Kruševac, Srbija
30. maj -1. jun 2018

8. SIMPOZIJUM

Hemija i zaštita životne sredine

sa međunarodnim učešćem

ENVIROCHEM 2018

8th SYMPOSIUM

Chemistry and Environmental Protection

with international participation

Knjiga izvoda

BOOK OF ABSTRACTS

СХД 1897

Srpsko hemijsko društvo
Serbian Chemical Society

OH

Sekcija za hemiju i zaštitu životne sredine
Environmental Chemistry Division

8. Simpozijum
Hemija i zaštita životne sredine

sa međunarodnim učešćem

8th Symposium
Chemistry and Environmental Protection

with international participation

KNJIGA IZVODA
BOOK OF ABSTRACTS

Kruševac 30. maj - 1. jun 2018

Naslov	**KNJIGA IZVODA** **8. simpozijum Hemija i zaštita životne sredine**
Title	*BOOK OF ABSTRACTS* *8th Symposium Chemistry and Environmental Protection*
Izdavač	**Srpsko hemijsko društvo** **Karnegijeva 4/III, Beograd, Srbija**
Publisher	*Serbian Chemical Society* *Karnegijeva 4/III, Belgrade, Serbia*
Za izdavača *For the publisher*	**Vesna Mišković - Stanković, predsednik Društva** *President of the Society*
Urednici *Editors*	**Vladimir Beškoski, Jelena Savović,** **Miloš Momčilović**
Tehnička prirema *Technical assistance*	**Sanja Živković**
Štampa *Printed by*	**DualMode štamparija, Beograd**
Tiraž *Circulation*	**120 primeraka** *120 copies*
ISBN	978-86-7132-068-9

POČASNI ODBOR

HONORARY COMMITTEE

Petar Pfendt
Dragan Veselinović
Mirjana Vojinović-Miloradov
Dragan Marković

NAUČNI ODBOR

SCIENTIFIC COMMITTEE

Ivan Gržetić, predsednik
Ilija Brčeski, potpredsednik
Vladimir Beškoski
Branimir Jovančićević
Tanja Brdarić
Vera Jovanović
Ljubiša Ignjatović
Aco Janićijević
Mira Aničić Urošević
Aleksandar Popović
Vladan Joldžić
Milica Balaban
Jelena Savović
Dubravka Milovanović
Milena Jovašević Stojanović
Ivana Ivančev Tumbas
Verka Jovanović
Jelena Radonić
Maja Turk Sekulić
Mališa Antić
Miloš Momčilović
Tatjana Šolević-Knudsen
Aleksandra Šajnović

ORGANIZACIONI ODBOR

ORGANIZING COMMITTEE

Bojan Radak, predsednik
Vladimir Beškoski, potpredsednik
Jelena Radonić
Maja Turk Sekulić
Branko Dunjić
Slavka Stanković
Rada Đurović Pejčev
Vladan Joldžić
Branimir Jovačićević
Mališa Antić
Dragan Manojlović
Goran Roglić
Gordana Gajica
Tatjana Šolević Knudsen
Ljubiša Ignjatović
Vesna Zlatanović Tomašević
Marina Mihajlović
Sanja Sakan
Dubravka Relić
Mira Aničić Urošević
Aleksandra Mihajlidi Zelić
Verka Jovanović
Milena Jovašević Stojanović
Ivan Gržetić
Aleksandra Šajnović
Anđelka Tomašević
Sanja Stojadinović
Milica Kašanin-Grubin
Milica Marčeta Kaninski
Vladimir Nikolić
Gvozden Tasić
Marija Lješević
Branka Lončarević
Aleksandra Žerađanin
Kristina Joksimović

IZVRŠNI ODBOR

EXECUTIVE COMMITTEE

Jelena Savović, predsednik
Dubravka Milovanović, potpredsednik
Sanja Živković, izvršni sekretar
Maja Milanović
Miloš Momčilović
Ivana Perović
Tijana Milićević

STUDENTSKI ODBOR

STUDENTS COMMITTEE

Slađana Savić, predsednik
Jelena Aleksić
Boško Vrbica
Katarina Kojić
Nada Vidović
Marko Jovanović
Milan Bukara
Luka Miladinović
Nataša Sekulić
Marija Ćurčić

SPONZORI I DONATORI
SPONSORS AND DONORS

МИНИСТАРСТВО ПРОСВЕТЕ,
НАУКЕ И ТЕХНОЛОШКОГ РАЗВОЈА

ХЕМИЈСКИ ФАКУЛТЕТ · УНИВЕРЗИТЕТ У БЕОГРАДУ

Institut za nuklearne
nauke Vinča

1889 TRAYAL
CORPORATION

Tehnološko
Metalurški
Fakultet
Univerzitet u Beogradu

Anahem
Laboratorija

PRIMAlab
a member of the Metrohm group

ANALYSIS
LABORATORY EQUIPMENT

Универзитет у Београду
ФАКУЛТЕТ ЗА
ФИЗИЧКУ ХЕМИЈУ

ИНСТИТУТ ЗА БИОЛОШКА ИСТРАЖИВАЊА
СИНИША СТАНКОВИЋ
ИБИСС
πανta ρει
УНИВЕРЗИТЕТ У БЕОГРАДУ

Henkel

Coca-Cola HBC
Srbija

SRBIJA
TURISTIČKA
ORGANIZACIJA
SRBIJE

LECO®
Delivering the Right Results

Sadržaj

PROGRAM / PROGRAMME

UTORAK / TUESDAY 29.05.2018.	
17:30	PRIJAVLJIVANJE/ REGISTRATION
18:30 - 20:00	Zajednički koktel / Get together cocktail

SREDA / WEDNESDAY 30.05.2018.	
08:30	PRIJAVLJIVANJE/ REGISTRATION
9:30 – 10:00	SVEČANO OTVARANJE SIMPOZIJUMA / OPENING CEREMONY Predsedavajući / Chairpersons: *Bojan Radak, Jelena Savović, Ivan Gržetić*
10:00 - 10:45	PLENARNO PREDAVANJE / PLENARY LECTURE (Predsedavajući / Chairperson: Ivan Gržetić) *Biodegradacija nafte u sedimentnim stenama i u životnoj sredini – prednosti i nedostaci* **Branimir Jovančićević**
10:45	SEKCIJA 1 / SESSION 1 Predsedavajući / Chairpersons: *Ivan Gržetić*
10:45 – 11:15	PREDAVANJE PO POZIVU / INVITED LECTURE 1 *Actuality and Perspectives of the Application of Electrochemical Methods in Environmental Analysis* **Ljubiša Ignjatović**
	USMENA IZLAGANJA / ORAL PRESENTATIONS
11:15- 11:30	*Ekološko pravna zaštita od negativnih tehnogenih uticaja* **Vladan Joldžić**
11:30- 11:45	**ANALYSIS obraćanje**
11:45-11:55	**LECO obraćanje**
11:55-12:15	Pauza za kafu / Coffee break

12:15-13:00	PLENARNO PREDAVANJE / PLENARY LECTURE (Predsedavajući / Chairperson: *Jelena Savović*) *Biosorption: Can we address water quality and contribute to the 'circular economy'?* **Stuart Gibb**
13:00-14:00	Pauza za ručak / Lunch break
14:00-15:30	Poster sekcija 1 / Studentska sekcija (**PP1/1-32, PPS/1-8)** (Predsedavajući / Chairperson: *Miloš Momčilović, Sanja Živković, Tijana Milićević*)
15:30	**Izlet Jastrebac**

ČETVRTAK / THURSDAY 31.05.2018.	
08:30	PRIJAVLJIVANJE/ REGISTRATION
9:00 – 9:45	PLENARNO PREDAVANJE / PLENARY LECTURE (Predsedavajući / Chairperson: *Vladimir Beškoski*) *Peroxo-methods for the synthesis of mixed metaloxide materials* **Viacheslav Avdin**, Igor Krivtsov, Marina Ilkaeva
9:45	SEKCIJA 2 / SESSION 2 Predsedavajući / Chairpersons: *Vladimir Beškoski*
9:45 – 10:15	PREDAVANJE PO POZIVU / INVITED LECTURE 2 *Zelena sinteza metalnih nanočestica korišćenjem ekstrakata biljaka - nove primene biljnih resursa* **Vladimir Mihailović**
	USMENA IZLAGANJA / ORAL PRESENTATIONS
10:15- 10:30	*Photochemical degradation of textile dye C.I. Reactive Blue 19 in a continuous photoreactor by means of sulfate radicals* **Nena Velinov**
10:30- 10:45	*Elektrohemijska dekolorizacija reaktivnih tekstilnih boja primenom ugljeničnih elektroda visoke poroznosti, dobijenih iz fenol-formaldehidnih smola* **Dragan Manojlović**
10:45-11:15	Pauza za kafu / Coffee break

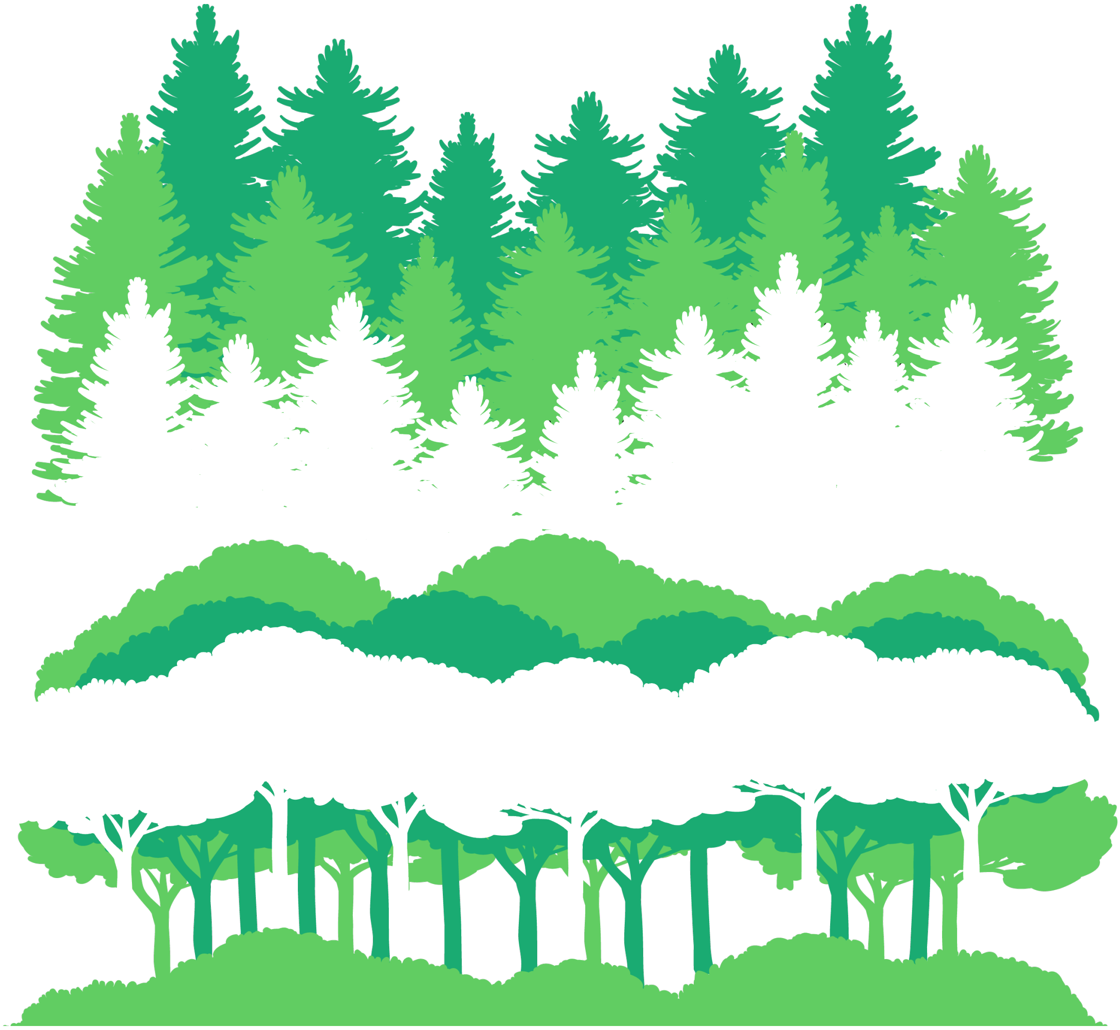
11:15 -12:00	PLENARNO PREDAVANJE / PLENARY LECTURE (Predsedavajući / Chairperson: *Ilija Brčeski*) *Primena dielektričnog barijernog pražnjenja u tretmanu voda* **Goran Roglić**
12:00	SEKCIJA 3 / SESSION 3 Predsedavajući / Chairpersons: *Ilija Brčeski*
12:00 – 12:30	PREDAVANJE PO POZIVU / INVITED LECTURE 3 *Challenges hindering the effective removal of arsenic from drinking water* **Malcolm Watson**
	USMENA IZLAGANJA / ORAL PRESENTATIONS
12:30- 12:45	*Enhanced phosphorus removal from water by KOH modified crab carapace, oyster and mussel shell* **Sabolc Pap**
12:45 - 13:00	*The chemical composition of volatile autolysis products of a potential phytoremediation plant species Bornmuellera dieckii Degen (Brassicaceae)* **Milica Todorovska**
13:00 -14:30	Pauza za ručak / Lunch break
14:30-15:00	ZELENA HEMIJA: Perspektive i mogućnosti primene u Srbiji *Diskusioni panel* **Vladimir Beškoski**
15:00	SEKCIJA 4 / SESSION 4 Predsedavajući / Chairpersons: *Dubravka Milovanović, Jelena Radonić*
15:00-15:30	PREDAVANJE PO POZIVU / INVITED LECTURE 4 *Exploring new horizons and sustainable technologies for highly efficient wastewater remediation and decontamination: Multifunctional biochar* **Maja Turk Sekulić**
	USMENA IZLAGANJA / ORAL PRESENTATIONS
15:30 - 15:45	*Sorption-desorption hysteresis of atrazine onto organoclays* **Anita Leovac Maćerak**
15:45 - 16:00	Pauza za kafu / Coffee break

16:00-17:30	*Poster sekcija 2* **(PP2/1-40)** (Predsedavajući / Chairperson: *Miloš Momčilović, Sanja Živković, Tijana Milićević)*
20:30	**SVEČANA VEČERA / GALA DINNER** Restoran Bagdala

PETAK / FRIDAY 01.06.2018.	
9:00	SEKCIJA 5 / SESSION 5 Predsedavajući / Chairpersons: *Tatjana Šolević-Knudsen, Aleksandra Šajnović*
9:00 – 9:30	PREDAVANJE PO POZIVU / INVITED LECTURE 5 *Towards widespread adoption of low cost air quality sensors - a necessity for effective calibration procedures* **Miloš Davidović**
	USMENA IZLAGANJA / ORAL PRESENTATIONS
9:30- 9:45	*Fotokatalitička degradacija ibuprofena u akvatičnom matriksu primenom nanokatalitičke smeše* ZnO/TiO_2 **Mirjana Vojinović Miloradov**
9:45-10:00	*Određivanje fipronila i njegovih metabolita u pilećim jajima i proizvodima od jaja korišćenjem gasne hromatografije-masene spektrometrije* **Aleksandra Tasić**
10:00-10:30	Pauza za kafu / Coffee break
10:30	SEKCIJA 6 / SESSION 6 Predsedavajući / Chairpersons: *Milena Jovašević Stojanović, Ivana Ivančev Tumbas*
10:30 – 11:00	PREDAVANJE PO POZIVU / INVITED LECTURE 6 *Today's cheap coal-derived electricity means future costly environmental pollution* **Gordana Medunić**
	USMENA IZLAGANJA / ORAL PRESENTATIONS
11:00- 11:15	*Trace element contamination (Pb, Zn, Cd, As, Ni) of floodplain sediments in a former ore mining area in Eastern Belgium* **Dubravka Relić**
11:15 - 11:30	*Assessment of potentially toxic elements bioavailability in the soil-plant-air system in different vineyard ambients in Serbia: biomonitoring, environmental and health risk implications* **Tijana Milićević**
11:30	SEKCIJA 7 / SESSION 7 Predsedavajući / Chairpersons: *Ljubiša Ignjatović, Vladan Joldžić*

11:30 – 12:00	PREDAVANJE PO POZIVU / INVITED LECTURE 7 *How green is biocatalysis?* **Jasmina Nikodinovic-Runić**
	USMENA IZLAGANJA / ORAL PRESENTATIONS
12:00- 12:15	*Primeri uticaja različitih strategija upravljanja otpadom na emisije gasova sa efektom staklene bašte u Republici Srbiji* **Marina Mihajlović**
12:15- 12:30	*Ispitivanje potencijala celuloze kao univerzalnog matriksa za analizu metala u biljkama pomoću WD-XRF* **Jovana Orlić**
12:30-12:45	*The influence of seawater physicochemical parameters on the content of trace elements in mussels and surface sediment* **Milica Ivković**
	ZATVARANJE SIMPOZIJUMA/ CLOSING CEREMONY

SPISAK IZLAGANJA
LIST OF PRESENTATIONS



SPISAK PLENARNIH PREDAVANJA
LIST OF PLENARY LECTURES

PL-1 Biodegradacija nafte u sedimentnim stenama i u životnoj sredini – prednosti i nedostaci
Branimir Jovančićević

PL-2 Biosorption: Can we address water quality and contribute to the 'circular economy'?
Stuart Gibb

PL-3 Peroxo-methods for the synthesis of mixed metaloxide materials
Viacheslav Avdin

PL-4 Primena dielektričnog barijernog pražnjenja u tretmanu voda
Goran Roglić

SPISAK PREDAVANJA PO POZIVU
LIST OF INVITED LECTURES

IL-1 Actuality and Perspectives of the Application of Electrochemical Methods in Environmental Analysis
Ljubiša Ignjatović

IL-2 Zelena sinteza metalnih nanočestica korišćenjem ekstrakata biljaka - nove primene biljnih resursa
Vladimir Mihailović

IL-3 Challenges hindering the effective removal of arsenic from drinking water
Malcolm Watson

IL-4 Exploring new horizons and sustainable technologies for highly efficient wastewater remediation and decontamination: Multifunctional biochar
Maja Turk Sekulić

IL-5 Towards widespread adoption of low cost air quality sensors - a necessity for effective calibration procedures
Miloš Davidović

IL-6 Today's cheap coal-derived electricity means future costly environmental pollution
Gordana Medunić

IL-7 How green is biocatalysis?
Jasmina Nikodinovic-Runić

SPISAK USMENIH IZLAGANJA
LIST OF ORAL PRESENTATIONS

OP-1 Ekološko pravna zaštita od negativnih tehnogenih uticaja
Vladan Joldžić

OP-2 Photochemical degradation of textile dye C.I. Reactive Blue 19 in a continuous photoreactor by means of sulfate radicals
Jelena Mitrović, Miljana Radović, Slobodan Najdanović, Nena Velinov, Danijela Bojić, Aleksandar Bojić

OP-3 Elektrohemijska dekolorizacija reaktivnih tekstilnih boja primenom ugljeničnih elektroda visoke poroznosti, dobijenih iz fenol-formaldehidnih smola
Viacheslav Avdin, Dmitry Zherebtsov, Katarina Lelek, Goran Roglić, Dragan Manojlović, Kristina Buskina, Chettichipalayam Prabhaharan Sakthi Dharan

OP-4 Enhanced phosphorus removal from water by KOH modified crab carapace, oyster and mussel shell
Sabolc Pap, Lisa Shearer, Mark A. Taggart, Barbara Bremner, Stuart Gibb

OP-5 The chemical composition of volatile autolysis products of a potential phytoremediation plant species Bornmuellera dieckii Degen (Brassicaceae)
Milica Todorovska, Niko Radulović

OP-6 Sorption-desorption hysteresis of atrazine onto organoclays
Anita Leovac Maćerak, Ivana Ivančev-Tumbas, Đurđa Kerkez, Božo Dalmacija

OP-7 Fotokatalitička degradacija ibuprofena u akvatičnom matriksu primenom nanokatalitičke smeše ZnO/TiO_2
Mirjana Vojinović Miloradov, Mladenka Novaković, Ivana Mihajlović, Goran Štrbac, Maja Petrović, Dragana Štrbac

OP-8 Trace element contamination (Pb, Zn, Cd, As, Ni) of floodplain sediments in a former ore mining area in Eastern Belgium
Dubravka Relić, Dragana Milanović, Theodoros Potouridis, Wilhelm Püttmann

OP-9 Određivanje fipronila i njegovih metabolita u pilećim jajima i proizvodima od jaja korišćenjem gasne hromatografije-masene spektrometrije
Aleksandra Tasić, Ksenija Nesić, Ljubiša Ignjatović, Nebojša Vuković

OP-10 Primeri uticaja različitih strategija upravljanja otpadom na emisije gasova sa efektom staklene bašte u Republici Srbiji
Marina Mihajlović , Mića Jovanović

OP-11 Assessment of potentially toxic elements bioavailability in the soil-plant-air system in different vineyard ambients in Serbia: biomonitoring, environmental and health risk implications

Tijana Milićević, Mira Aničić Urošević, Dubravka Relić, Sandra Škrivanj, Gordana Vuković, Aleksandar Popović

OP-12 Ispitivanje potencijala celuloze kao univerzalnog matriksa za analizu metala u biljkama pomoću WD-XRF

Jovana Orlić**,** Marija Krstić, Teodora Krsmanović, Konstantin Ilijević, Ivan Gržetić

OP-13 The influence of seawater physicochemical parameters on the content of trace elements in mussels and surface sediment

Slavka Stanković, Ana Perosević, Nikola Petrović, Milica Ivković, Marija Kojić, Milena Radomirović, Antonije Onjia

POSTER PREZENTACIJE
POSTER PRESENTATIONS

PP1/1 Assessment of influential factors on the geochemistry of the soil-biota system in the Prašnik forest
Maja Ivanić, Gordana Medunić, Željka Fiket, Gordana Marović, Jasminka Senčar, Martina Furdek Turk, Goran Kniewald

PP1/2 Procena stepena kontaminacije toksičnim elementima zemljišta oko industrijskih objekata Srema: Kspef faktor
Maja Poznanović, Sanja Sakan, Dragan Manojlović, Sandra Škrivanj

PP1/3 The Electrochemical Behaviour of Purpurin in an Aqueous Solution of $LiNO_3$
Jelena Senćanski, Maja Pagnacco, Stevan Blagojević, Milica Vujković

PP1/4 Oscillatory Reaction as a Tool to Determine Purpurin Concentration
Kristina Stevanović, Jelena Maksimović, Jelena Senćanski, Stevan Blagojević, Milica Vujković, Maja Pagnacco

PP1/5 Adsorpcija estrogenih hormona na modifikovanim ugljeničnim tkaninama
Danijela Prokić, Marija Vukčević, Marina Maletić, Jelena Rusmirović, Tatjana Đurkić

PP1/6 Karbon kriogel kao adsorbent za uklanjanje Cd(II), Zn(II) i Ni(II) jona iz vode
Marija Vukčević, Marina Maletić, Ana Kalijadis, Biljana Babić, Tatjana Đurkić, Mila Laušević

PP1/7 PAH diagnostic ratio and source analysis in the vicinity of industry sampling sites
Anka Cvetković, Milena Jovašević Stojanović, Dušanka Matijević, Stamenko Dikanović, Nebojša Vuković

PP1/8 Monitoring industrijskog zemljišta na teritoriji Republike Srbije
Stamenko Dikanović, Anka Cvetković, Nebojša Vuković, Dušanka Matijević

PP1/9 Human health risk assessment due to heavy metals in surface soil surrounding "Nikola Tesla A" thermoelectric power plant
Milan Tanić, Mirjana Ćujić, Marko Daković, Ljiljana Janković Mandić, Snežana Dragović, Denis Dinić

PP1/10 The evidence of hopane producing microbial communities in Kovin lignite deposit (Serbia)
Danica Mitrović, Nataša Đoković, Dragana Životić, Achim Bechtel, Ksenija Stojanović

PP1/11 Coniferous families as dominant source of precursor organic matter in lignite from the Kostolac Basin (Serbia)
Nataša Đoković, Danica Mitrović, Dragana Životić, Achim Bechtel, Ksenija Stojanović

PP1/12 Sorpciono ponašanje klomazona u poljoprivrednim zemljištima
Rada Đurović-Pejčev, Svjetlana Cupać, Zorica P. Tomić, Vojislava Bursić, Tijana Zeremski

PP1/13 Electrocatalitic Behaviour Of Serpentinite Modified Carbon Paste Electrode
Jelena Čović, Jelena Milićević, Milan Momčilović, Aleksandra Zarubica, Aleksandar Bojić, Marjan Ranđelović

PP1/14 Primena testova fitotoksičnosti kod fotofemijskih procesa
Anđelka Tomašević, Natasa Šekuljica, Ana Dugandžić, Dunja Dabić, Slobodan Petrović, Dušan Mijin

PP1/15 Uticaj hloridnih i fluoridnih jona na fotokatalitičku degradaciju nikosulfurona i karbofurana u vodi
Dušan Mijin, Anđelka Tomašević, Slavica Gašić, Rada Đurović-Pejčev, Nevena Prlainović, Ana Dugandžić, Aleksandar Marinković

PP1/16 Značaj geohemijskih i mineraloških karakteristika sedimenata za predviđanje procese degradacije terena
Milica Kašanin-Grubin, Aleksandra Šajnović, Gordana Gajica, Vladimir Simić, Ksenija Stojanović, Ilija Brčeski, Branimir Jovančićević

PP1/17 Sezonske varijacije koncentracija neorganskih anjona u atmosferskim aerosolima
Žaklina Todorović, Ivana Sredović Ignjatović, Ljubiša Ignjatović, Antonije Onjia

PP1/18 Uticaj različitih doza g-zračenja na hidrolitičku stabilnost modifikovanih urea-formaldehidnih (UF) smola
Vojislav Jovanović, Suzana Samaržija-Jovanović, Sonja Jevtić, Branka B. Petković, Gordana Marković, Milena Marinović-Cincović

PP1/19 First study of electrochemical behavior of herbicide pethoxamid and its voltammetric determination in river water
Sonja Jevtić, Vesna Vukojević, Slađana Đurdjić, Marija V. Pergal, Dragan Manojlović, Branka B. Petković, Dalibor M. Stanković

PP1/20 Sequestration of lindane in contaminated sediment amended with carbon-rich sorbents
Snežana Maletić, Marko Grgić, Jelena Belin, Srđan Rončević, Marijana Kragulj Isakovski, Jasmina Agbaba, Božo Dalmacija

PP1/21 Adsorption potential of hydrochars obtained from sugar beet pulp toward alachlor
Marijana Kragulj Isakovski, Snežana Maletić, Jelena Tričković, Jasmina Agbaba, Srđan Rončević, Aleksandra Tubić, Božo Dalmacija

PP1/22 Komparacija efikasnosti metode fitoremedijacije procednih voda deponije primenom Eichhornia crassipes
Katarina Antić, Szabolcs Pap, Dragan Adamović, Maja Turk Sekulić, Jelena Radonić

PP1/23 Preconcentration of heavy metals by the solid-phase extraction disk based on activated carbon derived from waste tires
Ksenija Kumrić, Radojka Vujasin, Đorđe Petrović, Aleksandar Devečerski, Latinka Slavković-Beškoski, Ljiljana Matović

PP1/24 Lead isotope ratio as a tool for considering dissolving mechanism of soil components by Macrolepiota procera
Slađana Đurđić, Vesna Vukojević, Jelena Mutić

PP1/25 Analytical approach for detection of ergosterol in mushrooms based on modification free electrochemical sensor
Vesna Vukojević, Slađana Đurdjić, Tanja Ćirković Veličković, Jelena Mutić, Dalibor M. Stanković

PP1/26 Application of a Venturi reactor for cavitation purification process of wastewaters from phenol
Sandra Petković, Borivoj Adnađević, Jelena Jovanović, Mihajlo Gigov, Marko Pavlović

PP1/27 Motor-oil removal from self-assembled 3D-reduced graphene oxide
Jelena Jovanović, Mihajlo Gigov, Sandra Petković, Borivoj Adnađević

PP1/28 Primena sveobuhvatne dvodimenzionalne gasne hromatografije sa masenom spektrometrijom (GCxGC-MS) za rešavanje nerazložene složene smeše (Unresolved Complex Mixture - UCM) naftnih ugljovodonika u procesima bioremedijacije
Kristina Joksimović, Aleksandra Žerađanin, Mila Ilić, Jelena Avdalović, Srđan Miletić, Tanja Jednjak, Vladimir Beškoski

PP129 Deterioracija betona u hidroelektranama- hemijski i mikrobiološki faktori
Marija Lješević, Gordana Gojgić-Cvijović, Bojana Stanimirović, Vladimir Beškoski, Ilija Brčeski

PP1/30 Primena Micro-Oxymax respirometra za procenu toksičnosti bakra na model organizmu Daphnia magna
Branka Lončarević, Marija Lješević, Marijana Marković, Dragica Jakovljević, Gordana Gojgić-Cvijović, Vladimir Beškoski

PP1/31 Ispitivanje naftnih zagadjujućih supstanci u uzorcima sedimenta na lokalitetu Toplane Novi Beograd

Aleksandra Žeradjanin, Marija Lukić, Mila Ilić, Jelena Avdalović, Jelena Milić, Tanja Jednak, Vladimir Beškoski

PP1/32 Comparative study of alachlor removal from water by UV photolysis and UV/persulfate process

Tajana Đurkić, Jelena Molnar Jazić, Jasmina Agbaba, Aleksandra Tubić, Marijana Kragulj Isakovski

……

PP2/1 Electrochemical behavior and nanomolar quantification of polydatin. Application on food supplements

Slađana Đurđić, Vesna Vukojević, Jelena Mutić, Dalibor M. Stanković

PP2/2 Uranium and thorium content in mushroom Macrolepiota Procera and their bioconcentration factors

Vesna Vukojević, Slađana Đurdjić, Jelena Mutić

PP2/3 Interaction of chlorophenols with microplastic in water

Aleksandra Tubić, Maja Lončarski, Tamara Apostolović, Snežana Maletić, Jelena Tričković, Dejan Krčmar, Jasmina Agbaba

PP2/4 Synthesis of 5-nitroisatin-3-thiosemicarbazone in a green solvent

Milica Z. Zlatković, Sandra S. Konstantinović, Vlada B. Veljković

PP2/5 Next generation low cost magnetic activated carbons for future arsenic removal from water

Sabolc Pap, Mark A. Taggart, Jelena Radonić, Maja Turk Sekulić

PP2/6 Is the Danube along Novi Sad overdosed by diazepam?

Maja Milanović, Jelena Radonić, Maja Turk Sekulić, Mirjana Vojinović Miloradov, Nataša Milić

PP2/7 Organsko-geohemijsko ispitivanje sedimenata iz arheološkog nalazišta Vinča (Beograd, Srbija)

Aleksandra Šajnović, Milica Kašanin-Grubin, Kristina Penezić, Sanja Stojadinović, Gorica Veselinović, Branimir Jovančićević

PP2/8 Persistent organic compound across Serbia – Indications of soil and vegetation (moss) pollution

Gordana Vuković, Tijana Milićević, Mira Aničić Urošević, Snježana Herceg Romanić, Gordana Mendaš, Miloš Ilić, Aleksandar Popović

PP2/9 Procena kontaminacije sedimenta reke Dunav organohlornim pesticidima

Maja Brborić, Branislav Vrana, Jelena Radonić, Mirjana Vojinović Miloradov, Sabolc Pap, Maja Turk Sekulić

PP2/10 Metode površinske jonizacije za merenje izotopskog sastava hlora
Filip Veljković, Boris Rajčić, Suzana Veličković

PP2/11 Asistencija mikrotalasa u hemiji: Sinteza novih mediuma za tretman otpadnih voda kontaminiranih emergentim polutantima
Olivera Paunović, Sabolč Pap, Nikola Bošković, Jelena Radonić, Maja Turk Sekulić

PP2/12 Brassicaceae in Phytoremediation: A review
Niko Radulović, Milica Todorovska

PP2/13 Preliminary investigation of polycyclic aromatic hydrocarbons in street dust of Pančevo, Serbia
Ivan Kojić, Tatjana Šolević Knudsen

PP2/14 Phthalate esters in glass jar metal lids from Serbian markets
Tatjana Šolević Knudsen, Mila Ilić, Srđan Miletić, Jelena Milić, Jelena Avdalović

PP2/15 Razvoj hromatografske metode za određivanje tragova veštačkih zaslađivača u vodi
Eleonora Gvozdić, Ivana Matić Bujagić, Svetlana Grujić, Tatjana Đurkić

PP2/16 Određivanje odabranih steroida u uzorcima komunalne otpadne vode
Ivana Matić Bujagić, Zorica Jauković, Svetlana Grujić, Eleonora Gvozdić, Mila Laušević

PP2/17 Emisija teških metala u urbanim sredinama
Snežana Aksentijević, Ana Kremić, Jelena Kiurski

PP2/18 Karakteristike aromatične frakcije mulja iz jezera Tehirgiol (Rumunija)
Sanja Stojadinović, Aleksandra Šajnović, Branimir Jovančićević, Mariana Golumbeanu, Roxana Almasan, Ilija Brčeski

PP2/19 Rangiranje lokacija na teritoriji grada Kruševca na osnovu sadržaja teških metala u zemljištu primenom PROMETHEE metode
Danijela Stojadinović, Tanja Nikolić

PP2/20 Čađ kao faktor kvaliteta vazduha na teritoriji grada Vranja
Tanja Nikolić, Danijela Stojadinović

PP2/21 Contamination influences of building construction site on surrounding environment in Serbia
Miljan Šunjević, Vladimir Rajs, Boris Obrovski, Mirjana Vojinović Miloradov, Miljana Zeković, Darko Reba

PP2/22 Adsorpcija i katalitička razgradnja zagađivača u prisustvu zeolita
Suzana Rogan, Maja Milojević-Rakić, Bojana Nedić Vasiljević, Snežana Uskoković-Marković, Vera Dondur, Ljubiša Ignjatović

PP2/23 Liverworts as potent bioaccumulators of environmental heavy metals: A review
Sonja Filipović, Niko Radulović

PP2/24 Conocephalum conicum (L.) Dum., biosensor of an environmental pollution with phytoremediation potential
Niko Radulović, Sonja Filipović, Marko Mladenović

PP2/25 Effects of power of ultrasound on the removal of cyprodinil from water by lignocellulosic-Al_2O_3 biosorbent
Nena Velinov, Jelena Mitrović, Milica Petrović, Miloš Kostić, Danijela Bojić, Aleksandar Bojić

PP2/26 Sadržaj As, Cd, Cr, Ni i Pb u zemljištu tipa gajnjača na području Radmilovca
Bojana Stanimirović, Jelena Popović-Đorđević, Radojka Maletić, Boris Pejin, Aleksandar Đorđević, Ilija Brčeski

PP2/27 Sadržaj torijuma-232, urana-235 i urana-238 u unutrašnjim organima divljih ptica sa područja Vojvodine
Željko Mihaljev, Brankica Kartalović, Nenad Popov, Sandra Jakšić, Milica Živkov-Baloš

PP2/28 Vaskularne biljke kao bioindikatori zagađenosti zemljišta u urbanim ekosistemima
Tatjana Sekulić, Vladanka Stupar, Zlata Živković

PP2/29 Razvoj originalne LIBS aparature na bazi TEA CO_2 lasera za primenu u zelenoj analitičkoj hemiji
Miloš Momčilović, Sanja Živković, Jelena Savović

PP2/30 Spektroskopija laserski indukovane plazme za evaluaciju efikasnosti biosorpcije teških metala iz otpadnih voda na ljuskama suncokreta
Sanja Živković, Jelena Stevanović, Jelena Petrović, Jelena Savović, Miloš Momčilović

PP2/31 Ispitivanje neorganskog sastava sedimenata Đerdapskog jezera (Srbija)
Gordana Gajica, Milica Kašanin-Grubin, Snežana Štrbac, Lukas Hagemann, Nebojša Vasić, Jan Schwarzbauer, Branimir Jovančićević

PP2/32 Postupak određivanja sadržaja gasovite faze BTEX jedinjenja (benzen, toluen, etilbenzen, ksileni) sa sorbenta metodom GC-FID
Đurica Katnić, Miloš Tošić, Željka Nikolić, Milena Pijović, Ivana Raičević, Boris Rajčić, Gvozden Tasić, Dubravka Milovanović

PP2/33 Određivanja sadržaja BTEX jedinjenja u uzorcima građevinskog materijala i otpada sa mineralnim uljima kao glavnom komponentom, metodom GC/FID Headspace
Miloš Tošić, Željka Nikolić, Jelena Georgijević, Tanja Brdarić, Gvozden Tasić, Vladimir Nikolić, Dubravka Milovanović, Milica Marčeta Kaninski

PP2/34 Nanostructured titanium-dioxide thin films for environmental applications
Ana Grce, Dejan Pjević, Momir Milosavljević, Rolf Grieseler, Peter Schaaf

PP2/35 Determination of the BTEX compounds in concrete using Headspace GC-FID
Branislava Savić, Ana Grce, Tanja Brdarić, Jelena Georgijević, Marija Ječmenica Dučić, Boris Rajčić, Milica Marčeta Kaninski

PP2/36 Validation Procedures for Determination of Polycyclic Aromatic Hydrocarbons (PAH) in Water
Mina Seović, Adrijana Šutulović, Danka Aćimović, Đurica Katnić, Miloš Tošić, Dubravka Milovanović, Milica Marčeta Kaninski

PP2/37 Determination of phenol and phenolic compounds in crude mineral oils and waste mineral oil samples by GC-MS
Adrijana Šutulović, Branislava Savić, Željka Nikolić, Marija Ječmenica Dučić, Mina Seović, Boris Rajčić, Tanja Brdarić

PP2/38 Kontinualno merenje emisija zagađujućih materija iz termoelektrana na ugalj prema zahtevima SRPS EN 14181
Marko Pavlović, Mihajlo Gigov, Sandra Petković, Miroslav Sofrenić

PP2/39 Risk assessment of emerging pollutants in the aquatic environment
Maja Sremački, Maja Petrović, Dušan Milovanović, Ivana Mihajlović, Mirjana Vojinović Miloradov

PP2/40 Application of BCR sequential extraction for study of Rare Earth Elements distribution in soil from Serbia
Jelena Mutić, Vesna Vukojević, Slađana Đurđić

PP2/41 Cleaning the engine using H2E ECC technology
Dragan Adamović, Mirjana Vojinović Miloradov, Vojin Močević, Jelena Radonić, Maja Turk Sekulić, Savka Adamović, Sabolč Pap

PP2/42 Waste-based alternative adsorbents for the remediation of radionuclides contaminated waters: Have we a new solution?
Nikola Bošković, Romana Kištof, Maja Turk Sekulić, Sabolč Pap, Polonca Trebše, Jelena Radonić, Jasmina Kožar Logar

STUDENTSKI RADOVI

STUDENTS' PAPERS

PPS/1 Bioakumulacija esencijalnih i toksičnih elemenata u šipurku
Studenti: Lazar Vujošević, Irena Miljković
Mentor: Jelena B. Popović–Đorđević

PPS/2 Sadržaj i dnevni unos barijuma u odabranom povrću
Studenti: Tamara Adžić, Irena Miljković
Mentor: Jelena B. Popović–Đorđević

PPS/3 Sadržaj odabranih elemenata u realnim uzorcima vode sa teritorije Požege, Srbija
Studenti: Ivana Maloparac, Simona Jaćimović
Mentor: Nebojša Pantelić

PPS/4 Optimizacija degradacije tekstilne boje Reactive Black 5 netermalnim plazma-tretmanom u prisustvu TiO_2
Student: Slađana Savić
Mentor: Goran Roglić

PPS/5 Procena potencijalnog zdravstvenog rizika upotrebe pijaće vode na području Požege na osnovu sadržaja barijuma i stroncijuma
Studenti: Simona Jaćimović, Ivana Maloparac
Mentor: Aleksandar Ž. Kostić

PPS/6 Određivanje sadržaja arsena, kadmijuma i olova u različitim uzorcima meda primenom optički emisione spektrometrije sa induktivno spregnutom plazmom
Studenti: Jovan Novaković, Maja Grigorov
Mentor: Biljana Kaličanin

PPS/7 Naftni zagađivači u drumskoj prašini Pančeva, Srbija
Studenti: Nada Vidović, Ivan Kojić
Mentor: Tatjana Šolević Knudsen

PPS/8 Praćenje sadržaja toksičnih metala (As, Cd i Pb) u odabranim vrstama medicinskog bilja
Studenti: Sandra Kalauzović, Maja Grigorov, Jovan Novaković
Mentor: Biljana Kaličanin

PLENARNA I SEKCIJSKA PREDAVANJA

PLENARY AND SESSION LECTURES

Biodegradacija nafte u sedimentnim stenama i u životnoj sredini – prednosti i nedostaci

Petroleum biodegradation in sedimentary rocks and in the environment - advantages and disadvantages

Branimir Jovančićević[1a]

[1]Univerzitet u Beogradu, Hemijski fakultet, Studentski trg 12-16, 11001 Beograd, Srbija,

[a]bjovanci@chem.bg.ac.rs

Nafta je složena smeša različitih zasićenih i aromatičnih ugljovodonika i azot, sumpor, kiseoničnih (NSO) jedinjenja. Nastaje u sedimentnim stenama u fazi katageneze krakovanjem kerogena pod dejstvom toplote i mineralnih katalizatora, na povišenom pritisku u toku geološkog vremena koje se meri milionima godina [1]. Akumulirana u rezervoarskim stenama podložna je različitim promenama koje su izazvane ispiranjem vodom, krakovanjem, deasfaltovanjem i biodegradacijom. Ukoliko je temperatura u rezervorskim stenama niža od 66 °C, stvaraju se pogodni uslovi za razvoj anaeronih mikroorganizama koji u velikoj meri mogu da izmene sastav nafte [2].

Ukoliko se nafta antropogenim uticajima, kao polutant, nadje u životnoj sredini (recentnim sedimentima, zemljištu, podzemnim i površinskim vodama) ona se takodje menja kao posledica fotooksidacionih reakcija, sorpcije, migracije, isparavanja, taloženja čestica, emulzije, površinskog spiranja, disperzije i biodegradacije. U životnoj sredini zagadjenom naftom postoje uslovi za razvoj aerobnih mikroorganizama. Pod njihovim dejstvom sastav nafte, kao zagadjujuće supstance, i njena količina, se menjaju u velikoj meri [3].

U ovom radu biće dat pregled rezultata onih istraživanja koja se odnose na biodegradaciju nafte u geološkim uslovima [4-6], i biodegradaciju nafte kao polutanta u životnoj sredini [7-9].

Biodegradacijom nafte u rezervoarskim stenama prvo se razradjuju *n*-alkani. Podložni razgradnji su i izoprenoidni alifatični ugljovodonici, a medju njima i najobilniji C_{19}, pristan i C_{20}, fitan. Iz aromatične frakcije, relativno lako se razgradjuju fenantren i njegovi metil-izomeri. Konačno, u poslednjim fazama mikrobiološke razgradnje svoj sastav i strukturu menjaju i policiklični alkani tipa sterana i terpana [2].

Uklanjanjem *n*-alkana, nafta gubi svoj parafinski karakter. Na taj način ona postaje bolja sirovina za dobivanje benzina visokog oktanskog broja. S te strane, biodegradacija nafte je poželjan proces. Medjutim, ovim procesom se razgradjuju najpouzdaniji bilološki markeri. Zbog toga je iz ugla organsko-geohemijskih istraživača koji imaju zadatak da procene poreklo i geološku istoriju nafte na osnovu njihove raspodele, biodegradacija vrlo nepoželjna.

U zemljištu i u površinskim vodama koji su zagadjeni naftom, dejstvom aerobnih mikroorganizama postiže se sličan efekat. U relativno kratkim vremenskim periodima biodegradacionim procesima može se razgraditi velika količina potencijalno toksičnih naftnih organskih jedinjenja. U tom smislu ovaj proces u prirodi se i pospešuje. Na taj način on postaje vrlo pouzdan remedijacioni postupak. Bioremedijacija se danas smatra vrlo pouzdanom tehnikom za prečišćavanje recentnih sedimenata, zemljišta i površinskih i podzemnih voda od nafte kao zagadjujće supstance [10-13].

Literatura

1. Schwarzbauer, J., Jovančićević B. *Fundamentals in Organic Geochemistry - Fossil Matter in the Geosphere* (2015), Springer, 158 pp.
2. Head. I.M., Jones D.M., Larter, S. *Nature* 426 (2003) 344-352.
3. Jovančićević, B., Antić, M., Pavlović, I., Vrvić, M., Beškoski, V., Kronimus, A., Schwarzbauer J. *Water Air and Soil Pollution* 190 (2008) 299-307.
4. Jovančićević, B., Polić P.,Vitorović D. *Journal of the Serbian Chemical Society* 63 (1998) 397-418.
5. Stojanović, K., Jovančićević, B., Pevneva, G.S., Golovko, J.A., Golovko, A.K., Pfendt, P. *Organic Geochemistry* 32 (2001) 721-731.
6. Šolević, T., Stojanović, K., Bojesen-Koefoed, J., Nytoft, H.P., Jovančićević, B., Vitorović, D. *Organic Geochemistry* 39 (2008) 118-134.
7. Jovančićević, B., Polić, P., Vrvić, M., Sheeder, G., Teschner, T., Wehner, H. *Environmental Chemistry Letters* 1 (2003) 73-81.
8. Antić, M., Jovančićević, B., Ilić, M., Vrvić, M.M., Schwarzbauer, J. *Environmental Sciences and Pollution Res*earch 13 (2006) 320-327.
9. Ilić, M., Antić, M., Antić, V., Schwarzbauer, J., Vrvić, M., Jovančićević, B. *Environmental Chemistry Letters* 9 (2011) 133-140.
10. Jovančićević, B., Antić, M., Vrvić, M., Ilić, M., Novaković, M., Saheed, R.M., Schwarzbauer, J. *Journal of the Serbian Chemical Society* 73 (2008) 577-583.
11. Novaković, M., Ramadan, M.M.A., Šolević Knudsen, T., Antić, M., Beškoski, V., Gojgić-Cvijović, G., Vrvić, M.M., Jovančićević B. *Environmental Chemistry Letters* 10 (2012) 287-294.
12. Muftah, M.A.R., Šolević-Knudsen, T., Antić, M., Beškoski, V., Vrvić,M.M., Schwarcbauer, J., Jovančićević, B. *Journal of the Serbian Chemical Societ* 75 (2013) 1035-1043.
13. Beškoski, V., Miletić, S., Ilić, M., Gojgić-Cvijović, G., Papić, P., Marić, M., Šolević-Knudsen, T., Jovančićević, B., Nakano, T., Vrvić, M.M. *CLEAN – Soil, Air, Water* (2018) doi: [10.1002/clen.201600023].

Biosorption: Can we address water quality and contribute to the ”circular economy”?

Stuart Gibb[1a], Yuan Li[1,2], Sabolc Pap[1,3], Ian Rae[1], Zulin Zhang[2], Mark Taggart[1]

[1]Environmental Research Institute, North Highland College-UHI, University of the Highlands and Islands, Thurso, Scotland, UK

[2]Environmental and Biochemical Sciences Group, The James Hutton Institute, Aberdeen, Scotland, UK

[3]Department of Environmental Engineering and Occupational Safety and Health, Faculty of Technical Sciences, University of Novi Sad, Novi Sad, Serbia

[a]stuart.Gibb@uhi.ac.uk

High quality water is of critical importance to both natural ecosystems and to human health. However, according to the UN, the global human population is expected to rise by around one third by 2050 (to 9.3 billion) placing increased pressure on limited, and unevenly distributed water resources. In addition, an increasing number of organic and inorganic hazardous compounds produced by anthropogenic activity are being discharged into the water environment. Inorganic water pollutants include metals, radioactive substances, fertilizers, etc., while organic pollutants include hydrocarbons, pesticides, pharmaceuticals, etc. These can be transported, immobilised, degraded, or bio-accumulated in the environment (water, air, soil) and ecosystems (plants, animals). As a result, contaminants in the aquatic environment can present eco-toxicological risks, and further exacerbate pressures on water resources for humans - causing elevated risks to food security, socio-economic well-being and human health.

While a wide range of physical, chemical and biological procesess are currently used in water treatment and remediation, all suffer from particular disadvantages. Given the growing and diversifying scale of pollution problems, new, effective, low-cost and sustainable approaches are now required. ‘Biosorption’ offers several advantages in terms of the removal of contaminants from water and their immobilisation: it often employs low-cost, waste, natural or sustainable materials; the process is metabolically-independent (*cf.* bioaccumulation) and can involve a range of physico-chemical mechanisms including physisorption, ion-exchange, surface complexation and microprecipitation.

As biosorption may use by-products or wastes from other industries (e.g., food and drink sector), the approach is also consistent with the principles of the ’circular economy’, i.e., an alternative to a traditional linear economy (make, use, dispose) in which we seek to re-use or recycle materials to extract the maximum value from them whilst minimising waste and resource consumption.

This presentation will provide an introduction to the principles of biosorption and the mechanisms involved, before using brief case studies to illustrate the potential of biosorption in the remediation of wastewater. One particular focus for biosorption research has been on the removal of dissolved metals (including transition and heavy metals) from aqueous media. Case studies will be presented on strontium removal from a simulant radioactive wastewater (generated through nuclear fission), and on copper removal from wastewater arising from the distillation of Scotch whisky.

Given the broad range of mechanisms involved in ’biosorption’, there has been a recognition that the technique has significant potential for the removal of organic contaminants from aqueous media. A further case study will be presented showing new data on the performance of a diverse range of biosorbents (derived mainly from industrial and agricultural wastes) for the removal of target and priority human pharmaceuticals.

While research (especially at the bench-scale) on biosorption has been extensive in recent decades, translation and application to pilot plants or the industrial scale has been somewhat limited. The presentation will highlight some of the barriers and factors involved, and identify issues that the R+D community must address if biosorption is to be more widely accepted and reach its full potential. These include:

- Enhancement of biosorbent performance, selectivity and stability (e.g. using encapsulation, biofilms, stabilisation);

- Better identify the biosorption mechanisms at play in relation to biosorbent-sorbant combinations (for metals, organics, etc.);

- Create new, improved, and simplified mathematical models for the description of multi-sorbate systems;

- Utilise multidisciplinary approaches to consider not only biosorbent performance, but also factors such as raw material availability, biosorbant production cost, LCA, etc.;

- Undertake pilot scale studies to bridge the gap between bench and full-scale applications - particularly for priority substances that are poorly removed using existing techniques, or, that present high toxicological risks to either ecosystems or human health;

- Improve life cycle analysis (LCA): To assess all the environmental impacts associated with the biosorbent ’life’ cycle - from raw material production through to processing, disposal, recycling and/or regeneration.

Peroxo-methods for the synthesis of mixed metaloxide materials

Viacheslav Avdin[1a], Igor Krivtsov[1,2], Marina Ilkaeva[2]

[1]Nanotechnology Education and Research Center, Chemical Department, South Ural State University

[2]Department of Physical and Analytical Chemistry, University of Oviedo

[a]avdinvv@susu.ru

Mixed oxides of Group IV metals and alkaline earth metals find application as ceramic semiconductors, biocompatible materials, adsorbents and catalysts. Such approaches as sol-gel method, nonhydrolytic methods, solvotermal synthesis are the most often used for their synthesis [1–7]. At the moment, there is no universal method that would allow satisfying all the requirements for synthesis and the properties of the resulting oxide material. A significant problem arising in the preparation of mixed metaloxides is the difference in the rates of hydrolysis of different metals. To equalize the rates of hydrolysis, prehydrolysis of a less active precursor, and to lower activity of a more active precursor, a single molecular precursor or organic ligands are being used. Particular attention deserves such parameters of the synthesis as the ratio and concentration of precursors, temperature, reaction time, drying methods, the nature of the solvent.

Peroxo methods are based on the intermediate reaction with H_2O_2. In this case, peroxo-hydroxo complexes with the $[M(O\text{-}O)(OH)_x]^y$ composition are formed. We have developed several methods for obtaining mixed MO_x/SiO_2 oxides using peroxo route.

1. Mixed TiO_2/SiO_2 oxides from precursors based on titanium peroxo tartrate and silicic acid [2]. The TiO_2/SiO_2 based hydrogel is prepared by precipitating TiO_2 and SiO_2 from aqueous solutions of sodium silicate and titanium oxysulfate. The hydrogel is washed with water and dissolved in hydrogen peroxide in the presence of tartaric acid. A clear, non-opalescent, bright orange solution is formed. It is slowly evaporated in a water bath until formation of a polymer gel, dried in vacuo and then calcined in air at 470°C. The obtained samples consist of a silicate matrix, with TiO_2 granules. The granules have a size of about 5 nm and 100% anatase phase. The surface area is <300 m^2/g.

2. The use of a precursor on the basis of peroxotitanic and silicic acids [3]. The method is similar to the previous one, except organic ligands not are used. The hydrogel based on TiO_2 and SiO_2 is dissolved in excess of hydrogen peroxide. After dissolving the hydrogel, a bright orange solution is left to decompose hydrogen peroxide. An orange precipitate forms, which is aged and washed with water. Peroxo xerogels consist of a condensed matrix of segregated silica and titanium dioxide, which contains peroxo groups. Peroxo groups decompose above 250°C. The transition of anatase-rutile in TiO_2 granules is observed at lower temperatures than in samples obtained without peroxo stage.

3. A hydrothermal peroxo method for preparation of highly crystalline titania-silica [4]. The method is similar to the previous one up to the stage of obtaining a solution of the peroxocomplex of titanium and silicic acid. HNO_3 is added to the resulting bright orange

solution to pH 2, transferred to an autoclave and thermostated. The precipitate is then washed with water and dried. In this process, the silica is adsorbed on pre-formed TiO_2 particles. This separates the particles of titania from each other and controls the crystals growth. It was possible to obtain a sample with photocatalytic activity five times higher than that of the commercial catalyst Evonik P25 in the methylene blue decomposition reaction.

Peroxo-route for the synthesis of MgO/ZrO_2 mixed oxides [8]. In the first stage, the solutions of $MgSO_4$ and $ZrOCl_2$ are co-precipitated with alkali. The obtained hydrosol was washed with water and dissolved in H_2O_2. Then the Pechini-type method was applied. This method provides a highdegree of incorporation of magnesium ions into the crystalline lattice of zirconia, thus forming cubic magnesia-stabilized zirconia phase with a general formula $Mg_xZr_{x-1}O_{2-x}$. A homogeneous distribution of acidic and basic sites is observed on the surface. The sample exhibited high activity and selectivity with respect to the mesitylene in the self-condensation reaction of acetone.

Peroxide precursors are inexpensive, non-toxic, environmentally friendly, do not require the use of special conditions. The use of a peroxide stage in combination with other common methods allows to successfully control the structure and properties of mixed metal oxide materials.

References

1. Kakihana, M., Kobayashi, M., Tomita K., Petrykin V., *Bull. Chem. Soc. Japan*. 83 (2010) 1285–1308.
2. Krivtsov, I.V., Ilkaeva, M.V., Samokhina V.D., Avdin V.V. et al. *J. Sol-Gel Sc. Tech.* 67 (2013) 665–669.
3. Ilkaeva, M., Krivtsov, I., Avdin V., Khainakov S. et al. *Col. Surf. A*. 456 (2014) P. 120–128.
4. Ilkaeva, M., Avdin V., Khainakov S. et al. *J. Col. Interface Sc.* 444 (2015) 87–96.
5. Truijen, I., Hardy, A., Van Bael, M.K., Van den Rul, H., Mullens J. *Thermochimica Acta*. 456 (2007) 38–47.
6. Kobayashi, M., Petrykin, V., Tomita, K., Kakihana M. *J. Crystal Growth*. 337 (2011) 30–37.
7. Ennaoui, A., Sankapal, B.R., Skryshevsky, V., Lux-Steiner, M.Ch. *Solar Energy Mat. Solar Cells*. 90 10 (2006) 1533–1541.
8. Krivtsov, I., Faba, L., Díaz, E., Ordóñez, S., Avdin V. et al. *App. Catal. A* 477 (2014) 26–33

Primena dielektričnog barijernog pražnjenja u tretmanu voda

Dielectric Barrier Discharge in Water Treatment

Goran Roglić[1a]

[1]Hemijski fakultet, Univerzitet u Beogradu, Beograd, Srbija

[a]groglic@chem.bg.ac.rs

Rast stanovništva, urbanizacija i porast životnog standarda kao i ekspanzija industrije i potrošnje hrane dovode do porasta potrošnje vode. Na taj način se troše rezerve sveže vode što dovodi do potrebe za razvojem novih tehnologija u tretmanu otpadnih voda. Ozbiljan problem predstavlja i intenzivno ispuštanje novih zagađujućih supstanci kao što su tekstilne boje, pesticidi, lekovi i supstance koje se koriste u proizvodnji sredstava za higijenu i kozmetičke preparate. Tradicionalni načini prerade vode koji obuhvataju sedimentaciju, koagulaciju-flokulaciju, biološki tretman i filtraciju često nisu dovoljni da ispune standarde kvaliteta vode. Ove supstance čak i u malim količinama mogu da utiču na zdravlje ljudi i imaju uticaj na vodene organizme.

Značajna istraživanja usmerena su ka novim tehnologijama kojima je moguće udaljiti ove rastvorne supstance iz vode. Tehnologije koje daju dobre rezultate u tretmanu vode su membranski postupci i unapređeni oksidacioni procesi. Unapređeni oksidacioni procesi su procesi koji pri ambijentalnim uslovima (pritisak i temperatura) generišu dovoljnu količinu hidroksilnih radikala da utiču na prečišćavanje vode. Hidroksilini radikal je neutralna kratkoživeća oksidaciona vrsta sa izraženim oksidacionim potencijalom. U reakcijama sa organskim molekulima hidroksilni radikal se ponaša kao elektrofil. Mehanizam delovanja mu je složen ali se može svrstati u sledeće grupe reakcija: a) adicija na dvostruku vezu ugljenik-ugljenik, b) supstitucija na aromatičnom prstenu; c) apstrakcija atoma vodonika i d) monoelektronska oksidacija.

Najznačajniji procesi u kojima dolazi do generisanja hidroksilnog radikala i koji su našli primenu u tretmanu voda su: 1. UV/H_2O_2 2. Ozon/vodonik peroksid (Perokson process), 3. Ozon/UV, 4. Fentonova reakcija (gvožđe (II) ili (III) sa vodonik peroksidom); 5. Fotokataliza.i u novije vreme netermalni plazma tretmani [1].

Netermalna plazma se karakteriše temperaturom elektrona koja je znatno viša od temperature gasa u kojoj se generiše. U prisustvu vode u netermalnoj plazmi dolazi do generisanja reaktivnih kiseoničnih i azotovih vrsta. Između ostalih vrsta generišu se i hidroksilni radikali. Relaksacijom pobuđenih vrsta u niže energetsko stanje dolazi do emisije UV zraka koji takođe učestvuju u degradaciji organskih molekula. U tretmanu vode netermalnom plazmom postoje dva pristupa: generisanje plazme u tečnosti i generisanje plazme u kontaktu sa tečnošću. Generalno, sva ova pražnjenja se mogu podeliti na pražnjenje direktno u tečnoj fazi, pražnjenja u gasnoj fazi sa tečnom elektrodom (elektrodama) i pražnjenje u mehurićima u tečnosti. Po tipu pražnjenja i konstrukciji reaktora razlikujemo tri glavna tipa električnih pražnjenja: tinjavo pražnjenje, dielektrično barijerno pražnjenje i pulsno korona pražnjenje [2,3].

Kod dielektričnog barijernog pražnjenja pražnjenje se odvija između dve elektrode od kojih je barem jedna prekrivena tankim slojem dielektričnog materijala (kao što su staklo ili kvarc).

Dielektrični barijerni reaktor sa padajućim vodenim filmom je okarakterisan (generisanje reaktivnih kiseoničnih i azotovih vrsta u vodi) [4] i uspešno primenjen za uklanjanje različitih zagađujućih supstanci iz vodenih rastvora (pesticida [5], tekstilnih boja [6,7], farmaceutika [8], surfaktanata [9]). Katalizatori pospešuju degradaciju i utiču na efikasnost mineralizacije (HPK i ukupni organski ugljenik) u tretmanu zagađujućih supstanci dielektričnim barijernim pražnjenjem [10]. Pored toga analizirani su proizvodi degradacije i ispitana je toksičnost rastvora posle tretmana. Pokazano je da je dielektrično barijerno pražnjenje pogodna metoda za uklanjanje zagađujućih supstanci čak i u visokim koncentracijama.

Literatura

1. Stefan, M. I. (2018): Advanced oxidation processes for water treatment. Fundamentals and applications / edited by Mihaela I. Stefan. London: IWA Publishing.
2. Jiang B., Zheng J., Qiu S., Wu M., Zhang Q., Yan Z., Xue Q., *Chem. Eng. J.*, 236 (2014), 348–368.
3. Hijosa-Valsero M., Molina R., Montràs A., Müller M., Bayona J. M., *Environ. Technol. Rev.,* 3(1), (2014) 71–91
4. Kovačević V. V., Dojčinović B. P., Jović M., Roglić G. M, Obradović B. M., Kuraica M. M. *J. Phys. D: Appl. Phys.* 50 (2017) 155205
5. Jović M. S., Manojlović D. D., Stanković D., Dojčinović B. P., Obradović B. M., Gašić U. M., Roglić G. M., *J. Hazard. Mater*, 260 (2013) 1092–1099
6. Dojčinović B. P., Roglić G. M., Obradović B. M., Kuraica M. M., Kostić M. M., Nešić J., Manojlović D. D., *J. Hazard. Mater*, 192(2), (2011) 763–771
7. Dojčinović B. P., Roglić G. M., Obradović B. M., Kuraica M. M., Tosti T. B., Marković M. D., Manojlović D. D. *J. Serb. Chem. Soc.* 77(4), (2012) 535-548
8. Marković M., Jović M., Stanković D., Kovačević V., Roglić G., Gojgić-Cvijović G., Manojlović D., *Sci. Total Environ.*, 505 (2015) 1148–1155
9. Aonyas M. M., Nešić J., Jović M., Marković M., Dojcinović B., Obradović B., Roglić G. M., *CLEAN - Soil, Air, Water*, 44 (4), (2016), 422–429
10. Jović M. S., Dojčinović B. P., Kovačević V. V., Obradović B. M., Kuraica M. M., Gašić U. M. and Roglić G. M., *Chem. Eng. J.*, 248 (2014), 63–70

Actuality and Perspectives of the Application of Electrochemical Methods in Environmental Analysis

Ljubiša M. Ignjatović[1a]

[1]Faculty of Physical Chemistry, University of Belgrade, Belgrade, Serbia

[a]ljignjatovic@ffh.bg.ac.rs

The author of this text sincerely beleives that electroanalytical methods have perspectives in environmental analysis and will try to point that out.

First of all, the weak points of the use of electochemical methods (and related techniques) in the analysis of real environmental samples have to be mentioned: limited selectivity, need for sample preparation, time-consuming analysis, high-educated personals. Although, the strong points of the mentioned methods are: sensitivity, the unique posibility for speciation analysis, simplicity of the instruments operation, low cost of instruments and of an analysis, and the possibility of investigation of oxidation and reduction mechanisms of the investigated substances. The last is very important in order to the prediction of the behaviour of the biologicaly active substanes, not only in the environment but in the living organism also. During my many years of work, I have been convinced that these advantages are still dominant.

Previous analytical applications of electrochemical methods, which are definitely irreplaceable in the future, are: direct and indirect potentiometric measurements (pH value, redox potential, titrations endpoint); conductometric measurements (conductivity of liquid and solid samples); measuring the content of water in samples (Karl Fischer titrations that are necessarily carried out with electrometric endpoint detection based on biamperometric or bivoltametric measurements), potentiometric and amperometric determinations of gases in the air and gases dissolved in liquids (e.g. O_2, NH_3, CO_2) and biologically active molecules.

Nowadays, the conductivity measurements are used to detect ions present in the sample (mixture) which are previously separated by an ion exchange column. This combination, ion chromatography coupled with conductometric detection, became a powerful method for ionic components determination. Its advantages are obvious: *multispecies analysis* – several species (e.g. anions, cations) can be determined simultaneously in one run; *high selectivity* – optimized columns and eluents improve separations; *low detection limits*; preconcentration allows to reach the ng/L (ppt) range; *high precision and accuracy*, because with the proper temperature control high-precision conductometry can be done with errors in the range of 0.1%; *high degree of automation* allows large sample series and monitoring.

Polarography and voltammetry are the names of analytical methods based on current – potential measurements in electrochemical cells. The analytical signal is the current, normally a faradaic current, which flows through the cell during the reaction of the analyte at the working electrode with small surface. The analyte can be a cation, an anion or a molecule. The term **polarography** is used when the current – potential curve is measured by using a liquid working electrode whose surface can be renewed periodically or continuously (e.g. by drops). This includes the classical dropping mercury electrode and the subsequently developed static mercury drop electrode. **Voltammetry** includes all methods in which the current – potential measurements are made at stationary and fixed working electrodes, irrespective of their material composition: the hanging mercury drop, the thin mercury film, glassy carbon (including nafion-coated and modified), carbon paste, graphite and ceramic, electrodes made from noble metals (Pt, Au), chemically modified electrodes (B-doped diamond, fluorinated B-doped diamond, meniscous modified or heavy-amalgamated Ag) as well as molecularly imprinted conducting polymer and sol-gel film electrodes. Various methods are assigned to the terms polarography and voltammetry. These differ in the measuring technique and the type of electric potential used to enable determination process: direct current methods, pulse methods (*Square wave, normal pulse and differential pulse*) and as most sensitive **- stripping methods** (a*nodic, catodic and adsorptive stripping voltammetry*).

Poor selectivity, as the main disadvantage of polarography and voltammetry in analysis of the environmental samples can be overcome by combination of liquid chromatographic separation of components in the sample (ions, organic molecules) and voltammetric detection. A pre-requirement is that the measured substances must be able to be either reduced or oxidized: anions (nitrite, nitrate, sulfide, sulfite, azide, halides, oxohalides, thiocyanate, thyosulfate, cyanide...), transitional metals, organic substances (f.e. a large number of pesticides). It can be concluded that modern voltammetric methods can even now play a very useful role in monitoring of trace amounts of various electrochemically active pollutants and that their low investment and running costs, selectivity, sensitivity and robustness make them competitive with modern separation and spectrometric methods. Therefore, further attention should be given to their development, improvement and to their combination with appropriate methods for preliminary separation of those substances from various environmental and biological matrices, food and beverages.

References

1. Ignjatović, Lj.M., Marković, D.A., Veselinović, D.S., Bešić, B.R., *Electroanalysis* 5 (1993) 529-533.
2. Zima, J., Švancara, I., Barek, J., Vytras, K., *Critical Reviews in Analytical Chemistry* 39 (2009) 204-227.
3. Stević, M.C., Ignjatović, Lj.M., Ćirić-Marjanović, G., Marjanović, B., Barek, J., Zima, J., *J. Electroanal. Chem*. 677-680 (2012) 69-77.

Zelena sinteza metalnih nanočestica korišćenjem ekstrakata biljaka - nove primene biljnih resursa

Green synthesis of metal nanoparticles using plant extracts - new application of plant resources

Vladimir Mihailović[1a], Jelena Katanić[1], Nikola Srećković[1], Nevena Mihailović[1]

[1]Institut za hemiju, Prirodno-matematički fakultet, Univerzitet u Kragujevcu, Kragujevac, Srbija

[a]vladam@kg.ac.rs

Koriščenje nanotehnologije za dobijanje različitih proizvoda u istraživačkim i razvojnim delatnostima je u porastu. Uzimajući u obzir veličinu nanočestica (1-100 nm), njihov različit oblik i veliku površinu kojom mogu delovati, nanočestice ispoljavaju specifične fizičko-hemijske osobine i nalaze veliku primenu kao hemijski senzori, katalizatori, elektronske komponente, farmaceutski proizvodi, u medicinskoj dijagnostici i kao antimikrobni agensi [1,2].

Sinteza metalnih nanočestica tradicionalno se oslanja na dva pristupa, fizički i hemijski. U slučaju fizičkih procesa sinteze nanočestica gotovo uvek je potrebno primeniti visoku temparaturu, pritisak ili dovođenje velike količine energije, dok većina hemikalija koje se koriste u hemijskom načinu sinteze, uključujući reaktante, polazni materijal i rastvarače, može biti toksična i zagađujuća za okolinu i biološke sisteme. Međutim, već duže vreme poznato je da se i mikroorganizmi i biljke mogu iskoristiti za dobijanje metalnih nanočestica. Danas, intenzivno se vrši proučavanje bioloških načina sinteze nanočestica korišćenjem različitih mikroorganizama, algi i biljaka. Korišćenje mikroorganizama u sintezi pokazalo je niz nedostataka, kao što je izbor odgovarajućeg mikroorganizma, vreme i obezbeđivanje aseptičkih uslova za njihovo gajenje i dodatno vreme za sintezu i prečišćavanje dobijenog proizvoda. Međutim, poslednjih godina broj publikovanih rezultata koji govore o sintezi metalnih nanočestica pomoću ekstrakata biljaka naglo raste. Postupak dobijanja nanočestica korišćenjem biljnih ekstrakata podrazumeva redukciju metalnih jona pod dejstvom fitojedinjenja prisutnih u ekstraktu i formiranje nanočestica metala koje su stabilizovane fitojedinjenjima, takođe, prisutnim u ekstraktu. Najveći broj istraživanja postupaka sinteze nanočestica pomoću biljnih ekstrakata se bavi sintezom nanočestica srebra. Pored toga, do sada, publikovani su i rezultati o biološkoj sintezi nanočestica zlata, gvožđa, paladijuma, olova, bakra i drugih elemenata. Fitosinteza nanočestica srebra i zlata pomoću biljnih ekstrakata poslednjih godina je od velikog interesovanja zbog njihove značajne antibakterijske i antikancerogene aktivnosti [2,3].

Podaci govore da skoro svi postupci fitosinteze koriste vodu kao rastvarač, a samo mali broj publikacija govori o metodama kod kojih se koriste aceton, etil-acetat, petrol etar, etanol ili metanol u ovim vrstama sinteza. Metoda sinteze uz pomoć biljnih ekstrakata predstavlja jednostavan postupak koji uključuje mešanje ekstrakta biljke sa vodenim rastvorom soli izabranog metala. Reakcija se odvija, najčešće, na sobnoj temperaturi i traje od nekoliko minuta do nekoliko sati. Osim pomenutih prednosti ovog vida sinteze nanočestica, metode koje se primenjuju su i reproduktivne, a metalne nanočestice, nastale u ovom ekološki prihvatljivom postupku, su veoma stabilne. Rezultati su pokazali da konstituenti biljnih ekstrakata, poput cikličnih peptida, askorbinske kiseline, limunske kiseline, eugenola, elaginske kiseline, elagitanina, galne kiseline, epikatehin galata i teaflavina imaju ključnu ulogu u bioredukciji jona metala i stabilizaciji nanočestica srebra. Pomenuta jedinjenja su identifikovana na površini dobijenih nanočestica pomoću FT-IR spektralnih podataka, međutim, pravi mehanizam po kom ova jedinjenja učestvuju u formiranju nanočestica nije u velikoj meri ispitivan korišćenjem čistih jedinjenja [3].

Protokoli koji se baziraju na primeni biljnih ekstrakata u sintezi metalnih nanočestica u potpunosti ispunjavaju kriterijume zelene sinteze. Priroda rastvarača (vodena sredina) i jednostavna procedura (nema primene visokog pritiska, na niskim temperaturama i nema upotrebe toksičnih hemikalija), kao i redukujući i stabilizirajući agensi (fitojedinjenja) odgovaraju principima zelene hemije. Postupci su pogodni i za dobijanje proizvoda u velikim razmerama, laki su i jednostavni za izvođenje, jeftiniji su, ekološki prihvatljiviji i bezbedniji za terapeutsku upotrebu. Koristeći ovakav pristup zelene hemije, opisani su postupci sinteze različitih metalnih nanočestica uz pomoć oko 200 biljaka iz različitih familija. Uzimajući u obzir sve pomenute prednosti u odnosu na druge metode, ova procedura sinteze metalnih nanočestica u jednom koraku postala je održiva alternativa konvencionalnim fizičkim, hemijskim, čak i mikrobiološkim metodama sinteze. Dosadašnji rezultati upućuju na nove mogućnosti primene biljnih resursa, uključujući i biljni otpad iz prehrambene industrije, što dodatno naglašava ekološku prednost ovog načine zelene sinteze metalnih nanočestica nad tradicionalnim metodama [3,4].

Zahvalnica: Ovaj rad je podržan od strane Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije u okviru projekat broj III43004

Literatura

1. Chung, I.M., Park, I., Seung-Hyun, K., Thiruvengadam, M., Rajakumar, G., *Nanoscale Res. Lett.* 11 (2016) 40-54.
2. Patil, M.P., Kim, G.D., *Appl. Microbiol. Biotechnol.* 101 (2017) 79-92.
3. Rajan, R., Chandran, K., Harper, S.L., Yun, S.I., Kalaichelvan, P.T., *Ind. Crops. Prod.* 70 (2015) 356-373.
4. Makarov, V.V., Love, A.J., Sinitsyna, O.V., Makarova, S.S., Yaminsky, I.V., Taliansky, M.E., Kalinina, N.O., *Acta Naturae* 6 (2014) 35-44.

Challenges hindering the effective removal of arsenic from drinking water

Malcolm Watson[1a], Aleksandra Tubić[1], Jasmina Nikić[1], Jasmina Agbaba[1]

[1]Faculty of Sciences, University of Novi Sad, Novi Sad, Serbia

[a]malcolm.watson@dh.uns.ac.rs

The natural contamination of groundwater sources with arsenic is a widespread problem in many countries around the globe, including Serbia. Due to the toxicity and carcinogenicity of arsenic and its compounds, most countries have adopted the WHO recommendation of a maximum allowable concentration of 10 µg/l for arsenic in drinking water.

Many different processes may be successfully applied to remove As from drinking water, including conventional or advanced coagulation and adsorption on a variety of filter media, such as granular ferric oxides/hydroxides, iron oxide coated sands and iron/manganese binary oxides [1,2]. However, As is never found alone in groundwaters, and other water constituents such as phosphates, natural organic matter (NOM), silicates and sulphates, have been shown to negatively influence the As removal efficacy of these treatment processes, even at otherwise acceptably low concentrations.

Over the last 15 years, our research group has examined the quality of many local groundwaters [3,4]. In laboratory and pilot scale investigations, we have demonstrated that as a result of the complex mixtures of contaminants found in the waters, treatment solutions for arsenic containing drinking waters are often more technologically and economically challenging than expected based on As concentrations alone. This work aims to briefly illustrate some of these challenges, using phosphates and NOM as examples.

Phosphate anions have very similar chemical structures to arsenic oxyanions, and therefore can compete for adsorption sites on the surface of adsorbents. Any adsorbent which is effective at removing As, will therefore also remove phosphate. In a recent pilot scale investigation, groundwater from Srem was investigated which contained inital arsenic and phosphate concentrations of 120 µg/l and 1.4 mg/l, respectively. Due to its non-hazardous nature, this phosphate concentration, more than 12 times higher than the As concentration, already satisfies the drinking water quality criteria for phosphates.

The adsorbent investigated successfully removed arsenic below 0.5 µg/l. However, it also removed phosphate equally effectively, with arsenic and phosphate displaying very similar breakthrough curves. The higher phosphate concentration means that a majority of the adsorption sites were wasted on phosphate removal instead of arsenic removal, decreasing the amount of water which can be effectively treated by a certain amount of filter media, and significantly increasing the final treatment cost.

The effect of NOM on As removal is harder to define, as its complex and varying structure has different functional groups which allow it to interact with As in various ways. NOM has been shown to oxidise As(III) to As(V), form complexes with As, and may compete with As for adsorption on flocc and sorbent surfaces. Figure 1 is from an investigation into how the interactions between As and humic acid (HA, used as a model for NOM) can effect the coagulation process, with the optimal coagulant dose required to maximise As removal depending on both the initial As and HA concentrations [4].

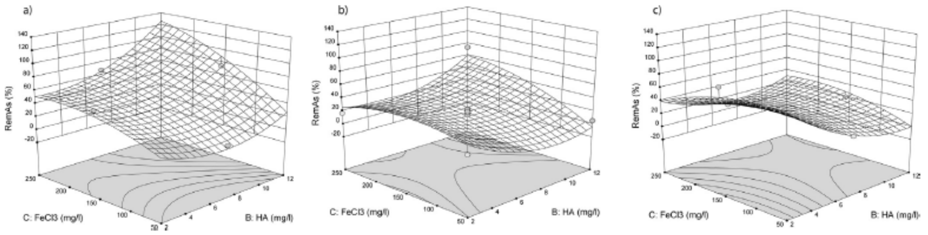


Figure 1: Response surface for As removal, depending on $FeCl_3$ dose and NOM concentration, at initial As concentrations of: a) 20, b) 110 and c) 200 μg/l.

The different response surfaces reflect how interactions between As and NOM change depending on their respective concentrations. At low As concentrations (Fig 1a), As removals were improved with increasing humic acid concentratoins, whereas at higher As concentations (Fig 1c) the opposite was observed.

The presence of other common water constituents in a particular water soruce can therefore have various, yet largely negative impacts on As removal efficacies. The natural variation in water source quality therefore dictates that in-depth laboratory and pilot scale investigations are effectively required to ensure that the chosen technologies will perform as expected under real treatment conditions.

Acknowlegment: This work was financed by the kind support of the Provincial Secretariat for Higher Education and Scientific Research, Republic of Serbia, Autonomous Province of Vojvodina 142-451-2826/2017-01/02.

References

1. Tubić, A., Agbaba, J,. Dalmacija, B., Ivančev-Tumbas, I., *J. Environ Sci Health A.* 45 (2010) 363–369
2. Nikić, J., Agbaba, J., Watson, M., Maletić, S., Molnar Jazić, J., Dalmacija, B., *Water Sci. Technol. Water Supply* DOI: 10.2166/ws.2016.015
3. Tubić, A., Dalmacija, B., Agbaba, J., Ivančev-Tumbas, I., Klašnja, M., Dalmacija M., *Water Sci. Technol.* 61 (2010) 3169-3177
4. Watson, M. A., Tubić, A., Agbaba, J., Nikić, J., Maletić, S., Molnar Jazić, J., Dalmacija, B., *J. Hazard. Mater.* 312 (2016) 150-158.

Exploring new horizons and sustainable technologies for highly efficient wastewater remediation and decontamination: Multifunctional biochar

Maja Turk Sekulić[1a], Tatjana Šolević Knudsen[2], Nikola Bošković[1], Đorđe Vukelić[1], Jasmina Kožar Logar[3], Jelena Radonić[1], Pap Sabolč[1,4]

[1]Faculty of Technical Sciences, Department of Environmental Engineering and Occupational Safety and Health, University of Novi Sad, Novi Sad, Serbia

[2]Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Belgrade, Serbia

[3]Department for low and medium energy physics, Jožef Stefan Institute, Ljubljana, Slovenia

[4]Environmental Research Institute, North Highland College, University of the Highlands and Islands, Thurso, UK

[a]majaturk@uns.ac.rs

The occurrence of different toxic organic and inorganic contaminants in water is an environmental issue that must be addressed to avoid damage to ecosystems and human health. Inspired by this current issue, in this work, we have fabricated multifunctional biochar and activated carbons capable for highly efficient capture, identification and removal of toxic metals, radionuclides, emerging, priority and hazardous priority substances from water samples. To find facile, eco-friendly and cost-effective routes for developing multifunctional materials, which have the capability to resolve many of the challenges associated with wastewater problem, here, we report:

- The novel design and synthesis details of multifunctional biochar and activated carbons which precursors were lignocellulosic raw materials (sweet/sour cherry, apricot and plum kernels) as fruit processing industry waste [1];
- Characterization of multifunctional materials performed by elemental analysis, Scanning Electron Microscopy, Energy-dispersive X-ray Spectroscopy, Fourier Transform Infrared Spectroscopy and Brunauer, Emmett and Taller technique [2];
- Detailed evaluation of their capability for highly efficient separation of heavy metals ions (Pb^{2+}, Cd^{2+}, Ni^{2+}), chlorophenols, pharmaceutical compounds (sulfamethoxazole, carbamazepine, diclofenac, naproxen, ketoprofen and ibuprofen) and radionuclides;
- The batch studies performed by varying different process conditions: the initial pH of the water solution, adsorbent dosage, contact time, temperature and initial adsorbate concentrations;
- The time dependant adsorption results fitted to four diffusion and four reaction kinetic models;

- Equilibrium data fitted to three isotherm models (for better insight into the adsorption process);
- Calculated thermodynamic parameters of the process: Gibbs energy, enthalpy and entropy;
- The best conditions for achieving maximum efficiency of biochar, a carbon-rich low-cost by-product of naturally abundant waste biomass, which exhibits heterogeneous surface chemistry and strong binding affinity via oxygen-containing group on the surface [3];
- Desorption and regeneration study results;
- Two-stage CSTR reactor design for the real samples treatment;
- Eco-design of the multifunctional materials production process [4];
- Life cycle assessment, comparative adsorption study and cost analysis of the process [4].

Performed study showed encouraging results that are highly beneficial for the development of alternative wastewater management technologies, as well as for modern organic waste disposal solution. Fabricated multifunctional biochar and activated carbons were found to be a promising low-cost and eco-friendly solution for the removal of wide range of micropollutants from aqueous waste as part of sustainable technology involving slurry reactors.

Acknowledgement

This study has been financially supported by CEEPUS student exchange program, Training and research in environmental chemistry and toxicology, Slovenia (CIII-SI-0905-04-1718) and Ministry of Education, Science and Technological Development of the Republic of Serbia (III46009 and TR3401).

References

1. Pap, S., Radonić, J., Trifunović, S., Adamović, D., Mihajlović, I., Vojinović Miloradov, M., Turk Sekulić, M. *J. Environ. Manag.* 184 (2016) 297–306.
2. Pap, S., Knudsen, T.Š., Radonić, J., Maletić, S., Igić, S.M., Sekulić, M.T. *J. Clean. Prod.* 162 (2017) 958–972.
3. Turk Sekulic, M., Pap, S., Stojanovic, Z., Boskovic, N., Radonic, J., Solevic Knudsen, T. *Sci. of the Total Environ.* 613–614 (2018) 736–750.
4. Vukelic, Dj., Boskovic, N., Agarski, B., Radonic, J., Budak, I., Pap, S., Turk Sekulic, M. *J. Clean. Prod.* 174 (2018) 1620–1628.

Towards widespread adoption of low cost air quality sensors - a necessity for effective calibration procedures

Miloš Davidović[1a], Dušan Topalović[1,2], Viša Tasić[3], Milena Jovašević-Stojanović[1]

[1]Vinca Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia

[2]School of Electrical Engineering, University of Belgrade, Belgrade, Serbia

[3]Mining and Metallurgy Institute Bor, Bor, Serbia

[a]davidovic@vinca.rs

One of the most important factors for increasing usefulness and relevance of air pollution data on a personal level would certainly be an increase in its spatial resolution. Current state of affairs in air quality monitoring networks at state or local level is such that they typically provide a wealth of high resolution temporal data, but monitoring stations are on the other hand mainly located at a few strategically important places in urban area. This low spatial resolution is a big barrier towards providing personally relevant information to citizens which would then be able to answer questions such as: what is the level of air pollution on routes and places they frequent, what are the associated health risks, and finally what can they do about it and at what cost? Part of the solution to this complex puzzle may be in low-cost air quality sensors (LCS).

LCS's are an emerging technology and are now commercially available for gases, particulate matter and meteorological parameters in a wide variety of designs and capabilities. However, the data sets generated by devices composed of selected LCS are often of questionable data quality. There are some protocols for calibration LCS in laboratory and in the field, but such procedures are extensive and appropriate for testing performance only during sensor development, but are certainly not practically feasible for testing of each commercial LCS [1, 2]. Developing, optimizing, and refining experiments and statistical modelling techniques for LCS-AQ calibration and validation is the mandatory step on the route of obtaining reliable and meaningful data [3, 4]. This work elaborates an important part of LCS deployment – its effective calibration procedure. We will describe our current work on calibration procedures for sensors for gaseous pollutants: ozone and carbon monoxide and sensors for particulate matter. In validation campaigns described in this work we have used combination of quality checks and mid-level validation, together with several statistical modeling approaches in order to observe which sensors have desirable level of performance and to later derive calibration curves or more complex calibration models. Calibration models were based on simple linear regression (LR), multiple linear regression (MLR) and artificial neural networks (ANN).

Mid-level validation of particulate matter low cost sensors was done via collocation with lab-grade instruments in laboratory office space in Institute Vinca and the results were collected for several weeks. Low cost instruments included two Sharp GP2Y1010AU0F compact optical dust sensors connected to Arduino platform (1 channel output), Alphasense CompactOPC sensor (16 channels from 0.38 to 17 μm) and Dylos DC1700 PM unit (2 channels corresponding to "large" and "small" particles). Lab grade instruments included

TSI NanoScan SMPS Model 3910 and TSI Optical particle sizer 3330 (17 channels from 0.3um to 10um). Basic quality check of two Sharp sensors showed that they did not have malfunctions and are surprisingly reliable when used in combination with Arduino platform. Sharp sensors mutually correlate with correlation coefficient cc~0.98. In comparison with lab grade instruments, they correlate best with OPS first channel cc~0.75 and cc steadily declines for channels corresponding to larger particles. Dylos channels best correlate with OPS 0.5-0.721µm for "small" particles with cc~0.60, and with OPS 2.156 µm for "large" particles with cc~0.978. Best performing low cost sensor was certainly Alphasense OPC with cc over 0.90 for corresponding channels. Performed validation steps clearly show to which particulate matter size range individual sensor channels correspond, enabling one to derive meaningful calibration curves.

LCS's for gaseous pollutants were deployed within multi-sensor platform AQMesh. Platforms were collocated with Automatic Monitoring Station Stari Grad belonging to the State Network run by the Serbian Environmental Protection Agency (SEPA), in two 1-month periods in late summer and early autumn 2015. CO and O3 sensors in AQMesh platform passed low level validation (criteria was percentage of collected data), and were considered for development of calibration models. Choice of predictors for MLR and ANN models utilized both statistical reasoning and heuristics to avoid overfitting calibrated sensor with co-varying gas species. Improvements in sensor performance with sophisticated ANN models compared to LR were significant, resulting in relative residuals less than 15% for concentration of pollutant approximately ranging from 175 µg/m^3 to 400 µg/m^3, while for O3 in the range from 40 µg/m^{3}to 120 µg/m^3.

References

1. Spinelle, L., Aleixandre, M. and Gerboles, M. 2013.Report EUR 26112 EN
2. Papapostolou V., Zhang H., Feenstra B.J., Polidori A., Atmospheric Environment, 171, 82-90
3. World Meteorological Organization, 2018., https://www.wmo.int/pages/prog/arep/gaw/documents/Draft_low_cost_sensors.pdf
4. Lewis A., Edwards P., 2016. Nature, 535, 29-31

Today’s cheap coal-derived electricity means future costly environmental pollution

Gordana Medunić[1a]

[1]Faculty of Science, Department of Geology, University of Zagreb, Zagreb, Croatia

[a]gmedunic@geol.pmf.hr

My multidisciplinary research [1-6] has been focused on highly sulphurous (4-6% total S) soil polluted with Croatian superhigh-organic-sulphur (SHOS) Raša coal due to coal mining, utilization, and combustion activities [1]. Large amounts of sulphur, potentially toxic trace metals (V, U, Zn, Cu, Pb, Cd, etc.), metalloids (Se), and organic pollutants (PAHs) were released into an acid-vulnerable, coastal karst environment (Istrian Peninsula, North Adriatic, Croatia). It is also an urban, densely populated touristic region. The principal objectives of the papers published in journals Science of the Total Environment [2] and Environmental Earth Sciences [3] were to determine the distributions of the mentioned pollutants and REEs in soil and SHOS coal. For that purpose, me and my colleagues from various scientific disciplines (biology, chemistry, physics, biochemistry, toxicology, metallurgy, technology) have addressed the problem by applying several analytical approaches to determine toxicity potential of polluted soil for life forms (animals and plants). In other words, we have subjected soil samples to cytotoxic and genotoxic tests [2]. As results have been indicative of statistically significant toxicity potential, our work has warranted further research on this environmental topic. We found decreased REE values away from a coal-fired power plant [3]. Hereby, REEs could be applied as a proxy for the determination of the pollution impact on soil with particles emitted from coal-fired industries. We also found out that selenium is slightly increased in seawater, clover and foliage specimens collected close to unlined coal ash by-products [4]. This indicates Se leaking problem in the study area. Our recent paper [5] reports total Se and other potentially toxic elements (As, Cd, Cu, Cr, Hg, Pb, Sr, U, V, and Zn) in lettuce, potato, and tissues (liver, kidney, heart, and muscle) of three non-migratory bird species (pigeon, jay, and black coot) from a Raša Bay area. Results point at selenium contamination of stream water (up to 78 µg/L total Se in a non-filtered sample), which is well above the Croatian regulatory threshold of 10 µg/L total Se. The stream drains a site of the former coal-separation unit, and an associated bottom sediment contains up to 10.8 mg/kg total Se, which is also above the safe level of 0.60 mg/kg total Se. Moreover, values of Mo, U, V, and Sr, elements commonly elevated in SHOS coal varieties, were also increased in majority of water samples as well as in analysed vegetables, soil, and aquatic sediments. Although Cu, Zn, Pb, and V were slightly increased in liver samples of birds, more in black coot than the other two birds, selenium values were found to be adequate for their normal growth. Our latest paper [6] was focused on chemical and toxicological evaluation of aqueous extracts of soil using Lemna (Lemna minor L.) bioassay and additional biochemical indicators - photosynthetic pigments, lipid peroxidation, antioxidative enzymes and glutathione. Elevated levels of PAHs (up to 15,765 ng/L) and trace metals were detected in extracts compared to control soil. Trace metals accumulated in L. minor were mostly in accordance with their concentrations in extracts. The results showed that extracts induced significant growth inhibition and other phytotoxic effects in L. minor. Those effects can be related to damage caused by increased production of reactive oxygen species and impaired antioxidant levels. The connection among the phytotoxicity, a distribution of analyzed contaminants, and distances from the coal-fired power plant is clearly established.

The lecture will summarize the most important findings of this multidisciplinary comprehensive research, and introduce an audience into future international collaborations aimed at detailed examinations of pollutant cycles in the environment, and applications of clean-up bioremediation strategies.

References

1. Medunić, G., Rađenović, A., Bajramović, M., Švec, M., Tomac, M., *MGPB* 34 (2016a) 27-45.
2. Medunić, G., Ahel, M., Božičević Mihalić, I., Gaurina Srček, V., Kopjar, N., Fiket, Ž., Bituh, T., Mikac, I., *Sci. Total Environ.* 566 (2016b) 306-319.
3. Fiket, Ž., Medunić, G., Kniewald, G., *Environ. Earth Sci.* 75 (2016) 598, doi:10.1007/s12665-016-5410-2.
4. Medunić, G., Kuharić, Ž., Krivohlavek, A., Fiket, Ž., Rađenović, A., Gödel, K., Kampić, Š., Kniewald, G., *Int. J. Oil Gas Coal Technol.* (2017) doi: 10.1504/IJOGCT.2018.10006334.
5. Medunić, G., Kuharić, Ž., Fiket, Ž., Bajramović, M., Singh, A.L., Krivohlavek, A., Kniewald, G., Dujmović, L., *MGPB* 41(3) (2018)
6. Radić, S., Medunić, G., Kuharić, Ž., Roje, V., Maldini, K., Vujčić, V., Krivohlavek, A., *Chemosphere* 199 (2018) 191-200.

How green is biocatalysis?

Jasmina Nikodinovic-Runic[1a], Jelena Radivojevic[1], Lidija Djokic[1], Sanja Jeremic[1]

[1]Institute of Molecular Genetics and Genetic Engineering, University of Belgrade, Belgrade, Serbia

[a]jasmina.nikodinovic@imgge.bg.ac.rs

The emergence and the advancements of green chemistry, that is the development of more environmentally friendly and sustainable chemical products and processes, found their place amongst the most significant developments in the chemical sciences in recent years. Green chemistry evolved around a set of twelve principles (defined by Anastas and Warner in 1998, including avoidance of solvents, the use of ambient reaction conditions, the adoption of atom-efficient chemical reactions and a preference for catalytic rather than stoichiometric transformations, avoidance of waste formation, limitations to resource and energy use and the greater use of renewables) in the belief that, through their application, clean chemical technology will result. Twenty years on, the concern has been raised that many unsubstantiated research data are easily labelled as 'green', citing one of twelve principles, without critical assessment or meaningful comparisons between a new, supposedly 'green', product, process or transformation and an existing equivalent that it is designed to replace [1].

Biocatalysis as the use of enzymes in chemical synthesis comes with economic and environmental advantages so it has impacted chemical synthesis in multiple industries, including food, pharmaceuticals, fine chemicals, polymers, and fuels [2-4]. Biocatalysis is considered to have many advantages in the context of green chemistry covering 10 out of 12 principles (Table 1), and can be produced from cheap and renewable resources [6,7]. However, biocatalysts can be more than merely 'green', and some recently developed enzymes outperform the best chemocatalytic alternatives, even for reactions never before observed in biology [6-8].

Table 1 Green Chemistry and Biocatalysis (adapted from [3])

Green chemistry principle	Biocatalysis
1 Waste prevention	Significantly reduced waste
2 Atom economy	More atom- and step-economical
3 Less hazardous synthesis	Generally low toxicology
5 Safer solvents and auxiliaries	Usually performed in water
6 Energy efficiency	Mild conditions/energy efficient
7 Renewable feedstocks	Enzymes are renewable
8 Reduced derivatizations	Avoids protection/deprotection steps
9 Catalysis	Enzymes are catalysts
11 Real-time analysis	Applicable
12 Inherently safer processes	Mild and safe conditions

While enzymes are highly active at ambient temperature, and thus considered ecologically and economically viable, such a favourable assessment does not always apply, raising concern of ‘How green biocatalysis really is?’ More recently, it has been emphasized that a more comprehensive analysis of the overall biocatalytic process needs to be considered, which includes factors such as enzyme stability under operating conditions, viability of cofactor regeneration systems, downstream processing, and product-extraction procedures, in addition to the price of enzymes and reactors [9].

To assess a given biocatalytic process quantitatively, the Sheldon E-factors can be calculated, which consider the mass of the desired product and the mass of by-products [10]. The result will differ from case to case, but such an analysis is needed early on and will help to define the “greenness” of a given industrial biocatalytic process.

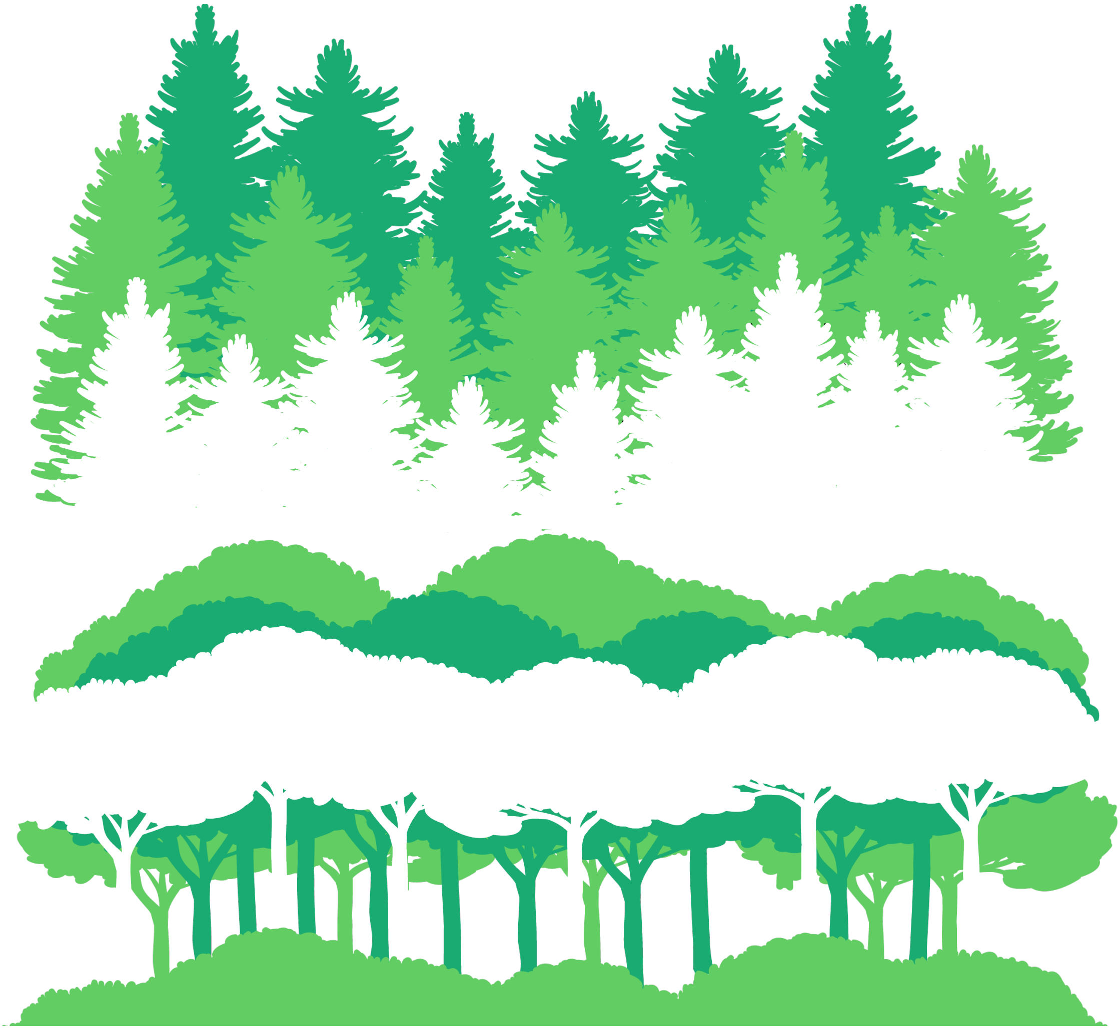
Although we can all agree that seeking cleaner chemical technology is a plausible aim, ‘green’ now has a much wider non-chemical meaning equating to ‘in harmony with the environment’, and chemistry is necessary but not sufficient to reach such a global objective. Moreover, enzymes in organic synthesis are becoming more and more important, but they do have limitations, therefore biocatalysis and chemocatalysis should continue to be complementary approaches in the development of ecologically acceptable products and processes.

References

1. Winterton, N., *Clean Technol. Environ. Policy* 18 (2016) 991-1001.
2. Schoemaker, H.E., Mink, D., Wubbolts, M.G., *Science* 299 (2003) 1694-1697.
3. Sheldon, R. A., Pereira, P. C., *Chem. Soc. Rev.* 46 (2017) 2678-269.
4. Narancic, T., Davis, R., Nikodinovic-Runic, J., O’Connor K.E., 37 (2015) *Biotechnol. Lett*. 943-954.
5. Challener, C., *Pharmaceutical Technol.* 40 (2016) 8.
6. Badenhorst, C.P.S., Bornscheuer, U.T., *Trends Biochem. Sci.* 43 (2018) 180-198.
7. Bornscheuer, U.T., *Philos. Trans. R. Soc. A* 376 (2018) 20170063
8. Hammer S.C., Knight A. M., Arnold F. H., *Curr. Opin. Green Sustain. Chem.*7 (2017) 20-30.
9. Reetz, M.T., *Chem. Rec.* 16 (2016) 2449-2459.
10. Ni, Y., D. Holtmann, D.H., Hollmann, F., *ChemCatChem* 6 (2014) 930-943.

USMENA IZLAGANJA

ORAL PRESENTATION



Značaj ekološkog prava za zaštitu od negativnih tehnogenih uticaja

The importance of the environmental law for the protection of negative technogenic influences

Vladan Joldžić[1a]

[1]Institut za kriminološka i sociološka istraživanja (IKSI), Beograd, Srbija

[a]vladanj@eunet.rs

U modernim državama generalna obaveza ekološko pravne zaštite uspostavljena je ustavima, takođe i u Srbiji [1]. Ali i mogućnost integrisanja elemenata međunarodnog prava u zakonodavstva (čl. 16.) [1]. Služeći se time ugradili smo više desetina konvencija i njihovih aneksa, od značaja za našu temu, u domaće zakonodavstvo [2, 3]. A neke od ”inostranih produkata”, poput onog koji se odnosi na registraciju, evaluaciju, autorizaciju i restrikcije u vezi hemikalija i na bazi legislativnih rezultata EU [4], adaptirajući ih [5]. Takođe razvijamo i originerne elemente zakonodavstva Srbije, poštujući znanja struka. Obzirom na brojnost istih ukazujemo da je logično da se njihovom sagledavanju pristupi kroz svojevrsnu Sistematiku ekološkog prava [6], koja mora da obuhvata grupne objekte prema kojima regulišemo poželjne oblike ponašanja fizičkih i pravnih lica, i to spram: 1. medijumima (vodama, vazduhu, zemljištu) i 2. drugim produktim prirode (npr. rudama, šuma...), te 3. radom stvorenim vrednostima životne sredine. Ukazujemo da uz potrebu za rečenom sistematikom, obzirom na oblasti privređivanja koje iskazuju značajan tehnogeni uticaj na radnu i životnu sredinu, raste i potreba za poznavanjem regulative posmatrane po dotičnim oblastima [7], a naročito: energetici, hemijskoj industriji, rudarenju, metalskoj industriji, elektro industriji, ali i gradnji, poljoprivredi, posebno proizvodnji hrane, te u finalu i postupanju sa materijama na kraju njihovog životnog ciklusa (otpadima). Pristupajući ekološko pravnom sagledavanju svake od ovih oblasti to činimo poštujući, redom: Ustav [1], te zakon o implementaciji tekstova međunarodnog prava [8], potom generalni zakon namenjen zaštiti životne sredine [9], te niz raznovrsnih specijalističkih zakona, kakav je na prvom mestu onaj o hemikalijama [10], praćen drugim, poput zakon o farmaceutskoj produkciji [11], rudarstvu [12], ali i brojnih sub-specijalističkih, kakav je Zakon zakon o sredstvima za zaštitu bilja [13] ili pak onaj o cevnom transportu ugljovodonika [14]. Praktično svi ovi zakoni praćeni su masama podzakonskih akata, najčešće pravilnika [15, 16]. Unutar ovih propisa sve je potrebnije, zato i češće, pozivanje na standarde za raznovrsne procese i proizvode, čime se doprinosi istovremeno njima ali i zaštiti radne i životne sredine.

Literatura

1. Ustav Republike Srbije, *Službeni glasnik Republike Srbije*, br. 83/2006.g., čl.: 74, 87, 97, 99. i 195.
2. Joldžić Vladan (2011): *Ekološko-pravna zaštita kao razvojno promenljiva - teorijsko-praktički pristup*, IKSI, Beograd, str. 105.-139.
3. Joldžić Vladan (2008): *Ekološka politika. Od ideje do izgradnje međunarodnog*

ekološkog prava, IKSI, Beograd, str: 211.-411.

4. Regulation (EC) No 1907/2006 of The European Parliament and of the Council, of 18 December 2006, concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), Official Journal of the European Union, OJ L 396, 30.12.2006.
5. Pravilnik o ograničenjima i zabranama proizvodnje, stavljanja u promet i korišćenja hemikalija koje predstavljaju neprihvatljiv rizik po zdravlje ljudi i životnu sredinu, *Službeni glasnik Republike Srbije*, br. 89/2010, 71/2011, 90/2011 i 56/2012.g.
6. Joldžić Vladan (2010): *Ekološko pravo – Opšti i Poseban deo*. Deo II - O logici konkretizacije i formiranja Sistematike Posebnog dela Ekološkog prava, IKSI, Beograd, str 142.-151.
7. Joldzic Vladan (2007): Ecology Law – General Part, *3.2.1. Development of the Ecology Law Protection and the Possibilities of its Systematization*, publisher: IKSI, Belgrade, pp. 31-46.
8. Zakon o zaključivanju i izvršavanju međunarodnih ugovora, *Službeni glasnik Republike Srbije*, br. 32/2013.g.
9. Zakon o zaštiti životne sredine, *Službeni glasnik Republike Srbije*, br. 135/2004, 36/2009, 36/2009 - dr. zakon, 72/2009 - dr. zakon, 43/2011 - odluka US i 14/2016.g.
10. Zakon o hemikalijama, *Službeni glasnik Republike Srbije*, br.: 36/2009, 88/2010, 92/2011, 93/2012 i 25/2015.g.
11. Zakon o lekovima i medicinskim redstvima, *Službeni glasnik Republike Srbije*, br.: 30/2010 i 107/2012.g.
12. Zakon o rudarstvu i geološkim istraživanjima, *Službeni glasnik Republike Srbije*, br. 101/2015.g.
13. Zakon zakon o sredstvima za zaštitu bilja, *Službeni glasnik Republike Srbije*, br. 41/2009.g.
14. Zakon o cevovodnom transportu gasovitih i tečnih ugljovodonika i distribuciju gasovitih ugljovodonika, *Službeni glasnik Republike Srbije*, br. 104/2009.g.
15. Pravilnik o sadržini i načinu vođenja liste odobrenih supstanci, liste zabranjenih supstanci i liste sredstava za zaštitu bilja, *Službeni glasnik Republike Srbije*, br. 10/2017.
16. Uredba o određivanju aktivnosti čije obavljanje utiče na životnu, *Službeni glasnik Republike Srbije*, br. 109/2009 i 8/2010.g.

Photochemical degradation of textile dye C.I. Reactive Blue 19 in a continuous photoreactor using sulfate radicals

Jelena Mitrović[1a], Miljana Radović[1], Slobodan Najdanović[1], Nena Velinov[1],
Danijela Bojić[1], Aleksandar Bojić[1]

[1] Department of Chemistry, Faculty of Sciences and Mathematics, University of Nis

[a]jelenam81@gmail.com

The textile industry is considered as the most polluting industrial sector due to the quantity and constituents of the produced effluents. Therefore, it is logical to look for an economical and feasible technique for remediation of such hazardous environmental effluents. The amount of generated textile wastewater can reach more than 300 L per kg of product [1].The main adverse effects of dyes in the environment are their inhibitory effect on aquatic photosynthesis, ability to deplete dissolved oxygen and toxicity to the flora, fauna and humans [2]. Also, if the dyes are broken down anaerobically, aromatic amines are generated, which are very toxic, carcinogenic, genotoxic and mutagenic compounds [3].

In this context, sulfate radicals-based advanced oxidation processes (SR-AOPs), one of the in situ chemical oxidation technologies, is a promising method for degradation oforganic pollutants. Additionally, a higher mineralization degree for the oxidation of organic pollutants could be obtained because sulfate radical ($SO_4^{-\bullet}$) is a strong oxidant with a redox potential of 2.5-3.1 V. Generally, peroxydisulfate (PS, $S_2O_8^{2-}$) is the preferred reagent as a source of sulfate radicals in laboratory studies because it is quite cheap, highly stable and easily soluble [4]. Peroxydisulfate can be activated by heat [5], UV light [6], ultrasound [7] and transition metal ions [8] to produce sulfate radicals.

In this study, the photooxidative decolorization of C.I. Reactive Blue 19 (RB19) in a continuous photoreactor was investigated.Peroxydisulfate ($S_2O_8^{2-}$) was used as a source of sulfate radicals, and was activated by UV light. Concentration of textile dye was followed at 592 nm by a UV-Vis spectrophotometer. Peroxydisulfate and UV light showed negligible effect when they were used independently, but with their combination complete removal of RB19 dye was achieved. Removal efficiency of RB19 was sensitive to the operational parameters such as initial concentrations of $S_2O_8^{2-}$, initial RB19 concentration, light intensity, initial pH value and flow rate. The rate of decolorisation was accelerated with increasing in peroxydisulfate concentration and intensity of UV light. Decolorisation is faster at low initial pH values. Increasing in flow rate leads to the decrease of residence timein reactor, which had negative impact on removal efficiency of RB19 dye(Figure 1.).

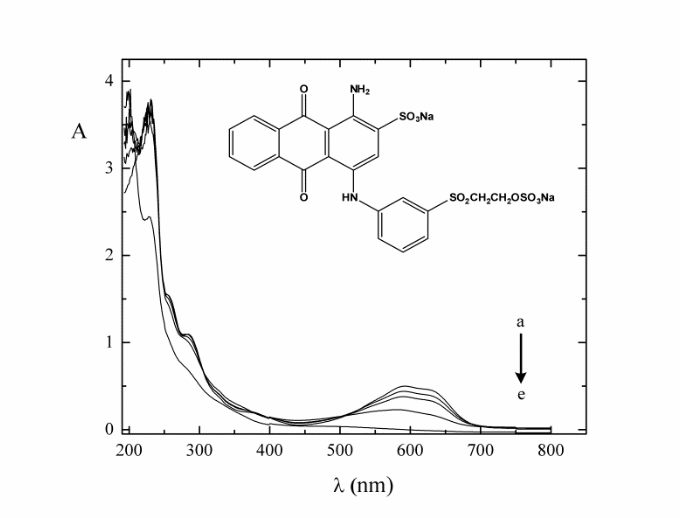


Figure 1. UV/Vis spectral changes of RB19 dye during irradiation: initial RB19 concentration was 50 mg dm^{-3}, initial $S_2O_8^{2-}$ concentration was 0.1 mmol dm^{-3}, flow rate: a) 0 ml min^{-1} (before irradiation), b) 30 ml min^{-1}, c) 15ml min^{-1}, d) 7.5 ml min^{-1}, e) 1.5 ml min^{-1}, native pH, UV light intensity was 1950 μW cm^{-2}, temperature was 25 ± 0.5 º C. Inset represents chemical structure of RB19.

Acknowelgments

This work was financed by the Serbian Ministry of Education, Science and Technological Development through the Grant No TR34008.

References

1. Bilinska L., GmurekM., LedakowiczS., *Process Saf. Environ. Prot.* 109 (2017) 420-428.
2. Navaro P., Gabaldon, J.A., Gomez-Lopez V.M., *Dyes Pigm.*136 (2017) 887-892.
3. Torres-Luna J.R., Ocampo-Perez R., Sanchez-Polo M., Rivera Utrilla J., Velo-Gala I., Bernal-Jacome L.A., *Chem. Eng. J.* 223 (2013) 155-163.
4. Tsitonaki, A., Petri, B., Crimi, M., MosbÆk, H., Siegrist, R.L., Bjerg, P.L., *Crit. Rev. Environ. Sci. Technol.* 40 (2010) 55-91.
5. Fan Y., JiY., KongD., LuJ., ZhouQ., *J. Hazard. Mater.* 300 (2015) 39-47.
6. Sharma J., Mishra I.M. , Kumar V., *J. Environ. Manage.* 156 (2015) 266-275.
7. YinR., GuoW., WangH., DuJ., ZhouX., WuQ.,ZhengH., ChangJ., RenN., *Chem. Eng. J.*335 (2018) 145-153.
8. PanX., YanL., Qu R., WangZ., *Chemosphere* 196 (2018) 95-104.

Elektrohemijska dekolorizacija reaktivnih tekstilnih boja primenom ugljeničnih elektroda visoke poroznosti, dobijenih iz fenol-formaldehidnih smola

Use of high porous carbon electrodes, prepared from phenol-formaldehyde resin in electrochemical decolorisation of reactive textile dye

Viacheslav Avdin[1], Dmitry Zherebtsov[1], Katarina Lelek[2], Goran Roglić[2],
Dragan Manojlović[2a], Kristina Buskina[1],
Chettichipalayam Prabhaharan Sakthi Dharan[1]

[1]South Ural State University, 76, Lenin prospekt, Chelyabinsk, Russia, 454080

[2]Univerzitet u Beogradu – Hemijski fakultet, Studentski trg 12-16, Beograd

[a]manojlo@chem.bg.ac.rs

Procenjena količina proizvedenih tekstilnih boja je preko 7 x 10^5 tona godišnje. Značajne količine sintetičkih boja ispuštaju se u životnu sredinu u vidu industrijskih otpadnih voda. Realna je procena da se javlja gubitak od 1-2 % u proizvodnji i 1-10 % pri upotrebi boja. Za reaktivne boje u tekstilnoj industriji, njihov gubitak može biti oko 4% što predstavlja veoma značajan problem za životnu sredinu[1].

U okviru primene unapređenih oksidacionih procesa, posebna pažnja se posvećuje primeni elekrohemijskih katalitičkih procesa uz korišćenje zelenih reagenasa [2, 3].

U ovome radu ispitana je efikasnost degradacije tekstilne boje Reactive Blue 52 primenom ugljeničnih elektroda dobijenih iz fenol-formaldehidnih smola. Elektrode su pripremljene dodatkom praha fenol-formaldehidne smole (СФПР-054) kao veziva zrncima grafita (ВПГ-4) dimenzija 50-90 µm uz dodatak različitih količina hidratisanog gvožđe(III)-nitrata za dobijanje katalitičkog efekta. Ovako pripremljena smesa je zagrevana u inertnoj atmosferi do 950 ^{o}C brzinom od 90 ^{o}C/sat. Poroznost tako dobijenih elektroda je iznosila između 38 i 40%. Polazna koncentracija boje je 30 mg/L a kao elektrolit korišćen je 0,1 M natrijum-sulfat. U elektrolit je dodat vodonik peroksid tako da je njegova koncentracija bila 1, 3, 5, 7 i 10 mM vodonik-peroksida bez korekcije pH.

Elektrohemijska dekolorizacija primenom anodne polarizacije u podeljenoj ćeliji (Nafion perfluorovana membrane) se pokazala veoma efikasnom. Primenom elektroda koje ne sadrže gvožđe nakon 30 minuta elektrolize pri struji od 30 mA i naponu elektrolize od (4,2 V) postignuta je efikasnost od 69,95% uz dodatak 1 mM vodonik-peroksida dok je pod istim uslovima za elektrodu koja sadrži 1% gvožđa postignuta efikasnost od 95%. Povećanje sadržaja peroksida do 3 mM pokazuje pozitivan uticaj na dekolorizaciju dok dalje povećanje nema proporcionalan efekat ili čak ispoljava i negativno dejstvo na dekolorizaciju.

Ispitani sistem pokazuje osobine elektro-Fenton sistema [4] i stoga smatramo da je primenljiv za degradaciju organskih zagađujuíh supstanci.

Literatura

1. Dojčinović Biljana., Primena reaktora na bazi dielektričnog barijernog pražnjenja za dekolorizaciju reaktivnih tekstilnih boja, Doktorska disertacija, Hemijski Fakultet Beograd (2011).
2. Comninellis, Christos; Chen, Guohua (2010): Electrochemistry for the environment. New York, London: Springer
3. Jović M., Manojlović D., Stanković D., Marković M., Anđelković I., Papan J., Roglić G., *CLEAN - Soil, Air, Water*, 42 (6), (2014), 804–808
4. H.He, Z.Zhou *Crit. Rev. Env.Sci.Tec.*47(21), (2017) 2100-2131

Enhanced phosphorus removal from water by KOH modified crab carapace, oyster and mussel shell

Sabolc Pap[1a], Lisa Shearer[1], Mark A. Taggart[1], Barbara Bremner[1], Stuart W. Gibb[1]

[1]Environmental Research Institute, North Highland College, University of the Highlands and Islands, Castle Street, UK

[a]szabolcs.pap@uhi.ac.uk

The use of phosphorus (P) fertiliser is extensive within modern food production and intensive farming systems. The vast majority of P for the fertiliser industry currently comes from mined rock-phosphate, which is a finite terrestrial resource. Hence, the recovery and re-use of valuable P from waste is now highly desirable. P recovery from wastewater, through the adsorption of P onto natural, solid, waste material may provide one solution. Ideally, this would be a low cost/low energy solution that would create a P-rich material (low in other sorbed contaminants) for use in agriculture as a fertilizer [1].

Crab carapace, oyster and mussel shell, waste by-products from the seafoodindustry, are generated in millions of tons annually. Currently, large quantities of these materials are simply discarded as waste (i.e. to landfill). Therefore, a feasible approach may be to convert these solid wastes into high value-added products.

In this study, calcium-rich biosorbents were modified with potassium hydroxide (KOH) to improvetheir adsorption capacity. The preparation process was divided into two stages:demineralization and activation. In the demineralization, raw materials were soaked with 1 M HCl for 2 h to eliminate mineral salts.The material was then washed with water until the pH of the filtrate approached neutral, and dried at 105 °C. Next, the demineralized material was heated at 600°C for 2 h. The thermally treated material was mixed at a mass ratio of 1:1 with a suitable KOH solution, and the mixture was placed into a crucible. The crucible was heated to 700°C for 1 h. Finally, the product was washed with Milli-Q water (EASYpure® II, 18.2 MΩ) several times and the resultantbiosorbentsdried in oven at 105°C for 2 h.

Thermal activation was found P removal efficiency from 35 to 63% for crab carapace, from 9 to 18% for mussel and from 17 to 42% for oyster shell (no activation vs 600ºC heating only; at 23 mg/L initial P concentration). As shown in Fig. 1, KOH treated biosorbents were also significantly effective for P removal i.e. efficiency was increased from 18to 99% using mussel shell removal.Meanwhile, crab carapace and oyster shell biosorbents removed 97 % and 75 % of P, respectively.

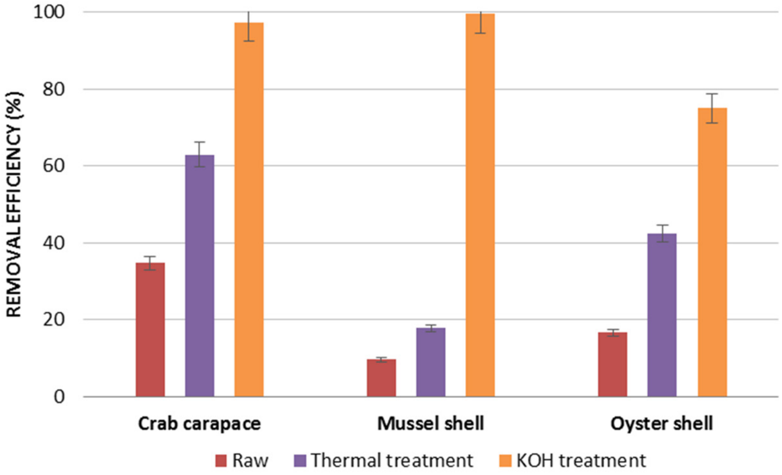


Figure 1: Removal efficiency of phosphorous ontocrab carapace, oyster and mussel shell(initial concentration: 23.64 mg L^{-1}; initial pH: 5.1; agitation time: 120 min; agitation speed: 150 rpm; dose of biosorbent: 10 g L^{-1})

This study explored the potential utilisation of crab carapace, oyster and mussel shell as a low-cost and sustainable material for phosphorus removal.Further experiments will investigatethe potential mechanisms which are involved in the adsorption process.In order to identify the mechanisms involved in the overall removal processand to quantity their respectivecontributions, a detailed physico-chemical characterization of the biosorbentswill be implemented (i.e., utilising TGA, FTIR, BET, SEM-EDX and XPS).

Acknowledgments

This work was undertaken with as part of the ‘Phos4You’ project with financial support from the InterReg Nordwest Europa programme.

References

1. Dai, L., Tan, F., Li, H., Zhu, N., He, M., Zhu, Q., Zhao, J. *J. Environ. Manage.*198(2017) 70-74.

The chemical composition of volatile autolysis products of a potential phytoremediation plant species *Bornmuellera dieckii* Degen (Brassicaceae)

Milica Todorovska[1a], Niko Radulović[1]

[1]Department of Chemistry, Faculty of Sciences and Mathematics, Serbia

[a]mimatod@gmail.com

In recent years, serious contamination of soil by metals has repeatedly been reported [1], therefore the development of new and efficient technologies for removing soil contaminants is an important matter. The environmentally friendly solution to this problem is phytoremediation, a technology for reducing the level of contaminants in the soil by plants. Metal hyperaccumulating plants have recently gained considerable attention in phytoremediation [1]. The ability of Brassicaceae plant taxa, and, more specifically, *Bornmuellera* genus, to bioaccumulate heavy metals has previously been reported [2,3,4]. The genus *Bornmuellera* Hausskn. is one of the smallest in the European flora [5] presented with three species (*B. baldaccii, B. dieckii* and *B. tymphaea*) distributed across the Balkan peninsula. All three species are known to thrive on serpentine soils and are endemic to such regions [5]. Serpentine (ophiolithic, ultramafic) rocks are naturally characterized by calcium deficiency and a high concentration of other metals (iron, magnesium, nickel, cobalt and chromium), and a reduced amount of nutrients [6]. The largest serpentine areas in Europe are located in the Balkan peninsula and are widespread in Serbia [6]. Precisely on this soil type and among obligatory serpentinophyte plant taxa, one should search for potential candidates for phytoremediation.

Having in mind a plethora of evidence suggesting the involvement of sulfur-rich peptides and small proteins in heavy metal tolerance and detoxification of xenobiotics and the extent of cadmium accumulation correlated with the increased levels of glutathione, phytochelatin, thiol, and sulfur compounds [7], we were prompted to perform a detailed chemical analysis of the essential oil and autolyzate of *B. dieckii* and to try to correlated it with the phytoremediation potential of this taxon. The plant material used for the chemical analyses was collected in 2007 during the flowering period of *B. dieckii*. Hydrodistillation of dry plant material yielded a small amount of a foul(cabbage-like)-smelling essential oil (0.01%, w/w). Autolysis experiments were conducted according to a previously reported procedure [8]. GC-MS analyses of the essential oil enabled the identification of more than 100 constituents, among which many components were sulfur-containing, for example 6-(methylthio)hexenenitrile (8.3%), 1-(methylthio)-3-pentanone (0.3%), 3-(methylthio) propanal (0.2%) and 4-(methylthio)-2-butanone (tr.). A GC-MS analysis of the autolyzate, on the other hand, enabled the identification of 42 components, in total, among which the major ones were found to be nonacosane (50.5%), hentriacontane (22.7%), pinoresinol (4.3%), as well as kaempferol (1.17%), 4-hydroxybenzoic acid (0.65%) and other phenolic compounds such as vanillin, vanillic acid, propiovanillon, acetovanillon and coniferyl aldehyde. The isothiocyanates ((5-isothiocyanatopentyl)-(methyl)sulfane and 1-isothiocyanato-5-(methylsulfinyl) pentane), corresponding to the nitriles detected in the essential oil, were also identified in the autolyzate. Knowing that sulfur-containing and phenolic compounds play an important role in metal decontamination, based on the chemical composition of its essential oil and autolyzate, and previously reported data for other species from this genus, one may conclude that there is significant potential for the use of *B. dieckii* in phytoremediation.

Acknowledgments: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172061).

References

1. Salt, D., et al. *Nature.* 13 (1995) 468-474.
2. Palmer, C. E., Warwick, S., Keller, W. *Int. J. Phytoremediation*. 3 (2001) 245-287.
3. Dar, M.I., et al. (2015) Roles of Brassicaceae in Phytoremediation of Metals and Metalloids. In: Ansari A., Gill S., Gill R., Lanza G., Newman L. (eds) Phytoremediation. Springer, Cham
4. Pantola, R. C., Alam, A.. *Int. J. Sci. Res. Environ. Sci.* 2 (2014) 120-138.
5. Marin, P.D., Petković, B., Vajs, V., Tešević, V. *Bocconea* 5 (1997) 563-569.
6. Marin, P.D., Tatić, B. *Bocconea* 13 (2001) 140-150.
7. Cobbett, C., Goldsbrough, P. *Annu. Rev. Plant Biol.* 53 (2002) 159-182.
8. Radulović, N., Dekić, M., Stojanović-Radić, Z. *Food Chem*. 129 (2011) 125-130.

Sorption-desorption hysteresis of atrazine onto organoclays

Anita Leovac Maćerak[1a], Ivana Ivančev-Tumbas[1], Đurđa Kerkez[1], Božo Dalmacija[1]

[1]Department of Chemistry, Biochemistry and Environmental Protection, Faculty of Sciences, University of Novi Sad, Novi Sad, Serbia

[a]anita.leovac@dh.uns.ac.rs

In order to improve the sorption capacity of the clays, they are usually modified with various organic cations, such as quaternary ammonium cations, which can be represented as $[(CH3)_3NR]^+$ or $[(CH3)_2NR_2]^+$ where R is carbon substituent. Insertion of cationic surfactants between layers of clay, changes the surface from very hydrophilic to hydrophobic [1]. In this way, the basal space between the layers increases, resulting in the formation of new sorption sites for sorption of organic substances. Organoclays are used as effective sorbents for removing organic compounds from water and air, as well as sorptive barriers for the remediation of contaminated groundwater and landfills [2].

Sorption of the herbicide depends on the complex interactions of sorbates and sorbents, the geochemical composition of the sorbents, and the conditions under which the sorption occurs.

The aim of this study was to investigate sorption-desorption hysteresis of atrazine onto two organoclays in synthetic water matrix. Atrazine was listed in Water Framework Directive (WFD, 2000) [3] as prirority substance. The organoclays used were tetramethylammonium kaolinite (TMA-K) and tetramethylammonium bentonite (TMA-B) prepared according to Groisman et al., (2004) [4]. Hysteresis indices (*HI*) were calculated for three sorbate equilibrium concentrations (C_e = 0.01, 0.05, 0.5 mg/l). A detailed description of the preparation and analysis of herbicide, organoclays and aqueous matrix, as well as sorption and desorption experiments was published in Leovac Maćerak (2017) [5].

HI values of atrazine for TMA-K were lower (*HI* = 1.93, 1.30, 0.63) compared to TMA-B (*HI* = 3.18, 4.43, 6.88) for C_e = 0.01, 0.05, 0.5 mg/l, respectively. Atrazine was more easily desorbed from TMA-K than TMA-B. Five times higher specific surface area and micropore content of TMA-B compared to TMA-K could be the reason for such sorption-desorption behaviour of atrazine.

Acknowledgement: The research was financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia within the projects OI17208 and III43005.

Literatura

1. Park, Y., Ayoko, G.A., Frost, R.L. *J. Colloid Interface Sci.* (2011) 292-305.
2. Zhu, R., Zhu, J., Ge, F., Yuan, P. *J. Environ. Manage.* (2009) 3212-3216.

3. Council Directive 2000/60/EC, OJ L327/1, 22.12.2000, p. 1-7
4. Groisman, L., Rav-Acha, C., Gerstl, Z., Mingelgrin, U. *Appl. Clay Sci.* (2004) 159-166.
5. Leovac Maćerak, A. (2017). Doktorska disertacija, PMF, Novi Sad.

Fotokatalitička degradacija ibuprofena u akvatičnom matriksu primenom nanokatalitičke smeše ZnO/TiO_2

Photocatalytic degradation of ibuprofen in the aquatic matrix using a nanocatalytic mixture of ZnO / TiO2

Mirjana Vojinović Miloradov[1a], Mladenka Novaković[1], Ivana Mihajlović[1], Goran Štrbac[2], Maja Petrović[1], Dragana Štrbac[1]

[1]Univerzitet u Novom Sadu, Fakultet tehničkih nauka

[2]Univerzitet u Novom Sadu, Prirodno-matematički fakultet

[a]miloradov@uns.ac.rs

Razvojem naprednih analitičkih tehnika, širok spektar sintetičkih, organskih supstanci je detektovan u površinskoj, podzemnoj, komunalnoj otpadnoj i pijaćoj vodi [1]. Usled intezivne upotrebe u humane i veterinarske svrhe, lekovi kao i njihovi metaboliti se kontinuirano unose u vodene matrikse [2]. Jedna od najznačajnijih karakteristika farmaceutiskih komponenata je detekcija u niskim koncentracionim nivoima (mikrogramskim, µg/L ili nanogramskim, ng/L). Dugoročno izlaganje niskim koncentracijama farmaceutskih polutanata, može dovesti do negativnih efekata po prirodne ekosisteme. Iako je veliki broj aktivnih farmaceutiskih komponenata prisutan na tržištu, grupe od najvećeg značaja po ekološki status prirodnih recipijenata predstavljaju: nesteroidni antiiflamatorni lekovi, antibiotici, beta blokatori, lekovi protiv epilepsije i drugi.

Ibuprofen, je komercijalno dostupan farmaceutik iz grupe nesteroidnih antiiflamatornih lekova i koristi se u tretmanu reumatskih bolesti, bolova u mišićima i imflamatornih stanja i povišene temperature. Ibuprofen se izlučuje u vodene siseme u vidu svojih konjugata (hidroksi-ibuprofen, karboksi-ibuprofen). Ekotoksikološki testovi su pokazali da ibuprofen izaziva visoku akutnu toksičnost, kao i da ima negativan uticaj na biodiverzitet.

Kako je mnogobrojnim istraživanjima utvrđeno da farmaceutske rezidue ne podležu procesu biološke degradacije kao sekundarnom tretmanu u postrojenjima za prečišćavanje voda, implementacija unapređenih oksidacionih procesa predstavlja veliki potencijal kao tehnološko rešenje eliminacije ove grupe mikropolutanata. Poluprovodnici na nano nivou se ponašaju kao efikasni katalizatori u destrukciji organskih zagađujućih komponenata. Tradicionalni titanijum dioksid je najčešće proučavan fotokatalizator, ali zbog svojih ograničavajućih karakteristika, neophodna je primena novih, sintetizovanih nanomaterijala.

Proces fotokatalitičke razgradnje ibuprofena ispitivan je primenom novog sintetizovanog nanomaterijala ZnO/TiO_2. Početna koncentracija ibuprofena iznosila je 5,4 mg/L. Kinetika procesa fotokatalitičke razgradnje ispitivana je dodavanjem 40 mg nanomaterijala vodenom rastvoru koji sadrži ibuprofen pod dejstvom UV lampe. Kako bi se ispratila kinetika procesa, odgovarajući alikvoti od 10 mL su izdvojeni u vremenskom intervalu od 5-60 minuta. Uzorci su profiltrirani kroz kvantitativni filter papir, a zatim kroz sirindž filtere prečnika 0,45 µm (Agilent Technologies), kako bi se sprečila zamućenost vodenog rastvora. Profiltrirani uzorci su kvantitativno preneti u vijale i analizirani na na uređaju za tečnu hromatografiju pod visokim pritiskom. HPLC metoda za analizu ibuprofena se sastoji od dve mobilne faze: 50% 0,1% sirćetne kiseline u ultrapure vodi i 50% acetonitrila. Razdvajanje je izokratsko i retenciono vreme ibuprofena je iznosilo 11 minuta (rT= 11 min). Talasna dužina je podešena na 220 nm, a protok na 0,8 mL/min.

Tabela 1. Efikasnost uklanjanja ibuprofena pomoću fotokatalizatora ZnO/TiO_2

Vreme fotokatalitičke degradacije, min	Koncentracija ibuprofena, mg/L	Procenat uklanjanja ibuprofena, %
0	5,47	0,03
5	4,24	22,55
10	2,41	55,90
20	1,63	70,17
30	1,48	72,94
40	1,47	73,08
50	0,68	87,55
60	0,43	92,08

Na osnovu preliminarnih rezultata fotodegradacije emergentnog mikropolutanta ibuprofena, može se zaključiti da novi katalitički nanomaterijal ima potencijal za fotodegradaciju izabranog farmaceutika. Dalja istraživanja biće usmerena na optimizaciju ključnih parametara fotokatalize.

Zahvalnica

Istraživanje je finansijski podržano od strane Pokrajinskog Sekretarijata AP Vojvodine u okviru projekta „Sinteza i primena novih nanostrukturnih materijala za razgradnju organskih polutanata iz procednih voda komunalnih deponija u Vojvodini“, 114-451-1821/2016-03, 142-451-2479/2017-01.

Literatura

1. Vojinović Miloradov M, Španik I, Turk Sekulić M, Radonić J, Vyviurska O, Mihajlović I. 2014.: Occurrence, Physico–Chemical Characteristics and Analytical Determination of Emerging Substances, Faculty of Technical Sciences, Novi Sad.
2. Li, G., Nie, X., Gao, Y., An, T. (2016) Can environmental pharmaceuticals be photocatalytically degraded and completely mineralized in water using g- C_3N_4/TiO_2 under visible light irradiation?-Implications of persistent toxic intermediates. Applied Catalysis B: Environmental, 180, 726–732.

Trace element contamination (Pb, Zn, Cd, As, Ni) of floodplain sediments in a former oremining area in Eastern Belgium

Dubravka Relić[1a], Dragana Milanović[2], Theodoros Potouridis[2], Wilhelm Püttmann[2]

[1]Faculty of Chemistry, University of Belgrade

[2]Institute for Atmospheric and Environmental Sciences, Goethe-University Frankfurt am Main, Germany

[a] dradman@chem.bg.ac.rs

Soil is a natural resource that plays a major role for humans, animals, and plants. Its main functions are for example,the cultivation of fruits and vegetables, the provision of various raw materials, and the removal of pollutants from rainwater during infiltration. Since the beginning of industrialization, soils in many regions have been heavily impacted by various human activities. Among anthropogenic sources also the ore mining and smelting of ores, notably in the 19th and 20th centuries, are considered as further reason for soil pollution. The present study aimed to examine the element contamination of soils and river sediments in a former Pb/Zn ore mining area in Eastern Belgium in the border triangle Belgium-Germany-Netherlands [1]. Ore mining and smelting was stopped in the area in the year 1922. At two selected flood plain locations in the study area, sediment profiles were analysed for the following heavy and semi-metals: Pb, Zn, Cd, Ni, and As. Furthermore, the focus was to reconstruct the history of deposition of these metals.The element amounts of the respective samples and their mobility and bioavailability were estimated applying two extraction methods. Samples were digested with *aqua regia*, while elements leaching into acetic acid were considered. The solutions obtained from both sample preparations were analysed by ICP-MS.

Two soil profiles were examined within the two main production centers in this area, Kelmis and Bleiberg. Profile 1 with 28 cm length was taken in Kelmis within the flood zone of the Hohnbach River. This sampling location lies 1 km away from the former ore processing plants and close to the former mining area. This profile was devided into 8 sub-sections. The Profile 2 with 24 cm length was dug on a meadow in the wind direction from the slag deposit and former Bleiberg production facilities and divided into 7 sub-sections. The obtained results showed that Zn was the predominating element in all samples of Profile 1.The amounts ranged from 1.3 to 2.1 g/kg, while Pb ranged from 0.5 to 0.8 g/kg. Significantly lower amounts were measured for Cd (2.9–5.6 mg/kg), As (1.5–43.4 mg/kg), and Ni (17.9–33.9 mg/kg) [1]. Based on the PCA (Principal component analysis) of *aqua regia* extracted elements in Profile 1, the highest concentrations of Zn, As, and Pb were detected in a depth of 20 cm, while the highest concentration of organic matter (Corg), water, and Cd were determined in the surface and subsurface samples in 0 and 4 cm depth, respectively (Fig. 1a). These parameters showed a significant decrease from the profile surface to the tread depth. On the other hand, with increasing depth, the pH value increased from 5.3 to 5.6,and Ni is the element that follows the pH gradient. With respect to the mobility of elements from Profile 1, the highest As amount was detected in the surface soil sample, while Pb and pH values increased with depth (Fig. 1b). The mobile fractions of Cd and Ni showed an increase from the soil surface to a depth of 20 cm, especially from

8 to 20 cm. Zn showed the highest mobility in surface samples and in the samples from 8 cm to 20 cm depth. The increasing extent of mining and smelting in Kelmis is reflected in the continuous increase in metal concentration from the bottom of the profile to the depth of 20 cm.

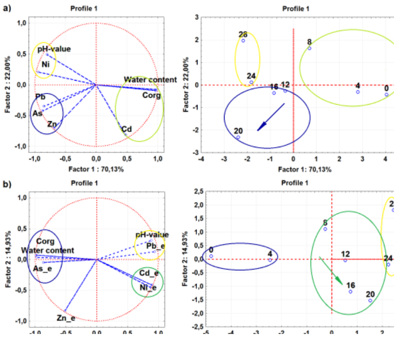


Figure 1. PCA (R and Q mode) of samples from Profile 1: a) factor scores of *aqua regia* element content and b) factor scores of acid-soluble element fractions

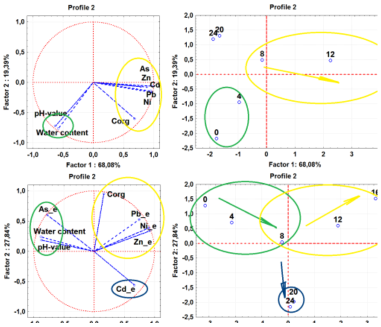


Figure 2. PCA (R and Q mode) of samples from Profile 2: a) factor scores of *aqua regia* element content and b) factor scores of acid-soluble element fractions

Samples of Profile 2 differ from samples of Profile 1 with respect to the organic matter content and pH values.The highest pH value and water contents were determined in the upper part of the profile (Fig. 2a). All metals and Corg showed an increase in concentrations from the soil surface down to a depth of 16 cm depth which could represent the heyday of mining in the village of Bleiberg. Corgshows a very similar trend with the analysed metals. Therefore, it can be assumed that the concentration of Corg in the soil was also influenced by the mining industry. According to Dejonghe, et al.[2], since 1859, large amounts of coal have been used to run pumps that pumped water out of the Bleiberger pits.The most abundant heavy metals were Pb and Zn with concentrations ranging from 0.1 to 13.7 g/kg for Pb and from 1.9 to 29.1 g/kg for Zn. Significantly lower values were measured for Cd (4–73.6 mg/kg), As (9.7–363 mg/kg) and Ni (15.1–50.8 mg/kg). Similarities in element behaviour (Fig.2a) suggest a common source of contamination and in this case, the cause can be seen in the nearby smelter. Similar to Profile 1, acid-soluble As showed the highest concentration in surface samples,which decreased continuously with depth (Fig. 2b). For both profiles, the higher As concentrations of the mobile fractions might be attributed to atmospheric deposition and its enrichment in surface samples. Furthermore, for mobile fractions of Pb, Ni, and Zn, and quantity of Corg,an increase was observed from the surface to a depth of 16 cm, while Cd was the only element with the most mobile quantity at the lower most sample of profile 2, at 24 cm depth.

Conclusively, the contents of Pb, Zn, Cd, and As found in the floodplain soils were very high in the study area. The highest contamination of the area occurred during the heyday of mining through ore transport, processing, and smelting, but after the shutdown of the mining and smelting activities the floodplain sediments were further contaminated by material mobilized from dumps of slag and other residual materials.

References

1. Milanović D, Master thesis (2017) at Johann Wolfgang Goethe-Universität, Frankfurt am Main.
2. Dejonghe, L., Ladeuze, F., & Jans, D. (1993). *Memories pour servir a l'Explication des cartes Geologiques et Minieres de la Belgique, 33*, 1-483.

Determination of fipronil and its metabolites in chicken eggs and egg products using gas chromatography-mass spectrometry

Aleksandra Tasić[1a], Ksenija Nesić[1], Ljubiša Ignjatović[2], Nebojša Vuković[3]

[1]Institut of Veterinary Medicine of Serbia, Belgrade, Serbia

[2]Faculty of Physical Chemistry, University of Belgrade, Belgrade, Serbia

[3]City Institute for Public Health Belgrade, Belgrade, Serbia

[a]alekstasic79@gmail.com

The scandal that broke in Europe in July 2017, when millions of eggs were withdrawn for the shelves of stores across Germany and the Netherlands due to high levels of the pesticide fipronil, has proved the need for improving and validating methods for its accurate and precise determination. Fipronil is a broad-spectrum insecticide that belongs to the phenylpyrazole chemical family. Fipronil is used as an active substance in veterinary products against flees and ticks in dogs and cats. Its two major metabolites are fipronil sulfone and fipronil desulfinyl [1,2]. A GC-MS analysis was carried out using a GC Clarus 680 PerkinElmer system comprising an autosampler and a gas chromatograph interfaced with an MS Clarus SQ8T instrument under the following conditions: capillary column Elite-5MS (30 x 0.25 mm ID x 0.25 µm df, composed of 95% dimethyl polysiloxane and 5% Phenyl), operating in the electron impact mode at 70eV. Helium (99.999%) was used as the carrier gas at the constant pressure of 22.5 psi and an injection volume of 2 µL was employed at the injector temperature of 250 ºC; the temperature of the ion-source was 280 ºC. Mass spectra were taken at 70eV; a scan interval of 0.2 seconds and fragments from 50 to 400 Da. The oven temperature program was initially set at 70 °C for 3 minutes and then ramped up to 150 °C at 25 °C/min , then to 200 °C at 3 °C/min, and finally to 280 °C at 8 °C/min for 10 min. Total GC running time was 41.87 min. The software was adapted to handle mass spectra and the chromatograms were Turbo Mass Ver 6.1.0. Stock standard solutions (10 µg ml^{-1}) composed of fipronil desulfinyl, fipronil and fipronil sulfone were supplied by Dr. Ehrenstorfer (Germany). Working solutions were obtained by appropriate dilutions with ethyl acetate. Matrix-matched solutions were also prepared by serially diluting the intermediate solution with blank eggs and eggs products sample extracts containing none of the tested analytes to perform matrix-matched calibration with the same concentrations as in the solvent.

Fipronil residues were extracted using the modified QuEChERS technique with acetonitrile and then purified using the dispersive solid phase extraction (d-SPE) cleanup. For the eggs, 5 g of sample, 5 ml of water, 10 mL of acetonitrile, 1.6 g of $MgSO_4$, and 0.4 g of NaCl were used in the liquid-liquid partition, while 80 mg of C18, 80 mg of primary and secondary amine and 150 mg of $MgSO_4$ were employed in the dispersive solid-phase extraction. Final extracts of acetonitrile were concentrated using a gentle stream of nitrogen and reconstituted into ethyl acetate. To achieve the best possible extraction results, extracts were re-purified using the C18 column before the analysis. Final extracts were evaluated by fast GC-MS analysis using the SIR (selected ion recording) mode with ion ratios for confirmation. Under the optimized conditions, the method was validated according to linearity, recovery, and precision.

The retention times of fipronil desulfinyl, fipronil and fipronil sulfone were 16.76, 21.28 and 24.40 min, respectively. Lindane was used as an internal standard and its retention time was 13.33 min. The linearity of the analytical response across the studied range of concentrations (0.005 – 0.040 mg kg^{-1}) was excellent, obtaining correlation coefficients higher than 0.99 (Table 1). The average recoveries of the pesticides from all matrices ranged from 86 to 104%, for fortification levels of 0.01, 0.02 and 0.040 mg kg^{-1}. The precision values, expressed as RSD values, were less than 10% for the pesticide in all matrixes. Matrix components, such as proteins and lipids, can induce ion suppression or enhancement effects. Thus, matrix effects were calculated to avoid any inaccurate quantifications of the analytes in different samples. The matrix effects, LOD and LOQ of this method are also outlined in Table 1.

Table 1. Linear regression parameters of the calibration curve

Compound	Regression equation	R^2	LOD (µg/kg)	LOQ (µg/kg)	Matrix effect, %
Fipronil desulfinyl	y=0.467132x + 0.402220	0.99983	1.2	4	- 98.2
Fipronil	y=0.482711x + 0.153820	0.99974	0.9	3	- 98.7
Fipronil sulfone	y=0.449708x - 0.003798	0.99859	0.9	3	- 98.5

Finally, the proposed method was successfully applied to monitoring fipronil and its metabolites in real samples, specifically egg products imported from EU member states and used further in the process of manufacturing products for our market. Good linearities were obtained and the quantification confirmed a minor matrix effect. Successful application of this method is relevant to monitoring the impact of fipronil contamination on the environment, primarily through monitoring the presence of fipronil in food, which will provide better insights into the present situation of the environment. This method, with certain modifications, may be employed in the future to test matrices such as soil and water.

References

1. Simon-Delso, N. *et al*, *Environ Sci Pollut Res* 22 (2015) 5-34.
2. Zheng, W. *et al*, *J. Chromatogr. B* 1072 (2018) 60-69.

Primeri uticaja različitih strategija upravljanja otpadom na emisije gasova sa efektom staklene bašte u Republici Srbiji

Estimation of several municipal solid waste strategies on greenhouse gas emissions in Republic of Serbia

Marina Mihajlović[1a], Mića Jovanović[2]

[1]Inovacioni centar Tehnološko-metalurškog fakulteta, Beograd, Srbija

[2]Tehnološko-metalurški fakultet, Univerzitet u Beogradu, Beograd, Srbija

[a]msavic@tmf.bg.ac.rs

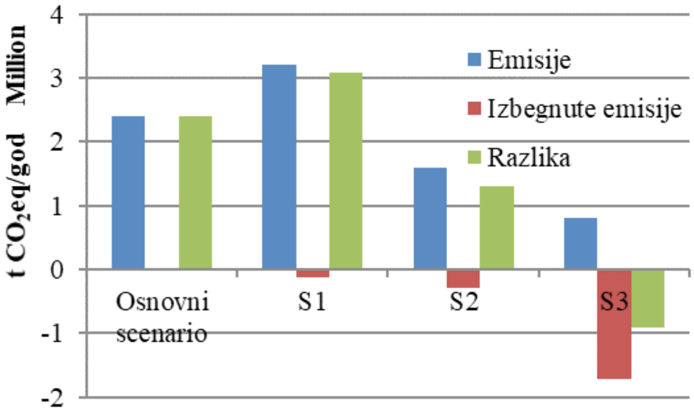
U hijararhiji upravljanja otpadom deponovanje je najmanje poželjna opcija. Istovremeno, ocenjuje se da se u zemljama u razvoju više od 90 % otpada odlaže na deponije. U sklopu procesa pristupanja Evropskoj uniji, Srbija je transponovala evropsku regulativu u oblasti upravljanja otpadom, pre svega kroz Uredbu o odlaganju otpada na deponije [1]. U Srbiji se godišnje generiše oko 2.374.374 tona otpada, a samo oko 60% obuhaćeno je organizovanim prikupljanjem i odlaganjem [2,3]. Podaci o recikliranim količinama otpada variraju od 1-10%, te se može oceniti da je ono zanemarljivo. Strategija upravljanja otpadom [2] postavila je kao jedan od dugoročnih ciljeva (2015-2019) povećanje količina ponovno iskorišćenog i reciklovanog ambalažnog otpada (staklo, papir, karton,metal i plastika) na 25%.

Deponovanje otpada je od posebnog značaja za GHG emisije budući da se deponijski gas uglavnom sastoji od oko 50 % metana i 50 % ugljen-dioksida. Metan je od posebnog značaja jer je njegov potencijal globalnog zagrevanja 21 put veći u odnosu na ugljen dioksid [4]. Važno je istaći da plitke deponije, dubine manje od 5 metara, usled aerobnih uslova, ne generišu metan odnosno, udeo metana u deponijskom gasu je veoma mali [5].

U ovom radu analizirani su efekti nekoliko scenarija u upravljanju otpadom u Republici Srbiji na emisije gasova sa efektom staklene bašte, u daljem tekstu GHG (*engl. Greenhouse Gas Effect*). Analiza je sprovedena upotrebom softvera ”*Tool for Calculating Greenhouse Gases (GHG) in Solid Waste Management (SWM-GHG calculator)*” koji je razvio nemački IFEU (*ger. Institut für Energie- und Umweltforschung Heidelberg*).

Analiza je obuhvatila četiri scenarija: bazni i tri scenarija unapređenog upravljanja otpadom. Parametri baznog scenarija odgovaraju trenutnom stanju u Republici Srbiji. U unapređenim scenarijima, označenim brojevima 1-3 varirani su parametri udela organizovanog prikupljanja i odlaganja otpada, udeo reciklaže, kao i tehnologije tretmana otpada.

Prosečan sastav otpada preuzet je iz odgovarajuće publikacije [6]. Scenario 1 odgovara trenutno prisutnim trendovima koje karakteriše samo povećanje obuhvata organizovanog prikupljanja, bez prikupljanja ili tretmana deponijskog gasa i neznatnog povećanja udela reciklaže. Scenario 2 opisuje osnovne ciljeve definisane Strategijom [2]. Scenario 3 opisuje savremeni sistem upravljanja otpadom, sa značajnim udelom reciklaže i dobijanja električne energije iz spaljivanja deponijskog gasa. Rezultati su prikazani na slici 1.



Slika 1. Procena GHG emisija

Rezultati pokazuju da će se GHG emisije zapravo povećati ukoliko promene u sektoru upravljanja otpadom ne budu sveobuhvatne. Ukoliko se sprovede samo jednostavni prelazak sa smetlišta na regionalne deponije, bez primene mera koje uključuju spaljivanje deponijskog gasa, može se očekivati porast GHG emisija za oko 700.000 $tCO_{2\ eq}$/god, odnosno za 28%.

Literatura

1. Uredba o odlaganju otpada na deponije (Sl. glasnik RS, br. 92/2010).
2. Vlada RS, Strategija upravljanja otpadom za period 2010-2019. godine, (Sl. glasnik RS br. 29/10).
3. Miltojević, V., Ilić Krstić, I,, Petković, A. *Int J Environ Sci Technol* 14 (2017) 1853-1864.
4. www.unfccc.int/ghg_data/items/3825.php
5. Abushammala, MFM., Basri, NEA., Kadhum, AAH., Basri, H., El-Shafie, AH., Sharifah Masturaet, SA. *Int J Environ Sci Technol* 11(2014) 377-384.
6. Waste statistics and waste management in the Republic of Serbia, 2008-2010, Ćeranić, M., Dostanić, D., Dimić, G., Vignjević, A., Kržalić, Ćosić, Z. Statistical Office of the Republic of Serbia, Belgrade, http://pod2.stat.gov.rs/ObjavljenePublikacije/G2012/pdfE/G20126012.pdf

Assessment of potentially toxic elements bioavailability in the soil-plant-air system in different vineyard ambients in Serbia: biomonitoring, environmental and health risk implications

Tijana Milićević[1a], Mira Aničić Urošević[1], Dubravka Relić[2],Sandra Škrivanj[2], Gordana Vuković[1], Aleksandar Popović[2]

[1]Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia,

[2]University of Belgrade, Faculty of Chemistry, Studentskitrg 12-16, 11000 Belgrade, Serbia

[a]tijana.milicevic@ipb.ac.rs

Monitoring of potentially toxic elements (PTEs) in agricultural soil represents the first measure of caution regarding food safety while research into element bioavailability should be a step forward in understanding the element transportation chain. Five experiments were performed in the different grapevine growing areas in Serbia (experimental, commercial, and organic vineyard) for investigating element bioavailability accompanied by an assessment of the ecological implications and human health risk and the plant materials (leaves and mosses) were tested as potential air biomonitors.The element (Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Ca, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sb, Sr, V, Zn) and some rare earth element (Ce, Dy, Er, Eu, Ga, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, Y, Yb) concentrations were measured in the soil and plant samples by inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS). In addition, the single extraction procedures (CH_3COOH, Na_2EDTA, $CaCl_2$, NH_4NO_3, deionised H_2O), and pseudo-total digestion were applied to determine the elements mobility and bioavailability from the soil[1,2].

The first experiment.The study was conducted in the experimental vineyard ambient during 2013/2014. The extraction with deionised H_2O during 16 h was tested for the first time as an alternative to commonly used extraction procedure [1]. Similarities between the plant parts and the plant species were identified. Applying ecological risk assessment formulas, the most polluted parcel in the experimental vineyard was determined. In addition, the leaves of some grapevine species showed abilityto accumulate some PTEs from the soil. ***The second experiment.*** An integrated approach to the investigation of PTEs was applied to the soil and leaves collected from the commercial vineyard through the entire grapevine season. To assess atmospheric particle deposition, the saturation isothermal remanent magnetisation measurement (SIRM) of the leaf samples was performed. Notable environmental implications of the soil samples were estimated for As, B, Cd, Co, Cr, Cu, Mn, Ni, Sr. The most bioavailable PTEs from soil to leaves were Mn, Ni, Sr, followed by Cr, Cu, while Cd, Co were strongly-bonded in the soil. According to the correlations between biogeochemical index (BGI) and biological accumulation coefficient (BAC), Cu and Na mostly bioaccumulated in the leaves from the soil, while bioaccumulation of B, Cd, Sb, Sr was influenced by the other atmospheric sources. The significant correlations between the element concentrations and SIRM values in leaves and in parallel with the concentrations in the moss bags[3] imply that the leaves (*Cabernet sauvignon* and *Sauvignon blanc*) indicate Co, Cr, Ni air pollution in the vineyard ambient. ***The third experiment.*** During the vineyard season 2015,the moss (*Sphagnum girgensohnii*and*Hypnum cupressiforme*) bags were exposed along transects in the commercial vineyard parcels to investigate an appropriate period of the element enrichment in the mosses[3]. The elements were significantly enrichedin the moss bags during 2-month exposure, and the enrichment gradually increasedup to 6-months. The 6-month exposure could be recommended for comparative studies among different vineyards because it reflects the airpollution during the entire grapevine season. Both species reflected the spatio-temporal changes of element concentration in the vineyard. Finally, both the moss bags and the topsoil analyses suggested that vineyard represents a dominant diffuse pollution source of As, Cr, Cu, Ni, Fe, V. ***The fourth experiment.***This study was conducted for investigating element bioavailability in the soil–grapevine system accompanied by an assessment of the ecological implications and human health risk. The most suitable extractants for assessing the element bioavailability were $CaCl_2$, NH_4NO_3, Na_2EDTA, but deionised H_2O could be suitable, as well [1]. The most bioavailable element in the soil–grapevine system was Ba. Contamination factor implied a moderate soil contamination ($1<CF<3$). According to BAC, the grape seeds and leaves mostly accumulated Cu and Zn from the soil, respectively. The influence of atmospheric deposition on the air-exposed grapevine parts (leaves and grape skin) was observed ($RF>1$). Nevertheless, low adverse health risk effects ($HI<1$; $R\leq1\times10^{-6}$) were estimated for farmers and grape/wine consumers. ***The fifth experiment.*** During 2016/2017 the experiment was conducted in the organic vineyard. The environmental implications of the soil showed not high soil contamination. The grapes grown in the organic vineyard (*Panonia and Regent*) were safe for the consumption; non-carcinogenic or carcinogenic risks were not assessed. The concentrations of PTEs in the organic grapevines were lower than in the previous studied experimental and commercial vineyards [1,2]. There was an indication that only airborne Al, Cr, Cu, Ni, Pb deposition have an influence to the outer parts of grapevine (leaf and grape skin) ($RF>1$). The moss bag biomonitor implies lower element accumulations in the exposed mosses in the organic than in the commercial vineyard [3].

References

1. Milićević, T., Relić, D., Škrivanj, S., Tešić, Ž., Popović, A., *Chemosphere*. 171 (2017a)284–293.
2. Milićević, T., AničićUrošević, M., Relić, D., Vuković, G., Škrivanj, S., Popović, A., *Sci. Total Environ.*626 (2018) 528–545.
3. Milićević, T., AničićUrošević, M., Vuković, G., Škrivanj, S., Relić, D., Frontasyeva, M.V., Popović, A., *Ecotoxicol. Environ. Saf.* 144 (2017b) 208−215.

Ispitivanje potencijala celuloze kao univerzalnog matriksa za analizu metala u biljkama pomoću WD-XRF

Investigation of the potential of cellulose as a universal matrix for metal analysis in plants by WD-XRF

Jovana Orlić[1a], Marija Krstić[2], Teodora Krsmanović[2], Konstantin Ilijević[2], Ivan Gržetić[2]

[1]Univerzitet u Beogradu, Inovacioni centar Hemijskog fakulteta

[2]Univerzitet u Beogradu, Hemijski fakultet.

[a] jovanaorlic@chem.bg.ac.rs

Biljke su, zbog svog visokog potencijala za usvajanje i akumulaciju metala, kao i zbog svakodnevne upotrebe od strane čoveka, često analizirana vrsta uzoraka. Dosadašnje spektrometrijske tehnike koje su u rutinskoj upotrebi zahtevaju vreme koje je neophodno za pripremu uzoraka, kao i materijalne resurse koji podrazumevaju: primenu agresivnih metoda digestije, korozivne i toksične hemikalije, što nije u saglasnosti sa principima zelene hemije. Kada je direktna analiza čvrstih uzoraka u pitanju, XRF je jedna od vodećih tehnika, stoga se postavlja pitanje može li se koristiti i za analizu biljnih matriksa.

Biljni matriks može imati raznolik sadržaj elemenata sa širokim koncentracionim opsegom. Prilikom kalibracije XRF uređaja, neophodno je ispuniti zahtev da matriks standarda koji se koriste za kalibraciju bude istovetan matriksu uzoraka koji se analizira. Često je teško naći dovoljan broj standarda koji će sadržati željene elemente u odgovarajućim koncentracijama. Poznato je da celuloza ima matriks sličan matriksu biljaka i ta osobina je čini potencijalnim univerzalnim matriksom [1]. Dodavanjem tečnih standardnih rastvora elemenata u čistu celulozu bilo bi moguće uticati na odabir elemenata koje želimo određivati, kao i na njihov koncentracioni opseg .Tečni standardni rastvor koji je ovom prilikom korišćen za pripremu sintetičkih celuloznih standarda je sadržao 20 elemenata: Na, Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, Ag, Cd, In, Tl, Pb i Bi.

Biljni uzorci, kao i celulozni sintetički standardi se za XRF analizu pripremaju presovanjem praškastog uzorka u čvrste pelete. Na osnovu različitih načina pripreme uzoraka, kreirane su tri metode. Prva metoda je kreirana pomoću sintetičkih standarda načinjenih od čiste celuloze sa standardnim dodatkom analiziranih elemenata (C). Čista celuloza prilikom presovanja daje stabilne pelete, ali je tokom pripreme biljnih uzoraka potreban dodatak voska kao vezivnog sredstva, jer to vodi ka dobijanju peleta koji su stabilni i u uslovima visokog vakuuma koji vladaju unutar uređaja tokom analize. Iz tog razloga je druga metoda kreirana pomoću peleta od celuloze sa dodatkom 20 % voska (CV). Kada količina uzorka nije dovoljna za pripremanje regularnog peleta, moguće je napraviti pelet sa uzorkom u tankom sloju koji se nanosi na nosač borne kiseline. Treća metoda je kreirana pomoću standarda od celuloze nanete na nosač borne kiseline u tankom sloju (TS).

Performanse kreiranih metoda ispitane su karakterizacijom analitičkih parametara. Osetljivost svih metoda je visoka, posebno za elemente četvrte periode. Kreirane metode su pokazale linearnost u prilično širokom opsegu koji je ovom prilikom testiran (od 0 do 500 ppm). Limiti detekcije i kvantifikacije sve tri metode su zadovoljavajuće niskih vrednosti za gotovo sve elemente, osim za pojedine lake elemente (Na, Mg). Međutim, koncentracija lakih elemenata u biljnim uzorcima je obično visoka, stoga su nešto više vrednosti detekcionih i kvanitifikacionih limita i dalje na zadovoljavajućem nivou.

Kao najlakši određivan element, Na pokazuje zadovoljavajuću tačnost tek pri koncentracijama većim od 100 ppm, ali se tačnost drastično povećava sa povećanjem atomskog broja. Prelazni metali četvrte periode pokazuju najveću tačnost pri određivanju i jako niskih koncentracija. Tačnost određivanja je dodatno proverena i potvrđena analizom sertifikovanih referentnih materijala (NIST SRM 1573a Tomato leaves i NIST SRM 1575a Pine needles).

Sintetički celulozni standardi su naknadno digestovani i analizirani na ICP-OES (Indukovano spregnuta plazma sa optičkom emisionom spektrometrijom) uređaju. Koeficijenti korelacije očekivanih i izmerenih koncentracija elemenata u sintetičkim celuloznim standardima pokazali su jako visoke vrednosti, i na taj način je potvrđeno da su vrednosti koncentracija elemenata sintetičkih standarda pouzdane.

Može se zaključiti da se celuloza sa dodatkom tečnog standarda može pouzdano koristiti za pripremu sintetičkih standarda za kalibraciju WD-XRF uređaja za određivanje metala u biljnim uzorcima. Priprema uzoraka je jednostavna i ne zahteva upotrebu agresivnih i potencijalno toksičnih hemikalija. Metoda je dovoljno precizna i tačna, brza i jednostavna. Takođe, moguća je analiza velikog broja elemenata u širokom analitičkom opsegu koncentracija.

Literatura

1. Evans, C.C., Analyst, 1970. 95 (1136): p. 919-929.
2. Marguí, E., Hidalgo M., Queralt I.*,Spectrochimica Acta Part B: AtomicSpectroscopy*, 2005. 60 (9–10): p. 1363-1372.
3. Reidinger, S., Ramsey M.H., Hartley S.E., *New Phytol*., 2012. 195 (3): p. 699-706.

The influence of seawater physicochemical parameters on the content of trace elements in mussels and surface sediment

Slavka Stanković[1a], Ana Perosević[2], Nikola Petrović[1], Milica Ivković[1], Marija Kojić[3], Milena Radomirović[1], Antonije Onjia[1]

[1]Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia

[2]BIO-ICT Centre of Excellence, University of Montenegro, Podgorica, Montenegro

[3]Institute for Technology of Nuclear and Other Mineral Raw Materials, University of Belgrade, Belgrade, Serbia

[a]slavka@tmf.bg.ac.rs

The concentrations of Al, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Sr, Zn, and Hg were studied in surface sediment and the mussel *Mytilus galloprovincialis* collected from the coastal area of Montenegro, in Boka Kotorska Bay at three locations during four seasons, in the year 2014-2015. The study investigated the impacts of seawater temperature, salinity, dissolved oxygen, and total organic carbon (TOC) on the metal contents in the surface sediment and mussels.

The influence of seawater physicochemical parameters on the content of toxic metals in mussels and surface sediment from three locations in four different seasons was analysed by Pearson correlation coefficient (*r*), principal component analysis (PCA) and cluster analysis (CA). Both PCA and CA were used to discriminate groups of samples according to a similarity of chemical composition.

It is well-known that concentrations of trace elements in sediments are much higher than those in the overlying water (1), and sediments reflect the prevailing quality of marine ecosystems (2). However, metal concentrations in sediments may not represent the biologically available fraction and considering that, living organisms are increasingly used as bioindicators of marine pollution (3). Mussels especially are valuable bioindicators because of their wide geographical distribution, sessile nature and easy sampling. As a sedentary, filter-feeding animal, the mussel *Mytilus galloprovincialis* is a known as a good bioaccumulator of trace elements (4). Trace elements can be accumulated in mussel tissues to concentrations much higher than those found in a marine environment. They are probably absorbed both from water and from ingested phytoplankton and other suspended particles (5). Although these elements occur naturally in marine environments, and some of them are essential in small quantities, at higher concentrations they can be very toxic to organisms, and some of them are harmful even at low concentrations. Mussels contaminated with trace elements can cause human poisoning and promote diseases, since they are consumed as a food (6).

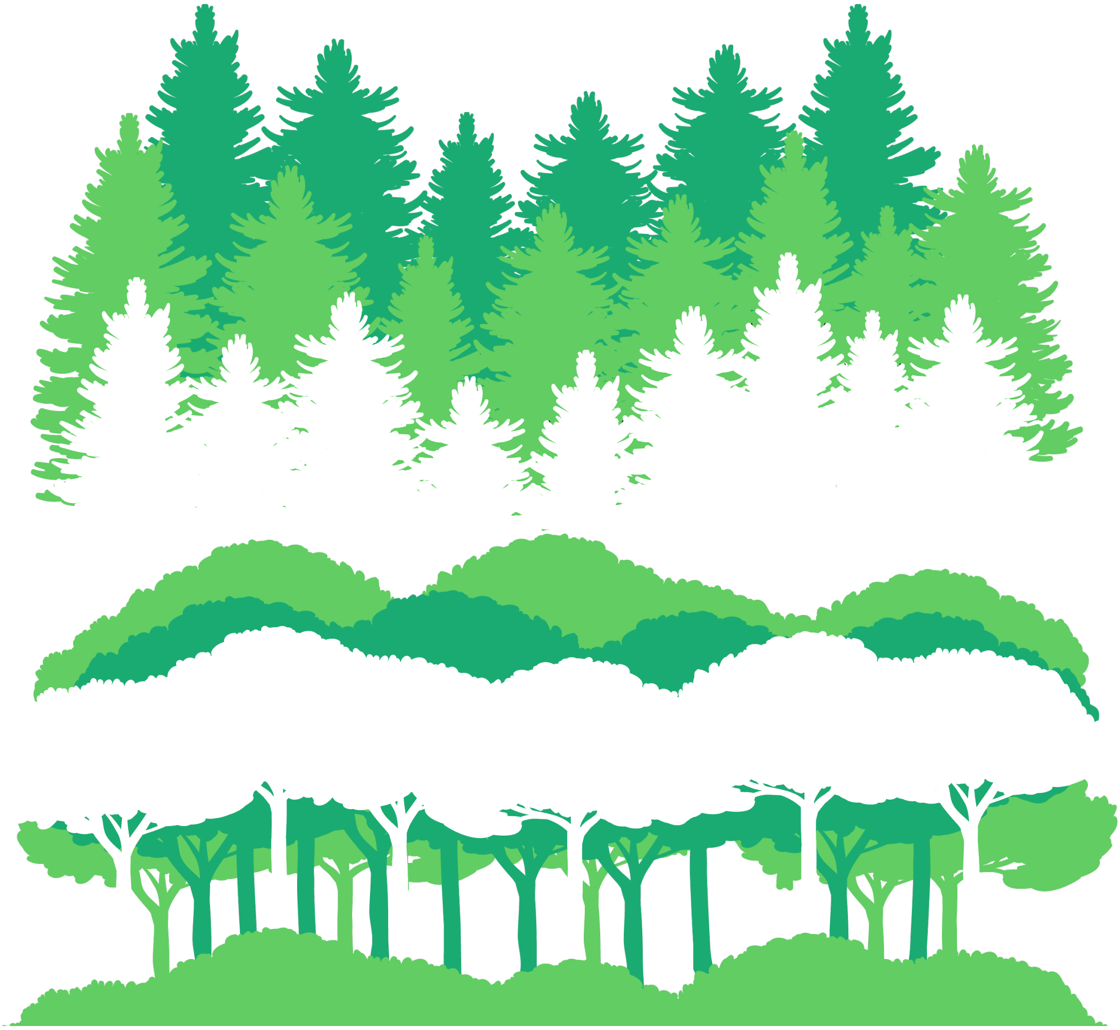
Bioaccumulation of trace elements in mussels and an surface sediment is influenced not only by environmental concentrations, but also by seawater physicochemical parameters: temperature, salinity, dissolved oxygen and total organic carbon (TOC). The strong correlation was not found between different elements in the mussel and sediment samples with seawater temperature and salinity, but temperature and salinity did have a high positive correlation.

It was also noticed that dissolved oxygen was in a strong negative correlation with temperature and salinity and, related to that, all elements which were positively correlated with temperature at the same time were negatively correlated with O_2 and *vice versa*, excepting Hg. Different levels of O_2, as well as different temperature and salinity in water where mussels were grown, did not have a significant effect on Hg concentration in mussel tissues. Also, a consistent pattern of TOC effects on trace element concentrations in mussels could not be found, since TOC effects are probably metal-specific. Besides other environmental impacts, the impact of element concentrations from surface sediments on their concentrations in mussels has also been observed.

Literatura

1. Salas, P.M., Sujatha, C.H., Ratheesh Kumar C.S., Cheriyan, E. *Marine Poll. Bull.* 119(2) (2017) 191–203.
2. Tanaskovski, B., Petrović, M., Kljajić, Z., Degetto, S., Stanković, S. *Maced. J. Chem. Chem. En.* 33(1) (2014) 139–150.
3. Stanković, S., Stanković, R., A. (2013). In: Lichtfouse, E., et al. (eds) Green materials for energy, products and depollution, Environmental Chemistry for a Sustainable World, vol 3. Springer, Dordrecht, pp151–228. https://doi.org/10.1007/978-94-007-6836-9_5.
4. Stanković, S., Kalaba, P., Stanković, A., *Environ. Chem. Lett.* 12 (2014) 63–84.
5. Spada, L., Annicchiarico, C., Cardellicchio, N., Giandomenico, S., Di Leo, A. *Mediterr. Mar. Sci.* 14 (2013) 99–108.
6. Tanaskovski, B., Jović, M., Mandić, M., Pezo, L., Degetto, S., Stanković, S. *Ecotox. Environ. Safe* 130 (2016) 65–73.

POSTER PREZENTACIJE
POSTER PRESENTATIONS



Assessment of influential factors on the geochemistry of the soil-biota system in the Prašnik forest

Maja Ivanić[1], Gordana Medunić[2a], Željka Fiket[1], Gordana Marović[3], Jasminka Senčar[3], Martina Furdek Turk[1], Goran Kniewald[1]

[1]Division for Marine and Environmental Research, Ruđer Bošković Institute, Zagreb, Croatia

[2]Faculty of Science, Department of Geology, University of Zagreb, Zagreb, Croatia

[3]Institute for Medical Research and Occupational Health, Zagreb, Croatia

[a]gmedunic@geol.pmf.hr

The Prašnik forest, located in the south-western part of the Pannonian Basin (Croatia), is a temperate rainforest and the last remnant of the Slavonian rainforest. As a unique phytocoenosis, it was recognized and protected as a special forest vegetation reserve since 1965. Focus of the present study were soil, mushroom and moss samples from this forest. The principal objectives of the study were determination of (i) levels of metals/metalloids in soil, moss and mushroom samples, and (ii) radionuclide activities in soil samples. The main aims of the presented study were to assess: 1) the influence of pedological substrate on the element composition in mosses and mushrooms, as sensitive bioindicators of air quality and environmental health, and 2) the influence of atmospheric deposition on the soil radionuclide composition in this area. Due to its position in the area of warfare during 1990s, the Prašnik rainforest was mined and until 2015 unavailable to visitors. Other than that, as a highly protected area of great biological importance, it was excluded from human exploitation activities since 1928 and is therefore considered free of anthropogenic influence except for contaminants delivered via natural pathways, air or water. Previous studies confirmed only slight and locally restricted influence of the war activities on the soil geochemistry [1], while geochemical composition of both mosses and mushrooms showed prevailing influence of the local substrate [2] and atmospheric deposition [3]. The multielement analysis of soil, moss and mushroom samples was performed by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS) using an Element 2 instrument (Thermo, Bremen, Germany). All samples, after digestion in the microwave oven (Multiwave 3000, Anton Paar, Graz, Austria), were analysed for total concentration of 28 elements. Radionuclides in the soil samples were analysed gamma-spectrometrically using GMX series gamma-X HPGe and/or Ge(Li) detector (resolution 2.24 keV on 1.33 MeV 60Co, relative efficiency 74.2%; resolution 1.78 keV on 1.33 MeV 60Co, relative efficiency 16.8%). Counting time was 80,000 s or higher and depended on sample activities. Results of the multielement analysis were in agreement with the data reported in European Geochemical Atlas (FOREGS) [4] for this area. Slightly higher levels than expected by the FOREGS were observed only for Cd, Pb and Zn. The calculated bioaccumulation factors ($BAF=C_{moss\ or\ mushroom}/C_{soil}$; C- concentration) suggest slight ($BAF=10^{-2}-10^{-1}$) to moderate ($BAF=10^{-1}-1$) accumulation of majority of elements (Figure 1) in both mosses and mushrooms (Figure 1). Only Cu in mushrooms exhibited BAF>1.

Anthropogenic radionuclides, ^{137}Cs and ^{134}Cs, were present in all samples and reflect the global contamination of the biosphere caused by nuclear tests and accidents in Chernobyl in 1986 and Fukushima in 2011, respectively (Table 1). Other detected radionuclides are considered to be of natural origin (Table 1).

Figure 1. Average bioaccumulation factors in moss and mushroom samples.

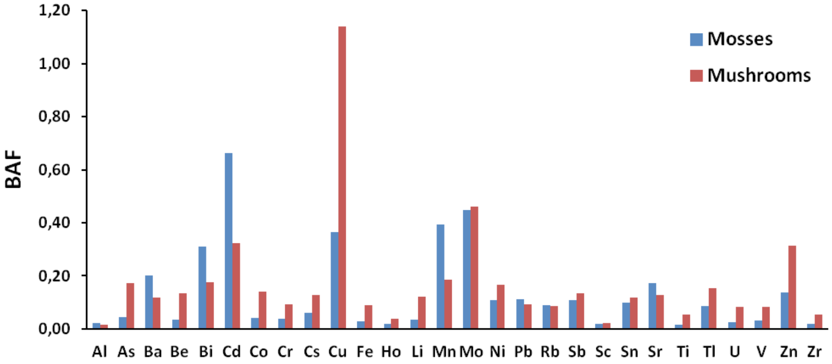


Table 1. Average radionuclide activity concentration in soil samples.

Activity concentration / Bq kg^{-1}									
^{238}U	**^{226}Ra**	**^{210}Pb**	**^{235}U**	**^{232}Th**	**^{228}Ra**	**^{40}K**	**^{7}Be***	**^{137}Cs**	**^{134}Cs**
66.2	44.6	55.6	2.7	42.3	42.3	542.4	13	30.8	1.6

References

1. Mesić Kiš, Ivana; Karaica, Bojan; Medunić, Gordana; Romić, Marija; Šabarić, Jasenka; Balen, Dražen; Šoštarko, Kristijan. Soil, bark and leaf trace metal loads related to the war legacy (The Prašnik rainforest, Croatia). *MPGB* 31(2) (2016) 13-28.
2. Fiket, Željka; Medunić, Gordana; Furdek Turk, Martina; Ivanić, Maja; Kniewald, Goran. Influence of soil characteristics on rare earth fingerprints in mosses and mushrooms: example of a pristine temperate rainforest (Slavonia, Croatia). *Chemosphere* 179 (2017) 92-100.
3. Medunić, Gordana; Marović, Gordana; Senčar, Jasminka. Radionuclides in soil, mosses, and mushroom of the Prašnik rainforest (Croatia) *Geologica Macedonica - zbornik na trudovi* (2016) 451-452.
4. Salminen, R. (Chief Editor) et al. FOREGS Geochemical Atlas of Europe, Part 1: Background Information, Methodology and Maps. (2005) Available online at: http://www.gtk.fi/publ/foregsatlas/

Procena stepena kontaminacije toksičnim elementima zemljišta oko industrijskih objekata Srema: Kspef faktor

Assessment of contamination level of the toxic elements in soils surrounding industrial facilities in Srem: Kspef factor

Maja Poznanović[1a], Sanja Sakan[2], Dragan Manojlović[3], Sandra Škrivanj[3]

[1]Geološki zavod Srbije, Beograd, Srbija

[2]Centar izuzetnih vrednosti za hemiju i inženjering životne sredine, IHTM, Univerzitet u Beogradu, Beograd, Srbija

[3]Hemijski fakultet, Univerzitet u Beogradu, Beograd, Srbija

[a]maja.poznanovic@gzs.gov.rs

U proceni stepena kontaminacije toksičnim elementima, pored upoređivanja sadržaja sa standardnim vrednostima ili poznatim fonom elemenata u zemljištu, koriste se pristupi koji podrazumevaju upotrebu različitih koeficijenata. Jedan od njih je i "Secondary phase enrichment factor" (Kspef), pogodan za utvrđivanje stepena obogaćena (kontaminacije) datim elementima u odnosu na prirodnu distribuciju u nekontaminiranim uzorcima (Cai et al, 2011). U ovom radu, upotrebom Kspef koeficijenta procenjen je stepen kontaminacije zemljišta toksičnim elementima: Cu, Cr, Ni, Co, Zn, Pb, Cd i As, na prostoru oko industrijskih objekata na teritoriji Srema.

Uzorci zemljišta su sakupljani tokom oktobra 2010. godine na 45 lokaliteta u 15 industrijskih oblasti, kao i 7 na prostoru južnog Srema, gde nisu značajno izraženi antropogeni uticaji (srednje vrednosti sadržaja elemenata uzete su kao referentne - BG). Za ispitivanje raspodele metala u zemljištu primenjena je metoda sekvencijalne ekstrakcije (Sakan et al., 2007). Određivanje sadržaja toksičnih elemenata izvršeno je tehnikom ICP/AES.

Za najveći broj uzoraka vrednosti koeficijenta ispitivanih elemenata su u intervalu $0 < \text{Kspef} < 3$, čime se uzorkovano zemljište svrstava u grupu sa odsustvom ili minornim obogaćenjem. Međutim, osim u slučaju Ni i Co, Kspef vrednosti drugih ispitivanih elemenata su na pojedinim lokalitetima bile van ovog opsega. U slučaju hroma to se odnosi na zemljište uzorkovano uz ispusni kanal fabrike kože u Rumi, sa umerenim povećanjem ovim elementom (Kspef =3,32) i sadržajem od 141 mg/kg. Kako se u industriji kože oslobađa Cr (VI), koji je detektovan u zemljištu oko kožara najviše kao Cr (III), usled redukcije u prisustvu npr. glina, on se može asosovati sa oblicima nerastvornih kristalnih struktura ili kompleksirati sa organskom materijom zemljišta (Kabata Pendias, 2011; Gitet at al, 2013). Kspef vrednost Cu u uzorku uzetom iz napuštenog voćnjaka, udaljenog 250 m od istog postrojenja iznosi 0,29. Od ukupne koncentracije bakra u podpovršinskom sloju od 553 mg/kg, najveći deo (455 mg/kg) je koncentrovan u rezidualnoj fazi. Povećan sadržaj ovog elementa je najverovatnije posledica upotrebe fungicida na bazi bakra, koji se koristi u voćarstvu i vinogradarstvu (Kabata Pendias, 2011), koja se dogodila dosta ranije u odnosu na uzorkovanje. U slučaju olova, Kspef од 4,71 и 3,36 registrovani su na lokalitetima udaljenim 300 m od fabrika celuloze i šećerane, odnosno neposredno uz fabriku izolacionog materijala. Obzirom da su ove vrednosti niže od vrednosti definisanih u referentnom uzorku (16,1 mg/kg), ne može se govoriti o značajnoj kontaminaciji zemljišta. Na lokalitetu u neposrednoj blizini starog postrojenja za proizvodnju gume, Kspef iznosi 0,48. Međutim, prisustvo olova u organskoj fazi od 44,7 mg/kg od ukupnih 49,9 mg/kg, može ukazati na antropogeni uticaj na sadržaj ovog elementa. Jedan od razloga mogu da budu ostaci dotrajalih guma, koje su u jednom periodu bili odloženi na ovom lokalitetu. Vrednosti Kspef koje ukazuju na umereno obogaćenje cinkom, izražene su na lokalitetima u kojima je sadržaj iznad BG (49,7 mg/kg), te je moguće pretpostaviti da povećan sadržaj cinka može biti posledica uticaja različitih izvora kontaminacije. U uzorcima u kojima Kspef vrednosti za Cd ukazuju na umereno ili umereno povećano obogaćenje, sadržaj kadmijuma je sličan sadržaju u referentnom uzorku. Isti zaključak može da se izvede i za As, osim u zemljištu s detektovanim umerenim obogaćenjem arsenom. Kontaminacija je najverovatnije posledica sagorevanja goriva u procesu proizvodnje cementa.

Vrednosti koeficijenata Kspef za većinu elemenata ukazuju na odsustvo ili minornu kontaminaciju na lokalitetima čak i sa visokim sadržajima elemenata, kao i umereno povećanu kontaminaciju u slučaju sadržaja nižih ili ekvivalentnih onim referentnim. Na osnovu toga može se zaključiti da upotreba ovog koefcijenta nije uvek adekvatna za procenu kontaminacije toksičnim elementima. Razlog tome je što se usled antropogenih aktivnosti u životnu sredinu oslobađaju i proizvodi kao nosioci toksičnih elementa u kojima oni teško postaju mobilni ili procesa redistribucije u zemljištu usled prirodnog procesa raspadanja minerala ili procesa koji sledi posle kontaminacije (npr. kompleksiranje i oksido-redukcija).

Literatura

1. Cai J., Cao Y., Tan H., *J. Environ. Monit.* 13 (2011) 2450-2456.
2. Gitet H., Subramanian PA., Minilu D., *Talanta* 116 (2013) 626-629.
3. Kabata Pendias A., *Trace elements in soils and plants.* (2011).
4. Sakan S., Gržetic I., Đorđević D., *Environ. Sci. Pollut. Res*. 14 (4) (2007) 229-237.

The Electrochemical Behaviour of Purpurin in an Aqueous Solution of $LiNO_3$

Jelena Senćanski[1a], Maja Pagnacco[2], Stevan Blagojević[1], Milica Vujković[2]

[1]Institute of General and Physical Chemistry, Belgrade, Serbia

[2]Faculty of Physical Chemistry, University of Belgrade, Belgrade, Serbia

[a]jsencanski@iofh.bg.ac.rs

Li-ion batteries have become the main power source for numerous portable electronic devices (mobile phones, laptops and electric vehicles) in the last decade. These batteries contain many hazardous substances including organic electrolyte which is flammable and toxic. To develop more environmentally friendly batteries, numerous studies have focused on its replacement with an aqueous electrolyte [1,2]. Furthermore, the transition metal oxides [1-3], from which the cathode material is actually built, have a harmful impact on the environment. As a result, these need to be replaced with less toxic cathode materials such as organic ones.

The aim of this work is to examine purpurin, an extract of the Madder plant, in an aqueous solution of lithium salt in order to establish its applicability as a cathode material for lithium aqueous rechargeable batteries. The examination was done by means of cyclic voltammetry in an aqueous solution of Li salt. The cyclic-voltammograms are presented in Fig. 1 and Fig. 2.

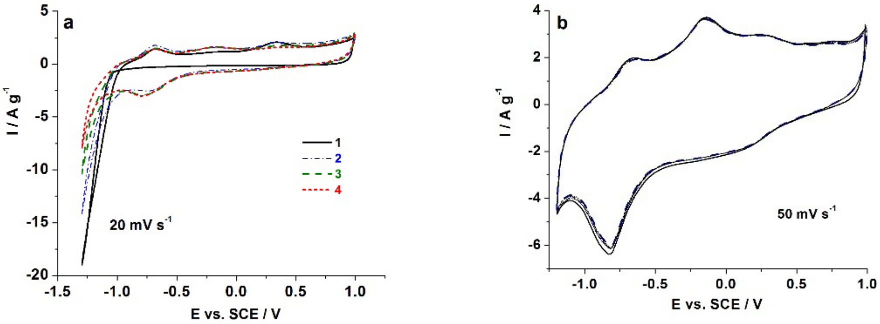


Fig. 1. The CVs of purpurin in an aqueous solution of $LiNO_3$, measured at a scanning rate of 20 mV s^{-1} over the initial four cycles (a) and at a scanning rate of 50 mV s^{-1} for the subsequent 10 cycles (b).

The initial four cycles for the material examined in an aqueous solution of $LiNO_3$ at a scanning rate of 20 mV s^{-1} are presented in Fig. 1a. After the initial two cycles, the redox activity of the material became stable while charging/discharging. Therein, the well-defined redox peaks correspond to lithiation/delithiation processes. The cyclic-voltammograms presented in Fig. 1b performed at a scanning rate of 50 mV s^{-1} contain three anode peaks positioned at -0.66V, -0.14V and 0.29V (vs.SCE) belonging to delithiation process as well as two anode peaks positioned at -0.82V and 0.17V (vs. SCE) belonging to the lithiation process.

The shapes and positions of the cathode and anode peaks are similar at various scanning rates, ranging from 5 to 400 mVs^{-1}, demonstrating the material's ability to support high currents. A capacity fade matching the increase of the polarisation speed was also observed, as had been expected. The values of the capacity during the first 180 cycles at a polarisation rate of 50 mV s^{-1} are given in Fig. 2b. The capacity values were found to range between 42 and 39 mAh g^{-1} for the cathode capacity and between 41 and 37 mAh g^{-1} for the anode capacity. The capacity retention after 180 charge/discharge cycles was found to be 93% for the cathode capacity and 90% for the anode, indicating the structural stability of the purpurin during its charging/discharging cycling in an aqueous solution of $LiNO_3$.

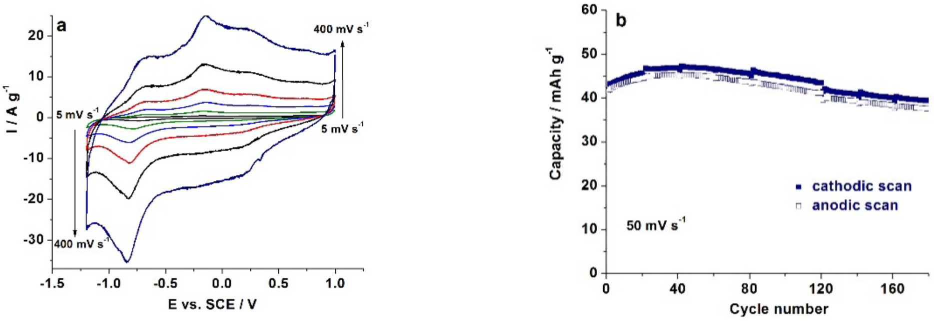


Fig. 2. The CVs of purpurin in an aqueous solution of $LiNO_3$ at the scanning rates: 5, 20, 50, 100, 200 and 400 mV s^{-1} (a); and the capacity values of purpurin during the initial 180 cycles at a scanning rate of 50 mV s^{-1} (b)

References

1. F. Wang, S. Xiao, Z. Change, Y. Yang, Y. Wu, *Chem. Commun*. 49 (2013) 9209-9211.
2. J.Senćanski, D.Bajuk Bogdanović, D.Majstorović- E. Tchernychova, J.Papan, M. Vujković, *J. Power Sources*, 342 (2017) 690-703.
3. R.B. Shivashankaraiah, H. Manjunatha, K.C. Mahesh, G.S. Suresh, T.V. Venkatesha, *J. Solid State Electr*. 16 (2012) 1279-1290.

Oscillatory Reaction as a Tool to Determine Purpurin Concentration

Kristina Stevanović[1], Jelena Maksimović[1], Jelena Senćanski[2a], Stevan Blagojević[2], Milica Vujković[1], Maja Pagnacco[1]

[1]Faculty of Physical Chemistry, University of Belgrade, Belgrade, Serbia

[2]Institute of General and Physical Chemistry, University of Belgrade, Belgrade, Serbia

[a]jsencanski@iofh.bg.ac.rs

Purpurin (1,2,4-trihydroxyanthraquinone) was extracted from the Madder plant (*Rubiatinctorum*). Its red-colored rhizomes and roots, are the main source of red dye purpurin. Recent studies [1] have shown purpurin to have strong antioxidant and enzyme inhibition activity. According to cytotoxicity results, purpurin induces cell proliferation, as well. Purpurin may also replace the cathode material of lithium-ion batteries, which contain toxic and high-cost cobalt. Doing so would help reduce the cost of commercial batteries and make them more environmental friendly.

The Briggs-Rauscher (BR) oscillating reaction [2,3] was applied to determine concentration levels of purpurin. The BR reaction itself is an oxidation of malonic acid ($CH_2(COOH)_2$) using a mixture of hydrogen peroxide (H_2O_2) and potassium iodate (KIO_3), catalyzed by manganous ion (Mn^{2+}) in an acidic (H_2SO_4) aqueous solution [3]. As an extremely sensitive matrix toward different active analytes, the BR reaction is used to determine concentration, antioxidatives/antiradicals, and the catalytic activity of analytes [4].

This work has aimed to analyze the difference in BR reaction dynamics after the addition of purpurin (Figure 1.) as well as to measure purpurin concentration at differing levels.The calibration curve, obtained by measuring the response of the BR system to purpurin perturbations, was used successfully to determine unknown concentrations of purpurin in test samples.

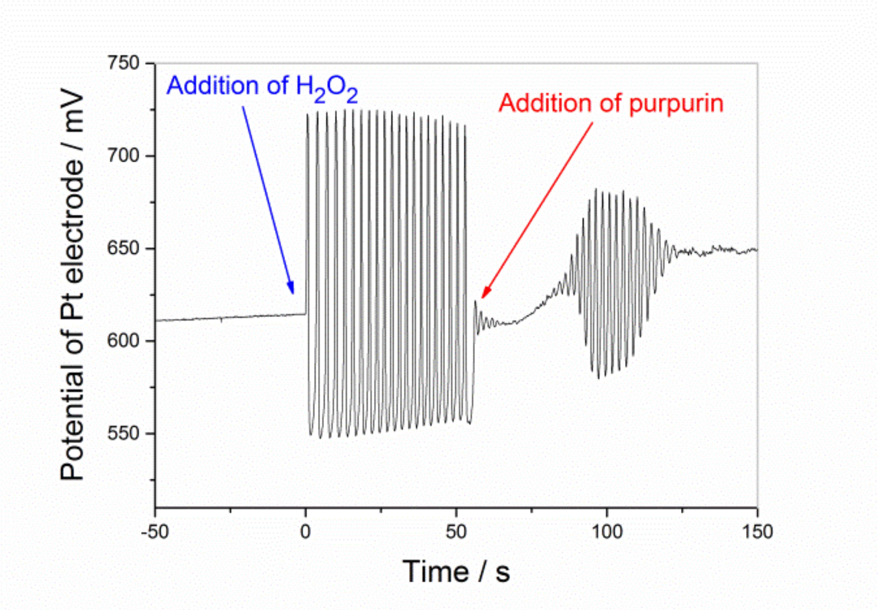


Figure 1. The Briggs-Rauscher system behaviour ([Malonic acid]$_0$= 0.0789 M, [$MnSO_4$]$_0$=0.00752 M, [$HClO_4$]$_0$=0.0300 M, [KIO_3]$_0$=0.0752M, [H_2O_2]$_0$=1.2690 M) after the addition of purpurin ([Purpurin]$_0$= 1.314×10^{-5} M).

Based on the obtained results, the method of using the BR reaction appears to be a potential tool that may prove useful in investigating the redox-reaction of purpurin as an electrode material in rechargeable metal-ion batteries. Due to the fact that very low concentrations of purpurin are able to be measured by the Briggs-Rauscher reaction (by the order of magnitude 10^{-6} M), the results obtained in this work may be applied further to studying the changes in aqueous electrolytic solutions during the charging/discharging of purpurin-based metal-ion batteries.

References

1. Zengin G., Degirmenci N.S., Alpsoy L. and Aktumsek A., *Hum ExperimToxicol*. 35(2016) 544–553.
2. Furrow S.D.,*J ChemEduc.* 89 (2012) 1421-1424.
3. Briggs T.S., Rauscher W.C.,*J Chem Ed.*50 (1973), 496-496.
4. Cervellati R., Höner K., Furrow S.D., Neddens C., Costa S.,*HelvChimActa.* 84 (2001) 3533-3547.

Adsorpcija estrogenih hormona na modifikovanim ugljeničnim tkaninama

Adsorption of estrogenic hormones on modified carbon cloth

Danijela Prokić[1a], Marija Vukčević[2], Marina Maletić[1], Jelena Rusmirović[1], Tatjana Đurkić[2]

[1]Inovacioni centar Tehnološko-metalurškog fakulteta, Beograd, Srbija

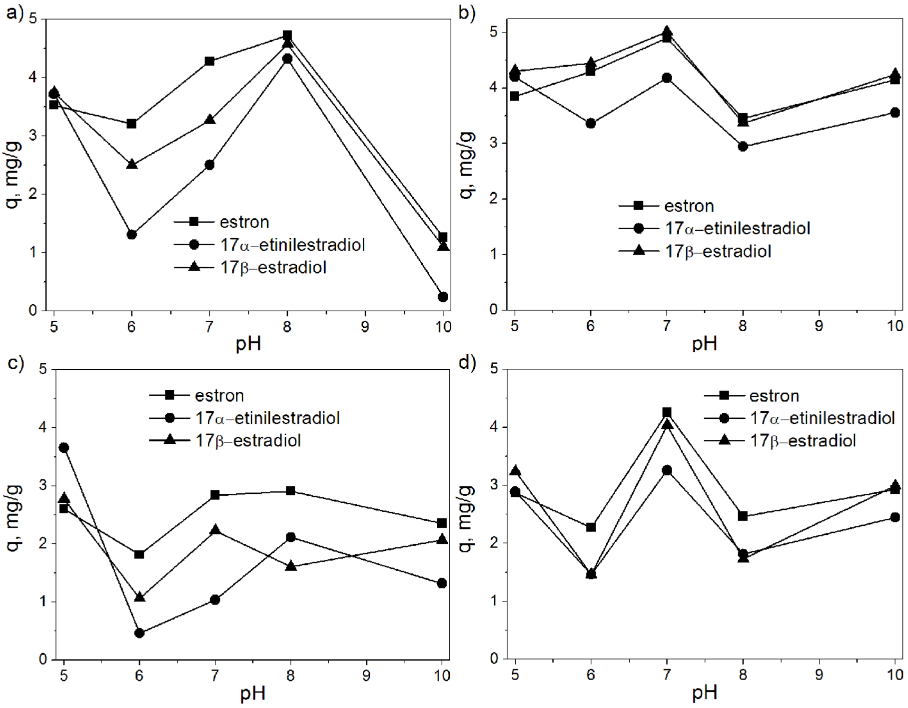
[2]Tehnološko-metalurški fakultet, Univerzitet u Beogradu, Beograd, Srbija

[a]dprokic@tmf.bg.ac.rs

Estrogeni hormoni su široko rasprostranjeni i prisutni u skoro svim vodenim matricama uključujući površinske vode, podzemne vode i otpadne vode [1,2]. Ova jedinjenja dospevaju u životnu sredinu uglavnom preko efluenata postrojenja za prečišćavanje otpadnih voda, koja nisu projektovana za uklanjanje ovih jedinjenja u potpunosti [3]. Čak i tercijarno tretirane otpadne vode sadrže tragove ovih hormona (reda veličine ng/L), što može uticati na promenu funkcije endokrinog sistema i fiziološki status ljudi i životinja [4]. Estrogeni hormoni su do sada sa manje ili više uspeha uklanjani iz vode na različite načine, kao što su membranska filtracija, fotohemijska oksidacija, razgradnja različitim biološkim procesima i sl [5]. Jedan od načina uklanjanja ovih jedinjenja iz vode je i adsorpcija. Neki od materijala koji su do sada korišćeni kao sorbenti su: granulisani aktivni ugalj, hitin, hitozan [6].

Tokom eksperimentalnih istraživanja, sprovedenih u okviru ovog rada, korišćene su modifikovane ugljenične tkanine, kao sorbenti za adsorpciju estrona, 17β-estradiola i 17α-etinilestradiola. Hemijska modifikacija podrazumevala je tretiranje površine aktivnih ugljeničnih tkanina rastvorima HNO_3, HCl i KOH, a uticaj ovih tretmana na hemiju površine aktivne ugljenične tkanine ispitan je infracrvenom spektroskopijom sa Furijeovom transformacijom (FTIR). Ispitivana je zavisnost adsorpcije od početne pH vrednosti rastvora hormona, kao i od vremena kontakta između adsorbenta i adsorbata.

Primenjeni hemijski tretmani dovode do promene u sadržaju funkcionalnih grupa prisutnih na površini ugljeničnih tkanina, što je pokazano FTIR analizom. Uticaj promene hemije površine, kao i uticaj početne vrednosti pH rastvora na adsorpciju hormona ugljeničnim tkaninama, prikazan je na slici 1. Najveću efikasnost u adsorpciji ispitivanih hormona pokazali su uzorci nemodifikovane ugljenične tkanine, pri početnoj pH vrednosti rastvora 8 i tkanine modifikovane sa HNO_3, pri pH = 7. Takođe, pokazano je da se modifikacijom sa HNO_3 smanjuje uticaj početne pH vrednosti rastvora na adsorpciju.



Slika 1. Uticaj pH vrednosti na adsorpciju hormona na: a) nemodifikovanoj ugljeničnoj tkanini i ugljeničnim tkanininama modifikovanim sa: b) HNO_3, c) HCl i d) KOH

Praćenjem adsorpcije ispitivanih hormona na ugljeničnoj tkanini modifikovanoj sa HNO_3, ispitana je i kinetika adsorpcije. Dobijeni rezultati su pokazali da adsorpcija hormona na modifikovanoj ugljeničnoj tkanini prati kinetiku pseudo-drugog reda.

Zahvalnica: Ovaj rad finansiralo je Ministarstvo prosvete, nauke i tehnološkog razvoja, Republike Srbije, kroz projekat ON 172007

Literatura

1. Vulliet ,E., Wiest, L., Baudot, R., Grenier-Loustalot M.F., *J. Chromatogr. A* 1210 (2008) 84-91.
2. Naldi, A.C., Fayad, P.B., Prevost, M., Sauve S., *Chemistry Central Journal* 10 (2016) 30 (1-17).
3. Johnson, A.C., Sumpter, J.P., *Environ. Sci. Technol.* 35 (2001) 4697–4703.
4. Grover, D.P., Balaam, J., Pacitto, S., Readman, J.W., White, S., Zhou J.L., *Chemosphere* 84 (2011) 1512–1520.
5. Silva CP., Otero M., Esteves V., *Environ. Pollut.* 165 (2012) 38-58.
6. Zhang, Y., Zhou, J.L., *Water Research* 39 (2005) 3991–4003.

Karbon kriogel kao adsorbent za uklanjanje Cd(II), Zn(II) i Ni(II) jona iz vode

Carbon cryogel as an adsorbent for removal of Cd(II), Zn(II) and Ni(II) ions from water

Marija Vukčević[1a], Marina Maletić[2], Ana Kalijadis[3], Biljana Babić[4], Tatjana Đurkić[1], Mila Laušević[1]

[1]Tehnološko-metalurški fakultet, Univerzitet u Beogradu, Beograd, Srbija

[2]Inovacioni centar Tehnološko-metalurškog fakulteta, Beograd, Srbija

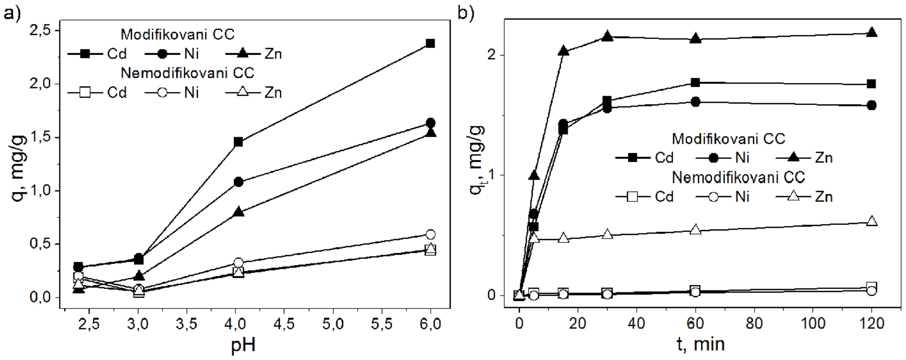
[3]Institut za nuklearne nauke “Vinča”, Univerzitet u Beogradu, Beograd, Srbija

[4]Institut za fiziku, Univerzitet u Beogradu, Beograd, Srbija

[a]marijab@tmf.bg.ac.rs

Zagađenje vodenih tokova teškim metalima je jedan od najakutnijih ekoloških problema današnjice. S obzirom na to da teški metali nisu biorazgradivi, oni se akumuliraju u životnoj sredini i na taj način ulaze u lanac ishrane ljudi i životinja, pa kao veoma toksične materije, mogu izazivati niz opasnih i često neizlečivih bolesti. Iz tog razloga, istraživači godinama u nazad razvijaju nove i usavršavaju postojeće tehnike za prečišćavanje otpadnih voda od ovih zagađujućih materija [1]. Za prečišćavanje vode zagađene teškim metalima mogu se koristiti različite metode: hemijska precipitacija, elektrohemijski tretmani, filtracija, reverzna osmoza, jonska izmena, membranski procesi, adsorpcija. Jedna od najčešće korišćenih je adsorpcija, koja zbog mogućnosti regenerisanja adsorbenta, odgovarajućim desorpcionim procesom, predstavlja veoma efektivnu i ekonomičnu metodu. Zahvaljujući razvijenoj specifičnoj površini i poroznosti, kao i prisustvu funkcionalnih grupa na površini, različiti ugljenični materijali pokazuju visoku efikasnost u uklanjanju teških metala iz vode. Karbon kriogel (CC) predstavlja ugljenični materijal razvijene mezoporoznosti čije se adsorpcione karakteristike mogu poboljšati optimizacijom i kontrolisanjem parametara dobijanja. U ovom radu je ispitana mogućnost uklanjanja jona teških metala (Cd^{2+}, Ni^{2+} i Zn^{2+}) iz vode, korišćenjem karbon kriogela i hemijski modifikovanog karbon kriogela.

Prvi korak u sintezi karbon kriogela je polikondenzacija rezorcinola i formaldehida, u prisustvu natrijum-karbonata kao katalizatora. Organski kriogel pripremljen je sol-gel tehnologijom uz naknadno sušenje postupkom zamrzavanja, dok je karbonizacija organskog kriogela vršena u inertnoj atmosferi argona na temperaturi od 800 ^{o}C [2]. U cilju poboljšanja adsorpcionih karakteristika karbon kriogela, izvršeno je hemijsko modifikovanje korišćenjem 5 M HNO_3. Karakterizacija materijala izvršena je merenjem specifične površine BET metodom, određivanjem tačke nultog naelektrisanja metodom masene titracije, kao i određivanjem vrsta funkcionalnih grupa prisutnih na površini materijala, metodom infracrvene spektroskopije sa Furijeovom transformacijom (FTIR). Ispitan je uticaj pH vrednosti rastvora, početne koncentracije jona metala u rastvoru, kao i vremena kontakta na adsorpciju teških metala uzorcima karbon kriogela.



Slika 1. Zavisnost adsorpcionog kapaciteta uzoraka karbon kriogela od:
a) početne pH vrednosti rastvora jona teških metala i b) vremena kontakta

Primenjenom hemijskom modifikacijom karbon kriogela ne dolazi do bitnijih promena u specifičnoj površini i poroznosti materijala. S druge strane, ovim postupkom dolazi do izmene površinske hemije materijala, uvođenjem novih, i povećanjem broja postojećih kiselih površinskih grupa, što je pokazano FTIR analizom i smanjenjem vrednosti tačke nultog naelektrisanja sa $pH_{PZC} = 9,3$ na $pH_{PZC} = 3,1$. Adsorpcija jona teških metala na modifikovanom i nemodifikovanom karbon kriogelu vršena je na pH = 6, jer pri ovoj pH vrednosti materijali pokazuju najveći adsorpcioni kapacitet, a ujedno je izborom ove pH izbegnuta precipitacija hidroksida metala. Izmene u hemiji površine dovode i do izmena adsorpcionih karakteristika karbon kriogela. Kako površinske grupe predstavljaju aktivna mesta za adsorpciju jona teških metala, povećanje količine površinskih grupa kod modifikovanog karbon kriogela dovodi do višestrukog povećanja adsorpcionog kapaciteta.

Zahvalnica: Ovaj rad finansiralo je Ministarstvo prosvete, nauke i tehnološkog razvoja, Republike Srbije, kroz projekat ON 172007.

Literatura

1. Vukčević, M, Pejić, B., Kalijadis, A., Pajić-Lijaković, I., Kostić, M., Laušević, Z., Laušević, M., *Chem. Eng. J.* 235 (2014) 284-292.
2. Babić, B., Kaluđerović, B., Vračar, Lj., Krstajić, N., *Carbon* 42 (2004) 2617-2624.

PAH diagnostic ratio and source analysis in the vicinity of industry sampling sites

Anka Cvetković[1a], Milena Jovašević Stojanović[2], Dušanka Matijević[1], Stamenko Dikanović[1], Nebojša Vuković[1]

[1]Institute of Public Health of Belgrade, Belgrade, Serbia

[2]Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia

[a]anka.filipovic@gmail.com

Air-quality policies have delivered many improvements according to EEA, 2017 [1] Reduced emissions have improved air quality in Europe but a large proportion of European populations and ecosystems are still exposed to air pollution that exceeds European standards. PM_{10} concentrations continued to be above the EU limit value in large parts of Europe in 2015 [1]. PM is a complex heterogeneous mixture with different chemical species bonded on PM surfaces-polycyclic aromatic hydrocarbons (PAHs) are one of the major significance.

In this paper particle-associated polycyclic aromatic hydrocarbons (PAHs) concentration were analyzed in PM_{10} ambient air in residential region of Smederevo and Obrenovac, sites with strong influence of industrial activities of steelmaking industry and termal power plant located nearby. In period November 2016. – July 2017. the total of 185 PM samples were collected at Smederevo site. At Obrenovac sampling period was between Jan 2012. to Dec 2013. and total of 127 PM_{10} samples were collected. PM_{10} were analyzed for a total of 16 EPA priority PAHs by Gas Chromatography with Mass Selective Detector. As a first step in identification of emission sources, we used PAH diagnostic ratios. These method is simple and useful for preliminary source identification as well as for validity statistical modeling as it comes by collecting data from numerous studies [2-11]. The obtained ratios in this paper are in the expected values compared to the previous studies [11].

According to diagnostic ratio Ind/(BghiP+Ind): 0.47-0.46 during H and NH respectively, and BghiP/Ind (1.1), diesel was dominant emission source at Smederevo in both seasons. At Obrenovac diagnostic ratio Ind/(BghiP+Ind) was 0.44 (H)-0.62 (NH), what is similar as at Smederevo. Ratio of Flt/(Flt+Pyr) and BaA /Chry was 0.48(H) to 0.47 (NH) and 0.91(H) to 0.67(NH) respectively, have shown that gasoline has also significant impact to source emmision for PAHs in air in both season at Smederevo. Aaccording to ratio Flt/(Flt+Pyr), what is 0.48 gasoline is source emission in summer at Obrenovac. This was confirmed with BaA /Chry ratio: 0.44 (NH) and 0.62 (H). Coal combustion was dominant source in both season at Smederevo (the ratio of B[a]P/BghiP was 1.25 (H) and 0.91(NH) while at Obrenovac it was 0.55 in NH and 0.72 in H what is marker for vehicles as source emission. Ratio Ant/(Ant+Phe) confirm impact of wood combustion in both season (>0.1) at Smederevo and in winter at Obrenovac (1.30).

The principal emission of PAHs associated with PM_{10} in this study according to diagnostic ratio was combustion (gasoline, diesel, wood and coal). Application of receptor modelling Positive Matrix Factorization (EPA PMF) [12-14] to resolve 3-5 different source contribution has shown that major sources to total PAH concentrations depending on the sampling site and season: traffic 1 (diesel and gasoline exhaust), stationary sources, wood and coal combustion.

Acknowledgments

This work was supported in part by the Ministry of education, science and technological development through INGEMA project III41028.

References

1. EEA 2017, https://www.eea.europa.eu/publications/air-quality-in-europe-2017
2. Tang, N., Hattori, T., Taga, R., Igarashi, K., Yang, X., Tamura, K., Kakimoto, Mishukov, V.F., Toriba, A., Kizu, R., Hayakawa, K.,. Atm. Environ. 39 (2005) 5817-5826.
3. Teixeira, E.C., Mattiuzi, C.D.P., Feltes, S., Wiegand, F., Santana, E.R.R.,. RS. An. Acad. Bras. Ciencias 84 (3) (2012)245-261
4. Tobiszewski M., Namieśnik J. Environ. Pollut. 162 (2012) 110-119
5. Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S. Org Geochem 33 (2002) 489-515
6. Zencak Z, Klanova J, Holoubek I, Gustafsson Ö. Environ.Sci.Technol. 41 (2007) 3850-5.
7. Agudelo-Castaned D. M., Teixeira E.C. Atm. Environ., 96 (2014) 186-200
8. Akyüz, M., Çabuk, H. Sci. Tot. Environ., 408, (2010) 5550-5558.
9. Park, S.-U., Kim, J.-G., Jeong, M.-J., Song, B., Arch Environ Contam Toxicol.., 60, (2011) 576-589
10. Kim E.J, Oh J., Chang Y.S. Sci. Total Environ. 311, (2003)177-189
11. Cvetković A., Jovašević-Stojanović M., Marković D., Ristovski Z.,. Atm. Environ., 112 (2015) 335-343
12. Paatero, P, (1999) J. Comput. Graph. Stat. 8, 854-888.
13. Polissar, A.V., Hopke, P.K., Paatero, P., Malm, W.C., Sisler, J.F., 1998 J. Geophys. Res. 103 (15), 19045-19057
14. Hopke P.2001. A guide to Positive Matrix Factorization, http://www.epa.gov/ttn/amtic/files/ambient/pm25/workshop/laymen.pdf,USA,pp.16

Monitoring industrijskog zemljišta na teritoriji Republike Srbije

Monitoring of industrial soil on the territory of the Republic of Serbia

Stamenko Dikanović[1a], Anka Cvetković[1], Nebojša Vuković[1], Dušanka Matijević[1]

[1]Gradski zavod za javno zdravlje Beograd, Beograd, Srbija

[a]stamenko.dikanovic@zdravlje.org.rs

Zagađenje vode, vazduha i zemljišta organskim jedinjenjima kao što su policiklični aromatični ugljovodonici (polycyclic aromatic hydrocarbons - PAHs) i polihlorovani bifenili (polychlorinated biphenyls – PCBs) predstavlja veliki problem sa aspekta ugrožavanja životne sredine. Mnoga jedinjenja iz ove grupe su genotoksična [1] i mogu izazvati pojavu mutacija i neke vrste kancera. Zbog izuzetno malog stepena degradacije i male rastvorljivosti u vodi, ova organska jedinjenja su veoma postojana u životnoj sredini. Policiklični aromatični ugljovodonici se nalaze se na listi prioritetnih zagađivača po klasifikaciji EPA (Environmental Pollution Agency).

Polihlorovani bifenili (PCB) su aromatska, sintetska, hemijska jedinjenja koja se ne pojavljuju prirodno u životnoj sredini. Pripadaju kategoriji otpadnih jedinjenja i podležu posebnom postupku karakterizacije. PAH-ovi nastaju na visokim temperaturama u procesima pirolize različitih organskih jedinjenja prisutnih u prirodi, odnosno pri nepotpunom sagorevanju organskih jedinjenja na visokim temperaturama (požari u šumama i prerijama, vulkanska aktivnost, požari izazvani aktivnošću čoveka), ali se najveća količina oslobađa pri sagorevanju fosilnih goriva [2-7]. Iako PAH-ovi mogu biti u prirodi sintetizovani prirodnim putem, aktivnošću nekih bakterija [2] i biljaka, najveća količina u životnoj sredini potiče iz sagorevanja uglja [8-10] jer fosilna goriva sadrže znatne količine aromatičnih ugljovodonika koji su nastali tokom njihovog formiranja pri inkubaciji organske materije pod specifičnim uslovima bez prisustva kiseonika.

Predmet ovog rada je monitoring industrijskog zemljišta na teritoriji Republike Srbije. U uzorcima zemljišta određivan je sadržaj perzistentnih organskih polutanata (policikličnih aromatičnih ugljovodonika i polihlorovanih bifenila). U periodu od januara do decembra 2017. godine uzorkovano je 250 uzoraka industrijskog zemljišta, na više od 30 različitih lokacija na teritoriji Srbije. Lokacije obuhvaćene monitoringom su industrtijska zemljišta u krugu industrijskih postrojenja, u Subotici, Šapcu, Obrenovcu, Kraljevu i Kragujevcu. Ukupni sadržaj 16 EPA prioritetnih policikličnih aromatičnih ugljovodonika određivan je je tehnikom gasne hromatografije sa masenim detektorom. Ukupni sadržaj polihlorovanih bifenila (7 PCB kongenera) određivan je tehnikom gasne hromatografije sa masenom spektrometrijom kao i detektorom sa zahvatom elektrona (ECD).

Dobijeni rezultati pokazuju da polovina od ukupnog broja uzoraka (50,0%) ne sadrži policiklične aromatične ugljovodonike (koncentracija manja od LOQ odnosno 0,010 mg/kg). Od preostalog broja uzoraka 75% uzoraka sadrži PAH-ove u koncentraciji ispod 1,0 mg/

kg, što je granična vrednost propisana Uredbom[7] (srednja vrednost sume PAHova iznosila je 0,310 mg/kg). Srednja vrednost ukupne koncentracije PAHova u preostalim uzorcima (25%) iznosila je 4,440 mg/kg. U analiziranim uzorcima zemljišta u okviru industrijskih pogona u Kraljevu detektovana je najveća koncentracija sume PAHova (maksimalna vrednost ukupne koncentracije PAHova iznosila je 25.920 mg/kg). Najveća koncentracija Benzo(a)pirena dobijena je na istoj lokaciji i iznosila je 4.054 mg/kg. Pored Kraljeva, koncentracije PAH-ova koje su jednake ili veće od dozvoljenih, detektovane su u barem jednom uzorku industrijskog zemljišta na teritoriji industrijskih pogona u Kragujevcu, Nišu, Subotici, Peokuplju, Somboru i Šapcu. Analizom rezultata dobijenih na određivanje sadržaja PCB zaključeno je da 3,6% (9 uzoraka) od ukupnog broja analiziranih uzoraka sadrži pomenute kontaminante iznad granične vrednosti (0,02 mg/kg).[7] Od tog broja u 5uzoraka ukupna koncentracija PCB-a bila je do 0,1 mg/kg; u 2 uzoraka od 0,2-1,0 mg/kg, dok isti broj uzoraka sadrži PCB u koncentracijama od 1,0-2,0 mg/kg. Najzagađenije zemljište u odnosu na sadržaj PCB-a bilo je industrijsko zemljište opštine Zrenjanin.

Reference

1. P.A. White, J.B. Rasmussen, C.Blaise, Environ.Toxicol.Chem., (1998)17, 286-303
2. W. Wilcke, J. Plant Nutr. Soil Sci., (2000)163, 229-248
3. EJ Kim, J. Oh, Y.S. Chang, Sci. Total. Environ (2003) 311, 177-189
4. Ravindra K., Sokh R., Grieken R., Atm. Environ., (2008) 42 (13), 2895-2921
5. Ratola N., Alves A., Lacorte S., Barceló D., Environ. Monit. Assess., (2012) 184 (2) 985–999
6. Katsoyiannis, A.J. Sweetman, K.C. Jones, Environ. Sci. Technol.,(2011) 45 (20) 8897–8906
7. Cristale, F.S. Silva, G.J. Zocolo, M.R.R. Marchi, Environ. Pollut., (2012) 169 210–21
8. N.T. Edwards, J. Environ. Qual., 12, 427-441 (1983)
9. S.R. Wild, K.C. Jones, Environ. Toxicol. Chem., 12, 5-12 (1993)
10. S.R. Wild, K.C. Jones, Environ. Pollut., 88, 91-108 (1995)
11. “Sl. glasnik RS”, br. 88/2010

Human health risk assessment due to heavy metals in surface soil surrounding “Nikola Tesla A” thermoelectric power plant

Milan Tanić[1a], Mirjana Ćujić[2], Marko Daković[3], Ljiljana Janković Mandić[2],
Snežana Dragović[2], Denis Dinić[1]

[1]Chemical, Biological, Radiological and Nuclear Centre, Kruševac, Serbia
[2]Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia
[3]Faculty of Physical Chemistry, University of Belgrade, Belgrade, Serbia

[a]milantanic@yahoo.com

Due to increased energy demands, nowadays coal-based thermoelectric power plants (TEPP) represent one of major sources of environmental pollution [1]. Coal combustion leads to accumulation of heavy metals (HMs) in combustion by-products whose disposal and atmospheric emission are main pathways for dispersion of HMs in the soil surrounding TEPPs. HMs from soil may reach human body via variety of pathways, therefore the resident population near TEPPs should be considered to be continuously exposed to soil and coal combustion residuals contaminated by HMs. The TEPP “Nikola Tesla A” is the largest TEPP in Serbian electric power industry. It is located near Obrenovac, (35 km from Belgrade), in the area identified as the Serbian region most threatened by pollution from coal mining and coal combustion.The aim of the present study was to assess carcinogenic and non-carcinogenic health hazard for residents associated with HMs in soil.

The potential human health riskwas estimated for exposures to minimal, mean and maximal total measured concentration of selected HMs – Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn. In case of Cr, 6:1 ratio of Cr(III):Cr(VI) was applied as recommended by US EPA. Surface soil samples (10 cm depth) were collected at 30 locations distributed 1, 2, 4, 6, 8, and 10 km to the west, southwest, south, southeast, and east directionfrom the TEPP “Nikola Tesla A”. Total concentrations of HMs were measured by atomic absorption spectrometer. The US EPA risk assessment model [2] was exploited for risk calculation taking into account ingestion of soil, inhalation of resuspended soilparticles and dermal exposure to HMs in soil.

The cancer risk was evaluated through the excess lifetime cancer risk – *ELCR*, and non-carcinogenic risk was expressed as the hazard quotient – *HQ*. According to US EPA, the cancer risk below $10^6$is considered to be negligibly small, and risk of 10^4 to be sufficiently large that remediation is desirable. Cancer risk between 10^6 and 10^4 are generally considered acceptable [3].The value of *HQ* should be less than unity to consider risk from systemic toxicity negligible. The total cancer risk, $ELCR_{total}$, is calculated as a sum of all *ELCR* for all HMs and all exposure routes considered. The overall non-carcinogenic risk is expressed as hazard index, *HI*, equal to the sum of all *HQ* for all HMs and all accounted exposure routes[2].

Risk assessment from non-carcinogenic effects showed that risk from ingestion of soil particles by children and adults comprises almost whole *HI*. Dermal risk existed only for exposition to Cd in soil, and it was negligible for both categories (4×10^9 to $3 \times \mathbf{10}^3$). Risk arose from inhalation exposure was not respective because calculated $HI$was so benevolent with maximal value of 1×10^8 for both children and adults. Although none of HQ for any single HM was above the reference value of one, aggregate HI for children fell in the range from 1.04 to 2.60 with a mean value of 1.79. Cobalt ($0.47 < HI < 1.00$), Fe ($0.42 < HI < 0.94$) and Mn ($0.11 < HI < 0.44$) were identified as contaminants of most concern.

Among HMs measured, only Cd, Co, Cr(VI), Ni and Pb are recognized as human cancerogens [2]. The $ELCR_{total}$fell in the range from $1 \times 10^5$to 5×10^5. Ingestion of soil contributed the largest to the $ELCR_{total}$, followed by insignificant contribution from inhalation. There was no risk induced by dermal exposure. According to Institute of Public Health of Serbia, the standardized cancer incidence for in 2014 for the City of Belgrade (where the municipality of Obrenovac belongs) was 2.60×10^3 for males and 2.15×10^3 for females [4]. These values are very high in comparison to the risk assessed in this study; therefore, the risk provoked by exposure to HMs in soil made portion of the real cancer risk that was completely insignificant.

The estimated carcinogenic risk in this research was in the acceptable range. Estimated non-carcinogenic risk suggests that adults are not endangered due to HMs in soil, while children population is under elevated risk from deleterious health effects. Ingestion of soil was identified as a primary pathway of HMs harming to human health.

References

1. Tanić M., Ćujić M., Gajić B., Daković M., Dragović S., *Environ. Earth Sci.*, 77 (2018) 28.
2. US Department of Energy, RAIS The Risk Assessment Information System, https://rais.ornl.gov, (2009).
3. US Environmental Protection Agency, Role of the Baseline Risk Assessment in Superfund Remedy Selection Decisions, Office of Solid Waste and Emergency Response, Washington, 1991.
4. Institute of Public Health of Serbia, Health Statistical Yearbook of Republic Serbia 2016, Institute of Public Health of Serbia, Belgrade, 2017.

The evidence of hopane producing microbial communities in Kovin lignite deposit (Serbia)

Danica Mitrović[1a], Nataša Đoković[1], Dragana Životić[2], Achim Bechtel[3], Ksenija Stojanović[4]

[1] University of Belgrade, Innovation Center of the Faculty of Chemistry, Studentski trg 12-16, 11000 Belgrade, Serbia

[2] University of Belgrade, Faculty of Mining and Geology, Đušina 7, 11000 Belgrade, Serbia

[3] Montanuniversität Leoben, Department of Applied Geosciences and Geophysics, Peter-Tunner-Str. 5, A-8700 Leoben, Austria

[4] University of Belgrade, Faculty of Chemistry, Studentski trg 12-16, 11000 Belgrade, Serbia

[a]danicamitrovic87@gmail.com

Lignite from the "Kovin" deposit is of Upper Miocene (Pontian, 6 Ma) age. Based on petrographic (maceral) analysis this lignite is typical humic coal. Main organic matter precursors originated from conifer families (gymnosperms), mainly from *Cupressaceae*, *Taxodiaceae*, *Phyllocladaceae* and *Pinaceae* and to a lesser extent from grasses and shrubs (angiosperms). Nonetheless, ferns, fungi, aquatic macrophyta and bacteria, which were present in precursor organic matter in minor quantities, also contribute significantly in comprehensive interpretation of palaeoconditions in the peat environment. The best indicators for various changes in diagenetic microbial communities are hopanoid biomarkers.

Biomarker analysis of hopanes in aliphatic fraction (mass fragmentogram *m/z* 191) of extractable organic matter of lignites from the Kovin deposit shows distribution of hopanoids that suggests active microbial communities during early diagenesis. The distributions are not equivalent in all samples but show different abundances of following hopanoids: C_{27} 17β(H)-hopane, C_{29} 17β(H)21β(H)-hopane, C_{31} 17α(H)21β(H)22(R) hopane, C_{30} hop-17(21)-ene and C_{28} neohop-13(18)-ene.

Pronounced domination of C_{27} 17β(H)-, C_{29} 17β(H)- and/or C_{30} 17β(H)21β(H)-hopane is frequent in immature organic matter [1-3]. Methanotrophic bacteria (*Methylococcus capsulatus* or *Methylomonas methanica*) give precursor hopanoid lipids that are functionalized at C-29 position and could be main producers of C_{27} 17β(H)- and particularly, C_{29} 17β(H)21β(H)-hopane [4].

C_{31} 17α(H)21β(H)22(R) hopane is primarily produced by heterotrophic bacteria that use organic matter of higher plants as a source of food [1, 5].

Methanotrophic and chemoautotrophic bacteria both produce C_{30} hop-17(21)-ene [6, 7]. It can be also readily formed by isomerisation of diploptene (C_{30} hop-22(29)-ene), which, in turn, might originate from diplopterol found in several eukaryotic phyta (e.g. ferns, mosses, lichens, fungi) as well as in hopanoid producing bacteria.

This is the first time that C_{28} neohop-13(18)-ene has been identified in lignite since it has so far been reported in black shales [8] and lake sediments [9]. However, bacteria producing neohopenes with other than C-30 atoms has not been discovered yet, therefore possibilities for its genesis and distribution throughout the sediment remain to be uncovered.

Input of mixture of methanotrophic, chemoautotrophic and heterotrophic microbial communities is demonstrated by high relative abundances of various hopanoids present in aliphatic fraction of extractable organic matter of Kovin lignite samples. Besides expected distributions of hopanes, the existence of C_{28} neohop-13(18)-ene is intriguing and remains to be clarified.

The investigation of hopanoids in lignite is important, since determination of bacteria communities contributes to better reconstruction of depositional environment during peat accumulation. Moreover, impact of methanotrophic bacteria to precursor organic matter is indicative for an active methane cycle at the time of deposition.

References

1. Vu, T.T.A., Zink, K.G., Mangelsdorf, K., Sykes, R., Wilkes, H., Horsfield, B., *Org. Geochem.* 40 (2009) 963-977.
2. Stefanova, M., Ivanov, D.A., Utescher, T., *Org. Geochem.* 42 (2011) 1363-1374.
3. Fabiańska, M.J., Kurkiewicz, S., *Int. J. Coal Geol.* 107 (2013) 24-44.
4. Neunlist S., Rohmer, M., *Biochem. J.* 231 (1985) 635-639.
5. Thiel, V., Blumenberg, M., Pape, T., Seifert, R., Michaelis, W., *Org. Geochem.* 34 (2003) 81-87.
6. Freeman, K.H., Hayes, J.M., Trendel, J.M., Albrecht, P., *Nature* 343 (1990) 254-256.
7. Duan, Y., Wu, B., Zheng, G., Zhang, H., Zheng, C., *Sci. Bull.* 49 (2004) 369-373.
8. Sinninghe Damsté, J.S., *Book of Abstracts, 18th International Meeting on Organic Geochemistry,* Maastricht, the Netherlands (1997) 659-660.
9. Nytoft, H.P., Bojesen-Koefoed, J.A., Christiansen, F.G., *Org. Geochem.* 31 (2000) 25-39.

Coniferous families as dominant source of precursor organic matter in lignite from the Kostolac Basin (Serbia)

Nataša Đoković[1a], Danica Mitrović[1], Dragana Životić[2], Achim Bechtel[3], Ksenija Stojanović[4]

[1] University of Belgrade, Innovation Center of the Faculty of Chemistry, Studentski trg 12-16, 11000 Belgrade, Serbia

[2] University of Belgrade, Faculty of Mining and Geology, Đušina 7, 11000 Belgrade, Serbia

[3] Montanuniversität Leoben, Department of Applied Geosciences and Geophysics, Peter-Tunner-Str. 5, A-8700 Leoben, Austria

[4] University of Belgrade, Faculty of Chemistry, Studentski trg 12-16, 11000 Belgrade, Serbia

[a] ndjokovicpost@gmail.com

The Smederevsko Pomoravlje field of Upper Miocene (Pontian, 6 Ma) age is located in the western part of the Kostolac lignite Basin, Serbia. The field is still under exploration. In this study a comprehensive biomarker analysis of extractable organic matter isolated from lignite samples has been performed in order to determine the sources of organic matter (OM).

Pulverised lignite samples were extracted by an azeotropic mixture of dichloromethane and methanol (88:12, v:v) using a Soxhlet's apparatus. Extracts were dissolved in a mixture of *n*-hexane : dichloromethane (80:1, v:v) and asphaltenes were precipitated. The hexane-soluble organic compounds (maltenes) were separated into saturated hydrocarbons, aromatic hydrocarbons and NSO fraction (polar fraction, which contains nitrogen, sulphur, and oxygen compounds) using column chromatography. All fractions were analysed by gas chromatography-mass spectrometry analysis (GC-MS). Polar fraction was derivatized by N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) prior to GC-MS.

The main constituents of saturated and aromatic fractions are diterpenoids, which indicates significant contribution of gymnosperms to precursor OM. Dominant compounds in the saturated fraction are pimarane and 16α(H)-phyllocladane, whereas simonellite and dehydorabietane prevail in aromatic fraction. A high abundance of pimarane indicates that the coal forming plants belonged to the conifer families *Pinaceae, Taxodiaceae* and *Cupressaceae*, while high amount of 16α(H)-phyllocladane suggests *Taxodiaceae*, *Podocarpaceae*, *Cupressaceae*, *Araucariaceae* and *Phyllocladaceae*. Abundant abietane type diterpenoids in aromatic fraction imply contribution of *Pinaceae* to precursor OM [1].

In polar fraction, fatty alcohols ranged from n-C_{12} to n-C_{28} with a sharp prevalence of long-chain homologues (n-C_{22} – n-C_{28}) are identified. *n*-Alkanoic acids in range from n-C_6 to n-C_{30} are also present in high amount. This class of biomarkers is characterised by a notable predominance of even over odd homologues, maximising at $C_{16:0}$ (hexadecanoic acid). The obtained results indicate terrestrial origin as well, and skeletons, which are produced primarily by conifer vascular plants (cutin and suberin) [2].

Other constituents of polar fraction are kauranol, 3-ketosimonellite, ferruginol, 6,7-dehydroferruginol, β-sitosterol and stigmastanol. The presence of kauranol and phenolic abietanes approves the contribution from *Taxodiaceae* and *Cupressaceae* to precursor OM [3-5].

The comprehensive biomarker analysis of lignite from the Kostolac Basin, which is typical humic coal, indicates that the main sources of OM were gymnosperms (conifers) which belonged to the families *Pinaceae, Taxodiaceae*, *Cupressaceae* and *Araucariaceae*.

The study of vegetation assemblage in precursor organic matter of lignite is important for further reconstruction of palaeoenvironment and palaeoclimate during peat accumulation. On the other hand, preservation of organic matter i.e. organic carbon content and other utilization properties of lignite depend on sources of precursor biomass.

References

1. Otto, A., Wilde, V., *Bot. Rev.* 67 (2001) 141-238.
2. Fabiańska, M.J., *Chemometr. Intell. Lab. Syst.* 72 (2004) 241-244.
3. Otto, A., Simoneit, B.R.T., *Org. Geochem*. 33 (2002) 1241-1251.
4. Otto, A., Simoneit, B.R.T., Wilde, V., Kunzmann, L., Püttmann, W., *Rev. Palaeobot. Palynol.* 120 (2002) 203-215.
5. Otto, A., Simoneit, B.R.T., Rember, W.C., *Rev. Palaeobot Palynol.* 126 (2003) 225-241.

Sorpciono ponašanje klomazona u poljoprivrednim zemljištima

Sorption behavior of clomazone in agricultural soils

Rada Đurović-Pejčev[1a], Svjetlana Cupać[2], Zorica P. Tomić[2], Vojislava Bursić[3], Tijana Zeremski[4]

[1]Institut za pesticide i zaštitu životne sredine, Beograd, Srbija

[2]Poljoprivredni fakultet, Univerzitet u Beogradu, Beograd, Srbija

[3]Poljoprivredni fakultet, Univerzitet u Novom Sadu, Novi Sad, Srbija

[4]Institut za ratarstvo i povrtarstvo, Novi Sad, Srbija

[a]rada.djurovic@pesting.org.rs

Klomazon (IUPAC: 2-(2-hlorobenzil)-4,4-dimetil-1,2-oksazolidin-3-on) je selektivni herbicid iz grupe izoksazolidinona, koji se na osnovu svojih fizičko-hemijskih karakteristika može svrstati u grupu pesticida koji predstavljaju potencijalne kontaminante dubljih slojeva zemljišta i podzemnih voda.

Kada dospe u zemljište, količina slobodne frakcije molekula klomazona koja može da učestvuje u detoksifikacionim mehanizmima, kao što su mobilnost, degradacija i usvajanje biljkama, direktno je određena veličinom sorpcije ovog herbicida za zemljišne čestice, pri čemu poznavanje njegovog sorpcionog koeficijenta (K_d) pruža mogućnost za procenu rizika od kontaminacije dubljih slojeva zemljišta pa čak i podzemnih voda ovom agrohemikalijom. Cilj ovog rada je s toga bio usmeren na proučavanje sorpcionog ponašanja klomazona u četiri različita poljoprivredna zemljišta (rendzina, pseudoglej, černozem i smonica) sa područja Republike Srbije, i utvrđivanje korelacije između veličine sorpcije i sadržaja glavnih sorbujućih komponenti zemljišta (organska materija (OM) i glina). Sadržaji pomenutih komponenti u proučavanim zemljištima su bili sledeći: 1,98% OM-e i 23,4% gline u rendzini, 2,21% OM-e i 35,5% gline u pseudogleju, 3,33% OM-e i 28,9% gline u černozemu, odnosno 3,29% i 45,2% u smonici.

Za proučavanje sorpcionog ponašanja klomazona i određivanje njegovih K_d konstanti za pomenuta četiri tipa zemljišta je korišćen *batch* metod [1], zasnovan na ravnotežnoj raspodeli molekula klomazona u sistemu zemljište/zemljišni rastvor. Svaki sistem se sastojao od smeše 2 g zemljišta i 10 mL rastvora određene koncentracije (0,5 – 15 μg/mL) klomazona u 0,01 M $CaCl_2$, koja je homogenizovana 24 h radi dostizanja ravnotežne raspodele ovog jedinjenja između dve faze sistema. Nakon centrifugiranja, vodena faza je analizirana HPLC-om opremljenim sa PDA detektorom, pri čemu su K_d koeficijenti klomazona za proučavana zemljišta računati kao odnos koncentracije pesticida koja je sorbovana za zemljište (C_s) i koncentracije jedinjenja koja je zaostala u vodenoj fazi (C_e), u uslovima ravnotežne raspodele. Adsorpcione izoterme su dobijene primenom Frojndlihove jednačine na eksperimentalno dobijene rezultate, pri čemu su Frojndlihovi koeficijenti K_f i n, dobijeni primenom linearne forme Frojdlihove jednačine.

Dobijeni rezultati su ukazali da je sorpcija klomazona najveća za smonicu, odnosno da opada u sledećem nizu: smonica (K_d=4,80 mL/g)> černozem (K_d=4,07 mL/g)> pseudoglej (K_d=3,92 mL/g)> rendzina (K_d=3,21 mL/g), pri čemu ne postoji statistički značajna korelacija K_d vrednosti samo sa sadržajem OM-e ili gline. Suprotno, višeregresiona analiza ukazuje na statistički značajnu korelaciju (nivo poverenja – 95%) K_d vrednosti sa sadržajem obe komponente zemljišta (K_d = 1,2712 + 0,4249 * w(OM) + 0,04744 * w(gline)), što ukazuje da su i organska materija i glina komponente u zemljištu koje učestvuju u sorpciji molekula klomazona, i da se sklonost ka zadržavanju ovog herbicida u nekom zemljištu može predvideti na osnovu poznatog sastava tog zemljišta.

Da je sorpcija klomazona za zemljište tipa smonica najizraženija, odnosno da sorpcija opada u nizu smonica > černozem > pseudoglej > rendzina, ukazuju i vrednosti Frojndlihovih K_f koeficijenata, koje za pomenuta zemljišta imaju sledeće vrednosti: K_f=5,48 (smonica), K_f=4,41 (černozem), K_f=3,98 (pseudoglej) i K_f=3,10 (rendzina). Dobijene vrednosti Frojndlihovih *1/n* koeficijenata ukazuju da su izoterme za zemljišta tipa pseudoglej (1,00) i rendzina (1,01) C-tipa (linearna zavisnost između sorbovane količine klomazona i količine ovog pesticida koja zaostaje u rastvoru), odnosno L-tipa (snažna sorpcija molekula klomazona za sorpcione centre zemljišta pri nižim koncentracijama pesticida opada kako koncentracija jedinjenja raste) u slučaju černozema (0,96) i smonice (0,94). Regresiona analiza ukazuje na statistički značajnu korelaciju *1/n* koeficijenata sa sadržajem OM-e (1/n = 1,0492 - 0,02097 * w(OM)), odnosno K_f vrednosti sa sadržajima OM-e i gline (K_f= 0,5585 + 0,6168 * w(OM) + 0,0573 * w(gline)).

Rad je realizovan kao deo projekata TR 31043 i OI 176010.

Literatura

1. OECD, 1997. OECD guidelines for testing of chemicals, proposal for updating guideline 106-adsorption/desorption using a batch equilibrium method, Paris.

Electrocatalitic Behaviour Of Serpentinite Modified Carbon Paste Electrode

Jelena Čović[1a], Jelena Milićević[2], Milan Momčilović[2], Aleksandra Zarubica[1],
Aleksandar Bojić[1], Marjan Ranđelović[1]

[1]Faculty of Sciences and Mathematics, Department of Chemistry, University of Niš, 33 Višegradska Str., 18000 Niš, Serbia

[2]Institute of Nuclear Sciences "Vinča", University of Belgrade,P. O. Box 522, 11001 Belgrade, Serbia

[a]covic.jelena91@gmail.com

Sample of natural serpentinite was collected from southern part of Serbia and thoroughly characterized for its morphological, structural and electrochemical characteristics. SEM technique has provided a detailed insight into the surface morphology of serpentinite indicating irregularly shaped particles and lamellar aggregates which are characteristic of lizardite mineral. The elemental composition of a sample was identified by EDX analysis confirming the presence of elements typical for this mineral rock such as Mg, Si, Fe, Al, Cu and Zn which are main constituents. Additionally, Ca and Ni are present as trace elements. The crystal phases detected by using XRD technique are lizardite and tiny amount of periclase.

Electrochemical characteristics and sensing properties were examined in three-electrode cell using carbon paste electrode which contained serpentinite powder and graphite in 1:1 weight ratio. For this purpose, redox reactions of potassium ferrocyanide in aqueous solutions as benchmark media were examined. Moreover, sensitive electrocatalytic properties were tested toward pesticide tebufenozide (TBF). Voltammetric analyses have, in all cases, shown that serpentinite modified carbon paste electrode (S-CPE) possess superior electrocatalytic activity in contrast to bare CPE for the red-ox reactions of $K_4[Fe(CN)_6]$. The enlargement of the peak currents, higher electroactive surface area, and the decline of the peak-to-peak separation are a proof of reversible and faster electron transfer kinetics for S-CPE. The effect of pH on the electrochemical behaviour of TBF was investigated in Britton-Robinson buffer solutions in range from 2.0 to 7.0 and showed the best analytical performance at pH 5.0 (Fig. 1).

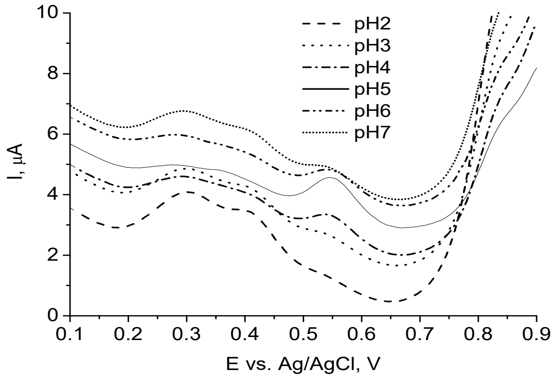


Fig. 1. DPSV curves for 9.96 ng cm^{-3} of TBF at S-CPE in Britton-Robinson buffer (pH 2.0–7.0), initial potential +0.1 V, end potential +0.9 V, accumulation potential −0.35 V, accumulation time 120 s, and the scan rate 50 mV s^{-1}

The oxidation peak of TBF appeared at +0.5 V vs. Ag/AgCl under conditions optimized for the determination of TBF in the differential pulse stripping voltammetry: initial potential +0.1 V, end potential +0.9 V, accumulation potential −0.35 V, accumulation time 120 s, and the scan rate 50 mV s^{-1}.

Keywords: Serpentinite, Carbon paste electrode, Potassium ferrocyanide, Tebufenozide, Voltammetry.

References

[1] F.J. Wicks, E.J.W. Whittaker, Serpentine textures and serpentinization, *Can.Mineral.*15 (1977) 459–488.
[2] V. Marecek, Z. Samec, J. Weber, The dependence of the electrochemical charge transfer coefficient on the electrode potential. Study of the Fe(CN)63−/Fe(CN)64− redox reaction on polycrystaline au electrode in KF solutions, *J. Electroanal. Chem.* 94 (1978) 169.
[3] C. Cannes, F. Kanoufi, A.J. Bard, Cyclic voltammetry and scanning electrochemical microscopy of ferrocenemethanol at monolayer and bilayer-modified gold electrodes, *J. Electroanal. Chem.* 547 (2003) 83–91.
[4] M. Ranđelović, M. Momčilović, B. Matović, B. Babić, J. Barek, Cyclic voltammetry as a tool for model testing of catalytic Pt- and Ag-doped carbon microspheres, *J.Electroanal. Chem.* 757 (2015) 176–182.

Uticaj hloridnih i fluoridnih jona na fotokatalitičku degradaciju nikosulfurona i karbofurana u vodi

The effect of chloride and fluoride anions on the photocatalytic degradation of nicosulfuron and carbofuran in water

Dušan Mijin[1a], Anđelka Tomašević[2], Slavica Gašić[2], Rada Đurović-Pejčev[2], Nevena Prlainović[1], Ana Dugandžić[3], Aleksandar Marinković[1]

[1]Tehnološko-metalurški fakultet, Univerzitet u Beogradu, Beograd, Srbija

[2] Institut za pesticide i zaštitu životne sredine, Beograd, Srbija

[a]kavur@tmf.bg.ac.rs

Neorganske soli koje su normalno prisutne u površinskim i podzemnim vodama imaju značajan uticaj na fotodegradacione procese organskih jedinjenja, uključujući i pesticide [1,2]. Prisustvo sulfata, fosfata, hidrogenfosfata, karbonata, bikarbonata, hlorida, fluorida, nitrata i ostalih anjona može prouzrokovati snižavanje efikasnosti fotokatalitičke degradacije. Naime, navedeni anjoni poseduju sposobnost da se adsorbuju na površini fotokatalizatora TiO_2 i ZnO i na taj način blokiraju šupljine i $^{\cdot}OH$ radikale (hydrohyl radicals scavengers) što dovodi do smanjenja brzine reakcije fotokatalize [2,3,4].

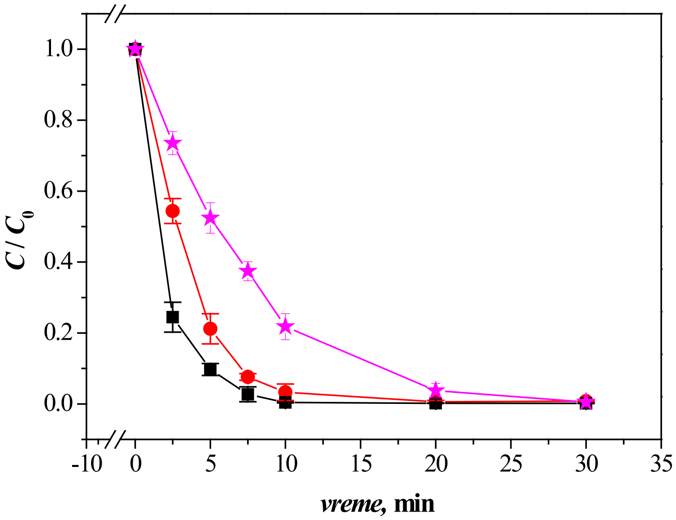
U ovom radu je ispitivana fotokatalitička degradacija sulfonilurea herbicida nikosulfurona i karbamatnog insekticida karbofurana u vodi koja sadrži hloridne i fluoridne jone. Cilj istraživanja je bio da se utvrdi kako prisutni joni utiču na stepen fotodegradacije navedenih aktivnih materija pesticida.

Nikosulfuron (98,1%) i karbofuran (99,5%) dobijeni su od Galenika-Fitofarmacija, Srbija i FMC Corporation, SAD. Sve hemikalije korišćene u eksperimentima su bile analitičke čistoće. Fotokatalizatori TiO_2 (P-25 Degussa) i ZnO (Merck) nabavljeni su od proizvođača.

Vodeni rastvori nikosulfurona i karbofurana ozračivani su pomoću 300 W Osram ultra-vitalux lampe koja produkuje polihromatsku svetlost (315-400 nm). Stepen degradacije nikosulfurona i karbofurana određivan je primenom UV spektroskopije i tečne hromatografije (HPLC).

Rezultati ispitivanja za nikosulfuron prikazani su na slici 1. Na osnovu dobijenih rezultata može se zaključiti da prisustvo oba anjona inhibira rakciju fotokatalize nikosulfurona u vodi. Takođe se zaključuje da je inhibicija izraženija u prisustvu jona fluorida nego hlorida.

Tokom istraživanja utvrđeno je da se degradacija rastvora karbofurana u prisustvu jona hlora odvijala sporija u odnosu na degradaciju bez dodatka NaCl. Reakcija fotokatalize karbofurana u prisustvu Cl^- jona je pseudo-prvog reda i brža je u prisustvu 0,1% NaCl (k = 0.088 min^{-1}) nego u prisustvu 0,5% NaCl (k = 0.069 min^{-1}), ali su obe reakcije sporije od reakcije u kojoj je koncentracija hlorida jednaka nuli (k = 0.107 min^{-1}).



Slika 1. Uticaj hloridnih i fluoridnih jona na fotodegradaciju nikosulfurona (20 mg L^{-1}), pri pH=5,0 i u prisustvu TiO_2 (2 g L^{-1}). Značenje simbola: (¢) bez soli; (□) NaCl; i (★) NaF. Koncentracija soli 20 mM.

Zahvalnica

Autori ovog rada se zahvaljuju Ministarstvu obrazovanja, nauke i tehnološkog razvoja Republike Srbije na finansijskoj pomoći (Projekti broj III 46008, 172013 i TR 31043). Takođe, zahvaljuju se kompanijama Galenika-Fitofarmacija, Srbija i FMC Corporation, USA, za standarde nikosulfurona i karbofurana dobijene kao poklon.

Literatura

1. Tomašević, A., Mijin, D., Kiss, E., *Sep. Sci. Technol.* 45 (2010) 1617-1627.
2. Wang Y., Lu, K., Feng, C., *J. Rare Earths.* 31 (2013) 360-365.
3. Behnajady, M.A., Modirshahla, N., Hamzavi, R., *J. Hazard. Mater. B* 133 (2006) 226-232.
4. Daneshvar, N., Aber, S., Seyed Dorraji, M.S., Khataee, A.R.M., Rasuolifard,H., *Sep. Purif. Technol.* 58 (2007) 91-98.

Primena testova fitotoksičnosti kod fotohemijskih procesa

Application of phytotoxicity testing for photochemistry processes

Anđelka Tomašević[1a], Natasa Šekuljica[2], Ana Dugandžić[3], Dunja Dabić[4], Slobodan Petrović[4], Dušan Mijin[4]

[1]Institut za pesticide i zaštitu životne sredine, Beograd, Srbija

[2]Inovacioni centar Tehnološko-metalurškog fakulteta, Univerzitet u Beogradu, Beograd, Srbija

[3]Institut za puteve, Beograd, Srbija

[4]Tehnološko-metalurški fakultet, Univerzitet u Beogradu, Beograd, Srbija

[a]andjelka.tomasevic@pesting.org.rs

Nikosulfuron pripada grupi sulfonilurea herbicida. Koristi se kao selektivni sistemicni herbicid i njegovi ostaci su detektovani u zemljištu, vodama i nekim usevima. Iz vode se može odstraniti primenom različitih metoda, uključujući adsorpciju [1], primenu različitih bakterija [2] i fotohemijske procese [3,4].

U ovom radu je ispitivana fitotoksičnost i akutna toksičnost reakcionih proizvoda oksidacije nikosulfurona tokom foto-Fenton reakcije. Cilj istraživanja je bio da se utvrdi da li su fotoprodukti koji su nastali degradacijom herbicida nikosulfurona manje ili više toksični od polaznog jedinjenja.

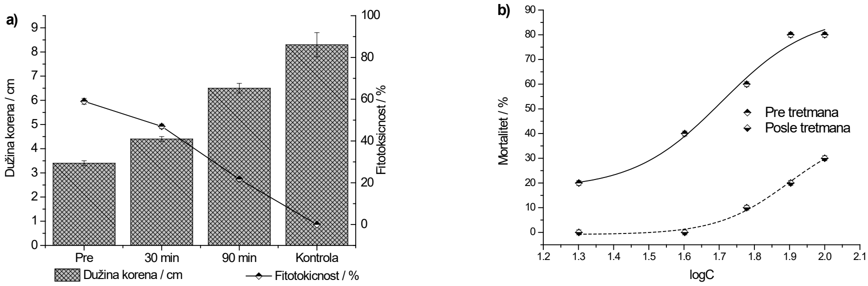
Foto-Fenton reakcija je izvedena osvetljavanjem rastvora nikosulfurona, fvožđe(II)-sulfata i vodonik-peroksida u vodi, pomoću Osram ultra vitalux® 300 W lampe, na sobnoj temperaturi uz mešanje. Promena koncentracije nikosulfurona praćena je metodom tečne hromatografije (SpectraSYSTEM P4000 sa UV detektorom).

Fitotoksičnost tokom reakcije je praćena korišćenjem literaturne metode [5]. Ukratko, uzeti su uzorci rastvora nakon 0, 30 i 90 minuta reakcije i njima je tretirano *Vigna mungo* seme u toku 5 dana. Posle 5 dana merena je dužina korena i određena fitotokisičnost u procentima.

Akutna toksičnost je određena primenom literaturne metode [6] korišćenjem račića *Artemia salina*. Uzorci pre i posle fotodegradacije sa odgovarajućim razblaženjima korišćeni su za određivanje akutne toksičnosti. Nakon 24 h inkubacije upoređuje se broj pokretnih i nepokretnih (uginulih) jedinki i određuje akutna toksičnost. EC_{50} vrednost je izračunata korišćenjem Probit metode.

Rezultati fitotoksičnosti su prikazani na slici 1a. Na osnovu dobijenih rezultata može se videti da primena foto-Fenton procesa smanjuje fitotoksičnost rastvora nikosulfurona. Dužina korena semena kod kontrolnog uzorka je bila 8,3±0,5 cm, a kod uzorka posle foto-Fenton reakcije 6,5±0,2 cm. Fitotoksičnost uzorka pre tretmana je bila 59,0±1,4 %, da bi se posle tretmana smanjila na 21,7±0,9 %.

Što se tiče akutne toksičnosti, rezultati dobijeni za uzorke pre i posle fotodegradacije prikazani su na slici 1b. EC_{50} vrednosti ukazuju na toksičnost ispitanih uzoraka. Pre tretmana foto-Fenton procesom EC_{50} je bila 51,0 %. Tokom reakcije EC_{50} rastvora dostigla je vrednost od 78,9 %. Dobijena vrednost ukazuje na smanjenje akutne toksičnosti. Dobijena EC_{50} vrednost uzorka posle tretmana je u oblasti 100 > EC50 > 75 % i može se klasifikovati kao uzorak niske toksičnosti. Sa druge strane, uzorak pre tretmana se klasifikuje kao toksičan (25 < EC50 < 75 %) [7].



Slika 1. a) Određivanje fitotoksičnosti; b) Određivanje EC_{50} ([nikosulfuron] = 48,8 µM, $[Fe^{2+}]$ = 144 µM, $[H_2O_2]$ = 176 µM, sobna temperatura).

Zahvalnica

Autori ovog rada se zahvaljuju Ministarstvu obrazovanja, nauke i tehnološkog razvoja Republike Srbije na finansijskoj pomoći (Projekti broj III 46008 i 172013).

Literatura

1. Vukčević, M., Kalijadis, A., Babić, B., Laušević, Z, Lauššević, M., *J. Serb. Chem. Soc.* 78 (2013) 1617-1632.
2. Zhang, H., Mu, W., Hou, Z., Wu, X., Zhao, W., Zhang, X., Pan, H., Zhang, S., *J. Environ. Sci. Health B* 47 (2012) 153-160.
3. Benzi, M., Robotti, E., Giantti, V., *Anal. Bioanal. Chem.* 399 (2011) 1710-1714.
4. Fenoll, J., Sabater, P., Navarro, G., Vela, N., Perez-Lucas, G.W., *J. Environ. Manage.* 130 (2013) 361-368.
5. Dugandžić, A.M., Tomašević, A.V., Radišić, M.M., Šekuljica, N.Ž., Mijin, D.Ž., Petrović, S.D., *J. Photochem. Photobiol., A Chem.* 336 (2017) 146–155.
6. Šekuljica, N.Ž., Prlainović, N.Ž., Jakovetić, S.M., Grbavčić, S.Ž., Ognjanović, N.D., Knežević-Jugović, Z.D., Mijin, D.Ž., *Clean* 44 (2016) 891–900.
7. Verma, Y., *Toxicol. Ind. Health* 24 (2008) 491– 500.

Značaj geohemijskih i mineraloških karakteristika sedimenata za predviđanje procese degradacije terena

Milica Kašanin-Grubin[1a], Aleksandra Šajnović[1], Gordana Gajica[1], Vladimir Simić[2], Ksenija Stojanović[3], Ilija Brčeski[3], Branimir Jovančićević[3]

[1]Univerzitet u Beogradu, IHTM, Njegoševa 12, Beograd

[2]Univerzitet u Beogradu, Rudarsko-geološki fakultet, Đušina 7, Beograd

[3]Univerzitet u Beogradu, Hemijski fakultet, Studentski trg 12-14, Beograd

[a] mkasaningrubin@chem.bg.ac.rs

Antropogeni uticaji na životnu sredinu započeli su pre nekoliko hiljada godina, ali su oni do industrijalizacije bili kratkotrajni i lokalizovani u vremenu i prostoru. Kasnije se stepen ljudskog uticaja na prirodno okruženje pojačavao i sada je znatno veći nego u bilo kom trenutku u ljudskoj istoriji. Tokom poslednjeg veka predeli se najčešće modifikuju i degradiraju rudarstvom, širenjem infrastrukture i urbanog razvoja [1] a efekti mogu da traju hiljadama, pa čak i milionima godina [2]. U cilju sprečavanja degradacije terena neophodno je razumeti kako će predeli reagovati na nametnute promene i to najpre u smislu a) verovatnoće da će predeo odgovoriti na nametnute promene, b) određivanja vremena, trajanja, brzine i načina odgovora i c) potencijala da se dat sistem vremenom stabilizuje [3].

Cilj ovog istraživanja je da se utvrdi značaj geohemijskog i mineroloških sastava sedimenata za određivanje osetljivosti terena na promene u životnoj sredini. U tu svrhu analizirano je 60 uzoraka sedimenata iz 5 neogenih jezerskih basena, a to su Loparski, Valjevski, Toplički, Aleksinački i Kremanski basen. Ovi baseni su posebno interesantni zato što nose fosilne i/ili mineralne resurse, i postoji mogućnost da pri površinskoj eksploataciji ovih resursa dođe do degradacije životne sredine.

Na svim uzorcima sedimenata određene su njihove minerološke, petrografske i geohemijske karakteristike. Sadržaji elemenata određeni su optičkom emisionom spektrometrijom sa indukovano spregnutom plazmom (ICP-OES), a mineralni sastav određen je rendgenskom difrakcijom praha (XRD). Sadržaj organskog ugljenika (Corg) određen je elementarnom analizom nakon uklanjanja karbonata hlorovodoničnom kiselinom. Električna provodljivost (EC) i pH su mereni u rastvoru 1 g fino sprašenog uzorka u 10 ml destilovane vode. Dostupni joni Na^+, K^+, Mg^{2+} i Ca^{2+} određeni su eksperimentom izluživanja tokom kog je 10 g uzorka potopljeno je u 100 ml destilovane vode i mućkano 24 h. Nakon toga materijal je filtriran i određene su koncentracije jona na ICP-OES-u. Disperznost sedimenata je određena pomoću odnosa EC i koeficijenta adsorpcije natrijuma (Sodium Adsorption Ration SAR).

Ispitivani sedimenti iz neogenih jezerskih basena su laporci sa promenjivim odnosom karbonanta i minerala glina, karbonatne stene izgrađene od kalcita ili dolomita, zatim bituminozni šejlovi i tufovi. U svim ispitivanim sedimentima uočena je statistički značajna pozitivna korelacija između pH i EC, kao i statitstički značajna negativna korelacija između pH i Corg. Odnos EC/SAR ukazuju na to da su laporci i tufovi najviše skloni disperziji prvenstveno zbog prisustva minerala glina. Međutim, bituminozni šejlovi koji su takođe bogati mineralima glina su znatno manje disperzni usled visokog sadržaja organske materije. S obzirom da disperznost sedimenata znatno pospešuje njihovu erodibilnost, samim tim utiče i na osetljivost terena i njegov odgovor na nametnute promene. Iz tog razloga, na osnovu dobijenih rezultata može se zaključiti da su minerološke i geohemijske karakteristike sedimenata, i stena uopšte, važne za određivanje osetljivosti terena na promene u životnoj sredini.

Literatura

1. Hooke, R.LeB, Martín-Duque, J.F., Pedraza, J., 2012. Land transformation by humans: a review. GSA Today, 22, 12, 4-10.
2. Schoorl, J.M., Temme, A.J.A.M., Veldkamp, T. 2014. Modelling centennial sediment waves in an eroding landscape – catchment complexity. Earth Surface Processes and Landforms, 39, 1526-1537.
3. Downs, P.; Gregory, K. 2004. River Channel Management; Towards Sustainable Catchment Hydrosystem. Hodder Arnold: London, 395p.

Sezonske varijacije koncentracija neorganskih anjona u atmosferskim aerosolima

Seasonal variations of concentrations of inorganic anions in atmospheric aerosols

Žaklina Todorović[1a], Ivana Sredović Ignjatović[2], Ljubiša Ignjatović[3], Antonije Onjia[4]

[1]Institut za nuklearne nauke “Vinča”, Univerzitet u Beogradu, Beograd, Srbija

[2]Poljoprivredni fakultet, Univerzitet u Beogradu, Beograd, Srbija

[3]Fakultet za fizičku hemiju, Univerzitet u Beogradu, Beograd, Srbija

[4]Tehnološko-metalurški fakultet, Univerzitet u Beogradu, Beograd, Srbija

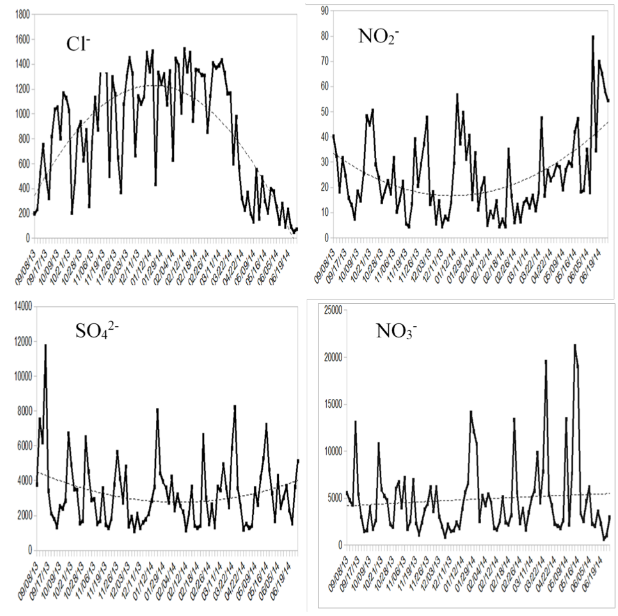
[a]zaklina@vinca.rs

Vodorastvorni joni čine jednu od glavnih komponenti atmosferskih aerosola. Neorganski anjoni, kao što su sulfati, nitrati i hloridi zajedno sa amonijum jonom, imaju veliki uticaj na hidroskopsku prirodu i kiselost aerosola. Njihove koncentracije značajno variraju u zavisnosti od lokacije i godišnjeg doba [1].

U ovom radu 94 uzorka atmosferskih aerosola analizirano je na sadržaj neorganskih anjona (hloridi, nitriti, nitrati i sulfati). Uzorkovanje je izvršeno u periodu od septembra 2013. godine do juna 2014. godine u Mirijevu, Beograd. 1 cm^2 svakog filtera je rastvaran u 10 ml dejonizovane vode i nakon mućkanja od 20 min. i filtriranja analiziran. Analiza je rađena na jonskom hromatografu Dionex DX 300 sa AS 11 analitičkom kolonom za razdvajanje. Kao mobilna faza korišćena je smeša metanola i hidroksidnih jona uz gradijentno eluiranje.

U analiziranih uzorcima atmosferskih aerosola detektovana su četiri neorganska anjona i to sulfati, nitrati, hloridi i nitriti. Koncentracije fluorida i fosfata su ispod kvantifikacionog limita. Dobijene su najveće koncentracije za nitrate koje su se kretale od 625 do 20396 ng m^{-3} i srednjom vrednošću od 5039 ng m^{-3}. Zatim slede sulfati sa koncentracijama od 1077 do 11705 ng m^{-3} i srednjom vrednošću od 3321 ng m^{-3}, hloridi sa koncentracijama od 53 do 1524 ng m^{-3} i srednjom vrednošću od 844 ng m^{-3}, dok su nitriti najmanje prisutni sa koncentracijama od 4,0 do 79 ng m^{-3} i srednjom vrednošću od 25 ng m^{-3}. Visoke koncentracije analiziranih anjona su očekivane, s obzirom da je u blizini mesta uzorkovanja industrijska zona u Pančevu, gradska deponija u Vinči i toplana.

Sezonske varijacije analiziranih anjona za ceo period uzorkovanja (od jeseni 2013. do leta 2014.) predstavljene su na slici 1. Vremenski trend ovih anjona predstavljen je kvadratnom krivom. Sulfati pokazuju trend povećanja koncentracija u jesen i leto sa minimalnim vrednostima u zimskom periodu. Povećana fotohemijska aktivnost je jedan od glavnih razloga za porast njihove koncentracije u ovom periodu [2]. SO_2 je dominantan antropogeni zagađivač vazduha koji sadrži sumpor. Nitriti pokazuju isti trend kao i sulfati. Za razliku od njih, hloridi pokazuju najveće koncentracije sa vrlo oštrim i značajnije višim pikovima u zimskom periodu. Nitrati ne pokazuju značajniji trend tokom celog analiziranog perioda već par većih porasta koncentracije ka letnjem periodu. Značajne sezonske varijacije analiziranih anjona ukazuju na uticaj različitih izvora, meteoroloških parametara i fizičko hemijskih procesa transformacija koji postoje u atmosferi.



Slika 1. Sezonske varijacije koncentracija (ng m^{-3}) hlorida, sulfata, nitrata i nitrita u atmosferskim aerosolima

Literatura

1. Wang, H., An, J., Cheng, M., Shen, L., Zhu, B., Li, Y., Wang, Y., Duan, Q., Sullivan, A., Xia, L., *Chemosphere* 148 (2016) 526-536.
2. Zhang, T., Cao, J.J., Tie, X.X., Shen, Z.H., Liu, S.X., Ding, H., Han, Y.M., Wang, G.H., Ho, K.F., Qiang, J., Li, W.T., *Atmos. Res*. 102 (2011) 110-119.

Uticaj različitih doza γ-zračenja na hidrolitičku stabilnost modifikovanih urea-formaldehidnih (UF) smola

The influence of different doses of γ-radiation on the hydrolytic stability of modified urea-formaldehyde (UF) resins

Vojislav Jovanović[1], Suzana Samaržija-Jovanović[1], Sonja Jevtić[1a],

Branka B. Petković[1], Gordana Marković[2], Milena Marinović-Cincović[3],

[1]Prirodno-matematički fakultet, Univerzitet u Prištini, Kosovska Mitrovica, Srbija

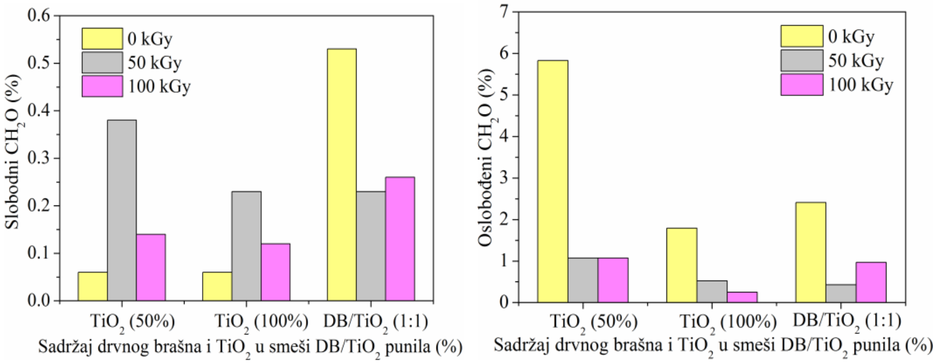
[2]Tigar, Pirot, Srbija

[3]Institut za nuklearnu nauku Vinča, Univerzitet u Beogradu, Beograd, Srbija

[a]jevticsonja88@gmail.com

Zbog emisije formaldehida (CH_2O) iz drvenih proizvoda, gde se urea- formaldehidne (UF) smole, između ostalog, koriste za impregnaciju drvenih panela koje se koriste u unutrašnjosti stambenih i drugih objekata poželjno je da procenat slobodnog formaldehida (CH_2O) u samoj smoli bude što manji, jer je poznato da formaldehid ima štetno dejstvo na čoveka, odnosno ceo živi svet. Pare formaldehida jako nadražuju disajne puteve. Koncentracije od 10-20 ppm otežavaju disanje, a koncentracije od 650 ppm mogu uzrokovati i smrt za samo nekoliko minuta. Često udisanje para niskih koncentracija mogu uzrokovati hronična oboljenja disajnih puteva. Simptomi i granice su individualni i javljaju se u širokim granicama izloženosti. Pojedine osobe mogu da osete simptome, kao što su iritacija očiju, grla, umor, glavobolja i mučnina, usled izloženosti i niskoj koncentaciji formaldehida (0.1 do 1 ppm). Osim slobodnog formaldehida, u samoj smoli, koji se spontano emituje, zbog niske otpornosti na vlagu, može doći do hidrolize UF smole što podrazumeva raskidanje samih veza u smoli (metilenetarskih) i dodatne emisije formaldehida u okolinu [1,2].

U ovom radu je ispitivana hidrolitička stabilnost modifikovanih UF smola sa “hvatačima” formaldehida, TiO_2 sa različitim sadržajem (3,75 g i 7,25 g) u UF smoli i kombinacijom TiO_2 i drvnog brašna (TiO_2/DB) u ekvimolarnim količinama. Tri modifikovane UF smole s odnosom formaldehida i uree (F/U) 0.8 s modifikovanim punilima su sintetizovani istim postupkom [3]. Hidrolitička stabilnost ispitivanih modifikovanih UF smola je određivana merenjem koncentracije oslobođenog formaldehida [4] iz modifikovane UF smole nakon kisele hidrolize. Zračenje sintetisanih modifikovanih smola je vršeno u vazdušnoj atmosferi u Co-60 radijacionoj jedinici na Institutu za nuklearne nauke, Vinča, Srbija. Uzorci smola su zračeni γ–zračenjem na sobnoj temperaturi i ukupnom apsorbovanom dozom od 50 kGy i 100 kGy [5].



Slika 1. Zavisnost koncentracije slobodnog i oslobođenog formaldehida od sadržaja i vrste punila u UF smoli pre i posle zračenja.

Pre zračenja najmanji procenat slobodnog formaldehida (0.06%) imaju uzorci koji su modifikovani TiO_2. Usled γ-zračenja dolazi do degradacije makromolekula što uzrokuje povećanje slobodnog formaldehida u zračenim uzorcima u odnosu na nezračene. Povećanje doze zračenja sa 50 kGy na 100 kGy dovodi do smanjenja količine slobodnog formaldehida u umreženoj UF smoli. Najmanji procenat slobodnog formaldehida nakon zračenja sa ukupnom apsorbovanom dozom od 100 kGy nalazi se u UF smoli koja sadrži 100% TiO_2 u količini od 0.12%. S druge strane i drvno brašno koje sadrži celulozu i hemicelulozu ima veliki broj hidroksilnih grupa, takođe reaguje sa slobodnim formaldehidom iz UF smole. γ-zračenjem je smanjen procenat oslobođenog formaldehida u svim ispitivanim modifikovanim UF smolama, posebno kod uzoraka smole sa TiO_2 u količini od 100% u izosu od 0.25%. To se objašnjava činjenicom da kisela hidroliza nakon zračenja dovodi do dodatnog umrežavanja u svim uzorcima, što rezultuje „hvatanjem“ formaldehida u toku samog procesa hidrolize. Uzorci ispitivane kompozitne smole sa TiO_2/DB pokazuju lošiju hidrolitičku stabilnot zbog povećane interakcije između hidroksilnih i karbonilnih grupa u drvnom brašnu i hidroksilnih grupa sa površine TiO_2, zbog čega dolazi do smanjene interakcije hibridnog punila sa polimernom matricom odnosno smanjuje se procenat slobodnih grupa koje bi inače reagovale sa formaldehidom i smanjile njegovu emisiju iz smole.

Literatura

1. T. Jahns, H. Ewen, and H. Kaltwasser, *J. Polym. Environ.*,11 (2003) 155.
2. G.E. Myers, *Forest. Prod. J.,* 35 (1984) 35.
3. Samaržija-Jovanović S, Jovanović V, Konstantinović S, Marković G, Marinović-Cincović M, *J. Therm. Anal. Calorim.,*104 (2011) 1159.
4. Walker J. F., Formaldehyde, 3rd ed., American Chemical Society Monograph Series, New Jork 251 (1967).
5. Marković V.M., Eymery R., Yuan H.C., *Radiat. Phys.Chem.,* 9 (1977) 625.

First study of electrochemical behavior of herbicide pethoxamid and its voltammetric determination in river water

Sonja Jevtić [1a], Vesna Vukojević[2], Slađana Đurđić[2], Marija V. Pergal[3], Dragan Manojlović[2], Branka B. Petković[1], Dalibor M. Stanković[2,4]

[1]Depatment of Chemistry, Faculty of Natural Science and Mathematics, University of Priština, Kosovska Mitrovica, Serbia

[2]Faculty of Chemistry, University of Belgrade, Belgrade, Serbia

[3]Institute of Chemistry, Technology and Metallurgy, Center of Chemistry, University of Belgrade, Belgrade, Serbia

[4]The Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia

[a]jevticsonja88@gmail.com

Pethoxamid (POA) is relatively new herbicide and it belongs to group of chloroacetamides. It inhibits the germination of target weeds in corn, soybeans, peas and beans, tobacco and other crops and it can affects on herbicide-resistant weeds. There are no many research records about this, in the future quite applicable, herbicide. Bearing in mind that pethoxamid is high soluble in water, with almost no sorption in soils [1], the leaching and runoff of this compound in ground and surface water is a real threat. Pethoxamid residues in soil, water food and feed of plant origin usually were determined by using liquid chromatography with tandem mass spectrometry (LC–MS/MS) [2] while some other analytical methods were used for determination of pesticides [3].

The electroanalytical methods are noted as fast and cost-effective analytical methods for determination of many analytes of environmental interest. As far as we know, this is a first report about electrochemical behavior of herbicide pethoxamid and its electroanalytical determination. This method is based on the electrochemical oxidation of pethoxamid in Britton-Robinson buffer solution at pH 4 at a boron-doped diamond electrode. This type of carbon electrode is almost resistant to contamination of surface with various chemical spaces, easy to maintain and has a very wide working potential window which could provide insight into the electrochemical oxidation of pethoxamid at high anodic potentials.

All electrochemical measurements (cyclic and square-wave voltammetry) were performed on PalmSens 3 potentiostat/galvanostat/impedance analyzer with PSTrace software (PalmSens BV, Netherlands). Three-electrode system in the electrochemical cell was consisted from Ag/AgCl (1M KCl) reference electrode and platinum wire counter electrode, while working electrode was boron-doped diamond electrode. BDD electrode was electrochemicaly prepared as it was written before [4]. Cyclic voltammetry provided a well defined oxidation peak at +1.35 V, and this peak was used as a peak of quantification at a optimal pH value 4 (Figure 1 a). The square-wave voltammetry was chosen as suitable technique for analytical determination of pethoxamid with an established optimal working conditions (pulse amplitude of 60 mV and frequency of 10 Hz).

The voltammograms obtained for standard solutions from 1 to 100 µM and corresponding calibration curve were shown on Figure 1 b.

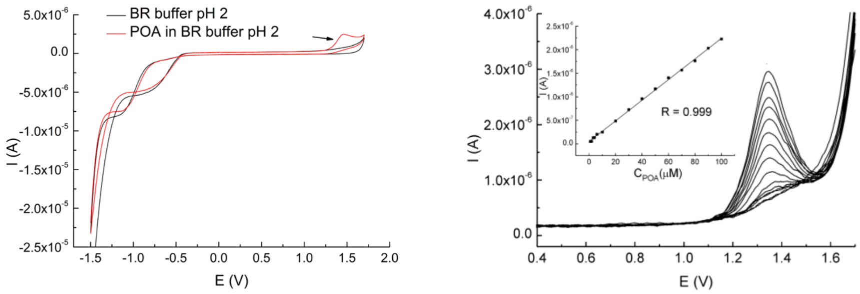


Figure 1. a) Cyclic voltammograms of BR buffer pH 2 with and without 100 µM of pethoxamid; b) SW voltammograms of different concentrations of pethoxamid at optimized working conditions in BR buffer, pH 4, at BDDE. Inserted figure: corresponding calibration curve

The method was applied for selective quantification of pethoxamid from spiked river water samples with good recovery of 92.0 to 104.6% for standard solutions of POA and good agreement with comparative HPLC method (97.6-98.1%). The results of this research indicate successful, fast, simple, reliable and cheap estimation of pethoxamid content in the surface water samples with no electrode surface modification and time-consuming sample preparation.

References

1. Hvězdová M. et al. *Science of the Total Environment* 613–614 (2018) 361–370
2. Arena M. et al., *EFSA Journal*, 15 (2017).
3. Liang H. C., Bilon N., Hay M. T., *Water Environment Research*, Volume 86 (2014)
4. Jevtić S., Stefanović A., Stanković D. M., Pergal M. V., Ivanović A. T., Jokić A., Petković B. B., *Diamond & Related Materials* 81 (2018) 133–137

Sequestration of lindane in contaminated sediment amended with carbon-rich sorbents

Snežana Maletić[1a], Marko Grgić [1], Jelena Belin[1], Srđan Rončević[1], Marijana Kragulj Isakovski[1], Jasmina Agbaba[1], Božo Dalmacija[1]

[1]Faculty of Sciences, University of Novi Sad, Novi Sad, Serbia

[a]snezana.maletic@dh.uns.ac.rs

Introduction. Lindane (LND) was ubiquitously used as an insecticide for more than 50 years all around the world, before it was banned and listed as a persistent organic pollutant at the Stockholm Convention [1]. The structural persistence of lindane leads to its accumulation in the sediment environment, which acts as a potential sink for this hazardous chemical [2]. These sediments may become a secondary source of pollution when they are eroded (e.g. due to flooding and bank erosion) and transported further downstream, which raises great concerns about the continuing risk of lindane [3]. The management, stabilization, and remediation of contaminated sediments remain challenging tasks for environmental engineers [3]. Traditional approaches do not always achieve risk reduction goals for human health and ecosystem protection and can even be destructive for natural resources. An alternative is to locally change the geochemistry to stabilize and sequester the contaminants and render them biologically unavailable. The main aim of this study was therefore to investigate the potential for improving sorption and sequestration of lindane in sediment by carbon-rich amendments such as activated carbon and humus.

Materials and methods. The sediment used in this study had the following characteristics: 31.6% clay, 11.9% silt, 15.6% coarse sand. The sediment was spiked with LND in methanol and left to age in the dark for 2 years. After aging, the sediment was amended with 0.1%; 0,5%; 1% and 10% of activated carbon (AC) and humus (HC). The amended sediment was left to age for 180 days in the dark with daily mixing, in order to investigate long-term effects of the sediment amendments. The efficacy of the amendments, with respect to its doses and aging time, was assessed by bioavailability tests using desorption with the XAD4 resin [4], *Zea mays* phytotoxicity and a phytoextraction test [4]. A two compartments model was used to describe the two-stage process LND desorption [2].

Results and discussion. The desorption kinetic data obtained by the two-compartment model (Fig. 1), showed that 67.1% of LND was found in the fast desorbing domain of organic matter (F_{rap}). The XAD beads sustained a constant driving force for LND release from sediment due to the beads' large sorption capacity for hydrophobic organic compounds [2]and 75% reduction for HCH, and 93% and 59% decrease for DDTs in aqueous equilibrium concentration, respec-tively. Similarly, the reduction efficiencies of DDT and HCH uptake by semipermeable membrane devices (SPMDs. Both carbon-rich amendments in all applied doses significantly reduced the LND bioavailable fraction. The results indicated that AC had a stronger ability to bind LND.

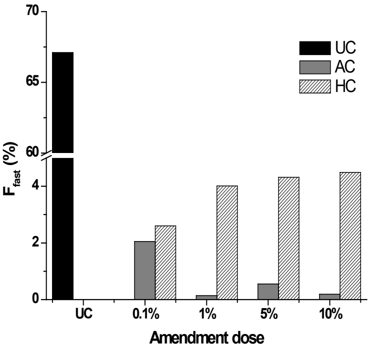


Figure 1. Percentage of LND bioavailable fraction

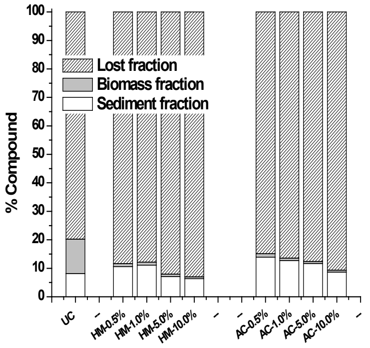


Figure 2. Distribution of LND

Zea mays germination test exhibited no adverse effect, hence 100% of all seeds were germinated in the observed period of time. LND accumulation in the plant biomass in the unamended sediment (UC) was significantly higher than in the all HC and AC amended sediment (Fig. 2). In the amended sediment, increasing the amendment dose led to a decrease in the accumulated LND in the plant biomass. No significant difference was observed between the two different amendments applied. From the residual concentrations, it can be noted that about 90% of the initial sediment concentration was removed (by processes like sequestration, (bio)degradation, or volatilization) [4]

Conclusion. The dose of 0.1% for both the carbon-rich amendments applied was enough to efficiently sequester and immobilize linden in sediment. This is confirmed by the phytoextraction test where a significantly lower amount of lindane was accumulated.

Acknowledgments. The authors gratefully acknowledge the support of the Provincial Secretariat for Higher Education and Scientific Research, Autonomous Province of Vojvodina (Project No. 114-451-2526/2017-02).

References

1. Miao, J., Chen, X., Xu, T., Yin, D., Hu, X., Sheng, D., *Chemosphere* (2018) 350-357.
2. Cornelissen, G., Rigterink, H., Ten Hulscher, D.E.M., Vrind, B.A., Van Noort, P.C.M., *Environ. Toxicol. Chem.* 20 (2001) 706–711.
3. Hua, S., Gong, J.-L., Zeng, G.-M., Yao, F.-B., Guo, M., Ou, X.-M., *Chemosphere* 177 (2017) 65–76.
4. Rončević, S., Spasojević, J., Maletić, S., Jazić, J.M., Isakovski, M.K., Agbaba, J., Grgić, M., Dalmacija, B., *Environ. Sci. Pollut. Res.* 23 (2016) 3239–3246.

Adsorption potential of hydrochars obtained from sugar beet pulp toward alachlor

Marijana Kragulj Isakovski[1a], Snežana Maletić[1], Jelena Tričković[1], Jasmina Agbaba[1], Srđan Rončević[1], Aleksandra Tubić[1], Božo Dalmacija[1]

[1]Faculty of Sciences, University of Novi Sad, Novi Sad, Serbia

[a]marijana.kragulj@dh.uns.ac.rs

Introduction. Alachlor is a chloroacetanilide herbicide used to control annual grasses and broad-leaved weeds, primarily in corn and soybeans. While the quantity of applied alachlor has decreased over the past few decades, contamination from leaching and runoff remains an issue. To protect water quality and human health, it is necessary to understand its adsorption mechanism onto carbon-rich materials as potential adsorbents for its removal [1]. Hydrochar (HC) is one such carbon-rich material and is obtained by the hydrothermal carbonization of biomass [2]. The main objective of this study was to investigate the adsorption potential of hydrochars produced from hydrothermally carbonizing sugar beet pulp, toward alachlor. Adsorption parameters for alachlor were determined for three different HCs obtained at three different temperatures: HC-180°C; HC-200°C and HC-220°C.

Materials and methods. All adsorption isotherms were performed in batch adsorption experiments. The background solution was 0.01 M $CaCl_2$ in distilled water with 100 mg/l NaN_3 as a biocide. The amount of hydrochar in each experiment corresponded to a sample/solution ratio that resulted in 20-80% uptake of alachlor. Flasks containing premeasured adsorbent and background solution were agitated in an ultrasonic bath for 15 min before a certain volume of methanol stock solution of alachlor was spiked and equilibrated at room temperature by continuous shaking for 24 h. The flasks were allowed to settle for 24 h and a sample of the supernatant was removed for gas-chromatographic determination of alachlor.

Results and discussion. All adsorption isotherms were described by the Freundlich and Langmuir models (Fig 1). Based on the results obtained from adsorption experiments in equilibrium conditions, it can be concluded that the adsorption process is better described by the Langmuir (R^2=0.981-0.994) model than the Freundlich model (R^2=0.964-0.990). The maximum sorption capacities, q_{max}, for all investigated HCs were in the range 1464-5579 mg/kg. Based on the good fit with the Langmuir model, it can be concluded that the monolayer adsorption occurs on a limited and fixed number of active sites that are identical in terms of affinity for the adsorbate. It is interesting to note that the highest q_{max} value was obtained for HC-220°C, indicating that increasing the temperature increases the carbon content, and thus increases the ability to adsorb organic compounds. These results are in line with other authors [3]

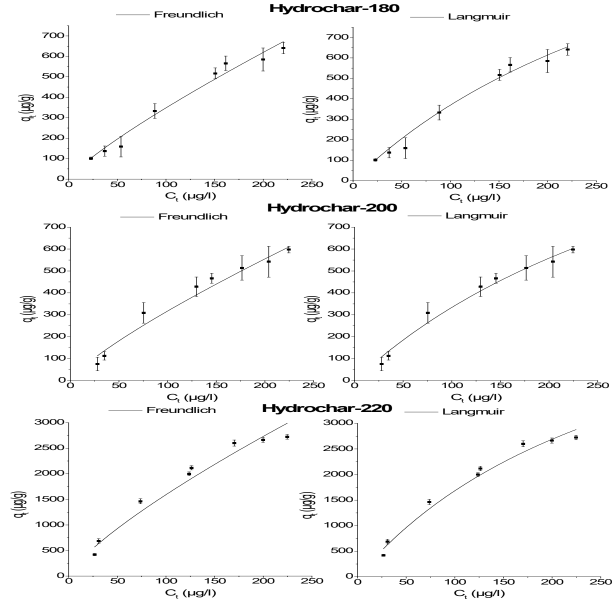


Figure 1. Adsorption isotherms of alachlor on investigated hydrochars

In addition, the type of adsorption process can be determined based on the separation factor R_L, which can be calculated using the obtained K_L value. The R_L value for adsorption of alachlor on all investigated HCs was lower than 1, suggesting that the adsorption process is favourable. At lower concentrations of adsorbates in the solution, a higher degree of adsorption is achieved, which gradually decreases as the concentration of alachlor in the solution increases.

Conclusion. Based on this results, it can be noticed that adsorption potential of hydrochars toward alachlor depend on the temperature of hydrothermal carbonization and used biomass.

Acknowledgments. The authors gratefully acknowledge the support of the Provincial Secretariat for Higher Education and Scientific Research, Autonomous Province of Vojvodina (Project No. 142-451-3597/2017-01/01).

References

1. Mendes, K.F., Hall, K.E., Spokas, K.A., Koskinen, C.W., Tornisielo, V.L. (2017) *Agronomy* 7, 64.
2. Han, L., Ro, K.S., Sun, K., Sun, H., Wang, Z., Libra, J.A., Xing, B. (2016) *Environ. Sci. Technol.* 50, 13274−13282.
3. Elaigwu S.E., Greenway G.M. (2016) *Int.J Ind. Chem.* 7, 449-456.

Komparacija efikasnosti metode fitoremedijacije procednih voda deponije primenom *Eichhornia crassipes*

Efficiency comparison of the phytoremediation of landfill leachate using *Eichhornia crassipes*

Katarina Antić[1], Szabolcs Pap[1], Dragan Adamović[1], Maja Turk Sekulić[1],

Jelena Radonić[1a]

[1]Departman za inženjerstvo zaštite životne sredine i zaštite na radu, Fakultet tehničkih nauka, Univerzitet u Novom Sadu, Novi Sad, Srbija

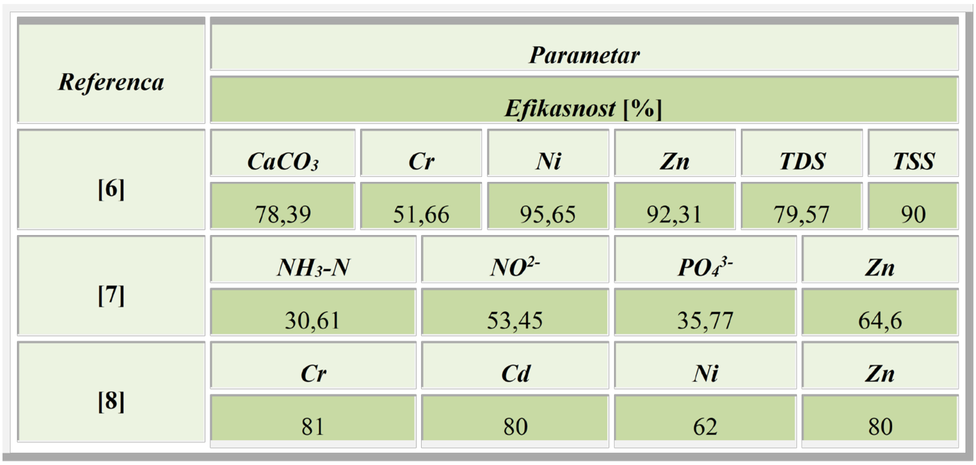
[a]jelenaradonic@uns.ac.rs

Proces formiranja deponijskog filtrata obuhvata rastvaranje čvrstih supstanci u vodi, pri čemu se ista procеđuje kroz telo deponije i izdvajanje rastvorenih ili suspendovanih materija nastalih biološkim i hemijskim procesima koji se neminovno odigravaju unutar tela deponije. Polutanti zastupljeni u okviru procednih voda komunalnih deponija čvrstog otpada klasifikuju se u četiri grupe: *rastvorljive organske komponente* (isparljive masne kiseline, varijateti huminskih i fluvinskih jedinjenja), *neorganske makrokomponente* (Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, Fe^{2+}, Mn^{2+}, Cl^-, SO_4^{2-}, HCO^{3-}), *teški metali* (Cd^{2+}, Cr^{3+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}) i *ksenobiotičke organske komponente* (ugljovodonici, fenoli, hlorovana alifatična jedinjenja, pesticidi, dioktil-ftalati) [1]. Usled kompleksnog hemijskog sastava, razvijene su različite metode zbrinjavanja i tretmana procednih voda deponija, te razlikujemo: *usmeravanje procednih voda* (mokra polja, recirkulacija, uporedni tretman procedne vode sa komunalnim otpadnim vodama u okviru opšteg kanalizacionog sistema), *biološki tretman*, *fizičko-hemijski tretman* i *membransku filtraciju* [2]. Naročito efikasnom u odnosu na konvencionalne tretmane procednih voda deponija, sa aspekta redukcije koncentracija teških metala, pokazala se alternativna metoda, fitoremedijacija.

Fitoremedijacija predstavlja ekonomski održivu i jednostavnu metodu koja se definiše kao projektovana primena zelenih biljaka u cilju ekstrakcije, akumulacije i stabilizacije zagađujućih materija. Aktivnostima korenovog sistema realizuje se izdvajanje zagađujućih materija i vode iz tretiranog medijuma, nakon čega otpočinje proces njihove degradacije, metabolisanja ili akumulacije u biljci, dok proces evapotranspiracije, koji se odvija u nadzemnom delu, podstiče kretanje vode kroz biljku. Unapređenje efikasnosti metode fitoremedijacije ostvaruje se primenom hiperakumulirajućih biljnih vrsta. Hiperakumulatori predstavljaju grupu biljaka koje apsorbuju toksične elemente i akumuliraju ih u nadzemnom delu biljke u nivoima znatno većim od uobičajenih koncentracija, pri čemu su negativni efekti navedene aktivnosti mali ili neznatni po biljke [3]. Hiperakumulacija teških metala uslovljena je primenjenom biljnom vrstom, karakterističnim parametrima tretiranog medijuma (pH, sadržaj organske materije, jonsko-izmenjivački kapacitet), kao i vrstama teških metala čije se koncentracije redukuju [4]. Visoko efikasnim u redukciji i monitoringu teških metala pokazale su se akvatične makrofite, naročito vodeni zumbuli (*Eichhornia crassipes*, familija *Pontederiaceae*) [5].

Efikasnost metode fitoremedijacije procednih voda deponija primenom vodenih zumbula eksperimentalno je ispitivana u okviru tri prethodno realizovana istraživanja. Rezultati istraživanja su prikazani u **Tabeli 1.**

Tabela 1. *Efiskasnost metode fitoremedijacije procednih voda sa deponijskih lokaliteta Moshi (India)* [6], *Pulau Burung (Malezija)* [7] *i Gradska deponija Novi Sad (Republika Srbija)* [8] *primenom Eichhornia crassipes*



Referenca	***Parametar***					
	***Efikasnost* [%]**					
[6]	$CaCO_3$	*Cr*	*Ni*	*Zn*	*TDS*	*TSS*
	78,39	51,66	95,65	92,31	79,57	90
[7]	NH_3-N	NO^{2-}	PO_4^{3-}	*Zn*		
	30,61	53,45	35,77	64,6		
[8]	*Cr*	*Cd*	*Ni*	*Zn*		
	81	80	62	80		

Prikazani eksperimentalni rezultati potvrđuju visoku efikasnost metode fitoremedijacije procednih voda deponije primenom *Eichhornia crassipes*, sa aspekta redukcije koncentracija teških metala, kao i sa aspekta redukcije koncentracija fosfata, nitrita, tvrdoće vode, ukupnih rastvorenih i suspendovanih materija.

Literatura

1. Kjeldsen, P., Barlaz, M.A., Rooker, A.P., Baun, A., Ledin, A.,Christensen, T.H. *Environ. Sci. Tech.* 4 (2002) 297-336.
2. Renou, S., Givaudan, G.J., Poulain, S., Dirassouyan, F., Moulin, P. *Journal of Hazardous Materials* 150 (2008) 468-493.
3. Baker, A.J.M., Brooks, R.R.J. *Biorecovery.* 1 (1989) 81-126.
4. Sarma, H. *J. Environ. Sci. Tech.* 4 (2011) 118-138.
5. Xian, X., Shokohifard, G. *Water Air Soil Pollut.* 45 (1989) 265-273.
6. Verma, S., Mishra, R., Pandit, B., Chatterje, A., Jadhav, S.S., Gaoture, S.P., Sarode, H.P. *Inter. J. Engin. Rese. Gene. Sci.* 3 (2015) 1234-1237.
7. Akinbile, O.C., Yusoff, S.M., Shian, M.L. Bioreme. Jour. 16 (2012) 9-18.
8. Antić, K., Pap, S., Radonić, J. *Zbornik radova FTN.* 7 (2017) 1335-1338.

Preconcentration of heavy metals by the solid-phase extraction disk based on activated carbon derived from waste tires

Ksenija Kumrić[1a], Radojka Vujasin[2], Đorđe Petrović[3], Aleksandar Devečerski[2], Latinka Slavković-Beškoski[4], Ljiljana Matović[2]

[1]Laboratory of Physics, Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia

[2]Laboratory of Materials Sciences, Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia

[3]Laboratory of Radioisotopes, Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia

[4]Laboratory of Chemical Dynamics and Permanent Education, Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia

[a]kkumric@vinca.rs

Introduction. Heavy metals are considered as serious inorganic pollutants which have toxic effects on human health, animals, plants and life in aquatic systems. Direct determination of heavy metals in environmental samples by the modern techniques is often difficult due to the complexity of sample matrix and the low concentrations of heavy metals. Therefore, separation and preconcentration of trace heavy metals prior to their analysis is required. The most widely used techniques for the separation and preconcentration of trace metals include liquid-liquid extraction (LLE) [1], cloud point extraction (CPE) [2], coprecipitation [3], ions exchange [4] and solid phase extraction (SPE) [5]. SPE is powerful tool for the preconcentration of analytes in environmental waters due to its advantages of high enrichment factor, high recovery, low cost, low consumption of organic solvents and the ease of automation. The choice of appropriate adsorbent is a crucial factor to obtain high recoveries and high enrichment factors in SPE procedure.

Over recent years there has been considerable interest in using low-cost waste materials as adsorbents of heavy metals from environmental samples. Activated carbon obtained from a waste tire has an adsorption capacity that is attractive and is greatly influenced by pore volume, surface area and pore size distribution [6]. The aim of this study was to evaluate the performance of SPE disks based on activated carbon derived from waste tires for the preconcentration of the selected heavy metals from aqueous solution before determination by differential pulse anodic stripping voltammetry.

Results and discussion. Carbon-based material used in this study was prepared by pyrolysis of waste rubber granules. The obtained carbon material was chemically activated using KOH as an activating agent (mass ratio of KOH/carbonized material was 4:1). Then, this material (100 mg) was dispersed in 6% Triton X-100. The dispersion was filtered through the filter paper with the pore size 1 - 2 mm using glass Büchner funnel as SPE disk holder. The disk was washed with HNO_3 and milli-Q H_2O, and dried at room temperature. After that, the prepared disk was ready to use for the preconcentration of the selected heavy metal ions, Pb(II), Zn(II), Cu(II) and Cd(II).

The aqueous sample solution (20 mL, pH 5.5) containing 1 mg L^{-1} of each heavy metal was passed through the SPE disk at a flow rate of 3 mL min^{-1}, the disk was dried under vacuum and the adsorbed heavy metal ions were desorbed with eluent (4 mL) at a flow rate of 1 mL min^{-1}. The concentration of heavy metal ions in the eluent was determined with a 797 VA Computrace polarography system (Metrohm, Switzerland) using the Metrohm's procedure for the voltammetric determination of Zn, Cd, Pb and Cu in water samples (no. 231/2 e). Various concentrations of HNO_3 and HCl were used for the elution of heavy metal ions from the SPE disk (Fig. 1).

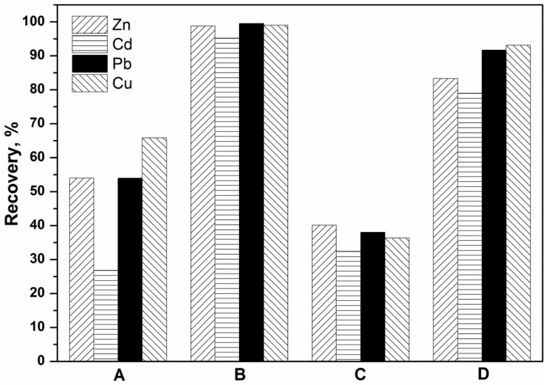


Fig. 1. The influence of various eluents on the recoveries of Zn, Cd, Pb and Cu (A, B: 0.1, 1 mol L^{-1} HNO_3, respectively; D, E: 0.1, 1 mol L^{-1} HCl, respectively)

Based on the presented results, it was found that quantitative recoveries (>95%) for all analyte ions were obtained with 1 mol L^{-1} HNO_3. Preliminary experiments demonstrated the feasibility of the developed SPE method for the determination of trace heavy metals in water samples. Further experiments will be oriented toward the optimization of the proposed method and determination of the detection limit for the investigated metals under the optimized conditions.

Acknowledgment. The authors acknowledge the support to this work provided by the Ministry of Education, Science and Technological Development of Serbia through the projects No. III 45006 and No. III 45012.

References

1. Igarashi, S., Takahashi, A., Ueki, Y., Yamaguchi, H., *Analyst* 125 (2000) 797-798.
2. Silva, E. L., Roldan, P. S., *J. Hazard. Mater.* 161 (2009) 142-147.
3. De Wuilloud, J. C. A., Wuilloud, R. G., Silva, M.F., Olsina, R. A.,Martinez, L. D., *Spectrochim. Acta Part B*57 (2002) 365-374.
4. Pehlivan, E., Altun, T., *J. Hazard. Mater.*140 (2007) 299-307.
5. Duran, A.,Tuzen, M., Soylak, M., *J. Hazard. Mater.*169 (2009) 466-471.
6. Mogolodi Dimpe, K., Mpupa, A., Nomngongo, P.N., *Spectrochim. Acta Part A* 188 (2018) 341-348.

Lead isotope ratio as a tool for considering dissolving mechanism of soil components by *Macrolepiota procera*

Slađana Đurđić[1a], Vesna Vukojević[1], Jelena Mutić[1]

[1]Faculty of Chemistry, University of Belgrade, Belgrade, Serbia

[a]sladjanadj@chem.bg.ac.rs

Macrolepiota procera belongs to saprophite species and is considered a wild edible mushroom (cap is a edible part of the mushroom). It usually inhabit forests, but also lake areas [1]. Mushrooms and corresponding soli samples originate from the Mountain Goč (Rasina district, Serbia). The surface area of soil (1.0 g) was subjected modified BCR sequential extraction procedure (F1 (easily soluble fraction), F2 (reducibile fraction, F3 (oxidizable fraction), R (residual fraction). Also, 0.5 g of soil was subjected to total digestion (pseudo total (PT) fraction) [2]. Mushrooms were divided into a cap and stipe and samples were digested with 4 mL HNO_3 and 1 mL H_2O_2. For determination of lead isotope ratios samples from each stage and mushroom samples were diluted and final concentration of lead was below 40 μg/L. In all samples was added Tl which final concentration was 2 μg/L.

NIST SRM 981 (Common Lead Isotopic Standard, USA) was used for making standard solutions and quality control, as well as for the correction isotope ratios on mass bias effect. NIST SRM 997 (Isotope Standard for Thallium, USA) was used as an internal standard. Inductively coupled plasma mass spectrometer (ICP-Q- MS, Thermo Scientific Xseries 2, UK) was used for determination of lead isotope ratios. ICP-Q-MS has no satisfactory accuracy and precision for lead isotope ratios analysis [3], therefore parameters such as dwell time and dead time of detector were optimized. Dwell time was optimized for each isotope (^{204}Pb was 0.100 s, ^{206}Pb, ^{207}Pb, ^{203}Tl, ^{205}Tl was 0.025 s), while the optimized dead time was 40 ns. Also, performed the corrections intensity ^{204}Pb with ^{202}Hg and ^{204}Hg. Obtained lead isotope ratios were corrected on mass bias effect usnig potential algoritam and external corection [3].

Results: Fractions are mostly difference by ^{208}Pb/^{206}Pb and ^{206}Pb/^{207}Pb. The ^{207}Pb/^{204}Pb was similar in all fractions. Isotope ratios such as ^{206}Pb/^{204}Pb and ^{208}Pb/^{204}Pb were similar in almost all factions, but in F1 were lowest. Also, in F1 was noticed the lowest ^{206}Pb/^{207}Pb (1.133) and largest ^{208}Pb/^{206}Pb (2.126). A low ^{206}Pb/^{207}Pb in easily soluble fraction of surface soil is a strong indicator of anthropogenic lead in the soil [4]. Comparing the obtained data (F1 and PT) with the literature, a similar distribution of ^{206}Pb/^{207}Pb in F1 with European gasoline can be noticed. European gasoline was characterized by a low ^{206}Pb/^{207}Pb and a high ^{208}Pb/^{206}Pb [2]. On the another hand, based on a high ^{206}Pb/^{207}Pb (1.177) in PT, it can be assumed presence of natural (litohgenic) lead in this fraction [4]. All lead isotope ratios in cap and stipe were similar. PCA (Principal Component Analysis) method was used to establish a relationship between lead isotope ratio in mushrooms and fractions. When used the PCA on F1 and mushrooms, there is no separation between cap, stipe and F1 (Figure 1A.), so it can be concluded that the mushroom adopted most available lead. Comparing F2 with cap and stipe, a partial separation of F2 was noticed (Figure 1B.). F2 fraction (Fe-Mn oxides) is an important scavengers of lead in the soil [4]. The mechanism of fungal oxidation of Fe and Mn is probably non-enzymatic, and oxidation involves certain metabolic products [5]. Partial overlap indicates a decreased ability of mushroom to completely dissolve Fe-Mn oxides. Larger grouping of PT is shown on Figure 1C. Biochemical degradation of minerals is based on the release of organic acids by the mushroom [5]. This can indicate that Macrolepiota procera has very small, or even does not has ability to dissolve the minerals. Metabolites such as oxalic and citric acid, which mushroom secretion through the mycelium, are not strong enough to destroy minerals [5].

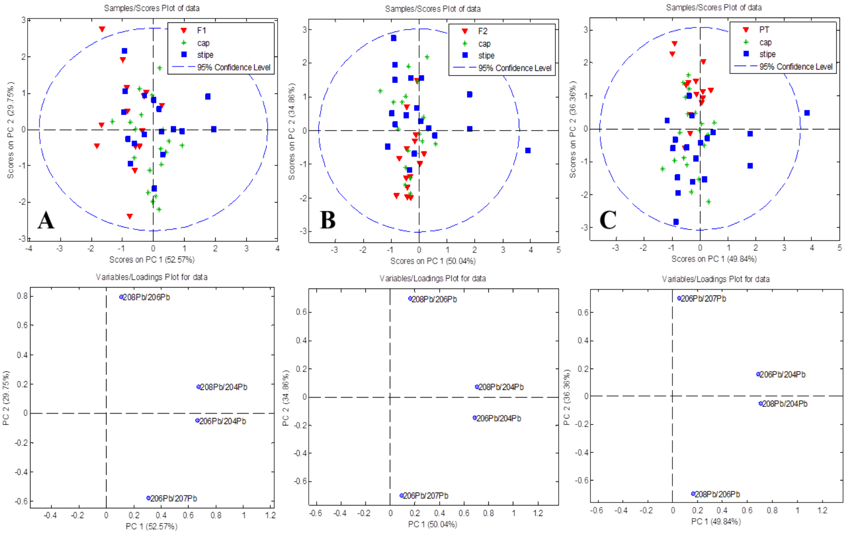


Figure 1. Score and loading plots for cap and stipe *vs* A) F1; B) F2 and C) PT.

References

1. Gucia, M., Jarzyńska, G., Rafał, E., Roszak, M., Kojta, A., Osiej, I., Falandysz, *J. Environ. Sci.* Pollut. Res. 19 (2012) 416-431
2. Bacon, J. R., Farmer, J. G., Dunn, S. M., Graham, M. C., Vinogradoff, S.I. *Environ. Pollut.* 141 (2006) 469-481
3. Marguí, E., Iglesias, M., Queralt, I., Hidalgo, M. *Talanta* 73 (2007) 700-709
4. Wong, C. S. C., Li, X. D. *Sci. Total Environ.* 319 (2004) 185-195
5. Gadd, G. M., Rhee, Y. J., Stephenson, K., Wei, Z. *Environ. Microbiol. Rep.* 4 (2012) 270-296

Analytical approach for detection of ergosterol in mushrooms based on modification free electrochemical sensor

Vesna Vukojević[1a], Slađana Đurđić[1], Tanja Ćirković Veličković[1], Jelena Mutić[1], Dalibor M. Stanković[1,2]

[1]Faculty of Chemistry, University of Belgrade, Belgrade, Serbia

[2]The "Vinča" Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia

[a]vvukojevic@chem.bg.ac.rs

Ergosterol is a major sterol found in the plasma membranes of fungi and protozoa, serving many of the same functions as cholesterol in animals and humans [1]. This compound can be usually named as provitamin D2. It is known to serve directly or either indirectly as bioactive sterol possessing several pharmacological functions such as anti-oxidative, cardiovascular, anti-inflammatory [2].

Several techniques are proposed for ergosterol quantification, dominantly based on chromatographic and NIR techniques. Due to advantages of electrochemical methods such as low-cost, easily manipulation steps, non-expensive equipment, the main goal of this work is to offer simple but satisfactory sensitive and selective electroanalytical procedure for ergosterol detection. Poor solubility of ergosterol limits its determination in water and based on this fact we tested ergosterol electrochemical behavior in various organic solvent in order to found optimum condition for its successful detection, and to test possible quantification in real mushrooms samples in comparison with standard methods.

All electrochemical measurements were done using a CHI 760b potentiostat/galvanostat (CH Instruments, USA). The working cell was equipped with standard three electrode system, where boron doped diamond (BDD) electrode was used as working, an Ag/AgCl and platinum wire as reference and counter electrodes, respectively. Electrochemical behavior of ergosterol was tested in different organic solvents (DMF, DMSO, ACN, and DCM) containing 0.1 M TBAHFP as supporting electrolyte. The best oxidation response,taking into account peak current and peak shape, was obtained in ACN as solvent. Before construction of calibration plot, oxidation response of 0.1 mM Erg was investigated using differential pulse (DPV) and square wave voltammetry. Significantly better response was obtained using SWV this technique was selected for all futher measurments. In order to achieve best analytical response SWV operating parameters, pulse amplitude and frequency, were optimized. Under optimized experimental conditions (pulse amplitude 70 mV, frequency 110 Hz) linear working range from 2 to 200 μM was estimated, with limit of detection of 0.7 μM (Figure 1).

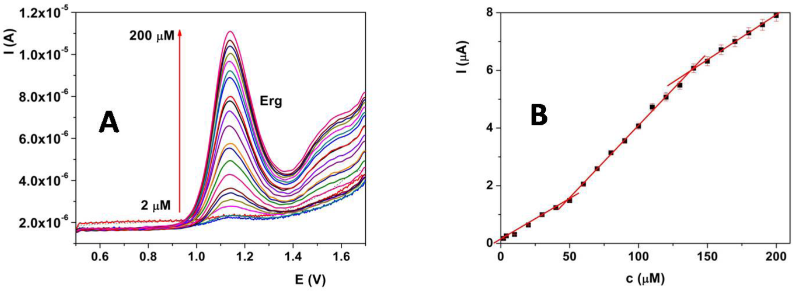


Figure 1. A) SWV voltammograms for different concentration of Erg in the range of 2 to 200 μM; B) calibration plot obtained from these measurements.

Selectivity of the developed procedure toward detection of ergosterol was tested using SWV under optimized experimental conditions. Some natural compounds, ascorbic acid, gallic acid and caffeine, were investigated as possible interfering substances (Figure 2). According to our results it can be considered that the proposed procedure offer satisfactory selective ergosterol determination and under developed parameters can be successfully used for application in real sample analysis.

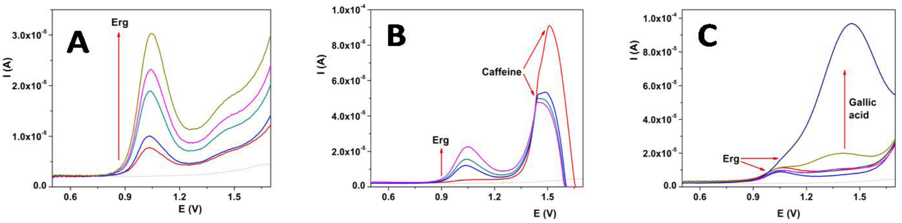


Figure 2. SWV voltammograms for different concentration of Erg in the presence of A) 500 μM of ascorbic acid; B) 500 μM of caffeince; C) different concentration (20 – 500 μM) of gallic acid.

Proposed methodology was successfully applied for estimation of Erg content in mushrooms extract with satisfactory results in comparison with spectrophotometric procedure. Obtained results clearly show that developed analytical methodology can be adequate replacement for the, up to date, used methods and open novel approach for ergosterol detection.

References

1. Mannock, D. A., Lewis, R. N. A. H., McElhaney, R. N. Biochimica *et biophysica acta*, 1798 (2012), 376–388.
2. .Muniroh, M. S., Sariah, M., Zainal Abidin, M. A., Lima, N., Paterson, R. R. M., *Microbiol Meth*, 100 (2014) 143-147

Application of a Venturi reactor forcavitation purification processof wastewaters from phenol

Sandra Petković[1a], Borivoj Adnađević[2], Jelena Jovanović[2], Mihajlo Gigov[1], Marko Pavlović[1]

[1]Rudarski institut d.o.o., Batajnički put 2, 11080 Beograd

[2]Fakultet za fizičku hemiju, Univerzitet u Beogradu, Studentski trg 12-16 11158 Beograd

[a] sandra.petkovic@ribeograd.ac.rs

The most common organic pollutant in industrial wastewaters is phenol. This pollutant exists in wastewaters from refineries, pharmaceutical industry, the paint industry, plastic, petrochemical industry, production of phenolic resins, processing of leather, disinfectants[1]. Improper handling and improper disposal of organic pollutants can lead to long-term consequences for the environmental impacts of water [2].

Hydrodynamic cavitation (HC) is a new, low cost and energy efficient method for wastewater treatment. The experimental reactor setup hydrodynamic cavitation with Venturi reactor as cavitating devicewas constructed.

The working characteristic of the device were determined: the flow and cavitation number dependence on cavitation number and downstream pressure.The influence of basic process parameters of hydrodynamic cavitation degradation of phenol, concentration of phenol (*Cph*), concentration of hydrogen peroxide ($c(H_2O_2)$), *pH*, temperature (*T*), number of passes (*n*) on the degree of reduction of phenol content in wastewaters are analyzed.

The optimal technological parameters of the investigated cavitation purification process of waste waters from phenol were determined. Based on the obtained results hydrodynamic cavitation in the presence of hydrogen peroxide is a simple, highly efficient method for the complete reduction of phenol content from wastewater. At the concentration of phenol of $50 mgL^{-1}$, $Cv = 0.5$, T=25°C, t=10 minwithout additional chemicals, the maximum achieved cavitation degree of phenol reduction is 12%.

The increase in temperature and in the concentration of hydrogen peroxide $H_2O_{2,}$ as well as the decrease in the values of the cavitation number of the cavitator and in the pH values of the solution leads to the increase in the degree of phenol reduction.

The values of the optimal reaction parameters of cavitation removal of phenol from wastewater are determined. Complete reduction of the phenol from the wastewaterunder the following reaction conditions: $Cph = 50 mgL^{-1}$, $c(H_2O_2) = 300 mgL\text{-}^{1}$, pH = 3, $Cv = 0.27$, T=25°C is achieved in a very short time interval of 10 minutes at the stoichiometric ratio of hydrogen peroxide H_2O_2 to phenol in the reaction mixture.

References

1. Busca, G, Berardinelli, S.,Resini, C., Arrighi, L., *J. Hazard. Mater.*, 160, 265-288 (2008)
2. J.H. Kim, K.K. Oh, S.T. Lee, S.W. Kim, S.I. Hong, *Process Bioc*hem.37 (2002) 1367.

Motor-oil removal from self-assembled 3D-reduced graphene oxide

Jelena Jovanović[1a], Mihajlo Gigov[2], Sandra Petković[2], Borivoj Adnađević[1]

[1] Fakultet za fizičku hemiju, Univerzitet u Beogradu, Studentski trg 12-16 11158 Beograd

[2] Rudarski institut d.o.o., Batajnički put 2, 11080 Beograd

[a] jelenaj@ffh.bg.ac.rs

A novel synthetic procedure for obtaining powdered graphene oxide (GO) was developed. The morphological, texture and basic physico-chemical properties of the synthesized GO were determined.

Figure 1. shows X-ray pattern of graphite, graphene oxide and graphene aerogel.

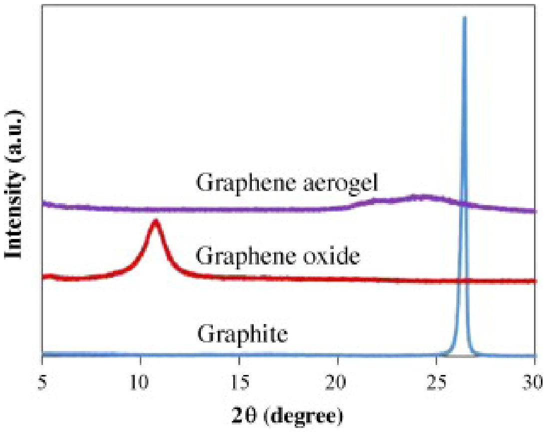


Figure 1. XRD pattern of graphite, reduced graphene oxide and graphene aerogel.

A microwave procedure for self-assembled 3D-reduced graphene oxide (3-D-rGO) was developed for first time. The texture properties *(specific area, specific volume, pore size distribution, bulk densities) and basic physico-chemical properties (XRD, FTIR, Raman spectrum) were determined.

Figure 2. shows raman spectrum of graphite, reduced graphene oxide and graphene aerogel.

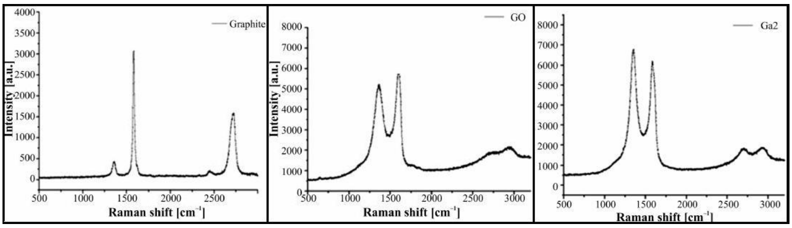


Figure 2. Raman spectrum of graphite, reduced graphene oxide and graphene aerogel.

The specific adsorption capacity of the sorbent against the motor-oil was determined by using the gravimetric method [1]. The effects of sorbent quantity (0.005-0.02 % mas), contact time (1-60 min) and temperature (10-40 °C) were investigated. Based on the obtained results it is concluded that:

a) the synthesized sorbent exhibited high specific adsorption capacity against the motor-oil,

b) the optimal sorbents quantity was 0.1% mas,

c) maximal specific adsorption capacity is achieved for contact time 5 minutes,

d) specific adsorption capacity of the sorbent increase with the increase in the temperature. The procedure for thermal regeneration of the used sorbent was developed.

References

1. Sokker, H.H., El-Sawy, N.M., Hassan, M.A., & El-Anadouly, B.E. , Adsorption of crude oilfrom aqueous solution by hydrogel of chitosan based polyacrylamide prepared by radiation induced graft polymerization. Journal of Hazardous Materials, 190(1), 359-365 (2011)

Primena sveobuhvatne dvodimenzionalne gasne hromatografije sa masenom spektrometrijom (GCxGC-MS) za rešavanje nerazložene složene smeše (Unresolved Complex Mixture - UCM) naftnih ugljovodonika u procesima bioremedijacije

Application of the comprehensive two-dimensional gas chromatography with mass spectrometry (GCxGC-MS) for the resolving of the Unresolved Complex Mixture (UCM) of petroleum hydrocarbons in bioremediation processes

Kristina Joksimović[1a], Aleksandra Žerađanin[2,3], Mila Ilić[2], Jelena Avdalović[2], Srđan Miletić[2], Tanja Jednjak[4], Vladimir Beškoski[3]

[1]Inovacioni centar Hemijskog fakulteta, Univerzitet u Beogradu, Beograd, Srbija

[2]Institut za hemiju, tehnologiju i metalurgiju, Univerzitet u Beogradu, Beograd, Srbija

[3]Hemijski fakultet, Univerzitet u Beogradu, Beograd, Srbija

[4]Brem Group d.o.o., Beograd, Srbija

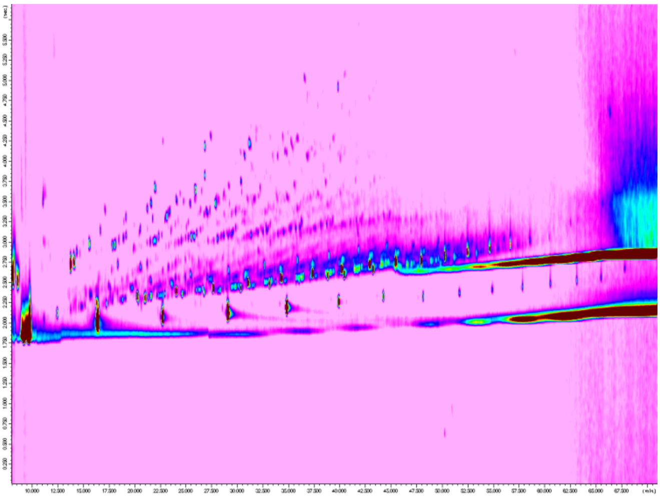
[a]kjoksimovic@chem.bg.ac.rs

Da bi biotehnološki proces bio uspešno realizovan neophodno je paralelno pratiti i analizirati mikrobiološke i hemijske parametre. Bioremedijacija predstavlja proces koji zahvaljujući mikroorganizmima uspeva, u velikoj meri ili pak potpuno, da zagađenu sredinu vrati u stanje pre zagađenja [1]. Uobičajene analitičke metode koje se primenjuju za praćenje sadržaja naftnih ugljovodonika tokom bioremedijacionih procesa obuhvataju najjednostavnija gravimetrijska određivanja, preko instrumentalnih FTIR, GC-FID, GC-ECD kao i GC-MS. Kvalitativni i kvantitativni sastav kompleksinh smeša, kao i analizu novonastalih metabolita (metabolomiks) daje nam sveobuhvatna dvodimenzionalna gasna hromatografija sa masenim spektrometrom GCxGC-MS [2,3].

Cilj ovog rada je proučavanje sastava naftnih ugljovodonika upotrebom GCxGC-MS u cilju utvrđivanja sastava dela smese poznate kao nerazložene složene smeše (Unresolved Complex Mixture - UCM) na uzorcima euro dizela, dizela D2 i zemljišta u procesu *ex situ* bioremedijaciji.

U radu su korišćeni uzorci euro dizela, dizela D2 i zemljišta uzorkovanih sa projektovane gomile (’’halde’’) za bioremedijaciju kompanije ”BREM GROUP” u Dobanovcima. Uzorci su nakon ekstrakcije i prečišćavanja analizirani gravimetrijski i upotrebom GC-FID, GC-MS i konačno GCxGC-MS (GCMS-QP2010Ultra, Shimadzu, Kyoto, Japan) sa GC×GC modulatorom (ZoexCorp). GC×GC-MS podaci su analizirani pomoću softvera ChromSquare 2.1.

Gravimetrijskom analizom kvantitativno se određuju ukupni naftni ugljovodonici (Total Petroleum Hydrocarbons–TPH), ali se ne identifikuju. Granica detekcije je oko 50 mg/kg zemljišta. Svi nepolarni ugljovodonici mogu se analizirati korišćenjem GC-FID. Pored ukupnog sadržaja ugljovodonika, dobijaju se podaci o vrsti naftnih ugljovodonika nafte (na osnovu upotrebljenih standarda), kao i stepen biorazgradnje. Granica detekcije je oko 0,1 mg/kg zemljišta. U slučaju nedostatka odgovarajućeg standarda, ovom tehnikom se ne mogu odrediti pojedine komponente smese i dominantan deo hromatograma često obuhvata UCM a dodatni problem je i činjenica da različita jedinjenja mogu imati ista retenciona vremena. Tehnika GC-MS se rutinski primenjuje za identifikaciju pojedinačnih ugljovodoničnih komponenti. I pored visokog stepena selektivnosti, nedostatak ovih metoda je u tome što mnoga različita jedinjenja mogu imati slične masene spektre, pa je njihova jasna identifikacija teška. Metoda koja pruža detaljniji uvid u hemijski sastav uzorka svakako je GCxGC-MS. Ovaj metod omogućava razdvajanje komponenti smeše u zavisnosti od tačke isparavanja (prva dimenzija) i polariteta (druga dimenzija). Na ovaj način se dobija mnogo detaljniji uvid u sastav analiziranog uzorka i omogućava analizu proizvoda metabolizma, kao i praćenje biodegradacije određenih komponenti smeše.



Slika 1. GCxGC-MS hromatogram uzorka dizela D2

Literatura

1. Beškoski, V.P., Gojgić-Cvijović, G.Đ., Milić, J.S., Ilić, J.S., Miletić, S.B., Jovančićević, B.S., Vrvić, M.M. *Hem.ind*. 66, (2012) 275-289.
2. Alam, S.M., Harrison, R.M. Chemical Science 7, (2016) 3968-3977.
3. Beškoski, V.P. Miletić, S. Ilić, M., Gojgić-Cvijović, G., Papić, P., Marić, N., Šolević-Knudsen, T., Jovančićević, B.S., Nakano, T., Vrvić, M.M., CLEAN – Soil, Air, Water, 45, (2017) 1600023.

Deterioracija betona u hidroelektranama- hemijski i mikrobiološki faktori

Deterioration of concrete in hydroelectric power plants- chemical and microbiological factors

Marija Lješević[1a], Gordana Gojgić-Cvijović[1], Bojana Stanimirović[2], Vladimir Beškoski[3], Ilija Brčeski[3]

[1]Centar za hemiju, Institut za hemiju, tehnologiju i metalurgiju, Univerzitet u Beogradu, Beograd, Srbija

[2]Institut Mol d.o.o., Stara Pazova, Srbija

[3]Hemijski fakultet, Univerzitet u Beogradu, Beograd, Srbija

[a]mljesevic@chem.bg.ac.rs

Degradacija betona može da bude posledica različitih fizičkih promena kao što su korozija, pucanje, preopterećenje itd. Osim fizičkih promena, na izdržljivost betona mogu da utiču i mikroorganizmi u procesu biodeterioracije. Iako biodeterioracija retko može biti direktan uzrok degradacije, ona znatno ubrzava druge štetne procese kao što su prodor hlorida i karbonacija koji narušavaju strukturu betona [1].

U procesima biodeterioracije mogu da učestvuju različiti mikroorganizmi kao što su bakterije, gljive, alge, lišajevi [2]. Oni utiču na procese deterioracije betona na tri načina: narušavanjem izgleda, što je posledica formiranja biofilma, mehaničkim pucanjem usled rasta i kretanja mikroorganizama i hemijskim putem usled ekskrecije metabolita [3]. Na početku, pH betonske površine je veoma visoka, pa će, ukoliko je vlažnost i količina hranljivih supstanci dovoljna, doći do kolonizacije alkalifilnim i tionskim bakterijama. Produkcijom oksidovanih sumpornih jedinjenja snižava se pH vrednost što povećava kolonizaciju betonske površine neutrofilnim, a potom i acidofilnim mikroorganizmima. Osim promene pH vrednosti, kiseline koje se proizvode direktno utiču na strukturni integritet betona pošto razgrađuju cementni materijal [2]. Usled deterioracije, troškovi održavanja betonskih konstrukcija je povećavaju, što svake godine prouzrokuje znatnu ekonomsku štetu [1, 2, 3].

U okviru ove studije ispitivan je odnos između mikrobnog rasta i različitih hemijskih svojstava uzoraka poreklom iz tri hidroelektrane u Srbiji (HE Đerdap, HE Potpeć, HE Uvac). Uzorkovanje je radjeno na dva mesta na svakoj lokaciji. Ispitivan je broj ukupnih, gvožđevitih, sulfat-redukujućih i tionskih bakterija, kvasaca i plesni kao i pH vrednost i sadržaj sulfata, nitrata, hlorida, mangana, gvožđa, magnezijuma i kalcijuma.

Vrednosti pH su bile u opsegu od 8,39- 9,09, koncentracije gvožđa su bile između 151,0- 61.100,0 mg/L, mangana 7,2- 4.900,0 mg/L, sulfata 37,4- 623,7 mg/L, nitrata 1,0- 11,3 mg/L, hlorida 88,2- 1.104,2 mg/L, kalcijuma 5,48- 19,93% i magnezijuma 0,11- 1,26%. Maksimalan broj ukupnih bakterija je bio $6,24 \times 10^8$ cfu/g, kvasaca i plesni $3,12 \times 10^5$ cfu/g, sulfat redukujućih bakterija $2,20 \times 10^3$ cfu/g , tionskih bakterija $2,50 \times 10^4$ cfu/g, a gvožđevitih bakterija 6.4 x 10^6 cfu/g.

Broj mikroorganizama i njihova aktivnost se uobičajeno povezuje sa osnovnim fizičko-hemijskim i hemijskim karakteristikama ispitivanih uzoraka. Hemijski faktori se u ovim uzorcima znatno razlikuju u zavisnosti od mesta uzorkovanja, zbog čega nije moguće odrediti jedan faktor koji bi bio indikator biodeterioracije. Ipak, uzorci uzeti iz HE Đerdap imaju najveći broj tionskih i sulfat-redukujućih bakterija, kao i najveću koncentraciju hlorida. Jedan od uzoraka uzetih iz HE Potpeć imao je najniži broj svih određivanih mikroorganizama kao i ekstremno visoke koncentracije gvožđa i mangana.

Literatura

1. Marquez-Penaranda, J.F., Sanchez-Silva, M., Husserl, J., Bastidas-Arteaga, E., *Mater. Struct.* 49 (2016) 4085-4099.
2. Wei, S., Jiang, Z., Liu, H., Zhou, D., Sanchez-Silva, M., *Braz. J. Microbiol.* 44 (2013) 1001-1007.
3. Noeiaghaei, T., Mukherjee, A., Dhami, N., Chae, S.R., *Constr. Build. Mater.* 149 (2017) 575-586.

Primena Micro-Oxymax respirometra za procenu toksičnosti bakra na model organizmu *Daphnia magna*

Using Micro-Oxymax respirometer for assesment of copper toxicity on model organism *Daphnia magna*

Branka Lončarević[1a], Marija Lješević[1], Marijana Marković[1], Dragica Jakovljević[1], Gordana Gojgić-Cvijović[1], Vladimir Beškoski[2]

[1]Institut za hemiju, tehnologiju i metalurgiju, Univerzitet u Beogradu, Beograd, Srbija

[2]Hemijski fakultet, Univerzitet u Beogradu, Beograd, Srbija

[a]brankakekez@chem.bg.ac.rs

Vodeni organizmi su izloženi brojnim hemijskim supstancama različitih mehanizama toksičnosti i da bi se okarakterisali međusobni efekti važna je uporedna analiza hemijskih podataka i odgovarajućeg biološkog odgovora (biomarkeri) [1]. Slatkovodni, planktonski beskičmenjak *Daphnia magna* je dobro poznat model u ekotoksikologiji, zbog svoje visoke osetljivosti na toksične supstance i relativno lake kultivacije u laboratorijskim uslovima. Većina istraživanja o proceni toksičnosti različitih hemijskih supstanci bazira se na ispitivanju akutne toksičosti i letalne ili efektivne koncentracije supstance koje dovode do neželjenog efekta u 50 % slučajeva (LC_{50}/EC_{50}), međutim neophodne su i detaljnije informacije o toksičnosti, koje bi uključile subletalne efekte i senzitivnije biomerkere [2]. Pošto bakar i njegova jedinjenja spadaju u vodeće zagađujuće supstance vode, sprovedene su i evaluirane brojne procene njegovih opasnosti i/ili negativnih efekata (US EPA 2007; EU 2007) [3]. Homeostaza bakra u akvatičnim organizmima uključuje regulisan unos, transport i ekskreciju koja je slična kao kod sisara. Studije na *D. magna*, koje su bile izložene subletalnim koncentracijama bakra, pokazuju pojačan oksidativni stres u jedinkama [4].

U ovoj studiji praćena je potrošnja O_2 i produkcija CO_2 kod jedinki *D. magna* tokom 48 h izlaganja Cu^{2+} jonima.

Respiracija *D. magna* (MicroBioTests Inc.) neonata praćena je 48 h pomoću dvanaestokanalnog Micro-Oxymax respirometra (Columbus Instruments, SAD). U intervalima od 4 h merena je koncentracija O_2, paramagnetnim senzorom, a CO_2 infra-crvenim senzorom, pri čemu je tokom celokupnog trajanja eksprerimenta sistem bio zatvoren. Uzorci su pripremani u providnim Micro-Oxymax bocama zapremine 500 mL u kojima je bilo po 100 mL tečne podloge i 20 neonata. Korišćen je AdaM medijum (Aachener Daphnien Medium) [5]. Koncentracija Cu^{2+} jona bila je 50 µg/mL i odabrana je prema literaturno određenoj EC_{50} vrednosti za $CuSO_4$ [6]. Jedinke nisu hranjene tokom eksperimenta i izlagane su na temperaturi od 20±2 ºC i fotoperiodu 16 h dan/8 h noć. Dobijeni podaci su evaluirani Micro-Oxymax softverom i određena je kumulativna potrošnja/proizvodnja gasova (µL). Nakon izlaganja praćena je imobilizacija neonata, a rezultati su izraženi kao procenat mortaliteta.

Dva dana nakon izlaganja *D. magna* sa Cu^{2+} jonima, zabeležen je mortalitet jedinki od 75 %. Test je bio validan, jer nije zabeležen mortalitet u kontrolnoj grupi. Kod organizama koji su bili izloženi jonima bakra kumulativna potrošnja O_2 je znatno manja tokom celog eksperimenta, dok je kumulativna produkcija CO_2 u prvih 24 h manja, a dalje razlike nisu uočene, što se može pripisati dekompoziciji imobilisanih jedinki. Na osnovu dobijenih rezultata zaključeno je da se test na MicroOxymax respirometru može koristiti kao dodatni parametar za procenu akutnih efekata toksičnih susptanci na organizam *D. magna*.

Literatura

1. Barata, P., Varo, I., Navarro, C. J., Arun, C., Porte, C, *Comp. Biochem. Physiol. Part C* 140 (2005) 175–186.
2. Bownik, A, *Sci. Total Environ***.** 601–602 (2017) 194–205.
3. Ha, Y-J., Kamo, M., Sakamoto, M, *Limnology* 18 (2017) 63-70.
4. Lushchak, V, *Aquat. Toxicol.* 101 (2011) 13-30.
5. Klüttgen, B., Dülmer, U., Engels, M., Ratte, T. H, *Wat. Res.* 28 (3) (1994) 743-746.
6. Guilhermino, L., Diamantino, T., Silva C., Soares, M. V, *Ecotoxicol. Environ. Saf.* 46 (2000) 357-362.

Ispitivanje naftnih zagadjujućih supstanci u uzorcima sedimenta na lokalitetu Toplane Novi Beograd

Determination of petroleum pollutants in sediment samples at the site of heating plant “Novi Beograd”

Aleksandra Žeradjanin[1,2a], Marija Lukić[2,3], Mila Ilić[1], Jelena Avdalović[1], Jelena Milić[1], Tanja Jednak[2,3], Vladimir P. Beškoski[2]

[1]Centar za hemiju – Institut za hemiju, tehnologiju i metalurgiju, Univerzitet u Beogradu, Beograd, Srbija

[2]Hemijski fakultet, Univerzitet u Beogradu, Beograd, Srbija

[3]Brem Group d.o.o., Beograd, Srbija

[a]adjuric@chem.bg.ac.rs

Nafta i naftni derivati kao što su dizel, benzin i mazut mogu dospeti u vodu, zemljište i sediment i predstavljaju rizik za životnu sredinu i čoveka [1-3]. Tehnologijom bioremedijacije, koristeći prirodnu sposobnost mikroorganizama da rastu na ugljovodonicima kao supstratima, nafta i naftni derivati se mogu ukloniti iz zagadjene životne sredine. Biološki tretmani su isplatljiviji i „prijateljski za okolinu”, a kao krajnji rezultat zagadjujuća supstanca se potpuno razgradjuje ili se dobijaju jedinjenja sa smanjenom toksičnošću. Da bi se vršili eksperimenti biodegradacije i bioremedijacije, neophodno je utvrditi poreklo i prirodu zagadjujuće supstance i okarakterisati autohtone mikroorganizme sa mesta zagadjenja.

Cilj ovog rada bio je da se identifikuju zagadjujuće supstance na teritoriji Toplane Novi Beograd. Uzorci su uzeti sa tri različita mesta na lokaciji. U uzorcima je praćen sadržaj ukupnih ugljovodonika nafte (TPH). TPH je ekstrahovan [ISO 16703] i gravimetrijski odredjen [DIN EN 14354]. Odredjivanje TPH gasnom hromatografijom vršeno je na gasnom hromatografu Agilent 7890A sa FID detektorom. Pored gasne hromatografije odredjivan je broj mikroorganizama na osnovnim i selektivnim podlogama.

Na osnovu dobijenih rezultata utvrdjeno je da su glavne zagadjujuće supstance na tačkama 1 i 2 u okviru lokacije Toplane Novi Beograd benzin i dizel, dok u tački 3 preovladava dizel sa manjom količinom mazuta. Ukupan sadržaj naftnih ugljovodonika u uzorku 1 je 3640 mg/kg, uzorku 2 2760 mg/kg, dok je u uzorku 3 taj broj oko deset puta veći, 28865 mg/kg. Tačka označena sa brojem tri je iznad remedijacione vrednosti na osnovu pravilnika i zakonskih propisa. U sva tri uzorka nadjen je veliki broj mikroorganizama koji razgradjuju ugljovodonike ~ 10^5 CFU/g, od kojih su dominantni rodovi *Pseudomonas, Achromobacter, Rhodococcus, Microbacterium* što je u skladu sa literaturom [1].

U okviru ovog rada uspešno su identifikovane zagadjujuće supstance i odredjeni rodovi dominantnih autohtonih mikroorganizama na lokaciji Toplane Novi Beograd.

Literatura

1. Beškoski, V., Gojgić-Cvijović, G., Milić, J., Ilić, M., Miletić, S., Jovančićević, B., Vrvić M. *Hem. Ind.* 66 (2012) 275-289.
2. Marić N., Petrović, R., Nikić, Z., Beškoski, V., Papić, P., Matić, I., Vrvić, M. *Zaštita Materijala* 58 (2017) 445 – 454.
3. Beškoski, P., Gojgić-Cvijović, G., Milić, J., Ilić, M., Miletić, S., Šolević, T., Vrvić, M. *Chemosphere* 83 (2011) 34-40.

Comparative study of alachlor removal from water by UV photolysis and UV/persulfate process

Tajana Đurkić[1a], Jelena Molnar Jazić[1], Jasmina Agbaba[1], Aleksandra Tubić[1],
Marijana Kragulj Isakovski[1]

[1]Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, University of Novi Sad

[a]tajana.djurkic@dh.uns.ac.rs

Abstract: Advanced oxidation processes, including direct UV photolysis and UV/persulfate, have been applied to investigate the degradation of alachlor in surface water. The results showed that in the presence of persulfate, removal of alachlor was higher than direct UV photolysis, which can be attributed to photolytic decomposition of persulfate, whereby highly reactive sulphate radicals ($SO_4^{\bullet -}$) are generated.

Introduction

Alachlor was chosen as a model compound for the chloroacetanilide herbicides identified as priority pollutants by the European Water Framework Directive (2013/39/EU). The Environmental Protection Agency classified alachlor as a B2 group carcinogen and it is known to be a highly toxic endocrine disruptor [1]. Advanced oxidation processes (AOPs) have attracted significant scientific attention for removal of organic contaminants from aquatic ecosystems. Today, the persulfate anion ($S_2O_8^{2-}$) has been gaining popularity as an alternative oxidant in the chemical oxidation of different organic pollutants from contaminated water, due to certain advantages, such as relatively low cost, high solubility in water, and easy storage and transport [2]. The main goal of this work was to investigate the efficiency of alachlor degradation using UV photolysis and a UV/persulfate process in surface water.

Experimental design

All experiments were performed in a commercial UV reactor with a quartz vessel equipped with low pressure Hg lamp (Philips TUV 16 W, emission at 253.7 nm). Surface water (Danube river) was spiked with an aqueous alachlor solution in order to obtain an initial concentration of about 100 µg/L. GC/MS was used for the alachlor analysis.

Results and discussion

Fig. 1 compares the photodegradation of alachlor by UV alone and by the UV/persulfate process, with reaction times from 10 to 420 s. As can be seen, UV photolysis achieved alachlor degradations from 3 to 85%, indicating that alachlor well absorbs UV radiation at a wavelength of 254 nm. Somewhat faster alachlor degradation was observed during the UV/persulfate process (with 0.029 mM $S_2O_8^{2-}$), as a consequence of the pollutant molecules being attacked

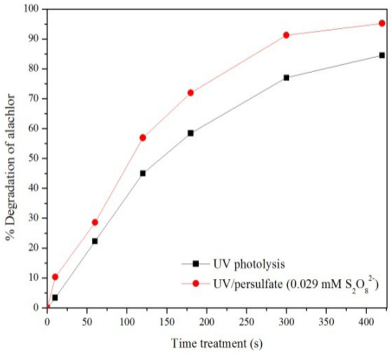


Figure 1. Degradation of alachlor in surface water using
direct UV photolysis and UV/persulfate process

by $SO_4^{\bullet-}$ radicals formed during $S_2O_8^{2-}$ photolysis. In order to examine the influence of the water matrix, these results were compared with our previous study [3] carried out in a synthetic matrix. In ultrapure water, nearly complete degradation of alachlor (97%) was achieved by the UV/persulfate process after just 14 s of the treatment. Thus, in the surface water matrix, a much longer (about 30 times) reaction time was required to achieve a similar level of removal. This is because some of the chemical species commonly present in surface waters can act as scavengers of the free $SO_4^{\bullet-}$ radicals or absorb the UV radiation, reducing the efficiency of the oxidative degradation of organic pollutants.

Conclusion

Advanced oxidation processes proved to be a promising technique for alachlor degradation in surface water. The impact of other constituents in the water matrix (natural organic matter, alkalinity) on efficiency the alachlor degradation will be the focus of future investigation.

Acknowledgements. The authors gratefully acknowledge the support of the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. III43005).

Literature

1. Wang, Q., Shao, Y., Gao, N., Chu, W., Deng, J., Shen, X., Lu, X., Zhu, Y., Wei, X., *J. Taiwan Inst. Chem. E.* 63 (2016) 379-385.

2. Sharma, J., Mishra, I.M., Kumar, V., J. *Environ. Manage.* 156 (2015) 266-275.

3. Đurkić, T., Molnar Jazić, J., Kragulj Isakovski, M., Tubić, A., Maletić, S., Agbaba, J., Dalmacija, B., Knjiga radova i apstrakata VI Memorijalni naučni skup iz zaštite životne sredine „Docent dr Milena Dalmacija“, 29-30.mart (2018) Novi Sad, pp. V-09.

Electrochemical behavior and nanomolar quantification of polydatin. Application on food supplements

Slađana Đurđić[1a], Vesna Vukojević[1], Jelena Mutić[1], Dalibor Stanković[1]

[1]Faculty of Chemistry, University of Belgrade, Belgrade, Serbia

[a]sladjanadj@chem.bg.ac.rs

In this work we demonstrated electrochemistry and determination of natural compound polydatin and its quantification in pills. Polydatin is most often found in grapes skin and presents a precursor of resveratrol which is present in wines and has an antioxidant ability. Biological effect of polydatin is widespread (antioxidant, anticancer, antibacterial, antiallergic, antiinflammatory effect) [1, 2].

Standard solution of polydatin ($1\cdot10^{-3}$ M) was prepared with mixture water:methanol (80:20, *v/v*). Britton-Robinson buffer solution (BRBS) was used as supporting electrolyte. Electrochemical measurements were performed on potentiostat/galvanostat CHI 760b (USA) utilizing conventional three electrode cell. As a working electrode boron doped diamond electrode was used (BDD, 3 mm diameter, 1000 ppm of boron doping level, Windsor Scientific, UK), 3M KCl Ag/AgCl as reference electrode, while as auxiliary (counter) electrode platinum wire of large surface was used. POLIDAL GHIMAS, pills with polydatin, were used as real samples. According to the manufacturer's declaration each pill contains 40 mg of polydatin. Also, pills were dissolved in a mixture methanol:water (20:80, *v/v*).

Electrochemical behavior of polydatin was tested in the potential range from -1.5 V to 2 V using cyclic voltammetry (Figure 1). It has been noticed that polydatin provides two oxidation peaks, one at around 0.73 V and second at around 1.3 V. In the reverse scan no reduction peak was observed. Influence of different pH on peak potential and current was studied in the pH range from 1 to 9. The best oxidation response which takes into account peak shape and peak current was observed in BRBS at pH=2.

Quantification of polydatin was done based on first oxidation peak using square wave voltammetry (SW). After optimization of the method (pulse amplitude 50 mV, frequency 70 Hz), linear working range from $1\cdot10^{-7}$ M to $7\cdot10^{-5}$ M was obtained. Polydatin in concentration range from $1\cdot10^{-7}$ M to $9\cdot10^{-6}$ M shows that the diffusion controlled process is responsible for the oxidation of polydatin on BDD electrode (Figure 2A, 2C). Limit of detection was calculated and it is equal to $6\cdot10^{-9}$ M, while limit of quantification was calculated and amounted to $2\cdot10^{-8}$ M. On the other hand, oxidation peak of polydatin is also showing linear dependence in concentration range from $2\cdot10^{-5}$ M to $7\cdot10^{-5}$ M, but with another slope (Figure 2B, 2C). In the area of higher concentrations adsorption phenomenon was responsible for the oxidation of polydatin.

The effect of two antioxidants (gallic and ascorbic acid) and alcaloid (caffeine) was tested on electrochemical response of polydatin. Negligible interferences effects were noticed.

The optimized SW method was applied for detection of polydatin in POLIDAL pills. Developed method shows excellent accuracy and precision toward detection of polydatin and was used for its quantification in the pharmaceutical samples.

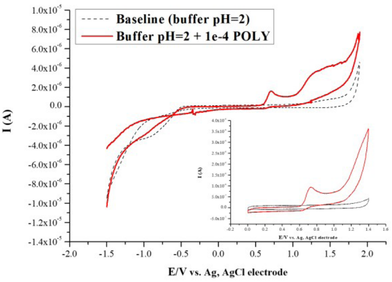


Figure 1. Cyclic voltammogram of $1\cdot10^{-4}$ M of polydatin in BRBS at pH=2 in full potential range of BDD electrode. Scan rate of 100 mV/s. Insert of figure shows the electrochemical response of polydatin in positive potential region.

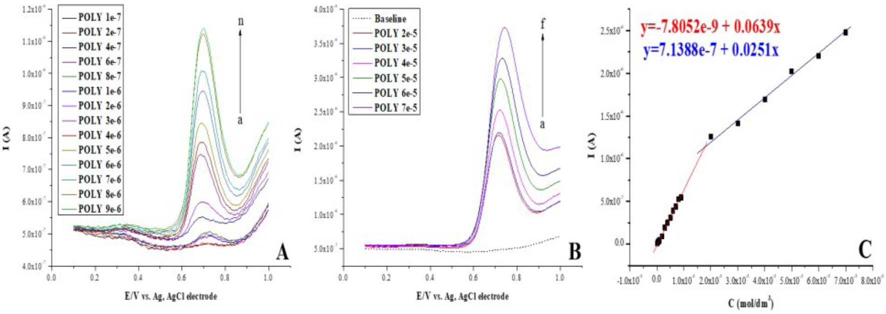


Figure 2. Voltammograms of dependence oxidation peak of different concentration of polydatin in BRBS pH=2 at BBD electrode; A) from a to n: $1\cdot10^{-7}$ - $9\cdot10^{-6}$ M; B) from a to f: $2\cdot10^{-5}$ - $7\cdot10^{-5}$ M; C) corresponding calibration curves.

References

1. Li, Y., Wang, L., Zhao, H., Du, L., Ye, B. *J. Electroanal. Chem.* 773 (2016) 39-46
2. Iacopini, P., Baldi, M., Storchi,P., Sebastiani, L. *J. Food Compos. Anal.* 21 (2008) 589-598

Uranium and thorium content in mushroom *Macrolepiota Procera* and their bioconcentration factors

Vesna Vukojević[1a], Slađana Đurđić[1], Jelena Mutić[1]

[1]Faculty of Chemistry, University of Belgrade, Belgrade, Serbia

[a]vvukojevic@chem.bg.ac.rs

Mushrooms species have significant role in biogeochemical cycling of elements and they are involved in transformation of both organic and inorganic compounds. The complex biochemical actions of macrofungi in soils lead to the uptake, transport, accumulation and hyperaccumulation of various chemical elements and compounds in mushroom fruiting bodies [1]. The bioaccumulation of metals in the mushrooms depends of numerous factors such as the type of geological bedrock, the physical characteristics of soil (pH,Eh), the amount of organic matter et cetera [2].

Macrolepiota procera is wild edible mushroom, widespread in Serbian forests. Mineral composition of this type of mushroom is a well-researched topic [3,4]. On the other hand, concentration of uranium and thorium in the fruiting bodies of these mushrooms, as well as the possibility of mushroom to adopt these elements from the soil is poorly researched. U and Th are the most abundant actinides in the terrestrial environments and distribution and behavior of these elements has received most attention.

The aim of this work was to determinate concentration of uranium and thorium in mushroom samples *Macrolepiota procera*. In order to examine the possibility of mushroom to accumulate uranium and thorium, we also determinate concentration of these metals in corresponding soil substrate.

The mushrooms and soil substrates samples, analyzed in this study, were collected at mountain Goc, Serbia. Caps and stipes of every collected mushroom were sampled separately to enable metal content determination for each anatomic part. Simulations with mushrooms, soil substrate samples from upper soil horizon (0-10 cm) were also collected. Digestion of mushroom samples was carried on by microwave digestion (Ethos 1, Advanced Microwave Digestion System, Milestone, Italy). The pseudo-total concentrations of elements in soil were determined using aqua regia. Determination of U and Th concentrations in all samples was carried out by ICP-MS (ICP-Q- MS, Thermo Scientific Xseries 2, UK).

Our results for U and Th concentrations were generally below 25 and 300 μg/kg dw in whole fruiting body of *M. Procera,* respectively. Content of these elements was higher in stipes than in caps in the case of Th, while content of U was equable in both anatomic part of mushroom (Figure 1).

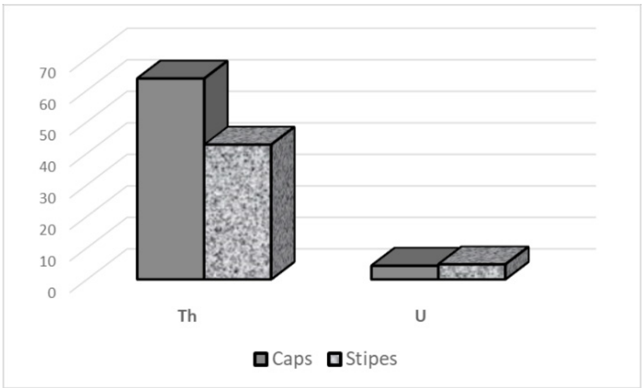


Figure 1. Average concentration (μg/kg) of U and Th in caps and stipes of *M. Procera*

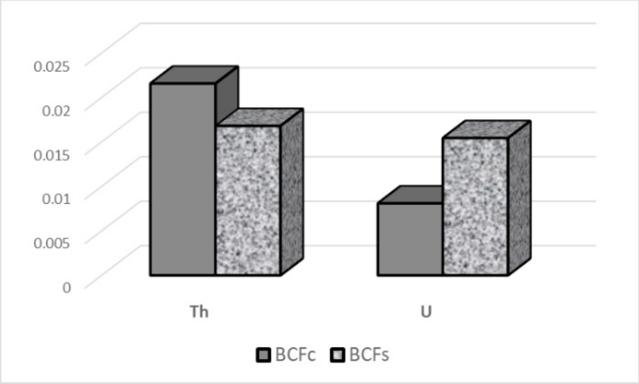


Figure 2. Calculated BCF values for caps and stipes of *M. Procera*

Bioconcentration factors were also calculated as ratio of U and Th concentration in caps or stipes and total concentration of these elements in soil. Obtained BCF values for these two elements were very low (BCF~0.02) with respect to total soil content (Figure 2).

Our results indicated that mushroom *Macrolepiota Procera* does not show ability to accumulate U and Th. In terms of bioconcentration and bioexclusion concept, these elements are bioexcluded in *M. Procera*.

References

1. Gadd, G., *Mycological Research* 111 (2007) 3-49
2. Damodaran, D., Vidya Shetty, K., Raj Mohan, B., *Ecotox Environ Safe* 104 (2014) 414–422
3. Stefanović, V., Trifković, J., Mutić, J., Tešić, Ž., *Environ Sci Pollut Res* 23 (2016) 13178–13190
4. Jarzunska, G., Gucia, M., Kojta, A., Rezulak K., Falandysz, J., J. *Environ Sci Heal B* 46 (2011) 741-751

Interaction of chlorophenols with microplastic in water

Aleksandra Tubić[1], Maja Lončarski[1a], Tamara Apostolović[1], Snežana Maletić[1], Jelena Tričković[1], Dejan Krčmar[1], Jasmina Agbaba[1]

[1]Department of Chemistry, Biochemistry and Environmental Protection, Faculty of Sciences, University of Novi Sad, Novi Sad, Republic of Serbia

[a]maja.loncarski@dh.uns.ac.rs

Abstract: Microplastic pollution presents an environmental hazard which has recently become a major cause of concern worldwide. In order to understand the possible impact of microplastics on the environment and human health, the knowledge of the interactions of these particles with other water pollutants needs to be expanded. This study aims to investigate interactions between microplastic particles of different origin and chlorophenols. Microplastics extracted from personal care products were found to have a higher affinity towards chlorophenols than clean microplastic particles.

Introduction

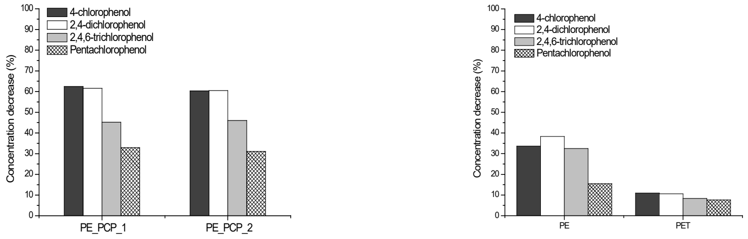
A significant amount of plastic is released into the environment, where over time, physical, chemical and biological processes break down large pieces into smaller ones [1]. Plastic components detected in the environment of less than 5 mm are termed microplastics. Primary microplastics are used in personal care products (PCPs) to improve their performance. Very little is known about the impact of microplastics on in-land waters and human health [2,3]. The aim of this study was to investigate interactions between microplastic particles of different origin and chlorophenols, which are known to be widespread environmental pollutants.

Materials and methods

For the purpose of this study, four chlorophenols (4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol) and four types of microplastics were investiated: low density polyethylene standard substance (PE), PE isolated from two PCPs (PE_PCP_1 and PE_PCP_2) and polyethylene terephthalate standard substance (PET). Isolation of polyethylene from PCPs was carried out according to the modified method [4]. Synthetic aqueous solution was prepared by the addition of selected chlorophenols to deionized water enriched with $CaCl_2$, $NaHCO_3$ and $MgSO_4 \cdot 7H_2O$. The degree of binding was monitored after a contact time of 96 h (mixing rate 200 rpm). Chlorophenols were analysed by GC/MSD, after liquid-liquid extraction and derivatization.

Results and Discussion

Figure 1 presents the changes in concentration of four investigated phenols, after 96 h contact time with microplastic particles. These results indicate that microplastic particles interact with the investigated chlorophenols. The highest affinity towards chlorophenols was observed in PE particles isolated from PCPs (Fig. 1a), probably due to possible changes in structure made during manufacturing, by adding different functional groups. The highest reductions in concentration were observed for 4-chlorophenol and 2,4-dichlorophenol (around 60% for both PE-PCP), while reductions in the concentrations of 2,4,6-trichlorophenol (45%) and pentachorlophenol (35%) were less notable.



(a) (b)

Figure 1. Decrease of chlorophenol concentrations in water, after 96 h contact time, with (a) microplastic extracted from PCP and (b) clean microplastics

The clean PE have similar affinities towards 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol (33-40% concentration decrease), while only 15% of pentachlorophenol interacted with these microplastic particles (Fig. 1b). The lowest interaction rate was observed for PET, with observed reductions in phenol concentrations of around 10%.

Conclusion

This study investigates the interaction of four chlorophenols with microplastic particles. It can be concluded that differences in chlorophenol structure and changes made to the microplastics during the production of personal care products have significant impacts on their possible interactions.

Acknowledgements: The authors gratefully acknowledge the support of the Provincial Secretariat for Higher Education and Scientific Research, Republic of Serbia, AP Vojvodina (142-451-2526/2017-02).

References

1. O’Brine T., Thompson R.C., (2010) Degradation of plastic carrier bags in the marine environment. Marine Pollution Bulletin, 60, 2279–2283.
2. Hidalgo-Ruz V., Gutow L., Thompson R.C., Thiel M., (2012) Microplastics in the marine environment: a review of the methods used for identification and quantification, Environmental Science & Technology, 46, 3060–3075.
3. Thompson R.C., Olsen Y., Mitchell R.P., Davis A., Rowland S.J., John A.W., McGonigle D., Russell A.E., (2004) Lost at sea: where is all the plastic? Science 304, 838.
4. Nuelle M-T.,. Dekiff J.H., Remy D., Fries E. (2014) A new analytical approach for monitoring microplastics in marine sediments, Environmental Pollution, 184, 161–169.

Synthesis of 5-nitroisatin-3-thiosemicarbazone in a green solvent

Milica Z. Zlatković[1a], Sandra S. Konstantinović[1], Vlada B. Veljković[1]

[1]Faculty of Technology, University of Niš, Leskovac, Serbia

[a]milica.zlatkovic@ymail.com

Green chemistry is a very important part of science. This concept implies the use of harmless reactants, green solvents, shorter reaction time, higher yield of products, as well as, their easily storage, biodegrability and recycling [1]. The replacement of conventional with alternative solvents is a very important task of green chemistry. Glycerol is one of the solvents that has widely been used as a substitute for conventional solvents and a cosolvent in the biocatalytic processes to improve the reaction selectivity, as well as in the processes for purification of organic chemicals [2,3].

In this paper, the synthesis of 5-nitroisatin-3-thiosemicarbazone was performed in conventional (methanol) and crude glycerol as an alternative solvent. The crude glycerol, a by-product in the production of biodiesel from sunflower oil, was obtained from the Laboratory for Chemical Engineering, Faculty of Technology, Leskovac. The excess of methanol was removed from the crude glycerol by distillation, and then its pH was adjusted by adding 85% H_3PO_4 to 4.5 [3,4]. Equimolar amounts of 5-nitroisatin and thiosemicarbazide were dissolved in crude glycerol and mixed. The mixture was refluxed for 15 minutes at 60^{o}C. The reaction was carried out at 60 ^{o}C to reduce the viscosity of the reaction mixture.After cooling at room temperature, the orange precipitate was separated by filtration, washed with ethanol and dried. The yield of the obtained compound was 93%. The same procedure was repeated in methanol, where pH was adjusted with H_2SO_4 to 4.5 [4]. The mixture was refluxed for 45 minutes at 50^{o}C, and the yield of the obtained product was 85%. 5-nitroisatin-3-thiosemicarbzone was identified by elemental microanalysis, and FTIR, UV/VIS, ^{1}H NMR and ^{13}C NMR spectroscopic methods.

The obtained results showed that the use of crude glycerol had a significant advantage over methanol, since the reaction time was reduced for 30 min., while the yield of the obtained product increased by 8%.

References

1. Gu, Y., Jerome, F., *Green Chem.*12 (2010) 1127-1138.
2. Konstantinović, S., Jovanović, M., Ilić, S., Banković Ilić, I., Veljković, V., Tehnological process for Schiff base synthesis in a crude glycerol as a green solvent, 2015, Leskovac.
3. Isahak, W.N.R.W., Azad, M.A.K., Jesmin, M., Ahsan, S., Rahman, M.M., Khanam, J.A., Islam, M.N., Shahriar, S.M.S., *Asian Pac. J. Trop. Biomed*. 2 (2012) 438-442.
4. Konstantinović, S., Zlatković, M., Ćirić, J., Ilić, S., Gojgić Cvijović, G., Veljković, V., *Hem.Ind*. 71 (2017) 487-494.

Next generation low cost magnetic activated carbons for future arsenic removal from water

Sabolc Pap[1,2a], Mark A. Taggart[1], Jelena Radonic[2], Maja Turk Sekulic[2]

[1]Environmental Research Institute, North Highland College, University of the Highlands and Islands, Thurso, UK

[2]Department of Environmental Engineering and Occupational Safety and Health, Faculty of Technical Sciences, University of Novi Sad, Novi Sad, Serbia

[a]szabolcs.pap@uhi.ac.uk

The development of advanced carbon materials that can efficiently remove pollutants from water is of great interest for environmental remediation and human safety. Magnetic activated carbons (MACs) are a class of carbonous sorbents that possess a high surface area, high porosity and magnetic properties. Compared with conventional activated carbons, MACs are generally more suitable for adsorption in slurry reactors due to their magnetic properties, which allows them to be easily removed from solution (simply by applying a magnet field). This process, in turn, makes lengthy filtration and/or centrifugation steps unnecessary [1].

Recognized as a highly toxic element, arsenic is abundant in our environment, with both natural and anthropogenic sources. There are a number of regions worldwide where arsenic is present in drinking water, particularly in groundwater, at elevated concentrations. Vojvodina (Serbia) is a Pannonian lowland, where high arsenic levels are present in groundwater (originating from geological sources). Effective arsenic removal technology is thus highly desirable to provide safe drinking water.

Here a MAC was generated from cherry kernels. The procedure for obtaining the carbonized cherry kernels (CScPA) (i.e., the parent material used to make the cherry kernel-derived MAC) has been described previously [2]. Our MAC was prepared by impregnating ferric chloride ($FeCl_3 \cdot 6H_2O$) into CScPA and then carbonizing the resulting composite material. Specifically, a 1:1 ratios of $FeCl_3 \cdot 6H_2O$ to CScPA (wt:wt) was employed. A mixture of 30g of CScPA and $FeCl_3 \cdot 6H_2O$ in 20 mL of Milli-Q water (EASYpure® II, 18.2 MΩ) was placed on an orbital shaker (IKA KS 260) and mixed at 150 rpm for 2 h. The mixture was then placed in oven at 105 °C until the water evaporated. The resulting solid was placed in a furnace and heated to 700 °C (and kept at this temperature for 2 h). After cooling to room temperature, the carbonized material was taken out and washed with Milli-Q until the pH of the solution reached a value of ~6.5-7.0. The solid material was dried in oven at 105 °C for 2 h.

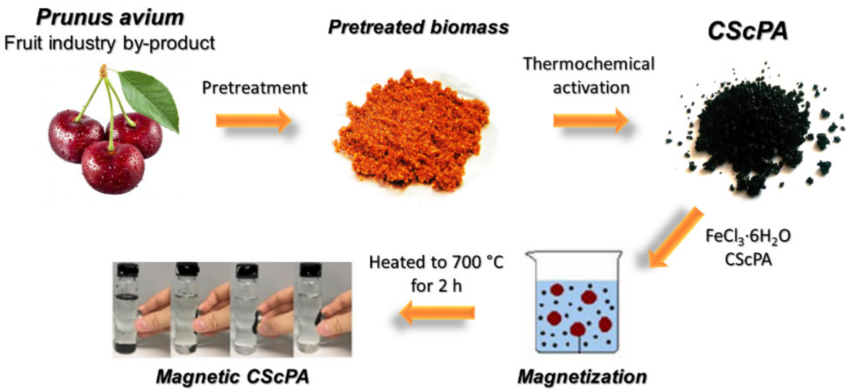


Figure 1: Preparation of magnetic activated carbon from cherry kernals

An arsenic adsorption experiment was conducted by adding 100 mg of MAC to 100 mL of 20 mg/L As(V) solution (shaken for 2 h; initial pH: 2; agitation speed: 150 rpm; temperature: 20 ± 2 ºC). The MAC removal efficiency was 20 %. Because, the efficiency of adsorption process depends on the selection of suitable operation conditions, further experiments will consider removal optimization of As(V) using response surface methodology (RSM) involving Box-Behnken design (BBD).

The production method provides MAC with a high surface area and magnetically active iron species at the surface. The initial adsorption study shows that the MAC has affinity toward As(V), and thererfore may be used as an adsorbent for arsenic removal in water treatment.

References

1. Cazetta, A. L., Pezoti, O., Bedin, K. C., Silva, T. L., Paesano Junior, A., Asefa, T., & Almeida, V. C. *ACS Sustainable Chem. Eng.*, 4(3) (2016) 1058-1068.
2. Pap, S., Radonić, J., Trifunović, S., Adamović, D., Mihajlović, I., Miloradov, M. V., Turk Sekulić, M. *J. Environ. Manage.* 184 (2016) 297-306.

Is the Danube along Novi Sad overdosed by diazepam?

Maja Milanović[1a], Jelena Radonić[2], Maja Turk Sekulić[2], Mirjana Vojinović Miloradov[2], Nataša Milić[1]

[1]Faculty of Medicine, University of Novi Sad

[2]Faculty of Technical sciences, University of Novi Sad

[a]maja.milanovic@mf.uns.ac.rs

Although residues of pharmaceuticals are identified as potential threat to the aquatic environment, only recently, the occurrence of benzodiazepines in the surface water acquired deserved attention. For decades, benzodiazepines are successfully used as anxiolytics, hypnotics, anticonvulsants, tranquilizers, muscle relaxants, etc. [1]. Probably the most known drug in this group is diazepam. Based on its frequent and global use, the aim of the study was to investigate the occurrence of diazepam and its active metabolite desmethyldiazepam in the Danube surface water.

The surface water samples were collected at seven representative locations (GC1, GC2, RO, RP, DR, DS, DL) along the Danube of the Novi Sad municipality during the four sampling campaigns. After solid phase extraction procedure, following the modified protocol set by Loos et al. [2], the residual concentrations of diazepam and desmethyldiazepam in the water samples were determined by liquid chromatography-electrospray ionization-tandem massspectrometry.

Although diazepam was under the limit of detection (0.1 ng/L) in all the water samples, its metabolite, desmethyldiazepam, occurred in the samples collected in spring, summer and autumn in the concentrations up to 3.4 ng/L. The obtained results could be explained by the fact that only 1% of the prescribed dose of diazepam is excreted in an unchanged form while active metabolite desmethyldiazepam usually takes between 22 and 43% [3]. Moreover, diazepam has affinity to adsorb to sediments which could be the additional reason for the absence of the parent compound in the analyzed samples [1]. These assumption could be confirmed by the previously performed studies [3, 4], in which diazepam was detected only in the sediment or in the hospital effluents.

Despite the absence of diazepam in analyzed samples, the detected low levels of its metabolite should not be neglected. It is still unknown what behaviour effects of aquatic organisms could provoke chronic exposure to low doses of diazepam and its metabolites. The obtained results provide important information that should be implemented into the database for the Danube River basin.

Acknowledgement: This research has been financially supported by Ministry of Education, Science and Technological Development, Republic of Serbia (III46009) and NATO Science for Peace Project ESP.EAP.SFP 984087.

References

1. Frick, J., Brodin, T., Heynen, M., Klaminder, J., Jonsson, M., Grabicova, K., et al. *Chemosphere* 176 (2017) 324-332.
2. Loos, R., Wollgast, J., Huber, T., Hanke, G. *Anal Bioanal Chem*. 387 (2007) 1469-1478.
3. Kosjek, T., Perko, S., Zupanc, M., ZanoškiHren, M., LandekaDragičević, T., Žigon, D., et al. *Water Res.* 46 (2012) 355-368.
4. Radović, T., Grujić, S., Petković, A., Dimkić, M., Laušević, M. *Environ. Monit. Assess.* 187 (2015) 1-17.

Organsko-geohemijsko ispitivanje sedimenata iz arheološkog nalazišta Vinča (Beograd, Srbija)

Organic geochemical investigation of sediments from the archeological site Vinča (Belgrade, Serbia)

Aleksandra Šajnović[1a], Milica Kašanin-Grubin[1], Kristina Penezić[2], Sanja Stojadinović[1], Gorica Veselinović[1],Branimir Jovančićević[3]

[1]IHTM, Univerzitet u Beogradu

[2]Biosens, Institut u Novom Sadu

[3] Hemijski fakultet, Univerzitet u Beogradu

[a] sajnovica@chem.bg.ac.rs

U okviru ovog istraživanja analizirano je deset uzoraka sedimenata iz arheološkog nalazišta Belo brdo iz Vinče, sa ciljem da se na osnovu rezultata organsko-geohemijskih ispitivanja dođe do novih saznanja o interakciji čovek/životna sredina tokom srednjeg i mlađeg neolita, kao i da se pouzdanije rekonstruišu uslovi u životnoj sredini i klimatske fluktuacije.

Arheološko nalazište Belo brdo u Vinči je eponimni lokalitet vinčanske kulture koja je dominirala prostorom centralnog Balkana u periodu srednjeg i ranog neolita (ca. 5300-4400 pre n.e.). Značaj lokaliteta se ogleda u bogatstvu pronađenog materijala koje je iskorišćeno kao osnova za izradu hronološkog sekvencioniranja ovog perioda praistorije. Lokalitet se nalazi na nepunih 15 km jugoistočno od Beograda, na desnoj obali Dunava. Uzorci V1-V4 su uzeti iz geološkog dela, dok su uzorci označeni sa V6-V10 uzeti iz arheoloških (kulturnih) slojeva. Uzorak V5 je na granici između arheološkog i geološkog dela i on potiče iz takozvanog “humusnog sloja” (paleozemljište). Iz arheoloških podataka je poznato da sloj iz kojeg je uzet uzorak V7 predstavlja ostatke kuće koja je gorela i koja je urušena. Tokom neolitakuće su pravljeneod blata, pleve, delom i balege. Uzorak V8 potiče iz sloja za nivelaciju, tipičnom za lokalitet Belo brdo, kojim je prekrivan ruševinski sloj gorelih objekata, radi dobijanja nove hodne površine. Za sloj nivelacijeje tipično korišćena vrsta glinovitog/praškastog materijala (sedimenata). Iako se pretpostavljaju lokacije sa kojih je ovaj materijal donošen, još uvek nije potpuno poznato odakle tačno potičematerijal za nivelaciju.

Rastvorna organska supstanca je izolovana pomoću ekstrakcije po Soxhlet-u, a potom je razdvojena hromatografijom na koloni na četiri frakcije različite polarnosti (zasićene i aromatične ugljovodonike, polarnu frakciju i frakciju masnih kiselina). Zasićeni i aromatični ugljovodonici analizirani su gasnohromatografsko-masenospektrometrijskom tehnikom. Pored navedenog, određen je i granulometrijski sastav ispitivanih sedimenata.

Svi ispitivani sedimenti su veoma sličnog granulometrijskog sastava i mogu se okarakterisati kao slabo vezani peskoviti alevriti. Sadržaj organske supstance u ispitivanim sedimentima varira u relativno širokom opsegu od 136 do 12030 ppm.Uzorke V1 i V2 karakteriše najveći sadržaj bitumena (>10000 pmm), što se može objasniti velikom bioprodukcijom organske supstance za vreme taloženja ovih uzoraka[1].

Raspodela i relativna obilnost *n*-alkana i diterpana ukazuju da je organska supstanca uzoraka formirana od viših i nižih biljnih organizama, uz učešće mikroorganizama (uzorci V1, V5, V7), akvatičnih makrofita i mahovina (uzorci V2 i V8), ili pretežno od viših kopnenih biljaka (uzorci V9 i V10). U geološkom sloju, a posebno u uzorcima V1-V3 pretežno su bile zastupljene drvenaste biljke, da bi se vremenom njihova obilnost smanjivala, na račun sve veće obilnosti trava, koje su bile dominantno zastupljene u humusnom sloju i sloju ispod njega.

Od diterpana u većini ispitivanih uzoraka identifikovani su samo pimaran i 16α(H)-filokladan. U uzorku V3 pomenuta jedinjenja su najzastupljenija u ukupnoj raspodeli zasićenih ugljovodonika, dok u uzorcima V1 i V2 nisu identifikovana. Pimaran i 16α(H)-filokladan su indikatori za plitke šumske močvare (baruštine).

Na osnovu dobijenih rezultata može se pretpostaviti da su uzorci V1 i V2 taloženi u dubljoj barsko-jezerskoj sredini sedimentacije sa velikom bioprodukcijom organske supstance, nakon čega je došlo do oplićavanja i stvaranja plitke baruštine (dubine ~ 1m) u kojoj je preovladavala šumska vegetacija (četinarsko drveće), a klima je bila pretežno vlažna i topla. Vremenom je došlo do promene ka suvoj i toploj klimi, što je uslovilo zasušivanje i zatrpavanje močvare i formiranje humusnoj sloja (paleozemljišta), na kojem su se nastanili ljudi tokom neolita. Tokom trajanja neolitskog naselja u Vinči može se pretpostaviti da je pretežno preovladavala suva i/ili toplija klima sa manjim oscilacijama. Uzorak V8, koji potiče iz sloja za nivelaciju, po raspodeli *n*-alkana se značajno razlikuje od ostalih uzoraka iz arheoloških slojeva, što je u saglasnosti sa činjenicom da je materijal za nivelaciju donošen sa strane. Ovaj uzorak karakteriše izrazita dominacija srednjelančanih i viših neparnih *n*-alkana, sa maksimumom na *n*-C_{25}, što ukazuje na značajan doprinos akvatičnih makrofita i mahovina [2], odnosno da je formiran u plitkoj sredini sedimentacije.

Literatura

1. Peters, K.E., Walters, C.C., Moldowan, J.M.(2005) The Biomarker Guide, Volume 2: Biomarkers and Isotopes in the Petroleum Exploration and Earth History. Cambridge University Press, Cambridge, UK.
2. Ficken, K.J., Li B., Swain, D.L., Eglinton, G. *Org. Geochem.* 31 (2000) 745–749.

Persistent organic compound across Serbia – Indications of soil and vegetation (moss) pollution

Gordana Vuković[1], Tijana Milićević[1a], Mira Aničić Urošević[1],
Snježana Herceg Romanić[2], Gordana Mendaš[2], Miloš Ilić[3], Aleksandar Popović[4]

[1]Institute of Physics Belgrade, University of Belgrade, 11080 Belgrade, Serbia,

[2]Institute for Medical Research and Occupational Health, 10001 Zagreb, Croatia

[3]Faculty of Sciences, University of Novi Sad, 21000 Novi Sad, Serbia

[4]Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia

[a]tijana.milicevic@ipb.ac.rs

Persistent Organic Compounds (POPs) include a range of substances such as intentionally produced polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) currently or once used in agriculture, industry or disease control. These compounds persist in the environment, bioaccumulate and biomagnify in the food chain, and are prone to long range atmospheric transport; once POPs have entered the air, they subsequently condense onto surfaces such as soil and vegetation. Raised to a global level, the Stockholm Convention on POPs aims to reduce and eliminate their release into environmental media and it has set the Global Monitoring Plan (GMP) recommended for international use [1]. In Serbia, the Convention entered into force in 2009 and no scientific articles focused on POPs in environmental media until now.

With reference to the GMP initiatives and ICP Vegetation 2015 under Convention on Long-Range Transboundary Air Pollution (LRTAP) [2], this study concerns 17 PCBs and seven OCPs in the topsoil and moss *Hypnum cupressiforme* Hedw. in Serbia. The samples were collected at 22 sampling sites (Figure 1a) during June and July 2017. Briefly, 5 g of topsoil and 1 g of moss samples were extracted using a mixture of n-hexane:acetone (1:1) and assisted by microwave (5 min up to 80°C, 10 min at 80°C). The PCBs (-28, -52, -101, -138, -153, -180, -105, -114, -118, -123, -156, -157, -167, -189, -60, -74, and -170) and OCPs (HCB, α-, β-, γ-HCH, *p,p′*-DDE, *p,p′*-DDD, and *p,p′*-DDT) were separated and analyzed on two gas chromatographic (GC) columns of different polarity (60 m × 0.25 mm, Rtx-5 film thickness of 0.25 µm; 30 m × 0.32 mm, Rtx-CL Pesticides film thickness of 0.32 µm) using a dual-column Agilent 7890B Series high-resolution G C System equipped with two electron capture detectors. The limits of detection (LOD) were calculated as the average of all determinations based on signal-to-noise ratio and the compound recovery.

The average recoveries were 72–105% and 73–116% while the LOD were within the range between 0.006 and 0.032 ng g^{-1}, and 0.016 and 0.302 ng g^{-1} for OCPs and PCB, respectively. The topsoil samples were mildly acidic to neutral (pH=4.78 − 8.01), with the highly variable content of soil organic matter (SOM=3.86 – 18.19) and the electric conductivity values (EC=19.54 µS to 320.00 µS). The abundances of the associated groups of chlorinated pollutants in the topsoil were: DDTs>PCBs>HCHs>HCB (Figure 1b). Except PCB-118, toxicologically relevant PCBs (-105, -114, -123, -156, -157, -167, and -189) in the topsoil were below LOD. Given the satisfying recoveries for POPs in the spiked moss samples, we recommend a microwave extraction as a suitable procedure for POP determination in line with time- and solvent-consuming Soxhlet extraction. The evaluation of the OCP and PCB levels in the real moss samples is in progress and their patterns possibly follow those in the topsoil [3].

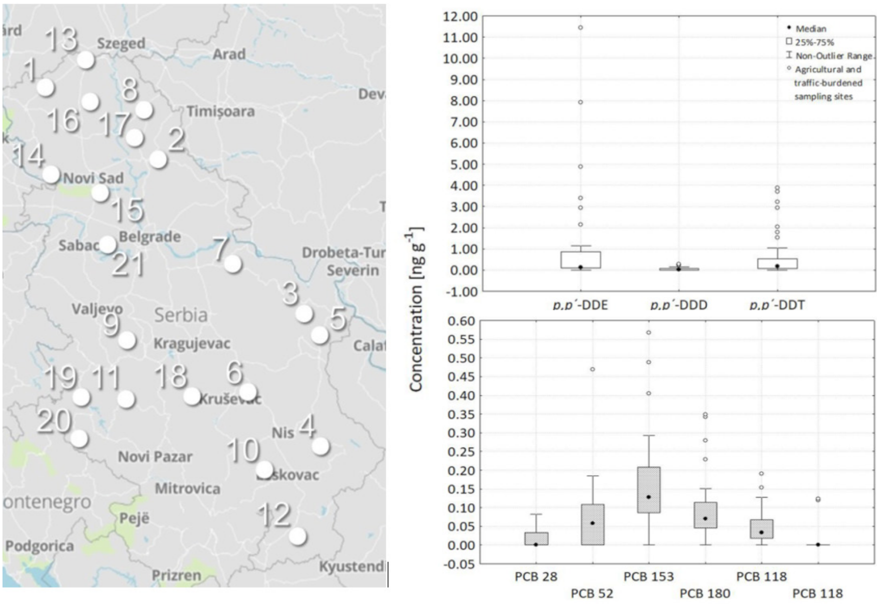


Figure 1. Map of the sampling sites across Serbia (a), and the levels of selected POP in the topsoil samples (b).

References

1. Stockholm Convention for Persistent Organic Pollutants (2001) http://chm.pops.int/, Accessed date: March 2018.
2. The International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (2015/16) https://icpvegetation.ceh.ac.uk/, Accessed date: March 2018.
3. Aničić Urošević, M., Vuković, G., Vasić, P., Jakšić, T., Nikolić, D., Škrivanj, S., Popović, A., *Ecol. Indic.* (2018) *accepted for publication*.

Procena kontaminacije sedimenta reke Dunav organohlornim pesticidima

Assessment of Danube River sediment contamination by organochlorine pesticides

Maja Brborić[1a], Branislav Vrana[2], Jelena Radonić[1], Mirjana Vojinović Miloradov[1], Sabolč Pap[3] , Maja Turk Sekulić[1],

[1]Departman za inženjerstvo zaštite životne sredine i zaštite na radu, Fakultet tehničkih nauka, Univerzitet u Novom Sadu

[2]Faculty of Sciences, Research Centre for Toxic Compounds in the Environment RECETOX, Masaryk University, Brno, Czech Republic

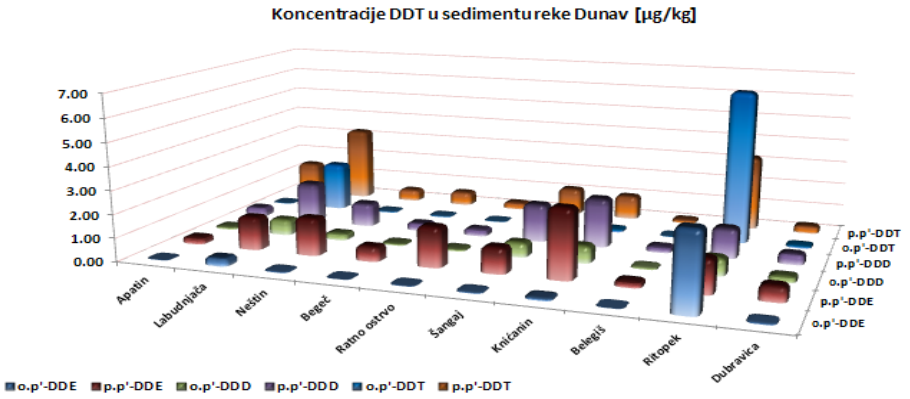
[2]Environmental Research Institute, North Highland College, University of the Highlands and Islands, UK

[a]majastupavski@uns.ac.rs

U cilju procene stepena kontaminacije akvatičnog sedimenta tokom 2012. godine na deset targetnih lokaliteta na teritoriji Republike Srbije, duž čitavog toka Dunava, sproveden je monitoring odabranih lipofilnih perzistentnih i emergentnih organskih jedinjenja. Uzorkovani sedimenti su ekstrahovani diholorometanom metodom Soxlet ekstrakcije (Büchi B-811 automatski ekstraktor), dok je prečišćavanje uzoraka izvršeno pomoću silikagela. Finalni ekstrakti nakon koncentrovanja tečnim azotom analizirani su gasnom hromatografijom-masene spektrometrije (GC 7890/MS-MS trostruki kvadrupol 7000B, Agilent). U radu su sprovedene dvostepene Pearsonove korelacije da bi se odredile veze između izmerenih parametara sedimenta koristeći statistički paket SPSS, verzija 22.0.

Na svim lokalitetima kvantifikovani su organohlorni pesticidi (DDT i njegovi metaboliti DDE i DDD) (Slika 1.). Sadržaj TOC u kolektovanim uzorcima sedimenta kretao se od 0,3% do 1,3%, ukazujući na značajnu varijaciju u prostornoj distribuciji, ali bez jasnog trenda. Srednje vrednosti koncentracija ΣDDE, ΣDDD i ΣDDT (suma o.p’ i p.p’) kretale su se u rasponu od 0,25 do 4,76, 0,31 do 2,86 i 0,16 do 9,84 µg·kg^{-1} d.w., respektivno, dok su se ukupne vrednosti ΣDDT kretale u rasponu od 0,70 do 16, µg·kg^{-1} d.w. sa srednjom vrednošću 5,08 µg·kg^{-1} d.w. i medijanom koja je iznosila 3,00 µg·kg^{-1} d.w. Vrednosti TOC su u velikoj meri korelisane sa koncentracijama ΣDDE ($r = 0,68$; $p<0.05$) i ΣDDD ($r = 0,66$; $p<0.05$), a u manjoj meri sa ΣDDT ($r = 0,34$; $p<0.05$). Utvrđene su značajne korelacije između koncentracija ΣDDT i ΣDDE ($r = 0,77$; $p<0.05$).

Zbog niskih proporcija DDE i DDD u tehničkim DDT, može se pratiti odnos DDT/(DDE+DDD) za sve uzorke sedimenta i ukoliko su dobijene vrednosti <1.0 generalno ukazuje na upotrebu u prošlosti, dok ukoliko je odnos > 1.0 ukazuju na trenutnu upotrebu DDT [2]. Odnos DDT/(DDE+DDD) u analiziranim uzorcima sedimenta reke Dunav u blizini Apatina, Labudnjače i Ritopeka ukazuje na činjenicu da se DDT u našoj zemlji i dalje koristi, iako je njihova upotreba krajem ’80-tih godina zabranjena. Na ostalim lokalitetima ovaj odnos je <1 i ukazuje na zagađenje izazvano u prošlosti.



Slika 1. *Koncentracioni nivoi DDT i njegovih metabolita u sedimentu reke Dunav na teritoriji Republike Srbije*

Upoređivanjem dobijenih vrednosti koncentracija DDT i njegovih metabolita sa vrednostima propisanih Uredbom o graničnim vrednostima zagađujućih materija u površinskim i podzemnim vodama i sedimentu i rokovima za njihovo dostizanje („Službeni glasnik RS”, br. 50/2012), može se zaključiti da na lokalitetu Ritopek vrednosti ΣDDT, ΣDDE i ΣDDD prelaze u znatnoj meri maksimalno dozvoljene koncentracije, dok vrednosti dobijene za ΣDDT ukupni ne ukazuju da je potrebno sprovesti remedijacione mere ni na jednom od ispitivanih lokaliteta. Na osnovu dobijenih rezultata, može se ustanoviti da duž toka reke Dunav na teritoriji Srbije još uvek postoje značajni potencijalni izvori zagađenja akvatičnih sistema orhanohlornim pesticidima, koje je neophodno opsežnijim monitoringom detektovati i sprečiti dalju upotrebu adekvatnim kontrolama pesticida koje se danas uvoze i proizvode u našoj zemlji, te bi se na taj način umanjili izrazito negativni ekotoksikološki efekti trenutno prisutni u akvatičnom sistemu.

Zahvalnica

Ovo istraživanje podržalo je Ministarstvo prosvete, nauke i tehnološkog razvoja Republike Srbije (III46009) i Ministarstvo obrazovanja Republike Češke (LO1214 i LM2011028).

Literatura

1. Li, P., Wang, Y., Huang, W., Yao, H., Xue, B., Xu, Y., Sixty-year sedimentary record of DDTs, HCHs, CHLs and endosulfan from emerging development gulfs: a case study in the Beibu Gulf, South China Sea. Bulletin of Environmental Contamination and Toxicology 92 (2014) 23–29.

Metode površinske jonizacije za merenje izotopskog sastava hlora

Methods of surface ionization for the measurement of chlorine's isotopic composition

Filip Veljković[1a], Boris Rajčić, Suzana Veličković

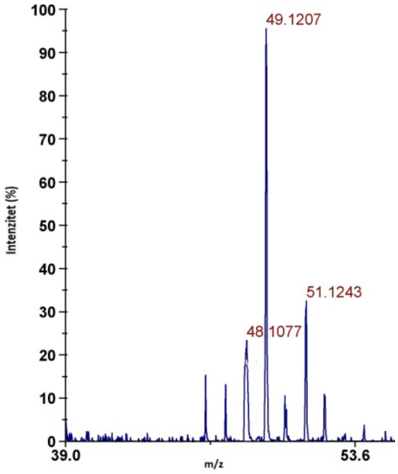
[1] Institut za nuklearne nauke „Vinča”, Univerzitet u Beogradu

[a]filipveljkovic@vin.bg.ac.rs

Jedinjenja hlorata i perhlorata koja se koriste kao herbicidi, pogonska čvrsta goriva i eksplozivi, i sve češće se prepoznaju kao zagađivači podzemnih voda [1]. Perhlorati su posebno opasni jer ometaju proizvodnju hormona u štitnoj žlezdi. Hlor je podložan izotopskom frakcionisanju fizičkim i hemijskim procesima. Varijacije u atomskim masama, kao i u zastupljenosti izotopa hlora su posledica njegovog izotopskog frakcionisanja tokom fizičkih, hemijskih i bioloških procesa. Upravo, te varijacije su korisne za određivanje porekla supstance i proučavanje ekoloških, hidroloških i geoloških procesa. Takođe, analizom izotopa hlora može se utvrditi i priroda zagađivača životne sredine odnosno da li je njegovo poreklo antropogeno ili ne. Informacije mogu biti važne iz pravnih razloga i za remedijaciju kontaminiranog područja [2, 3].

Hlor se u prirodi javlja u obliku dva stabilna izotopa ^{35}Cl i ^{37}Cl (relativnih atomskih masa, respektivno 34,968 8527 i 36,965 9026), čiji relativni izotopski sastav je 0,7553 i 0,2547 [4]. Merenje odnosa stabilnih izotopa hlora (n(^{37}Cl)/n(^{35}Cl)), kao i molske frakcije ^{36}Cl (n(^{36}Cl)/n(Cl)) pruža korisne informacije o poreklu hlorata i perhlorata u okruženju [2, 3]. Ranija merenja promene odnosa stabilnih izotopa hlora rađena su pomoću magnetnog masenog spektrometra sa površinskom jonizacijom u negativnom modu direktnim praćenjem jona Cl^- [5], ili određivanjem promena izotopskog sastava praćenjem jona jedinjenja CH_3Cl^+ [6]. Danas se metodom površinske jonizacije radi ispitivanja izotopskog sastava ne prate direktno joni hlora, već jedinjenja kao što su „superalkalni” klasteri tipa M_2Cl^+ (M-alkalni metali). Razlog je, vrlo niska energija jonizacije pomenutih klastera (u nekim slučajevima niža od energije jonizacije cezijuma) što omogućava njihovu vrlo jednostavnu detekciju u masenom spektru [7]. Iako je ova metoda precizna i pouzdana, vrlo je skupa.

Broj analiza izotopa hlora pomoću ugljovodonika koji u sastavu imaju hlor kao što je trihloretilen je u porastu, jer su ove vrste važni zagađivači životne sredine. Analiza kontinuiranog protoka trihloretilena molekula, bilo gasnom hromatografijom/izotopskom masenom spektrometrijom (GC/IRMS) ili sa masenom spektrometrijom GC/kvadrupol (GC/qMS), je inovativno analitičko rešenje, ali uprkos ranijim implementacijama, nedostaje joj rutinska aplikacija [8].



Slika 1. Maseni spektar Li_2Cl^+ klastera dobijenog LDI metodom.

Pored navedenih tehnika u površinske metode jonizacije spada i masenospektrometrijska metoda laserske desorpcije i jonizacije (LDI).

Preliminarni rezultati ukazuju da se „superalkalni“ klasteri tipa M_2Cl^+ mogu detektovati navedenom metodom. S obzirom na jednostavnost korišćenja i njenu ekonomsku isplatljivost, analiza i ispitivanje promene izotopskog sastava pomoću LDI metode može predstavljati važan korak u analitici.

Finansiranje je obezbeđeno od strane Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije, projekat broj OI 172019.

Literatura

1. Ader, M., Coleman, M., Doyle, S., Stroud, M., Wakelin, D., *Anal. Chem.* 73 (2001) 4946-4950.
2. Stewart, M., Spivack, J., *Rev. Min., Geochem.* 55 (2004) 231-254.
3. Böhlke, J., Sturchio, C., Gu, B., Horita, J., Brown, M., Jackson, A., Batista, J.R., Hatzinger, B., *Anal. Chem.* 77 (2005) 7838-7842.
4. Boyd, W., Brown, F., Loundsburg, M., *Can. J. Phys.* 3 (1955) 35-42.
5. Shields, S., Murphy, J., Garner, L., Dibeler, H., *J. Am. Chem. Soc.* 84 (1962) 1519-1522.
6. Kaufman, R., Long, A., Bentley, H., Davis, S., *Nature* 309 (1984) 338-340.
7. Neskovic, O., Veljkovic, M., Velickovic, S., Djeric, A., Miljevic, N., Golobocanin D., *Nukleonika* 47 (2002) S85-S87.
8. Bernstein, A., Shouakar-Stash, O., Ebert, K., Laskov, C., Hunkeler, D., Jeannottat, S., Sakaguchi-Söder, K., Laaks, J., Jochmann, A., Cretnik, S., Jager, J., Haderlein, B., Schmidt, C., Aravena, R., Elsner, M., *Anal. Chem.* 83 (2011) 7624-7634.

Asistencija mikrotalasa u hemiji: Sinteza novih mediuma za tretman otpadnih voda kontaminiranih emergentim polutantima

Microwave-Assisted Chemistry: Synthesis of new medium for the treatment of emerging pollutants contaminated water

Olivera Paunović[1a], Sabolč Pap[1,2], Nikola Bošković[1], Jelena Radonić[1], Maja Turk Sekulić[1]

[1]Fakultet tehničkih nauka, Departman za inženjerstvo zaštite životne sredine i zaštitu na radu, Univerzitet u Novom Sadu

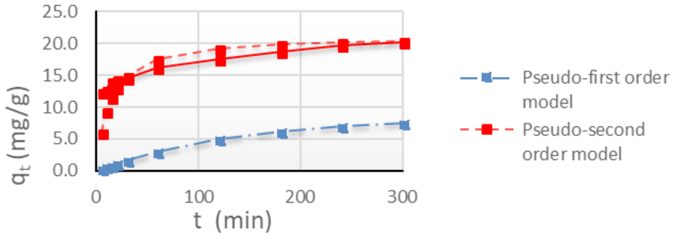
[2]Environmental Research Institute, North Highland College, University of the Highlands and Islands, UK

[a]o.paunovic88@gmail.com

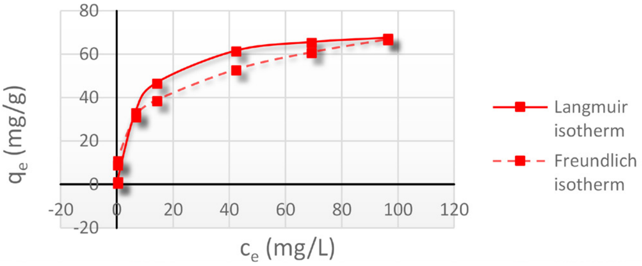
Farmceutici su primarno dizajnirani da izazivaju određene biohemijske procese u organizmu, da prolaze kroz ćelijsku membranu i veoma ih je teško deaktivirati pre nego što ispune svoju funkciju [1]. Kada se farmaceutici nađu u životnoj sredini, efekti se ispoljavaju na takozvanim „non-target“ organizmima, u čemu se ogleda njihov negativni uticaj na životnu sredinu [2]. Naproksen spada u arilacetatne kiseline, nesteroidne antiinflamatorne lekove.

Adsorpcija je veoma efikasna prilikom uklanjanja organskih materija iz vode. Nedostatak ove metode je visoka cena adsorbenata, zbog čega se intenzivno radi na razvijanju *low-cost* aktivnih ugljeva dobijenih iz otpadnih lignoceluloznih materijala.

U ovom radu prikazano je ispitivanje uklanjanja naproksena na aktivnom uglju dobijenom od koštica ringlova (*Prunus cerasifera Ehrh*.). Aktinivni ugalj dobijen je termohemijskom aktivacijom sirove biomase, kombinovanjem konvencionalne tehnike zagrevanja i mikrotalasa, uz KOH kao impregnaciono sredstvo Prilikom modelovanja adsorpcionog procesa korišćeni su kinetički modeli (Lagergrenov model pseudo-prvog reda (LMPR) i Ho-Mekejev model pseudo-drugog reda (HMMDR)) i ravnotežne izoterme (Lengmirova i Frojndlihova).



Slika 1: Kinetički modeli (LMPR i HMMDR)



Slika 2: Lengmirova i Frojndlihova adsorpciona izoterma

Tabela 1: Parametri primenjenih reakcionih kinetičkih modela i parametri analiziranih adsorpcionih izotermi za adsorpciju naproksena

Kinetički modeli	Parametar	Vrednost	Ravnotežne izoterme	Parametar	Vrednost
Lagergrenov model pseudo-prvog reda	R^2	0,994	Lengmirova izoterma	R^2	0,964
	K_1	-0,007		K_L	9,290
	qecal (mg/g)	8,383		q_0*(mg/g)*	73,137
	qeexp (mg/g)	21,111		q_{max} *(mg/g)*	73,020
Ho-Mekejev model pseudo-drugog reda	R^2	0,998	Frojndlihova izoterma	R^2	0,969
	K_2	0,004		K_F	18,395
	q_{ecal}*(mg/g)*	21,198		n	3,536

Poređenjem koeficijenata korelacije (R^2) primećuje se da se kinetika adsorpcije odvija po modelu pseudo-drugog reda, što se može zaključiti i iz dobijenih vrednosti za maksimalni adsorpcioni kapacitet (q_{ecal}).

Poređenjem korelacionih koeficijenata za Lengmirovu i Frojndlihovu izotermu, može se zaključiti da se adsorpcija može bolje opisati Frojndlihovom izotermom. *n* ima vrednost veću od 1, **što ukazuje na favorizovanost adsorpcije, maksimalni adsorpcioni kapacitet** aktivnog uglja za naproksen je 73,02 mg/g.

Na osnovu dobijenih rezultata se može zaključiti da se sintetisani aktivni ugalj može koristiti prilikom uklanjanja naproksena iz vode.

Literatura

1. Sanderson, H., Johnson, D., Wilson, C., Brain, R.,Solomon, K.,*Toxicology Letters* 144 (2003) 383-395
2. Silva, B., Costa F., Neves, I., Tavares, T., *SpringerBriefs in Molecular Science* (2015) 1-3

Brassicaceae in Phytoremediation: A review

Niko Radulović[1], Milica Todorovska[1a]

[1] Department of Chemistry, Faculty of Sciences and Mathematics, University of Niš, Višegradska 33, 18000 Niš, Serbia

[a]mimatod@gmail.com

The mustard family (Brassicaceae/Cruciferae) is a large angiosperm dicot plant family, which belongs to the order Brassicales. It encompasses a total of 338–360 genera and 3,709 species distributed worldwide on all continents except Antarctica [1]. Many cruciferous taxa are known to hyperaccumulate a very broad range of heavy metals and possess genes for resistance or tolerance to the toxic effects of a wide range of metals [2]. The use of plants in decontamination of soils contaminated with organic or inorganic compounds is called phytoremediation [3] and is generally regarded as more efficient and gainful compared with other remediation methods [4]. It is a natural and environmentally safe approach to decontaminate polluted sites. Members of the Brassicaceae plant family play a key role in the phytoremediation technology [2]. The purpose of this article is to review the use of both wild and cultivated Brassicaceae taxa in phytoremediation.

The Brassicaceae hyperaccumulating taxa include 87 species from 11 genera: *Alyssum* (46), *Arabis* (1), *Arabidopsis* (2), *Bornmuellera* (4), *Cardamine* (1), *Cochlearia* (1), *Peltaria* (2), *Pseudosempervivum* (2), *Stanleya* (1), *Streptanthus* (1), and *Thlaspi* (28) [2, 5]. The largest number of cruciferous hyperaccumulators is reported for nickel: *Alyssum* (45), *Bornmuellera* (4), *Cardamine* (1), *Peltaria* (1), *Pseudosempervivum* (2), *Streptanthus* (1), and *Thlaspi* (18). Ni-hyperaccumulators are distributed throughout southern Europe to the near East, the main hotspot being in the eastern Mediterranean (Turkey, Greece, Aegean), with the exception of *Streptanthus* from California. Palmer and co-workers suggested the next largest group are Zn hyperaccumulators: *Arabidopsis* (2), *Cochlearia* (1), and *Thlaspi* (17). The latter are reported from Europe, Turkey, western United States, and southern South America. Other reports of hyperaccumulation of metals include: Cd and $_{90}$Sr hyperaccumulation in UK populations of *Thlaspi caerulescens* and *Arabis stricta*, respectively, Se hyperaccumulation in *Stanleya* species from the western United States, and Pb hyperaccumulation in one *Alyssum* and two *Thlaspi* species from Europe. Several species were reported to hyperaccumulate more than one metal, for example, *Thlaspi caerulescens* (Cd, Ni, Pb, and Zn); *T. goesingense* and *T. ochroleucum* (Ni, Zn), and *T. rotundifolia* (Ni, Pb, and Zn) [2, 5].

In order to be effective in phytoremediation, a plant species must have a high growth rate, biomass buildup, be able to eradicate large amounts of contaminants, be tolerant to high levels of such contaminants and be well adapted to polluted environments [5]. This provides phytoremediation within a reasonable time period. A number of cruciferous taxa may not be suitable for direct use in phytoremediation due to low biomass and slow growth rate, but are valuable sources of genes for transfer to more desirable species [7]. They are well suited for genetic manipulations and *in vitro* culture techniques and are attractive candidates for the introduction of relevant genes aimed at phytoremediation. For phytoremediation of heavy metals, however, metal tolerance and hyperaccumulation may be more important than high biomass [6]. In this sense, Brassicaceae taxa are of utmost importance.

Acknowledgments: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172061).

References

1. Al-Shehbaz, I. A., Beilstein, M. A., Kellogg, E. A. *Plant Syst. Evol.* 259 (2006) 89-120.
2. Palmer, C. E., Warwick, S., Keller, W. *Int. J. Phytoremediation*. 3 (2001) 245-287.
3. Salt, D., et al. *Nature.* 13 (1995) 468-474.
4. Ali, H., Khan, E., Sajad, M. A. *Chemosphere*. 91 (2013) 869-881.
5. Dar, M.I., et al. (2015) Roles of Brassicaceae in Phytoremediation of Metals and Metalloids. In: Ansari A., Gill S., Gill R., Lanza G., Newman L. (eds) Phytoremediation. Springer, Cham
6. Chaney, R. L., et al. *Curr. Opin. Biotechnol.* 8 (1997) 279-284.
7. Pantola, R. C., Alam, A. *Int. J. Sci. Res. Environ. Sci.* 2 (2014) 120-138.

Preliminary investigation of polycyclic aromatic hydrocarbons in street dust of Pančevo, Serbia

Ivan Kojić [1], Tatjana Šolević Knudsen[2a]

[1] University of Belgrade, Innovation Center of the Faculty of Chemistry, Studentski trg 12-16, 11000 Belgrade, Serbia

[2] University of Belgrade, Institute of Chemistry, Technology and Metallurgy – Department of Chemistry, Njegoševa 12, 11000 Belgrade, Serbia

[a] tsolevic@chem.bg.ac.rs

Polycyclic aromatic hydrocarbons (PAHs) is a common name for a large group of organic compounds with two or more fused aromatic rings. PAHs are well known for their toxicity [1,2]. Because of that they keep attracting great interest on many environmental studies.

PAHs can have natural or anthropogenic origin. In nature, PAHs are produced during fires and volcanic eruptions, during formation of petroleum and coal, as a result of diagenesis of organic matter and by biosynthesis. The main anthropogenic sources of PAHs are processing of coal and crude oil, combustion and vehicle traffic [3].

Urban street dust is the sink of PAHs from different sources [4,5]. There is a general agreement that the higher amounts of PAHs in street dusts, the higher human exposure risk to these pollutants via inhalation, ingestion, or dermal contact [6].

The aim of this study was a preliminary investigation of PAHs in street dust of the Pančevo city, Serbia.

A representative composite street dust sample was collected from different locations in the Pančevo city. Using a set of stainless steel sieves the particles were fractioned into three sizes with diameters of: < 63 µm, 63 – 250 µm, and 250 – 500 µm. The street dust particles were extracted and the extracts were cleaned up and fractionated using column chromatography. PAHs were analysed by gas chromatography – mass spectrometry (GC-MS) in a selected ion monitoring (SIM) mode. The ions monitored were: $m/z = 128$ (naphthalene), $m/z = 152$ (acenaphthylene), $m/z = 154$ (acenaphthene), $m/z = 166$ (fluorene), $m/z = 178$ (phenanthrene and anthracene), $m/z = 202$ (fluoranthene and pyrene), $m/z = 228$ (benzo[a]anthracene and chrysene), $m/z = 252$ (benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[j]fluoranthene, benzo[e]pyrene and benzo[a]pyrene), $m/z = 276$ (indeno[1,2,3-c,d] pyrene and benzo[g,h,i]perylene), and $m/z = 278$ (dibenzo[a,h]anthracene).

The results showed that all PAHs investigated were present in the analysed composite sample. Furthermore, a non-target screening of the extracts indicated presence of some other environmentally important aromatic hydrocarbons such as: acetophenone, benzophenone, biphenyl and retene.

The analysis of the distribution pattern of the PAHs different in size in different size fractions revealed a possible size fractionation of three- and tetracyclic PAHs.

These results indicate that PAHs represent an important component in the street dust of the Pančevo city and point to the need for future investigation of the dust samples from this locality.

Acknowledgement

We thank the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project 17600) for supporting this research.

References

1. Aramandla R., Anthony E. A. *In Reproductive and Developmental Toxicology*, Edited by Ramesh C. G., Elsevier Inc., London, UK (2011) 577-591.
2. Darryl B. H., Aramandla R., Sanika C., Habibeh K., Anthony E. A. In *Reproductive and Developmental Toxicology*, Edited by Ramesh C. G., Elsevier Inc., London, UK (2011) 593-606.
3. Shields W. J., Ahn S., Pietari J., Robrock K., Royer L. In: *Environmental Forensics for Persistent Organic Pollutants,* edited by O'Sullivan, G, Sandau, C. Elsevier, AE Amsterdam, The Netherlands (2014) 1-20.
4. Wang X. S., Zhang P., Zhou H. Y., Fu J., *Inter. J. Environ. Study*, 69 (2012), 602–615.
5. Lee B. K., Dong T. T. T., *Jour. Hazard. Mat.*, 175 (2010) 540–550.
6. Wang X. S., Environ. Geochem. Health 40 (2018) 383-393.

Phthalate esters in glass jar metal lids from Serbian markets

Tatjana Šolević Knudsen[1a], Mila Ilić[1], Srđan Miletić[1], Jelena Milić[1],
Jelena Avdalović[1]

[1] Institute of Chemistry, Technology and Metallurgy, University of Belgrade,Belgrade, Serbia

[a]tsolevic@chem.bg.ac.rs

Phthalate esters are plasticizers which are used to impart flexibility in PVC resins but also in other resins such as polyvinyl acetates and polyurethanes. A wide range of consumer products contain specific members of this family of chemicals. Phthalate plasticizers are not chemically bound to PVC. Because of that they can enter the environment through losses during manufacturing processes and by leaching from final products [1]. Phthalate esters are suspected of having endocrine disrupting properties [2,3]. Exposure to high concentrations was shown to induce fetal death, cancer, liver and kidney injury and reproductive toxicity in animals [4,5,6]. Due to growing health concerns and environmental awareness, producers all over the world are increasingly forced to use non-phthalate plasticizers. However, phthalate esters are still found in many products, even in those which are used for food packaging and storage.

The aim of our study was investigation of glass jar metal lids for presence of phthalate esters. Different glass jars with screw-on metal lids were bought at supermarkets in Belgrade, Serbia. All metal lids had a plastic seal ring that goes between the glass lid and the rim of the jar.

The glass jars were washed according to the usual laboratory procedure, filled with distilled water, closed with screw-on metal lids and left upside-down for three days at room temperature. The water from glass jars was extracted with hexane. Hexane extracts were dried with Na_2SO_4, and evaporated to dryness under stream of nitrogen. Masses of all extracts were 0.2 mg. Procedural blank - a control sample containing distilled water in a glass jar without a metal lid was analyzed according to the same procedure. The resulting mass was negligible.

The extracts were analyzed by gas chromatography–mass spectrometry (GC–MS). GC–MS was conducted using an Agilent 7890A gas chromatograph (HP5-MS column, 30 m × 0.25 mm, 0.25 µm film thickness, He carrier gas, 1.5 cm3 min-1), coupled to an Agilent 5975C mass selective detector (70 eV).

GC-MS analysis revealed that most of the compounds identified in these extracts were phthalate esters. However, the lids were divided into two distinct groups, based on the number of carbon atoms in the alcohol chain of the phthalate esters identified.

One group contained phthalate esters with long alkyl chains (9, 10 or more C atoms). The second group contained phthalate esters with short alkyl chains (usually 4C atoms) with different degree of branching. Typical for the second group of lids were also squalene and 13-docosenamide, common plastic additives.

It can be concluded that, regardless of the type of the containing phthalate esters, 0.2 mg of these compounds can migrate from the investigated metal lids into distilled water with which it is in contact, during three days at room temperature. Considering the composition of food products which are usually packed in this kind of containers but also the fact that the increased temperature is usually used during their production process, it can be presumed that migration of phthalate esters from metal lids into the food products contained in the glass jars might be even higher.

Acknowledgement

We thank the Ministry of Education, Science and Technological Development of the Republic of Serbia (Projects 176006 and III 43004) for supporting this research.

References

1. Francisco G. C., Joaquín I., José A. D., in *Emerging Pollutants Origin Structure and Properties*, Wiley-VCH Verlag GmbH & Co., Weinheim, Germany, 2018, 274-280.
2. Jobling, S., Reynolds, T., White, R., Parker, M. G., Sumpter, J. P., *Environ. Health Perspect.* 103 (1995) 582–587.
3. Latini G., *Clin. Chim. Acta* 361 (2005) 20–29.
4. Lovekamp-Swan T., Davis B. J., *Environ. Health Perspect.* 111 (2003) 139–145.
5. Hauser R., Calafat A. M., *Occup. Environ. Med.* 62 (2005) 806–818.
6. Latini G., Del Vecchio A., Massaro M., Verrotti A., De Felice C., *Curr. Med. Chem.* 13 (2006) 2527–2534.

Razvoj hromatografske metode za određivanje tragova veštačkih zaslađivača u vodi

Development of chromatografic method for trace determination of artificial sweeteners in water

Eleonora Gvozdić[1a], Ivana Matić Bujagić[2], Svetlana Grujić[2], Tatjana Đurkić[2]

[1] Inovacioni centar Tehnološko-metalurškog fakulteta,

[2] Tehnološko-metalurški fakultet, Univerzitet u Beogradu

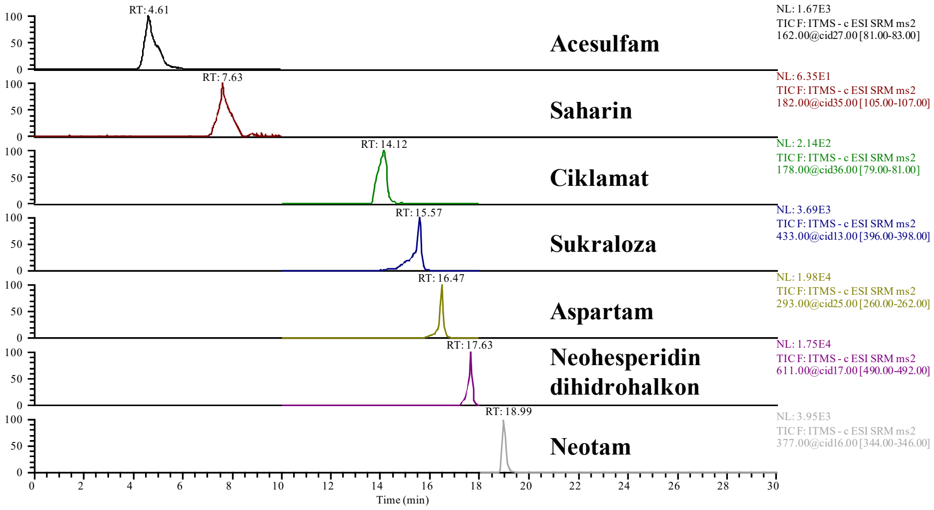
[a]egvozdic@tmf.bg.ac.rs

Nakon decenija upotrebe veštačkih zaslađivača kao aditiva u prehrambenim proizvodima, lekovima i sredstvima za oralnu higijenu, studije su dokumentovale njihovo prisustvo u životnoj sredini [1,2]. Veštački zaslađivači, zbog potencijalnih štetnih efekata po živi svet u okolini, pripadaju klasi emergentnih zagađujućih materija, a mogu se koristiti i kao indikatori zagađenja životne sredine komunalnim otpadnim vodama [1]. Za ove zagađujuće materije ne postoji referentna metoda određivanja u uzorcima voda, ali je u naučnoj literaturi opisano nekoliko metoda koje se najčešće baziraju na primeni tečne hromatografije u sprezi sa tandem masenom spektrometrijom (eng. liquid chromatography tandem mass spectrometry, LC-MS/MS) [1-4].

U ovom radu su prikazani razvoj i optimizacija tečno-hromatografske metode za analizu sedam odabranih veštačkih zaslađivača, sa ciljem optimalnog hromatografskog razdvajanja analita u što kraćem vremenskom periodu, u okviru LC-MS/MS analize. Maseni spektri odabranih veštačkih zaslađivača su snimljeni korišćenjem LTQ XL (Thermo Fisher Scientific, SAD) linearnog jonskog trapa, kao masenog spektrometra. Kao jonizaciona tehnika korišćena je elektrosprej jonizacija u negativnom režimu rada. Na osnovu rezultata MS^n analize odabrane su karakteristične reakcije fragmentacije za kvantitativno određivanje i potvrdu prisustva svakog analita koje su korišćene za dalji razvoj analitičke metode. Tečno-hromatografska analiza odabranih veštačkih zaslađivača izvršena je na Dionex UltiMate® 3000 HPLC sistemu (Thermo Fisher Scientific, SAD). U optimizaciji hromatografskog razdvajanja analita ispitane su dve reverzno-fazne kolone: Luna® C8 (3,0 mm × 150 mm × 3 µm) i Luna® C18 (4,6 mm × 150 mm × 3 µm), proizvođača Phenomenex, SAD. Testirani su i različiti sastavi mobilne faze sačinjene od dejonizovane vode i metanola ili acetonitrila. Takođe, ispitan je i dodatak aditiva amonijum-acetata (koncentracije 0,1 mol L^{-1}, u opsegu 1–10%), radi poboljšanja izgleda i oblika hromatografskih pikova analita. S obzirom na to da analiti ispoljavaju veći afinitet prema C18 koloni i eluiraju se na dužim retencionim vremenom, optimalno hromatografsko razdvajanje analita postignuto je primenom C8 kolone (slika 1) i gradijenta mobilne faze prikazanog u tabeli 1.

Tabela 1. Sastav i gradijent mobilne faze za hromatografsko razdvajanje odabranih veštačkih zaslađivača.

Vreme, min	Protok, mL min^{-1}	H_2O, %	CH_3OH, %	0,1 M CH_3COONH_4, %
0,00	0,33	84	15	1
8,00	0,33	84	15	1
13,00	0,33	34	65	1
15,00	0,33	0	100	0
20,00	0,33	0	100	0
20,01	0,33	84	15	1
30,00	0,33	84	15	1



Slika 1. Maseni hromatogrami smeše odabranih veštačkih zaslađivača dobijeni LC-MS/MS analizom standardnog rastvora koncentracije 500 ng mL^{-1}.

Zahvalnica

Ovaj rad je finansiralo Ministarstvo prosvete, nauke i tehnološkog razvoja Republike Srbije (broj projekta ON 172007).

Literatura

1. Buerge, I., Buser, H., Kahle, M., Muller, M., *Environ. Sci. Technol.* 43 (2009) 4381-4385.
2. Scheurer, M., Brauch, H., Lange, F.T., *Anal. Bioanal. Chem.* 394 (2009) 1585-1594.
3. Berset, J., Ochsenbein, N., *Chemosphere* 88 (2012) 563-569.
4. Arbelaez, P., Borrull, F., Pocurull, E., Marcé, R.M., *J. Chromatogr. A* 1393 (2015) 106-114.

Određivanje odabranih steroida u uzorcima komunalne otpadne vode

Determination of selected steroids in municipal wastewater samples

Ivana Matić Bujagić[1], Zorica Jauković[1], Svetlana Grujić[1], Eleonora Gvozdić[2a], Mila Laušević[1]

[1] Tehnološko-metalurški fakultet, Univerzitet u Beogradu,

[2] Inovacioni centar Tehnološko-metalurškog fakulteta, Beograd

[a]egvozdic@tmf.bg.ac.rs

Komunalne otpadne vode i efluenti iz postrojenja za prečišćavanje otpadnih voda predstavljaju značajan izvor zagađujućih materija u vodenoj sredini. Studije su pokazale da se steroidna jedinjenja u postrojenjima za tretman ne uklanjaju u potpunosti [1,2], kao i da prisustvo steroida u vodi, čak i pri veoma niskim koncentracijama, može izazvati brojne neželjene efekte [3]. U ovom radu analizirani su kompozitni uzorci otpadne vode, uzeti tokom pet dana sa dva ispusta komunalne vode u Novom Sadu. U uzorcima otpadne vode ispitivano je prisustvo 20 najčešće detektovanih steroidnih hormona i sterola optimizovanom metodom tečne hromatografije visokih performansi u sprezi sa tandem masenom spektrometrijom. Pored rastvornog oblika steroida, analizirana je i frakcija adsorbovana na suspendovanoj materiji.

Predtretman uzoraka izvršen je filtriranjem 1,0 L otpadne vode kroz filter sa staklenim vlaknima (veličine pora < 0,7 μm, LLG Labware, Francuska) da bi se odvojila frakcija adsorbovana na suspendovanim česticama. Za pripremu rastvornog dela uzoraka otpadnih voda korišćena je metoda ekstrakcije na čvrstoj fazi, dok je čvrsta, suspendovana frakcija pripremljena metodom ultrazvučne ekstrakcije. Rastvornom delu uzoraka, zapremine 100 mL, podešena je pH vrednost na 7,5. Potom su uzorci naneti na Oasis HLB kertridže (200 mg; 6 mL, Waters, SAD) koji su prethodno kondicionirani sa 5 mL metanola i 5 mL dejonizovane vode. Nakon nanošenja uzoraka, kertridži su osušeni pod vakuumom 10 min, a potom su analiti eluirani sa 15 mL metanola. Ekstrakti su upareni u struji azota, rekonstituisani do 1 mL pomoću metanola i filtrirani kroz 0,45 μm polivinililiden difluorid filtere (PVDF, Roth, Nemačka). Suspendovane čestice iz otpadne vode su ekstrahovane sa filtera ultrazvučnom ekstrakcijom sa 10 mL metanola u trajanju od 10 min. Potom je supernatant odvojen od taloga centrifugiranjem na 4000 o min^{-1} i postupak ekstrakcije je ponovljen još jednom sa 10 mL svežeg rastvarača. Supernatanti su spojeni i upareni u struji azota. Zatim su ekstrakti rekonstituisani i filtrirani kroz 0,45 μm PVDF filtere u bočice za dalju analizu. Tečno-hromatografska analiza je urađena na Dionex UltiMate 3000 LC sistemu (Thermo Fisher Scientific, SAD), a za razdvajanje analita je upotrebljena reverzno-fazna kolona Zorbax Eclipse® XDB–C8, dimenzija 150 mm × 3,0 mm sa 3,5 μm veličinom čestica (Agilent Technologies, SAD). Detekcija i kvantifikacija analita je izvršena pomoću linearnog jonskog trapa LTQ XL (Thermo Fisher Scientific, SAD), dok je kao jonizaciona tehnika korišćena hemijska jonizacija na atmosferskom pritisku.

U ispitivanim uzorcima otpadnih voda detektovani su samo steroli, dok steroidni hormoni nisu pronađeni. Analizom rastvornog dela uzoraka detektovani su koprostanol i holesterol (humani/životinjski steroli), kao i biljni steroli - stigmasterol, kampesterol i β-sitosterol, dok su u suspendovanoj frakciji dodatno pronađeni i fitosteroli dezmosterol i sitostanol (tabela 1).

Tabela 1. Minimalne i maksimalne koncentracije detektovanih analita u uzorcima otpadnih voda.

Analit	**Rastvorni deo uzoraka otpadne vode**		**Suspendovana frakcija uzoraka otpadne vode**	
	min *c*, μg L^{-1}	max *c*, μg L^{-1}	min *c*, μg L^{-1}	max *c*, μg L^{-1}
Koprostanol	13	49	7,3	381
Holesterol	6,3	48	14	365
Stigmasterol	0,20	0,60	3,1	19
Kampesterol	0,30	0,99	2,7	8,9
β-Sitosterol	2,0	20	38	74
Dezmosterol	-	-	1,5	3,9
Sitostanol	-	-	8,0	183

Iz dobijenih rezultata se jasno može uočiti da su koncentracije analita u netretiranoj otpadnoj vodi, posebno u suspendovanom delu, izuzetno velike što ukazuje na značaj analize suspendovane frakcije. Najviše koncentracije zabeležene su u slučaju humanih/životinjskih sterola, koprostanola i holesterola, u rastvornom (49 μg L^{-1} i 48 μg L^{-1}) i u suspendovanom delu (381 μg L^{-1} i 365 μg L^{-1}) uzoraka otpadnih voda, respektivno. Biljni steroli stigmasterol, kampesterol i β-sitosterol imaju znatno niže koncentracije u odnosu na humane/životinjske sterole, ali su koncentracije ovih sterola detektovane u suspendovanoj frakciji uzoraka otpadnih voda značajno veće od onih za odgovarajuću rastvornu frakciju uzoraka.

Zahvalnica

Ovaj rad je finansiran od strane Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije (broj projekta ON 172007).

Literatura

1. Chang, H., Wan, Y., Wu, S., Fan, Z., Hu, J., *Water Res.* 45 (2011) 732-740.
2. Furtula, V., Liu, J., Chambers, P., Osachoff, H., Kennedy, C., Harkness, J., *Water. Air. Soil Pollut.* 223 (2012) 1017-1031.
3. Bouman, A., Jan Heineman, M., Faas, M.M., *Hum. Reprod. Update* 11 (2005) 411-423.

Emisija teških metala u urbanim sredinama

Emission of heavy metals in urban areas

Snežana Aksentijević[1a], Ana Kremić[1], Jelena Kiurski[2]

[1] Visoka poslovno-tehnička škola strukovnih studija, Užice, Srbija

[2] Fakultet za ekonomiju i inženjerski menadžment, Univerzitet u Novom Sadu,

[a]sneza.aksentijevic@gmail.com

Depozicija i bioakumulacija zagađenog vazduha ima višestruke negativne efekte na vodene površine, zemljište, ekosisteme i ljude u urbanim i ruralnim područjima. Teški metali prisutni su u biosferi još od nastanka Zemlje [1]. U atmosferu dospevaju u vidu finih čestica prašine i u njoj se zadržavaju najčešće nekoliko dana do nekoliko sedmica. Mogu se transportovati na velike udaljenosti pre nego što se uklone iz atmosfere. Postoje tri načina unošenja teških metala u organizam: putem respiratornih organa, gastro-intestinalnog trakta i preko kože. Izlaganje ljudi povećanoj koncentraciji teških metala ukazuje da može doći do ozbiljnih negativnih zdravstvenih efekata: na mogućnost većeg broja bolesti kao što su kardiovaskularne, reproduktivni poremećaji, dermatitise, alergije i neke vrste kancera [2].

U radu su prikazani rezultati ispitivanja koncentracija suspendovanih čestica, frakcija PM_{10} i sadržaja teških metala, As, Cd, Ni i Pb u njima u najprometnijem delu grada Užica - merno mesto Narodno pozorište (Tabela 1). Ispitivanje teških metala As, Cd, Ni i Pb urađeno je po Uredbi o uslovima za monitoring i zahtevima za kvalitet vazduha ("Sl. glasnik RS", br. 11/2010 i 75/2010 i 63/2013) [3].

Tabela 1: Rezultati ispitivanja koncentracija suspendovanih čestica, frakcija PM_{10} i sadržaja metala u frakciji PM_{10} suspendovanih čestica

Parametar ispitivanja Pb			Suspendovane čestice, frakcija PM_{10}	Sadržaj metala u frakciji PM10 suspendovanih čestica			
			As	Cd	Ni		
Jedinica mere			µg/m³	µg/m³	ng/m³	ng/m³	ng/m³
Metoda			SRPS EN 12341	DM A14	DM A14	DM A14	DM A14
Granična vrednost za 1 dan (GV)			50	1	-	-	-
Br. uzorka	Primljeno	Završeno	Koncentracija				
1	17.03.2017	03.05.2017	62				
2	20.03.2017	03.05.2017	56				
3	21.03.2017	03.05.2017	56	47,1	< 1	1,3	17,5
4	23.03.2017	03.05.2017	48	31,8	< 1	0,9	10,0
5	27.03.2017	03.05.2017	41	57,7	< 1	1,0	9,8

6	27.03.2017	03.05.2017	47	19,0	< 1	0,4	10,3
7	29.03.2017	03.05.2017	44	34,8	< 1	1,6	18,4
8	31.03.2017	03.05.2017	47	23,6	< 1	0,4	8,2
9	03.04.2017	03.05.2017	44	20,3	< 1	0,9	18,5
10	04.04.2017	03.05.2017	39	20,8	< 1	0,4	15,5
11	06.04.2017	03.05.2017	32	15,2	< 1	<0,3	13,7
12	10.04.2017	03.05.2017	33	18,7	< 1	0,1	14,5
13	10.04.2017	03.05.2017	32	15,8	< 1	0,3	9,9
14	12.04.2017	03.05.2017	34	56,8	< 1	2,0	15,1
15	18.04.2017	03.05.2017	28	23,4	< 1	0,7	13,4
16	18.04.2017	03.05.2017	17	14,9	< 1	0,3	8,8

Vrednosti koncentracija suspendovanih čestica PM_{10} za 3-ći dan, prema “Sl. Glasniku Republike Srbije” br. 11/2010 i 75/2010 i 63/2013, član 22, prilog X, bile su iznad zakonski propisanih graničnih vrednosti (GV), ali prema kriterijumima za ocenjivanje kvaliteta vazduha na osnovu dnevnih vrednosti koncentracija zagađujućih materija (od 50 $\mu g/m^3$) kvalitet vazduha je prihvatljiv. Znatno su povećane koncentracije olova za sve uzorke.

Uzorkovanje vazduha je vršeno u jednoj od dve najprometnije ulice grada Užica, i prisustvo povećanih koncentracija ovog teškog metala može se objasniti i emisijom izduvnih gasova iz motornih vozila, koji pored olova mogu biti izvor i povećanih koncetracija kadmijuma. U samom gradu postoji i veliki broj individualnih kotlarnica u kojima se najviše kao gorivo koriste ugalj čije sagorevanje doprinosi emisiji arsena, a sagorevanje nafte u enegetskim postrojenjima doprinosi emisiji nikla, obzirom da su merenja izvršena u toku grejne sezone.

Godinama se pri kategorizaciji kvaliteta vazduha grad Užice nalazi u III kategoriji - **prekomerno zagađen vazduh** (gde su prekoračene tolerantne vrednosti, TV, za jednu ili više zagađujućih materija), tako da se moraju učiniti dodatni napori da se stanje poboljša: izmestiti tranzitni saobraćaj iz centralnih ka perifernim zonama grada; planiranje i projektovanje ozelenjavanja urbanih i zagađenih oblasti radi smanjivanja uticaja zagađenja koje prouzrokuje intenzivan protok automobila i najvažnije nastaviti sa gasifikacijom gradskih i individualnih kotlarnica.

Literatura

1. Morman, S. *Arsenic: A detective story in dust. EARTH*, (2010, June), 40-47.
2. Goletić, Š. *Teški metali u okolišu,* Zenica, (2005), 29-36.
3. Uredbe o uslovima za monitoring i zahtevima za kvalitet vazduha (“Sl. glasnik RS”, br. 11/2010 i 75/2010 i 63/2013)

Karakteristike aromatične frakcije mulja iz jezera Tehirgiol (Rumunija)

The characteristics of aromatic fraction in the mud of the Techirghiol lake (Romania)

Sanja Stojadinović[1a], Aleksandra Šajnović[1], Branimir Jovančićević[2], Mariana Golumbeanu[3], Roxana Almasan[4]; Ilija Brčeski[2]

[1]IHTM – Centar za hemiju, Univezitet u Beogradu, Njegoševa 12, Beograd, Srbija

[2]Hemijski fakultet, Univerzitet u Beogradu, Studentski trg 12-16, Beograd, Srbija,

[3]National Institute for Marine Research and Development "Grigore Antipa", Bd.Mamaia 300, Constanta, Romania

[4]Balneal and Rehabilitation Sanatorium Techirghiol, Constanta, Romania

[a] mrkics@chem.bg.ac.rs

Jezero Tehirgiol se nalazi u jugoistočnom delu Rumunije (Slika 1), na obali Crnog mora, od koga je odvojeno peščanim sprudom širine 100 m. Ovo jezero, čija je prosečna dubina 9 m je najveće slano jezero u Rumuniji i obuhvata površinu od 10,68 km^2. Visok salinitet jezera (55 g/l do 66 g/l) je rezultat male godisnje količine padavina, neposredne blizine Crnog mora i velikog intenziteta isparavanja [1, 2].

Slika 1. Tehirgiol jezero sa lokacijama uzorkovanja.

U ovom hipersalnom okruženju razvijen je jedinstveni ekosistem u Evropi, koji se karakteriše bogatim sapropelnim muljem koji se koristi u terapeutske svrhe.

U okviru ovog rada analizirani su aromatični ugljovodonici iz pet uzoraka sedimenata jezera Tehirgiol (Slika 1). Za ekstrakciju rastvorne organske supstance korišćena je smesa CH_2Cl_2/CH_3OH (9:1) u ekstrakcionom sistemu B-811, nakon čega je dobijeni ekstrakt razdvojen hromatografijom na koloni na zasićenu, aromatičnu i NSO frakciju. Zasićena i aromatična frakcija su potom analizirane pomoću gasnohromatografskomasenospektrometrijske tehnike.

Estri benzoeve kiseline su najdominantniji aromatični ugljovodonici u svim ispitivanim uzorcima. Pored njih, identifikovani su alkilbenzeni i PAH-ovi u znatno manjoj relativnoj obilnosti. Od PAH-ova dokazano je prisustvo kadalena, simonelita i retena, koji potiču od viših kopnenih biljaka, kao i PAH-ova koji su iz antropogenih izvora. U cilju određivanja porekla PAH-ova korišćeni su dijagnostički parametri: Fluranten/(Fluranten+Piren), ΣMetilfenantreni/Fenantren i LMW/HMW (odnos nisko- i visokomolekularnih PAH-ova). Vrednosti parametra Fluranten/(Fluranten+Piren) u opsegu 0,52-0,58, i relativne vrednosti odnosa LMW/HMW < 1 i ΣMetilfenantreni/Fenantren < 1 ukazuju na pirogene izvore ovih jedinjenja [3, 4, 5].

Prisustvo alkilbenzena, fenantrena i metilovanih fenantrena, vrednosti fenantrenskih maturacionih parametara, kao i tragovi drugih polikondenzovanih aromatičnih ugljovodonika karakterističnih za pirogeno/naftno zagađenje nedvosmisleno ukazuju i na prisustvo organske supstance antropogenog porekla u izolovanoj organskoj supstanci ispitivanog mulja.

Zahvalnica

Autori se zahvaljuju za podršku Ministarstvu prosvete, nauke i tehnološkog razvoja Republike Srbije (Broj projekta 176006).

Literatura

1. Barbulescu A., Barbes L. *Revista de Chimie (Bucharest)* 64 (2013), 868-874.
2. Barbulescu A., Maftei C. *Romanian Jouranal of Physics* 20 (2015), 1163-1170.
3. Perra G., Pozo K., Guerranti C., Lazzeri D., Volpi V., Corsolini S., Focardi S. *Marine Pollution Bulletin* 62 (2011) 874–877.
4. Grba N., Krčmar D., Kragulj Isakovski M., Molnar Jazić J. *Journal of Environmental Management* 182 (2016) 149-159.
5. Oyo-Ita I., Oyo-Ita O., Dosunmu M., Domínguez C., Bayona J., Albaigés J. 70 (2016) *Arch Environ Contam Toxicol.* ,372-382.

Rangiranje lokacija na teritoriji grada Kruševca na osnovu sadržaja teških metala u zemljištu primenom PROMETHEE metode

Location ranking based on heavy metal contents in soil in the area of Kruševac city using PROMETHEE method

Danijela Stojadinović[1a], Tanja Nikolić[2]

[1]Fakultet zaštite na radu, Univerzitet u Nišu

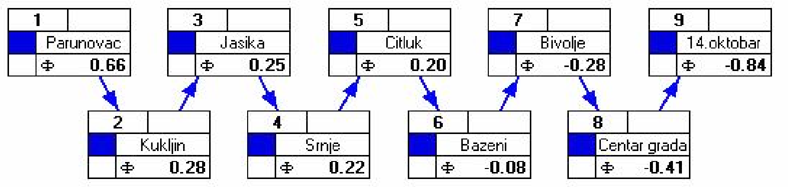
[2]Visoka tehnološko umetnička strukovna škola, Leskovac

[a]danijelastojadinovicks@gmail.com

Savremeno društvo se suočava sa ubrzanom kontaminacijom zemljišta teškim metalima usled industrijalizacije, brzog rasta svetske populacije i intenzivne primene agrohemikalija. Najznačajniji antropogeni izvori teških metala u životnoj sredini su hemijska i mašinska industrija. Teški metali se vremenom akumuliraju u zemljištu i biljkama i ulaze u lanac ishrane što može imati ozbiljne posledice po zdravlje ljudi i životinja [1]. Za razliku od zemljišta za poljoprivrednu namenu, urbana zemljišta, posebno u parkovima i stambenim zonama, mogu imati direktan uticaj na ljudsko zdravlje s obzirom na to da lako mogu dospeti u organizam. Smatra se da je ingestija prašine i zemlje jedan od glavnih puteva kojim su naročito deca izložena teškim metalima [2]. Stoga je razumljiva potreba za što boljim razumevanjem zagađenja urbanog zemljišta.

U ovom radu izvršeno je kompletno rangiranje mernih mesta u urbanoj sredini i okolini grada Kruševca na osnovu izmerenih nivoa koncentracija teških metala u zemljištu, primenom PROMETHEE II metode. Uzorkovanje zemljišta na teritoriji grada Kruševca vršeno je na mernim mestima: Srnje, 14. oktobar, Centar grada, Bazeni, Parunovac, Bivolje, Jasika, Čitluk i Kukljin. Praćeni su parametri teških metala u zemljištu: Hg, Pb, Cu, Cd, Ni, Zn, Cr, Br. Uzorkovanje i analizu je izvršio Gradski zavod za zaštitu zdravlja – Kruševac, na osnovu Pravilnika o dozvoljenim količinama opasnih i štetnih materija u zemljištu i vodi za navodnjavanje i metodama njihovog ispitivanja (Sl. gl. RS br. 23/94). Za analizu problema zagađenja zemljišta često se koriste metode MCDM (multi-criteria decision making). Primena PROMETHEE II metode podrazumeva definisanje odgovarajuće funkcije preferencije i dodeljivanje težine značajnosti (težinskog koeficijenta) svakom pojedinačnom kriterijumu. Određivanje težina značajnosti je veoma važan korak u svim višekriterijumskim metodama, pa tako i u metodi PROMETHEE II, gde donosilac odluke mora da bude dovoljno informisan i objektivan kako bi na adekvatan način dodelio težine svakom kriterijumu. PROMETHEE metod se bazira na određivanju pozitivnog ($\Phi+$) i negativnog toka ($\Phi-$) za svaku alternativu prema relacijama rangiranja, u korelaciji sa težinskim koeficijentima dobijenim za svaki kriterijum. Net flow (Φ) predstavlja razliku pozitivnog i negativnog toka preferencije i koristi se za kompletno rangiranje. Alternativa koja ima najveću Φ vrednost je najbolje rangirana [3].

Rangiranje devet mernih mesta (alternative) na osnovu stepena njihove kontaminacije teškim metalima (kriterujumi) izvršeno je primenom PROMETHEE II metode. Za funkciju preferencije odabrana je linearna funkcija, za sve definisane kriterijume, sa pragovima indiferencije (Q) i preferencije (P) u zonama 5% i 30%. Težinski koeficijenti su dodeljeni na osnovu udela svakog parametra – kriterijuma u ukupnom izmerenom zagađenju na svim posmatranim lokacijama i to: Hg - 0,07%, Pb - 11,73%, Cu - 9,71%, Cd - 0,08%, Ni - 31,15%, Zn - 32,36%, Cr - 14,49%, Br - 0,41%. Kompletno rangiranje alternativa PROMETHEE II metodom prikazano je na slici 1.



Slika1. PROMETHEE II kompletno rangiranje mernih mesta na kojima je vršeno uzorkovanje zemljišta.

Rezultati pokazuju da je najbolja – najmanje zagađena lokacija Parunovac, dok je najzagađenija – sa najlošijim kvalitetom zemljišta lokacija 14. oktobar. S obzirom na to da se raspolaže podacima o kvalitetu zemljišta koji obuhvataju i period kada je 14. oktobar radio sa punim proizvodnim kapacitetom, uz napomenu da danas radi sa smanjenim kapacitetom, potrebno je sagledavanje uticaja dominantnih industrija nakon dužeg praćenja i analiziranja zemljišta u njihovom okruženju.

Literatura

1. Suciu, I., Cosma, C., Todică, M., Bolboacă, S.D., Jäntschi, L., *Int. J.Mol. Sci.*9 (2008)434-453.
2. Chen, T-B., Zheng, Y-M., Lei, M., Huang, Z-C., Wu, H-T., Chen, H., Fan, K-K., Yu, K., Wu, X., Tian, Q-Z., *Chemosphere* 60 (2005) 542-551.
3. Nikolić, Đ., Milošević, N., Živković, Ž., Mihajlović, I., Kovačević, R., Petrović, N., *J. Serb. Chem. Soc.* 76 (2011) 625-641.

Čađ kao faktor kvaliteta vazduha na teritoriji grada Vranja

Soot as air quality factor in the area of Vranje city

Tanja Nikolić[1],Danijela Stojadinović[2a]

[1]Visoka tehnološko umetnička strukovna škola, Leskovac

[2]Fakultet zaštite na radu, Univerzitet u Nišu

[a]danijelastojadinovicks@gmail.com

Iako postoji opravdana zabrinutost u pogledu emisije polutanata vazduha iz antropogenih izvora, naše društvo se još uvek dobrim delom oslanja na upotrebu fosilnih goriva za različite primene. Industrijski procesi i sagorevanje goriva u energetskim postrojenjima i motornim vozilima spadaju u izvore sa najvećim uticajem na ukupno zagađenje vazduha urbanih sredina [1].U zimskim mesecima, kada je grejna sezona, dolazi do povećanih koncentracija zagađujućih materija, a tome doprinose i prirodni faktori: niska temperatura, povećana vlažnost, povećani atmosferski pritisak, vetar i padavine.

Prema Svetskoj zdravstvenoj organizaciji, zagađenje vazduha predstavlja najozbiljniju ekološku pretnju urbanoj populaciji, s obzirom na to da se povezuje sa tri miliona preranih smrti svake godine. Čađ je jedan od značajnih faktora promene kvaliteta vazduha. Može dospeti u organizam putem inhalacije vazduha u zatvorenom prostoru i spoljašnjoj sredini, ingestije kontaminirane hrane, kao i kontakta sa kožom [2]. Čađ može imati štetne posledice po zdravlje ljudi, pri čemu su posebno osetljiva deca, starije osobe i osobe obolele od kardiovaskularnih i respiratornih bolesti. Najčešće dolazi do nadražaja respiratorih puteva, otežanog disanja, kašlja, iritacije očiju i, pored toga, čađ ima značajnu ulogu u nastanku tumora pluća, kardiovaskularnog morbiditeta i mortaliteta [2,3].

U ovom radu analizirane su koncentracije čađi na teritoriji grada Vranja za vremenski period od 2012. do 2017. godine. Kontrola kvaliteta vazduha na ispitivanom području vrši se na dva merna mesta, u krugu Osnovne škole ”Svetozar Marković” i Zavoda za javno zdravlje Vranje. Merno mesto škole je u pravcu dominantnog severoistočnog vetra u odnosu na industrijsku zonu, tako da rezultati odražavaju uticaj industrijske zone za vreme strujanja ovog vetra, kao i uticaj lokalnih ložišta i saobraćajnica. Škola je smeštena u stambenoj zoni sa uglavnom zastupljenim individualnim stambenim objektima niske spratnosti, tako da zagađenje vazduha potiče od individualnih ložišta i saobraćajnih sredstava. Drugo merno mesto se nalazi u blizini centra grada i rezultati odražavaju uglavnom uticaj saobraćaja na kvalitet vazduha. Merno mesto se nalazi u blizini frekventnih saobraćajnica, kao i gradske toplane J.P. ”Novi dom” [4]. U tabeli 1 date su koncentracije čađi za analizirani vremenski period, na osnovu izvršenih merenja Zavoda za javno zdravlje Vranje.

Tabela 1. Koncentracije čađi na mernom mestu Osnovna škola ”Svetozar Markovič” (OŠ) i Zavod za javno zdravlje Vranje (ZJZV) za vremenski period od 2012. do 2017. godine

Godina merenja	Srednja godišnja koncentracija (µg/m³)		Maksimalno izmerena koncentracija (µg/m³)		Minimalno izmerena koncentracija (µg/m³)	
	OŠ	ZJZV	OŠ	ZJZV	OŠ	ZJZV
2012	13,72	19,65	71,7	231,5	6,1	8,4
2013	15,33	20,35	179,8	156,2	7,0	8,3
2014	13,63	15,96	80,6	87,6	7,5	8,4
2015	13,51	16,51	154,3	220,2	5,6	6
2016	10,1	12,29	75,9	93,4	5,3	5,9
2017	11,33	13,42	85,0	125,4	5,5	6

Srednje godišnje koncentracija čađi ne prekoračuju dozvoljenu graničnu vrednost (50 µg/m³) u posmatranom vremenskom periodu. Analizirajući mesečne koncentracije čađi, dolazimo do zaključka da su maksimalno zabeležene koncentracije izmerene u zimskom periodu, što se može povezati sa povećanom upotrebom fosilnih goriva u individualnim i kolektivnim ložištima. Sveopšte sagledavanje uticaja prirodnih i antropogenih činilaca ukazuje na njihov podjednako važan uticaj na prisustvo koncentracija čađi na analiziranim mernim mestima. Na prirodne činioce i dominantan severoistočan vetar koji duva u odnosu na industrijsku zonu ne može se puno uticati, ali uspostavljanjem kontrole nad antropogenim izvorima emisije može se smanjiti koncentracija čađi i time doprineti poboljšanju kvaliteta vazduha.

Literatura

1. Trumbulović-Bujić, Lj., Aćimović-Pavlović, Z., *Metalurgija*14 (2008)229-240.
2. Yakubu, O.H., *Environments* 5 (2018) 2-23.
3. Ilić, D., Jović, J., Mirković, M., Milošević, J., Đurić, S., Bukumirić, Z., Ćorac, A., *Praxis medica* 45 (2016) 35-39.
4. Zavod za javno zdravlje Vranje, http://www.zjzvranje.org.rs

Contamination influences of building construction site on surrounding environment in Serbia

Miljan Šunjević[1a], Vladimir Rajs[1], Boris Obrovski[1], Mirjana Vojinović Miloradov[1], Miljana Zeković[1], Darko Reba[1]

[1]Faculty of technical sciences, University of Novi Sad

[a]msunjevic@uns.ac.rs

One of the major sources of pollution is construction industry. There are a large number of environmental problems directly associated with pollution from building sites. The main concern pollution areas that construction industry is responsible are particle emission, air pollution, water pollution, noise pollution and soil pollution. Increasing pressure on construction industry to reduce pollution levels have made some effect, but despite the increasing efforts to reduce the environmental impact of construction processes, building sites are still an uncontrolled large source of pollution and adverse influence on the environment.

Rapid expansion of urbanization processes in Serbia generates large amounts of pollution that cumulatively cause severe degradation of environment. Situation with building sites environmental care in Serbia is inferior related to developed countries, due to inadequate legislation and ineffective control. In Serbia from 2014 concluding with 2016 there were 50.091 objects constructed (SYRS, 2017). Taking that into account it can concluded that there is average of 17.000 active building construction sites every year in Serbia. That large number of building sites is very hard to control and it is practically impossible to pay attention on environmental influence building sites produce. Causal relationship that occurs signifies the importance for changing building sites policies, particularly from the environmental point of view.

Construction, defined as all the activities that contribute to the creation, maintenance and operation of the built environment, is a fundamental component of the economic and social development of a country (E-CORE, 2005). However, significant challenges have to be faced, in terms of construction's influence on energy and climate change and its impact on natural resources (energy, water and materials) (EC, 2009).The amounts ofgaseous and solid waste can differ from site to site and depend on the architectural project, construction materials, management, storage and expertise of the workers on site. Commonly, construction companiesseparate only reusable and recyclable remains.The remaining waste after separation, such as concrete debris and the cut off piles were mixed with othertypes of waste and are being disposed as fill material. Waste removal is operated by construction companies themselves or by hiring others to remove and dispose it to waste off-sites. One of the main problems that occur is low level of recycling consciousness in Serbia, which can be seen through site management where site managers do not understand the benefit of construction waste segregation and believe that is waste of time and money. Commonly waste generated at construction sites are concrete, tiles, ceiling, steel, wood, materials package, aluminium, plastic, glass, and sand etc. Beside these materials, hazardous and potentially hazardous materials can be also found in construction sites such as asbestos-based materials, lead-based materials, mercury-containing electrical equipment, CFCs, PCBs, high corrosive materials, flammable materials, toxic and others emerging materials.

Cumulative effects of building site pollution (particle emission, air pollution, water pollution, noise pollution and soil pollution) can have a dramatic impact on environmental quality. To be able to have better environmental prevention, evaluation and control, contribution to environmental impacts reduction in construction building sites needs to be from the beginning of the construction process supported by contractors and other decision-makers, but also it requires governmental support and assistance. This type of the architectural research and investigation is rare and is sporadically preformed in Serbia.

Acknowledgement

The paper is supported by the Ministry of Education, Science and Technological Developmentof Serbia,Project No. III43008 “Development of methods, sensors, and systems for monitoring water, air and soil quality”.

References

1. Statistical Yearbook of the Republic of Serbia 2017 (2017), Statistical Office of the Republic of Serbia, page 310, ISSN 0354-4206
2. E-CORE, 2005, E-CORE Strategy for Construction RTD, Final Version, European Construction Research Network,http://www.eccredi.org/pages/StrategyReport.pdf
3. EC, 2009, Lead Market Initiative for Europe, Mid-term Progress Report, SEC,1198 final. http://ec.europa.eu/enterprise/policies/innovation/files/swd_lmi_midterm_progress.pdf
4. Marta Gangolells, Miquel Casals, Santiago Gassó, NúriaForcada, Xavier Roca, Alba Fuertes, A methodology for predicting the severity of environmental impacts related to the construction process of residential buildings, Building and Environment, Volume 44, Issue 3, 2009, Pages 558-571,ISSN 0360-1323, https://doi.org/10.1016/j.buildenv.2008.05.001.
5. S.G. Abramyan, Environmental Compliance During Construction, Procedia Engineering, Volume 150, 2016, Pages 2146-2149, ISSN 1877-7058, https://doi.org/10.1016/j.proeng.2016.07.255.
6. Yong Han Ahn, Chan Woo Jung, MinjaeSuh, MyungHwaJeon, Integrated Construction Process for Green Building, Procedia Engineering, Volume 145, 2016, Pages 670-676, ISSN 1877-7058, https://doi.org/10.1016/j.proeng.2016.04.065.

ADSORPCIJA I KATALITIČKA RAZGRADNJA ZAGAĐIVAČA U PRISUSTVU ZEOLITA

Adsorption and catalytic degradation of pollutants in the presence of zeolites

Suzana Rogan[1], Maja Milojević-Rakić[1a],Bojana Nedić Vasiljević[1], , Snežana Uskoković-Marković[2], Vera Dondur[1], Ljubiša Ignjatović[1]

[1]Fakultet za fizičku hemiju, Univerzitet u Beogradu,

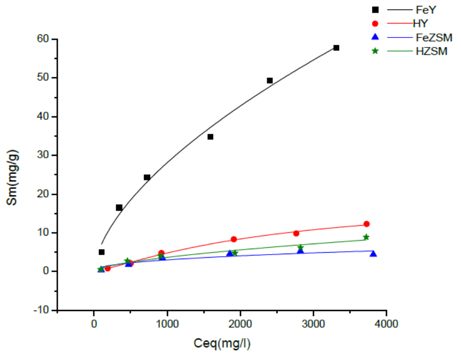
[2] Farmaceutski fakultet, Univerzitet u Beogradu, Srbija

[a]maja@ffh.bg.ac.rs

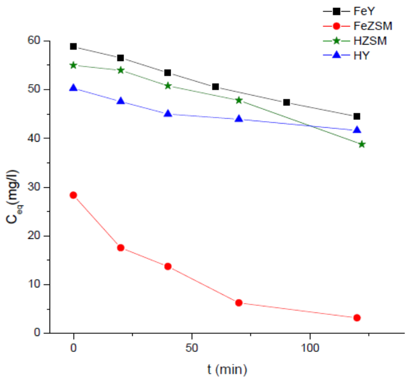
Pesticidi i naftne prerađevine predstavljaju izuzetno korisne industrijske proizvode, ali nažalost i su veliki zagađivači životne sredine. Veliki napori i finansijska sredstva se ulažu da bi se pronašla što efikasnija rešenja za uklanjanje ova dva tipa zagađivača, pre svega iz vodenih sredina[1,2].

U ovom radu proučavana je mogućnost otklanjanja zagađivača (glifosata i fenola), korišćenjem različitih vrsta zeolita. U slučaju glifosata, oni su služili kao adsorbensi, dok je u slučaju fenola ispitivan uticaj njihovog prisustva i katalitičkog delovanja u reakciji oksidacije fenola vodonik peroksidom. Ispitivani zeoliti u oba slučaja bili su HZSM, FeZSM, HY i FeY.

Iz adsorpcionih eksperimenata pokazano je da se adsorpcija na HZSM i FeY zeolitima može predstaviti Frojndlihovom izotermom, dok kod FeZSM i HY zeolita Langmir-Frojndlihova izoterma pokazuje bolje slaganje sa eksperimantalnim podacima (Slika 1). Pokazano je da se moć adsorpcije kreće u sledećem nizu FeZSM<HZSM<HY<FeY, te da je najbolji adsorbens za glifosat od ispitivanih zeolita FeY. Hidrofilniji HY zeolit bolje adsorbuje glifosat od nešto hidrofobnijeg HZSM zeolita. Pokazano je još i da, kad je u pitanju hidrofilan zeolit HY, jonska izmena Fe^{3+} jonima utiče na višestruko povećavanje količine adsorbovanog glifosta, dok je kod hidrofobnog HZSM zeolita sasvim suprotno. Naime, jonskom izmenom na ZSM zeolitu Fe^{3+} jonima, dolazi do opadanja količine adsorbovanog glifosata. Za uklanjanje glifosata iz vodenih rastvora, FeY zeolit se pokazao kao najbolji adsorbens.



Slika 1. Prikaz adsorpcionih izotermi glifosata na HZSM, FeZSM, HY i FeY zeolitu



Slika 2. Grafički prikaz smanjivanja koncentracije fenola u zavisnosti od reakcionog vremena na FeY, FeZSM, HZSM i HY zeolitu.

Što se tiče uticaja ispitivanih zeolitskih materijala na brzinu reakcije oksidacije fenola vodonik peroksidom, situacija je drugačija (Slika 2). Poznato je da hidrofobniji materijali bolje adsorbuju fenol[3], pa bi se očekivalo i da će ovakvi materijali pokazivati bolje katalitičke osobine. Hidrofobniji FeZSM zeolit je višestruko bolji katalizator od hidrofilnijeg FeY zeolita, čiji je uticaj na tok reakcije manji od uticaja zeolita HY i HZSM, za koje se i očekivalo da neće pokazivati katalitičku sposobnost. Kako oba zeolita imaju sličan sadržaj gvožđa (FeY=0,115 % i FeZSM=0,105 %) može se zaključiti da katalitička sposobnost FeZSM zeolita potiče od hidrofobnosti samog materijala. Tako se, od ispitivanih zeolita, kao najbolji katalizator pokazao FeZSM zeolit.

Literatura

1. Damjanović Lj., Rakić V., Rac V., Stošić D., Auroux A., J. Hazardous Mater. 184, (2010) 477-484.
2. Ying Y., Qi-Xing Z., Chemosphere58 (2005) 811-816.
3. Khalid M., Joly G., Renaud A., Magnaux P., Ind. Eng. Chem. Res. 43 (2004) 5275-5280.

Liverworts as potent bioaccumulators of environmental heavy metals: A review

Sonja Filipović[1a], Niko Radulović[1]

[1]Department of Chemistry, Faculty of Sciences and Mathematics, University of Niš, Višegradska 33, 18000 Niš, Serbia

[a]sonjafilipovic86@yahoo.com

The Marchantiophyta are a phylum of non-vascular land plants commonly referred to as liverworts with approximately 9000 species [1]. Liverworts have been investigated as monitors of pollution due to their ability to accumulate toxic elements [2]. Bryophytes have certain anatomical and morphological features, which rendered them suitable for their use as biomonitors/bioindicators. Although heavy metal accumulation in bryophytes is the field of interest, only few studies have been done on this topic: *Funaria*, *Jungermania*, *Scapania*, *Pellia*, *Conocephalum*, *Lunularia*, *Hylocomium*, *Hypnum*, *Marchantia*, *Pleurozium* and *Sphagnum* genera were investigated in this sense, while only seven species belong to the liverworts [3].

Morphology of bryophytes is significant in metal cation binding [3, 4, 5, 6]. *Conocephalum conicum* (L.) Dum., exhibits a significant correlation between concentrations of Cr and Co in soil and bioaccumulated amounts of these metals (11.33 mg/kg dry weight (d.w.); 7.15 mg/kg d.w.), and *Pellia epiphyla* (L.), was proven useful in pollution control, especially soil pollution with Cr (9.567 mg/kg d.w.), Cu (7.856 mg/kg d.w.) and Ni (11.67 mg/kg d.w.) [5]. Bioaccumulation ability (181 mg/kg d.w. Zn, 2.17 mg/kg d.w. Cd, 128 mg/kg d.w. Pb, 300-1000 mg/kg d.w. Hg) of *Scapania undulata* (L.) Dum., makes this species a valuable indicator of bioavailability and natural purificator of water as well as *Plagiochasma appendiculatum* Lehm. & Lindenb. which have shown the resistance to elevated Pb, Zn and Cr water levels [8, 9, 10]. High adsorption rates rendered *Marchantia polymorpha* L. as a hyper-accumulator for lead (2.276 µg/g d.w.; 7.792 p.p.m. d.w.) [3, 11]. Furthermore, the highest content of Hg in the aquatic plants ever is recorded in the liverwort species *Jungermannia vulcanicola* (Schiffn.) Steph. which contained 1.3% (836 µg/g-6060 µg/g) on a d.w. basis. The difference in the accumulated quantity originates from a varying distance from the apex and consequently different ability of cation binding and bioaccumulation [7]. Data on heavy metal concentration can also be deduced by monitoring the changes in the physiological parameters. Increase in proteins may be a defense mechanism since activation of phytochelatin synthase (PCS) in *C. conicum* [12, 13] together with constitutive metal(loid)-broadly responsive PCS by Cd, Cu, Hg, Pb etc. stress in *Lunularia curciata* was recorded [14]. This might clarify high resistance of this liverwort on elevated Cd concentrations (1.2% d.w.) compared to other plant species. Increased levels of chaperons, Hsp70, were also registered as a metabolic stress response in *C. conicum* being important as they play a central role in counteracting toxic effects of heavy metals. Enzymes controlling the physiological and biochemical processes are also influenced by intoxication. It was observed that toxi-tolerance of liverworts was conditioned by genetic differences, *L. curciata* (L.) Dum., compartmentalizes cadmium, which has a pleiotropic effect at the gene level showing an up-, and down-regulation of genes that encode cystathione γ-synthase and methyltransferase, tyrosine phosphatase enzyme, respectively [11, 15].

Bearing in mind all of the above mentioned, we could reckon that versatile and adaptable defense mechanisms counteracting heavy metal intoxication exist in liverworts and that the published results indicate this phylum as a prolific source of possible bioaccumulatiors, biosensors, and phytoremediators.

Acknowledgments: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172061).

References

1. Asakawa, Y., Ludwiczuk, A., Toyota, M., Hashimoto, T., Tori, M., Fukuyama, Y., Harinantenaina, L., *Heterocycles* 77 (2009) 99-150.
2. Richardson D.H.S (1981) *The biology of mosses,* Oxford: Blackwell Publishers
3. Sharma, S., *Aerobiologia*, 23(3) (2007) 181-187.
4. Carginale, V., Sorbo, S., Capasso, C., Trinchella, F., Cafiero, G., Basile, A., *Protoplasma* 223(1) (2004) 53-61.
5. Samecka-Cymerman, A., Marczonek, A., Kempers, A. J., *Arc. Environ. Contam. Toxicol.* 33(2) (1997) 162-171.
6. Samecka-Cymerman, A., Kempers, A. J., *Ecotoxicol. Environ. Saf.* 35(3) (1996) 242-247.
7. Satake, K., Soma, M., Seyama, H., Uehiro, T., *Arch. Hydrobiol*. (1983).
8. Vincent, C. D., Lawlor, A. J., Tipping, E., *Environ. Pollut.* 114(1) (2001) 93-100.
9. Samecka-Cymerman, A., & Kempers, A., J., *Ecotoxicol. Environ. Saf.* (1995) 31(1), 57-61.
10. Ghate, S., & Chaphekar, S. B., *Environ. Pollut*. 108(2) (2000) 173-181.
11. Briggs, D., *Nature*, 238 (5360) (1972) 166.
12. Miemyk, J., *Trends Plant Sci.* 2(5) (1997) 180-187.
13. Basile, A., Sorbo, S., Conte, B., Cardi, M., Esposito, S., *Environ. Pollut.* 182 (2013) 209-216.
14. Degola, F., De Benedictis, M., Petraglia, A., Massimi, A., Fattorini, L., Sorbo, S., Basile, A., *Plant Cell Physiol.* 55(11) (2014)1884-1891.
15. Basile, A., di Nuzzo, R. A., Capasso, C., Sorbo, S., Capasso, A., Carginale, V., *Gene* 356 (2005) 153-159.

Conocephalum conicum (L.) Dum., biosensor of an environmental pollution with phytoremediation potential

Sonja Filipović[1a], Niko Radulović1, Marko Mladenović[1]

[1]Department of Chemistry, Faculty of Sciences and Mathematics, University of Niš,

[a]sonjafilipovic86@yahoo.com

Increasing environmental pollution, mainly due to anthropogenic activities, seriously threatens to contaminate the ecosystems. Among the environmental contaminants one of the most hazardous one is the heavy metal pollution, since it does not undergo biodegradation, and can be accumulated in living organisms requiring a constant monitoring, as such [1]. Costly and drudgingly optimized methods, many of producing a residue rich in heavy metals, can be replaced by an environmental friendly, effective and affordable technological solutions such as phytoremediation and heavy metal pollution monitoring using the selected plant species, ”accumulators”[2].

Liverworts (Marchantiophyta, Hepaticae), the phyla of Bryophytes, represent one of the oldest terrestrial plants, with a great adaptational and harshest environmental conditions survival capability. Bryophytes are able to accumulate considerable amounts of heavy metals, due to their certain morphological and selected biochemical and enzymological responses developed to cope with this environmental threat [3]. They have been extensively employed as biomonitors of environmental pollution, but little is known about the behavior and localization of heavy metals and exact defense mechanisms [4]. Liverworts are suggested and currently studied in relation to uptake, and sub cellular localization of heavy metals [5,6], but only six species of this phyla (approximately 9000 species) have been investigated until now.

This work represents the first bio-monitoring-guided study of *Conocephalum conicum* (L.) Dum. (snake liverwort) collected from non-epilithic habitat on the Jastrebac mountain slopes, in Serbia. Plant material in our hands has been analyzed, and we report the chemical composition of the hydro distilled essential oil (0.03% w/w) and the ether extract (969.6 mg) of this liverwort species, in detail. A GC-MS analysis enabled the identification of 96.9% of the essential oil constituents, among which conocephalenol (15.4%), sabinene (28%), 1-octen-3-yl-acetate (5.4%) and isolepidozene (4.6%) where the dominant ones. The total of 91.9% of the ether extract constituents was also identified by the same method revealing the conocephalenol (16.9%), aristola-1(10),8-diene (11.3%), aristolene (7.5%) and brasila-5,10-diene (5.6%) as the most represented ones. This heavy metal tolerant liverwort [7, 8] has originated from the different localities (Italy, Poland) in the previous two studies, but it was comparable in secondary metabolite composition with our material. We could speculate, bearing in mind that the morphological characteristics accountable for the metal accumulation are always the same (high surface/volume ratio, absence or reduction of a cuticle, high absorption and ion exchange capacity on their cell wall, simple anatomic organization etc.) [9], that similarity of metabolism will result in similarity in the metabolic and molecular response to environmental pollution and activation of stress-related proteins. We could further deduce that *C. conicum* from Serbia could be used as an air pollution/bioaccumulation indicator. Phytoremediation (use of plants to remove, degrade or stabilize contaminants) potential of *C. conicum* is also attention grabbing, knowing that this liverwort absorbs heavy metals by cell walls and accumulates them in the parenchyma [7].

Although finding effective signals on environmental stress in *C. conicum* and clarifying its first line response to pollution, at a molecular level, clearly merits further exploration, we can conclude that the significance of novel natural biosensors and potential phytoremediation agents, such as *C. conicum*, is undeniable and obligatory.

Acknowledgments: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172061).

References

1. Tangahu, B. V., Sheikh Abdullah, S. R., Basri, H., Idris, M., Anuar, N., Mukhlisin, M., IJChER, (2011).
2. Sinha, R. K., Herat, S., Tandon, P. K., Phytoremediation: role of plants in contaminated site management. In Environmental bioremediation technologies Springer, Berlin, Heidelberg, (2007) 315-330.
3. Glime, J. M., Saxena, D, *Uses of bryophytes*, Today & Tomorrow’s Printers & Publ. (1991).
4. Sharma, S., *Aerobiologia*, 23(3) (2007) 181-187.
5. Samecka-Cymerman, A., Kempers, A. J., *Ecotoxicol. Environ. Saf.* 35(3) (1996) 242-247.
6. Samecka-Cymerman, A., Marczonek, A., Kempers, A. J., *Arc. Environ. Contam. Toxicol.* 33(2) (1997) 162-171.
7. Basile, A., Sorbo, S., Conte, B., Cardi, M., Esposito, S., *Environ. Pollut.* 182 (2013) 209-216.
8. Samecka-Cymerman, A., Marczonek, A., Kempers, A. J., *Arc.Environ. Contam. Toxicol.* 33(2) (1997) 162-171
9. Salemaa, M., Derome, J., Helmisaari, H. S., Nieminen, T., Vanha-Majamaa, I., *ScTEn* 324(1-3) (2004) 141-160.

Effects of power of ultrasound on the removal of cyprodinil from water by lignocellulosic-Al_2O_3 biosorbent

Nena Velinov[1a], Jelena Mitrović[1], Milica Petrović[1], Miloš Kostić[1], Danijela Bojić[1], Aleksandar Bojić[1]

[1] Faculty of Sciences and Mathematics, University of Nis

[a] nena.velinov@yahoo.com

Pesticides are chemicals used to eliminate or control a variety of agricultural pests that can damage crops and livestock and reduce farm productivity. However, only a minimal percentage actually reaches the crops, while the remainder ends up contaminating land, air and water. In this context, the leaching of pesticides to groundwater is an environmental and public health concern throughout the world, because many people use groundwater as drinking water [1]. Among the emerging remediation technologies for pesticide impurity, biosorption of pesticides using natural biomasses or agro-industrial wastes is known to be a feasible and efficient alternative considering numerous biosorbent sources, low operational costs, high removal efficiency and low secondary pollution risk [2-6].

In this study, the effect of power of ultrasound on removal of commonly used fungicide cyprodinil by chemically modified lignocellulosic biomass with Al_2O_3 (LC-Al_2O_3), was investigated. For biosorbent synthesis, *Lagenaria vulgaris* shell was used as a starting lignocellulosic material. Lignocellulosic biomasswas dried, grouned, chemically purified and chemically modified by small amount of Al_2O_3.

Ultrasound through its mechanical waves has been used as a means for enhancing the sorption process. Ultrasonic waves strongly enhance mass transfer between two phases through reducing the thickness of liquid films at the solid phase and thus the diffusion is enhanced [7]. Biosorption experiments were done at different ultrasound power from 0 to 50 W, while other parameters were kept constant (initial pH 7.0, initial cyprodinil concentration 12.0 mg dm^{-3}, sorbent dose 2.0 g dm^{-3}, temperature 25.0 ±0.2°C) (Figure 6). It is clear from the results that the presence of ultrasound does not change the removal efficiency of cyprodinil, but it speeds up the sorption process a lot. The removal efficiency in all three cases of different ultrasound power is 99.5%, but in the absence of ultrasound equilibrium is attained after 120 min period of time. In the presence of ultrasound with powers of 25 and 50 W, the equilibrium is attained considerably faster, after 40 and 20 min period of time, respectively. The stronger the acoustic power is, the greater is the intensity of ultrasonic field, which leads to the improvement of microstreaming, microturbulence, shock waves and microjets and to enhancement of mass transfer in the system and speed up the process of cyprodinil sorption [8].

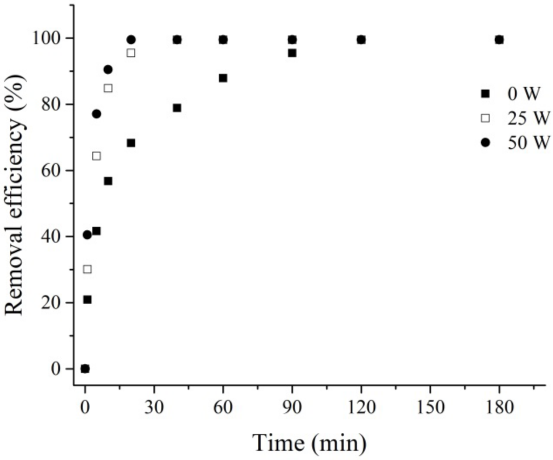


Figure 1. Effect of power of ultrasound on the cyprodinil sorption onto LC-Al_2O_3biosorbent.Initial pH 7.0, initial cyprodinil concentration 12.0 mg dm^{-3}, sorbent dose 2.0 g dm^{-3}, temperature 25.0±0.2ºC.

Acknowelgments

This work was financed by the Serbian Ministry of Education, Science and Technological Development through the Grant No TR34008.

References

1. Pionke H. B., Glotfelty D. W.,*Chemosphere*, 21 (1990) 813–822.
2. Taha S. M., Amer M. E., Elmarsafy A. E., Elkady M. Y.,*J Environ ChemEng*.2 (2014)2013–2025.
3. Vukčević M. M., Kalijadis A. M., Vasiljević T. M., Babić B. M., Laušević Z. V., Laušević M. D.,*Microporous. Mesoporous. Mater.*214(2015)156–165.
4. Rojas R ., Vanderlinden E., Morillo J., Usero J., El Bakouri H.,*Sci. Total. Environ.* 488–489(2014) 124–135.
5. Rojas R., Morillo J., Usero J., Vanderlinden E., El Bakouri H.,*J.Hydrol.*520(2015) 461–472.
6. Pinto M. de C. E., Gonçalves R. G. L., dos Santos R. M. M., Araújo E. A., Perotti G. F., dos S. Macedo R., Bizeto M. A., Constantino V. R. L., Pinto F. G., Trontoet J.,*Microporous.Mesoporous. Mater.*225(2016)342–354.
7. Entezari M., Keshavarzi A., *Ultrason. Sonochem.* 8(2001)213–216.
8. Entezari M. H., Soltani T., *J. Hazard. Mater.* 160(2008)88–93.

Sadržaj As, Cd, Cr, Ni i Pb u zemljištu tipa gajnjača na području Radmilovca

The content of As, Cd, Cr, Ni and Pb in Eutric Cambisols of Radmilovac area

Bojana Stanimirović[1,2a], Jelena Popović-Đorđević[3*], Radojka Maletić[3], Boris Pejin[4], Aleksandar Đorđević[3], Ilija Brčeski[2]

[1]Institut MOL d.o.o., Stara Pazova, Srbija

[2]Hemijski fakultet, Univerzitet u Beogradu

[3]Poljoprivredni fakultet, Univerzitet u Beogradu

[4]Institut za multidisciplinarna istraživanja – IMSI, Univerzitet u Beogradu

[a]mol@mol.rs

Gajnjače pripadaju redu automorfnih i klasi kambičnih zemljišta. Ova zemljišta su dobro aerisana sa odličnim filtracionim karakteristikama. Obrazuju se na supstratima bogatim bazama, rastresitim karbonatnim i beskarbonatnim sedimentima kao i na magmatskim i metamorfnim stenama. Kod nas su najčešće obrazovane na tercijernim ilovastim karbonatnim i beskarbonatnim sedimentima [1]. U Srbiji, gajnjača se nalazi u Šumadiji, Pomoravlju, Mačvi, Posavini, istočnoj Srbiji, Sremu, okolini Vršca i Bele Crkve, a do sada je kartirano 750.000 ha. Danas se najvećim delom koriste u poljoprivredne svrhe (>80% površina) [1].

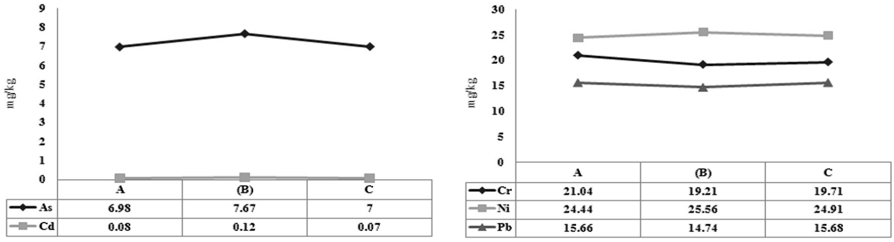
Mnogi elementi mogu biti toksični za biljke ukoliko se nađu u zemljištu u visokim koncentracijama. To se odnosi na elemente koji su esencijalni za biljke kao i na elemente koji nisu ni esencijalni ni korisni za biljke. U ove elemente spadaju teški metali. Povećane koncentracije ovih elementata mogu biti posledica njihove prirodne rasprostranjenosti ili antropogenog uticaja. Takođe, njihova akumulacija, mobilnost i rastvorljivost uglavnom zavise od specifičnih karakteristika zemljišta [2].

Cilj rada bio je da se utvrdi bezbednost i kvalitet zemljišta za gajenje poljoprivrednih kultura na osnovu sadržaja As, Cd, Cr, Ni i Pb u zemljištu tipa gajnjača na području Radmilovca.

Uzorci zemljišta uzeti su sa tri dubine: horizont **A**-0-55cm, (**B**)-55-103 cm i **C**-103-129 cm, i nekoliko lokacija na eksperimentalnom polju ”Radmilovac” koje pripada Poljoprivrednom fakultetu Univerziteta u Beogradu. Prema vrednostima aktivne kiselosti (pH u H_2O) zemljište je neutralno u humusnom horizontu i blago kiselo u pothumusnim horizontima, **A**-6,92; (**B**)-6,51; i **C**-6,34 [3]. Priprema uzoraka za hemijsku analizu urađena kao što je opisano u našem prethodnom radu [2]. Sadržaj As, Cd, Cr, Ni i Pb određen je analitičkom tehnikom indukovano spregnute plazme sa optičkom emisionom spektroskopijom (ICP-OES) [2]. Za svaku dubinu izvršena su merenja u tri ponavljanja. Eksperimentalni rezultati obrađeni su statističkom analizom uz primenu parametarskih testova ANOVA i Tukey ($p<0,05$).

Dobijeni rezultati pokazuju da je Cd detektovan u najmanjoj (0,09 mg/kg) a Ni

(24,97 mg/kg) u najvećoj prosečnoj koncentraciji. Posmatrano po horizontima, najveća koncentracija As, Cd i Ni zastupljena je u horizontu (**B**) (55-103 cm), Cr u horizontu **A (**0-55cm) a Pb u horizontima **A (**0-55cm i **C (**103-129 cm), **slika 1**. Sadržaj elemenata statistički se značajno razlikuje između horizonata (p<0,05).



Slika 1. Sadržaj As, Cd, Cr, Ni i Pb (mg/kg) u horizontima A, (B) i C u zemljištu tipa gajnjača

Koncentracije ispitivanih elemenata u sva tri horizonta niže su od maksimalno dozvoljenih koncentracija u zemljištu, propisanih *Pravilniku o dozvoljenim količinama opasnih i štetnih materija u zemljištu i vodi za navodnjavanje i metodama njihovog ispitivanja* [4]. Dobijeni rezultati ukazuju da zemljište tipa gajnjača na području Radmilovca nije zagadjeno toksičnim elementima i da je bezbedno za poljoprivrednu proizvodnju.

Rad je urađen u okviru projekata broj 46009, 172053 i 172017 koje finansira Ministarstvo prosvete, nauke i tehnološkog razvoja Republike Srbije

Literatura

1. Đorđević, A., S., Radmanović, *Pedologija*, Univerzitet u Beogradu – Poljoprivredni fakultet Beograd (2016)
2. Stanimirović B., Popović Djordjević J., Pejin B., Maletić R., Vujović D., Raičević P., Ž., Tešić, *Sci. Hort*. 237 (2018) 74–80.
3. Moravčević, V. M., Karakteristike gajnjače na području Radmilovca, master rad, Univerzitet u Beogradu, Poljoprivredni fakultet (2017)
4. *Pravilnik o dozvoljenim količinama opasnih i štetnih materija u zemljištu i vodi za navodnjavanje i metodama njihovog ispitivanja*, Službeni glasnik br. 23/94.

Sadržaj torijuma-232, urana-235 i urana-238 u unutrašnjim organima divljih ptica sa područja Vojvodine

Thorium-232, uranium-235 and uranium-238 content in internal organs of wild birds from the area of Vojvodina

Željko Mihaljev[1a], Brankica Kartalović[1], Nenad Popov[1], Sandra Jakšić[1], Milica Živkov-Baloš[1]

[1]Naučni institut za veterinarstvo „Novi Sad“

[a]zeljko@niv.ns.ac.rs

Do ,,tehnološki povećane prirodne radioaktivnosti’’ [1] dovodi nekontrolisana primena fosfatnih đubriva [2] što predstavlja najveći antropogeni izvor povećanja sadržaja urana i torijuma u zemljištu, a samim tim i u ostalim karikama lanca ishrane: zemljište-vegetacija-životinjski svet-čovek [3]. U tom cilju su sa lovno-šumskih gazdinstava na području Vojvodine sakupljeni uzorci unutrašnjih organa (bubrega) različitih vrsta divljih ptica, i to: **1.** Orao belorepan (Haliaeetus albicilla),**2.** Roda (Ciconia), **3.** Orao mišar (buteo buteo), **4.** Velika šumska ušara (Bubo bubo), **5.** Stepski soko (Falco cherrug), **6.** Rečni galeb (Larus ridibundus), **7.** Divlja patka (Anas platyrhynchos),**8.** Fazan (Phasianus colchicus), **9.** Prepelica (Coturnix coturnix) i **10.** Vodomar (Alcedo atthis). Sakupljeni uzorci divljih ptica pripremljeni su za merenje mikrotalasnom digestijom a sadržaj ukupnog Th i U određen je induktivno spregnutom plazmom sa masenom detekcijom [4]. Koristeći specifične aktivnosti za ^{232}Th, ^{235}U i ^{238}U dobijene su njihove koncentracije aktivnosti u ispitivanim uzorcima.

Na osnovu rezultata iz tabele 1. može se zaključiti da je najveći sadržaj torijuma izmeren u bubrezima orla belorepana (12,1 µg/kg) sa aktivnošću od 49,3 mBq/kg.

Tabela 1. Sadržaj Th i U i koncentracije aktivnosti ^{232}Th, ^{235}U i ^{238}U u uzorcima

Br.uzorka(bubrezi)	SadržajTh [µg/kg]	Aktivnost ^{232}Th [mBq/kg]	Sadržaj U [µg/kg]	Aktivnost ^{238}U [mBq/kg]	Aktivnost ^{235}U [mBq/kg]
1.	12,1 ± 1,5	49,3 ± 6,3	41,7 ± 2,9	463,1 ± 32,6	23,8 ± 1,7
2.	5,2 ± 1,3	21,2 ± 5,9	11,7 ± 1,4	129,3 ± 15,6	6,6 ± 0,8
3.	4,5 ± 0,1	18,5 ± 0,2	10,9 ± 3,1	121,2 ± 34,7	6,2 ± 1,8
4.	2,5 ± 0,3	10.1 ± 1,1	5,7 ± 0,8	62,7 ± 8,8	3,2 ± 0,5
5.	1,8 ± 0.2	7,2 ± 0,6	3,5 ± 0,5	38,6 ± 5,6	2,0 ± 0,3
6.	1,4 ± 0,3	5,8 ± 1,4	6,4 ± 1,4	70,8 ± 15,2	3,6 ± 0,8
7.	2,3 ± 0,4	9,2 ± 1,8	5,7 ± 0,3	63,3 ± 2,9	3,3 ± 0,2
8.	2,1 ± 0,2	8,6 ± 0,9	7,0 ± 0,7	77,1 ± 7,6	4,0 ± 0,4
9.	3,9 ± 0,2	16,0 ± 0,6	6,6 ± 0,7	72,7 ± 7,5	3,7 ± 0,4
10.	5,9 ± 0,2	24,0 ± 1,0	9,4 ± 0,6	104,1 ± 7,0	5,3 ± 0,4
Opseg	**1,4 – 12,0**	**5,8 – 49,3**	**3,5 – 41,7**	**38,6 – 463,1**	**2,0 – 23,8**

Najveći sadržaj urana (41,7 µg/kg) je takođe izmeren kod orla belorepana pri čemu je aktivnost ^{238}U iznosila 463,1 mBg/kg, dok je aktivnost ^{235}U iznosila 23,8 mBq/kg.Kod svih ostalih analiziranih uzoraka divljih ptica, sadržaj torijuma je bio veoma nizak i ujednačen a kretao se u intervalu od 1,4 (rečni galeb) – 5,9 (vodomar) µg/kg sa aktivnošću od 5,8 – 24,0 mBq/kg. Izmereni sadržaj urana je kod ostalih uzoraka bio takođe nizak i ujednačen a kretao se u intervalu od 3,5 (stepski soko) – 11,7 (roda) µg/kg, priče mu se aktivnost ^{238}U u ovim uzorcima kretala u opsegu od 38,6 – 129,3 mBq/kg a aktivnost ^{235}U u opsegu od 2,0 – 6,6 m Bq/kg. Za Vojvodinu, kao područje sa velikim mogućnostima za proizvodnju zdravstveno bezbedne hrane, od izuzetnog značaja je sistematsko praćenje nivoa radioaktivnosti životne sredine, jer ukoliko se kontaminira materijama sa tehnološki povišenim nivoom prirodne radioaktivnosti, može doći do povećanja doze koju primi stanovništvo od radioaktivnog zračenja [5]. Takođe možemo zaključiti da je induktivno spregnuta plazma sa masenom detekcijom vrlo osetljiva metoda za kvantitativno određivanje koncentracije Th i U u biološkom materijalu [6]. Zbog toga se može uspešno koristiti kao alternativna metoda za praćenje veoma niskih koncentracija Th i U u životnoj sredini [7]. Dobijeni rezultati doprinose boljem sagledavanju translokacije i nakupljanja prirodnih radionuklida u unutrašnjim organima divljih životinja što omogućuje procenu ekološkog stanja geografskih područja sa kojih ispitivana divljač potiče.

Zahvalnica: Ovaj rad je finansiralo ministarstvo prosvete, nauke i tehnološkog razvoja (br. Projekta TR 31084).

Literatura

1. Simić M., Kovačević J., Radošević B., Jović V., Prirodni kontaminanti životne sredine, *Tehnologija mesa*, 42 (2001) 45-57.
2. Mitrović B., Vitorović G., Stojanović M., Vitorović D., Radioaktivnost fosfatnih mineralnih proizvoda, *Vet. Glasnik* 65 (2011)123-140.
3. Mihaljev Ž., Ljubojević D., Ćirković M., Baloš M. Ž., Jakšić S., Kartalović B., Prica N., Radioactiviti of the Soil in Vojvodina (Northern Province of Serbia), Proceedings, First International Symposium of Veterinary Medicine, Scientific Veterinary Institute "Novi Sad", Novi Sad, (2015) 173-177.
4. Zoriy M. (2005): Determination of long-lived radionuclides at ultratrace level using mass spectrometric techniques, Forschungszentrum Jülich
5. Dželalija M. Ionizirajuće zračenje u biosferi, Sveučilište u Splitu, Kemijsko tehnološki fakultet (2006).

Vaskularne biljke kao bioindikatori zagađenosti zemljišta u urbanim ekosistemima

Plant bioindicators of soil pollution in urban ecosystems

Tatjana Sekulić[1a], Vladanka Stupar[1], Zlata Živković[1]

[1]Visoka tehnička škola strukovnih studija Požarevac

[a]tatjana.sekulic.84@gmail.com

U biološkom monitoringu zagađenosti zemljišta najčešće se koriste vaskularne biljke (vrste, njihove populacije i fitocenoze) kao fitoindikatori. One mogu precizno ukazati na prisustvo i intenzitet različitih zagađujućih materija (teški metali, hemijske materije, i td.) u zemljištu urbanih biotopa [1]. Primena viših biljaka u indikaciji zagađenosti zemljišta zasniva se na njihovoj sposobnosti da "absorbuju" metale (posebno teške metale) i druge toksične supstance iz zemljišta, i vrše njihovu akumulaciju, čime indukuju na relativno povećanje i širenje zagađenja na staništu. U biomonitoringu teških metala najčešće se analiziraju listovi i kora drveća, ali se koriste i koren i rizom.

Tako na primer, vrste indikatori serpentinistskih staništa, ukazuju na tla siromašna kalcijumom, a obogaćena magnezijumom, kao i niklom, hromom i kobaltom. Na Balkanu to su npr. *Halacsya sendtneri, Cheilanthes marantae, Asplenium cuneifolium, Silene paradoxa, Echium rubrum, Alyssum murale* itd. *Viola arsenica* je vrsta koja je indikator zemljišta koja su bogata arsenom. *Urtica dioica* i *Urtica urens* ukazuju na povećanu koncentraciju nitrata i nitrita u zemljištu i obično naseljavaju nitrifikovana staništa u urbanim sredinama.

Hiperakumulatori se definišu kao one vrste koje su sposobne da talože (akumuliraju) metale u koncentracijama koje su i do 100 puta veće od koncentracija koje su izmerene kod ostalih biljaka koje ne akumuliraju teške metale. Verovatno najpoznatiji hiperakumulator teških metala je vrsta *Thlaspi caerulescens*. Dok najveći broj biljaka pokazuje simptome toksičnosti pri koncentraciji cinka od oko 100 ppm, ova biljka akumulira cink u koncentraciji od 26.000 ppm bez ikakvih oštećenja. Mnoge biljke, uključujući i *T. caerulescens* pokazuju sposobnost naseljavanja (kolonizacije) staništa (zemljišta) koja su obogaćena olovom, cinkom i kadmijumom, tzv. kalaminska zemljišta. Ova vrsta zajedno sa vrstom *Brassica juncea* predstavlja model za istraživanje fiziologije i biohemije usvajanja teških metala.

Većina biljaka je osetljiva i na minimalne količine teških metala u podlozi, ali značajan broj vrsta opstaje na staništima koja se odlikuju velikim količinama teških i toksičnih metala. Takve biljke su, tokom evolucije, razvile brojne adaptivne mehanizme na osnovu kojih savladavaju nepovoljne uslove staništa [2].

Jedna od najinteresantnijih i najkontroverznijih biljaka za biološku indikaciju zagađenosti zemljišta u urbanim ekosistemima je *Ailanthus altissima* - kiselo drvo (pajasen) [3]. Ova vrsta potiče iz jugoistočne Azije, i preneta je na Evropski kontinent sredinom 18-tog veka, i danas je jedna od najbolje prilagođenih adventivnih lišćarskih vrsta na kompleksne uslove zagađenih gradskih biotopa. Stoga su i rađena istraživanja ukupne brojnosti, populacione strukture, kao i uporedna proučavanja morfo-fizioloških karakteristika jedinki koje se razvijaju u uslovima ekstremno zagađenog zemljiša na različitim ruderalnim staništima uže gradske zone Beograda. Totalnim prebrojavanjem populacija vrste *A. altissima*, tokom perioda 1990-1992. godine, konstatovano je prisustvo 7362 jedinke. Analizom zastupljenosti različitih uzrasnih klasa, utvrđena je najveća brojnost klijanaca, juvenila i izbojaka s jedne strane, kao i vegetativnih adulta s druge strane. Ovakav odnos ukazuje na pogodnost ekoloških uslova urbanih biotopa za razvoj i izuzetnu ekspanzivnost ove vrste. Za razliku od drugih vrsta drveća prisutnih u drvoredima i na ruderalnim staništima Beograda, kod kojih su patološke promene na listovima usled velike koncentracije zagađujućih materija uočljive već na prvi pogled, kiselo drvo uspeva na istim staništima bez ikakvih, makroskopski i mikroskopski, vidljivih oštećenja na listovima. Određene strukturne promene u uslovima zagađene sredine predstavljaju povećanu kseromorfizaciju koja odražava prilagođavanje na stresne uslove urbanih staništa. Promene u anatomskoj građi listova vrste *A. altissima* iz zagađene sredine ogledaju se u redukciji veličine ćelija palisadnog tkiva lica lista, u povećanju količine kristala i idioblasta, kao i upadljivim brojem hloroplasta u ćelijama mezofila.

Na osnovu prethodno navedenih podataka, može se zaključiti da su vaskularne biljke kao bioindikatori, osnova biološkog monitoringa zagađenosti zemljišta u urbanim biotopima, jer je diverzitet ruderalne flore uslovljen i srazmeran intenzitetu antropogenih uticaja u urbanim ekosistemima. Poznavanje ekologije i rasprostranjenja ovih vrsta i zajednica, kao i mehanizama njihovih adaptacija na uslove stresa (koji po pravilu vladaju u urbanim biotopima), predstavlja imperativ savremenih urbanoekoloških istraživanja.

Literatura

1. Cvijan M., Ekologija zagadjenih sredina, bioindikatori i monitoring sistem, skripta 1.deo, Biološki Fakultet Univerziteta u Beogradu (2000) Beograd.

2. Stevanović, B., Janković, M. Ekologija biljaka sa osnovama fiziološke ekologije biljaka. NNK Internacional (2001) Beograd, 514.

3. Jovanović S., Filipović V., Mačukanović M., Dražić G., Stevanović B., Rasprostranjenost i ekologija vrste *Ailanthus altissima* (Mill.) Swingle na području grada Beograda, Glasnik Instituta za botaniku i botaničke bašte Univerziteta u Beogradu (1997) Tom XXXI, 9–22.

Razvoj originalne LIBS aparature na bazi TEA CO_2 lasera za primenu u zelenoj analitičkoj hemiji

Development of the original LIBS apparatus based on TEA CO_2 laser for application in the green analytical chemistry

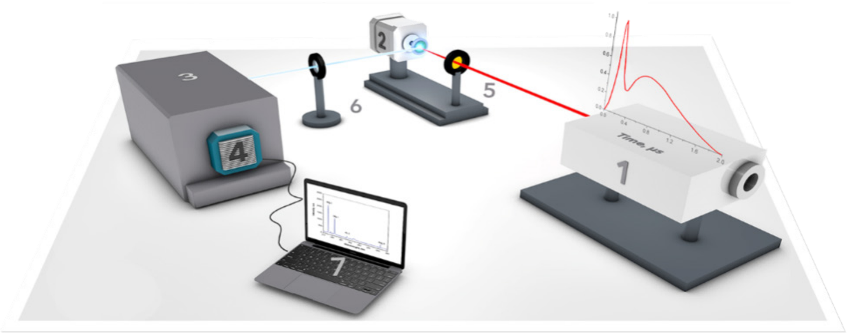
Miloš Momčilović[1a], Sanja Živković[1], Jelena Savović[1]

[1]Institut za nuklearne nauke “Vinča“

[a]milos@vinca.rs

Spektroskopija laserski indukovane plazme (Laser Induced Breakdown Spectroscopy, LIBS) je savremena metoda hemijske analize koja koristi optički signal iz laserski generisane plazme za proučavanje sastava materijala. LIBS se može koristiti za analizu uzoraka različite prirode i porekla zbog čega je našao primenu u brojnim oblastima [1]. U oblasti zaštite životne sredine LIBS je pogodan za brzu analizu opasnih metala i drugih zagađivača u vodi, zemljištu, biljkama, vazduhu, kao i za analizu otpada. Ono što posebno izdvaja LIBS od drugih spektrohemijskih metoda je mogućnost detekcije svih hemijskih elemenata iz periodnog sistema, uključujući i lake elemente (He, Li, Be, B, C, N, O...) koji se teško određuju drugim tehnikama, analiza čvrstih uzoraka bez potrebe za pripremom uzoraka, kao i mogućnost analize u realnom vremenu (*in situ, stand-off, remote*). Posebno treba istaći da se LIBS uklapa u koncept zelene analitičke hemije koja je prepoznata kao ključni deo zelene hemije [2]. Razvoj zelene analitičke hemije ima za cilj smanjenje negativnog uticaja hemijskih analiza na životnu sredinu. Najvažniji izazov za budućnost ove discipline jeste postizanje kompromisa između poboljšanja kvaliteta rezultata i povećanja ekološke prihvatljivosti analitičke metode. Danas, spektroskopske metode dominiraju u oblasti zelene analitičke hemije, a među njima posebno se, svojim karakteristikama i univerzalnošću, izdvaja LIBS. U najvećoj meri LIBS ispunjava postavljene principe zelene analitičke hemije koji razmatraju kompletan analitički proces koji uključuje uzorkovanje, pripremu, kao i sam proces analize uzoraka [2,3].

LIBS karakteriše velika fleksibilnost instrumentalne postavke. U zavisnosti od željene namene, optimizacija LIBS sistema može se postići izborom lasera određene energije, vremenskog trajanja laserskog impulsa (nanosekundni, pikosekundni, femtosekudni), kao i talasne dužine zračenja (ULJ, VID, IC). U praksi uobičajeno se koristi LIBS sistem koji se sastoji iz Nd:YAG lasera, spektrometra i detektora sa vremenskom rezolucijom. U okviru Laboratorije za fizičku hemiju INN Vinča razvijena je originalna LIBS aparatura koja se bazira na TEA (Transverzalno Ekscitovanom Atmosferskom) CO_2 laseru, Slika 1. Ovaj kompaktni, impulsni, nanosekundni laser, koji je takođe kompletno konstruisan u INN Vinča, radi u visoko multimodnom režimu i emituje zračenje u infracrvenom delu spektra na 10,6 µm. Analitička primena laserski indukovane plazme zahteva optimizaciju, odnosno razdvajanje intenziteta kontinualnog zračenja od intenziteta linijske emisije analita u cilju postizanja zadovoljavajućih granica detekcije za posmatrani element. Za razliku od komercijalno dostupnih LIBS aparatura u kojima se koristi vremensko razlaganje signala, u ovoj eksperimentalnoj postavci optimizacija je postignuta alternativnom metodom, korišćenjem vremenski-integraljene prostorno-razložene laserske spektroskopije. Na ovaj način izbegnuto je korišćenje generatora kašnjenja i skupih iCCD detektora.



Slika 1. LIBS eksperimentalna postavka [4]

Dosadašnja istraživanja vezana za analizu različitih tipova uzoraka pokazala su da je LIBS sistem koji koristi impulsni CO_2 laser po analitičkim performansama (selektivnost, osetljivost, granice detekcije) u potpunosti uporedljiv sa komercijalnim LIBS uređajima, u odnosu na koje je naš sistem znatno kompaktniji, robusniji i ekonomski isplativiji [4-6]. Kompaktnost LIBS-a je posebno značajna jer manji broj komponenti olakšava konstrukciju prenosivog LIBS uredjaja. Tekuća istraživanja usmerena su na optimizaciju TEA CO_2 LIBS-a za detekciju zagađenja vode i zemljišta teškim metalima.

Zahvalnica

Ova istraživanja su podržana od strane Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije (projekat br. 172019).

Literatura

1. Hahn D., Omenetto N., *Appl. Spectrosc*. 66 (2012)347-419.
2. Gałuszka A., Migaszewski Z., Namiesnik J., *TrAC* 50 (2013) 78-84.
3. Yihua H., Tang L., Wu X., Hou X., *Appl. Spectros. Rev.*42 (2007)119-138.
4. Zivkovic S., Savovic J., Trtica M., Mutic J., Momcilovic M. *J Alloy Comp* 700 (2017) 175-184.
5. Zivkovic S., Momcilovic M., Staicu A., Mutic J., Trtica M., Savovic J., *Spectrochim. Acta B* 128 (2017) 22-29.
6. Zivkovic S., Savovic J., Kuzmanovic M., Petrovic J., Momcilovic M., *Microchem. J.* 137 (2018) 410-417.

Spektroskopija laserski indukovane plazme za evaluaciju efikasnosti biosorpcije teških metala iz otpadnih voda na ljuskama suncokreta

Laser Induced Breakdown Spectroscopy for Efficiancy Evaluation of Sunflower Husk for Biosoption of Heavy Metals from Wastewater

Sanja Živković[1a], Jelena Stevanović[2], Jelena Petrović[1], Jelena Savović[1], Miloš Momčilović[1]

[1]Institut za nuklearne nauke "Vinča", Beograd

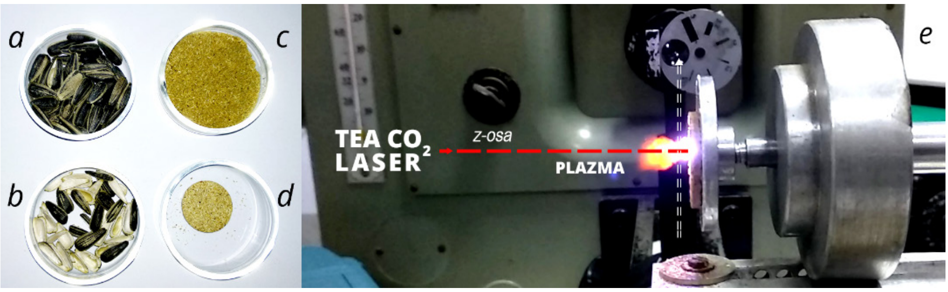
[2]Fakultet za fizičku hemiju, Univerzitet u Beogradu

[a]sanjaz@vinca.rs

Industrijske otpadne vode često imaju relativno visoki sadržaj teških metala koji, zbog svoje perzistentnosti i toksičnosti, mogu imati veoma štetan uticaj po životnu sredinu. Kako su količine čiste vode na planeti ograničene, neophodno je izvršiti prečišćavanje otpadnih voda. Biosorpcija kao nova tehnika, pored tradicionalnih fizičkih i hemijskih metoda za prečišćavanje voda, predstavlja primenu ekonomski isplativih, lako dostupnih i obnovljivih bioloških materijala za efikasno uklanjanje polutanata iz vode adsorpcijom [1,2].

Pre nego se neka metoda počne koristiti u industriji mora se ispitati u laboratorijskim uslovima. Cilj ovog rada bio je ispitivanje mogućnosti upotrebe ljuski semenki suncokreta kao bisorbenta za uklanjanje bakra i kadmijuma iz otpadnih voda, kao i upotreba relativno nove analitičke tehnike, spektroskopije laserski indukovane plazme (LIBS) za određivanje efikasnosti adsorpcije. Za razliku od standardnih spektrohemijskih tehnika, u LIBS-u nema klasične pripreme uzoraka, ne upotrebljavaju se agresivne hemikalije i što je najvažnije, nema hemijskog otpada [3,4].

Biosorbent je pripremljen temeljnim pranjem i ispiranjem dejonizovanom vodom, nakon čega je osušen, samleven i prosejan kroz milimetarsko sito. Ovaj materijal korišćen je za pripremu sintetičkih LIBS standarda, ispitivanje uticaja pH vrednosti i vremena adsorpcije, kao i za procenu efikasnosti sorpcije metala iz simuliranih uzoraka otpadnih voda. Plazma je generisana ozračivanjem uzorka TEA CO_2 laserskim zračenjem na atmosferskom pritisku, Slika 1. Primenom sintetičkih standarda konstruisane su kalibracione krive i postignuta je linearna zavisnost za Cu i Cd sa regresionim koeficijentima $r^2>0,95$. Dobijene kalibracione krive korišćene su za procenu limita detekcije (LOD) i određivanje koncentracija Cu i Cd u biosorbentu pre i posle tretmana simuliranog uzorka otpadne vode, kao i za procenu efikasnosti primenjenog biosorbenta.



Slika 1. LIBS analiza biosorbenta: a) semenke suncokreta; b) ljuske suncokreta; c) biosorbent - samlevene ljuske nakon sušenja; d) pastila dobijena presovanjem biosorbenta; e) LIBS analiza pastila biosorbenta

Postignuta je relativno niska granica detekcije reda veličine desetak ppm za oba elementa koja se daljom optimizacijom eksperimenta može sniziti. Uočeno je da koncentracija metala raste u biosorbentu sa porastom vremena kontakta i dostiže zasićenje posle 3h. Najveća efikasnost adsorpcije postiže se pri pH ≈ 5.

Dobijeni rezultati provereni su i potvrđeni referentom metodom. Svi uzorci biosorbenta pre i posle tretmana, kao i simulirani uzorci analizirani su na optičkom emisionom spektrometru sa induktivno spregnutom plazmom (ICP OES, Thermo Scientific 7400 Duo).

Na osnovu dobijenih rezultata može se zaključiti da se otpadna biomasa u vidu ljuski suncokreta može koristiti kao bisorbent za uklanjanje jona bakra i kadmijuma iz vode. Takođe, LIBS kao predložena metoda za analizu koncentracije bakra i kadmijuma u uzorcima biosorbenta predstavlja ekološki prihvatljivu alternativu za monitoring efikasnosti biosorpcije teških metala u otpadnim vodama.

Zahvalnica

Ova istraživanja su podržana od strane Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije (projekat br. 172019).

Literatura

1. De Gisi, S., Lofrano, G., Grassi, M., Notarnicola, M., *Sustainable Materials and Technologies* 9 (2016) 10–40.
2. Saleh,M., El-Refaey, A., Mahmoud A., *Soil & Water Res.* 11 (2016)53–63.
3. Zivkovic S., Momcilovic M., Staicu A., Mutic J., Trtica M., Savovic J., *Spectrochim. Acta B* 128 (2017) 22-29.
4. Zivkovic S., Savovic J., Kuzmanovic M., Petrovic J., Momcilovic M., *Microchem. J.* 137 (2018) 410-417.

Ispitivanje neorganskog sastava sedimenata Đerdapskog jezera (Srbija)

The investigation of inorganic composition of sediments from Djerdap Lake (Serbia)

Gordana Gajica[1], Milica Kašanin-Grubin[1], Snežana Štrbac[2], Lukas Hagemann[3], Nebojša Vasić[4], Jan Schwarzbauer[3], Branimir Jovančićević[5]

[1]Institut za hemiju, tehnologiju i metalurgiju , Univerzitet u Beogradu,

[2] Univerzitet EDUCONS, Faculty of Environmental Protection, Sremska Kamenica, Srbija

[3] RWTH Aachen University,Institute for Geology and Geochemistry of Petroleum and Coal, Germany

[4] Rudarsko-geološki fakultet, Univerzitet u Beogradu

[5] Hemijski fakultet, Univerzitet u Beogradu

[a]ggajica@chem.bg.ac.rs

Đerdapsko jezero formirano je 1972. godine kada je izgrađena hidroelektrana Đerdap 1 na Dunavu na srpsko-rumunskoj granici. Zapremina jezera je od oko 3.500 miliona m^3 sa suspedovanim opterećenjem od oko 8.900 kt a^{-1}.

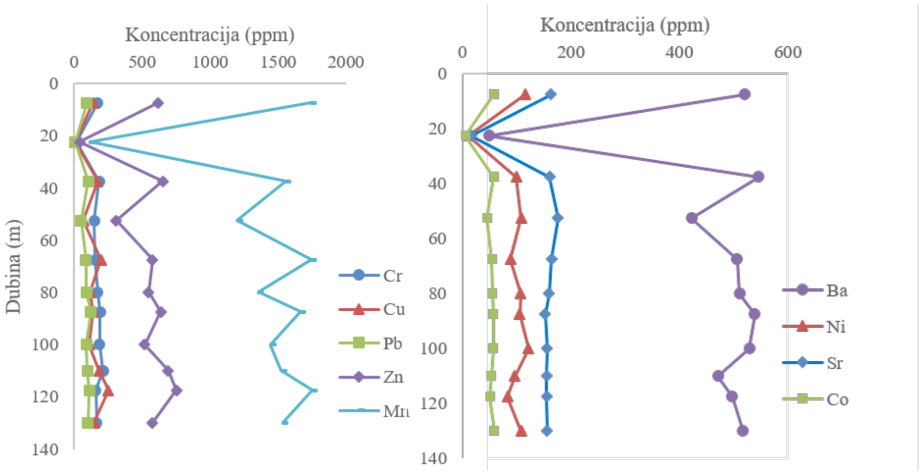
Cilj ovog istraživanja bio je ispitivanje neorganskog sastava sedimenata Đerdapskog jezera sa posebnim akcentom na teške metale u cilju utvrđivanja potencijalnog antropogenog zagađenja u ispitivanim sedimentima.

Da bi se dali odgovori na postavljeni cilj sedimenti su uzorkovani iz jezgra dubine 140 cm, tako da sedimentno jezgro predstavlja sedimente koji su se taložili od nastanka jezera do 2016. godine (oko 43 godine). Potom je sedimentno jezgro podeljeno na 11 uzoraka. Sadržaj metala određen je rendgenskom fluorescentnom spektrometrijom (XRF), kvalitativna analiza mineralnog sastava urađena je rendgenskom difraktometrijskom analizom (XRD) i na svim uzorcima je urađena granulometrijska analiza prosejavanjem i pipet analizom.

Dobijeni rezultati granulometrijske analize pokazuju da u većini uzorka dominira frakcija ispod 125 μm i da se uzorci uglavnom sastoje od alevrita i glina.

Rendgenska difraktometrijska analiza je pokazala da se uzorci sastoje od sledećih minerala: liskuna, hlorita, kalcita, dolomita, feldspata, smektita i kvarca.

Određen je sadržaj sledećih teških metala Ni, As, Cd, Zn, Pb, Cu, Hg, Cr, Mn, Ba, Sri Co.U koncentracijama ispod detekcionog limita za XRF(1 ppm)nalaze se As, Hg i Cd. Posmatrajući promene koncetracije teških metala sa dubinom isti trend imaju Zn, Pb, Cu, Cr i Mn, dok se Ni, Ba i Sr ponašaju drugačije (Slika 1). Najniže koncentracije teških metala primećene su na dubinama od oko 20 m, dok se najviše koncentacije većine teških metala nalaze na dubinama od oko 40 i 120 m. Ispitivani teški metali ne pokazuju korelaciju sa sadržajem organske supstance i frakcije glina. Nađene koncentracije ispitivanih elemenata u najvećoj meri ukazuju na geološko poreklo, i da je antropogeni uticaj mali. Da bi se dali precizniji odgovori buduća istraživanje biće usmerena ka detaljnijim mineraloškim analizama, određivanju dostupnih jona i izotopskom određivanju starosti sedimenata da bi se dali odgovorim o potencijalnom zagađenju ispitivanih sedimenata.



Slika 1. Promene koncentracije teških metala sa dubinom.

Postupak određivanja sadržajagasovite faze BTEX jedinjenja (benzen, toluen, etilbenzen, ksileni) sa sorbenta metodom GC-FID

Method of determining the content of the gaseous phase of the BTEX compound (benzene, toluene, ethylbenzene, xylenes) with the sorbent method GC-FID

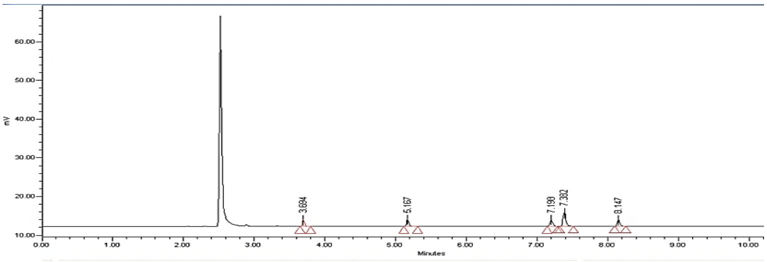
Đurica Katnić[1], Miloš Tošić[1], Željka Nikolić[1], Milena Pijović[1], Ivana Raičević[1], Boris Rajčić[1], Gvozden Tasić[1], Dubravka Milovanović[1a]

[1]Institut za nuklearne nauke Vinča, Univerzitet u Beogradu,

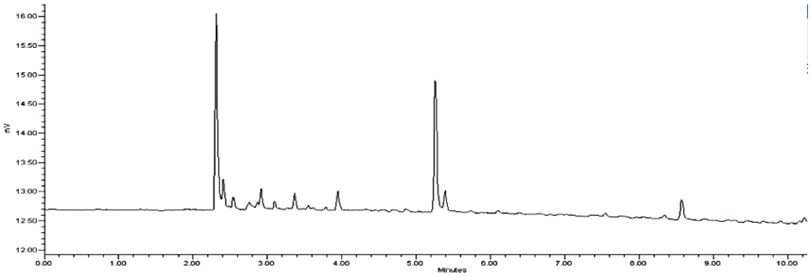
[a]dubravka.milovanovic@vin.bg.ac.rs

Monoaromatični ugljovodonici, kao što su BTEX jedinjenja (benzen, toluen, etilbenzen i izomeri ksilena), su lako isparljiva organska i mogu se smatrati nosiocima zagađenja poreklom iz antropogenih izvora [1]. U ovom radu je opisana metoda za kontrolu kvaliteta emisije BTEX jedinjenja iz građevinskih materijala u ispitnoj komori kao i za analizu uzoraka sa sorbenta. Metodajerazvijena u Laboratoriji za fizičku hemiju, Instituta za nuklearne nauke „Vinča“, modifikacijom standardnih metoda za određivanje isparljivih aromatičnih jedinjenja BTEX-a iz čvrstog otpada, otpadnog ulja, vodenih uzoraka, adsorbenasa za vazduh, zagađenog zemljišta [2, 3]. Korišćenesu Tenax cevčice kao adsorbensi pri uzorkovanju unutrašnjeg vazduha, kao i za ispitivanje vazduha iz ispitne komore za određivanje emisije isparljivih jedinjenja iz građevinskih materijala.

Validacionim protokolom definisani su sledeći kriterijumi za validaciju:specifičnost/selektivnost, linearnost, granica detekcije-LOD, granica kvantifikacije-LOQ, ponovljivost ipreciznost [4]. FID detektor je pokazao linearan odgovor u opsegu od 0,1 do 10 μg što pokazuje r ≥ 0,999.Metoda je tačna što pokazuje relativna standardna devijacija RSD ispod 5,0% i rikaveri koji se kreće od 83,9 do 105,6% za data jedinjenja što zadovoljava kriterijume validacije, zatim reproduktivna što pokazuje RSD koja je ispod 10,0%, kao i validna jer je kombinovana merna nesigirnost ispod 20,0% za dato jedinjenje [5,6]. Na osnovu retencionih vremena za sertifikovani standardni rastvor BTEX jedinjenja (Slika 1.), kvantitativno se određuje njihov sadržaj u uzorku (Slika 2.) upoređivanjem hromatograma.



Slika 1. Hromatogram za sertifikovani standardni rastvor BTEX jedinjenja



Slika 2. Hromatogram uzorka gasovite faze sa sorbenta

Ovim radom validirana je i razvijena savremena, pouzdana, precizna i tačna, analitička metoda za kontrolu kvaliteta emisije BTEX jedinjenja iz građevinskih materijala u ispitnoj komori kao i za analizu uzoraka sa sorbenta.

Zahvalnica

Ovaj rad je urađen pod pokroviteljstvom Ministarstva obrazovanja, nauke i tehnološkog razvoja Republike Srbije.

Literatura

1. Andrej I. Šoštarić, Mehanizmi uklanjanja lako isparljivih monoaromatičnih ugljovodonika (BTEX) iz ambijentalnog vazduha mokrom depozicijom, Beograd, 2017
2. Validation and Qualification in Analytical laboratories, www.labcompliance.com 8. Quantifying Uncertainty in Analytical Measurement, EURACHEM/CITAC Guide CG4, 2000
3. METHOD EPA 8260B - Volatile organic compounds by gas chromatography/ mass spectrometry (GC/MS)EPA 3810: 1986 Headspace
4. Volatile Organic Compounds (VOCs) thermally desorbed http://www.radiello.com/english/cov_term_en.htm
5. SRPS ISO/IEC 17025 -Opšti zahtevi za kompetentnost laboratorija za ispitivanje i laboratorija za etaloniranje
6. EURACHEM/CITAC, Guide 25, 2000. 5. Text on Validation of Analytical Procedure, ICH 6. Method Verification and Validation, www.fda.gov/ora/science 7.

Određivanja sadržaja BTEX jedinjenja u uzorcima građevinskog materijala i otpada sa mineralnim uljima kao glavnom komponentom, metodom GC/FID Headspace

Determination of the BTEX compounds in building materials and waste samples containing mineral oils as the main component using Headspace GC/FID

Miloš Tošić[1], Željka Nikolić[1], Jelena Georgijević[1], Tanja Brdarić[1], Gvozden Tasić[1],
Vladimir Nikolić[1], Dubravka Milovanović[1a], Milica Marčeta Kaninski[1]

[1]Institut za nuklearne nauke Vinča, Univerzitet u Beogradu

[a]dubravka.milovanovic@vin.bg.ac.rs

BTEX jedinjenja su lako isparljiva aromatična jedinjenja, klasifikovana kao toksična jedinjenja i kao takva su opasna po zdravlje ljudii životnu sredinu. Predmet istraživanja u ovom radu su BTEX jedinjenja u uzorcima građevinskog materijala sa mineralnim uljima kao glavnom komponentom. S obzirom da su ona sastavni deo mineralnih ulja, važno je odrediti njihovo prisustvo, koncentraciju i dalju distribuciju u životnu sredinu.

Tokom eksperimentalnog istraživanja, ispitivan je sadržaj BTEX jedinjenja: benzen, toluen, ksilen (o, p, m) i etilbenzen u uzorcima mineralnih ulja iz građevinskih materijala i otpada. Metoda za određivanje ovih jedinjenja, kao i za njihovu kvantifikaciju u uzorcima mineralnih ulja, razvijena je u Laboratoriji za fizičku hemiju, Instituta za nuklearne nauke „Vinča", Univerziteta u Beogradu, modifikacijom i unapređenjem standardnih metoda[1, 2].

Za potrebe ovog istraživanja,u eksperimentalnom delu, primenom Headspace ekstrakcije sa GC-FID tehnikom, određen je kvalitativni i kvantitativni sadržaj BTEX jedinjenja, što istovremeno predstavlja i validaciju ispitivane metode, kao i određivanje njene merne nesigurnosti (Tabela 1.).

Tabela 1. Proračun merne nesigurnosti na primeru spajka 50µg/ml

Jedinjenje	Merna nesigurnost (µg/ml)
Benzen	45,60 ± 5,50
Toluen	42,98 ± 6,70
Etilbenzen	39,61 ± 9,03
Orto-ksilen	46,70 ± 8,40
Meta-ksilen	46,95 ± 7,60
Para-ksilen	46,95 ± 7,60

Parametri za validaciju ove metode su bili: specifičnost, linearnost, granica detekcije (LOD), granica kvantifikacije (LOQ), ponovljivost i tačnost svakog jedinjenja.

Primenom opisane metode postignuta je pouzdana identifikacija ispitivanih jedinjenja. Identifikacija se ostvaruje poređenjem retencionih vremena ispitivanih jedinjenja sa retencionim vremenima analitičkih standarda. FID detektor pokazuje linearan odgovor u opsegu 0,1 do 10 µg , odnosno $R \geq 0,99$. Vrednosti standarda na kalibracionoj krivi su potvrdili preciznost metode. Relativna standardna devijacija RSD je ispod 5%, što dokazuje da je metoda tačna i reproduktivna [3-8].

Predstavljena metoda je validirana kao pouzdana, precizna i tačna za potrebe kontrole kvaliteta mineralnih ulja koja su korišćena ili će se koristiti u toku izgradnje građevinskih objekata, kao i za otpadni materijal.

Zahvalnica

Ovaj rad je urađen pod pokroviteljstvom Ministarstva obrazovanja, nauke i tehnološkog razvoja Republike Srbije (Projekat br. 172045 i 172019).

Literatura

1. EPA 3810: 1986 Headspace
2. METHOD EPA 8260B - Volatile organic compounds by gas chromatography/ mass spectrometry (GC/MS)
3. SRPS ISO/IEC 17025 -Opšti zahtevi za kompetentnost laboratorija za ispitivanje i laboratorija za etaloniranje
4. EURACHEM/CITAC, Guide 25, 2000.
5. Text on Validation of Analytical Procedure, ICH
6. MethodVerification and Validation, www.fda.gov/ora/science
7. Validation and Qualification in Analytical laboratories, www.labcompliance.com
8. Quantifying Uncertainty in Analytical Measurement, EURACHEM/CITAC Guide CG4, 2000

Nanostructured titanium-dioxide thin films for environmental applications

Ana Grce[1a], Dejan Pjević[1], Momir Milosavljević[1], Rolf Grieseler[2], Peter Schaaf[2]

[1]VINČA Institute of Nuclear Sciences,University of Belgrade, Serbia

[2] Institute of Materials Engineering and Institute of Micro- and Nanotechnologies Macro-Nano, Ilmenau University of Technology, Germany

[a]grce@vin.bg.ac.rs

Titanium-dioxide nanostructures and thin films are interesting for application in environmental protection, for water and air purification from toxic compounds, and photocatalytic degradation of water, where separation of H_2 is important for the development of new energy sources. Furthermore, they are interesting for fabrication of solar cells, various sensor applications, transparent conducting oxides (TCO), etc [1-3]. Stoichiometric TiO_2 phase has a wide optoelectronic band gap of ~3.2 eV, which makes it a dielectric at lower temperatures and a semiconductor at higher temperatures. It has a high absorption coefficient in the range of UV radiation, but low in the visible light region, and this makes significant constrains for its usage as a photocatalyst. For reducing energy gap, better absorption in visible light region and more efficient application it is necessary to add doping material species, which can be metal or non-metal ions.When used as a photocatalyst in form of a powder, TiO_2 nanoparticles are embedded in photosensitizing dyes which absorb visible light, or they are partly covered with nanoparticles of some transition metal to enhance injection of charge carriers. Recent developments involve the use of physical vapor deposition (vacuum evaporation or ion sputtering) to synthesize TiO_2 thin film structures, and ion implantation for their doping. The advantage of using physical vapor deposition is that the Ti:O ratio can be varied, and the films can be deposited on any supporting or large area substrates. On the other hand, ion implantation is a proven technique for introducing dopant atomic species into the crystal lattice of semiconductor materials.

In these experiments TiO_2 thin films were synthesized by physical vapor deposition (PVD) method, using three different procedures: (i) reactive d.c. ion sputtering of pure Ti target, using Ar ions and introducing O_2 in the deposition chamber; (ii) r.f. sputtering of TiO_2 target, using Ar + O_2 gas mixture; and (iii) reactive e-beam evaporation of pure Ti in the presence of introduced O_2. In case of reactive d.c. ion sputtering additional experiments involved a controlled introduction of nitrogen in the interaction chamber, which yielded doping of the deposited TiO_2 thin films, in reducing their band gap and enhancing absorption of visible light. The films were deposited to a thickness of a few hundred nm on silicon wafers and glass slide substrates. Structural and compositional characterization of samples included X-ray diffraction analysis (XRD), transmission electron microscopy (TEM, HRTEM), Rutherford backscattering spectrometry (RBS), and X-ray photoelectron spectroscopy (XPS). Optical characterizations were done by measuringthe transmission and diffuse reflection UV/VIS spectra. Photocatalytic activity was measured by determining the photodegradation rate of organic solutions.

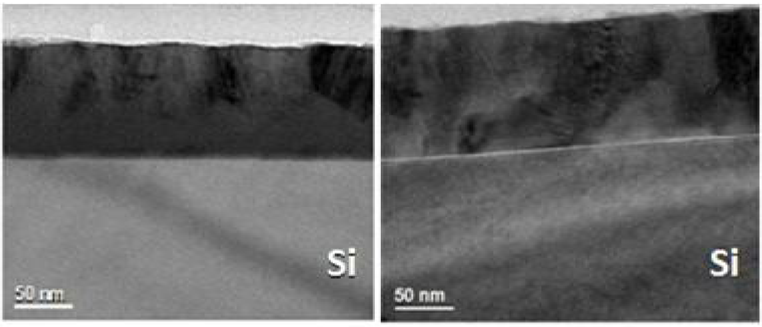


Fig. 1. Bright-field TEM cross-sectional imagesof two different samples, showing the fine polycrystalline nature of TiO_2 films deposited on Si wafers.

Structural characterization revealed that as-deposited samples grow in form of a mixture of very fine nanocrystalline grains of rutile and anatase TiO_2 phases and TiO. Hence, in order to homogenize the TiO_2 stoichiometry andinduce the growth of larger grains it was necessary to anneal the samples in air, at temperatures of 400 and 600 °C [4]. This procedure was performed on all samples after deposition. Bright-field cross-sectional images taken from two different TiO_2 films deposited on Si wafers are shown in Fig. 1. Sharp contrast regions within the films indicate their polycrystalline structure. The results of investigations showed that it is possible to tailor the structure and properties of the obtained TiO_2 thin films by adjusting the processing parameters.

Acknowledgments

This work was supported by the Serbian Ministry of Education, Science and Technological Development (Projects TR37021 and ON171023) and the German–Serbian bilateral collaborative project (DAAD PPP 50752549).

References

1. Karunagaran, B., Uthirakumar, P., Chung, S.J., Velumani, S., Suh, E.K.,*Mater. Charact.*58(2007)680–684.
2. Zhao, J.Yu.X., Zhao, Q.,*Mater. Chem. Phys.*69(2001)25–29.
3. Ko, K.H., Lee, Y.C., Jung,Y.J.,*J.ColloidInterface*283(2005)482–487.
4. Pjević, D., Obradović, M., Marinković,T., Grce, A., Milosavljević, M., Grieseler, R., Kups, T., Wilke, M., Schaaf, P., *Physica*B463(2015)20–25.

Determination of the BTEX compounds in concrete using Headspace GC-FID

Branislava Savić[1], Ana Grce[1a], Tanja Brdarić[1], Jelena Georgijević[1], Marija Ječmenica Dučić[1], Boris Rajčić[1], Milica Marčeta Kaninski[1]

[1]Vinča Institute of Nuclear Sciences, University of Belgrade

[a]grce@vin.bg.ac.rs

Presence of volatile organic contaminants in building materials negatively affects people's health. This study presents the validation of the analytical method, which has been developed for the simultaneous identification and quantification of BTEX compounds: benzene, toluene, ethylbenzene, xylene isomers (ortho-xylene, meta-xylene, para-xylene) in concrete by headspace gas chromatography method with flame ionization detection (HS-GC-FID).

The quality of the indoor air depends largely on outdoor air quality, but it also can be affected by a numerous other factors such as emissions from building materials (concrete, coatings, paint, lacquer) [1]. Due to the various sources of indoor air pollutants, to date there is no EU legislation relating to indoor air quality. Concrete is a composite building material which consists of water, aggregate (rock, crushed stone, sand, or gravel), and a binder or paste such as cement, and may contain additives [2]. As such, it presents a complex and challenging matrix for BTEX compounds analysis.

The qualitative and quantitative content of the BTEX compounds in polluted concrete was determined experimentaly by using headspace extraction with the GC-FID technique. The main emphasis was on assessing the parameters of validation such as selectivity, linearity, limit of detection (LOD), limit of quantification (LOQ), accuracy, precision (Table 1.) and estimation of measurement uncertainity.

The advanced method of BTEX compounds determination and quantification in concrete was developed in Department of Physical Chemistry, at Vinča Institute of Nuclear Sciences. Concrete was sampled from the building elementas at the construction sites, and the method was established by modifying the standard methods of volatile aromatic compounds (BTEX) determination from solid waste, waste oil, aqueous samples, adsorbent for air, contaminated soil, and sediments [3-5].

Using the method described above, reliable identification of the tested compounds was achieved by comparing the retention times of the test compounds with the retention times of the analytical standards. The FID detector showed a linear response in the range of 0.01 to 1 mg/kg and $R \geq 0.99$. The values of the standard on the calibration curve were confirmed by the accuracy of the method.

Table 1. Summary of the method validation data

Compound	**Regression equation**	**R**	**LOD (mg/kg)**	**LOQ (mg/kg)**	**Repeatability (RSD, %)**	**Precision (RSD, %)**	**Recovery (%)**
benzene	y=-60.08+319323.85x	0.999	0.003	0.01	0.04	0.04	77
toluene	y=-15.38+453551.97x	0.999	0.003	0.01	0.02	0.02	67
ethylbenzene	y=360.32+485261.49x	0.999	0.003	0.01	0.04	0.03	65
ortho-xylene	y=-147.5+456246.56x	0.999	0.003	0.01	0.02	1.92	69
meta-xylene	y=55029+488256.95x	0.999	0.003	0.01	0.03	0.05	33
para-xylene	y=55029+488256.95x	0.999	0.003	0.01	0.03	0.05	33

The developed method will be used for the control testing of BTEX compounds in concrete in residential buildings and other construction objects associated with a sick-building syndrome.

Acknowledgements

This study was financially supported by the “Serbian Ministry of Education, Science and Technological Development” (Grants No. 37021).

References

1. J.C. Chuang, S.R. Cao, Y.L. Xian, D.B. Harris, J.L. Mumford, Chemical characterization of indoor air of homes from communes in Xuan-Wei, China, with high lung-cancer mortality-rate, Atmos. Environ. Part A-General Top. 26 (1992) 2193–2201, lw0345.pdf.
2. S. Kubba, Handbook of Green Building Design and Construction: LEED, Butterworth-Heinemann, BREEAM, and Green Globes, 2012.
3. EURACHEM/CITAC, Guide 25, 2000. 5. Text on Validation of Analytical Procedure, ICH 6. Method Verification and Validation, www.fda.gov/ora/science 7.
4. Validation and Qualification in Analytical laboratories, www.labcompliance.com 8. Quantifying Uncertainty in Analytical Measurement, EURACHEM/CITAC Guide CG4, 2000.
5. EPA 3810: 1986 Headspace

Validation Procedures for Determination of Polycyclic Aromatic Hydrocarbons (PAH) in Water

Mina Seović[1a], Adrijana Šutulović[1], Danka Aćimović[1], Đurica Katnić[1], Miloš Tošić[1], Dubravka Milovanović[1], Milica Marčeta Kaninski[1]

[1]Vinča Institute of Nuclear Sciences, University of Belgrade

[a]mina050@vin.bg.ac.rs

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds made of two or more fused benzene rings.They are knownassoil and aquatic contaminants. Either naturally occurring or formed during the incomplete combustion of fossil fuels, low concentrations can usually be found just about everywhere in environment. PAH – contaminated areas pose a health risk to humans since these pollutants exert toxic, mutagenic, carcinogenic effects and potential endocrine-disrupting properties [1].The determination of PAH content in water is useful as an estimation of the pollution. It is a validated analytical method which is suitable for its intended purpose.

The method was developed atthe Department of Physical Chemistry, Vinča Institute of Nuclear Sciences. It is a modification of EPA Method 610 which uses Ultra-Performance Liquid Chromatography (UPLC) approach for the determination of PAHs. A number of PAHs that were determined are listed in Table 1. The following validation parameters were considered [2]:*accuracy, precision* (considered at two levels,repeatability and intermediate precision) [3], and *linearity –selectivity*[4]. The obtained results are presented in Table 1.

Table 1. Validation parameters

PAH	R_f (%)	RSD* (%)	RSD** (%)	Linearity, R^2	*RT*(min)
Acenaphthene	55.37	2.23	5.20	0.999	2.678± 0.2
Acenaphthylene	49.71	2.79	3.24	0.999	2.329± 0.2
Anthracene	92.93	2.63	6.34	0.999	3.222± 0.2
Benzo(a)anthracene	83.18	1.99	5.78	0.999	4.396± 0.2
Benzo(a)pyren	68.46	2.88	6.08	0.999	6.045± 0.2
Benzo(b)fluoranthene	89.86	2.05	5.09	0.999	5.221± 0.2
Benzo(ghi)perylene	41.45	2.30	7.01	0.999	7.280± 0.2
Benzo(k)fluoranthene	62.78	2.64	5.06	0.999	5.595± 0.2
Chrysene	87.12	2.68	6.89	0.999	4.621± 0.2
Dibenzo(a,h)anthracene	50.02	2.19	5.06	0.999	6.684± 0.2
Fluoranthene	80.63	3.10	5.65	0.999	3.484± 0.2
Fluorene	86.66	2.53	5.81	0.999	2.714± 0.2
Indeno(1,2,3-cd)pyrene	56.28	3.00	5.99	0.999	7.740± 0.2
Naphthalene	89.58	4.00	8.08	0.999	2.136 ± 0.2

Phenanthrene	102.45	2.15	5.43	0.999	2.957± 0.2
Pyrene	90.58	2.26	5.43	0.999	3.725± 0.2

*Repeatability; **Intermediate precision

A special attention was paid to selectivity. In this case selectivity has been proven by analyzing chromatograms of standard PAH mixture. Identification of PAH mix compounds is based on characteristic UV spectra as well as retention times (*RT*). This validation procedure has shown that liquid chromatographic method does resolve all 16 of the PAHs listed(Fig 1).

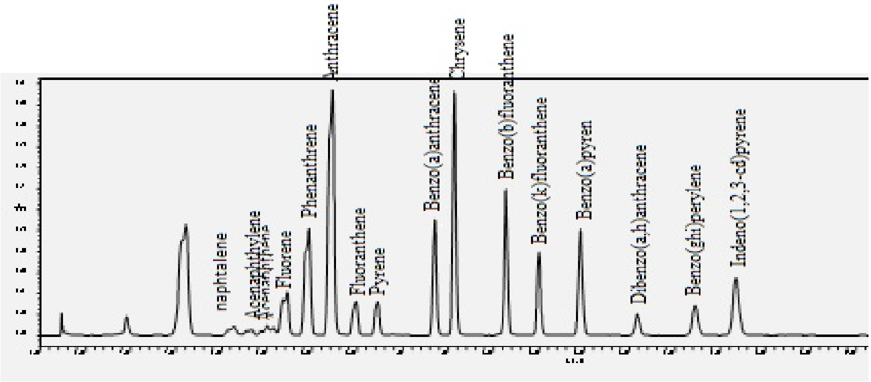


Figure 1.PAH mix chromatoram

References

1. Lee BD, Hosomi M (2001) Fenton oxidation of ethanol-washed distillation-concentrated benzo(a)pyrene: reaction product identification and biodegradability. Water Res 35(9):2314–2319.
2. [2]DubravkaDoležal, TatjanaTomić; Validation procedures for determination of total organic carbon in Water;Proceedings, XVII IMEKO World Congress, June 22 – 27, 2003.
3. International Conference on Harmonisation (ICH) ofTechnical Requirements for the Registration ofPharmaceuticals for Human Use, “Validation of analyticalprocedures: Methodology”, *ICH-Q2B*, Geneva, 1996.
4. DIN 38402 Part 51, “Calibration of analytical methods,evaluation of analytical results and linear calibrationfunctions used to determine the performance characteristicsof analytical methods”, 1986.

Determination of phenol and phenolic compounds in crude mineral oils and waste mineral oil samples by GC-MS

Adrijana Šutulović[1], Branislava Savić[1], Željka Nikolić[1], Marija Ječmenica Dučić[1], Mina Seović[1a], Boris Rajčić[1], Tanja Brdarić[1]

[1]Vinča Institute of Nuclear Sciences, University of Belgrade

[a]mina050@vin.bg.ac.rs

Phenol and phenolic compounds are ubiquitous contaminants in the environment due to their toxicity [1]. Anthropogenic emissions of phenols in the environment are product of the activity of chemical, pharmaceutical and process industries such as pulp, paper, wood, mineral (non-metallic), steel, metal, and petroleum industries [2].

The present study demonstrates the development and validation of the GC-MS method for determination of phenol, 2-chlorophenol and 2,4-dimethylphenol in mineral and waste oil samples.

The method is intended for quality control of mineral oils used as construction material and for used lubricating mineral oils (waste material). Mineral oils are mixtures of saturated hydrocarbons with different chain lengths and various properties both physical and chemical. They are by – products made from petroleum and are mainly used as lubricants for engines and technical instruments. Presented method's procedure involves a liquid-liquid extraction, derivatization step of the phenols, an optimization of the GC-MS operating conditions, an identification of target acetylated phenols and their quantification. It is derived from the modification of the standard method ISO/TS17182:2014 [3]. The component of interest was identified by comparison of the mass spectrum of analyte with the mass spectrum from standard solution. The following criteria were used for identification from spiked matrices: the retention time for each phenol compound corresponded to retention time of analyte from standard solution; at least two ions with characteristic m/z value were presented in mass spectrum as well as in mass spectrum of analyte from standard solution; SNR≥10. The blank and spiked matrices were analysed in order to avoid negative matrix effects. No interferences were observed. By recording the serial of certified reference material of phenols, diluted in few points, calibration curve was made in order to quantify these analytes from the oil samples.

Validation of this method was carried out with the aim to provide objective evidence that the requirements for determination of phenol compounds in mineral oil samples using GC-MS technique are satisfied. The following parametars of validation are conducted: limit of detection, limit of quantification (Table 1), precision, repeatability, accuracy, linearity, selectivity and working range [4]. The measurement uncertainty of method as quantitative indicator of its quality was determined as well [5].

Table 1. Limits of detection and quantification for target phenolic compounds

Compound	LOD (μg/ml)	LOQ (μg/ml)
Phenol	0.003	0.01
2-chlorophenol	0.004	0.01
2,4-dimethylphenol	0.025	0.08

By GC-MS tehnique, reliable identification, quantification and good resolution of analysed peaks were achieved. The results obtained confirmed that all requirements in the terms of the method validation are fulfilled and that the method is applicable for determination of phenol compounds in mineral and waste oil samples by GC-MS.

Acknowledgements

This study was financially supported by the "Serbian Ministry of Education, Science and Technological Development" (OI 172045).

References

1. Distribution of eleven priority phenolic compounds in soils from mixed landuse and assessment of health hazard for human population, Bhupander Kumar , Jyoti Tyagi , V. K. Verma , C. S. Sharma and A. B. Akolkar, Advances in Applied Science Research, 2014, 5(2):125-132
2. CENTRAL POLLUTION CONTROL BOARD (Ministry of Environment, Forests & Climate Change) PariveshBhawan, East Arjun Nagar Delhi - 110032 in AUGUST, 2016
3. ISO/TS17182:2014-Soil quality — Determination of some selected phenols and chlorophenols— Gas chromatographic method with mass spectrometric detection
4. EURACHEM/CITAC, Guide 25, 2000. 5. Text on Validation of Analytical Procedure, ICH
5. Quantifying Uncertainty in Analytical Measurement, EURACHEM/CITAC Guide CG4, 2000

Kontinualno merenje emisija zagađujućih materija iz termoelektrana na ugalj prema zahtevima SRPS EN 14181

Continious Emission Monitoring from Coal-Fired Power Plants according to EN 14181

Marko Pavlović[1a], Mihajlo Gigov[1], Sandra Petković[1], Miroslav Sofrenić[1]

[1]Rudarski institut d.o.o. Beograd, Srbija

[a]marko.pavlovic@ribeograd.ac.rs

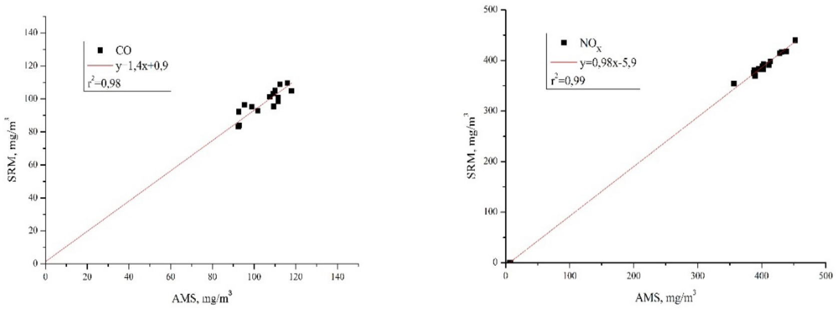
Kontinualno merenje emisije zagađujućih materija iz stacionarnih izvora zagađivanja vrši se automatskim mernim sistemom (AMS) kojim se osiguravaju podaci o koncentraciji i masenom protoku zagađujućih materija u otpadnom gasu tokom neprekidnog rada stacionarnog izvora zagađivanja [1].

U Srbiji postoji osam termoelektrana koje kao pogonsko gorivo koriste ugalj (lignit). Sa ukupnom snagom od 5.171 MW i 25 blokova u radu [2], ovi energetski objekti predstavljaju glavni izvor zagađivanja u našoj zemlji.

Termoelektrane na ugalj toplotne snage ložišta veće od 300 MWth, prema važećoj zakonskoj regulativi [3] u obavezi su da vrše kontinualni monitoring sumpor dioksida (SO_2), oksida azota NO_x (izražene kao NO_2), praškastih materija i ugljen monoksida (CO).

Za trajno ugrađene automatske merne sisteme na stacionarnim izvorima zagađivanja, Evropska direktiva o industrijskim emisijama [4] zahteva obezbeđenje kvaliteta u skladu sa Evropskom normom EN 14181 [5]. Uspostavljaju se tri nivoa obezbeđenja kvaliteta AMS (QAL1, QAL2 i QAL3) kojima se definišu postupci za ispunjavanje zahteva za sertifikaciju, verifikaciju, kalibraciju i stalnu proveru AMS tokom njegovog rada, kao i zahteva za mernu nesigurost koja je definisana zakonskom regulativom.

Na Slici 1 prikazane su kalibracione funkcije određene tokom inicijalne kalibracije uređaja za kontinualno merenje emisije – obezbeđenje poverenja nivoa 2 (QAL2), za CO i NO_x. Ispitivanja su sprovedena u termoelektrani na ugalj toplotne snage ložišta 838 MWth. Sprovedeno je 15 serija paralelnih merenja i određena je linearna zavisnost rezultata dobijenih automatskim mernim sistemom (AMS) i standardnim referentnim metodama (SRM) za određivanje masene koncentracije CO i NO_X. Dobijeni su koeficijenti korelacije (r^2) veći od 0,9 što ukazuje da je QAL2 procedura uspešno sprovedena.



a) b)

Slika 1. a) kalibraciona funkcija za CO, b) kalibraciona funkcija za NO_x

Obezbeđenje kvaliteta automatskih mernih sistema za kontinualno mernje emisije u skladu sa SRPS EN 14181 otvorilo je novo poglavlje monitoringa zagađujućih materija u termoelekranama u Srbiji. Kontinualno merenje emisije postalo je obaveza zahtevana evropskom i nacionalnom regulativom, naročito za velike stacionarne izvore zagađivanja, a samo pouzdan monitoring može formirati pravu sliku o kvalitetu vazduha i biti ozbiljna podloga za studije o proceni uticaja na životnu sredinu.

Literatura

1. Uredba o merenjima emisija zagađujućih materija u vazduh iz stacionarnih izvora zagađivanja, *Službeni glasnik Republike Srbije 5/16*, 2016;
2. http://eps.rs/Poslovanje-EE/Pages/Termoelektrane.aspx;
3. Uredba o graničnim vrednostima emisija zagađujućih materija u vazduh iz postrojenja za sagorevanje, *Službeni glasnik Republike Srbije 6/16*, 2016;
4. Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on Industrial Emissions (Integrated Pollution Prevention and Control), *European Commission*, 2010;
5. SRPS EN 14181:2015, Emisije iz stacionarnih izvora – Obezbeđenje kvaliteta automatskih mernih Sistema, *Institut za standardizaciju Srbije*, 2015.

Risk assessment of emerging pollutants in the aquatic environment

Maja Sremački[1],Maja Petrović[1], Dušan Milovanović[1], Ivana Mihajlović[1],
Mirjana Vojinović Miloradov[1a]

[1]Faculty of technical sciences, University of Novi Sad, Novi Sad, Serbia

[a]miloraodov@uns.ac.rs

Risk assessments (RA), based on fundamental knowledge of distribution, fate, exposure and effects, and are essential for safe utilisation ofchemical and their discharge into the environment. The risk assessment for the emerging substances comprises of several complex studies – quantification of spatial and temporal trends in fate, behaviour, exposure and effects, development of models (distribution, bioavailability and exposure-response), the effect of chemical mixtures, simultaneous exposure to chemical and non-chemical stressors, identification of traits that underpin sensitivity and adaptation for RA to key organisms, food security, ecosystem services and biodiversity, examination of how chemical risks can vary taking into consideration climate and demographic change, increasing urbanisation and a move towards low carbon economies and other.

Emerging pollutants reach the environment from numerous anthropogenic sources and are distributed throughout environmental compartments. Although abundant advances have been made in the sector of detection and analysis of trace pollutants, due to the continued development and refinement of techniques, a broadrange of emerging contaminants are jet to be identified and/or quantified. EmPcan be persistent and pseudo-persistent, chronically toxic even at low concentration levels. Comprehensive data on about the fate and behaviour in the environment, as well as on threats to ecological and human health, of EmPare still lacking. Furthermore, the ecotoxicological implications of the most EmP are largely unknown, because acceptable and reliable data for determination of risk to the environment are frequentlynon existent[1].

Potential ecological risk or risk quotient (RQ) of different emerging groups of substances in environmental compartments (water–sediment) has shown to be essentially high for pesticides, phthalates, antibiotics, anti-inflammatory drugs, β-blockers, and antiepileptic drugs[2].Concentration levels that have been reported for drug residues in surface waters (average of concentrations) are often in the range of ng/L-µg/L. The occurrence of β-blockers have been reported in low ng/L and µg/L [3].

The general principles and guidelines for environmental risk assessment (ERA) of new and existing chemicals have been introduced by European Medicines Evaluation Agency (EMEA), based on the comparison between the predicted environmental concentrations (PEC) and the predicted no effect concentrations (PNEC) estimated from standard toxicity assays [4,5].The criteria for interpreting the RQ, in RA studies, establish different risk levels defined as *low risk*(0.01-0.1), *medium risk* (0.1-1), and *high risk*(>1) [4,6], have been applied in the paper.

Different techniques were used to obtain concentration data for selected emerging xenobiotics – organochlorine pesticides (DDT and metabolites, atrazine, dieldrin, edndrin, heptachlor and other), phthalates and estrogens. Results obtained through target analyses were used to calculate daily load and RQ, for the purpose of risk assessment[7]. Pesticides lindane, endrin, dieldrin, endosulfane α, heptachlor, heptachlor, p',p'-DDT, hexachlorobenzene show a significantly high calculated RQ on almost every location where these substances were detected, which is a reason for concern due to direct endocrine disrupting effects, bioaccumulation characteristics and toxicity in aquatic system of EmP.

Acknowledgement

This paper is based upon the results from NATO Project DriWAQ-NS ESP.EAP. SFP 984087NATO and Project financed by the City of Novi Sad, City Administration for Environmental Protection no. 501-2/2017-56v-II.

References

1. Gavrilescu,M., Demnerová,K., Aamand,J.,Agathos,S.,Fava, F. (2015) New Biotechnology, 32 (1) 147-156 https://doi.org/10.1016/j.nbt.2014.01.001
2. Hernando, M.D., Mezcua, M., Fernández-Alba, A.R., Barceló, D. (2006) Talanta, 69 (2) 334-342, https://doi.org/10.1016/j.talanta.2005.09.037
3. Daughton, C.G., Ternes, T.A. (1999) Environmental Health Perspectives, 107 (6)907-938
4. EC, 1996, Technical Guidance Documents in Support of the Commission Directive 93/667/EEC on risk assessment for new notified substances and the Commission regulation (EC) 1488/94 on Risk substances, European Chemical Bureau, Ispra, Italy, 19th April 1996, part 1, 2 and 3.
5. FDA, Guidance for industry-Environmental assessment of human drugs and biologics applications, FDA, CDER/CBER, CMC 6, rev. 1, 1998.
6. Sanchez-Bayo, F., Baskaran, S., Kennedy I.R. (2002) Agriculture, EcosystEmP and Environment, 91(1-3) 37-57
7. Sremački M. (2017) University of Novi Sad, Faculty of Technical Science, http://nardus.mpn.gov.rs/handle/123456789/8924

Application of BCR sequential extraction for study of Rare Earth Elements distribution in soil from Serbia

Jelena Mutić[1a], Vesna Vukojević[1], Slađana Đurđić[1]

[1]Faculty of Chemistry, University of Belgrade, Belgrade, Serbia

[a]jmutic@chem.bg.ac.rs

The mobility of Sc, Y and lanthanoids (rare earth elements) and their impacts on ecosystems are still relatively unknown. Abundances of REEs in soils greatly depend on their parent material and pedogenic processes, organic matter content etc [1]. Scandium is a relatively widespread element in the Earth's crust with which abundance is higher than metals such as Pb and W. Due to the new tehnological development large amount of Sc has released to the environment and it has been used as a marker of environmental pollution [2]. Yttrium also has a wide application in modern industry and in recent years many authors investigate impact of this element to environment [3].Cartain lanthanoids such as neodymium, europium, or terbium are used in advanced clean energy technologies (hybrid cars) and also in products such as computers, smartphones and lighting[4].

The purposes of this study were to establish baseline concentrations of scandium, yttrium and lanthanides in soil samples from Serbia and to determine the fractions of these elements in soil based on BCR sequential extraction scheme.

Samples of soil were collected from two unpolluted, forest sites in central Serbia. Site S1 was unpolluted region on the Mountain Goč and site S2 was forest near city Trstenik The pseudo-total concentrations of elements in soil were determined using aqua regia and the geochemical fractions were assessed using a BCR sequential extraction procedure. Using this extraction we established the concentration of REE in exchangeable, reducible, oxidisable and residual fraction. Determination of REE concnentration in all samples was achived using ICP-QMS (ICP-Q- MS, Thermo Scientific Xseries 2, UK).

Based on obtained results, we can conclude that there are significant differences in content of Sc and Y in soil samples from two locations, while the total content of lanthanoids in average was similar between the two soil sites. The fractionation profile of Sc,Y and lanthanides shows that the greatest amounts of these element were found in the residual fractions,followed by oxidizable, reducible and water soluble, exchangeable fraction, in all soil samples (Figures 1,2). On the other hand, some difference in distribution of all examined elements was observed betwean soil samples from different location.

-

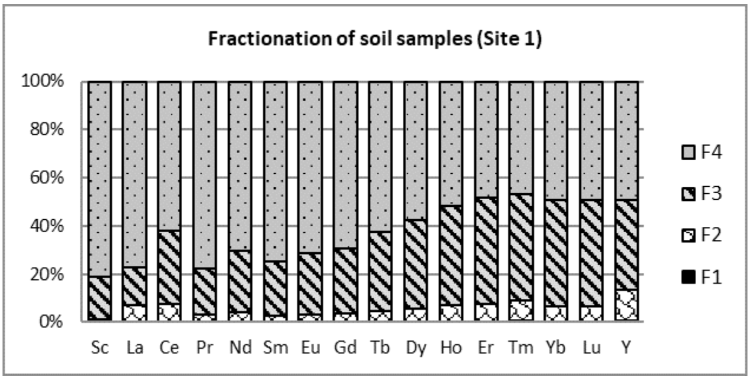


Figure 1. Distribution of REE in soil samples (Site 1)

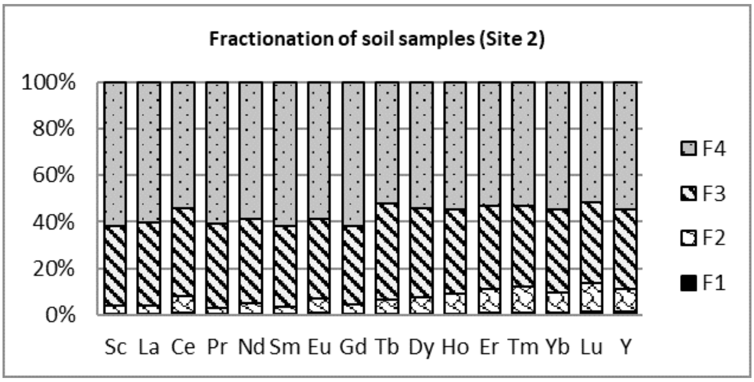


Figure 2. Distribution of REE in soil samples (Site 2)

Content of Sc, Y and lanthanoids in soil greatly depends on sampling location. According to results of sequential BCR extraction, the distribution of the REEs also varied with the type of soil. Those differences seem to be due to the parent material and its properties such as pH, clay content and organic matter. Applied BCR sequential extraction procedure showed that very small amounts of REE are bound with exchangeable fraction and we can conclude that they are slightly mobile in soils.

References

1. Tyler, G., *Plant Soil* 267 (2004) 191–206
2. Jerez, J., Isaguirre, A. C., Bazán, C., Martinez, L. D., Cerutti, S., *Talanta*124 (2014)89–94.
3. Jerez J., Isaguirre A.C., Bazán C., Martinez L.D., Cerutti S.,*Talanta* 124 (2014) 89–94
4. Reed, D.W., Fujita, Y, Daubaras, D.L., Jiao, Y, Thompson, V.S.,*Hydrometallurgy*166 (2016)34–40

Cleaning the engine using H2E ECC technology

Dragan Adamović[1a], Mirjana Vojinović Miloradov[1], Vojin Močević[2], Jelena Radonić[1], Maja Turk Sekulić[1], Savka Adamović[3], Sabolč Pap[1,4]

[1]Faculty of Technical Sciences, Department of Environmental Engineering and Occupational Safety and Health, University of Novi Sad,
[2]Hybrid Power System LLC Novi Sad, Serbia
[3]Faculty of Technical Sciences, Department of Graphic Engineering and Design, University of Novi Sad,
[4]Environmental Research Institute, North Highland College, University of the Highlands and Islands, UK
[a]draganadamovic@uns.ac.rs

H2E engine carbon cleaning (H2E ECC) system in the process of water alkaline electrolysis, in the presence of potassium hydroxide (KOH), generates hydrogen and oxygen in a volume ratio of 2:1 [1]. The obtained mixture of gases is introduced into the engine cylinders through the inlet manifold, while the engine is operating in a mode set by the H2E application during the additivation procedure. In controlled combustion conditions, degradation of carbon deposits occurs in the cylinder and the exhaust manifold [2].

In order to assess the impact of the H2E ECC process on the emission characteristics of the tested motor vehicles. The exhaust gas analysis were performed before and after the H2E ECC process.

The quantification of the target components in the exhaust mixtures was carried out using the gas analyser Stargas 898 Global Diagnostic System (Serial No. 3156) and the "Smokemeter 495/02."

The measurements were carried out on randomly selected used vehicles that are in regular usage and where it was possible to test the emission characteristics using the exhaust gas analysers prescribed for control on technical inspections. The measurements were included a sample of ten vehicles, four of which were with diesel engines and six vehicles were with petrol engines. The analyses were conducted in the period from 8/4/2017 to 1/2/2018 at the locations in Novi Sad (Serbia) and Ystad (Sweden). Measurements of exhaust gas emissions were conducted before and after treatment with the H2E ECC system, for each vehicle. Exhaust gas emission measurements were carried out according to the method described in the instructions of the exhaust gas analysers, while the treatments were carried out according to the procedure described in the directions of the H2E ECC system.

The results of testing the emission characteristics of the engines on four randomly selected vehicles with diesel engines that fulfil the Euro 3 and Euro 4 standards indicate a decrease in the opacity by an average of 60%.

The results of the emission test for six randomly selected petrol engines that fulfil

Euro 3, Euro 4 and Euro 5 standards indicate a decrease in carbon monoxide (CO) concentrations for an average of 77% and total hydrocarbons (HC) for an average of 84% in the exhaust gas stream.

It can be concluded that for all tested vehicles, emissions of exhaust gases (opacity on diesel engines) have dropped significantly, which is the result of more efficient combustion after performed the H2E ECC procedure.

The reduction in the concentration levels of CO and HC in the exhaust gas stream is the result of providing more favourable conditions for combustion of the air-fuel mixture after the treatment with H2E ECC system. This claim is supported by the data on the slight increase in carbon dioxide (CO_2) content, which generates as a result of complete combustion at the expense of the disappearance of HC and CO.

The significantly reduced CO and HC emissions in the petrol engine provide higher overall efficiency and longer service life of the catalyst in the exhaust system of the vehicle.

Reduced opacity in the diesel engine indicates on reduced particulate intake intensity within the particle filter (DPF), which diminishes many automatic regenerations of the filter, thereby providing a longer service life and higher efficiency of the catalytic converter of exhaust gases and particulate filters.

The reduced emission of gases in the exhaust section results in reduced accumulation of deposits in the inlet manifold to which it comes through the exhaust gas recirculation system (EGR)

Acknowledgement: This research was supported by Ministry of Education, Science and Technological Development, Republic of Serbia (III46009).

References

1. Ji, C., Wang, S., Zhang, B. Combustion and emissions characteristics of a hybrid hydrogen-gasoline engine under various loads and lean conditions. *Int. J. Hydrogen Energy* 35(2010), 5714–5722.
2. Song, H., Xiao, J., Yang, X., Yu, K., Huang, Z.The effects of surface temperature on the deposit behaviors of gasoline on a hot surface. *Fuel* 215 (2018), 111–122.

Waste-based alternative adsorbents for the remediation of radionuclides contaminated waters: Have we a new solution?

Nikola Bošković[1a], Romana Kištof[2], Maja Turk Sekulić[1], Sabolč Pap[4], Polonca Trebše[3], Jelena Radonić[1], Jasmina Kožar Logar[2]

[1] Department of Environmental Engineering, Faculty of Technical Sciences, University of Novi Sad, Serbia

[2] Department for low and medium energy physics, Jožef Stefan Institute, Ljubljana, Slovenia

[3] Faculty of Health Sciences, University of Ljubljana, Slovenia

[4] Environmental Research Institute, North Highland College, University of the Highlands and Islands, UK

[a] boskovicnikola16@gmail.com

Activated carbon is one of the most common adsorbent involved in water purification due to its high specific surface area. It is widely used as one of the first steps in drinking water preparation and in the removal process of industrial contaminants. Commercially available activated carbon is expensive and not always easily affordable. The synthesis and characterization of new activated carbons obtained from lignocellulosic precursors is therefore a topic widely studied by a number of researchers worldwide. The aim of this study is to find the appropriate and cheap raw material from agricultural, industrial or vegetable (lignocellulosic) wastes to reduce the cost of production by changing the synthesis of alternative activated carbon, characterize newly developed material and test its efficiency on different types of pollutants.

The alternative activated carbons derived from apricot (*Prunus armeniaca*), plum (*Prunus domestica*) and cherry/sour cherry (*Prunus avium/Prunus cerasus*) kernels were produced by thermo-chemical activation using phosphorous acid. The materials were already tested on wastewater polluted by heavy metals and pharmaceuticals and showed promised results [1,2,3]. The results were encouraging and the study was extended to radioactive inorganic micropollutants. Environmental water obtained in the vicinity of former uranium mine at Žirovski Vrh (Slovenia) was chosen due to its rather high content of radionuclides. Several experiments were performed on small, laboratory scale with simple, rapid and standardised method for their evaluation.

Activities of total radionuclides were firstly obtained by screening method of gross alpha/beta activity determination for water before and after usage. Activated carbon from plum showed remarkable results, lowering alpha and beta activity for 95.14% and 95.88%. Comparable commercial activated carbon gave 80.39% and 87.78% removal. High resolution gamma spectrometry was second analytical technique for water characterization before and after treatment by same types of activated carbons. Results showed that Ra-226 had highest removal of 48.80% with commercial activated carbon and lowest removal of 36.38% with cherry/sour cherry activated carbon. Highlighted results showed that U-238 had lowest removal of 29.75% with commercial activated carbon and highest removal of 48.75% with apricot activated carbon. Results of both methods were comparable what confirmed the usefulness of the rapid and simple screening method for evaluation of different adsorption tests and further routine monitoring of treated waters after economic removal of radioactive micropollutants on large scale. Screening method for determination of gross alpha/beta activity method seemed more suitable for that purpose.

Acknowledgement

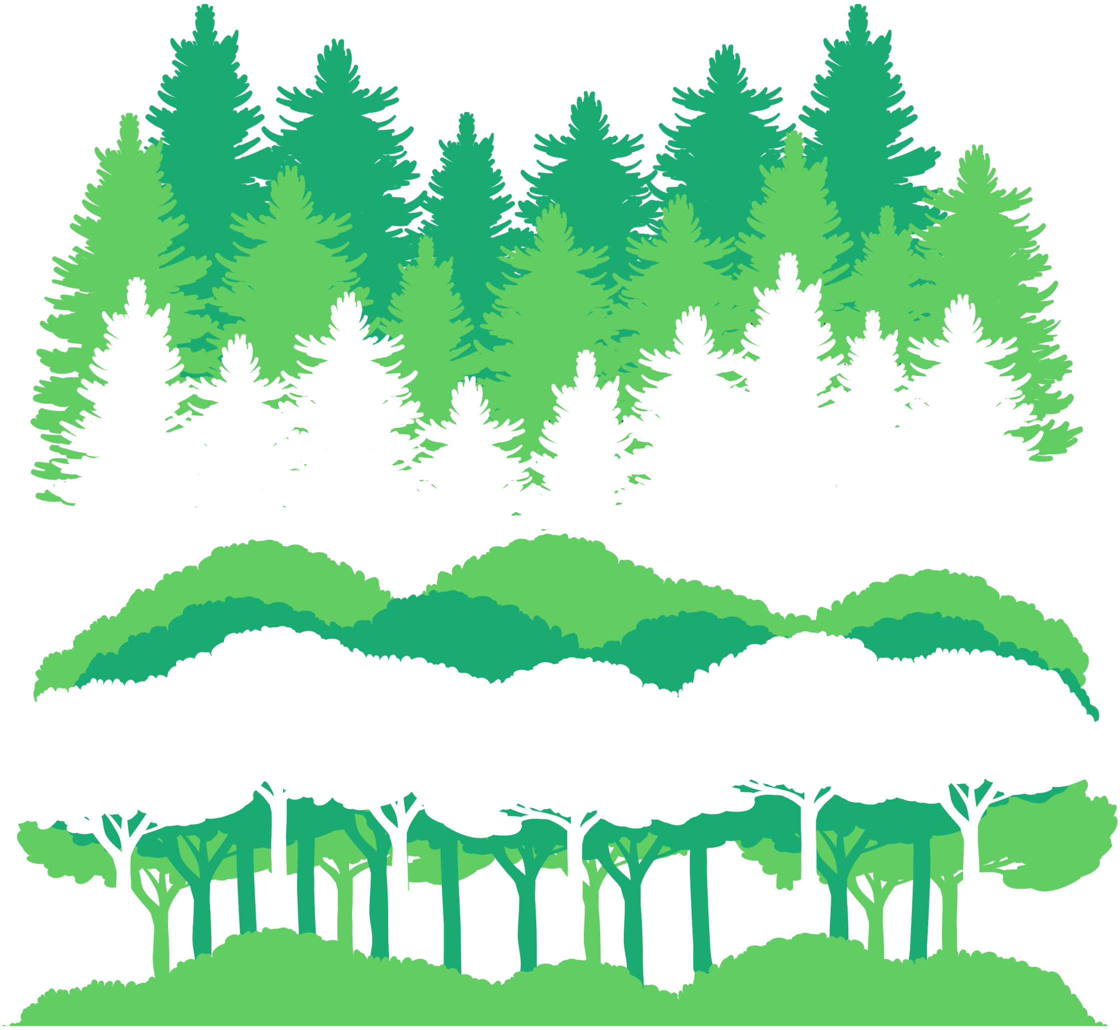
This study has been financially supported by CEEPUS student exchange program, Training and research in environmental chemistry and toxicology, Slovenia (CIII-SI-0905-04-1718).

References

1. Pap, S., Radonić, J., Trifunović, S., Adamović, D., Mihajlović, I., Vojinović Miloradov, M., Turk Sekulić, M. *J. Environ. Manag.* 184 (2016) 297–306.
2. Pap, S., Knudsen, T.Š., Radonić, J., Maletić, S., Igić, S.M., Sekulić, M.T. *J. Clean. Prod.* 162 (2017) 958–972.
3. Turk Sekulic, M., Pap, S., Stojanovic, Z., Boskovic, N., Radonic, J., Solevic Knudsen, T. *Sci. of the Total Environ.* 613–614 (2018) 736–750.

STUDENTSKI RADOVI

STUDENTS’ PAPERS



Bioakumulacija esencijalnih i toksičnih elemenata u šipurku

Bioaccumulation of essential and toxic elements in rosehip

Studenti: Lazar Vujošević[1a], Irena Miljković[1]

Mentor: Jelena B. Popović–Đorđević[1]

[1]Poljoprivredni fakultet, Katedra za hemiju i biohemiju, Univerzitet u Beogradu,

[a]lazar933@gmail.com

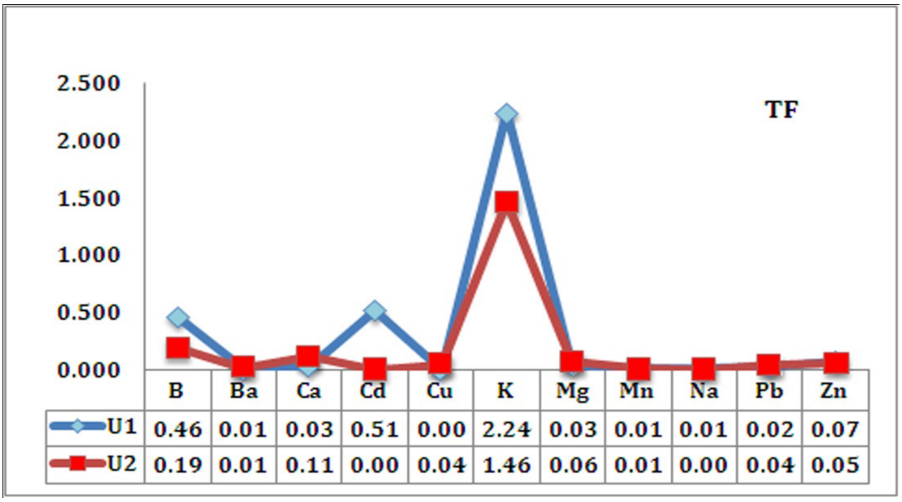
Kako raste svest potrošača o značaju ishrane za zdravlje, tako raste i potreba za proizvodnjom kvalitetnih plodova, gajenih u nekontaminiranim sredinama. Šipurak je plod divlje ruže (*Rosa canina* L.), najrasprostranjenije biljke iz porodice ruža (*Rosaceae* A.L.). Zbog svog prijatnog ukusa tradicionalno se koristi u prehrambenoj, a zbog lekovitog dejstva i u farmaceutskoj industriji. Zahvaljujući svojoj adaptivnosti prema različitim tipovima zemljišta šipurak je rasprostranjen na širokom području Evrope, Afrike i severne Azije [1].

Mineralne materije su od izuzetnog značaja, kako za biljku tako i za životinje i ljude. Prema zastupljenosti u sastavu biljnog materijala grupisane su u makro, mikro i ultramikroelemente. Prisustvo mineralnih materija je neophodno za brojne hemijske reakcije i procese u biljnom organizmu što direktno utiče na rast i razvoj biljke. Pojedini mikrolementi mogu biti toksični u višim koncentracijama (Fe, Zn, Co, Cu, Mn i dr) rezultujući promenama metaboličkih reakcija [2].

U prethodnom radu određen je mineralni sastav šipurka prikupljenog sa dve lokacije u centralnoj Srbiji, pri čemu su utvrđene razlike u sadržaju detektovanih elemenata [3]. Hemijski sastav biljaka uopšteno odražava elementarni sastav zemljišta na kom su gajene. Kod biljaka koje rastu na različitim ali nekontaminiranim zemljištima, uobičajene koncentracije elemenata u tragovima pokazuju prilično velike varijacije za svaki element, što je posledica uticaja različitih faktora. Biljke usvajaju elemenate koji su zastupljeni u zemljištu u rastvornim oblicima, kao i jonskim ili heliranim i kompleksnim oblicima [4].

Uzorci zrelog šipurka (**U1** i **U2**) sakupljeni su u toku oktobra 2016. godine sa dve lokacije u centralnoj Srbiji; **U1**–Mala Moštanica (opština Obrenovac, grad Beograd) i **U2**–Čačak (Moravički okrug). Bioakumulacija elemenata (transfer faktor–TF) izračunata je prema formuli $TF=C_p/C_z$; C_p je koncentracija elemenata u plodu šipurka a C_z je koncentracija istog elementa u uzorku zemljišta prikupljenom sa parcele na kojoj je uzgajan šipurak [5].

U uzorku šipurka **U1** (Mala Moštanica) nije detektovan (Cu), a u uzorku **U2** (Čačak) nisu detektovani kadmijum (Cd) i natrijum (Na) (TF=0). U uzorcima šipurka uzgajanog na obe lokacije uočena je visoka bioakumulacija kalijuma (TF>1), kao i veoma niska bioakumulacija aluminijuma (Al) i gvožđa (Fe) (TF<0,01). Vrednosti TF za esencijalne elemenate u uzorcima bile su u redosledu: **U1**–K>Zn>Ca=Mg>Na, **U2**–K>Ca>Mg>Zn (grafik 1).



	B	Ba	Ca	Cd	Cu	K	Mg	Mn	Na	Pb	Zn
U1	0.46	0.01	0.03	0.51	0.00	2.24	0.03	0.01	0.01	0.02	0.07
U2	0.19	0.01	0.11	0.00	0.04	1.46	0.06	0.01	0.00	0.04	0.05

Grafik 1. Transfer faktor (TF) za esencijalne i toksične elemente u uzorcima **šipurk**a

Male varijacije u vrednostima za TF kod oba uzorka utvrđene su za sledeće elemente: barijum (Ba), magnezijum (Mg), mangan (Mn), olovo (Pb) i cink (Zn). U uzorku **U1** vrednost transfer faktora za bor (B) bila je dvostruko veća nego u uzorku **U2** (grafik 1). Vrednosti TF za toksične i potencijalno toksične elemente bile su u redosledu: Cd>B>Pb>Ba=Mn u uzorku sa teritorije Male Moštanice **(U1)** i B>Pb=Cu>Ba=Mn u uzorku sa teritorije Čačka (**U2**). Najveće razlike između uzoraka u vrednostima za TF uočene su za kalijum, bor i kalcijum.

Rad je urađen u okviru projekata broj 46009 koje finansiran Ministarstvo prosvete, nauke i tehnološkog razvoja Republike Srbije.

Literatura:

1. Mratinić, E., Kojić, M. (1998). Samonikle vrste voćaka Srbije. Institut za istraživanja u poljoprivredi, Beograd.
2. Živkov–Baloš M., Mihaljev Ž., Ćupić Ž., Jakšić S., Apić J., Ljubojević D., Prica N. (2014). Savremena poljoprivreda 63 (4-5). 394-402.
3. Popović–Đorđević, J., Paunović, D., Milić, A., Aritonović, A., Brčeski, I. (2018). Mineralni profil šipurka iz centrale Srbije, XXXII savetovanje agronoma, veterinara, tehnologa i agroekonomista, Padinska Skela, Beograd, Zbornik naučnih radova, Vol. 24, (1-2), 179-185.
4. Kabata-Pendias A. (2011). Trace elements in soils and plants (4th ed,). CRC Press, New York.
5. Barać, N.M. (2017). Mobilnost i biodostupnost odabranih elemenata u poljoprivrednom zemljištu aluviona reke Ibar, doktorska disertacija Univerzitet u Beogradu, Tehnološko-metalurški fakultet, Beograd.

Sadržaj i dnevni unos barijuma u odabranom povrću

Content and daily intake of barium in selected vegetables

Studenti: Tamara Adžić[1a], Irena Miljković[1]

Mentor: Jelena B. Popović–Đorđević

[1]Poljoprivredni fakultet, Katedra za hemiju i biohemiju, Univerzitet u Beogradu

[a]adzict3@gmail.com

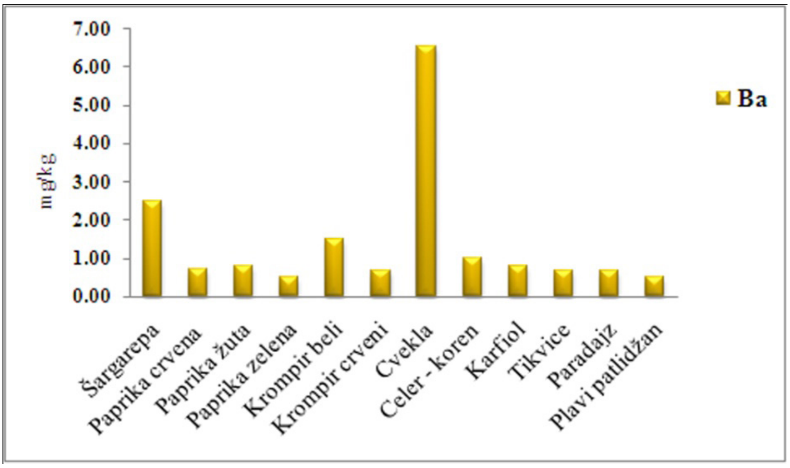
Zbog značaja povrća u ljudskoj ishrani stanovništva neophodno je da ono bude zdravstveno bezbedno. Hemijski sastav biljaka uopšteno odražava elementarni sastav zemljišta na kom su gajene, a na njihov međusobni odnos utiče veliki broj različitih faktora [1].

Barijum (Ba) je prirodni je sastojak minerala u kojima se nalazi u malim količinama, ali je široko rasprostranjen, posebno u magmatskim stenama, peščarima, uglju. Prisutan je u vodi, zemljištu i mnogim namirnicama [2]. Osim prirodne zastupljenosti, jedinjenja barijuma koriste se u industrijskoj proizvodnji plastike, keramike, stakla, insekticida [3]. Ljudska populacija izložena je, u značajanoj meri, jedinjenjima Ba kroz hranu, vodu ili preko vazduha. Negativni efekti Ba na ljudsko zdravlje uključuju abnormalnosti elektrokardiograma, ventrikularnu tahikardiju, hipertenziju i/ili hipotenziju, mišićnu slabost i paralizu [4]. Oralni unos kroz pijaću vodu i hranu je preovlađujući način unosa barijuma današnje populacije [2]. Glavni proces kojim Ba dospeva u biljke iz zemljišta je preko korena [5], što ukazuje da karakteristike zemljišta utiču na biodostupnost ovog elementa. Ipak, stepen bioakumulacije Ba iz zemljišta još uvek nije dobro razjašnjen [3].

Cilj rada bio je određivanje sadržaja barijuma u odabranim vrstama povrća. Pored toga izračunat je dnevni unos Ba kroz konzumiranje ispitivanog povrća.

Uzorci povrća (1–14) odabranih vrsta, u koje spadaju: 1– šargarepa, 2–4 paprika (crvena, žuta i zelena), 5–6 krompir (beli i crveni), 7– cvekla, 8–koren celera, 9– karfiol, 10– tikvice, 11– paradajz, 12– plavi patlidžan, 13–crni luk i 14–bundeva, sakupljeni su oktobru 2016. godine sa zelene pijace u Čačku (Moravi*čki okrug,* zapadna Srbija). Određivanje sadržaja Ba u povrću i izračunavanje dnevnog unosa Ba konzumiranjem povrća urađeno je prema literaturi [6,7].

U ispitivanom povrću, barijum nije detektovan samo u bundevi i crnom luku. Rezultati ukazuju da je korenasto (cvekla, šargarepa, celer) i krtolasto povrće (krompir) sadržavalo najveće količine Ba. Najveća koncentracija (6,51 mg/kg) detektovana je u cvekli, a najmanja u zelenoj paprici (0,50 mg/kg) (grafik 1). Vrednosti dnevnog unosa (DI-*daily inatake*) barijuma konzumiranjem ispitivanog povrća bile su u opsegu od 0,002 – 0,03 mg/kg.



Grafik 1. Sadržaj barijuma u odabranom povrću

Najveći dnevni unos Ba je putem cvekle (0,03 mg/kg), a najmanji kroz crvenu i zelenu papriku, tikvice, paradajz, plavi patlidžan i crveni krompir (0,002 mg/kg). Dobijeni rezultati ukazuju da se konzumiranjem ispitivanog povrća ne prekoračuje tolerantni dnevni unos (TDI-*tolerable daily inatke*) za Ba propisan od strane SCHER (*Scientific Committee on Health and Environmental Risks*) koji iznosi 0,2 mg/kg dnevno (2012). Dalja istraživanja o bioakumulaciji Ba u biljakama bila bi korisna za bolju procenu njegovog stanja u životnoj sredinini i izloženosti ljudi kroz lanac ishrane.

Istraživanja u radu deo su projekta br. 46009 koji finansira Ministarstvo prosvete, nauke i tehnološkog razvoja Republike Srbije.

Literatura

1. Kabata-Pendias, A. (2011). Trace elements in soils and plants (4th ed,). CRC Press, New York.
2. World Health Organization (2001) Barium and barium compounds, Geneva.
3. U.S. Department of health and human services, Agency for Toxic Substances and Disease Registry (ATSDR) (2007). Toxicological profile for barium and barium compounds.
4. SCHER (Scientific Committee on Health and Environmental Risks), (2012). Assessment of the Tolerable Daily Intake of Barium.
5. McBride, M.B., Shayler, H.A., Spliethoff, H.M., Mitchell, R.G., Marquez-Bravo, L.G., Ferenz, G.S., Russell-Anelli, J.M., Casey, L., Bachman, S. (2014). Environ Pollut. 194: 254–261.
6. Popović–Dordevic, J., Bokan, N., Dramicanin, A., Brceski, I., Kostic, A. (2017). *J Environ. Prot. Ecol.* 18 (3), 889–898.
7. Khan, K., Lu, Y., Khan, H., Ishtiaq, M., Khan, S., Waqas, M., Wei, L., Wang T. (2013). Food. Chem. Toxicol, 58, 449–458.

Sadržaj odabranih elemenata u realnim uzorcima vode sa teritorije Požege, Srbija

The contect of selected elements in real samples of water in the Požega area, Serbia

Studenti: Ivana Maloparac[1a],Simona Jaćimović[1]

Mentor: Nebojša Pantelić

[1] Poljoprivredni fakultet, Univerzitet u Beogradu

[a]maloparac993@gmail.com

Voda sačinjava 71% površine planete Zemlje i jedan je od osnovnih sastojaka svih živih bića. Značaj vode za piće ogleda se prevashodno u njenoj fiziološkoj ulozi u organizmu odnosno u održavanju metaboličkih procesa i razmene materije i epidemiološko-toksikološkom značaju, jer se preko vode mogu razviti i preneti razna bakterijska, virusna i parazitna oboljenja. Shodno tome, jako je vazno pratiti kvalitet vode koja se koristi za piće i u domaćinstvu, a posebno sadržaj potencijalno toksičnih elemenata [1] jer njihove povišene koncentracije u vodi mogu štetno da utiču na ljudsko zdravlje i uzrokuju mutagene ili kancerogene efekte u zavisnosti od supstanci.

Cilj ove studije bilo je ispitivanje kvaliteta vode u realnim uzorcima vode za piće sa teritorije Požege (Zlatiborski okrug) kroz sadržaj odabranih potencijalno toksičnih elemenata (aluminijum, kobalt, mangan, olovo, arsen). Uzorci, gradska voda Požega (**S1**), česmenska voda Gornja Dobrinja (**S2**), bunarska voda Gornja Dobrinja (**S3**), kao i basenska voda Gornja Dobrinja (**S4**), prikupljeni su i ispitivani u periodu april-jun 2017. godine.

Za određivanje sadržaja ispitivanih elemenata u uzorcima korišćena je analitička tehnika induktivno kuplovana plazma sa optičkom emisionom spektrometrijom, ICP-OES (eng. *Inductively coupled plasma* - *optic emission spectrometry*).

Aluminijum je jedan od najzastupljenijih metala u Zemljinoj kori, i prisutan je u okruženju u kombinaciji s drugim elementima kao sto su kiseonik, silicijum i fluor. Kao takav lako dospeva u organizam čoveka putem vode i hrane. Posledice trovanja aluminijumom mogu biti encefalopatija, abnormalni govor a neka poslednja istraživanja pokazuju da povišene koncentracije aluminijuma utiču na pojavu mentalnih i neurodegenerativnih oboljenja [2]. Prema Pravilniku o kvalitetu i ispravnosti pijaće voda Republike Srbije i Svetske zdravstvene organizacije (WHO), maksimalno dozvoljena koncentracija (MDK) aluminijuma je 50 μg/L. U uzorcima **S1** i **S2** izmerena je blago povišena koncentracija ovog metala (66,56 odnosno 53,21 μg/L), dok je u preostala dva uzorka, **S3** i **S4**, zabeležana znatno niža koncentracija aluminijuma od MDK (Tabela 1). Kobalt je važan esencijalni biogeni oligoelement, sastojak vitamina *B12* (cijanokobalamin) i bitan element eritropoeze. Kobalt u malim dozama u potpunosti se apsorbuje u probavnom sistemu a najvise se akumulira u jetri i bubrezima. U akutna stanja uzrokovana delovanjem povišene koncentracije kobalta ubrajaju se rinitis, konjunktivitis i stanje slično astmi. Prema pravilniku WHO koncentracija kobalta u pijaćoj vodi trebalo bi da bude $< 0,1$ μg/Lšto je i zabeleženo u uzorku **S4**, dok se opseg koncentracije*Co* u ostalim ispitivanim uzorcima kretao od 0,67 do 0,83 µg/L (Tabela 1). Iako su ove vrednosti blago povišene od MDK, njihov negativan uticaj na zdravlje ljudi se iskljucuje.

Neorganski oblici arsena, prisutni u zemlji, vodi i hrani bitno utiču na zdravlje ljudi i životinja [2], dok organski vezan arsen nema toksično dejstvo. Apsorbovani arsen se distribuira i deponuje u svim tkivima organizma. Sa druge strane, neorgansko olova se apsorbuje preko gastrointestinalnog trakta a izaziva hemolizu eritrocita i remeti hematopoezu. Posledice izloženosti povišenim koncentracijama olova su hronična nefropatija i oksidativna oštećenja biomakromolekula [2]. Sa druge strane, povećana koncentracija mangana može dovesti do promena u intelektualnom razvoju dece, zatim oštećenja respiratornog sistema kao i promene na koži. U svim ispitivanim uzorcima vode koncentracije arsena, olova i mangana su bile daleko ispod maksimalne dozvoljenih vrednosti, Tabela 1.

Tabela 1. Sadržaj elemenata [**µ**g/L] u ispitivanim uzorcima vode

Uzorci	*Al*	*Co*	*Mn*	*Pb*	*As*
S1	66,56	0,83	< 0,10	0,23	0,43
S2	53,21	0,69	< 0,10	0,60	0,73
S3	6,05	0,67	< 0,10	< 0,10	0,75
S4	10,16	< 0,10	0,40	2,06	0,62
MDK*	50	< 0,10	50	10	10

* Maksimalna dozvoljena koncentracija u vodi za ljudsku upotrebu ("Sl. list SRJ", 1999)

Kao zaključak možemo istaći da su svi ispitivani elementi u uzorcima vode sa teritorije Požege bili u granicama maksimalno dozvoljenih vrednosti, osim aluminijuma u uzorcima **S1** i **S2**, kao i kobalta u uzorcima **S1**, **S2** i **S3** gde su zabeležene blago povišene vrednosti. Dalja ispitivanja određenih makro- i mikroelemenata dalo bi kompletniju sliku o kvalitetu vode sa ovog područja.

Literatura

1. Chowdhury, S., Jafar Mazumder, M.A., Al-Attas, O., Husain, T, *Sci. Tot. Environ*. 569 (2016) 476-488
2. Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B.B., Beeregodwa K.N., *Interdiscip. Toxicol*. 7 (2014) 60-72

Optimizacija degradacije tekstilne boje *Reactive Black* 5 netermalnim plazma-tretmanom u prisustvu TiO_2

Optimization of degradation of textile dye *Reactive Black 5* using nonthermal plasma-treatment in the presence ofTiO_2

Student: Slađana Savić[1a]

Mentor: Goran Roglić

[1]Hemijski fakultet, Univerzitet u Beogradu

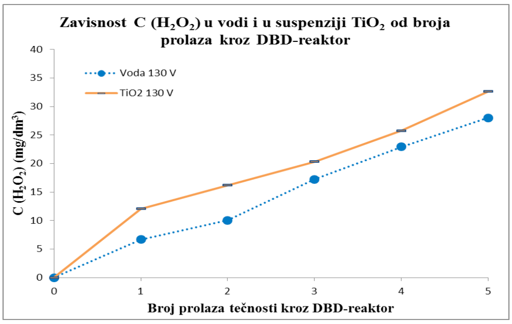
[a]sladjana.savic@rocketmail.com

Tekstilna boja *Reactive Black 5*(CAS 17095-24-8) se ubraja u reaktivne boje koje se hemijski vezuju za tkaninu. Kada se ova boja nađe u otpadnoj vodi predstavlja ne samo estetski problem, već i potencijalnu opasnost po životnu sredinu i ljudsko zdravlje. Jedna od tehnika unapređenih oksidacionih procesa za uklanjanje teško razgradivih organskih jedinjenja je i netermalna plazma, u kojoj nastaje veliki broj reaktivnih kiseoničnih i azotnih vrsta [1]. U ovom radu je korišćenreaktor sa dielektričnim barijernim pražnjenjem (DBD-reaktor), koji radi u protočnom režimu u prisustvu vazduha kao radnog gasa. [2] Kroz ovaj reaktor je više puta recirkulisana destilovana voda, suspenzija titan-dioksida, kao i rastvor tekstilne boje (sa i bez katalizatora), pri čemu su poređeni sledeći parametri:promena pH i provodljivosti i koncentracija H_2O_2. Kao heterogeni katalizator korišćen je TiO_2 (*Aeroxide TiO_2P25, Evonik industries*).

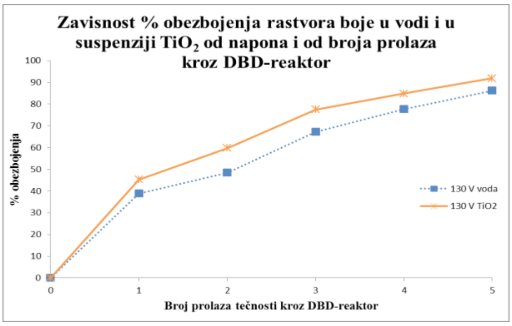
Određivanje sadržaja H_2O_2 zasniva se na principu razvijanja žute boje (A_{407}) nakon reakcije sa titanil-jonom, pri čemu nastaje pertitanska kiselina, H_2TiO_4.[3]Tretirane tečnosti, uz recirkulisanje, propuštane su kroz DBD-reaktor. Kombinovanjem različitih vrednosti frekvence i ulaznog napona struje odabrana je optimalna vrednost (150 Hz,130 V). U alikvotima prikupljenim nakon svakog prolaza su određivani temperatura, pH i sadržaj H_2O_2 (uz centrifugiranje pri analiziranju suspenzije TiO_2). Zatim je kroz DBD-reaktor propuštan rastvor boje (C = 200 mg/dm^3), pripremljen u destilovanoj vodi i u suspenziji TiO_2(C = 1000 mg/dm^3). Alikvoti su po potrebi centrifugirani, pa je u supernatantu određivana A_{590} i uz pomoć jednačine (1) računat % obezbojenja.

$$\%\ \text{obezbojenja} = (A_o - A_i)/A_o \times 100 \tag{1}$$

Sa slike 1 vidi se da koncentracija H_2O_2 raste povećanjem broja recirkulisanja tretirane tečnosti kroz DBD-reaktor, a pri svakom prolazu je veća C (H_2O_2) u prisustvu TiO_2.Na slici 2 se uočava analogan porast % obezbojenja tretiranog rastvora boje sa povećanjem broja prolaza tretiranograstvora boje kroz DBD-reaktor. Efikasnije uklanjanje boje je uočljivo u prisusutvu TiO_2. Ovaj uticaj se ogleda i na kinetiku obezbojavanja rastvora tretirane tekstilne boje.



Slika 1. Zavisnost C(H_2O_2) u vodi i u suspenziji TiO_2 od broja prolaza destilovane vode, odnosno suspenzije TiO_2 kroz DBD-reaktor.



Slika 2. Zavisnost % obezbojenja rastvora boje u vodi i u suspenziji TiO_2 od broja prolaza destilovane vode, odnosno suspenzije TiO_2 kroz DBD-reaktor.

Na ovaj način je dokazano da netermalna plazma pouzdano uklanja teško razgradive organske supstance, usled stvaranja reaktivnih kiseoničnih vrsta od kojih je najstabilnija H_2O_2. Tretman otpadne vode pomoću DBD-reaktora u prisustvu TiO_2 kao heterogenog katalizatora povećava efikasnost opisanog sistema, jer dovodi do povećanja koncentracije kiseoničnih vrsta (hidroksilnih radikala), kao što je navedeno kod [4].

Literatura

1. Atalay S. and Ersöz G.,*SpringerBriefs in Molecular Science*, *Springer Nature* (2016)
2. Brandenburg R, Kovačević V, Schmidt M, Basner R, Kettlitz M, Sretenović G, Obradović B, Kuraica M, Weltmann K., *Contributions to Plasma Physics*, 54(2014) 202–214.
3. Eisenberg G. *Industrial and Engineering Chemistry Analytical Edition*, 15 (1943) 327–328.
4. Dojčinović B, Roglić G, Obradović B, Kuraica M, Kostić M, Nešić J, Manojlović D.,*Journal of Hazardous Materials*, 192 (2011) 763–771.

Procena potencijalnog zdravstvenog rizika upotrebe pijaće vode na području Požege na osnovu sadržaja barijuma i stroncijuma

Potential health risk assessment of drinking water consumation from Požega area expressed through barium and strontium content

Studenti: Simona Jaćimović[1], Ivana Maloparac[1]

Mentor: Aleksandar Ž. Kostić[1]

[1]Poljoprivedni fakultet, Institut za Prehrambenu Tehnologiju i Biohemiju, Univerzitet u Beogradu

Pijaća voda predstavlja sastavni i neodvojivi deo svakodnevnog života. U tom smislu, očuvanje kvaliteta i dovoljnih količina vode za potrebe stanovništva je jedan od osnovnih zadataka svakog društva. Iako je najveći deo Zemlje pod vodom, svega 3% svetskih zaliha vode čini pijaća voda [1]. Sve veći stepen zagađenja životne sredine značajno ugrožava i izvore pitke vode zbog čega se smatra da će, u bliskoj budućnosti, voda postati jedan od najskupljih prirodnih resursa. Upravo iz tih razloga velika pažnja se poklanja očuvanju i praćenju kvaliteta voda posmatrano kroz njihove fizičko-hemijske i mikrobiološke karakteristike [2,3]. Iako se po zalihama pijaće vode Srbija ne može smatrati siromašnom zemljom (na listi Organizacije za hranu Ujedinjenih nacija (FAO) Srbija se po resursima pijaćih voda nalazi na 47. mestu od 180 rangiranih zemalja) postoje određeni delovi naše zemlje koji imaju problema ili sa kvalitetom (Vojvodina i Užice) [2] ili količinom dostupne vode (požarevački i čačanski region). Prema podacima Agencije za zaštitu životne sredine Srbije (SEPA) iz 2017. godine, kvalitet pijaće vode na području Požege, sa fizičko-hemijskog aspekta, smatra se prihvatljivim sa do 5% nepravilnosti. Za vodosnabdevanje na području grada Požege kao i nekoliko okolnih gradova (Čačak, Arilje, Lučani i Gornji Milanovac) koristi se regionalni vodovodni sistem ”Rzav”. Na osnovu činjenice da je ukupno vreme restrikcija vodom iznosilo 60 dana u godini tzv. indeks bezbednosti snabdevanja za ovaj sistem iznosi 16% i smatra se alarmantnim.

Cilj ovog rada je bio da se izvrši procena zdravstvenog rizika stanovništva Požege određivanjem koeficijenata rizika (KR) a na osnovu sadržaja dva potencijalno toksična elementa (stroncijum i barijum) određena ICP-OES (induktivno kuplovana plazma sa optičkom emisionom spektrometrijom) metodom. Pri tome određen je koeficijent kratkoročnog rizika (KR) kao pokazatelj opasnosti po zdravlje ljudi od pojave nekih akutnih poremećaja kao i koeficijent dugoročnog rizika (KR_{oral}) koji, pak, ukazuje na postojanje potencijalne opasnosti od pojave kancerogenih oboljenja. Četiri uzorka pijaće vode koji su ispitivani su prikupljeni u periodu april-jun 2017 i to: gradska voda Požega iz sistema Rzav (**U1**), česmenska voda Gornja Dobrinja (**U2**), bunarska voda Gornja Dobrinja (**U3**), kao i basenska voda Gornja Dobrinja (**U4**). Proračuni KR-vrednosti urađeni su primenom literaturnih podataka i obrazaca [2,4].

Dobijeni rezultati prikazani su u Tabeli 1.

Tabela 1. Rezultati za koncentracije odabranih elemenata i koeficijente zdravstvenog rizika za pijaće vode iz Požege

	U1		U2		U3		U4	
	Ba	Sr	Ba	Sr	Ba	Sr	Ba	Sr
c [mg/L]	0,016	0,110	0,015	00,108	0,137	0,402	0,021	0,320
KR	0,003	0,004	0,003	0,004	0,028	0,013	0,026	0,011
KR_{oral}	$1,6\cdot10^{-3}$	$5\cdot10^{-4}$	$1,5\cdot10^{-3}$	$5\cdot10^{-4}$	$1,4\cdot10^{-2}$	$1,9\cdot10^{-3}$	$1,3\cdot10^{-2}$	$1,5\cdot10^{-3}$
TNU* [mg/L]	* tolerantni nedeljni unos elementa - Ba: 0,7; Sr: 4,2[4]							
RfD_{oral}** [mg/L·kg]	** preporučene referentne vrednosti unosa elemenata – Ba: 0,2; Sr: 4,2[4]							

Kratkoročni rizik (KR) po zdravlje ljudi se smatra visokim i značajnim ukoliko prelazi vrednost 1 [2]. Na osnovu dobijenih rezultata za uzorke voda iz Požege može se zaključiti da su svi kratkoročni rizici daleko ispod vrednosti 1 i da, u tom smislu, upotreba ovih pijaćih voda sa stanovišta sadržaja ova dva potencijalno toksična elementa ne predstavlja značajan rizik za zdravlje ljudi. Ukoliko se posmatra dugoročni rizik po zdravlje ljudi usled potencijalne pojave kancerogenih oboljenja smatra se da je svaka vrednost KR_{oral} koeficijenta jednaka ili veća od 10^{-3} rizična za jednog odnosno srazmerno više stanovnika posmatrano na hiljadu žitelja na nekom području [2]. U tom smislu dobijeni rezultati ukazuju na postojanje slabog rizika od pojave kancerogenih oboljenja usled prisustva stroncijuma u pijaćoj vodi kao i u prva dva uzorka u slučaju barijuma. Sa druge strane, prisustvo barijuma u uzorcima **3** i **4** predstavlja potencijalni rizik za pojavu malignih oboljenja kod 13 tj.14 stanovnika Požege posmatrano na 1000 osoba.

Literatura

1. du Plessis, A., *Fresh water challenges of South Africa and its upper Vaal river (book).* chapter 1 (2017) 3-11.
2. Kostić, A.Ž., Pantelić, N.Đ., Kaluđerović, L.M., Jonaš, J.P., Dojčinović, B.P., Popović-Djordjević, J.B., *Expo Health*. 8 (2016) 227-238.
3. Pantelić, N., Dramićanin, A.M., Milovanović, D.B., Popović-Đorđević, J.B., Kostić, A.Ž., *Rom J Phys*. 62 (2017) 818.
4. Alfredo, K., Adams, C., Eaton, A., Roberson, J.A., Stanford, B., *The Potential Regulatory Implications of Strontium*. (2014) American Water Works Association.

Određivanje sadržaja arsena, kadmijuma i olova u različitim uzorcima meda primenom optički emisione spektrometrije sa induktivno spregnutom plazmom

Determining the content of arsenic, cadmium and lead in various types of honey using inductively coupled plasma optical emission spectroscopy

Studenti: Jovan Novaković[1a],Maja Grigorov

Mentor: prof. dr Biljana Kaličanin

[1]Medicinski fakultet, Departman za farmaciju, Univerzitet u Nišu

[a]novakovicjovan63@gmail.com

Med je prirodna supstanca koju stvaraju medonosne pčele. Predstavlja prirodni produkt veoma složenog hemijskog sastava. Oko 95% suve materije meda predstavljaju ugljeni hidrati, uglavnom fruktoza i glukoza, ali i oko 25 različitih oligosaharida. Osim šećera, med sadrži male količine aminokiselina, enzima, vitamina, flavonoida, fenola i minerala. [1]

Med je efikasan u zaustavljanju dijareja. Pozitivni efekti su dokazani i kod drugih gastrointestinalnih tegoba, bolesti respiratornog trakta, različitih infekcija itd. Takođe, med ispoljava antibakterijsko, antivirusoidno i antiparazitsko dejsvo, a potvrđena je i njegova efikasnost kao antioksidansa, antimutagena i antikancerogena. [1,2]

U medu se pored sastojaka koji koriste ljudskom zdravlju (Fe, Cu, Zn, Se...) mogu naći elementi čije prisustvo u medu može narušiti zdravlje ljudi i koji mogu predstavljati pokazatelj zagađenosti oblasti sa koje je med prikupljen (As, Cd, Pb, Hg...).Tako hronična izloženost arsenu dovodi do hiperpigmentacije kože, hiperkeratoze, polineuritisa, nenormalnog rada srca, nerava, jetre i bubrega; kadmijum je element toksičnosti nekoliko puta veće od arsena, poseduje kancerogeno dejstvo, izaziva anemiju, bolesti kostiju, oštećuje bubrege itd.; olovo je kumulativni otrov, deluje toksično na nervni sistem izazivajući subencefalopatske, neurološke i efekte u ponašanju, a dokazana je i njegova kancerogena aktivnost. [1]

Cilj ovog rada bio je određivanje sadržaja arsena, kadmijuma i olova u različitim uzorcima meda primenom optički emisione aspektrometrije sa induktivno spregnutom plazmom (ICP-OES).

Ispitivanje je vršeno na dvadeset uzoraka meda prikupljenih na teritoriji Republike Srbije. Šesnaest uzoraka meda je domaće proizvodnje, dok četiri uzorka predstavljaju med koji se može nabaviti u marketima. Uzorci su razvrstni prema njihovoj vrsti (livadski, šumski, lipov i bagremov). Za analizu, uzorci su pripremani postupkom mokre digestije. [3]

Sadržaj olova u analiziranim uzocima meda kretao se od 0,4 do 0,93mg kg^{-1}, saprosečnom vrednošću 0,685 mg kg^{-1}. Dobijene vrednosti olova bile su niže odnosno više od vrednosti dobijenih u analiziranim uzorcima meda autora iz zemalja regiona. Tako se sadržaj olova u medu iz Slovenije kretao od 1,86 do 4,3 mg kg^{-1}[4], a u medu iz Hrvatske se kretao od 0,01 do 0,84mg kg^{-1}. [3] Sadžaj olova u medu se kretao u granicama koje su propisane pravilnikom Republike Srbije, [5] odnosno pravilnikom koji propisuje EU, [6] osim u nekim uzorcima gde je sadržaj bio viši, što može biti posledica kontaminacije jer prisustvo olova u medu je najvećim delom aerogenog porekla.

Sadržaj kadmijuma u analiziranim uzorima meda se kretao od 0,02 do 0,09 mg kg^{-1}. Ove vrednosti su slične sa vrednostima koje su dobijali i drugi autori [7], a takođe odgovaraju dozvoljenim vrednostima sadržaja ovog elementa u medu propisanim u pravilniku EU. [6] Prisustvo kadmijuma u medu je poreklom iz biljaka.

Sadržaj arsena u svim analiziranim uzorcima meda bio je oko ili manji od 1 mg kg^{-1} što odgovara pravilniku koji je dala Evropska agencija za sigurnost hrane. [8]

Sadržaj Pb, Cd i As u analiziranim uzorcima meda kretao se u granicama koje propisuju različiti pravilnici, a koje su bezbedne za ljudsku upotebu, osim u manjem broju uzoraka meda gde je za neki od ovih metala sadržaj bio viši što može biti posledica eventualnog nepravilnog čuvanja meda, zagađenosti vaduha, zemlje, vode.

Zahvalnica: Ovaj rad je rađen u okviru Projekta br. 45017, koje finansira Ministarstvo prosvete, nauke i tehnološkog razvoja Republike Srbije.

Literatura

1. Bogdanov, S., Jurendić, T., Sieber, R., Gallmann, P., *American Journal of the College of Nutrition.* 27 (2008) 677-689.
2. Czipa, N., Andrasi, D., Kovacs, B.,*Food chemistry.*175 (2015) 536-542.
3. Bilandžić, N., Đokić, M., Sedak, M., Kolanović, B., Varenina, I., Končurat, A., Rudan, N., *Food Chemistry.* 128 (2011) 1160-1164.
4. Golub, T., Doberšek, U., Kump, P., Nečemer, M., *Food Chemistry*. 91 (2005) 593-600
5. Pravilnik o količinama pesticida, metala i metaloida i drugih otrovnih supstancija, hemioterapeutika, anabolika i drugih supstancija koje se mogu nalaziti u namirnicama, *Sl. Glasnik RS*. (2010)
6. EC commission decision amending Annex II to council directive. (2000)
7. Vanhanen, L. P., Emmeretz, A., Savage, G. P., *Food Chemistry*. 128 (2011) 236-240
8. www.efsa.europa.eu

Naftni zagađivači u drumskoj prašini Pančeva, Srbija

Oil Pollutants in the street dust of Pančevo, Serbia

Studenti: Nada Vidović[1a], Ivan Kojić[2]

Mentor: Tatjana Šolević Knudsen[2]

[1]Prirodno-matematički fakultet, Univerzitet u Banja Luci

[2]Inovacioni centar Hemijskog fakulteta, Univerzitet u Beogradu, ()

[a]vidovicnadaa@gmail.com

Cilj ovog rada bio je istraživanje i karakterizacija naftnih zagađivača u drumskoj prašini grada Pančeva u Srbiji. Ispitivana je i razlika u raspodjeli zagađujućih supstanci u frakcijama čestica različite veličine.

Reprezentativni kompozitni uzorak drumske prašine prikupljen je sa različitih lokacija grada Pančeva. Koristeći set sita od nerđajućeg čelika, čestice su frakcionisane u tri veličine sa prečnikom: <63 µm, 63 - 250 µm i 250 - 500 µm. Čestice drumske prašine su ekstrahovane, ekstrakti su prečišćeni i razdvojeni na frakcije koristeći hromatografiju na stubu adsorbensa.

Raspodjela n-alkana (m/z = 71), izoprenoida (m/z = 183), sterana (m/z = 217) i hopana (m/z = 191) ukazuje na prisustvo različitih naftnih derivata u uzorcima [1, 2]. Glavne komponente koje su identifikovane su bile mazut i ulje za podmazivanje. Dodatno, uočeno je i prisustvo najlakših naftnih derivata (najvjerovatnije motornog benzina).

Analiza ekstrakta u frakcijama različite veličine pokazala je da su najkrupnije čestice (250 - 500 µm) sadržale smješu različitih naftnih zagađivača i nativne organske supstance. Ovo zapažanje je najverovatnije rezultat većeg udjela biljnih i životinjskih ostataka u ovoj frakciji čestica.

Može se zaključiti da drumska prašina grada Pančeva sadrži smješu nativne organske supstance i različitih naftnih zagađivača. Naftni zagađivači identifikovani u uzorcima drumske prašine odgovaraju naftnim derivatima koji se najčešće koriste u Srbiji.

Reference

1. Kaplan I.R., Galperin Y., Lu S., Lee R. (1997): *Forensic Environmental Chemistry: diferentiation of fuel-types, their sources and release time.* Organic Geochemistry 27, 289-317.
2. Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. *The Biomarker Guide, Volume 2: Biomarkers and Isotopes in the Petroleum Exploration and Earth History*. Cambridge University Press, Cambridge, UK.

Praćenje sadržaja toksičnih metala (As, Cd i Pb) u odabranim vrstama medicinskog bilja

Monitoring the content of toxic metals (As, Cd and Pb) in selected types of medicinal herbs

Studenti: Sandra Kalauzović[1a], Maja Grigorov[1], Jovan Novaković[1]

Mentor: Biljana Kaličanin[1]

[1]Medicinski fakultetu, Departman za Farmaciju, Univerzitet u Nišu

[a]kalauzovics@gmail.com

Medicinsko bilje se u zemljama u razvoju tradicionalno koristi u prevenciji i lečenju nekih bolesti, mada se poslednjih decenija interesovanje za medicinsko bilje povećalo i u razvijenim zemljama. Pored direktne upotrebe za lečenje određenih bolesti, medicinsko bilje predstavlja i važnu sirovinu za proizvodnju farmaceutika u farmaceutskoj industriji. Medicinsko bilje sadrži brojne hemijske sastojke (fenole, flavonoidi...) [1], koji imaju pozitivno dejstvo na zdravlje ljudi. Međutim, biljne vrste mogu biti, zbog prisustva zagađivača na mestima na kojima se uzgajaju, onečišćene teškim metalima, pesticidima i mikroorganizmima. Obzirom na visoko toksično i kumulativno dejstvo teških metala, neophodno je praćenje i određivanje njihovog sadržaja u biljnim vrstama, koje se koriste za pripremu čajeva i drugih napitaka od medicinskog bilja. Tako je, u ovom radu, primenom optički emisione spektrometrije sa indukovano kuplovanom plazmom (ICP-OES) određivan sadržaj As, Pb i Cd u listu matičnjaka (*Melissa officinalis*), listu masline (*Olea Europea*), cvetu smilja (*Helichrysum arenarium*), plodu badelja (*Silybum marianum*) i listu virka (*Alchemilla vulgaris*). Odabrane biljne vrste, pored ostalog, imaju povoljno dejstvo kod bolesti jetre, tj. mogu se koristiti kao hipolipemici. Uzorci za analizu su pripremani metodom suve digestije [2].

U Tabeli 1, prikazan je totalni sadržaj toksičnih metala (As, Cd i Pb) u navedenom medicinskom bilju.

Određeni sadržaj As se kretao između $9{,}19\cdot10^{-3}$ i $1{,}18\cdot10^{-1}$ mg/kg, pri čemu je najniži sadržaj određen u biljnoj vrsti *Olea Europea*, a najviši u *Helichrysum arenarium*. Kada je u pitanju Cd, vrednosti suse kretale između $1{,}18\cdot10^{-2}$mg/kg u biljnoj vrsti *Olea Europea* i $1{,}18\cdot10^{-1}$ mg/kg u biljnoj vrsti *Silybum marianum*. Vrednosti, dobijene za sadržaj Pb kretale su se od $3{,}83\cdot10^{-2}$ u biljnoj vrsti *Melissa officinalis* do $5{,}33\cdot10^{-1}$mg/kg u *Helichrysum arenarium*.

Pravilnikom, koji se primenjuje u Republici Srbiji, propisane su vrednosti teških metala, koje se mogu nalaziti u čaju.Vrednosti za sadržaj metala analiziranih u ovoj studiji su znatno niže od vrednosti, koje propisuje naš Pravilnik [2].Ovim Pravilnikom propisane vrednosti za Pb su 2 mg/kg, za As su 1 mg/kg, dok vrednosti za Cd nisu date.

Svetska zdravstvena organizacija propisuje maksimalno dozvoljeni dnevni unos za teške metale, koji u slučaju Cd, Pb i As iznosi 70μg, 250μg i 150μg dnevno, za osobu prosečne telesne težine [3].

Tabela 1. Sadržaj As, Cd i Pb (mg/kg) u odabranim vrstama medicinskog bilja i RSD vrednosti (u %)

Uzorak	Sadržaj (u mg/kg)			RSD (u %)		
	As	Cd	Pb	As	Cd	Pb
Melissa officinalis	$4{,}96\cdot10^{-2}$	$1{,}38\cdot10^{-2}$	$3{,}83\cdot10^{-2}$	7,78	1,48	8,00
Olea Europea	$9{,}19\cdot10^{-3}$	$1{,}18\cdot10^{-2}$	$6{,}83\cdot10^{-2}$	14,26	11,11	5,77
Helichrysum arenarium	$1{,}18\cdot10^{-1}$	$5{,}20\cdot10^{-2}$	$5{,}33\cdot10^{-1}$	2,78	6,57	1,07
Silybum marianum	$5{,}34\cdot10^{-2}$	$1{,}18\cdot10^{-1}$	$1{,}18\cdot10^{-1}$	4,81	0,50	7,78
Alchemilla vulgaris	$4{,}14\cdot10^{-2}$	$3{,}22\cdot10^{-2}$	$3{,}94\cdot10^{-1}$	10,34	3,33	5,18

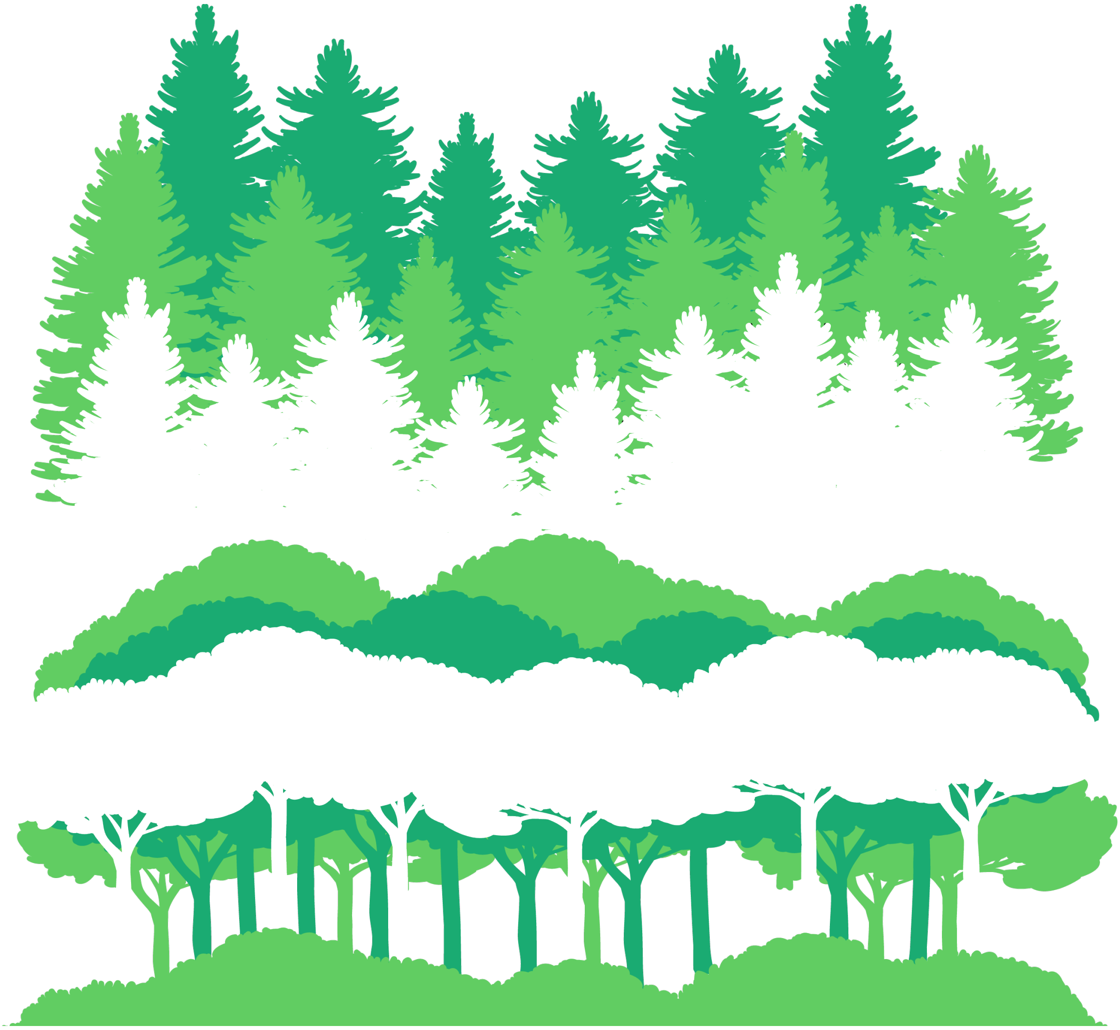
Rezultati dobijeni u ovom radu pokazuju da je primena ovih biljnih vrsta za ljudsku upotrebu bezbedna, sa aspekta ovih teških metala.Niske RSD vrednosti, ukazuju da je se ICP-OES može sa sigurnošću koristiti za određivanje sadržaja teških metala u ovim i sličnim uzorcima.

Zahvalnica: Ovaj rad rađen je u okviru Projekta br. 45017, koji finansira Ministarstvo prosvete, nauke i tehnološkog razvoja Republike Srbije.

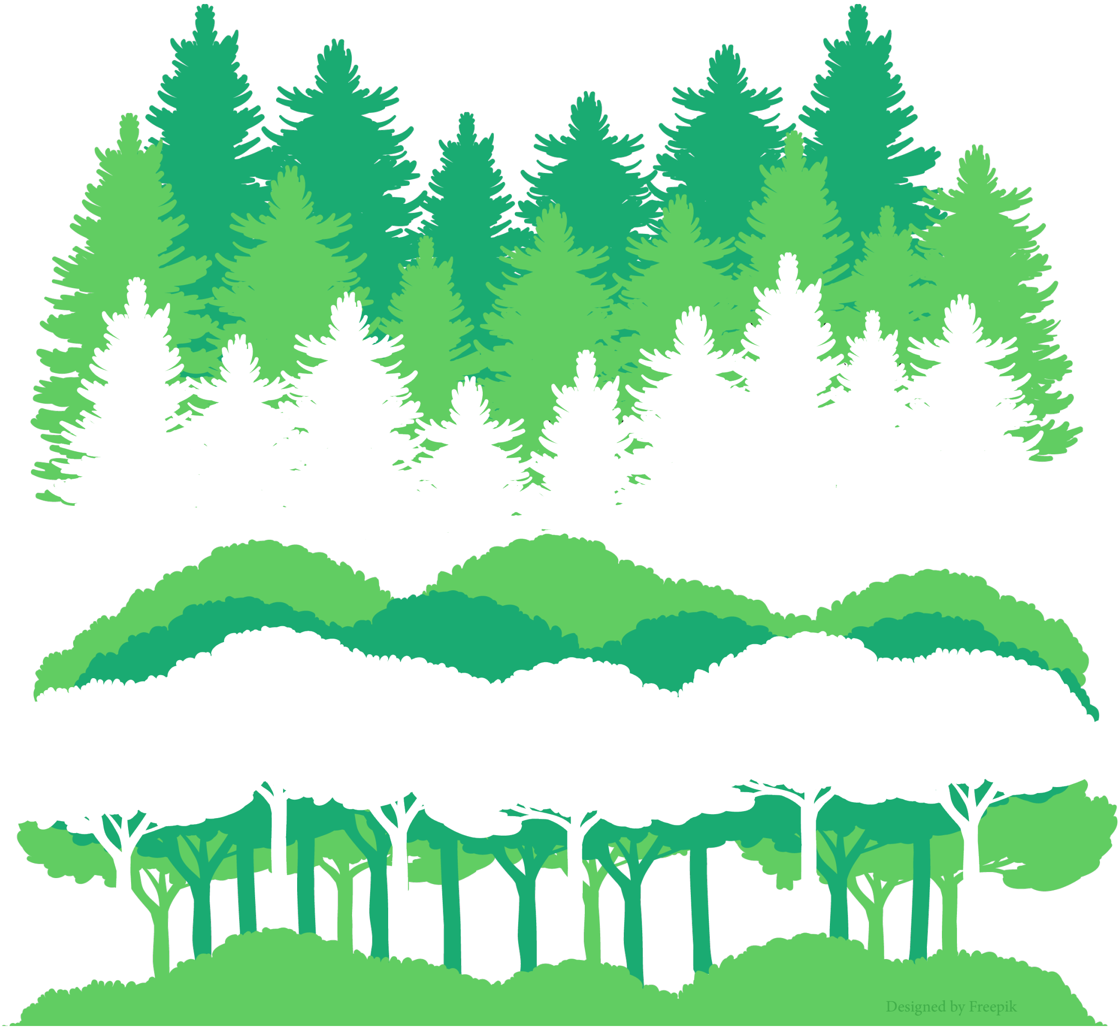
Literatura

1. Pourmorad F, Hosseinimehr S. J, Shahabimajd N. Antioxidant activity, phenol and flavonoid contents ofsome selected Iranian medicinal plants. African Journal of Biotechnology 2006; 5(11): 1142-1145.
2. Soylak M, Tuzen M, Narin I,Sari H. Comparison of Microwave, Dry and Wet DigestionProcedures for the Determination of Trace MetalContents in Spice Samples Produced in Turkey. JFDA2004; 12(3): 254-258.
3. Pravilnik o količinama pesticida, metala i metaloida i drugih otrovnih supstancija, hemioterapeutika, anabolika i drugih supstancija, koje se mogu nalaziti u namirnicama. Službeni list SRJ, br. 5/92, 11/92, 32/2002.
4. JECFA, 2005. Joint FAO/WHO Expert Committee on Food Additives. Sixty-vourthMeeting. Summary and Conclusions. WHO, Geneva.

REGISTAR AUTORA
AUTHOR INDEX



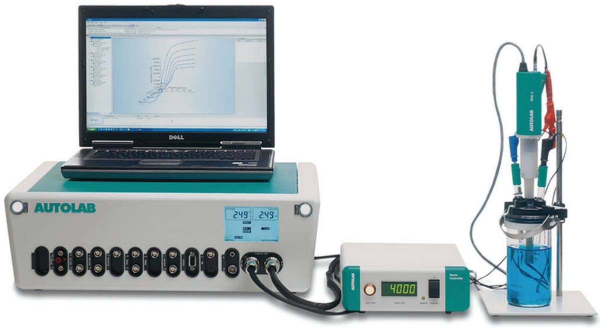
SPONZORI

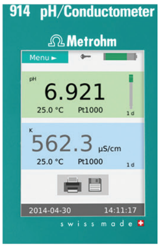


Институт ”Винча”

70 година

науке


AUTOLAB
4000


914 pH/Conductometer
Metrohm
Menu ▸
pH
6.921
25.0 °C Pt1000
562.3 µS/cm
25.0 °C Pt1000
2014-04-30 14:11:17
swiss made


Process Analyzer ADI 2045PL

INSTITUT MOL d. o. o.
Privredno društvo za hemiju, biotehnologiju i konsalting
Nikole Tesle 15, 22300 Stara Pazova, tel./faks: (022) 2100-325
(022) 317-652 e-mail: mol@eunet.rs http://www.mol.rs

INSTITUT MOL je osnovan 1993. godine. Bavi se hemijom životne sredine i razvojnim istraživanjima na polju hemije i biotehnologije.

Opremljene laboratorije za hemijsku analitiku (klasične i spektrofotometrijske analize, atomska apsorpciona i UV-VIS spektrofotometrija, gasna i gasno-masena hromatografija, IR spektrometrija, tečna hromatografija) uz dobar tim stručnjaka, učinili su INSTITUT MOL jednom od vodećih kuća u oblasti ekokarakterizacije životne sredine. Rezultat ovog rada su sledeća ovlašćenja: **Ovlašćenje za uzorkovanje i vršenje fizičko-hemijskih ispitivanja kvaliteta površinskih, podzemnih** i **otpadnih voda, Ovlašćenje za kontrolu kvaliteta vazduha u životnoj sredini** kao i **Ovlašćenje za karakterizaciju otpada.** Naše terenske ekipe su stručno i tehnički opremljeni za uzimanje uzoraka površinskih, podzemnih i otpadnih voda, vazduha i čvrstih materijala, kao i za pravilno rukovanje i transport svih uzoraka do Laborotorije za ispitivanje.

INSTITUT MOL je do sada radio veliki broj ispitivanja i istraživanja, na južnoevropskim prostorima, posebno na području analitike (hemijske i mikrobiološke) voda, zemljišta, vazduha. Rezultati su sadržani u desetinama elaborata i objavljivani su na stručnim skupovima.

INSTITUT MOL je uključen u interlaboratorijska ispitivanja u zemlji i u inostranstvu (IMEP-Belgija, ERA, LGC i SGS).

Rad laboratorije je usaglašen sa zahtevima standarda **SRPS ISO/IEC 17025:2006**- standarda za obavljanje poslova ispitivanja, **ISO 9001:2015**-sistem kvaliteta menadžmentom**,** standarda **ISO 14001:2015** –sistem upravljanja zaštitom životne sredine i standarda **BS OHSAS 18001:2007**- sistem upravljanja zaštitom zdravlja i bezbednošću na radu.

INSTITUT MOL was founded in 1993. It deals with environmental chemistry and developmental research in the field chemistry and biotechnology.

Equipped laboratories for chemical analytics (classical and spectrophotometrical analyses, atomic absorption and UV-VIS spectrophotometry, gas and gas mass chromatography, IR spectroscopy, liquid chromatography…) along with a great team of experts have made INSTITUT MOL one of the leading firms in the area of ecocharacterization of the environment. The results of this work are the following authorities: **The authority for sampling and testing of surface, ground water and wastewater quality, the authority for controlling air quality in the environment as well as the authority for the characterization of waste**. Our field teams are professionally and technically equipped for taking samples of surface, ground and waste water, air and solid materials, as well as for the proper handling and transport of all of the samples to the laboratories for testing.

So far, INSTITUT MOL has carried out large numbers of analyses and research in the southern area of Europe, especially in the field of water, land and air analytics (chemical and microbiological). The results can be found in dozens of studies and were published at professional conferences.

INSTITUT MOL is included in interlaboratory research in the country and abroad (IMEP – Belgium, ERA, LGC and SGS).

The functioning of the laboratory is determined according to the requests of the **SRPS ISO/IEC 17025:2006-** standard for the competence of testing laboratories, **ISO 9001:2015 standard-** Quality management system, **ISO 14001:2015 standard** – Environmental management systems and **BS OHSAS 18001:2007-**Occupational health and safety Management systems.

Anahem Laboratorija
Mocartova 10, 11160 Beograd, Srbija

Matični broj: 17615980; Šifra delatnosti: 7120
PIB: 103604091; Tekući račun: 205-81605-04
www.anahem.org; E-mail: analize@anahem.org
Tel.: 011 3422 800; Fax: 011 3422 900

ANAHEM Laboratorija je akreditovana prema SRPS ISO/IEC 17025 standardu od strane Akreditacionog tela Srbije (ATS) (Sertifikat o akreditaciji br. 01-261) za ispitivanje:

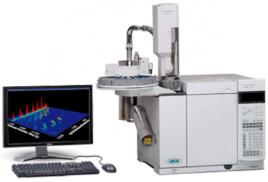
- **VODE** (voda za piće, otpadna, podzemna, površinska, tehnološka,...)
- **ZEMLJIŠTE** (zagađenje, kvalitet)
- **OTPAD** (sve vrste industrijskog, komunalni)
- **HRANU I HRANU ZA ŽIVOTINJE** (voće i povrće, dečija hrana, dijetetika, aditivi, stočna hrana,...)
- **PREDMETE OPŠTE UPOTREBE** (dečje igračke, posuđe, ambalaža, tekstilni materijal, deterdženti, kozmetika, duvanski proizvodi,...)
- **UZORKE SA POVRŠINA (brisevi)**
- **VAZDUH** (emisija, ambijentalni vazduh)
- **BUKU U RADNOJ OKOLINI I ŽIVOTNOJ SREDINI**
- **USLOVE RADNE OKOLINE** (fizičke,hemijske I biološke štetnosti, fizički parametri)

KONTAKTI

Analize vode: 065 847 39 34	voda@anahem.org
Analize otpada: 064 847 39 16	otpad@anahem.org
Analize predmeta opšte upotrebe: 065 847 39 55	predmeti@anahem.org
Analize hrane: 065 847 39 51	hrana @anahem.org
Analize vazduha: 064 847 39 21	vazduh@anahem.org
Analize radne okoline: 065 847 39 40	radnaokolina@anahem.org
Merenje buke: 065 847 39 41	buka@anahem.org

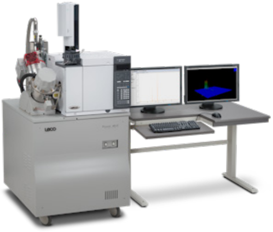
LINIJA LECO GASNIH HROMATOGRAFA

GCxGC-FID/ECD



Pegasus BT 4D - NOVO!

Pegasus GCxGC-TOFMS 4D



Pegasus GC-HRT 4D

Pegasus BT

Pegasus HT

Pegasus GC-HRT

- GCxGC-FID/ECD (sveobuhvatna dvodimenzionalna gasna hromatografija sa plameno-jonizacionim detektorom/detektorom elektronskog zahvata)
- Pegasus BT 4D (Benchtop GCxGC-TOFMS - sveobuhvatna dvodimenzionalna gasna hromatografija sa time-of-flight masenim spektrometrom)
- Pegasus 4D (GCxGC-TOFMS - sveobuhvatna dvodimenzionalna gasna hromatografija sa time-of-flight masenim spektrometrom)
- Pegasus GC-HRT 4D (GCxGC-high resolution TOFMS - sveobuhvatna dvodimenzionalna gasna hromatografija sa time-of-flight masenim spektrometrom visoke rezolucije)
- Pegasus BT (Benchtop GC-TOFMS - gasna hromatografija sa time-of-flight masenim spektrometrom)
- Pegasus HT (HT GC-TOFMS - gasna hromatografija sa time-of-flight masenim spektrometrom velike propusne moći)
- Pegasus GC-HRT (GC-high resolution TOFMS - gasna hromatografija sa time-of-flight masenim spektrometrom visoke rezolucije)

Ovlašćeni predstavnik za teritoriju Srbije, Crne Gore, R.Makedonije i Albanije
ANNAFER D.O.O., Đorđa Servickog 4, 21000 Novi Sad, Srbija
Olgica Gaal, mob: +381-63 598 361, email: olgica_gaal@leco.com

MI SE BAVIMO ANALITIKOM I EKSPERIMENTALNOM HEMIJOM

www.chem.bg.ac.rs

TRAYAL
KORPORACIJA AD

Web: www.trayal.rs
E-mail: headoffice@trayal.rs
Tel. +381 37 428090
Fax. +381 37 428507
Centrala: +381 37 422328

CIP - Каталогизација у публикацији - Народна библиотека Србије, Београд

54(048)
502/504(048)
577.1(048)
66(048)

СИМПОЗИЈУМ Хемија и заштита животне средине са међународним
учешћем (8 ; 2018 ; Крушевац)

Knjiga izvoda = Book of Abstracts / 8. simpozijum Hemija i zaštita životne sredine sa međunarodnim učešćem, Kruševac 30. maj - 1. jun 2018. = 8th Symposium Chemistry and Environmental Protection with International Participation; [urednici Vladimir Beškoski, Jelena Savović, Miloš Momčilović]. - Beograd: Srpsko hemijsko društvo = Serbian Chemical Society, 2018 (Beograd : DualMode). - 256 str. : ilustr. ; 24 cm

Tekst na srp. i engl. jeziku. - Tiraž 120. - Bibliografija uz svaki sažetak. - Registar.

ISBN 978-86-7132-068-9

a) Хемија - Апстракти b) Животна средина - Заштита - Апстракти c)
Биохемија - Апстракти d) Биотехнологија - Апстракти
COBISS.SR-ID 264762380

Prethodni skupovi iz oblasti hemije i zaštite životne sredine

Previous symposia on chemistry and environmental protection

1. JUGOSLOVENSKI SIMPOZIJUM — Beograd, 1985.

2. JUGOSLOVENSKI SIMPOZIJUM — Vrnjačka Banja, 1993.

1. REGIONALNI SIMPOZIJUM — Vrnjačka Banja, 1995.

3. JUGOSLOVENSKI SIMPOZIJUM — Vrnjačka Banja, 1998.

4. JUGOSLOVENSKI SIMPOZIJUM — Zrenjanin, 2001.

2. REGIONALNI SIMPOZIJUM — Kruševac, 2003.

5. SIMPOZIJUM — Tara, 2008.

6. SIMPOZIJUM — Vršac, 2013.

7. SIMPOZIJUM — Palić, 2015.

ISBN 978-86-7132-068-9

9 788671 320689