

9th Croatian-Slovenian-Serbian Symposium on Zeolites



PROCEEDINGS

Editors

Ivona Nuić

Matjaž Mazaj

Aleksandra Daković

Zagreb, 2021



Statue of Grgur Ninski (Bishop Gregory of Nin), Split, sculpted by Ivan Meštrović. Gregory of Nin, 10th-century Croatian bishop who defended the usage of old Croatian language in liturgical services instead of Latin. According to tradition, after rubbing his big toe, your wish will come true...

Front-page: Panoramic view of historic old town of Split (the palace of Diocletian), waterfront, West coast and Marjan hill

Proceedings of the 9th Croatian-Slovenian-Serbian
Symposium on Zeolites

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SYMPOSIUM ON ZEOLITES

September 23-25, 2021
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9th Croatian-Slovenian-Serbian Symposium on Zeolites

23rd-25th September 2021, Split, Croatia

Time	Thursday, 23. 09. 2021	Time	Friday, 24. 09. 2021	Time	Saturday, 25. 09. 2021
8:30-9:00	Registration				
9:00-9:30	Opening				
	<i>chair Bronić</i>		<i>chair Rakić</i>		<i>chair Vukojević Medvidović</i>
9:30-10:15	PL Mintova	9:00-9:45	PL Giordano	9:00-9:45	PL Migliori
10:15-10:45	IL Byrne	9:45-10:15	IL Žerjav	9:45-10:15	IL Ugrina
		10:15-10:30	OP Kalebić	10:15-10:30	OP Labtim d.o.o.
10:45-11:15	 <i>Coffee break</i>	10:30-11:00	 <i>Coffee break</i>	10:30-10:45	CP Jasika d.o.o.
	<i>chair Novak Tušar</i>		<i>chair Bosnar</i>	10:45-11:00	CP Alumina d.o.o.
11:15-11:20	CP Labtim d.o.o.	11:00-11:15	OP Hrenović	11:00-11:15	Closing remarks and <i>Coffee break</i> 
11:20-11:35	OP Bosnar	11:15-11:30	OP Ivanković		
11:35-11:50	OP Šktjanc	11:30-11:45	OP Dikić		
11:50-12:05	OP Medak	11:45-12:00	OP Vukojević Medvidović		
12:05-12:20	OP Palčić	12:00-12:15	OP Vukojević Medvidović		
12:20-12:35	OP Rac	12:15-12:30	OP Mužek		
		12:30-12:45	OP Nuić		
12:35-14:00	 <i>Lunch</i>	12:45-14:00	 <i>Lunch</i>		
	<i>chair Zabukovec Logar</i>				
14:00-14:45	PL Valtchev				

14:45-15:15	IL Markiv			<p>PL = plenary lecture IL = invited lecture OP = oral presentation CP = company presentation</p>
15:15-15:30	OP Vu			
15:30-15:45	 <i>Coffee break</i>			
	<i>chair Trgo</i>			
15:45-16:00	OP Stojanović			
16:00-16:15	OP Pavlović			
16:15-16:30	OP Smiljanić			
16:30-16:45	OP Dimitrijević	16:00-18:00	<i>Diocletian Palace walking tour</i>	
16:45-17:00	OP Novaković	19:00-	<i>Conference dinner</i>	
17:00-17:15	OP Dib			

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Boris Subotić: 75th anniversary of life and 52 years of scientific work

Dr. sc. Boris Subotić is a retired senior scientist at the Ruđer Bošković Institute. He is a well-known and internationally recognized scientist in the field of microporous and mesoporous materials, especially zeolites.

Dr. sc. Boris Subotić was born on December 02, 1946. in Dugo Selo, near Zagreb, Croatia. He achieved the BS degree at the Faculty of Science, University of Zagreb, and was employed in the Laboratory for Colloid Chemistry of the Ruđer Bošković Institute in 1969. In 1976 he obtained the Ph.D degree in Chemistry at the Ruđer Bošković Institute and the University of Zagreb. In 1988 he became a co-founder and member of the Laboratory for the Synthesis of New Materials, and from 1995 to 2011 he was the head of the same laboratory. He was also a member of the Institute's Scientific Council for a long time, and from 2005 to 2009 he was a member of director's advisory team and President of the Institute's Commission for Innovation. He was also co-founder of the Croatian Zeolite Association and the first president of the Association.

During his long scientific work, he established the research of zeolites at the



Dr. sc. Boris Subotić

Ruđer Bošković Institute (synthesis, characterization and application) with a special emphasis to investigation of mechanisms of crystallization and transformation of zeolites. In this context, he established theoretical basis of the model of autocatalytic nucleation of zeolites, and together with co-workers, experimentally proved validity and significance of the model. In the meantime, together with the coworkers, he developed the model of crystallization of zeolites based on the population balance theory, including all relevant subprocesses (mechanism and kinetics of precipitation amorphous aluminosilicate precursor, its dissolution as well as nucleation and crystal growth of zeolites). The results of more recent investigations showed that crystallization of zeolites in heterogeneous systems (aluminosilicate hydrogels) occur via formation/transformation of three different

alumino-silicate precursors (gel, worm-like particles and condensed aggregates), and that crucial importance in the process of crystallization play the core-shell nano-precursors (3–20 nm in size) formed at the very early stage of the crystallization process. For this reason his very recent and present investigations are focused on the investigation of chemical and structural properties of the core (amorphous silica)@shell (TAA-polysilicates) and their influence on the course of crystallization and properties of products (zeolites).

Besides the main directions of investigation, dr. Boris Subotić and co-workers also studied solution-mediated transformations of thermodynamically less stable types of zeolites (mainly zeolite A) and some other materials (orthombic barium fluoride) to more stable ones (zeolite P, hydroxysodalite, cubic zeolite P), thermodynamics and kinetics of exchange of cations from solution with the host ions from zeolites, mechanochemical transformations of zeolites to amorphous phase, high-temperature transformations of zeolites, amorphous aluminosilicates to ceramics, etc.

Dr. sc. Boris Subotić is still very active scientist publishing regularly in prestigious world's journals.

He has published more than two hundred scientific papers, and between them more than hundred are included in Web of Science Core Collection. The number of citations of dr. sc. Boris Subotić is about 3000, and his h-index is 29. He is the author

of five chapters in books and four patents. He has been the supervisor of one post-doctoral fellowship, ten PhD thesis and four master's theses.

Also for a great contribution in establishing of cooperation with many scientists, what is, in addition to scientific results, nice way to enrich knowledge of our and world's culture and art.

We wish him many years of good health and fruitful work.

Congratulations are joined by the Slovenian Zeolite Association and the Serbian Zeolite Association.

Tatjana Antonić Jelić (*Croatian Zeolite Association*)

PREPARATION AND ANTIBACTERIAL ACTIVITY OF COMPOSITES BASED ON THYMOL/CARVACROL AND CLINOPTILOLITE

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ABSTRACT

Composites based on clinoptilolite and monoterpene phenols - thymol and carvacrol were prepared by supercritical solvent impregnation (SSI) at 30 MPa and 35 °C during 18 h in supercritical carbon dioxide (scCO₂). The composites were characterized in detail and their antibacterial activity was tested towards two potentially pathogenic bacteria; *Escherichia coli* and *Staphylococcus aureus*.

Key words: thymol, carvacrol, antibacterial activity, clinoptilolite, supercritical solvent impregnation.

INTRODUCTION

Due to antimicrobial properties, phenols and polyphenols obtained from plant essential oils are intensively studied. Thymol [2-Isopropyl-5-methylphenol] and carvacrol [5-Isopropyl-2-methylphenol] are major components of oregano (*Origanum vulgare*) used from ancient times [1]. Both compounds exhibit antimicrobial, antioxidant, anti-inflammatory, antitumor, antimutagenic, analgesic, anti-parasitic and insecticidal properties [1,2]. The use of bioactive compounds is most favourable if they are immobilized on suitable carriers. In this work natural zeolite – clinoptilolite was tested as a carrier of thymol and carvacrol, and antibacterial activity of the prepared composites towards Gram negative *Escherichia coli* DSM 498 and Gram positive *Staphylococcus aureus* ATCC 25923 were studied.

EXPERIMENTAL

Preparation of the composites

Zeolitic tuff (Z) with about 70 wt. % of natural zeolite – clinoptilolite from Vranjska Banja deposit (Serbia) was used in experiments. Z was converted into NH₄-form (NH₄-Z) using a solution of ammonia acetate (1 mol dm⁻³) and H-form (H-Z) using the following procedure. NH₄-Z was firstly calcined in air at 550 °C and the calcined product was treated with 0.6 mol dm⁻³ HCl at 70 °C. The obtained product was washed with distilled water until the negative reaction to Cl⁻ and dried overnight at 60 °C to a constant mass.

Crystalline thymol and liquid carvacrol (purity > 99%, Sigma Aldrich, Germany) were impregnated onto H-Z in a high-pressure view cell using a static mode at optimized conditions (35 °C, 30 MPa, time interval of 18 h, decompression rate of 1.5 MPa min⁻¹) using CO₂ as supercritical fluid. The obtained composites were denoted as T-Z (thymol-containing zeolite) and C-Z (carvacrol-containing zeolite).

Characterization of synthesized composites

The content of thymol and carvacrol in composites were determined by thermogravimetric analysis (TGA) using a SDT Q-600 simultaneous DSC-TGA instrument (TA Instruments), as well as by C, H, N analysis using Varian EL III C,H,N,S/O Elemental Analyzer (Elementar, Langensfeld, Hesse, Germany). Crystallinity of the samples was examined by PXRD method using Ultima IV Rigaku diffractometer equipped with Cu K_{α1,2}

radiation using a generator voltage (40.0 kV) and a generator current (40.0 mA). The PXRD patterns were recorded in the 2θ range $5 - 45^\circ$ with a scanning step of 0.02° and the scan rate of 5°min^{-1} . Specific surface area was measured by N_2 adsorption–desorption experiments (Micromeritics ASAP 2020) and calculated according to the Brunauer, Emmett, Teller (BET) method. Interactions of the phenols and zeolite lattice were studied by Fourier Transform Infrared (FTIR) Spectroscopy. The FTIR spectra were recorded in the range $4000\text{--}450\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} at room temperature, using Nicolet iS10 (Thermo Scientific) spectrometer.

Antibacterial activity test

Antibacterial activity of the composites was tested in different water media: phosphate buffer solution (PBS), commercially available spring water (Gala, Serbia, SW), and lake water (Sava Lake, Belgrade, Serbia, SL) toward Gram negative *E. coli* DSM 498 and Gram positive *S. aureus* ATCC 25923. Firstly, bacteria were pre-grown on the Nutrient agar (NA, Torlak, Serbia) for 16 h at $37\pm 0.1^\circ\text{C}$ to obtain cultures in a *log* phase of growth. All water media were sterilized before the tests by autoclaving ($121^\circ\text{C}/20\text{ min}$) and the composite samples by UV light in UV chamber for 30 min.

The experiments were performed as follows: into 10 cm^3 of bacterial biomass suspended in a sterile water media 0.1 g of each composite (T-Z or C-Z) was added, and incubated in a thermostatic water bath during 24 h at $37\pm 0.1^\circ\text{C}$ with shaking at 105 rpm. As a positive control (without antibacterial activity), the bottles with 0.1 g of H-Z in all studied media with bacteria were set up. The number of viable bacterial cells was determined at the beginning of the experiment, after 1 h (short contact) and after 24 h (long contact). After 1 and 24 h the aliquot of 0.1 cm^3 was plated by a spread plate method directly on NA and another amount of the sample (1 cm^3) was serially diluted ($10^{-1}\text{--}10^{-7}$). Diluted samples have also been plated onto NA and incubated for 24 h at $37\pm 0.1^\circ\text{C}$. After incubation the bacterial colonies grown on NA were counted. The number of bacteria was reported as CFU (Colony Forming Units) per one cm^3 , logarithmically transformed and the antibacterial activity was finally expressed as the percent of reduction of the log of CFU cm^{-3} according to the Equation (1). All experiments were done in triplicate.

$$\text{Reduction (\%)} = \frac{\log \text{CFU cm}^{-3} (t_0) - \log \text{CFU cm}^{-3} (t)}{\log \text{CFU cm}^{-3} (t_0)} \times 100 \quad (1)$$

where t_0 presents the initial number of bacteria and t is the number of bacteria after time of contact (1 or 24 h).

Desorption of thymol and carvacrol from composites

Leaching of thymol and carvacrol from the composites were studied after antibacterial activity tests. The concentration of the phenols was measured photometrically using a UV-VIS spectrophotometer Cary 100 Scan (Varian) at $\lambda_{\text{max}} = 274\text{ nm}$.

RESULTS AND DISCUSSION

The conversion of Z into H-Z significantly increased the specific surface area of Z from $42\text{ m}^2\text{ g}^{-1}$ to $230\text{ m}^2\text{ g}^{-1}$ (H-Z) suggesting that the modification led to a partial pore opening of clinoptilolite lattice. PXRD analysis (not shown) confirmed that the modification is not accompanied by loss of zeolite crystallinity.

Thermal properties of the phenols and composites are presented in Fig.1. Thermogram of H-Z shows rather continual weight loss (10.0 wt.%) up to 350°C . The thermal decomposition of thymol and carvacrol (not shown in the Figure) proceeds as one-step-process up to 160°C with DTG maxima centred at 119°C (thymol) and 148°C (carvacrol). Fig. 1 shows that the composites have similar thermal behaviour: T-Z displays a strong DTG maximum at 134 and

C-Z at 135 °C, indicating that the SSI procedure successfully loaded phenols onto H-Z. Thymol and carvacrol content obtained from TGA agrees well with C, H, N analysis: 23.0 wt.% of thymol was obtained for T-Z and 19.2 wt.% of carvacrol for C-Z.

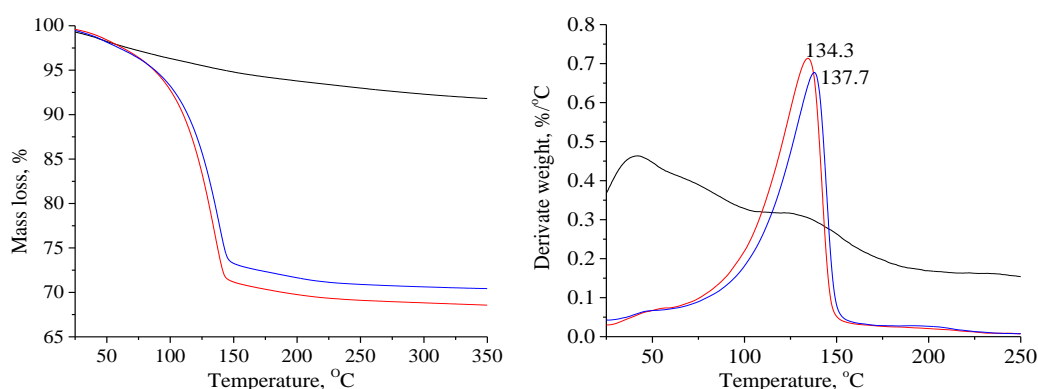


Figure 1. TG and DTG curves of H-Z (black line), T-Z (red line) and C-Z (blue line)

Fig. 2 shows FTIR spectra, which confirm the presence of the phenols on the composites. A broad band at 3580 – 3160 cm^{-1} corresponds to the phenolic –OH stretching vibrations, bands at 3000 – 2850 cm^{-1} belong to the C-H symmetric and asymmetric stretching vibration [3], while the bands between 1620 and 1417 cm^{-1} originate from C=C stretching vibrations in phenolic ring of thymol and carvacrol [4]. The bands attributed to the out-of-plane C-H wagging and bending vibrations from isoprenoids at around 804 cm^{-1} and at 945 cm^{-1} , respectively, were ascribed to phenols presented in the zeolite lattice [5]. Taking into account band positions it can be concluded that there is no significant difference between free and immobilized phenols suggesting that the interactions of the phenols and Z do not include formation of covalent bonds.

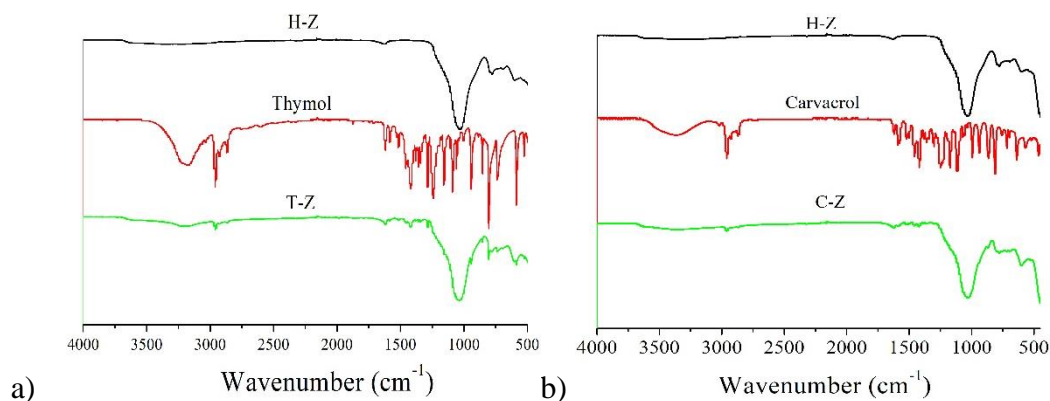


Figure 2. FTIR spectra of H-Z, thymol and T-Z (a) and H-Z, carvacrol and C-Z (b).

Antibacterial activity

Antibacterial activity was investigated toward Gram negative *E. coli* and Gram positive *S. aureus* in different water media (Table 1.). According to previous studies, H-Z did not exhibit any antibacterial activity towards examined strains (data not shown). After 1 h of contact in SL, T-Z exhibited a significant antibacterial activity toward both strains (62.6 and 72.2 % toward *E. coli* and *S. aureus*, respectively). In other water media, T-Z exhibited bactericidal effect after only 1 h of contact, except in the case of *S. aureus* in SW, where bactericidal effect appeared after 24 h. The C-Z exhibited bactericidal activity toward both examined strains in all media after 1 h of contact. Considering the obtained results, it is evident that C-Z shows better antibacterial activity than T-Z in the case of short-term exposure. This suggests that mechanism of the antibacterial action is influenced by chemical structure of bioactive compound.

Table 1. Percent of reduction in number of *E. coli* and *S. aureus* after 1 and 24h of contact with T-Z and C-Z in different water media.

Water medium	Reduction (%)							
	T-Z				C-Z			
	<i>E. coli</i>		<i>S. aureus</i>		<i>E. coli</i>		<i>S. aureus</i>	
	1 h	24 h	1 h	24 h	1 h	24 h	1 h	24 h
PBS	100±0	100±0	100±0	100±0	100±0	100±0	100±0	100±0
SW	100±0	100±0	70±0	100±0	100±0	100±0	100±0	100±0
SL	65±7	100±0	71±2	100±0	100±0	100±0	100±0	100±0

t_0 *E. coli* 2.1×10^7 CFU cm⁻³; *S. aureus* 7.0×10^6 CFU cm⁻³ (experiment with thymol)

t_0 *E. coli* 7.6×10^6 CFU cm⁻³; *S. aureus* 1.5×10^7 CFU cm⁻³ (experiment with carvacrol)

Desorption of thymol and carvacrol from the composites

Leaching of thymol and carvacrol from the T-Z and C-Z were determined in all water media after antibacterial tests (Table 2). Although antibacterial activity of C-Z is more pronounced than that of T-Z, the amount of thymol leached from T-Z is significantly higher than carvacrol leached from C-Z. This could be explained by weaker interactions between thymol and zeolite.

Table 2. Percentage of the leached thymol/carvacrol from the composites T-Z and C-Z after 24 h of the contact.

Water media	% of the leached phenols			
	<i>E. coli</i>		<i>S. aureus</i>	
	Thymol	Carvacrol	Thymol	Carvacrol
PBS	23.2	8.6	22.7	6.2
SW	26.3	7.2	26.1	8.1
SL	32.9	8.6	28.1	8.9

CONCLUSION

Components of the essential oils such as thymol and carvacrol can be successfully immobilized onto natural zeolite - clinoptilolite by the supercritical solvent impregnation. The composites that contained 23.0 wt.% of thymol and 19.2 wt.% of carvacrol showed bactericidal activity toward both Gram-negative *E. coli* and Gram-positive *S. aureus*. This suggests their potential use as disinfectant agents. It is worth noticing that the impregnation of these phenols by supercritical solvent impregnation used in this work is a novel and an environmentally friendly approach in the preparation of materials with antibacterial properties.

ACKNOWLEDGEMENTS

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