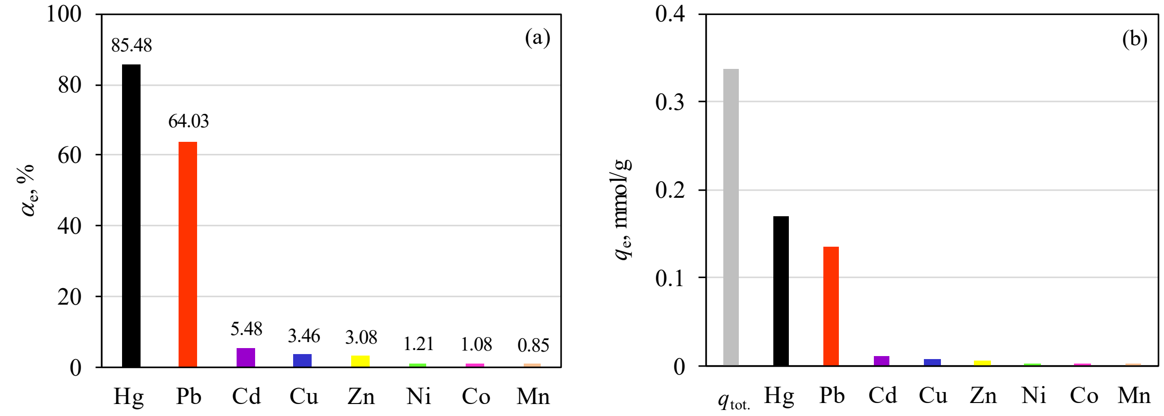


Figure 3. Selectivity of FeSZ towards Hg in the presence of seven divalent heavy metal cations in a multi-component equimolar system, expressed in terms of α_e (a) and q_e (b).

Figure 3a shows that a significant amount of Hg (85.48%) was sorbed even in the presence of equimolar concentrations of the other seven heavy metals. This indicates an extremely high affinity of Hg for FeSZ, as well as FeSZ pronounced selectivity for Hg over other metal cations in both single-component and binary systems. In addition, a significant reduction in the removal of other cations except Pb was observed. The sorption capacity of Hg decreased slightly in the presence of other heavy metals (Figure 3b), indicating that Hg is preferentially sorbed on FeSZ, with the competitive effect of the other seven heavy metal cations being almost negligible. The total sorption capacity of FeSZ in the multi-component system increased compared to that in the binary and single-component systems, due to the higher total concentration of heavy metals (16 mmol/L) and, consequently, the greater driving force of the process. Ultimately, the selectivity in all tested systems follows the same order: Hg > Pb > Cd > Cu > Zn > Ni > Co > Mn.

The selectivity of a sorbent depends on the nature of its functional groups, as well as on the hydrated ionic radius and electronegativity of the heavy metals. Based on the hydrated ionic radius, the affinity of heavy metals is expected to follow the sequence: Pb > Ni > Cu > Hg > Co > Cd > Zn > Mn, as ions with smaller hydrated radii can diffuse more easily onto the surface of the solid [4]. Furthermore, higher electronegativity corresponds to greater affinity for the sorbent. Accordingly, the expected affinity sequence is: Pb > Hg > Ni > Cu > Co > Cd > Zn > Mn [5]. However, the theoretical affinity differs from the experimental results. Given the well-known high affinity of Hg for sulfide species, a two-step chemical modification of natural zeolite was carried out to immobilize sulfide species on the zeolite surface. According to the solubility product constants of metal sulfides, the expected selectivity sequence is: Hg > Cu > Pb > Cd > Zn > Co > Ni > Mn [6]. Although minor deviations occur, this sequence closely matches the experimentally determined order.

CONCLUSION

The prepared FeSZ exhibited absolute selectivity toward Hg in all tested systems regardless of the presence of one or more additional heavy metal cations. This finding justifies the implementation of zeolite modification. The pronounced selectivity of FeSZ toward Hg can be attributed to the nature of the sorbent and the complex sorption mechanism, which, in addition to ion exchange, involves complexation with sulfide species. Accordingly, FeSZ represents a highly promising sorbent for the remediation of mercury-contaminated environments.

Acknoweldgement

This work was supported by the bilateral Croatian-Slovenian project “Application of modified natural sulfur-based zeolites for remediation of mercury-contaminated soil from the Idrija mine area in Slovenia” (2025–2026), founded by the Croatian Ministry of Science, Education and Youth of the Republic of Croatia and Slovenian Research and Innovation Agency (ARIS) as well as by the project ANTARES (IP-UNIST-28) granted by the European Union – “NextGenerationEU” and the project ExtremEarth (J7 60124) founded by ARIS.

REFERENCES

[1] T. Teršič, H. Biester and M. Gosar, *Geoderma*, 2014, **226-227**, 213–222.

[2] L. Wang, D. Hou, Y. Cao, Y. Sik Ok, F.M.G. Tack, J. Rinklebe and D. O'Connor, *Environ. Int.*, 2020, **134**, 105281.

[3] U. Schwertmann, R. M. Cornell, Iron Oxides in the Laboratory, Preparation and Characterization, Second Completely Revised and Extended Edition, Wiley-VCH, Weinheim, 2000, 121-123.

[4] Liu, A. Khan, Z. Wang, Y. Chen, S. Zhu, T. Sun, D. Liang, H. Yu, *Water*, 2020, **12** 1027. E. R. Nightingale, J. Phys. Chem., 1959, **63**, 1381-1387.

[5] D. R. Lide, Handbook of Chemistry and Physics, 79th ed. CRC Press, Boca Raton, 1998, 5-93.

[6] J. F. Blais, Z. Djedidi, R. Ben Cheikh, R. D. Tyagi, G. Mercier, *Pract. Period. Hazard., Toxic, Radioact. Waste Manag.*, 2008, **12**, 135-149.

DEPENDENCE OF ACID BLUE 111 ADSORPTION EFFICIENCY ON pH VALUE USING MODIFIED NATURAL CLINOPTILOLITE

Stevan Stupar[1], Nemanja Vučković[1], Dušan Mijin[2], Sanja Jevtić[2], Jelena Dikić[3]
[1]University of Criminal Investigation and Police Studies, Faculty of Forensic Sciences and Engineering, Cara Dušana 196, 11080, Belgrade, Serbia
[2]University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia
[3]Innovation center of the Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade
E-mail: stevan.stupar@kpu.edu.rs

ABSTRACT

Technological advances have benefited humanity but also increased environmental pollution, with the textile industry being a major source of water contamination. Anthraquinone dyes, such as Acid Blue 111, are widely used in textiles [1]. Acid Blue 111 is a representative anthraquinone dye containing the anthraquinone chromophore in its structure. Adsorption is a mass transfer process in which a solid substance, known as an adsorbent, removes dissolved adsorbat from wastewater by selectively attracting them to its surface. Depending on the nature of the interactions between the adsorbent surface and pollutant, adsorption can be classified as either chemical or physical. Dye adsorption is typically a physical process, primarily controlled by Van der Waals forces, dipole-dipole interactions, and related mechanisms [2]. Zeolites, microporous aluminosilicates with high surface area, are effective adsorbents due to their selective adsorption properties [3].

The utilized adsorption method comprised the use of the anthraquinone dye solution, Acid Blue 111, and the iron-modified natural clinoptilolite (FeZ) particles in a thermostated glass reactor. The pH value of the solution was adjusted using 0.1 mol/L sulfuric acid. The changes in dye concentrations in the liquid phase were followed using a UV-Vis spectrophotometer. Adsorption kinetics were studied at pH 3.0–6.8 (CAB111 = 50 mg/L, Cads = 1 g/L, t = 120 min, T = 293.15 K, ω = 750 rpm) and fit a pseudo-second-order model. Maximum adsorption capacity (8.62 mg/g) and dye removal (77%) occurred at pH 3. Higher pH reduced adsorption efficiency. At aqueous dye solution without any pH modification (pH 6.8), adsorption capacity and the percentage of dye removal were decreased to $q_e = 4.92$ mg/g and 46.5% of removed dye. Adsorption rates are in a good agreement with the adsorption capacity and the dye removal efficiency trends. Thus, the adsorption rate in the most effective system (pH 3) was $k_2 = 0.059$ g/(mg min) while at a pH 6.8, the adsorption rate was $k_2 = 0.010$ g/(mg min). At higher pH values, the deprotonation of functional groups on the zeolite surface leads to the formation of negatively charged sites, which hinder the adsorption of AB111 dye molecules due to Coulombic repulsive forces [1].

Keywords: Natural zeolite, clinoptilolite, dye adsorption, Acid Blue 111, wastewater treatment.

REFERENCES

[1] S. Stupar, M. Vuksanović, Lj. Totovski, R. Jančić Heinemann, Dušan Ž. Mijin, *Sci. Sinter.* 2021, **53,** 91-117

[2] A. Kausar, M. Iqbal, A. Javed, K. Aftab, Z. H. Nazli, H. N. Bhatti, S. Nouren, *J. Mol. Liq.*, 2018, **256**, 395-407

[3] N. Grifasi, B. Ziantoni, D. Fino, M. Piumetti, *Environ. Sci. Pollut. Res.*, 2025,**32**, 27805–27840

FLUORESCENT DETECTION OF CIPROFLOXACIN USING Tb^{3+}-EXCHANGED ZEOLITES

Srna Stojanović[1], *Katarina Rondović*[1], *Marko Dević*[2], *Kristina Mojsilović*[2], *Rastko Vasilić*[2], *Vladislav Rac*[3], *Ljiljana Damjanović-Vasilić*[1]
[1]University of Belgrade, Faculty of Physical Chemistry, Studentski trg 12-16, 11000 Belgrade, Serbia
[2]University of Belgrade, Faculty of Physics, Studentski trg 12-16, 11000 Belgrade, Serbia
[3]University of Belgrade - Faculty of Agriculture, Nemanjina 6, 11080 Belgrade, Serbia

E-mail:srna@ffh.bg.ac.rs

The development of luminescent materials for detection of emerging contaminants has attracted significant attention in recent years [1]. In this context, the fluoroquinolone antibiotic ciprofloxacin (CIP), frequently detected in aquatic environments, represents an important target compound due to its persistence and incomplete removal. [2]. Among various analytical approaches for antibiotic detection, fluorescence-based techniques have gained considerable interest owing to their high sensitivity and selectivity [2].

This study demonstrates the application of Tb^{3+}-exchanged zeolites as fluorescence-based sensors for the detection of CIP in aqueous solution. The materials were prepared by an aqueous ion-exchange process in which Tb^{3+} ions were introduced into ZSM-5 and β zeolite frameworks using a dilute terbium(III) nitrate solution. The samples were calcined at different temperatures in order to examine the effect of calcination on the fluorescence emission of Tb^{3+} ions. Materials were characterized by X-ray powder diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy with energy-dispersive X-ray spectroscopy (EDS), low-temperature N_2 adsorption and fluorescence spectroscopy.

EDS analysis indicated higher terbium loading in Tb-β (6.29 ± 0.24 wt%) compared to Tb-ZSM5 (1.57 ± 0.22 wt%) zeolite. Fluorescence detection of CIP was performed by monitoring changes in the intensities of characteristic Tb^{3+} emission bands assigned to the $^5D_4 \rightarrow {}^7F_j$ transitions (j = 6, 5, 4, 3) at 488, 543, 584 and 619 nm, respectively, in Tb-β and Tb-ZSM5 suspensions. After adsorption of CIP, an increase in Tb^{3+} emission intensity was observed for Tb-β and Tb-ZSM5 with increasing CIP concentration. The fluorescence response depended on terbium loading, zeolite structure and solution pH. The enhanced Tb^{3+} emission, in alkaline conditions, is attributed to the formation of complexes between CIP and Tb^{3+} involving anionic CIP species, suggesting efficient energy transfer from CIP to Tb^{3+} ions (antenna effect). These results highlight the potential of Tb-β and Tb-ZSM5 as dual-function materials for simultaneous detection and removal via adsorption of fluoroquinolone antibiotic, offering a promising approach for environmental monitoring applications.

Keywords: Ciprofloxacin, Fluoresence, Tb^{3+}-exchanged zeolites, ZSM-5 zeolite, β-zeolite

ACKNOWLEDGEMENT

This research was funded by the Science Fund of the Republic of Serbia, grant number 7309 ZEOCOAT and Ministry of Science, Innovation, and Technological Development of the Republic of Serbia (451-03-34/2026-03/200146, 451-03-136/2025-03/200162, 451-03-137/2025-03/200162 and 451-03-34/2026-03/200116).

REFERENCES

[1] F. Caroleo, G. Magna, M. L. Naitana, L. Di Zazzo, R. Martini, F. Pizzoli, M. Muduganti, L. Lvova, F. Mandoj, S. Nardis, M. Stefanelli, C. Di Natale, R. Paolesse, *Sensors*, 2022, **22**, 2649

[2] Q. Ren, P. Yang, J. Liu, Y. Chen, S. Ouyang, Y. Zeng, P. Zhao, J. Tao, *J. Hazard. Mater.*, 2021, **1188**, 339191

NOVEL MENTHOL-ENRICHED CHITOSAN/ZEOLITE COMPOSITES AS WATER DISINFECTANTS

Jelena Dikić[1], Sanja Jevtić[2], Katarina Sokić[2], Nikola Milašinović[3], Mirjana Minceva[4], Jelena Pajnik[4]

[1]Innovation Centre of the Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia
[2]Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia
[3]Faculty of Forensic Sciences and Engineering, University of Criminal Investigation and Police Studies, Cara Dušana 196, Belgrade, Serbia
[4]TUM School of Life Sciences, Technical University of Munich, Alte Akademie 8, Freising, Germany
E-mail:jdikic@tmf.bg.ac.rs

The growing demand for safe, sustainable water disinfection treatment has increased the need for the development of advanced functional materials as alternatives to conventional chemical treatments. In this work, a novel, environmentally friendly approach for the preparation of menthol-enriched chitosan/zeolite composite beads for water disinfection was investigated. Natural clinoptilolite from the Slanci deposit (Serbia) was incorporated into a chitosan matrice to obtain highly porous structures with enhanced loading capacity, while menthol, a bioactive compound with proven antibacterial activity, was loaded into the composite beads via supercritical CO_2 impregnation, a green, solvent-free technology.

First, 2.0000 g of chitosan was dissolved into the 100.0 cm^3 of 2 % acetic acid. Then, different amounts of zeolite (0, 20, 50, and 100 wt.% with respect to the dry mass of chitosan) were loaded into the chitosan matrices. Thermal and FTIR characterization demonstrated successful incorporation of menthol into the composite. SEM analysis revealed a well-developed, stable porous morphology achieved through supercritical CO_2-assisted drying. The antibacterial performance of the obtained materials was evaluated against *Escherichia coli* DSM 498 and *Staphylococcus aureus* ATCC 25923 by disc diffusion method. While unloaded composites showed no zone of inhibition, menthol-loaded materials exhibited clear zone around the samples (1-3 mm), demonstrating the functional efficiency of the prepared composites.

This study presents a promising step toward the development of sustainable, bio-based disinfection materials by combining natural zeolites, biopolymers, and supercritical CO_2 technology with bioactive compounds, such as menthol. The proposed approach opens new perspectives for the design of high-performance materials for the disinfection of water, as well as for similar environmental applications.

Acknowledgment: This work was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Contract No. 451-03-136/2025-03/200135 and 451-03-136/2025-03/200287) and the bilateral project between Republic of Serbia and Federal Republic of Germany (No. 001545243 2025 13440 003 000 000 001 03 006).

APTES-MODIFIED ZEOLITE IMMOBILIZED IN ALGINATE BEADS FOR EFFICIENT Ag(I) REMOVAL FROM AQUEOUS SOLUTIONS

Jelena Dimitrijević [1], Jelena Dikić [2], Jelena Petrović [1], Marija Simić [1], Marija Koprivica [1], Marija Ercegović [1], Sanja Jevtić [3]
[1]Institute for Technology of Nuclear and Other Mineral Raw Materials, 86 Franchet d'Esperey St., 11000 Belgrade, Serbia
[2]Innovation Centre of the Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia
[3]Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia
E-mail:j.dimitrijevic@itnms.ac.rs

ABSTRACT

Hybrid alginate-based beads incorporating APTES-modified natural zeolite (ANZ-alg) were synthesized and evaluated for the removal of Ag(I) ions from aqueous solutions. The developed composite material combines the ion-exchange capacity of clinoptilolite, the functional reactivity of aminosilane groups, and the structural stability of alginate matrix, resulting in enhanced adsorption performance. Results of scanning electron microscopy (SEM) and pH_{PZC} analysis, confirmed successful immobilization and provide insight into surface charge behavior. Batch adsorption experiments demonstrated rapid uptake and high removal efficiency of Ag(I) ions, indicating strong affinity between the adsorbent and metal ions. The adsorption mechanism is governed by a combination of ion exchange, coordination interactions between Ag(I) ions and amine groups, and electrostatic interactions influenced by surface charge. The synergistic effect of zeolite, APTES functionalization, and alginate matrix significantly contributes to the overall adsorption performance. The obtained results indicate that ANZ-alg beads represent a promising, stable, and environmentally friendly material for efficient removal of silver ions from contaminated water.

Keywords: zeolite; alginate beads; APTES; adsorption; hybrid adsorbent

INTRODUCTION

The presence of heavy metals in aquatic systems represents a major environmental concern due to their toxicity, persistence, and bioaccumulation potential. Among them, silver ions (Ag^+) have attracted increasing attention due to their widespread application in electronics, catalysis, medical devices, and antimicrobial products. Despite their industrial importance, uncontrolled discharge of silver into water systems poses significant ecological risks [1]. Adsorption has been recognized as one of the most efficient and economically viable methods for the removal of metal ions from aqueous solutions. In this context, natural zeolites, particularly clinoptilolite, have been extensively studied due to their well-defined porous structure, high surface area, and significant cation-exchange capacity [2,3]. However, their performance can be limited by insufficient functional groups and difficulties in handling fine particles. To overcome these limitations, surface modification of zeolites using organosilanes has been widely explored. Functionalization with (3-aminopropyl)triethoxysilane (APTES) introduces amine groups capable of forming strong coordination interactions with metal ions such as Ag(I), thereby enhancing adsorption efficiency[3,4]. In addition, immobilization of zeolite particles within polymer matrices, such as alginate, represents an effective strategy for improving mechanical stability, facilitating separation, and enabling uniform distribution of active components. Alginate-based beads provide a three-dimensional porous network that enhances accessibility of adsorption sites and improves overall performance [5,6].

In this study, APTES-modified zeolite was immobilized within alginate beads (ANZ-alg), and its efficiency for Ag(I) removal from aqueous solutions was investigated. Special attention was given to the role of surface charge (pHPZC) and the synergistic interaction between zeolite, functional groups, and polymer matrix in the adsorption process.

EXPERIMENTAL

Natural clinoptilolite-rich zeolitic tuff obtained from the Zlatokop deposit near Vranjska Banja (Serbia) was used after grinding and sieving (<125 µm). Sodium alginate (Sigma-Aldrich) was used as the polymer matrix for bead formation. Calcium chloride dihydrate (Lach-Ner) was used as the crosslinking agent. 3-Aminopropyltriethoxysilane (APTES, ≥98%, Sigma-Aldrich) was used for surface functionalization of the zeolite. All solutions were prepared using deionized water, and all chemicals were of analytical grade.

Natural clinoptilolite-rich zeolite was functionalized with 3-aminopropyltriethoxysilane (APTES, ≥98%) following a previously reported procedure with slight modifications. The silanization process resulted in the covalent attachment of APTES molecules onto the zeolite surface through Si–O–Si bonds, introducing surface-bound amine groups ($-NH_2$) [4].

The modified zeolite, denoted as ANZ, was used as component for further bead preparation.

Immobilization of ANZ was carried out by incorporation into an alginate matrix. A defined amount of ANZ was dispersed in sodium alginate solution under constant stirring. The obtained suspension was added dropwise into $CaCl_2$ solution, leading to the formation of spherical beads. After preparation, the beads were washed with deionized water and stored under ambient conditions prior to use.

Adsorption experiments were conducted using a batch system. A fixed amount of adsorbent (0.02 g) was added to 40 mL of Ag(I) solution. All experiments were performed at room temperature (25 °C) under constant agitation (220 rpm). After the desired contact time, suspensions were filtered, and residual Ag(I) concentrations were determined using atomic absorption spectroscopy (AAS). All experiments were performed in triplicate, and average values were reported.

The surface morphology of the prepared ANZ-alg beads was examined using scanning electron microscopy (SEM, JEOL JSM-6610LV).

The pH_{PZC} of ANZ-alg beads was determined using the pH drift method. A series of solutions with different initial pH values were prepared, and a fixed amount of adsorbent was added to each solution. After equilibration, the final pH values were measured, and the pH_{PZC} was determined as the point where the initial and final pH values were equal.

RESULTS AND DISCUSSION

SEM analysis (Fig.1) confirmed the formation of spherical ANZ-alg beads with a heterogeneous and rough surface morphology. The surface appears irregular, with visible embedded zeolite particles within the alginate matrix, indicating successful immobilization of the inorganic phase.

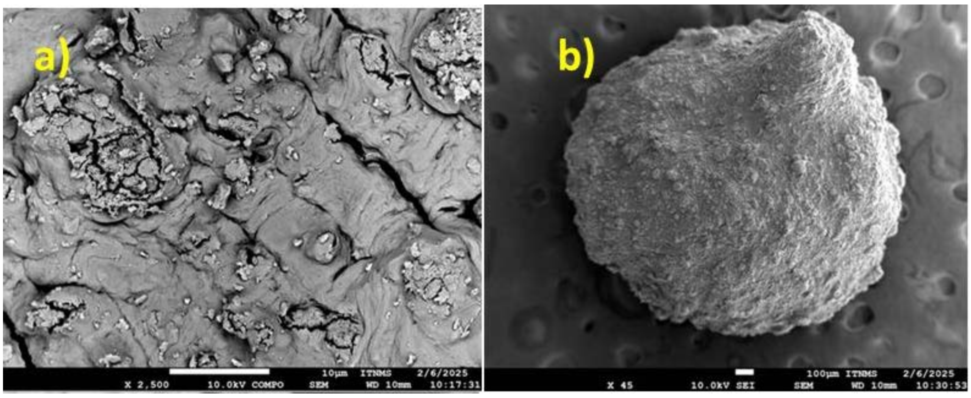
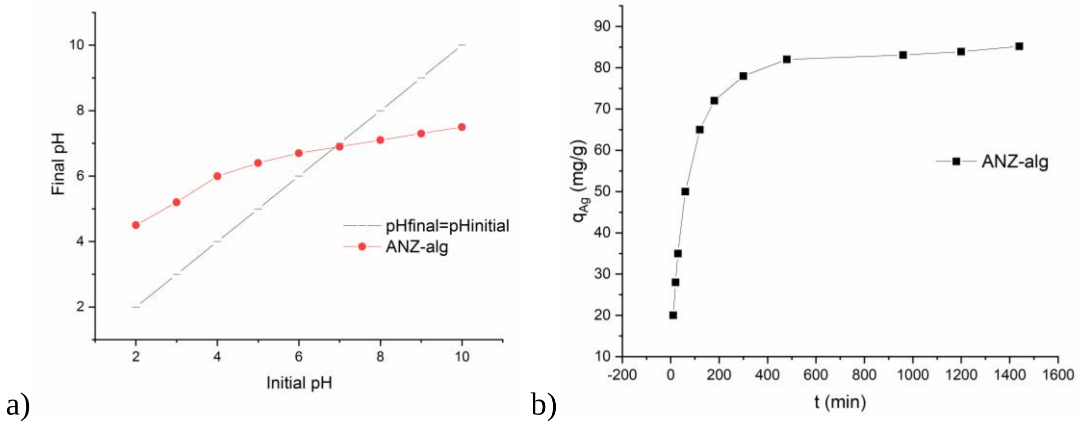


Figure 1. SEM micrographs of ANZ-alg adsorbent: a) surface morphology showing rough and heterogeneous structure with embedded zeolite particles, and b) spherical bead morphology.

The observed porous and non-uniform structure suggests the presence of multiple active sites and diffusion pathways, which can facilitate the transport of Ag(I) ions toward the interior of the beads. Such morphology is favorable for adsorption processes, as it enhances both accessibility and interaction between the adsorbent and metal ions [7,8].

The pHPZC value of ANZ-alg beads was determined using the pH drift method and is presented in Fig. 2a. The obtained pH_{PZC} was approximately 6.9. At pH values below pHPZC, the surface of the adsorbent is positively charged, which leads to electrostatic repulsion with Ag^+ ions and consequently lower adsorption efficiency. In contrast, at pH values above pHPZC, the surface becomes negatively charged, promoting electrostatic attraction between the adsorbent and Ag^+ ions and enhancing the adsorption process [8]. This behavior indicates that surface charge plays an important role in the adsorption mechanism. In addition to electrostatic interactions, the presence of amine functional groups introduced by APTES modification enables coordination interactions with Ag(I) ions, further contributing to the overall adsorption performance [4,7].



a) b)

Figure 2. a) Determination of pH_{PZC} of ANZ-alg beads using the pH drift method: variation of final pH as a function of initial pH. b) Effect of contact time on Ag(I) adsorption onto ANZ-alg beads.

The adsorption of Ag(I) onto ANZ-alg beads (Fig. 2b) is characterized by a rapid initial uptake within the first 20-30 min, followed by a slower approach to equilibrium. The initial stage corresponds to adsorption on readily available surface sites, while the later stage is controlled by diffusion of Ag(I) ions into the interior of the beads and gradual saturation of active sites [6].

Such behavior is consistent with the structural characteristics of the material and the pH_{PZC} results, indicating that both electrostatic interactions and diffusion processes contribute to the overall adsorption mechanism.

To further describe the adsorption process, kinetic analysis was performed using pseudo-first-order (PFO) and pseudo-second-order (PSO) models. The PFO model showed weaker agreement with experimental data, with lower correlation coefficient ($R^2 = 0.83$) and noticeable deviation between calculated and experimental adsorption capacities.

In contrast, the PSO model provided an excellent fit, with $R^2= 0.9961$ and calculated adsorption capacity ($q_{e,cal} = 86.4$ mg/g) is very close to the experimental value ($q_{e,exp} = 85.0$ mg/g) .

These results indicate that the adsorption process is predominantly governed by chemisorption, involving electron sharing or exchange between Ag(I) ions and active sites on the adsorbent[4,5] .Overall, the adsorption of Ag(I) onto ANZ-alg beads can be described by a synergistic mechanism involving ion exchange within the zeolite structure, coordination interactions with amine groups, electrostatic attraction controlled by surface charge, and diffusion through the alginate matrix [3,4,8].

CONCLUSION

ANZ-alg beads showed efficient adsorption of Ag(I) ions, with rapid uptake and high adsorption capacity. The adsorption process is influenced by surface charge behavior, with enhanced performance at pH values above pH_{PZC}. Kinetic analysis confirmed that the pseudo-second-order model provides the best description of the process, indicating that chemisorption is the dominant mechanism. The combined effects of ion exchange, coordination interactions, and electrostatic attraction make ANZ-alg beads a promising material for silver removal from aqueous systems.

REFERENCES

[1] C. Wang, S. Leng, Y. Xu, Q. Tian, X. Zhang, L. Cao, J. Huang, *Minerals* 2018, **8**, 145

[2] S. Jevtić, I. Arčon, A. Rečnik, B. Babić, M. Mazaj, J. Pavlović, D. Matijaševic, M. Nikšić, N. Rajić, *Microporous and Mesoporous Materials*,2014, **197**, 92-100.

[3] X. Han, Z. Cao, R. Wang, P. He, Y. Zhang, J. Yu, Y. Ge, *Constr Build Mater* 2020, **259**, 119713.

[4] J. Dimitrijević, J. Petrović, A. Marinković, J. Dikić, M. Koprivica, M. Simić, S. Jevtić, *Macedonian Journal of Chemistry and Chemical Engineering*, 2025, **44**, 331-347.

[5] B. Nedić Vasiljević, M. Milojević-Rakić, M. Ranković, A. Jevremović, L. Ignjatović, N. Gavrilov, S. Usković-Marković, A. Janošević Ležaić, H. Wang, D.Bajuk-Bogdanović, *Molecules*, 2025, ***30***, 3267

[6] I. Cosme-Torres, M.G. Macedo-Miranda, P. Ibarra-Escutia, M. Manjarrez-Olvera, V. Albíter-López, A. Trujillo-Segura, *MRS Adv,* 2020, **5**, 3247-3256.

[7] L.D. Anbealagan, T.L. Chew, Y.F. Yeong, Z.A. Jawad, C.D. Ho, *IOP Conf Ser Mater Sci Eng* 2021, **1195,** 012047.

[8] S. Wang, Y. Peng, Chemical Engineering Journal 2010, **156,** 11-24.

PREPARATION, CHARACTERIZATION, AND KINETICS OF ZEOLITE/ALGINATE COMPOSITES

Bojana Rajičić[1], Mihaela Novaković[1], Katarina Sokić[1], Jelena Pajnik[3], Jelena Dikić[2], Sanja Jevtić[1]

[1] University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia
[2]Innovation center of the Faculty of Technology and Metallurgy, Belgrade, Serbia
[3]TUM School of Life Sciences, Technical University of Munich, Freising, Germany
E-mail:bojanarajicic8@gmail.com

ABSTRACT

In this study, the adsorption of Ni(II) and Zn(II) ions from mono- and binary aqueous solutions was investigated using alginate beads with and without zeolite. The adsorption behavior was evaluated for both hydrated and dehydrated beads. The results showed that the incorporation of zeolite slightly enhances the adsorption of single ions. However, dehydrated beads exhibited significantly higher adsorption capacity compared to hydrated ones, especially in binary systems. The adsorption kinetics followed a pseudo-second-order model, indicating that chemisorption is the dominant mechanism.

Keywords: zeolite, nickel, zinc, monocomponent solution, binary solution

INTRODUCTION

Nowadays, the removal of heavy metals from wastewater remains a major environmental challenge. Among available techniques, ion exchange is one of the most effective methods, where toxic metal ions are replaced by less harmful cations. Due to their stability, ion-exchange capacity, and low cost, natural zeolites are widely used for this purpose [1]. Natural zeolites have demonstrated the ability to remove metal ions such as Ni(II) and Zn(II) from aqueous solutions [1]. However, powdered adsorbents present limitations such as aggregation, reduced active surface area, and operational issues in column systems and their direct use is not possible. In contrast, spherical beads provide improved mechanical stability and easier handling. The preparation of the defined shapes with polymer matrices is usually used. Alginate is a biopolymer with high adsorption capacity and chemical stability in aqueous environments, making it a suitable matrix material [2]. The aim of this study was to synthesize alginate beads with and without zeolite and evaluate their adsorption properties toward Ni(II) and Zn(II) ions.

EXPERIMENTAL

Preparation and characterization of the beads

The zeolite sample (10 g, particle size 0.063-0.125 mm) was first suspended in 1 dm^3 2.0 M NaCl, in order to obtain the Na-Z [3]. The suspension was stirred for 24 h on a magnetic stirrer at a temperature of 25 °C. The sample was then filtered and washed with distilled water until a negative reaction for Cl^- ions was observed, after which it was dried in an oven at 50 °C. The resulting sample was designated as Na-Z.

The Na-alginate solution was prepared by dissolving 3 g of Na-alginate in 100 cm^3 of deionized water. The solution was stirred for 24 h on a magnetic stirrer at a speed of 300 rpm. Then, 4 g of Na-Z was suspended in one part of the polymer solution, and then the suspension was treated with an ultrasonic in order to homogenize the suspension.

Spherical beads were prepared by a syringe pump (Razor A-99) through a 20 G needle, with a flow rate of 70 cm^3 h^{-1}. The suspension with and without zeolite was added dropwise to

0.1 M $CaCl_2$. The formed beads were left in 0.1 M $CaCl_2$ for better crosslinking. After 24 h, the beads were washed with distilled water and used in further experiments. There were two series of the beads: hydrated and dehydrated. The dehydrated beads were dried at the air until the constant mass.

Kinetics of adsorption of Ni^{2+} and Zn^{2+} onto beads with and without zeolite

The adsorption kinetics were investigated from monocomponent and binary solutions, where the concentration of each metal was 100 mg dm^{-3}. In all experiments, the ratio of solid to liquid phase was 1:100. One series of experiments was performed with hydrated beads, and the other with dehydrated ones. The samples were stirred in a water bath at a temperature of 25 °C. Samples were taken at precisely defined time intervals (0.5, 1, 2, 4, 6 and 24 h). The concentration of metal ions in the samples was determined using a Varian-55B AA series flame atomic absorption spectrometer (AAS). The adsorption capacity at time t was calculated using equation 1:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where q_t is the amount of metal ions adsorbed per gram of sample at time t (mg g^{-1}), C_o is the initial concentration of metal in solution (mg dm^{-3}), C_t is the concentration of M^{2+} at time t , V is the volume of solution (dm^3) and m is the mass of the beads (g).

Desorption of metal ions from saturated adsorbents

Metal desorption from saturated samples was tested in distilled water at 25 °C in a water bath. The suspensions were stirred at 105 rpm, with a solid-liquid ratio of 1:100. After 24 h, the suspensions were separated and the metal concentration was determined by AAS.

RESULTS AND DISCUSSION

Table 1 shows that the hydrated bead has a larger diameter and mass compared to the dehydrated ones. The data obtained are in accordance with expectations, given that hydrated beads contain water molecules in their structure. The presence of the zeolite in the beads influences on the diameter and mass that increase slightly with the addition of the zeolite.

Table 1. Comparison of dimensions and particle size

bead type	alginate		with zeolite	
	hydrated	dehydrated	hydrated	dehydrated
diameter (mm)	3	1	4	1.5
mass (g)	0.0174	0.00062	0.0178	0.00104

From Figure 1, it is evident that the color of the beads is different. Zeolite beads have an intense yellow color, which comes from the presence of zeolite, while only alginate beads are colorless.

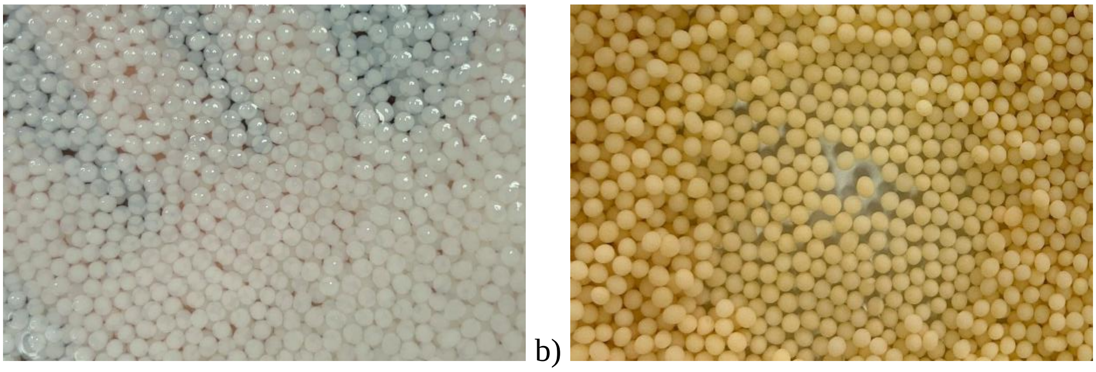


Figure 1: Hydrated alginate beads without (a) and with (b) zeolite

Comparing the adsorption of metal ions in hydrated and dehydrated beads, dehydrated beads adsorb almost three times higher amount of metal ions compared to hydrated beads. Adsorption occurs predominantly on the surface of the particles, which can be explained by the larger specific surface area of dehydrated beads compared to hydrated ones. Hydrated beads have the specific surface area around 4 and the dehydrated in the range of 100 to 300 g m^2 for the beads without and with zeolite, respectively.

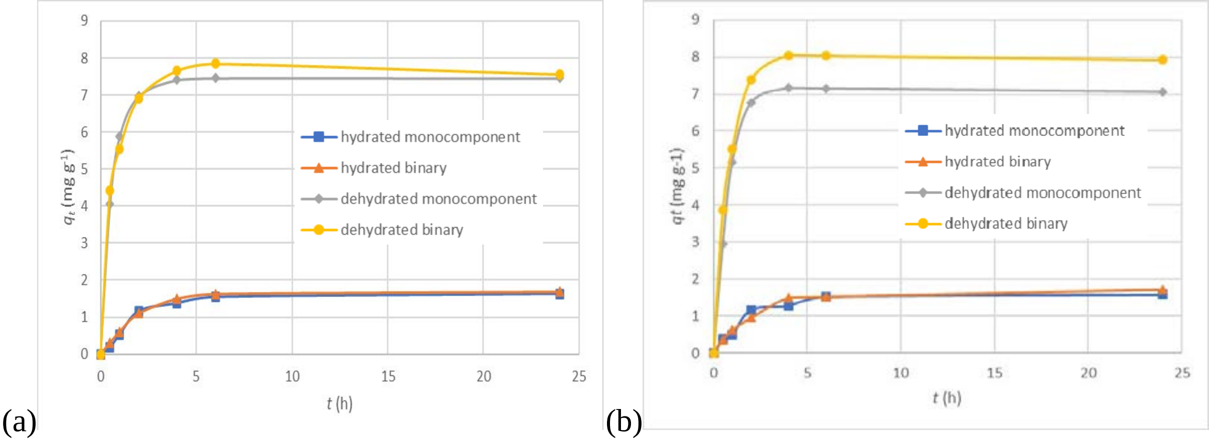


Figure 2: Comparison of Ni^{2+} adsorption kinetics on hydrated and dehydrated alginate beads with zeolite (a) and without zeolite (b)

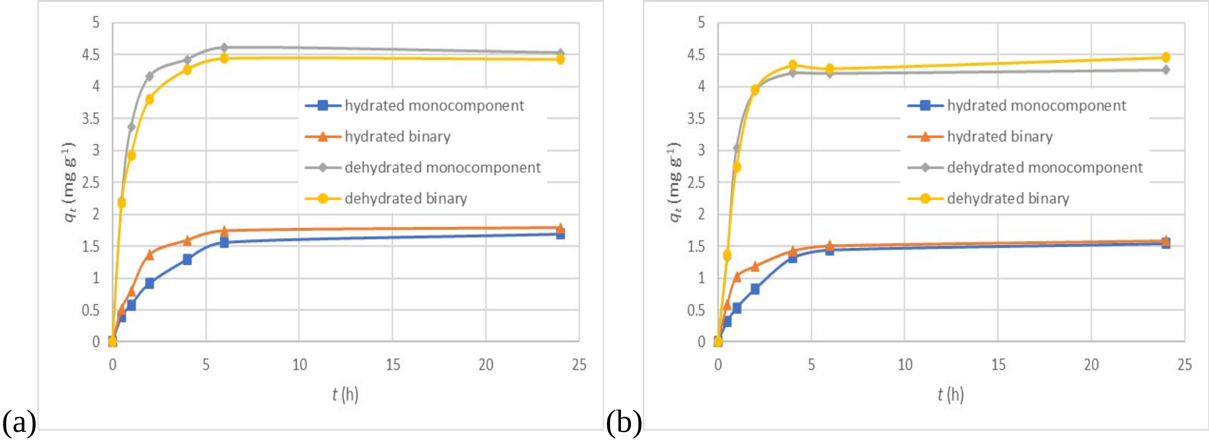


Figure 3: Comparison of Zn^{2+} adsorption kinetics on hydrated and dehydrated alginate beads with zeolite (a) and without zeolite (b)

It is seen from the curves on Figs. 2 and 3 that at the beginning (approximately in the first 2 h), the adsorption of the Ni^{2+} and Zn^{2+} increases sharply. Afterwards, the adsorption proceeds gradually. The adsorption kinetics followed a pseudo-second-order model, indicating that chemisorption is the dominant mechanism. The process involves ion exchange, surface diffusion, and intraparticle diffusion. According to the present results, the surface diffusion occurs more rapidly at the beginning, while intraparticle diffusion becomes dominant as time progresses.

During desorption, the results presented in Tables 2 and 3 show that nearly complete desorption of metal ions occurs in hydrated beads, whereas only about 5% of metal ions are desorbed from dehydrated beads. The maximum concentrations allowed for Ni^{2+} and Zn^{2+} ions in water are 0.02 and 3 mg dm^{-3}, respectively. The measured Ni^{2+} concentrations exceed the regulatory limit, whereas Zn^{2+} concentrations remain within acceptable levels.

Table 2. Concentration of Ni^{2+} ions after desorption in mg dm^{-3}

bead type		hydrated		dehydrated	
		alginate	with zeolite	alginate	with zeolite
Solution	monocomponent	1.15	1.62	1.0426	0.3301
	binary	1.24	1.52	0.6601	0.2619

Table 3. Concentration of Zn^{2+} ions after desorption in mg dm^{-3}

bead type		hydrated		dehydrated	
		alginate	with zeolite	alginate	with zeolite
Solution	monocomponent	1.6	1.5	0.806	0.3961
	binary	1.17	1.58	0.96	0.458

CONCLUSION

The study showed that the adsorption capacity of alginate beads, with or without zeolite, for Ni^{2+} and Zn^{2+} ions is higher in dehydrated beads. Adsorption of a single metal ion was higher in binary than in monocomponent solutions, while similar adsorption capacities were observed for beads with and without zeolite. The adsorption process proceeds through ion exchange, followed by surface and intraparticle diffusion, and the kinetics are best described by the pseudo-second-order model. The desorption process is highly dependent on the hydration state of the beads, with hydrated beads enabling nearly complete release of metal ions, whereas dehydrated beads strongly retain the adsorbed ions.

REFERENCES

[1] Đ. Stojaković, J. Milenković, S. Stupar, Z. Veličković, N. Rajić, *Desal. Water Treat.*, 2016, **57**, 18748-18754.

[2] C. Mahamadi, P. Zambara, *European Journal of Scientific Research*, 2012, **71**, 581-589.

[3] N. Rajić, Đ. Stojaković, M. Jovanović, N. Z. Logar, M. Mazaj, V. Kaučić, *Appl Surf Sci.*, 2010, **257**, 1524-1532.

MINERALOGICAL CHARACTERIZATION OF THE ZLATOKOP ZEOLITIC TUFF BY QUANTITATIVE RIETVELD ANALYSIS

Ana S. Radosavljević-Mihajlović, Ivana Jelić, Jovica Stojanović, Slavica Mihajlović, Nikola Vuković
Institute for technology of nuclear and other raw materials, Franche d Eperea 86, 11000 Belgrade, Serbia
a.radosavljevic@itnms.ac.rs

ABSTRACT

Quantitative mineralogical and structural analysis of zeolitic tuff from the Zlatokop deposit was performed using X-ray powder diffraction and Rietveld refinement. The sample is dominated by clinoptilolite (77.2%), with minor quartz, feldspars, and mica. Structural refinement confirms Ca-clinoptilolite as the main phase, with Ca^{2+} as the dominant exchangeable cation despite comparable site occupancies with Na^{+}. This is supported by cation exchange capacity (CEC) values (Ca^{2+} 94 meq/100 g), indicating strong electrostatic stabilization within channels A and B. Refined channel dimensions (A ≈ 10.5 × 5.73 Å; B ≈ 6.21 × 7.15 Å) confirm the structural suitability of Ca^{2+} for ion exchange. The results highlight the high ion-exchange potential and structural stability of Zlatokop clinoptilolite.

Keywords: Rietveld method, zeolitic tuff, Ca-clinoptilolite

INTRODUCTION

Zeolitic tuffs are formed by diagenetic alteration of volcanic ash and are widely used due to their ion-exchange and adsorption properties. Quantitative phase analysis using X-ray powder diffraction combined with Rietveld refinement represents a reliable method for determining mineral composition and structural characteristics of zeolite-rich materials. Clinoptilolite-rich tuffs are particularly important due to their high cation-exchange capacity and structural stability. This study presents a quantitative and structural analysis of Ca-clinoptilolite from the Zlatokop deposit using Rietveld refinement.

EXPERIMENTAL

Powdered samples (<63 µm) were analyzed by X-ray diffraction using a Philips PW-1710 diffractometer (Cu Kα radiation, 40 kV, 30 mA). Data were collected over a 2θ range of 4–65° with a step size of 0.02°. Quantitative and structural refinement was performed using the Rietveld method implemented in the FullProf software package. Structural visualization was carried out using VESTA.

RESULTS AND DISCUSSION

Crystal-chemical analysis revealed that Ca is the dominant cation, with a Si/Al ratio of 4.64, while the bulk chemical composition (SiO_2 = 63.64 wt%, Al_2O_3 = 12.40 wt%, Fe_2O_3 = 0.92 wt%, CaO = 4.93 wt%, MgO = 1.02 wt%, Na_2O = 0.20 wt%, K_2O = 1.80 wt%, LOI = 15.4 wt%) further confirms that the Zlatokop zeolitic tuff is rich in Ca-clinoptilolite, consistent with previous studies [8]. Quantitative XRD analysis indicates that the tuff is dominated by clinoptilolite (77.2%), with minor quartz (8.8%), albite (6.3%), muscovite (3.8%), orthoclase (3.2%), calcite (0.7%), and traces of pyrite [9]. Representative SEM photomicrographs of the samples are shown in Fig. 1, illustrating the typical morphology of the zeolite crystals.

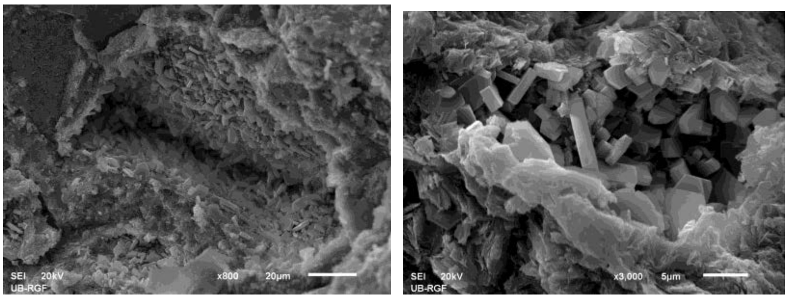


Figure 1. SEM photomicrograph of Zlatokop zeolitic tuff at ×800 and ×3,000 magnifications

SEM analysis of Ca-clinoptilolite reveals well-defined prismatic and plate-like crystals, whereas monoclinic symmetry is determined from X-ray diffraction results. The crystals are elongated with rectangular cross-sections and smooth surfaces, forming dense, irregular aggregates, while smaller crystals occupy the interstitial spaces between larger ones. The 5 *μm* scale bar indicates that individual crystals are in the micrometer size range.

Strucutural analysis

Based on previous studies [10], the structure of Ca-clinoptilolite from the Zlatokop deposit was refined in the *C*2/*m* space group, with a disordered distribution of Si and Al over the tetrahedral sites, using initial parameters from the KT model [11]. The structure of Ca-clinoptilolite was refined in the C2/m space group using a disordered Si/Al distribution model. Only clinoptilolite and quartz were included in the refinement. The refined proportions are 87.7% clinoptilolite and 12.3% quartz. Refinement indicators (RB < 5–7%) confirm good agreement between observed and calculated intensities, despite elevated Rwp values due to the presence of amorphous material and microstructural effects typical of natural samples. Minor deviations in the 2θ range are attributed to preferred orientation and microstrain. Refined X-ray powder diffraction patterns of Ca-clinoptilolite are presented in Figure 3, while the corresponding structural and profile parameters, along with the refinement factors, are summarized in Table 1.

Table 1. XRPD profile data for zeolitic tuff phases: Ca-clinoptilolite and quartz.

Space groupe	Prof. fun.	Parameter of unit cell (Å)					ρ (g/cm^3)	RB(%)	RF(%)	R_{wp}	R_p
		a…	***b…***	***c…***	***β …***	**V(Å^3)**					
**C*2/*m*	*pV*	17.68	18.00	7.416	116.40	2114.78	2.390	4.8	6.3	20.8	19.81
***P3221*	pV	4.918	4.918	5.410		113.353	5.281	7.0	5.3		

*Ca-clinoptilolite; **Quartz

The goodness-of-fit (GoF) is 3.1, and χ^2 is 9.5; such deviations are typical for complex natural structures with multiple phases and an amorphous component (Fig. 2).

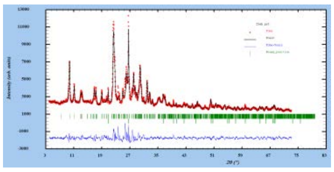


Figure 2. Rietveld refinement of the XRPD pattern of zeolitic tuff (Zlatokop), including observed and calculated profiles, difference curve, and Bragg positions.

Analysis of tetrahedral positions

The tetrahedral sites (Si1–Si5) in Ca-clinoptilolite exhibit variable distortion [12] due to interactions with neighboring tetrahedra and extra-framework Ca^{2+} cations. Silicon predominates at all T-sites, with T3 being nearly pure Si (SOF = 0.97) and T5 showing the lowest Si occupancy (SOF = 0.32). All oxygen atoms (O1–O10) are fully occupied, maintaining a stable framework. Among the tetrahedra, Si4 is the most symmetrical, while Si5 shows the greatest distortion, likely due to its framework position and interactions with channel cations [13]. Si–O bond lengths (1.613–1.649 Å) and T–O–T angles (108.8°–110.1°) indicate that the tetrahedra largely preserve near-ideal geometry, with minor local distortions. Among the sites, Si4 is the most symmetrical, whereas Si5 shows the highest distortion, reflecting its interaction with channel cations. These structural variations influence local acidity, cation distribution, and channel geometry.

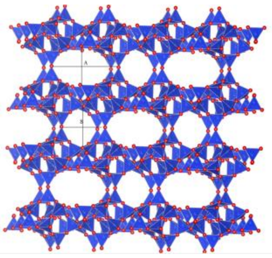


Figure 3. Structure of Ca-clinoptilolite showing channels A (10-membered rings) and B (8-membered rings) with approximate experimental dimensions.

Figure 3 shows the structure of Ca-clinoptilolite with two types of channels: channel A (larger, rectangular, formed by 10-membered rings) and channel B (smaller, formed by 8-membered rings). In the literature, their effective pore sizes are approximately 3.1 × 7.5 Å for channel A and 3.6 × 4.6 Å for channel B [13]. However, the experimental crystallographic values are larger (A ≈ 10.5 × 5.73 Å, B ≈ 6.21 × 7.15 Å) because they represent oxygen–oxygen framework distances defining the channel walls rather than the true accessible pore openings. These discrepancies arise from local tetrahedral distortions and different definitions of channel boundaries in the crystallographic model. The physicochemical and structural properties of clinoptilolite largely depend on the type and content of extraframework cations. In Ca-clinoptilolite, Na–O, Ca–O, K–O, and Mg–O bonds average approximately 2.45 Å, 2.62 Å, 2.85 Å, and 2.16 Å, respectively, with cations coordinated by 6–8 framework oxygen atoms in distorted polyhedral environments. The refined site occupancy factors for the extraframework cations (Na1 = 0.0942, Ca2 = 0.216, K3 = 0.143, Mg = 0.127) indicate that calcium occupies its positions to the greatest extent. Ca, despite a site occupancy similar to Na, dominates ion exchange due to its divalent charge and favorable coordination in channels A and B, as indicated by CEC values: Ca^{2+} 94, Na^{+} 0.9, K^{+} 16.4, Mg^{2+} 10.7 meq/100 g [14]. Calcium exhibits the highest cation-exchange capacity due to strong electrostatic interactions with the framework and sufficient mobility for exchange, Fig.4.

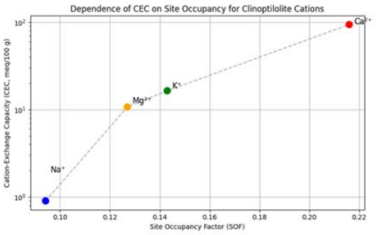


Figure 4. Dependence of total cation exchange capacity (CEC meq/100g on occupancy factor (SOF).

The diagram shows a clear positive correlation between site occupancy factor and cation exchange capacity (CEC), indicating that higher occupancy of exchangeable sites is associated with increased ion-exchange potential. Ca^{2+} exhibits the highest occupancy and CEC values, confirming its dominant role in the clinoptilolite structure and its strong preference in exchange processes compared to Na^{+}, K^{+}, and Mg^{2+}.

CONCLUSION

Based on the results of quantitative Rietveld analysis, the presence of 12 % quartz in the sample does not significantly affect the structural and crystal-chemical properties of Ca-clinoptilolite present in the zeolitic tuff. These results also confirm that Ca^{2+} is the dominant exchangeable cation in clinoptilolite, while Na^{+}, K^{+}, and Mg^{2+} play secondary roles, determined by their structural environment. Site occupancy factors further indicate the preferential distribution of Ca^{2+} within the available exchange sites of the clinoptilolite framework, reflecting its structural stability and cation selectivity. This crystal-chemical characteristic explains the high selectivity of clinoptilolite for divalent cations and highlights its efficiency in environmental and technological ion-exchange applications.

ACKNOWLEDGMENTS

The authors express their gratitude to the Ministry of Science, Technological Development and Innovations of the Republic of Serbia for the financial support of this research within the framework of project number 451-03-136/2025-03/200023.

REFERENCES

[1] F.A. Mumpton, In Mineralogy and Geology of Natural Zeolites, M.S.A. Short Course Notes, Vol. 4, F.A. Mumpton (ed.), Mineralogical Society of America, Washington, D.C., 1977, p. 1.

[2] R. Bonetto, P. Zalba, M. Conconi, M. Manassero, Revista Geológica de Chile, 2003, **30**(1), 103–115.

[3] R. Snellings, L. Machiels, G. Mertens, J. Elsen, *Geologica Belgica,* 2010, **13**(3), 183–196.

[4] H. Rietveld, J. Appl. Crystal. 1969, **2**: 65-71.

[5] J. Rodriguez-Carvajal, Fullprof: A Program for Rietveld Refinement and Pattern Matching Analysis," Abstract of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUC*r,* Toulouse, France, 1999, 127.

[6] A. Radosavljević-Mihajlović, J. Stojanović, V. Kašić, J. Lemić, Bulletin of Geoinstitute, 2003, **38**:149-155.

[7] K. Momma, F. Izumi F. J Appl Crystallogr. 2011; **44:**1272-1276.

[8] K. Mihajlović, J. Stojanović, S. Mihajlović, I. Jelić, A. Radosavljević-Mihajlović *In Proceedings of the 56th International October Conference on Mining and Metallurgy (IOC 2025),* Bor Lake, Bor, Serbia, 22–25 October 2025.

[9] K. Mihajlović, J Stojanović, A Radosavljević-Mihajlović, I Jelić, S. Mihajlović, N. Vuković, V. Kašić, *Geološki anali Balkanskoga poluostrva, 2025,* ***18,***

[10] K. Koyama,Y, Takeuchi, Zeitschrift für Kristallographie, 1977, **145**: 216-239.

[11] S.Li, J. Zhang, Y. Wang, Microporous and Mesoporous Materials*,* 2013, **174**, 69–76

[12] D. Breck, *Zeolite molecular sieves: Structure, chemistry, and use.* New York, 1974, NY: John Wiley & Sons.

[13] D. Akporiaye, K. Tsuji, K. Kaneko. Applied Sciences, 2023, **15**(7), 3955.

[14] V. Inglezakis, A. Zorpas, A. *Handbook of Natural Zeolites.* 2012**,** Bentham Science Publishers, Sharjah, UAE.

Gold sponsors

AstrineXLab

Altium

MC LABOR

Regular sponsors

WIKA

ANALYSIS
LABORATORY EQUIPMENT

Student grants support

FEZA

minerals
an Open Access Journal by MDPI