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***on Analytical and Environmental Problems***

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**Organized by:**

SZAB Kémiai Szakbizottság Analitikai és Környezetvédelmi Munkabizottsága

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*Institute of Pharmaceutical Analysis, University of Szeged  
Department of Inorganic and Analytical Chemistry, University of Szeged*

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Environmental Protection*

## CHARACTERIZATION OF NATURAL ZEOLITE (CLINOPTILOLITE) AS ONE OF THE HIGH CATION EXCHANGE CAPACITY GEOPOLYMER MATERIAL

**Nenad Grba<sup>1</sup>, Marina Šćiban<sup>2</sup>, Dejan Krčmar<sup>1</sup>, Sanja Panić<sup>2</sup>, Mirjana Petronijević<sup>2</sup>, Slaven Tenodi<sup>1</sup>, Đurđa Kerkez<sup>1</sup>, Kristiana Zrnić Tenodi<sup>1</sup>, Dragan Radulović<sup>3</sup> and Božo Dalmacija<sup>1</sup>**

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### Abstract

The aim of this research is to subject one of the specific and locally used natural zeolite (clinoptilolite) from Vranjska Banja, Serbia with high cation exchange capacity. Mineralogical - X-Ray Diffraction Analysis (XRD), Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) and determination of cation exchange capacity (CEC) were investigated. Results showed homogenous structure with dominant clinoptilolite - heulandite type zeolites as most abundant minerals. The important aspect of this research is possibility of wider usage of natural zeolite-clinoptilolite due to cost-efficiency aspects of this natural material that can be exploited in large amount from several Serbian deposits e.g. "Zlatokop" (Vranjska Banja) and "Igroš Vidojević" (Brus), Serbia. The present of higher, but also extremely concentration of heavy metals in Pannonian, Internal Dinarides and wider European region lead us to boost novel high performance but economically viable techniques. The starting points are geochemical characterization of novel geo- materials before further water-treatment implementation.

### Introduction

Natural zeolites are hydrated aluminosilicate minerals with valuable physicochemical properties, such as cation exchange, molecular sieving, catalysis and sorption. In the past decades, natural zeolites have found a variety of applications in adsorption, catalysis, building industry, agriculture, soil remediation, and energy. The use of natural zeolites for environmental applications is gaining new research interests mainly due to their properties and significant worldwide occurrence. Natural zeolite have also been reported for removal of anions and organics from water systems [1, 2, 3]. These materials are abundant and low-cost resources and have been found in many areas of the world. In this paper we will examine the characterization of zeolite (clinoptilolite) from the territory of the Republic Serbia.

The aim of this work is to determine the consistent, homogeneity and high CEC capacity for local and economically most affordable materials in order to be used on field investigations on groundwater and industrial wastewater most suitable purification/remediation material in order to recommend it for best available water treatment technology as main adsorbent.

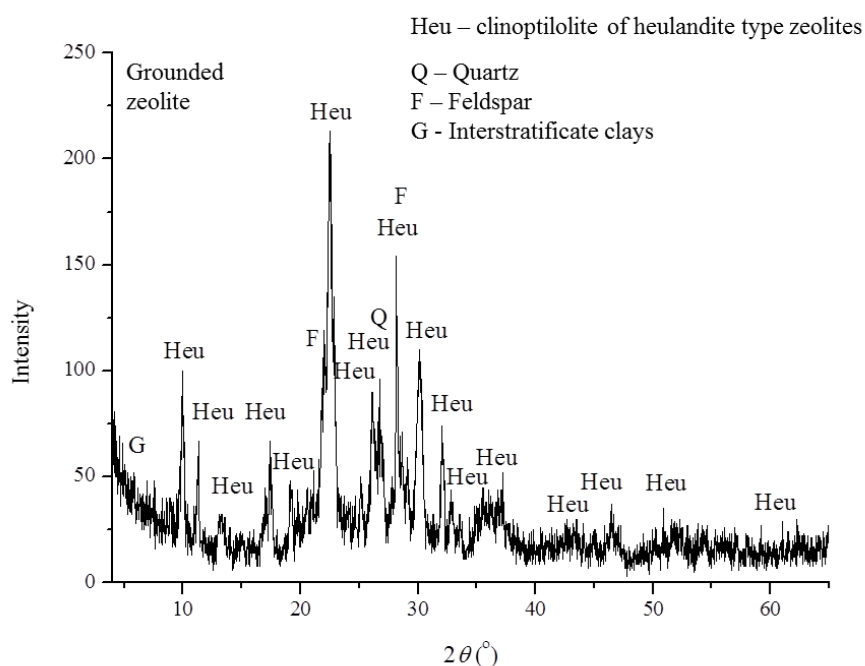
The need for new geomaterial with high to superhigh cation exchange capacity (CEC) have been stated in many scientific papers and field investigations [1]. The aim of this study is to characterize zeolites from the investigated area of Serbia, in this case specific geochemical composition from natural zeolite (clinoptilolite) from Vranjska Banja, Serbia.

## Experimental

The primary sample of zeolite, natural zeolite (clinoptilolite) from Vranjska Banja, Serbia ca. 1 kg, was prepared and dried by Standard methods for sample preparation (SRPS B.B8.080.) in Dryer - "Binder" (sample distributor Jones). The sample was analyzed for mineralogical - XRD analysis, SEM/EDS and determination of CEC. XRD and SEM analysis of the matrices were done in order to elucidate the microscopic structures and morphology of surfaces and CEC analysis will show specific content of exchangeable cations in clinoptilolite sample. Examination of the mineral composition of the sample was investigated by X-ray automatic powder diffractometer PHILIPS, model PW-1710. X-ray diffraction analysis was used to determine and monitor the phase composition of the sample. The intensities of diffracted  $\text{CuK}\alpha$  X-rays radiation ( $\lambda=1.54178\text{\AA}$ ) were measured at room temperature at intervals of  $0,02^\circ 2\theta$  and a time of 1 s in the range from  $4$  to  $65^\circ 2\theta$ . The X-ray tube was loaded with a voltage of 40 kV and a current of 30 mA, while the slots for directing the primary and diffracted beam were  $1^\circ$  and 0.1 mm. Method for determination of exchangeable cations  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  and cation exchange capacity was DM 10-0/40.

## Results and discussion

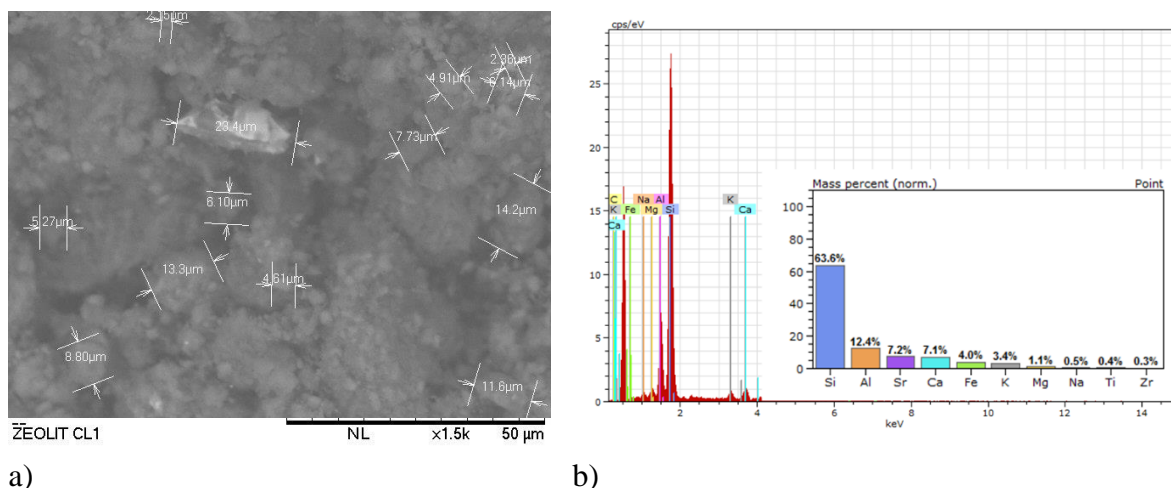
The sample was examined by X - ray diffraction on a polycrystalline sample (powder). The diffractogram of the tested sample is presenting the clinoptilolite - heulandite type zeolites as most abundant minerals.



**Figure 1.** The diffractogram of the clinoptilolite (natural zeolites) from Vranjska Banja

The presence of the following minerals was determined in the analyzed sample: clinoptilolite-heulandite type zeolites, feldspar, quartz, interstratified clays, carbonates and mica. The most common minerals are zeolite and then feldspar, while quartz is significantly less common. Of the feldspar, plagioclase is predominantly represented, relative to K-feldspar. Semiquantitative share crystalline phases (minerals) is as follows: zeolites  $\approx 85\%$ , feldspars  $\approx 10\%$ , clays  $\leq 5\%$ , quartz 2-3%. Carbonates, respectively calcite and mica are present in the trace.

The next important targeted analysis of sample surfaces is Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) method and results can be seen from Figure 2. The SEM-micrograph shows from several to tens micrometers semi-homogeneous structure and macro/meso-porosity. The brighter areas in the crystallites represent feldspar and darker areas clinoptilolite as in study from [4].



**Figure 2.** SEM-micrograph (a) and (b) EDS spectrum of the natural zeolite (clinoptilolite) sample

Generally, the important ratio for classification of zeolite from clinoptilolite type is Si/Al and according to the EDS analysis it was round 5.3 and accordingly higher than prescribed value of 4.5 [2] for this type. Additionally, previous studies support this examination with also similar Ca, Fe, K, Mg and Na content (Table 1) and similar chemical composition on globescale<sup>1</sup>.

**Table 1.** Results of EDS analysis from natural zeolite (clinoptilolite) from Vranjska Banja, Serbia compared with other related zeolites (clinoptilolite) samples

Element	[norm. wt.%]	[norm. wt.%] <sup>4</sup>	[norm. wt.%] <sup>3</sup>
<b>Silicon</b>	<b>69.98</b>	<b>65.63</b>	70.90
<b>Aluminium</b>	<b>13.19</b>	<b>12.97</b>	12.40
Calcium	7.49	3.08	2.54
Iron	4.19	1.48	1.21
Potassium	3.57	1.33	4.46
Magnesium	1.12	1.41	0.83
Sodium	0.44	0.95	0.28
<b>CEC (meq/g)</b>	1.2	/	1.6–1.8

The results of determining the content of exchangeable cations are shown in Table 2:

**Table 2.** Results of determining the content of variable cations of zeolite samples (meq/100g)

Sample/ions	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Σ <sub>cations</sub>
Natural zeolite (clinoptilolite) from Vranjska Banja, Serbia	2,53	48,47	68,61	3,36	<b>122,97</b>

Due to many study observed in paper from Wang and Peng, 2008 the CEC value could clasify this zeolite as higher in the class with high potential for local but also comercial near region used as adsorbent with superhigh cation exchange capacity regarding previous [4,5] but also ongoing and future studies.

### Conclusion

This research shows good potential and high CEC capacity of zeolite (clinoptilolite) from Vranjska Banja, Serbia. Future application will be based on this geochemical scanning of clinoptilolite as potentially well structure and geo-chemically powerful purification material.

### Acknowledgements

The authors acknowledge financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 451-03-68/2020-14/200125 and No. 451-03-68/2020-14/200134) and the Innovation Fund of the Republic of Serbia (Grant No. 5717). The authors also acknowledge PhD Goran Kitić and MSc Jovana Stanojev from BioSense Institute (Novi Sad, Serbia), for the technical support from SEM/EDS analysis.

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# *26<sup>th</sup> International Symposium on Analytical and Environmental Problems*

*Szeged, Hungary  
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**University of Szeged**



**Final Program**



## *26<sup>th</sup> International Symposium on Analytical and Environmental Problems*

### **Supporting Organizations**

*Hungarian Academy of Sciences*

*Institute of Pharmaceutical Analysis, University of Szeged*

*Department of Inorganic and Analytical Chemistry, University of Szeged*

### **General information**

*The Symposium features recent findings from leading industrial and academic experts in the field of analytical chemistry and environment related problems.*

### **Symposium Chairman:**

*István Ilisz, DSc, professor of chemistry*

*University of Szeged, Institute of Pharmaceutical Analysis*

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*University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection*

## **TIMETABLE**

### **Monday**

**9<sup>00</sup>-9<sup>15</sup>: Opening Ceremony**

**9<sup>15</sup>-12<sup>45</sup>: Oral Presentations: Session I**

**13<sup>30</sup>-16<sup>15</sup>: Poster session I**

### **Tuesday**

**9<sup>15</sup>-12<sup>45</sup>: Oral Presentations: Session II**

**13<sup>30</sup>-16<sup>30</sup>: Poster session II**

**16<sup>30</sup>: Closing Remarks**

**Oral Presentations: Monday (Session I)**

**Session Chair:** Dr. István Ilisz (*University of Szeged, Institute of Pharmaceutical Analysis*)

9<sup>15</sup>-9<sup>30</sup>

**EMISSIVE Zn(II) METALLOMESOGEN BASED ON TRIDENTATE TERPYRIDINE LIGAND**  
**Adelina A. Andelescu**, Benoît Heinrich, Emilie Voirin, Evelyn Popa, Massimo La Deda, Giuseppe Di Maio, Otilia Costişor, Bertrand Donnio, Elisabeta I. Szerb\*

9<sup>30</sup>-9<sup>45</sup>

**HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC ENANTIOSEPARATION OF SOME AMINO COMPOUNDS WITH PHARMACEUTICAL RELEVANCE ON ION-EXCHANGER-BASED CHIRAL STATIONARY PHASES**

**Attila Bajtai**, Dániel Tanács, Enikő Forró, Ferenc Fülöp, Wolfgang Lindner, Antal Péter, István Ilisz

9<sup>45</sup>-10<sup>00</sup>

**AMMONIA TRANSPORT ACCIDENT EXPOSURE ANALYSIS**

**Jovana Bondžić**, Maja Petrović

10<sup>00</sup>-10<sup>15</sup>

**STRUCTURAL AND MAGNETIC PROPERTIES OF THREE 1D COPPER(II) COORDINATION POLYMERS**

**Ildiko Buta\***, Peter Lönnecke, Evamarie Hey-Hawkins, Marius Andruh, Otilia Costisor

10<sup>15</sup>-10<sup>30</sup>

**COULD HUMIC SUBSTANCES BE GOOD ANTIOXIDANTS?**

**A. Csicsor**, E. Tombácz

10<sup>30</sup>-10<sup>45</sup>

**RECOGNITION OF RENEWABLE ENERGY AMONG BUSINESS STUDENTS**

**László Berényi<sup>1</sup>**, Nikolett Deutsch<sup>2</sup>

**Coffee Break**

**Session Chair:** Dr. Tünde Alapi (*University of Szeged, Department of Inorganic and Analytical Chemistry*)

11<sup>15</sup>-11<sup>30</sup>

**POULTRY WASTEWATER TREATMENT USING *PORPHYRIDIUM* SPP.**

**Zamfira Dincă**, Anamaria Iulia Török, Ana Moldovan, Emilia Neag, Cecilia Roman

11<sup>30</sup>-11<sup>45</sup>

**IMPROVING THE PERFORMANCE OF THE POLYSULFONE MEMBRANES INDUCED BY THE PRESENCE OF IONIC LIQUIDS: RHEOLOGICAL INVESTIGATIONS**

**Adina Maria Dobos**, Mihaela Dorina Onofrei, Lavinia Lupa, Anca Filimon

11<sup>45</sup>-12<sup>00</sup>

**MODELING THE FUNCTIONALIZED POLYSULFONE FIBERS BY THE ELECTROSPINNING PROCESS AND CONTROL OF SOLUTIONS PARAMETERS**

**Anca Filimon**, Niculae Olaru, Florica Doroftei

12<sup>00</sup>-12<sup>15</sup>

**CHARACTERIZATION OF NATURAL ZEOLITE (CLINOPTILOLITE) AS ONE OF THE HIGH CATION EXCHANGE CAPACITY GEOPOLYMER MATERIAL**

**Nenad Grba**, Marina Šćiban, Dejan Krčmar, Sanja Panić, Mirjana Petronijević, Slaven Tenodi, Đurda Kerkez, Kristiana Zrnić Tenodi, Dragan Radulović and Božo Dalmacija

12<sup>15</sup>-12<sup>30</sup>

**PREPARATIVE PURIFICATION OF OCHRATOXIN A BY LIQUID-LIQUID CHROMATOGRAPHY**

**Zsófia Hegedűs**, Dominik Szabó, Csaba Vágvölgyi, András Szekeres

*26<sup>th</sup> International Symposium on Analytical and Environmental Problems*

12<sup>30</sup>-12<sup>45</sup>

NOVEL COBALT COMPLEXES WITH GLYOXIMES: SYNTHESIS, PHYSICO-CHEMICAL ANALYSIS AND BIOLOGICAL STUDY

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Henrietta Ágoston, Erzsébet Mernyák

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Milica Baloš, Vojislava Bursić, Vuković Gorica, Rada Đurović-Pejčev, Tijana Stojanović, Aleksandra Petrović, Dušan Marinković, Bojana Špirović Trifunović, Bojan Konstantinović

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Florina Stefania Rus, Radu Banica, Calin Ladasiu

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Cristina Mosoarca, Alexandra Ioana Bucur, Radu Banica, Corina Orha, Maria Poienar, Raul Bucur

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Adina Căta, Ioana M. C. Ienașcu, Mariana N. Ștefănuț

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Aleksandra M. Cavic, Dragan Dj. Solesa, Snezana M. Aksentijevic, Jelena S. Kiurski

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Ákos Kristóf Csete, Ágnes Gulyás

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A. Csicsor, E. Tombác

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**IMPACT OF THE LAND COVER CHANGE ON THE ABUNDANCE OF FARMLAND BIRDS**

Nándor Csikós

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Zsuzsanna Csilla Dávid, Norbert Kúsz, László Bakacsy, Judit Hohmann, Andrea Vasas

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Mircea Laurentiu Dan, Alin Faur, Cristian George Vaszilcsin

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Mirjana Petronijević, Nataša Đurišić-Mladenović, Sanja Panić, Igor Antić, Predrag Kojić, Dragan Govedarica, Milan Tomić

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Maria Elena Rădulescu-Grad, Simona Funar-Timofei

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Mirela Ahmadi-Vincu, Gabriela Garban, Florin Muselin, Robert Ujhelyi, Zeno Gârban

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Vesna Gvoić, Maja Lončarski, Aleksandra Tubić, Sanja Vasiljević, Dejan Krčmar, Jasmina Agbaba, Miljana Prica

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Petru Hididis, Mircea Nicolaescu, Roxana Muntean, Norbert Kazamer, Cosmin Codrean, Viorel-Aurel Serban

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Madalina Ivanovici, Florina-Stefania Rus, Paulina Vlazan, Paula Svera(Ianasi), Stefan Danica Novaconi

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Tamara Ivetić, Jelena Petrović, Olivera Klisurić, Svetlana Lukić-Petrović

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Zoltán Jákói, Laura Haranghy, Cecilia Hodúr, Sándor Beszédes

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Sladana Dorontić, Olivera Marković, Aurelio Bonasera, and Svetlana Jovanović

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Gyula Kajner, Albert Kéri, Ádám Béltéki, Sándor Valkai, András Dér, Zsolt Geretovszky, Gábor Galbács

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Djurdjica Karanovic, Milica Hadnadjev-Kostic, Tatjana Vulic and Marija Milanović

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Dejan Kepić, Jovana Prekodravac, Bojana Vasiljević, Dragana Jovanović, Duška Kleut, and Biljana Todorović Marković

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**GIS-BASED METHODOLOGY FOR COMPLEX UGS PROVISION ASSESSMENT THROUGH THE CASE STUDY OF SZEGED, HUNGARY**

Ronald A. Kolcsár, Nándor Csikós, Péter Szilassi

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**DETECTION OF THE EFFICIENCY OF ENZYMATIC AND FERMENTATION PROCESSES BY DIELECTRIC MEASUREMENT**

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## 26<sup>th</sup> International Symposium on Analytical and Environmental Problems

### Oral Presentations: Tuesday (Session II)

**Session Chair:** Dr. Daniela Sojic Merkulov (*University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection*)

9<sup>15</sup>-9<sup>30</sup>

**THE MECHANOCHEMICAL IMPLEMENTATION OF THE ENVIRONMENTALLY FRIENDLY ASYMMETRIC TRANSFER HYDROGENATION OF KETONES**

**Vanessa Judit Kolcsár, György Szöllösi**

9<sup>30</sup>-9<sup>45</sup>

**PHOSPHORAMIDE CHIRAL CATALYSTS FOR ENVIRONMENTALLY FRIENDLY ASYMMETRIC ORGANOCATALYTIC PROCESSES**

**Viktória Kozma, György Szöllösi**

9<sup>45</sup>-10<sup>00</sup>

**“SMART” MOLECULAR ENGINEERING OF METALLOMESOGENS BASED ON Pt(II) TERPYRIDINE COORDINATION COMPLEXES**

**Evelyn Popa, Benoît Heinrich, Adelina A. Andelesc, Massimo La Deda, Giuseppe di Maio, Emilie Voirin, Bertrand Donnio and Elisabeta I. Szerb**

10<sup>00</sup>-10<sup>15</sup>

**DEVELOPING NEW ECOLOGICAL MATERIAL WITH APPLICATIONS IN CONSTRUCTION INDUSTRY AND POLLUTION REDUCTION**

**Florina-Stefania Rus, Stefan Novaconi, Madalina Ivanovici, Paulina Vlazan**

10<sup>15</sup>-10<sup>30</sup>

**ARSENIC UPTAKE IN TOMATO AND CABBAGE IRRIGATED WITH ARSENIC-CONTAMINATED WATER**

**Sirat Sandil, Victoria Vetesi, Peter Dobosy, Mihaly Ovari, Anna Fuzy, Gyula Zaray**

10<sup>30</sup>-10<sup>45</sup>

**POLY (VINYLIDENE FLUORIDE)/TiO<sub>2</sub>-CNT NANOCOMPOSITE ULTRAFILTRATION MEMBRANES FOR WASTEWATER TREATMENT**

**Elias Jigar Sisay, Ákos Fazekas, Zsuzsanna László**

### **Coffee Break**

**Session Chair:** Dr. Róbert Bekecz (*University of Szeged, Institute of Pharmaceutical Analysis*)

11<sup>15</sup>-11<sup>30</sup>

**ANALYTICAL POSSIBILITIES OF CARBON NANOTUBE BUCKYPAPERS DOPED BY GOETHITE**

**I. Y. Tóth and Á. Kukovecz**

11<sup>30</sup>-11<sup>45</sup>

**STUDYING BEER DEALCOHOLIZATION BY REVERSE OSMOSIS**

**Áron Varga, † Edit Márki, Eszter Bihari-Lucena, Márta Ladányi, Beatrix Szabó-Nótin, András Koris**

11<sup>45</sup>-12<sup>00</sup>

**APPLICATION OF HIGH POWER UV LEDs IN HETEROGENEOUS PHOTOCATALYSIS**

**Máté Náfrádi, Tamás Hlogyik, Luca Farkas, Tünde Alapi**

12<sup>00</sup>-12<sup>15</sup>

**THE MOST COMMON SYNTHETIC CANNABINOIDS IN THE LAST YEAR; FOCUSING ON THEIR METABOLITES IN BIOFLUIDS**

**Tímea Körmöczi, Éva Sija, Róbert Bekecz**

## ***26<sup>th</sup> International Symposium on Analytical and Environmental Problems***

12<sup>15</sup>-12<sup>30</sup>

**ULTRAHIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC ENANTIOSEPARATION OF SOME  $\beta^2$ -AMINO ACIDS**

**Dániel Tanács, Ferenc Fülöp, Antal Péter, István Ilisz**

12<sup>30</sup>-12<sup>45</sup>

**Xe\*-EXCIMER LAMP VERSUS LOW PRESSURE MERCURY VAPOR LAMP – THE COMPARISON OF THE EFFICIENCY OF 185 nm WITH 172 nm RADIATION, BASED ON H<sub>2</sub>O<sub>2</sub> FORMATION AND COUMARIN OXIDATION**

**Tünde Alapi, Luca Farkas, Daniele Scheres Firak**

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