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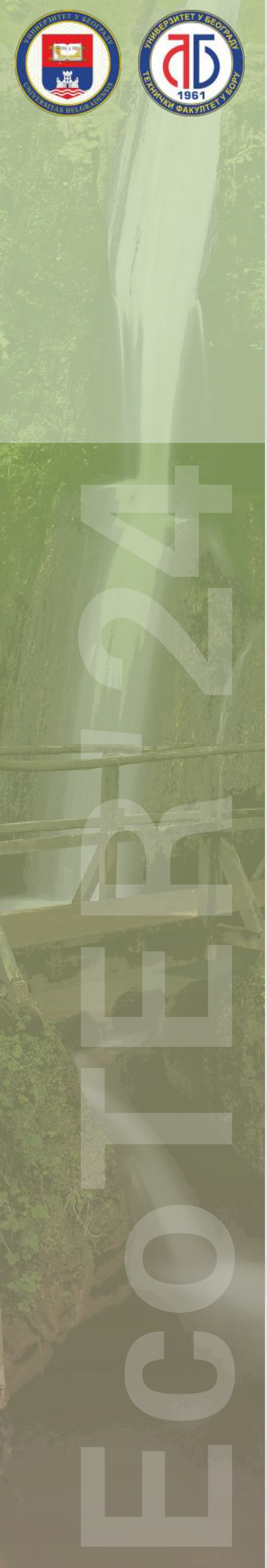

31st International conference

Ecological Truth & Environmental Research

Editor
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PROCEEDINGS

Hotel Sunce, Sokobanja, Serbia
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PREFACE

The 31st international conference Ecological Truth & Environmental Research – EcoTER'24 focuses on showing the latest research findings and innovations in the field of ecology, environmental protection and sustainable development. The conference will be held in Sokobanja (Serbia) in hotel Sunce in the period of 18–21 June 2024.

The aim of the conference is to connect the experts in various fields in order to transform attitudes and behaviors in everyday practices, as well as in the industry and economy sector which is essential for achieving the desired changes that our society must undergo.

The 31st international conference Ecological Truth & Environmental Research – EcoTER'24 is organized by the University of Belgrade, Technical Faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology; the University of Montenegro, Faculty of Metallurgy and Technology – Podgorica; the University of Zagreb, Faculty of Metallurgy – Sisak; the University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Society of Young Researchers – Bor.

These Proceedings encompass 119 papers from the authors coming from the universities, research institutes and industries in 15 countries: Brazil, Norway, USA, Spain, Austria, Libya, Italy, Israel, Slovenia, Croatia, Romania, Bulgaria, Montenegro, Bosnia and Herzegovina, North Macedonia, and Serbia. It is a great honor and pleasure to cordially wish a warm welcome to all the participants of the conference.

As a part of this year's conference, the 6th Student Section – EcoTERS'24 will be held. We appreciate the contribution of the students and their mentors who have also participated in the conference and hope that students will continue to explore and to be curious, since education is a never-ending process, and knowledge is continuously growing.

The organization of the EcoTER'24 conference has been financially supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia.

The support of the Donors and their willingness and ability to cooperate has been of great importance for the success of the EcoTER'24 conference. The organizing committee would like to extend their appreciation and gratitude to the Platinum donors of the conference – Serbia ZiJin Copper doo Bor and HBIS SERBIA, to the Gold donor of the conference – Elixir Group, as well as to the Silver donor of the conference – Serbian Chamber of Engineers.

We would like to express our sincere appreciation to all the authors who have contributed to the Proceedings. We would also like to express our gratitude to the members of the scientific, organizing and honorary committees, reviewers, speakers, chairpersons and all the conference participants for their support of the EcoTER'24. Sincere thanks go to all the people who have contributed to the successful organization of the EcoTER'24.

Prof. Snežana Šerbula,

President of the scientific and organizing committee

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APPLICATION OF NATURAL ZEOLITE – CLINOPTILOLITE IN WATER TREATMENT BY ADSORPTION AND PHOTOCATALYSIS

Nevenka Rajić[1*], Jelena Pavlović[2]

[1]Faculty of Ecology and Environmental Protection, University Union – Nikola Tesla, Cara Dušana 62–64, 11158 Belgrade, SERBIA

[2]Institute of Soil Science, Teodora Drajzera 7, 11000 Belgrade, SERBIA

[*]*nrajic@unionnikolatesla.edu.rs*

Abstract

The adsorptive and photocatalytic performance of the Serbian clinoptilolite-rich zeolitic tuff (ZT) is reported. Mg^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} adsorption studies, as well as kinetics and thermodynamics, were conducted by ZT under carefully controlled temperature, pH, grain size, and solid/liquid weight ratio conditions. ZT has a good adsorption capacity for the metal cations under study. By converting ZT to Fe-containing ZT (Fe-ZT and Fe_3O_4-ZT), the ZT becomes effective at eliminating phosphate and nitrate ions, which are typically found in surface and groundwater, as well as the antibiotic ciprofloxacin, which is one of the most used antibiotics and is present in wastewater as an organic micropollutant. It was also found that ZT exhibits photocatalytic activity in the decomposition of common organic dyes such as methylene blue (MB). The photocatalytic activity was ascribed to trace amounts of the Fe species as a minor satellite phase in the tuff. Sn-containing ZT (Sn-ZT) also shows catalytic activity in the MB degradation. The ZT decomposes MB in an eco-friendly manner at room temperature, atmospheric pressure, and visible light irradiation.

Keywords: zeolite, clinoptilolite, toxic metal cations, adsorption, photocatalysis.

INTRODUCTION

Zeolites are crystalline porous minerals with a three-dimensional lattice structure composed of a network of corner-sharing tetrahedra, TO_4 (T=Si, Al), which have Si and Al atoms in the center of the tetrahedra. Because the crystal structure contains geometrically precise structured channels and cages, only species of the appropriate size can diffuse through the lattice. Zeolites can, therefore, be used in ion exchange, adsorption, separation procedures, and molecular sieves. Zeolites can also be employed as heterogeneous catalysts by being transformed into strong solid acids [1,2].

Clinoptilolite is the most prevalent kind of natural zeolite. With a pore diameter of up to 0.7 nm, eight- and ten-member ring channels show an open reticular structure readily accessible [3,4]. Two channels (A and B) are parallel to the c-axis. The ten-membered rings in the A channels have a tightly compressed aperture of 0.31 x 0.75 nm, while the eight-membered rings in the B channels have an aperture of 0.36 x 0.46 nm. The C channels comprise eight-membered rings parallel to the a-axis with an aperture of 0.28 x 0.47 nm. Water molecules occupy extra-framework sites specific to crystallography, as do

exchangeable alkali and alkali earth cations. Due to differences in the Si/Al ratio, clinoptilolite samples from various regions have varying ion-exchange capacities.

We have studied the adsorption and photocatalytic properties of clinoptilolite from the Slanci deposit in Serbia. The clinoptilolite's ability to exchange cations with different heavy metal cations frequently present in wastewater and its ability to adsorb certain anions and exhibit photocatalytic activity have all been thoroughly examined.

MATERIALS AND METHODS

Zeolitic tuff (ZT) from the Serbian deposit Slanci (Veliko selo, Belgrade) was used in experiments. Clinoptilolite content determined by a semiquantitative X-ray diffraction analysis (using the Rietveld refinement method Topas-Academic v.4) was 80 wt.%, feldspar – 16 wt.% and quartz – 4 wt.%. The cation exchange capacity (CEC), measured by standard procedure [5] was 162 mmol M^+/100 g. For all the experiments, the grain size was chosen in the range 0.063–0.125 mm, for which preliminary tests proved that it is an optimal range for experimental work and achieving high capacity [6,7]. Before the experiments, the samples were sieved, washed with deionized water to remove impurities, and dried in an oven at 105°C overnight to a constant mass. All samples were converted into Na-rich form (Na-ZT) by treatment with 2 mol dm^{-3} of NaCl for 24 h at 70°C to achieve the best possible exchange capacity.

Conversion of ZT into Fe-ZT, Fe_3O_4-ZT, and Sn-ZT

The ZT was converted into Fe-containing ZT (Fe-ZT) using a two-step procedure: 1) treatment of ZT with a water solution of $Fe(NO_3)_3$ in an acetate buffer (pH=3.6) followed by the addition of 0.1M NaOH until pH~7, and 2) heating of the product at 80°C until a constant mass. The ZT was also converted to Fe_3O_4-ZT by alkaline co-precipitation of $FeCl_3 \cdot 6H_2O$ and $FeSO_4$ water solution in a molar ratio of 2:1, and to avoid the formation of non-magnetic iron oxide particles, the synthesis was performed under N_2 atmosphere. The obtained product was heated at 80°C until a constant mass. Conversion of ZT into Sn-ZT included: 1) treatment of ZT with 1 mol dm^{-3} HCl at 100°C for 4 h followed by treatment with 0.2 mol dm^{-3} NH_4OH at 65°C for 0.5 h to obtain H-form of clinoptilolite (H-ZT), and 2) treatment of H-ZT with the ethanolic solution of $SnCl_2$ (8.8 mmol dm^{-3}) and NH_4OH followed by calcination at 400°C for 2h.

Fe-ZT surface was examined by transmission electron microscopy (TEM) by using a 200-kV TEM microscope (JEM-2100 UHR, Jeol Inc., Tokyo, Japan) equipped with an ultra-high-resolution, objective-lens pole-piece having a point-to-point resolution of 0.19 nm. Electron diffraction patterns (EDPs) and TEM images were recorded by 2k charge-coupled device camera using Digital Micrograph™ (Gatan Inc., USA) as a user interface. Elemental compositions of samples were obtained by a Carl Zeiss SupraTM 3VP (Zeiss, Jena, Germany) field-emission gun scanning electron microscope (FEG-SEM) equipped with an EDS detector (Oxford Analysis) with the INCA Energy system for quantification of elements. The specific surface area of samples was determined by the nitrogen sorption method using an automatic sorption analyzer (Micrometrics ASAP 2020, Norcross, GA, USA).

Adsorption studies of M(II) ions onto ZT

The M(II) sorption (M – Mg, Mn, Ni, Cu, Zn, Pb) was studied at 25–55°C. The suspensions of Na-ZT and the chosen M(II) solution (100–400 mg M dm^{-3}) were shaken at about 100 rpm for 24 h in a thermostated water bath (Memmert WPE 45, Germany). M(II) solutions were prepared by dissolving $M(NO_3)_2$ (Fluka, p.a.) in deionized water. The M(II) concentrations were measured by AAS (Varian SpectrAA 55B atomic absorption spectrophotometer, SpectraLAb inc., Markham, ON, Canada).

Adsorption studies of nitrate, phosphate, and ciprofloxacin onto Fe-ZT and Fe_3O_4-ZT

Solutions of KNO_3 and KH_2PO_4 (1–6 mmol dm^{-3}) were used for nitrate and phosphate adsorption. Adsorption of ciprofloxacin (CIP) was studied for the initial CIP concentrations from 0.04 to 0.2 mmol dm^{-3}. The adsorption experiments were carried out at pH~5, for which CIP is present as a cation. KNO_3, KH_2PO_4, and CIP (supplied by Aldrich) were dissolved in deionized water. The concentration of adsorbates was measured using a UV-Vis spectrometer (Lambda 365 spectrophotometer, Perkin Elmer Inc., Waltham, MA, USA).

All adsorption experiments were carried out by a batch method under controlled conditions: the thermostated bath temperature was maintained constant to within ± 0.1°C, the zeolite samples were weighted to four-digit accuracy, and the solution concentrations were determined with four-digit accuracy. All chemicals used were analytical-grade reagents. The adsorbate concentration was measured in filtrate after solid/liquid separation.

The concentration of adsorbate on adsorbents was calculated using the using the following formula:

$$q_t = \frac{C_0 - C_i}{m} \cdot V \qquad (1)$$

where C_0 and C_i are concentrations of the adsorbate in aqueous solution (mg dm^{-3}) before and after the contact with ZT (Fe-ZT or Fe_3O_4-ZT), respectively; V is the solution volume in dm^3, and m is the mass of the ZT (Fe-ZT or Fe_3O_4-ZT) in g.

Photocatalytic test

Photocatalytic tests were carried out using a batch reactor system equipped with a 50 cm^3 Pyrex glass cell and a circulating water jacket to keep the temperature constant at 25°C during the reaction (Figure 1).

Suspension contained water solution of MB (C_0 = 10 mg dm^{-3}) and ZT or Sn-ZT in the concentration of 0.2 g dm^{-3} at different pH (pH = 3, 6, or 9), was continuously stirred by magnetic stirrer for 30 min to achieve an adsorption/desorption equilibrium and then irradiated for 300 min by using Osram Ultra Vitalux lamp/300 W, served as the visible light source and positioned 10 cm above the photocatalytic reactor. The concentration of MB was followed colorimetrically at λ=664 nm by UV/VIS spectroscopy (Lambda 365 spectrophotometer, Perkin Elmer).

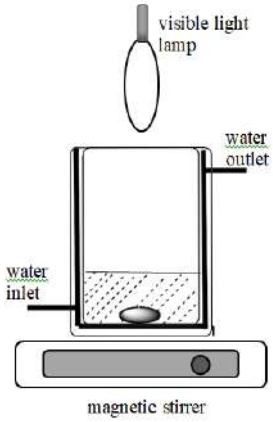

Figure 1 *The schematic presentation of the reactor system used in photocatalytic tests*

RESULTS AND DISCUSSION

Conversion to Fe-ZT, Fe_3O_4-ZT, and Sn-ZT resulted in the production of novel phases that covered the ZT surface. An EDS analysis revealed that there was a significant decrease in exchangeable cation content for Fe-ZT, Fe_3O_4-ZT, and Sn-ZT when compared to ZT and that the decrease in exchangeable cation content for Fe (as well as Sn) content was significantly greater than that for ZT. This indicates that 1) an ion exchange reaction happened, and 2) precipitation of the Fe (or Sn species) at the ZT surface occurred during the conversion of ZT to Fe-ZT/Fe_3O_4-ZT/Sn-ZT. The Fe content in Fe-ZT rose from 0.21 (ZT) to 18.1 wt.%, Fe_3O_4-ZT from 0.40 (ZT) to 5.63 wt.%, while the Sn content was 14.9 wt.%. Figure 2 depicts the Fe-ZT surface as a representative example of cover at the ZT surface.

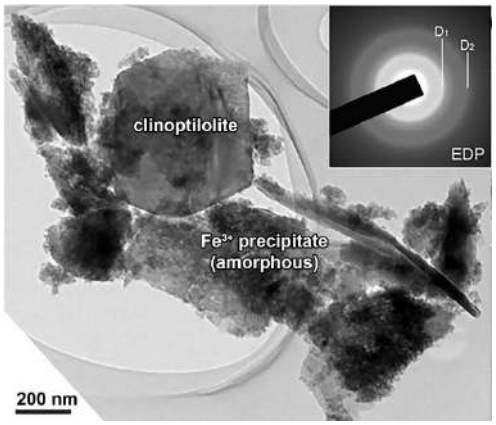

Figure 2 *TEM image of Fe-ZT: bright-field image of clinoptilolite sheets coated with a precipitate rich in Fe(III). The amorphous nature of the Fe(III) precipitate is confirmed by its electron diffraction pattern (EDP) in the upper right corner*

Accumulation of the Fe- and Sn-containing precipitates increases the specific surface area of ZT from 28.6 to 140.3 $m^2\ g^{-1}$ for Fe-ZT, to 45.2 $m^2\ g^{-1}$ for Fe_3O_4-ZT and to 78.0 $m^2\ g^{-1}$ for Sn-ZT. It seems likely that the increase in the specific surface can be attributed to forming a second porous system at the ZT surface. Powder XRD analysis showed that the conversion did not affect the crystallinity of ZT. TEM analysis showed amorphous Fe(III) precipitates on

Fe-ZT, and an abundant coverage of the ZT plates by rounded magnetite nanocrystals on Fe_3O_4-ZT, and X-ray photoelectron spectroscopy (XPS) exhibited the presence of SnO_2 on Sn-ZT. According to the XPS depth profiles, the Fe and Sn concentrations decrease from the samples' top to bottom.

Adsorption experiments showed that Na-ZT can capture the investigated cations from water media through an endothermic ion exchange reaction. Specifically, metal ions from an aqueous solution that come into contact with the Na-ZT replace Na^+ ions from the clinoptilolite lattice. Even though all the metal ions under study have hydrated radii that are noticeably larger than the clinoptilolite's lattice aperture, the ion exchange process does not seem to be restricted by intra-particle diffusion. One offered explanation is that the cations' coordination sphere changes as the reaction progresses [8]. Table 1 displays the Na-ZT's removal efficiency and ionic radii [9] of the removed cations.

Table 1 *Removal efficiency (%) of Na-ZT towards M(II) at the initial concentration of 1.5 mmol M(II) dm^{-3} at 25°C*

M(II)	Removal, %	Ionic radius, pm
Mg	60	66
Mn	47	82
Ni	15	70
Cu	84	73
Zn	50	74
Pb	100	119

The removal efficiency increases with temperature for all of the cations under study. Thus, when the temperature rose from 25 to 45°C, the removal efficiency towards Cu(II) increased by about 14%. Furthermore, the pseudo-second-order rate model provides the most accurate description of the cations' adsorption kinetics. However, only for Mn^{2+} and Ni^{2+} does the rate of adsorption increase with temperature, and only for Mn^{2+} does the increase become statistically significant. This may be because the hydrolysis of metal ions affects the adsorption kinetics [10,11].

The adsorption kinetics for nitrate and phosphate anions agrees reasonably well with the Lagergren pseudo-second-order model. The maximum affinity for the phosphate ions Fe-ZT was found at pH~6.5. The ^{31}P NMR analysis, according to Kaplanec *et al*. [12], showed the intricacy of the phosphate adsorption mechanism, which consists of a more substantial covalent bonding between the phosphate ion and Fe(III) and also electrostatic interactions. The phosphate is bound as a bidentate ligand most of the time. Temperature increases the removal efficiency of both phosphate and nitrate ions. The Langmuir isotherm, which produces the Langmuir constant (R_L) values in the range of 0–1, suggests favourable adsorption. As part of their adsorption mechanism, nitrate ions partially bind by ion exchange, replacing hydroxyl ions [13].

Adsorption of CIP onto Fe_3O_4-ZT is very fast [14]. Over 80% of the maximum adsorption capacity is reached within the first ten minutes. The Langmuir isotherm model explains the equilibrium adsorption data, while the Lagergren pseudo-second-order equation describes the

adsorption kinetics. The adsorption mechanism most likely involves strong electrostatic interactions between the cationic form of CIP and the negatively charged Fe_3O_4-ZT surface.

Sn-ZT showed a high photocatalytic activity in the degradation of methylene blue, which could mainly be ascribed to the presence of photocatalitically active SnO_2 at the surface of ZT [15]. However, the clinoptilolite lattice and SnO_2 particles work together synergistically. ZT's adsorption affinity for cationic organic dyes draws more molecules to the surface, which produces hydroxyl radicals that open up many active sites for the adsorption of intermediates. Moreover, the lattice prevents the SnO_2 particles from aggregating, which usually reduces their activity. Electron-hole recombination accompanying photocatalysis is possible because oxide particles are attached to specific crystallographic sites in the lattice.

ZT demonstrates remarkable photocatalytic activity in the degradation of MB as well [16]. The total degradation of MB is affected by pH, which peaks at pH=6 (70% for C_0=10 mg MB dm^{-3} for 300 min). The photodegradation process follows the Langmuir–Hinshelwood kinetic model. The entire dye degradation process is caused by the combined action of the Fe(III) species, which are generally present as impurities in zeolitic tuffs. When MB is exposed to visible light, these species also impact its initial adsorption and degradation. Comparable results are obtained from zeolitic tuffs in other regions [17]. Fe impurities play a role in photocatalysis, as evidenced by the fact that photocatalytic activity rises with increasing Fe content.

CONCLUSION

One of the most common natural zeolites, clinoptilolite, is a mineral resource in R. Serbia. This study's results suggest that clinoptilolite is a valuable adsorbent for various contaminants and can be applied to wastewater treatment in environmentally friendly processes. It exhibits photocatalytic activity, which is currently one of the most promising ways to eliminate organic micropollutants such as organic dyes.

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