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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PROCEEDINGS OF THE
9th CROATIAN-SLOVENIAN-SERBIAN
SYMPOSIUM ON ZEOLITES

September 23-25, 2021
Split, Croatia

Organizers
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SLOVENIAN ZEOLITE ASSOCIATION
SERBIAN ZEOLITE ASSOCIATION

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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				
	chair Bronić		*chair Rakić*		*chair Vukojević Medvidović*
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	☕ *Coffee break*	10:30-11:00	☕ *Coffee break*	10:30-10:45	CP Jasika d.o.o.
	chair Novak Tušar		*chair Bosnar*	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 *Coffee break* ☕
11:20-11:35	OP Bosnar	11:15-11:30	OP Ivanković		
11:35-11:50	OP Škrjanc	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	🍽 *Lunch*	12:45-14:00	🍽 *Lunch*		
	chair Zabukovec Logar				
14:00-14:45	PL Valtchev				

14:45-15:15	IL Markiv			PL = plenary lecture IL = invited lecture OP = oral presentation CP = company presentation
15:15-15:30	OP Vu			
15:30-15:45	☕ *Coffee break*			
	chair Trgo			
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	*Diocletian Palace walking tour*	
16:45-17:00	OP Novaković	19:00-	*Conference dinner*	
17:00-17:15	OP Dib			

CONTENTS

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 Chemisty 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.


Dr. sc. Boris Subotić

During his long scientific work, he established the research of zeolites at the 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 sub-processes (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*)

THE EFFICIENCY OF NATURAL CLINOPTILOLITE FOR CIPROFLOXACIN REMOVAL FROM AQUEOUS MEDIA

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ABSTRACT

Adsorption of the antibiotic ciprofloxacin (CIP) from an aqueous solution by calcium-rich clinoptilolite (CLI) was investigated. Obtained results showed that natural CLI possesses a high adsorption efficiency in the removal of CIP at 283, 288 and 293 K and at pH= 5. Adsorption kinetics studied for the initial CIP concentrations of 15–75 mg dm^{-3} follow Lagergren's pseudo-second order equation and the adsorption is best represented by the Langmuir model. The adsorption mechanism involves strong electrostatic interactions between aluminosilicate lattice of CLI and the cationic form of CIP accompanied by an ion-exchange reaction. The CIP saturated CLI was successfully regenerated by a cold atmospheric pressure plasma treatment.

Key words: clinoptilolite, ciprofloxacin, adsorption, plasma treatment.

INTRODUCTION

The use of antibiotics in both human and veterinary medicine is constantly increasing, while water pollution by these organics is generally poorly regulated. Antibiotics present in water media have different adverse effects on environment as well as human health. They belong to organic micropollutants (OMPs) and cannot be efficiently removed from water by conventional water treatment processes. Consequently, it is of great importance to find acceptable alternative technologies for their removal from water.

CIP is widely applied antibiotic for treatment of both human and animal bacterial infections because of its excellent activity against Gram-positive and Gram-negative bacteria. Thus, it has been found in wastewater effluents in concentrations from ng to mg dm^{-3}, with extremely high concentration of up to 50 mg dm^{-3} near drug manufacturing plants [1]. Moreover, due to the CIP zwitterionic nature, the charge is strongly pH dependent.

CLI is the most abundant natural zeolite. It has been extensively studied for adsorption of inorganic pollutants from water [2,3]. Reports on usability of CLI in pharmaceuticals removal are rather scarce [4]. This could be explained by the fact that adsorption of these organics has mostly been found as an irreversible process.

This study shows an excellent adsorption efficiency of CLI in CIP removal from water media. Spent adsorbent is recovered by cold atmospheric pressure plasma treatment which is novel method in regeneration of mineral adsorbents.

EXPERIMENTAL

Clinoptilolite-rich zeolitic tuff (Z) obtained from the deposit Slanci (near Belgrade, Serbia) was used as a starting material. Rietveld analysis showed that Z contains CLI as the major mineral phase (> 80 wt.%), quartz (< 7.5 wt.%) and feldspar (< 13 wt.%). The cation exchange capacity (CEC) of the CLI determined by a standard procedure was 162 mmol M^{+}/100

g. The particle size used in the experiments was in the range of 0.063-0.125 mm for which previous experiments showed that it is optimal one.

Characterization: Rigaku SmartLab diffractometer with CuKα radiation (λ = 1.54178 Å) was used for analysis of the mineral phases present in the samples. The PXRD patterns were recorded in the 2θ range 5–65°. Elemental analysis of the CLI phase was determined by a Carl Zeiss Supra^{TM} 3VP field-emission gun scanning electron microscope (FEG-SEM) equipped with EDS detector with INCA Energy system for quantification of elements. A simultaneous thermogravimetric (TGA) and differential thermal analysis (DTA) was performed using a SDT Q-600 instrument (TA Instruments). The specific surface areas and porosity characteristics were determined by N_2 adsorption isothermally at -196 °C, using a Micrometrics ASAP 2020, and the specific surface area of sample (S_{BET}) was calculated according to the BET method. The zeta potential of CLI was measured by a Zetasizer NanoZS90 (Malvern Instruments Ltd., UK).

Adsorption tests: The adsorption tests were performed by a batch method. The adsorption capacity was studied for different initial CIP concentration (15, 25 50 and 75 mg dm^{-3}) and temperatures (283, 288 and 293 K) at pH= 5. About 0.2 g of the zeolite was suspended in 50,0 cm^3 of the certain concentration of CIP solution and left under shaking in a thermostated water bath from 5 to 60 min. Solid phase was recovered by centrifugation and the CIP concentration in filtrate was measured by an UV-VIS spectrophotometer (Perkin Elmer Lambda 365) at λ= 278 nm according to a standard procedure [5].

Adsorbent regeneration: A surface dielectric barrier discharge (SDBD) source with a segmented electrode operating in air for 20 min was used for plasma treatment of the spent CLI.

RESULTS AND DISCUSSION

The PXRD pattern (Figure 1) showed that CLI was the main mineral phase. Diffractions at 2θ = 26.6° and 27.1° correspond to the presence of quartz and feldspar, respectively, which are major sattelite phase [6].

Elemental analysis of CLI showed that the Si/Al molar ratio is 5.03 which is the common value for natural clinoptilolite. Furthermore, the specific surface area (S_{BET}) was 23.57 m^2 g^{-1} which is in accordance with reported values for S_{BET} (usually in the range 15–40 m^2 g^{-1}).

Zeta potential measurements showed that CLI has a negatively charged surface in the whole range of pH values (Figure 2).

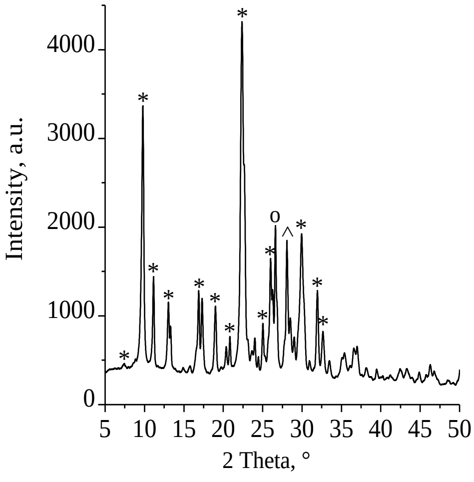

Figure 1. PXRD patterns of CLI (* – clinoptilolite, ° – quartz and ^ – feldspar).

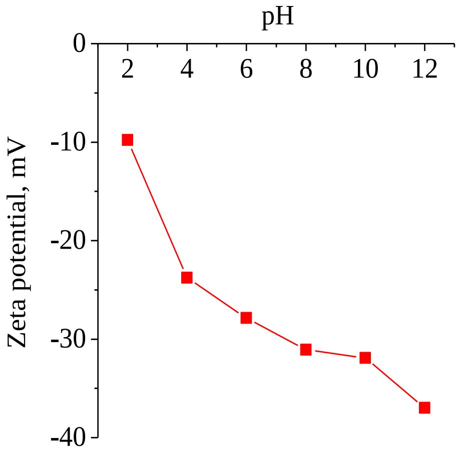

Figure 2. pH dependence of surface charging of CLI.

Since CIP molecule mainly exists as a zwitterion at neutral pH with a shift towards positively charged species at pH < 5.9 and towards anionic form at pH > 8.9, the pH of the solution strongly affects its adsorption performance [7]. Study of dependence of the adsorption capacity with pH showed that the best results can be obtained at pH= 5 (not shown). Accordingly, all experiments were done at pH= 5. Adsorption isotherms were studied at 283, 288 and 293 K. The equilibrium data were analysed by several empirical adsorption isotherm models [8]. Among the two-parameter models the Langmuir model gave the best results. The CIP uptake onto CLI increases rather sharply in the first 10 min for all studied temperatures and initial CIP concentrations. More than 80% of the maximum adsorption capacity was achieved in this 10 min period, indicating fast adsorption kinetics.

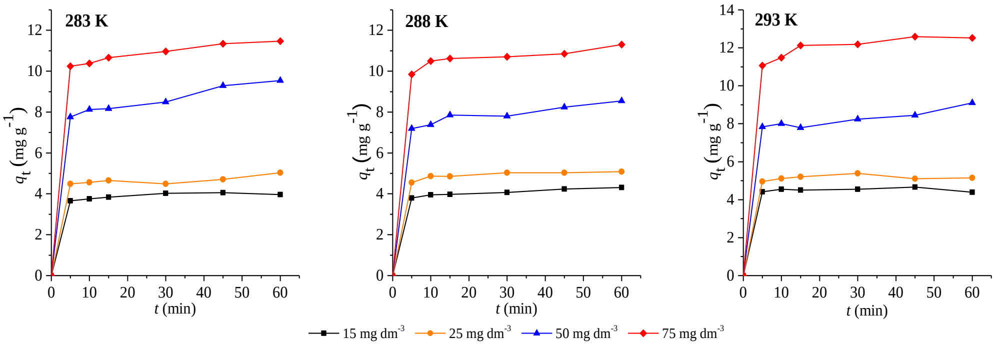

Figure 4. Adsorption kinetics for CIP on CLI for different temperatures; q_t is the amount of the adsorbed CIP (mg per 1 g of adsorbent) after time *t*.

Two reaction–based kinetic models were applied in order to describe the adsorption experimental data (Figure 4). Satisfactory fits were obtained only by the Lagergren's pseudo-second-order kinetic model (Table 1). Moreover, to investigate the influence of intra-particle diffusion on the CIP adsorption, the data were further processed by the Weber–Morris mass transfer model [9]. This did not result in agreement with experimental data suggesting that the intra-particle diffusion is not present in the adsorption.

Table 1. Rate constants for Lagergren's pseudo-second order kinetic model for the CIP adsorption on CLI (R^2 is the correlation coefficient of the linear regression).

C_0, mg CIP dm^{-3}	**CLI**			
	T, K	**k_2, g mg^{-1} min^{-1}**	**q_e, mg g^{-1}**	**R^2**
15	283	0.3393	4.09	0.9999
	288	0.2490	4.28	0.9998
	293	0.2275	4.82	0.9996
25	283	0.1896	4.90	0.9988
	288	0.2900	5.13	0.9999
	293	0.4011	5.24	0.9995
50	283	0.0436	9.78	0.9983
	288	0.0703	8.63	0.9991
	293	0.0714	8.94	0.9989
75	283	0.0868	11.58	0.9997
	288	0.0886	11.28	0.9991
	293	0.0443	13.27	0.9982

C_0 – initial CIP solution concentration (mg dm^{-3}); k_2 – pseudo-second-order rate constant, g mg^{-1} min^{-1}; q_e – adsorption capacity, mg g^{-1}.

Regeneration of the adsorbent. The CIP adsorption onto CLI includes an ion exchange reaction at the CLI surface (results are not shown) which is irreversible (results are not shown). Since the adsorbent reusability is the most important issue for the operational cost of wastewater treatment based on the adsorption, we tested cold atmospheric pressure plasma for regeneration of the spent CLI. The results showed that more than 90% of the initial adsorbent capacity can be recovered in five cycles by the plasma treatment (Figure 5). This recommends cold plasma treatment as an environmentally friendly method suitable for the recycling of CIP saturated CLI.

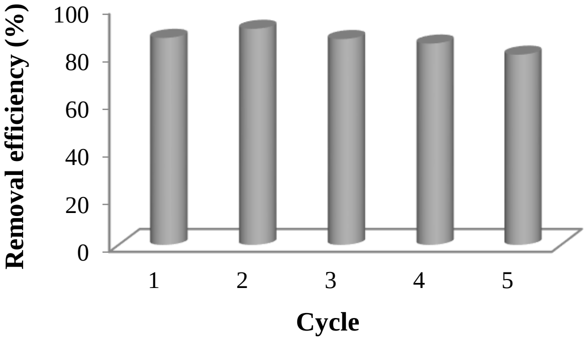

Figure 5. CLI removal efficiency through 5 adsorption cycles (C_0= 25 mg dm^{-3}; solid:liquid= 1:100; pH= 5; T= 21 °C).

CONCLUSION

The study shows that cost effective and environmentally friendly natural clinoptilolite can be a promising adsorbent for the removal of antibiotic ciprofloxacin from water media. The spent clinoptilolite can be successfully regenerated by cold atmospheric pressure plasma treatment.

ACKNOWLEDGEMENTS

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