



# PROCEEDINGS



*27th*  
*International*  
*Conference*  
*Ecological*  
*Truth and*  
*Environmental*  
*Research*

**EDITOR**

*Prof. Dr Snežana Šerbula*

18-21 June 2019, Hotel Jezero, Bor Lake, Serbia



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**27<sup>th</sup> INTERNATIONAL CONFERENCE**

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## **TABLE OF CONTENTS**

### **Plenary Lectures**

<b><i>Slobodan Jovanović, D. Randelović</i></b> EVALUATION OF URBAN BIOTOPES – TOOL FOR BIODIVERSITY PROTECTION AND SUSTAINABLE DEVELOPMENT OF CITIES	3
<b><i>Nataša Valentić, J. Petković-Cvetković, N. Banjac, B. Božić, G. Ušćumlić</i></b> TOWARDS DEVELOPING GREEN CHEMISTRY METHOD FOR SYNTHESIS OF NEW SUCCINIMIDES AS THE ANTIMICROBIAL AGENTS	16

### **Conference Papers**

<b><i>Ana Čučulović, J. Stanojković, R. Čučulović, M. Sabovljević, S. Nestorović, N. Radaković, D. Veselinović</i></b> ACTIVITY LEVELS OF <sup>137</sup> Cs AND <sup>40</sup> K IN MOSS COLLECTED IN 2018 FROM NP ĐERDAP	28
<b><i>Ivana Jelić, A. Kostić, J. Bošnjaković, V. Komadinić, R. Šerović</i></b> ESTIMATION OF HAZARDOUS MINING AND QUARRYING WASTE QUANTITY IN THE REPUBLIC OF SERBIA	34
<b><i>Velimir Komadinić, J. Bošnjaković, I. Jelić</i></b> APPLICATION OF STANDARD ISO 14001 IN THE ENVIRONMENTAL PROTECTION SYSTEM	41
<b><i>Jovana Bošnjaković, V. Komadinić, I. Jelić</i></b> ECO-INDUSTRIAL PARKS	47
<b><i>Milica Branković, D. Anđelković, G. Kocić, S. Mitić</i></b> GC-MS ANALYSIS OF BOSCALID IN APPLE ORCHARD SAMPLES FROM THE REGION OF JABLANICA – VUČJE	53
<b><i>Milica Branković, D. Anđelković, B. Zlatković, T. Anđelković, I. Kostić</i></b> SCREENING OF SEVEN ANIONS IN SOIL AND WATER SAMPLES FROM THE LALINAC SALT MARSH	58
<b><i>Umirzak Jussipbekov, M. Oshakbayev, A. Utelbayeva, O. Torebekov, U. Aksakalova</i></b> OIL SLUDGE OF MANGYSTAU REGION OF THE REPUBLIC OF KAZAKHSTAN	64
<b><i>Jovana Galjak, J. Đokić, I. Dervišević, G. Milentijević</i></b> FLY ASH DISPERSION MODELING IN EXTREME WEATHER CONDITIONS FROM LANDFILL IN OBILIĆ	70
<b><i>Miloš Kostić, M. Radović Vučić, M. Petrović, S. Najdanović, N. Velinov, D. Bojić, A. Bojić</i></b> ORGANIC DYE REMOVAL FROM AQUEOUS SOLUTIONS BY ULTRASOUND SYNTHESIZED LAYERED Mg/Co/Al DOUBLE HYDROXIDE	78

<b>Miljana Radović Vučić, M. Kostić, M. Petrović, J. Mitrović, N. Velinov, D. Bojić, A. Bojić</b>	CuO INCORPORATED $\text{Bi}_6\text{O}_6(\text{OH})_3(\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ WITH SUPERIOR PHOTOCATALYTIC ACTIVITY FOR DECOLORIZATION OF DYE	84
<b>Mira Stanković, D. Bartolić, M. Prokopijević, O. Prodanović, D. Đikanović, J. Simonović Radosavljević, K. Radotić</b>	FLUORESCENCE SPECTROSCOPY AND PRINCIPAL COMPONENT ANALYSIS IN THE HONEY SAMPLES CLASSIFICATION	89
<b>Tatjana Anđelković, D. Bogdanović, I. Kostić, G. Nikolić, B. Kostić, G. Kocić</b>	DETERMINATION OF PHTHALATES IN PVC BY FTIR AND A PRECIPITATION METHOD	93
<b>Tatjana Anđelković, D. Bogdanović, I. Kostić, G. Kocić</b>	STUDY OF DI-N-ETHYL HEXYL PHTHALATE MIGRATION FROM PLASTIC MATERIALS	99
<b>Tatjana Anđelković, I. Kostić, G. Kocić, T. Cvetković, D. Bogdanović</b>	INVESTIGATION OF AMMONIUM HYDROXIDE EFFECT ON DnBP EXTRACTION FROM MILK SAMPLES	105
<b>Irena Nikolić, D. Đurović, V. Radmilović, S. Marković, V. Radmilović</b>	CHARACTERIZATION OF ELECTRIC ARC FURANCE SLAG BY XRD, SEM/EDS AND THERMAL ANALYSIS	110
<b>Slaven Tenodi, D. Krčmar, S. Rončević, A. Tubić, M. Grgić, K. Zrnić, B. Dalmacija</b>	COMPARISON OF DIFFERENT RISK ASSESSMENT METHODS FOR EVALUATION OF GROUNDWATER IN LANDFILL AREAS	115
<b>Milica Veličković, M. Panić, Đ. Nikolić</b>	PREDICTION OF OZONE CONCENTRATION IN BELGRADE URBAN AREA USING ANNs APPROACH	122
<b>Danijela Voza, M. Vuković, I. Milošević</b>	INTEGRATION OF ARTIFICIAL NEURAL NETWORKS INTO MODELLING MORAVA RIVER SYSTEM WATER QUALITY	129
<b>Jelena Ivaz, M. Radovanović, P. Stojković, D. Petrović, V. Milić, S. Stojadinović, M. Žikić</b>	ANALYSIS OF CO EMISSIONS IN BOR AND ZAJEČAR	135
<b>Mladen Radovanović, J. Ivaz, P. Stojković, D. Petrović, V. Milić, S. Stojadinović, M. Žikić</b>	ANALYSIS OF ENVIRONMENTAL POLLUTION WITH DUST FROM NON-METALLIC OPEN PITS	142
<b>Ana Radojević, S. Šerbula, J. Milosavljević, T. Kalinović, J. Kalinović, M. Nujkić</b>	EVALUATION OF SOIL POLLUTION IN THE BOR AREA	148
<b>Tanja Kalinović, S. Šerbula, A. Radojević, J. Kalinović, J. Milosavljević</b>	INDICATION OF THE POLLUTION EMITTED FROM THE QUARRY	154
<b>Jelena Milosavljević, S. Šerbula, A. Radojević, J. Kalinović, T. Kalinović</b>	ASSESSMENT OF SOIL CONTAMINATION WITH HEAVY METALS BY SOIL POLLUTION INDICATORS	160
<b>Senad Čerčić, H. Husić</b>	ENDANGERING GROUND BY SURFACE MINING WORKS ON THE AREA OF THE MUNICIPALITY BANOVIĆI	166
<b>Jelena Vranković, K. Zorić, B. Tubić</b>	ACTIVITY OF GLUTATHIONE S-TRANSFERASE IN <i>Cepaea vindobonensis</i> (GASTROPODA: HELICIDAE) FROM POLLUTED AREA	172



<b>Nenad Stavretović, Đ. Petrov, M. Ocokoljić, J. Petrović</b> <i>Lagerstroemia indica</i> L. IN CLIMATE CHANGE CONDITIONS IN BELGRADE	178
<b>Nenad Stavretović, J. Petrović, M. Ocokoljić, Đ. Petrov</b> MEDITERRANEAN HERBACEOUS PLANTS IN CLIMATE CHANGE CONDITIONS IN BELGRADE GREEN AREAS	183
<b>Alexander I. Smirnov, E.R. Agletdinova, R.F. Mustafin, Z.R. Zaynutdinova, A.R. Musina, R.N. Umetbayev</b> MODERN MANIFESTATIONS OF A KARST IN THE TERRITORY OF THE REPUBLIC OF BASHKORTOSTAN	189
<b>Dragana Štrbac, M. Novaković, G. Štrbac, I. Mihajlović, M. Petrović</b> DICLOFENAC, IBUPROFEN AND KETOPROFEN PHOTOCATALITIC DECOMPOSITION BY TiO <sub>2</sub> NANO POWDER	195
<b>Milica Branković, D. Anđelković, B. Zlatković, T. Anđelković, I. Kostić</b> UPTAKE OF COPPER BY WATER LETTUCE IN MULTIPLY METAL-CONTAMINATED WATER	199
<b>Milica Petrović, S. Najdanović, M. Radović Vučić, M. Kostić, J. Mitrović, N. Velinov, A. Bojić</b> ELECTROCHEMICAL OXIDATIVE DEGRADATION OF TWO SYNTHETIC DYES IN WATER BY ELECTROSYNTHESIZED Ti/Bi <sub>2</sub> O <sub>3</sub> ANODE	205
<b>Marija Koprivica, J. Petrović, M. Petrović, M. Mihajlović, J. Milojković, M. Kojić, Z. Lopičić</b> PAULOWNIA LEAVES AND THEIR HYDROCHAR FOR Pb <sup>2+</sup> IONS REMOVAL FROM AQUEOUS SOLUTION	210
<b>Marija Kojić, J. Petrović, M. Petrović, M. Mihajlović, M. Koprivica, J. Milojković, T. Šoštarić</b> REMOVAL OF Cd (II) USING HYDROCHARS PREPARED FROM SUBSTRATE FOR CULTIVATING MUSHROOMS	215
<b>Nevena Pantić, N. Popović, M. Prokopijević, D. Spasojević, R. Prodanović, D. Đikanović, O. Prodanović</b> OPTIMIZATION OF HORSERADISH PEROXIDASE ENCAPSULATION WITHIN TYRAMINE-ALGINATE FOR PHENOL REMOVAL	220
<b>Miloš Prokopijević, N. Pantić, D. Spasojević, O. Prodanović, J. Simonović Radosavljević, D. Đikanović, R. Prodanović</b> IMMOBILIZATION OF TYRAMINE-HRP ONTO TYRAMIDE-CARBOXYMETHYL CELLULOSE MATRIX FOR WASTEWATER TREATMENT	224
<b>Veselin Bežanović, M. Novaković, D. Štrbac, D. Adamović</b> ADSORPTION OF METHYLENE BLUE FROM AQUEOUS SOLUTION USING ACTIVATED CARBON NORIT HYDRODARCO C	228
<b>Dragana Tamindžija, A. Volarić, D. Radnović</b> CHARACTERIZATION OF CHROMATE RESISTANT AND REDUCING BACTERIAL STRAINS	233
<b>Ana Volarić, D. Tamindžija, D. Radnović</b> HEXAVALENT CHROMIUM REDUCTION OF INDIVIDUAL BACTERIAL STRAINS AND CONSORTIA	240
<b>Radmila Pivić, A. Stanojković-Sebić, Z. Dinić, J. Maksimović</b> THE QUALITY OF IRRIGATION WATER AND ASSESMENT OF ITS USE IN TOPLICA DISTRICT	247

<b>Borislav Malinovic, T. Djuricic, D. Bjelic</b>	ELECTROCOAGULATION OF TEXTILE DYEING WASTEWATER CONTAINING AN AZO DYE	253
<b>Jasmina Agbaba, J. Nikić, M. Watson, A. Tubić, M. Kragulj Isakovski, S. Maletić, B. Dalmacija</b>	ARSENIC REMOVAL FROM GROUNDWATER BY <i>IN LINE</i> COAGULATION	258
<b>Mihajlo Stanković, J. Damjanović</b>	NEWFOUND RARE SPECIES OF COCCINELLID, <i>Henosepilachna argus</i> , IN SPECIAL NATURE RESERVE “ZASAVICA”	264
<b>Mihajlo Stanković</b>	OVERVIEW OF NECESSARY TYPES FOR NATURE PROTECTION OF EUROPE IN A SPECIAL NATURE RESERVE ZASAVICA	270
<b>Gordana Šekularac, M. Ratknić, M. Aksić, N. Gudžić, T. Ratknić, S. Eremija, T. Ćirković-Mitrović, D. Marković, A. Đikić</b>	CLIMATE AS A FACTOR OF WATER DEFICIT AND REAL EVAPOTRANSPIRATION IN THE SOIL WATER BALANCE OF THE PART OF CENTRAL SERBIA	279
<b>Maja Sremački, B. Obrovski, M. Petrović, I. Mihajlović, M. Vojinović Miloradov, J. Radić</b>	ENVIRONMENTAL EVALUATION OF GROUNDWATER QUALITY IN THE PROTECTED AREA OF LAKE ZOBNATICA	284
<b>Danijela Lukić, G. Milojević Miodragović</b>	RAPID ALERT SYSTEM FOR FOOD AND FEED - RASFF AND REPUBLIC OF SERBIA	290
<b>Mirjana Vojinović Miloradov, M. Sremački, I. Mihajlović, M. Petrović, B. Obrovski, K. Sabadoš, V. Kicošev, T. Keser, P. Dragičević, J. Radić</b>	SENS WETLANDS PROJECT: OVERVIEW OF THE INTERREG IPA PROJECT BETWEEN CROATIA AND SERBIA	296
<b>Dragana Bartolić, M. Stanković, A. Mitrović, D. Mutavdžić, J. Simonović Radosavljević, K. Radotić</b>	VIABILITY ASSESSMENT OF MAIZE ( <i>Zea mays</i> L.) SEEDS CONTAMINATED WITH AFLATOXIN USING FLUORESCENCE SPECTROSCOPY	301
<b>Ivana Milenković, D. Bartolić, M. Algarra, Lj. Kostić, M. Nikolić, K. Radotić</b>	THE EXAMINATION OF ECOTOXIC EFFECT OF FOLIC ACID BASED CARBON DOTS ON MAIZE	305
<b>Marina Đukić, T. Kragulj, M. Purić, G. Vuković, V. Bursić, N. Puvača, A. Petrović</b>	MERCURY CONTAMINATION OF SEAWATER, SEDIMENT AND FISH FROM BAR MUNICIPALITY	311
<b>Marina Đukić, G. Vuković, V. Bursić, A. Petrović, D. Marinković, B. Konstantinović, N. Puvača</b>	OCCURANCE OF CYANOBACTERIAL TOXINS IN LUDAŠ LAKE	316
<b>Slavica Sladojevic, M. Rakanovic, J. Penavin-Skundric, Z. Levi, R. Petrovic, D. Bodroza</b>	STUDY OF OBSERVING ADSORPTION OF HEXA VALENT CHROMIUM FROM AQUEOUS ENVIRONMENT ON MORDENITE	322
<b>Gordana Milojević Miodragović, Lj. Torović</b>	REGISTRATION OF UNSAFE TOYS ON THE RAPID ALERT SYSTEM FOR NON-FOOD CONSUMER PRODUCTS (RAPEX)	328

<b>Maša Knez Hrnčič, S. Šostar Turk, S. Stavbar, Ž. Knez</b>	
REMOVAL OF COMMONLY USED ANTIBIOTICS FROM HOSPITAL WASTEWATER	332
<b>Mirko Gojić, I. Ivanić, T. Holjevac Grgurić, S. Kožuh, O. Beganović, D. Čubela</b>	
MICROSTRUCTURAL PROPERTIES AND DYNAMIC-MECHANICAL BEHAVIOUR OF CuAlMn SHAPE MEMORY ALLOY	337
<b>Vladan Mičić, J. Budinski-Simendić, S. Pavlović, V. Teofilović, A. Aroguz, I. Krakovsky, J. Pavličević</b>	
SUPERCRITICAL FLUIDS AS GREEN SOLVENTS	343
<b>Branislava Lazić, B. Popović, S. Poznanović</b>	
ECOLOGICAL ADVANTAGES OF ORGANIC GROWING COTTON	349
<b>Valentina Simić, M. Šljivić, S. Belošević, M. Milosavljević, I. Karabegović</b>	
OPTIMIZATION OF FLAVONOID EXTRACTION USING MICROWAVE-ASSISTED EXTRACTION AS ECO-FRIENDLY TECHNIQUE	356
<b>Suzana Polić, S. Ristić, B. Radojković, B. Jegdić</b>	
LASER CLEANING OF CORROSION, EFFICIENT AND ENVIRONMENTALLY FRIENDLY METHOD	362
<b>Irma Dervišević, A. Dervišević, J. Galjak, J. Đokić</b>	
RECYCLING VALUABLE AND HAZARDOUS METALS FROM WEEE AND GREEN TECHNOLOGIES	369
<b>Branka Kaluderović, Đ. Čokeša, M. Marković, J. Hranisavljević, V. Mandušić,</b>	
INFLUENCE OF MODIFICATION OF ACTIVE CARBON MATERIAL SURFACE ON ITS ANTIMICROBIAL PROPERTIES	376
<b>Đuro Čokeša, M. Marković, M. Gajić-Kvašček, S. Radmanović, S. Šerbula</b>	
ISOTHERMAL TITRATION CALORIMETRY STUDY OF Cu BINDING TO HUMIC ACIDS FROM TECHNOSOLS ON RECLAIMED Cu POST FLOTATION TAILINGS (BOR, SERBIA)	382
<b>Uroš Stamenković, S. Ivanov, I. Marković, D. Gusković, S. Marjanović</b>	
THE EFFECTS OF DIFFERENT AGING TREATMENTS ON THE MICROHARDNESS AND THERMAL DIFFUSIVITY OF THE EN AW-6060 AND EN AW-6082 ALUMINUM ALLOYS FROM 6000 SERIES	386
<b>Milan Radovanović, V. Nedelkovski, A. Simonović, Ž. Tasić, M. Petrović Mihajlović, M. Antonijević</b>	
ELECTROCHEMICAL BEHAVIOR OF STAINLESS STEEL 316L IN RINGER'S SOLUTION IN THE PRESENCE OF L-TRYPTOPHAN	392
<b>Ana Simonović, I. Veljković, M. Radovanović, Ž. Tasić, M. Petrović Mihajlović, M. Antonijević</b>	
THE INHIBITORY EFFECT OF N-ACETYL-L-LEUCINE ON CORROSION OF BRASS IN SYNTHETIC ACIDIC RAIN SOLUTION	398
<b>Yavor Lukarski, I.V. Atanasov, C.A. Argirov</b>	
PROTECTION OF THE PERSONNEL FROM IRRADIATION DURING PYRO-METALLURGICAL PROCESSING OF METALLIC RADIOACTIVE WASTE ON THE BASE OF MODEL CALCULATIONS	404
<b>Eugene Buško, E. Shavalda</b>	
ASSESSMENT OF THE ENVIRONMENTAL SITUATION IN EUROPEAN COUNTRIES USING NEUTRON ACTIVATION ANALYSIS	412
<b>Irina Kandić, I. Čeliković, A. Kandić, M. Gavrilović, P. Janačković</b>	
ASSESSMENT OF ANNUAL EFFECTIVE DOSE DUE TO INGESTION OF <sup>137</sup> Cs, <sup>40</sup> K AND <sup>210</sup> Pb IN MEDICINAL HERBS FROM SERBIA AND FROM MONTENEGRO	418

<b>Branislava Lazić, B. Popović, S. Poznanović</b>	
INTEGRATED PEST MANAGEMENT IN COTTON GROWING	424
<b>Jasmina Jovanović Mirković, G. Kocić, C. Alexopoulos, N. Miljković, D. Dejković</b>	
DEPOSITING CADMIUM AND THE THERAPEUTIC EFFECT OF $\alpha$ -LIPOIC ACID IN THE TISSUE OF LIVER AND KIDNEY RATS	430
<b>Jasmina Jovanović Mirković, G. Kocić, C. Alexopoulos, N. Miljković, D. Dejković</b>	
DISPOSAL OF LEAD AND PHYSIOLOGICAL EFFECT OF GLUTATHIONE IN THE LIVER AND KIDNEY TISSUE IN RATS	435
<b>Jasmina Jovanović Mirković, G. Kocić, C. Alexopoulos, N. Miljković, D. Dejković</b>	
PATHOPHYSIOLOGICAL EFFECTS OF COPPER AND PHYSIOLOGICAL ROLE OF $\alpha$ -LIPOIC ACID THROUGH THE ACTIVITY OF ENDONUCLEASES IN RATS	440
<b>Radmila Ilić, D. Milošević, I. Stanojević, S. Filipović, M. Milosavljević, M. Šljivić, T. Vasić</b>	
HERBICIDE EFFICACY IN CONTROLLING WEEDS IN ALFALFA	445
<b>Sanja Mitić, Ž. Mitić, S. Živanović, S. Stojanović, M. Radenković, S. Najman, D. Savić, M. Trajanović</b>	
CHARACTERIZATION OF <i>Saccharomyces cerevisiae</i> YEASTS BY MATRIX ASSISTED LASER DESORPTION/IONIZATION-TIME OF FLIGHT MASS SPECTROMETRY	450
<b>Dragan Pajić, I. Ristanović-Ponjavić, L. Ivančajić</b>	
SOIL CONTAMINATION TESTING AT THE AGRICULTURAL AREAS OF THE TERRITORY OF BELGRADE	456
<b>Živče Šarkočević, B. Stojčetić, S. Marković, D. Lazarević</b>	
SWOT ANALYSIS OF POTENTIAL PROJECTS OF RENEWABLE ENERGY SOURCES IN THE MUNICIPALITY OF STRPCE	459
<b>Ljiljana Brašanac-Bosanac, T. Čirković-Mitrović, S. Eremija</b>	
FOREST-BASED BIOMASS AS ALTERNATIVE ENERGY SOURCE IN SERBIA	465
<b>Vojislav Krstić, B. Krstić</b>	
ACTUAL STATE OF APPLICATION OF MOTOR VEHICLE AGGREGATES	471
<b>Vojislav Krstić, B. Krstić</b>	
THE POSSIBILITY OF IMPROVING THE SECURITY OF TRANSPORT OF DANGEROUS CARGO FROM THE ASPECT OF A VEHICLE	478
<b>Oliver Slivoski, I. Andreevski, G. Kozarov, S. Stavreva</b>	
PUBLIC WATER SUPPLY AS AN ALTERNATIVE ENERGY	485
<b>Gordana Šekularac, N. Gudžić, M. Aksić, M. Ratknić, T. Ratknić, T. Čirković-Mitrović, S. Stajić, S. Gudžić, D. Marković</b>	
CLIMATE ASSESSMENT ACCORDING TO THE DROUGHT INDEX OF THE PART OF CENTRAL SERBIA	491
<b>Aleksandra Ivanović, N. Stavretović, J. Petrović, V. Golubović Čurguz</b>	
DEGRADATION OF THE MAKIŠ MARINA GREEN AREA DUE TO ANTHROPOGENIC IMPACTS	497
<b>Aleksandra Ivanović, N. Stavretović, V. Golubović Čurguz, J. Petrović</b>	
NEGATIVE EFFECTS OF ANTHROPOGENIC IMPACTS ON THE HEALTH STATUS OF TREES: A CASE STUDY OF MAKIŠ MARINA IN BELGRADE	504

<b>Milica Lukić, D. Filipović</b>	LANDSCAPE EVALUATION FOR THE PURPOSES OF ECOTOURISM – CASE STUDY OF BURGENLAND	511
<b>Dorđe Vojinović</b>	BACKCASTING AND TNA (Technology Needs Assessment) METHODS FOR SELECTION OF TECHNOLOGIES FOR REDUCTION OF GHG EMISSIONS IN TRANSPORT SECTOR IN BOSNIA AND HERZEGOVINA	519
<b>Ladislav Lazić, D. Cerinski, J. Baleta, M. Lovrenić-Jugović</b>	IMPROVING FUEL UTILISATION EFFICIENCY BY OXYGEN-ENRICHED AIR COMBUSTION	529
<b>Vlastimir Vučić, M. Radović Vučić</b>	ANALYZING ENERGY SECURITY FROM AVAILABILITY PERSPECTIVE –ENERGY POLICY DEVELOPMENT IN THE REPUBLIC OF SERBIA	535
<b>Vlastimir Vučić, M. Radović Vučić</b>	RENEWABLE ENERGY POLICY DRIVERS – ESTIMATING ECONOMIC IMPACTS OF DEPLOYING RENEWABLES	540
<b>Vlastimir Vučić, M. Radović Vučić</b>	THE EVOLVING CONCEPT OF ENERGY SECURITY – WHETHER CULTURE PLAYS A ROLE IN SECURING SUFFICIENT ENERGY SUPPLIES?	545
<b>Jasna Simonović Radosavljević, N. Pantić, J. Stevanić, D. Đikanović, A. Mitrović, L. Salmén, K. Radotić</b>	STRUCTURAL CHARACTERISATION AND ORIENTATION OF CELL WALL POLYMERS IN MAIZE LEAVES	551
<b>Marina Đukić, T. Stanković, A. Popović, T. Stojanović, M. Petrović</b>	WIDESPREAD OF ASIAN FLY ( <i>Drosophila suzukii</i> , MATSUMURA) IN DIFFERENT PLANTATIONS	555
<b>Vladimir Razlutskiy, K. Zorić, J. Đuknić, M. Moroz, B. Tubić, S. Anđus, N. Marinković, M. Paunović</b>	THE IMPACT OF ALIEN SPECIES ON MACROZOOBENTHOS COMMUNITIES AND ASSESSMENT OF WATER QUALITY BY BIOTIC INDICES	560
<b>Branko Stajić, N. Radaković</b>	GROWTH OF TURKISH HAZEL ( <i>Corylus colurna</i> L.) IN THE BEECH-TURKISH HAZEL FOREST IN THE AREA OF “DJERDAP” NATIONAL PARK	565
<b>Bratimir Nešić, V. Alivojvodić, M. Stamenović, V. Pavićević</b>	ECONOMIC AND ENVIRONMENTAL EFFECTS OF COMPOSTING TECHNOLOGY WITHIN THE REGIONAL WASTE MANAGEMENT CENTRE IN LESKOVAC, SERBIA	572
<b>Jelena Pavličević, B. Ikonić, M. Jovičić, O. Bera, A. Aroguz, S. Sinadinović-Fišer, O. Govedarica, M. Janković</b>	MATERIAL FLOW MANAGEMENT: ZERO EMISSION CONCEPT AND CIRCULAR ECONOMY	579
<b>Ivan Ristić, I. Krakovsky, S. Cakić, J. Tanasić, B. Pilić, V. Aleksić, J. Budinski-Simendić</b>	SYNTHESIS OF BIOBASED THERMOPLASTIC POLYURETHANE ELASTOMERS	585

<b><i>Vesna Alivojvodić, J. Drobac, P. Maksić, M. Stamenović</i></b>	
SETTING THE FRAMEWORK FOR DEVELOPMENT OF SUSTAINABLE DESIGN CURRICULUM	591
<b><i>Jelena Drobac, V. Alivojvodić, P. Maksić, M. Stamenović</i></b>	
SUSTAINABLE FASHION: A PUSH TOWARD CIRCULAR FASHION	596
<b><i>Branislava Lazić, B. Popović, S. Poznanović</i></b>	
ECOLOGICAL FOOTPRINT OF TEXTILE FIBERS	602
<b><i>Jaroslava Budinski-Simendić, D. Kojić, G. Marković, S. Jovanović, T. Erceg, N. Vukić, Lj. Tanasić, S. Samaržija-Jovanović</i></b>	
THE VULCANIZATION PROPERTIES OF HYBRID ELASTOMERIC MATERIALS BASED ON WASTE RUBBER POWDER	608
<b><i>Boban Spalović, S. Milić, D. Medić, I. Đorđević, B. Ilić</i></b>	
METHODS FOR REMOVING COPPER FROM WASTEWATER	615
<b><i>Ivan Đorđević, S. Milić, D. Medić, B. Spalović, B. Ilić</i></b>	
REMOVAL OF Cr <sup>3+</sup> FROM ELECTROPLATING WASTEWATER USING DIFFERENT ADSORBENTS	622
<b><i>Milanka Negovanović, L. Kričak, J. Majstorović, D. Tošić</i></b>	
TOXIC FUMES FROM BLASTING	627
<b><i>Author Index</i></b>	
	635

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## REMOVAL OF Cd (II) USING HYDROCHARS PREPARED FROM SUBSTRATE FOR CULTIVATING MUSHROOMS

Marija Kojić<sup>1\*</sup>, Jelena Petrović<sup>1</sup>, Marija Petrović<sup>1</sup>, Marija Mihajlović<sup>1</sup>,  
Marija Koprivica<sup>1</sup>, Jelena Milojković<sup>1</sup>, Tatjana Šoštaric<sup>1</sup>

<sup>1</sup>Institute for Technology of Nuclear and Other Mineral Raw Materials,  
86 Franchet d'Esperey St., 11000 Belgrade, SERBIA

\*[m.kojic@itnms.ac.rs](mailto:m.kojic@itnms.ac.rs)

### Abstract

*In this study, the sorption capacity of Cd (II) removal from aqueous solution was investigated using hydrochar obtained from substrate for cultivating mushrooms. In order to increase the adsorption capacity, hydrochar was previously modified with 2M KOH. The obtained results showed that alkally modification increased the sorption capacity from 41.5 mg/g to 53.5 mg/g. Structural characterization of alkally modified and unmodified hydrochars were performed by Fourier transform infrared spectroscopy (FTIR). According to obtained results of FTIR analysis, the increased of the oxygen functional groups (OFG) in alkally modified hydrochars was observed, which is contributed to the increase in the adsorption capacity of this hydrochar. Results indicated that substrate for cultivating mushrooms can be converted into hydrochar as a sorbent for sorption of Cd (II), and the presence of OFGs play important role in the hydrochar's high adsorption capacity.*

**Keywords:** substrate for cultivating mushrooms hydrochars, Cd(II) removal, alkally modification

### INTRODUCTION

Excessive increased of population, industrialization and agricultural activities have caused contamination of water and soil with heavy metals [1]. The presence of these pollutants in the waters can have negative effects on the environment, because heavy metals are highly toxic and not degradable. Elements such as Cd, Hg, Ag, Se and Pb can be extremely toxic, while Cu, Zn, Mn, Fe, Ni and Co are considered essential for the functioning of living organisms and they are toxic in higher concentrations [2]. Cadmium is one of the most toxic heavy metal. Phosphoric fertilizers, wastewaters from industry, batteries, and dyes are often responsible for bringing Cd (II) into the aquatic environment [3]. Constant exposure to Cd (II) can cause various diseases in human such as lung cancer, prostate proliferative lesions, bone fractures, kidney dysfunction, and hypertension [2]. In order to avoid mentioning negative health effects, industrial wastewater should be purified and recycled using appropriate methods.

In recent years, various conventional wastewater treatments methods have been used, such as: precipitation, ion exchange, adsorption, electrochemical processes and membrane processes [3]. However, adsorption relative to other technology is the most commonly used method because it is efficient, environmentally friendly and economical [4]. A large number

of different sorbents have been investigated for water purification, especially waste biomass. Biosorbents are by-products of agriculture that are easily accessible, high efficiency, and ability to remove organic and inorganic compounds from water [5]. Research on biosorbents was mainly focused on application of biochar from the pyrolysis process [2]. However, lately a greater emphasis is placed on the using of hydrochar, which is obtained during hydrothermal process. Kambo and Dutta [6] states that hydrochar has substantially greater adsorption capacity than biochar, considering that it is richer in functional groups on its surfaces and also it has lower surface area and porosity.

Hydrothermal carbonization (HTC) is thermochemical technology that can treat various types of organic waste materials into functional products with minimal environmental pollution [7]. HTC is operated in water as a reaction medium, moderate temperatures (180–260°C) and autogenous pressure [8]. The products obtained from HTC of feedstock are a carbon-rich solid product (hydrochar), process water and small amount of gas. The process parameters such as pressure, temperature, reaction time and biomass and water ratio has a significant impact on degree of carbonization of waste organic matter [9]. In contrast to feedstocks, the hydrochar is characterized by higher mass and energy density, better dewaterability, and improved combustion performance as a solid fuel [10]. HTC has been considered for various purposes, such as catalysis, adsorption, fuel, electrochemistry, template synthesis, nanostructured materials [11]. A number of studies have been performed on hydrothermal carbonization of a wide range of waste organic matter: food waste, animal manure, glucose etc. [9].

Petrovic *et al.* [12] examined the adsorption of  $Pb^{2+}$  from aqueous solution with alkally modified hydrochar and found that the hydrochar showed the highest  $Pb^{2+}$  sorption capacity of 137 mg/g. Elaigwu *et al.* [13] compared the adsorption capacities of the hydrochars and biochars, and found that hydrochars were able to adsorb the Pb (II) and Cd (II) more efficiently in contrast to biochars.

The aims of this study were to investigate the efficiency of substrate for cultivating mushrooms hydrochar as a sorbent for the removal of Cd (II) from wastewaters. Besides, the sorption capacity between alkali-modified and unmodified hydrochars will be compared, as well as their structural changes.

## **MATERIALS AND METHODS**

Substrate for mushroom cultivation (SM) is obtained from the local mushroom industry located in the vicinity of Belgrade. The compost used is from the following components: wheat straw, urea, gypsum and horse manure.

### **HTC hydrochar preparation**

The HTC experiments were carried out in 250 ml autoclave reactor (Carl Roth, Model II). The HTC reactor was equipped with a cooling system and controller for pressure and temperature. To analyse the effect of the HTC temperature on 200°C were adopted under the same reaction time of 1 h. For each test, 10 g of SM feedstock was mixed with 150 ml of deionized water into autoclave. The autoclave was held at final temperature at 60 min and the



reactor was cooled down to the room temperature. The hydrochar was washed with deionized water and then dried at 105°C for 24 h.

#### *Alkaline modification*

Alkaline hydrochar modification was carried out according to the procedure shown in the paper Petrovic *et al.* [12].

#### *Adsorption studies and characterization of hydrochar*

A stock solution of 100 mg L<sup>-1</sup> Cd<sup>2+</sup> was prepared by dissolving Cd (NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O. For adsorption experiment, 0.025 g of one of hydrochars (unmodified (SM-200) or alkali-modified (SM-KOH-200)) was mixed with 25 ml of Cd<sup>2+</sup> solutions. The flasks were capped and shaken at room temperature for 120 min at 250 rpm. After that, the mixtures were filtered and the concentrations of Cd<sup>2+</sup> were determined by atomic absorption spectroscopy (Perkin Elmer, AAS Analyst 300). The solids remaining on the filter were collected and dried at 105°C for Fourier transform infrared spectroscopy (FTIR; Thermo Scientific Nicolet iS50 FT-IR spectrometer in transmission mode) analysis. Materials were recorded in the spectral range 4000–400 cm<sup>-1</sup>.

Adsorption capacities  $q_e$  (mg/g) were calculated as follows:

$$q_e = (C_0 - C_e) \times V/m$$

where  $V$ , is the volume of the Cd<sup>2+</sup> solution (L),  $m$  is the amount of adsorbent (SM-200 or SM-KOH-200) (g);  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of the Cd<sup>2+</sup> ions (mg L<sup>-1</sup>), respectively.

## **RESULTS AND DISCUSSION**

The FTIR analysis was carried out to explain the internal chemical structural changes of SM-200 and SM-KOH-200 after adsorption of Cd (II). The FTIR spectrums are presented in Fig. 1. The intensity of the peak 3280 cm<sup>-1</sup> was associated to -O-H stretching vibration from hydroxyl and carboxyl groups in the SM-200 and SM-KOH-200 [2,12]. The two bonds at around 2920 and 2850 cm<sup>-1</sup> probably originated from vibration of aliphatic C-H stretching in cellulose from wheat straw [14].

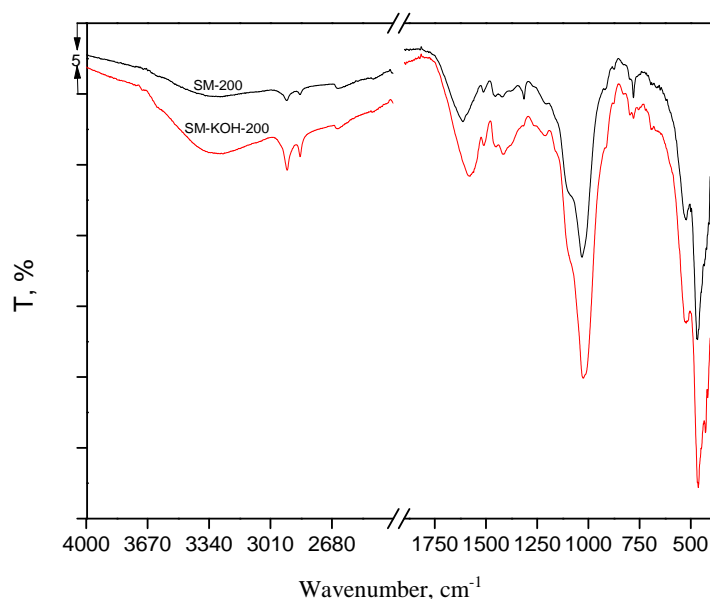
The bonds at 1620 cm<sup>-1</sup> could be attributed to C=O vibrations [15]. The band at 1521 cm<sup>-1</sup> are the results of the of N-O nitro groups, which can originated from protein and uric acid in horse manure [16]. The bonds at 1420 cm<sup>-1</sup> were associated with aromatic C=C stretching, indicating the presence of lignin in the hydrochars [17]. The stretching -COR aliphatic ethers and -COH primary alcohols were attributed to the bonds at 1030 cm<sup>-1</sup> [11]. The absorbance peaks at around 779 and 470 cm<sup>-1</sup>, presented to the aromatic C-H bending vibration and aliphatic C-H stretching vibrations [11].

Based on research Han *et al.* [2], it can be noticed that there are a large number of active functional groups (-COOH, -CO, -OH) that can form complexes with Cd (II) on the surface of the hydrochars.

Similar observation was also noticed in this paper. The Figure 1 showed that SM-KOH-200 had a significantly higher intensity of peak at 3280, 1620 and 1030 cm<sup>-1</sup> compared to SM-200. This confirmed that SM-KOH-200 had more OFG in contrast to SM-200, which SM-

KOH-200 improved ability to adsorb Cd(II). Petrovic *et al.* [12] and Sun *et al.* [18], also found that alkaline modification of the hydrochars increased the number of OFGs, which had an impact on the improvement of the metal adsorption capacity to the hydrochars.

The results from FTIR analysis was confirmed by determining the preliminary adsorption capacity of the applied hydrochars. The adsorption capacity of the SM-KOH-200 was  $q_e=53.5$  mg/g, while the SM-KOH showed smaller capacity ( $q_e=41.5$  mg/g). It can be shown that alkally modified hydrochar had more OFGs on their surface, and thus more electron donating sites for adsorption of Cd (II) ions.



**Figure 1** FT-IR spectra of SM-200 and SM-KOH-200 after Cd (II) sorption

## CONCLUSION

Based on this paper, we can conclude that alkaline modification contributed to the increase of OFG in hydrochars, which increased the adsorption capacity from 41.5 mg/g for SM-200 to 53.5 mg/g for SM-KOH-200. It showed that these materials could be used as low cost adsorbents in wastewater treatment and that HTC is sustainable method for conversion of this type of biomass.

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