



УНИВЕРЗИТЕТ У БАЊОЈ ЛУЦИ
UNIVERSITY OF BANJA LUKA

ПРИРОДНО-МАТЕМАТИЧКИ ФАКУЛТЕТ
FACULTY OF NATURAL SCIENCES AND MATHEMATICS



Number of Protocol: 18/1.455/19

Date: Marth 05, 2019

The United Nations Educational, Scientific and Cultural Organization
(UNESCO), PARIS headquarters, 7 Place Fontenoy
75007 Paris, France

Re: REPORT ON THE PROJECT SCIENTIFIC AND FIELD ACTIVITIES for the grant.

Please find enclose the scientific activities report on the grant:

“Hybrid Metallic/Carbon Nanomaterials Made from Mining Industry Sludge and Their Applications in Adsorption/Catalysis Treatment of Emerging Pharmaceuticals in Water”

Contract number: 4500355075

Principal investigator: Dr Maja STANISAVLJEVIĆ

Team members: Savka Janković, MA in physical chemistry and Dragana Milisavić, MA in physical chemistry

Institutions participating in implementation of the proposed research project:

1. HOME INSTITUTION: University of Banja Luka, Faculty of Science, Laboratory for Organic Chemistry, Mladena Stojanovića 2, 78000 Banja Luka Tel/Fax: +387/51/319-142, Dr BALABAN Milica (balabanm@pmfbl.org) , <http://www.pmfbl.org>
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3. ADVISORY AND SUPPORT INSTITUTION: Shinshu University, Center for Energy and Environmental Science, Wakasato 4-17- 1, Nagano, Japan 380-8553 Tel/Fax: +81/26-228-1057, Dr Katsumi KANEKO (kkaneko@shinshu-u.ac.jp) <http://www.shinshu-u.ac.jp/>

SUMMARY

The Project “Hybrid Metallic/Carbon Nanomaterials Made from Mining Industry Sludge and Their Applications in Adsorption/Catalysis Treatment of Emerging Pharmaceuticals in Water” supported the research of young PhD postdoctoral researcher Dr Maja Stanisavljević, who repatriated to Bosnia and Herzegovina after completing her PhD at Mendel University in Czech Republic. She narrowly specialized the quantum dots, a metallic nanomaterial, during her PhD study. In discussions with the host team from University of Banja Luka, she developed the idea to try to introduce the small metallic “spots” the on the classical nanoporous (activated) carbon material. The University of Banja Luka hosted this idea and even further, the project was developed so to use the mining waste water, containing significant ammounts of metal ions as the source for the carbon treatment. This hybrid material, developed through the project should have the capability to adsorb various toxic organic molecules within the small pores in the carbon material. However, at the same time, it should also be able to degrade them since there are these metallic nano-spots on the surface which should serve as the catalyst. The project experiments are going timely, focusing on the various pharamaceutical molecules often present in the waste water, and most particularly diclophenac and tetracycline. The project team gained the state-of-the-art training at the Eastern Finland University (host institution) and also have got the significant support in material characterisation from the Shinshu University, Nagano (support institution). Project gained also the industrial support from the Bosnian carbon factory, the iron mine and other stakeholders as reported in the detailed scientific report. Also, the large dissemination event was held “A road to activated carbon in Bosnia and Herzegovina” which attracted 63 visitors including some foreign partners from Italy. Bulgaria and Finland. All of the conference presentations and the summer schools were attended timely and one peer reviewed paper was published. The second paper is in the preparation phase as well as the national patent application.

INTRODUCTORY NOTE: The following report contains the descriptions of the contents of activities performed within the project, which are aligned according to the original timing list submitted with the project application.

A 1. Field work on sampling of the sludge at Omarska iron mine

Performed timely, the samples collected.

Since the first step in the project development was the study of the quality of the mining sludge, in order to extract as many useful metal ions as possible, the project team has visited the largest iron mine in Bosnia and Herzegovina. It is the Omarska iron mine in vicinity of the Prijedor city. The deposits here are estimated up to 100 million tons of iron. The ore type is limonite which is known to produce plenty of the sludge and products other than iron.



Picture 1. Project team performing sampling of the waste sludge in the Omarska iron mine

The project team first had a seminar with the technical director and the field engineers who expressed interest in the project contents and potential for further increase in efficiency of the extraction of iron from the ore, or indirectly from sludge as is drafted in the project. The project team was then given the safety training for field work and has visited the processing plant as well as four accumulation lakes. The sampling was performed from the so called “Emergency lake” in which the sludge is standing for the longest period of time. This fact should contribute to the simplification of the later processes since probably most of the eventual organic byproducts from the soil have degraded on the water environment and also the metals should have

oxy or oxyhydroxide forms which are easier to process and extract later. Samples were packed in the 3L glass jars and pH was adjusted to $\text{pH} < 2$ for conservation. The iron mine staff have provided the project team with the earlier data for the last 40 years, in the form of studies on quality of the ore. These data are the useful guiding documents for the optimization of the metal ion extraction process to be developed within the project.

Finally, this visit was finished with the discussion stressing out the importance of the remediation of the soil and also the water around the mining sites, not only in Bosnia and Herzegovina, but also all over the world. Since large financial and labour recourses are involved in the mining activities, maximal exploitation of the materials with minimum waste remaining is both economically and environmentally a goal for the future. The permanent permission for sampling was therefore granted to the project team for the whole duration of the project and the importance of the potential or the project idea in the, at least partial resolution for the application of the accumulated waste was recognized by this industrial subject.

ADDITIONAL VALUE TO THIS ACTIVITY: From the budget for local travel, the project team have realized also visits to the 3 factories, potential stakeholders of the projects realized by project team, and the best students from Chemistry Department were also involved in these activities.



Picture 2. Project team, together with the students from Chemistry department in the visit of the “RS silicon” factory in Mrkonjić Grad.

The project team have visited three stakeholders, industrial companies in need of the nanoporous materials in their technologies or in search of the resolution for the environmental threats their work might pose to the environment. The first visit was to the “RS Silicon” factory which has over 300 workers on 2 location in Bosnia and Herzegovina and is producing pure silicon metal. However, they produce a lot of the by-product, the microsilica in the quantities of few tons per day. This material is also a hybrid which deserves attention for the future research. It contains about 95% of SiO_2 , however, it contains also a traces of other metals and carbon shell around the particles. Due to this fact, this material represents an inverse material of what is the goal for the project, namely the material which is the metal from “inside” but carbon from “outside”. It should be interesting for the future comparative studies of adsorption of pharmaceuticals which are the subject of the study. Around 10kg of the waste microsilica sample was collected during the visit and conserved in the laboratory.

The second trip to stakeholders was to the “Tehnosint” company which is a successful producer of the lubricants for motor vehicles and pumps. This company have shown interest in the project results since they are aware of the scientific reports that activated carbons are important material for lubricant industry. Namely, activated carbon is used for rejuvenation or reclamation of the used lubricating oils.

The company will follow the progress of the project in hopes that the hybrid activated carbons produced through the project could one day also be tested for the removal of the toxic metal ions or carcinogen hydrocarbons from the used oils. The company is developing the line for recycle of the used motor and lubrication oils, the first one in Bosnia and Herzegovina. The project members have got guarantees for the access to the factory laboratory premises if needed for any kind of testing. The instrumentation in the laboratory is the state-of-the-art characterization equipment with highest safety standards and the laboratory is currently in the process of accreditation.



Picture 3. Project team with students during the visit to the “Tehnosint” company in Laktaši



The third study trip of the project team and department students to the stakeholders was to the „Destilacija“ company in Teslić city. This factory is over 130 years old and is very closely related to the project subject. Namely, the factory is performing the pyrolysis of the wood chips after the dry distillation of the wood.

The distillation gains products such as the natural acetic acid sold for food industry and many more. The pyrolysis of the wood in the subsequent processes results in the charcoal which is sold for the barbeque purposes. However, this is practically the half-product for the production of the activated carbon and the company is therefore showing interest in the project results. Hopefully, after the laboratory testing for the production of the activated carbon from Bosnian raw materials (wood and fruit stones) and their hybridization with the metal ions from the mining waste, publications by the project team should show the direction for the future development of the factory as well.

The project team has collected the samples of the half-pyrolyzed samples from the factory for the future work. The Raman spectroscopy of the samples have shown pronounced G-band in the material, indicating that the graphene phase in this material is more dominant. This means that material should have good mechanical properties and therefore potential for multiple regeneration after application in the filtration processes. The project team included this material as one to be used in the series for preparation of the hybrid activated carbon to be enriched with metal ions from the mining sludge, since the main material is exclusively Bosnian cellulose material as the project goal demands.



Picture 4. Project team and students with the engineers in “Destilacija” factory

A 2. Purify the sludge by acid digestion and separation of the iron ions in concentrated solution

Performed timely, the ionic solutions of the iron and manganese in high concentrations obtained, the detailed analysis of other metals performed at the sub-contracting national accredited laboratories. The results have shown that the mining waste indeed contains mostly iron, however, also a high level of the manganese concentrations too. They are followed by the silica and also by the traces of the lead and aluminium.



Picture 5. Separation of the iron from other metals of the mining waste extract

Separation was performed using the strong acid digestion, combination of the sulphuric and nitric acid. For this purpose the digestion apparatus (COD reactor) was purchased through the project. After acidic digestions, the oxidized sludge were than dissolved in boiling water and filtrated to remove the sand (SiO_2). In later stages, the Fe was separated from other

metals by the precipitation using ammonium chloride and ammonium hydroxide. This method was highly effective rendering the solution completely clear.

In later phases the manganese was also precipitated in the form of manganese sulphate which had very high crystallinity (XRDs for the paper which was published on this part of the study, performed by support institution, Shinshu University).



Picture 6. *PhD student from the support institution Shinshu University, Hironori SUGIYAMA working on the adsorption experiment*

In this part of the study, a young visitor was accepted from the project supporting institution, Shinshu University, Nagano, Japan. Hironori SUGIYAMA is the PhD student at this university, doing his PhD thesis also on carbon materials, mostly on carbon fibers which are also a widely studied filtration and adsorption material. His travel and living expenses were covered by Japanese resources, in particular “Global Leader Program for Fiber Renaissance”. He participated in all the project activities along his 5 months long stay at the University of Banja Luka. He was working on the digestion experiments, ionic separation experiments. He gave the important contribution by introducing the team to a simple methylene blue adsorption from solution method which, by means of Dubinin-

Radushkevich method gives a preliminary information on the specific surface of the obtained carbon materials. He will also perform the characterisation experiments in Nagano for the final phases of the project.

A 3. Characterization of the oxidized sludge and nanomaterials synthesized from sludge

Performed timely, the dry sludge was sent to the collaborating laboratory at Shinshu University, Nagano and analysis reports obtained (XRD, XRF techniques). The contents of the sludge are already described in the previous section.

A 4. Conduct the sampling of the cellulose waste from plums, cherries and peaches in Western Bosnia regions

Samples collected timely at the locations of the plum fruit farm, nuts production plant and at the wood chips production company. Samples were preserved in the refrigerator device bought from the project budget. The locations and the data on the harvest and quantities of generation of this form of waste were also collected.

A 5. Attend International summer schools on Nanosciences and Nanotechnologies (N&N)

Performed timely by team member Savka JANKOVIĆ.

ADDITIONALLY: Presentation of the part of the preliminary results on carbon materials treated with mining waste at the international conference held in parallel to the summer school.



Ms JANKOVIĆ attended a 12th International Summer Schools on N&N, OE & Nanomedicine held in Thessaloniki (Greece) from 30th June till 7th July 2018. This summer school was divided in three complementary schools that covered the significant areas in the N&N field: 1. Nanosciences & Nanotechnologies; 2. Organic electronic; 3. Nanomedicine. The lectures were reviewing the current trends and knowledge in the fields of NN in general (mainly in School 1) and in parallel focused in three main Application areas, the Organic Electronics (School 2), Nanomedicine (School 3). Also, it was talk about the laboratory facilities for developing and characterizing technics nanoscale materials.

In addition, at the same event, Ms. Janković also participated in the NN18-15th International Conference on N&N, where on 3th of July she orally presented a work named “*NaHCO₃ as a Modifier of SWCNTs’ Membrane Structure via Spherical Crystals Formation*”. This is one of the preliminary experiments in project where the project team have tested the strength of the hybrid inorganic/carbon materials on the commercial carbon materials before starting the central experiments of the project. As the part of this education activity, on July 4, Ms. Janković also visited Aristotel University of Thessaloniki, where she visited laboratories for organic, inorganic, analytical and physical chemistry. The follow-up workshop agreed on future collaborations with this University, which offered to help with sample characterizations for the project. Overall this activity gave the education to the team about the newest developments in carbon sciences necessary for the development of the further project activities.



Picture 7. Team member S. JANKOVIĆ with the hosts from Thessaloniki, Aristotle University, Greece

A 6. Preparation of the active carbon from the local waste

Samples prepared partially in the collaborating lab (before the arrival of the equipment) followed by preparation in UNIBL laboratory (in June 2019, after lengthy public procurement procedure and arrival of the cylindrical oven).

The conditions used variations of the temperatures and thermally programmed pyrolysis ranging in length from 30-180 minutes, also the tests were performed for application of the water and CO₂ gas as the agent for introduction of the nanopores. At the present water (steam) appears to be very effective agent, producing much for nanopore volume, and more experiments are on the way to confirm this.

A 7. Impregnation of the prepared active carbon with different concentration of the iron solution dry and thermally treat impregnated carbon

Experiments conducted timely. The solutions of iron ions of different concentrations were used in this experiment.

The higher concentrations have shown that metal ions are more likely to form larger particles on the outer surfaces of the activated carbon, while lower concentrations improve the dispersion and later attachment of the metal ions inside the nanopores.

A 8. Characterization of hybrid iron/carbon nanomaterials

Experiments conducted timely at the home institution of Banja Luka and at the support institution Shinshu University, Nagano, Japan.

The characterisations performed are: x-ray photoelectron spectroscopy, BET specific surface measurements and x-ray diffraction measurements.

BET method is showing very clearly that the metal ions if used in moderate to lower concentrations are indeed getting into the nanopores, and the data supports this by showing clear decrease in nanopores volume (data already published in the article within the project).

XPS method have given the data on the nature of liaison between the carbon surface and the metal ions used for preparations of the hybrid metal/carbon materials. It looks from this perspective that the metal ions choose the oxygenated sites on the surface of carbon and attach there during the preliminary adsorption, while this attachment is later strengthened by subsequent heat treatments. Most probably, the metal ions or nanoparticles forms along the carbon surface become partially encapsulated within the structure. This phenomenon is under investigation by the Shinshu University collaborators who are preparing the XPS-C-peak deconvulsion data in order to determine this. They are also attempting the delicate high-resolution transmission electron microscopy which is at the moment showing hard to perform on these granular material.

A 9. Acquainting with the state-of-the-art techniques in batch adsorption and techniques in following the degradation of organic pollutants

Study visit conducted timely by team members Savka JANKOVIĆ and Dragana MILISAVIĆ at the host institution of Eastern Finland University

Team members, Dragana MILISAVIĆ, and Savka JANKOVIĆ realized a one month visit (Oct-Nov 2019.) at Eastern Finland University in Kuopio, Finland. They have had an intensive training on the state-of-the-art techniques necessary for the project. This visit was realized through a partnership with Professor Amit Bhatnagar's project team which was the planned host institution from the very beginning of the project application. During the following weeks, Ms Milisavić studied the adsorption of pharmaceuticals (diclofenac, tetracycline and cephalexin) on natural minerals from Egypt for a month, while Ms Janković, investigated the adsorption of pharmaceuticals (diclofenac, tetracycline, cephalexin) on activated cellulose made from waste of the tobacco industry. At the end of each week, a weekly report was written to Professor A. Bhatnagar, on the basis of which the professor assigned new assignments at the beginning of each following week. In the third week of the visit team members started a new study of the adsorption of toxic metals on the composite made from minerals with active carbon and cellulose with active carbon. In the first phase of the experiment, they studied method of synthesis of these composites and then they continued with an adsorption study. During the last week of the visit, methods of characterization of these samples were mastered. Young researchers independently measured the chromium content of post-absorption samples using AAS.



As a result of this visit, future collaboration and joint publication was agreed. Two scientific papers have been published on the topics that young researchers from the Faculty of Natural Sciences and Mathematics worked on. In both papers, the authors thanked to Ms Milisavić and Ms Janković for their work in the acknowledgements of the paper.

Some of the tasks performed by S. Janković in Finland:

- pH experiments: adsorption of diclofenac on cellulose
- Measurements the concentration after adsorption with UV/VIS spectrophotometer
- Adsorption of 2.5 ppm diclofenac on cellulose- Kinetic study (m (adsorbent) = 0.002g)
- Experiments with different dosage of adsorbent
- Measurements of pH after adsorption
- Experiment with different concentrations of DCF (2.5, 5, 10 and 20 ppm)
- Preparing biochar and CNC biocomposite
- Adsorption of 20 ppm diclofenac on cellulose- Kinetic study (m (adsorbent) = 0.004g)
- pH study
- Preparing the solutions for salt impact experiment
- Preparing 50 and 20 ppm solution of DCF
- Preparing samples for salt impact experiment: Adsorption of DCF on cellulose
- Preparing samples for isotherms study for pure CNF
- Preparing samples for salt impact experiment (KCl, NaNO₃, MgSO₄): Adsorption of DCF on cellulose
- Adsorption of Co and Cd on Biochar + CNC composite
- Salt influence experiment (on DCF adsorption) by using carbonate
- Isotherms study for pure CNC (adsorption of DCF) Preparing the samples and measuring the absorbance after 2h shaking
- Algae – Soxhlet extraction

Some of the tasks performed by D. Milisavić in Finland:

- Preparing samples for pH experiment: adsorption of tetracycline on bentonite/biochar composite
- Preparing samples for lead (II) ion adsorption on clays, determination of pH pzc, shaking for 24 h on 200 rpm
- Preparing samples for pH experiment for tetracycline adsorption on red clay, shaking for 24 h on 200 rpm
- Washing bentonite after modification and preparing for drying over the night at 60 °C
- Preparing samples for pH experiment for tetracycline adsorption onto bentonite, shaking for 4 h on 200 rpm
- Preparing samples of acid activated clay for pHpzc experiment, shaking for 24 h on 200 rpm
- Preparing samples of K-DM clay for for pHpzc experiment, shaking for 24 h on 200 rpm
- Preparing samples for dosage experiment: tetracycline adsorption onto bentonite, shaking for 4 h on 200 rpm
- Determination of Cation Exchange Capacity for bentonite with Methylene Blue
- Preparing samples for dosage experiment: tetracycline adsorption onto bentonite, shaking for 4 h on 200 rpm

- Preparing samples for pH experiment: lead (II) ion adsorption onto bentonite, shaking for 24 h on 200 rpm
- Preparing samples for pH experiment: ciprofloxacin adsorption onto bentonite, shaking for 24 h on 200 rpm
- Preparing samples for pretest for acid and alkaline modified bentonite: adsorption of tetracycline and ciprofloxacin, shaking for 4 h on 200 rpm
- Preparing samples from day before for measuring the absorbance with UV/Vis spectrophotometer
- Preparing samples for kinetics experiment: Adsorption of tetracycline onto bentonite
- Preparing samples for kinetics experiment: Adsorption of ciprofloxacin onto bentonite
- Determination of Cation Exchange Capacity for bentonite, N-kaolinite and red clay with Methylene Blue
- Preparing samples for isotherms experiment: Adsorption of tetracycline onto bentonite
- Filtration and preparing samples of isotherms experiment for measuring the absorbance by UV/Vis spectrophotometer
- Determination of Cation Exchange Capacity for kaolinite with Methylene Blue
- Preparing samples for kinetics experiment: lead (II) ion adsorption onto bentonite, red clay, acid activated clay and natural clay, short time kinetics
- Preparing samples for kinetics experiment: lead (II) ion adsorption onto bentonite, red clay, acid activated clay and natural clay, long time kinetics
- Preparing samples for isotherm experiment: lead (II) ion adsorption onto natural clay and acid

A 10. Lecture at host institution on the innovative points in present project

Performed timely.

The team members shared with the colleagues from Finish team the complete project idea. They also gave the presentation on the rich sources of the mining waste in Bosnia and Herzegovina and the diversity of the cellulose waste in forestry industry, fruit processing industry and generated in the field of Bosnian thriving agricultural activities.

The presentation also gave an overview of the stakeholders in Bosnia who have shown interest in the project. The method for extraction of the metal ions from the mining sludge from Omarska mine have been shown and discussion was performed on the subject of the metal analysis and their separation.



Picture 8. Project team members with the team of the host institution Eastern Finland University



A 11. Give a lecture at home institution, sharing the experience from University of Eastern Finland with colleagues with discussion on results and perspectives of the project

Performed timely.

Team members who spent one month on exchange in Finland presented the report to the colleagues at the home institution University of Banja Luka. They have shared the experience gained at the host institution and discussed with colleagues about the new arrangements in the laboratory necessary for the equipment arriving through the project. The plan for the adsorption from solution and sample conservation laboratory arrangements were agreed. Also, some improvements in the laboratory lighting and holders for the atmospheric conditions were suggested in order to perform the experiments in the controlled manner for best reproduction of the results later.



Picture 9. D. MILISAVIĆ giving lecture at the home Institution University of Banja Luka, Chemistry Department about one month exchange at the Eastern Finland University

A 12. Presentation at the Congress on Green and Sustainable Chemistry (EuGSC) in York, UK.

Substituted.

Due to late arrival of the project budget, this conference was substituted by the NANOFis conference in Austria.

Team member Dr Maja Stanisavljević attend the 3rd International conference on integrated functional nano systems, which was held on November 22-24, 2017 in Graz, Austria. Conference is jointly organized by the Materials Center Leoben Forschung GmbH and Techkonnex – HighTech Promotion. For this conference, the team members prepared the presentation named “Novel Nanoporous Carbon/Iron Oxide Needle Catalyst for SO₂ Degradation” which was presented in the poster section. This work was performed in the first part of the study where different activated carbons were impregnated by the metal solutions (iron and manganese regenerated from the mining waste as planned through the project).

Since the project equipment public procurement procedure was not yet completed, the team opted to test the materials as adsorbents for the sulphur dioxide, instead of pharmaceuticals. This part of the experiment was co-financed by BlowUp project (EIT raw materials-funded, grant number 16320).

During the conference variety of nanomaterials applications have been presented, with special insight in application of nanomaterials for micro- and nanoelectronics to photonic devices. Valuable knowledge for the project was collected at the sessions where different characteristics of nanomaterials were discussed. A lot was learned about the advances that have been made to overcome some shortcomings of carbon nanomaterials towards their industrial application, some new nanomaterials applications as well as novel materials were presented and discussed.



Picture 10. Team member Dr Stanisavljević at the opening and poster sessions at the NANOFis conference in Gratz, Austria

ADDITIONAL value to the activity: the paper containing part of the experimental results on materials from the project was published in the peer-reviewed journal *Materials Today: Proceedings*, with appropriate acknowledgment to UNESCO/IUPAC/PhosAgro.

Reference to the paper:

Stanisavljević, M., Janković, S., Milisavić, D., Čađo, M., Kukrić, Z., Stević, D., ... & Atlagić, S. G. (2019). Novel Nanoporous Carbon/Iron Oxide Catalyst for SO₂ Degradation. *Materials Today: Proceedings*, 7, 920-929.

A 13. Perform series of batch adsorption/catalytic degradation of the diclofenac and tetracycline with carbon impregnated with four different concentrations of iron solutions.

Performed timely.

ADDITIONAL VALUE TO THE ACTIVITY: two largest pharmaceutical factories visited by team members, S. JANKOVIĆ, D. MILISAVIĆ and support institution Shinshu University visitor, H. SUGIYAMA.



Picture 11. Project team visiting the pharmaceutical factory "Blagoleks"

Team members Dragana Gajić, Savka Janković, and Hironori Sugiama visited in December 2018 the pharmaceutical factory „Blagoleks“ in Bijeljina. As part of this visit, young researchers first orally presented their work and the UNESCO project to members of the “Blagoleks” experts team. After that, together with the main pharmacist and other engineers, they visited the laboratories for the production of pharmaceuticals, quality control and the wastewater treatment plant at the disposal of this factory.

The factory management emphasized that the doors of this laboratory are open for analysis and project cooperation as well as for future graduation or master theses.



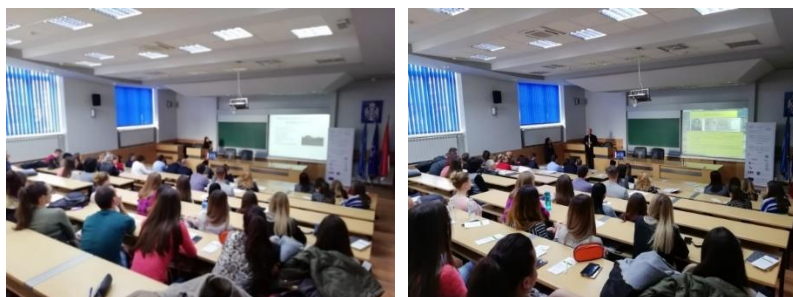
Picture 12. Team members visiting pharmaceutical factory "Bosnalijek", Sarajevo

The team members visited also the leading pharmaceutical factory in Bosnia and Herzegovina "Bosna Lijek" located in Sarajevo. The engineers and factory management informed them about the production process and the chemical laboratory for quality control of raw materials and finished

products. During this visit, the hosts particularly presented their wastewater treatment plant, where they expressed interest for the materials developed within the project. Namely, as they are also producers of the diclophenac and tetracycline, they are in constant search for optimal methods for adsorption and degradation of the traces of these products in their waste water. The company has also given valuable suggestions for the performance tests for the materials produced. In particular, they have confirmed that the project direction towards the intensive mixed adsorption studies rather than focusing on the individual adsorption studies is very valuable. In their example and also in most of the real sector, the waste waters are indeed most of the time a complex mixture of different contaminants.

A 15. Workshop for guests, experts for mining industry in Bosnia on results and perspectives of the project with open discussions about potential pilot plants configuration

Performed timely.



Picture 13. Workshop lectures at the Faculty of Natural Sciences and Mathematics

The workshop included a number of guests from the industry. Lecturers were Prof dr Tanya Tsoncheva from Bulgarian Academy of Sciences an expert in activated carbon preparation, Prof dr Toni Nikolić from Federal institute for geology in Sarajevo, Prof dr Suzana Gotovac Atlagić who specialized in nanocarbons during her 5 years stay in Japan

and also, the present project team, represented by D. Milisavić gave the report on the methods learned in Finland. Particularly important for the future directions of the project was the lecture by Prof Nikolić. Namely, he had given the lecture on the potential of the low-value coal which is widely present in Bosnia and Herzegovina.

Although this material has a low calorically value for the heating purposes, it is a valuable recourse for production of the activated carbon and should be as such studied, both as a classical activated carbon and as the hybrid materials as developed through the present project. **ADDITIONAL VALUE TO THE ACTIVITY:** national patent office representatives who were present during the workshop in the audience, suggested to write the patent and the text is in preparation. Their experts support is granted through the national funding and the budget for the patent is already planned within the present project.

A 16. Writing the paper for peer reviewed journal

Paper in preparation.

The paper will summarize the data on the prepared carbons, based on Bosnian nuts shells, wood chips, low value coal and the plum stones as the sources of the cellulose. The data for the characterization is already mostly obtained from the host institution in Finland and the support institution in Japan. All the samples were analysed as pristine (as-prepared) and also after the treatment with iron and manganese solution obtained exclusively from the mining waste. Later, adsorption of the pharmaceuticals on these materials and their kinetic of adsorption as well as the findings on the process of degradation of the organic molecules when they are adsorbed on the metallic nanoparticles generated, will be shown. The materials are clearly showing increased adsorption as well as the degradation potential for the pharmaceuticals studied. The project team aims also at testing the hybrid carbon/metal materials regeneration testing which are now feasible in the home institution after the equipment purchase through the project is completed. Namely, the ultimate goal of the project will be to confirm that the materials produced are indeed capable of performing multiple cycles of the adsorption/degradation of the pharmaceutical contaminants.

The paper is expected to be sent to the publisher in the autumn of 2019.



A 17. Presentation of the results at the renowned Junior EUROMAT congress

Performed timely by team member Ms Dragana MILISAVIĆ.

Ms Milisavić attended the Junior EUROMAT 2018 conference from July 8-12, 2018, where she had an oral presentation of the part of the project study „Enhanced nanoporous carbons as adsorbents for mixed phenolic acids“. This scientific report was based on the introductory experiments for the project studying the mixed adsorption of salicylic acid and benzoic acid on nanoporous carbons synthesized from olive and peach stone. The presentation have also shown future possibilities in Bosnia and Herzegovina for producing nanoporous carbon from waste materials, especially saw dust, based on data from UNPD-funded study.



Picture 14. Team member, Dragana MILISAVIĆ presentation at the Junior EUROMAT congress (Budapest, Hungary)

The presentation gave opportunity to discuss and connect with young colleagues from Germany, Poland, Hungary, South Korea, United Kingdom about possible solutions for the air, water and soil contaminations in the frame of Energy, Transportation and Environment session.

At this conference, Ms Milisavić also attended round table “Raw materials, clean and efficient energy”, where professors and scientist from Hungary and Belgium discussed with young scientists about new technologies and new green materials, which were

synthesized and used in the last decade as a source of energy, as well as new “no waste” technologies. Valuable connections for the progress of the project were made with colleagues from Croatian Department of Materials, from University of Zagreb, who offered the support for the project in characterization of carbon materials synthetized within the project.

Principal investigator:

Dr Maja STANISAVLJEVIĆ

Dean of the Faculty:



Prof dr Goran TRBIĆ