

Advances in Science, Technology & Innovation  
IEREK Interdisciplinary Series for Sustainable Development

Attila Çiner · Md Firoz Khan · Amjad Kallel ·  
Jesús Rodrigo-Comino · Mario Parise · Rahim Barzegar ·  
Zeynal Abiddin Ergüler · Nabil Khelifi · Imran Ali *Editors*

# Recent Research on Environmental Earth Sciences, Geomorphology, Soil Science, Paleoclimate, and Karst

Proceedings of the 1st MedGU, Istanbul 2021  
(Volume 4)

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# Advances in Science, Technology & Innovation

## IEREK Interdisciplinary Series for Sustainable Development

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**ASTI series has now been accepted for Scopus (September 2020). All content published in this series will start appearing on the Scopus site in early 2021.**

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# Recent Research on Environmental Earth Sciences, Geomorphology, Soil Science, Paleoclimate, and Karst

Proceedings of the 1st MedGU, Istanbul 2021  
(Volume 4)

*Editors*

Attila Çiner  
Eurasia Institute of Earth Sciences  
Istanbul Technical University  
Istanbul, Türkiye

Amjad Kallel  
Sfax National School of Engineering  
University of Sfax  
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(RIME)  
Université du Québec  
en Abitibi-Témiscamingue (UQAT)  
Amos, QC, Canada

Nabil Khelifi  
DAAD Alumni Researcher  
Heidelberg, Germany

ISSN 2522-8714                      ISSN 2522-8722 (electronic)  
Advances in Science, Technology & Innovation  
ISBN 978-3-031-42916-3              ISBN 978-3-031-42917-0 (eBook)  
IEREK Interdisciplinary Series for Sustainable Development  
<https://doi.org/10.1007/978-3-031-42917-0>

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The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

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## About MedGU



Steps toward the creation of a Mediterranean Geosciences Union (MedGU)

Mediterranean Geosciences Union (MedGU) aims to create a unique federation that brings together and represents the Mediterranean geoscience community specializing in the areas of Earth, planetary, and space sciences.

MedGU will be structured along the lines of American Geophysical Union (AGU) and European Geosciences Union (EGU).

The plan is to establish a large organization for the Mediterranean region that is more influential than any one local geoscience society with the objective of fostering fundamental geoscience research, as well as applied research that addresses key societal and environmental challenges.

MedGU's overarching vision is to contribute to the realization of a sustainable future for humanity and for the planet.

The creation of this union will give the Earth sciences more influence in policy-making and in the implementation of solutions to preserve the natural environment and to create more sustainable societies for the people living in the Mediterranean region. It is hoped that the union will also provide opportunities to Mediterranean geoscientists to undertake interdisciplinary collaborative research. MedGU plans to recognize the work of the most active geoscientists with a number of awards and medals.

Although MedGU has not yet been officially inaugurated, its first annual meeting is planned for November 2021 in Istanbul. This will provide a forum to achieve a consensus for the formation of this non-profit international union of geoscientists. Membership will be open to individuals who have a professional engagement with the Earth, planetary, and space sciences, and related studies, including students and retired seniors.

Nabil Khélifi and Attila Çiner have taken an ambitious approach to the launch of the first MedGU Annual Meeting 2021 and hope to develop it in the near future into the largest international geoscience event in the Mediterranean and the broader MENA region. Its mission is to support geoscientists based in this region by establishing a Global Geoscience Congress.

It is expected that hundreds of participants from all over the world will attend this first MedGU Annual Meeting 2021, making it one of the largest and most prominent geosciences events in the region. So far, over 1300 abstracts have been submitted from 95 countries. The meeting's sessions will cover a wide range of topics with more details available on the Conference Tracks.

This first 2021 Annual Meeting will have a "hybrid" format, with both in-person and virtual participation. Springer, its official partner, will publish the proceedings in a book series (indexed in Scopus) as well as a number of special issues in diverse scientific journals (for more details, see Publications). The official journal of MedGU is Mediterranean Geoscience Reviews (Springer).

## Conference Tracks

The scientific committee of the MedGU invites research papers on all cross-cutting themes of Earth sciences, with the main focus on the following 16 conference tracks:

- Track 1. Atmospheric Sciences, Meteorology, Climatology, Oceanography
- Track 2. Biogeochemistry, Geobiology, Geoecology, Geoagronomy
- Track 3. Earthquake Seismology and Geodesy
- Track 4. Environmental Earth Sciences
- Track 5. Applied and Theoretical Geophysics
- Track 6. Geo-Informatics and Remote Sensing
- Track 7. Geochemistry, Mineralogy, Petrology, Volcanology
- Track 8. Geological Engineering, Geotechnical Engineering
- Track 9. Geomorphology, Geography, Soil Science, Glaciology, Geoarcheology, Geoheritage
- Track 10. Hydrology, Hydrogeology, Hydrochemistry
- Track 11. Marine Geosciences, Historical Geology, Paleoceanography, Paleoclimatology
- Track 12. Numerical and Analytical Methods in Mining Sciences and Geomechanics
- Track 13. Petroleum and Energy Engineering, Petroleum Geochemistry
- Track 14. Sedimentology, Stratigraphy, Paleontology, Geochronology
- Track 15. Structural Geology, Tectonics and Geodynamics, Petroleum Geology
- Track 16. Caves and Karst, a special session on the occasion of International Year of Caves and Karst

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UMR 8591, Meudon, France

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## Preface

This proceedings volume is based on 57 papers accepted and presented during the 1st Mediterranean Geosciences Union (MedGU-21) Conference organized in Istanbul, Turkey, in 2021 under the auspices of Springer Nature. Although more than half of the contributions come from the Mediterranean region, many other countries around the globe also actively participated in developing this volume. In detail, almost half of this volume's papers (29) are related to the Environmental Earth Sciences. In the second part, a total of 19 articles contain works from Geomorphology, Soil Science, Landslides, Paleoclimate, Geoarcheology, and Geoheritage.

Last but not the least, the third part includes nine papers dealing with karst research. These were submitted to the special session on the occasion of the International Year of Caves and Karst (IYCK), declared for 2021 by the International Union of Speleology (UIS) under the auspices of UNESCO. Following the main goals of IYCK, the focus was on all spheres related to the fragile karst environment, especially regarding important issues such as the protection of caves and their natural resources and sustainability.

The book is relevant to all researchers and students on the topics mentioned above, presenting an updated view on field studies, laboratory analyses, and modeling in earth sciences.

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Md Firoz Khan  
Amjad Kallel  
Jesús Rodrigo-Comino  
Mario Parise  
Rahim Barzegar  
Zeynal Abiddin Ergüler  
Nabil Khelifi  
Imran Ali

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## About the Editors



**Attila Çiner** is a Sedimentology and Quaternary Geology Professor at the Eurasia Institute of Earth Sciences at Istanbul Technical University, Turkey. After graduating from the Middle East Technical University in Ankara (1985), he obtained his M.Sc. degree at the University of Toledo, USA (1988), and his Ph.D. at the University of Strasbourg, France (1992). He works on the tectono-sedimentary evolution of basins and Quaternary depositional systems such as moraines, fluvial terraces, alluvial fans, and deltas. He uses cosmogenic nuclides to date these deposits. He primarily focuses on the glacial deposits and landscapes and tries to understand paleoclimatic and paleoenvironmental changes since the Last Glacial Maximum. Lastly, he was part of the Turkish Antarctic Expedition. He spent two months working on the site recognition and decision of the future Turkish scientific research station to be implemented on the continent. He is Editor-in-Chief of *Mediterranean Geoscience Reviews* and Chief editor of *Arabian Journal of Geosciences*, both published by Springer. He has published more than 100 peer-reviewed articles and book chapters.



**Dr. Md Firoz Khan** is an Associate Professor at the Department of Environmental Science and Management, North South University, since 2022 and a Leader of the AEROSOL LAB (pollutAnts-hEalth inteRactiOn eStimatiOn Lab). Before that, he taught Environmental Science and Geoinformatics for eight years in multiple countries, including Malaysia and China. His fields of expertise include but are not limited to air pollution/causes and effects, atmospheric chemistry, environmental chemistry, air pollution modeling, environmental toxicology, etc. He received his education in Japan (Ph.D.), the UK (M.Sc.), and Bangladesh (B.Sc.). He is an author or co-author of >110 peer-reviewed research articles published in many top-tiering journals. He engages with >20 research grants as a PI or CoPI received from national and international funding bodies in environmental research. Dr. Firoz is a lead lecturer and developer of a micro-credential online course titled “Chemometrics in Air Pollution” under the Future Learn Website. He evaluates research grants from the SWISS National Science Foundation (SNSF) and the Qatar National Research Fund (QNRF). Under his supervision (main and co-supervision), around 30 research students have received undergrad, postgrad, and Ph.D. degrees in air

pollution-health interaction. With immense experience in air pollution research, Dr. Firoz plays a vital role as an Associate Editor in several journals, i.e., *Observation and Modeling of Air Pollution* (a special issue of Sustainability, MDPI, Impact Factor: 3.889); *Elementa: Science of the Anthropocene* (Impact Factor 6.053, California University Press); *Frontiers in Environmental Engineering—Air Pollution Management* and *Arabian Journal of Geosciences* (Springer, Impact Factor: 1.827); and also serves as an expert member to Atmospheric Environmental Remote Sensing Society (AERSS) (Working Group-8: Air Quality, Climate, and Health).



**Dr. Amjad Kallel** is currently an Associate Professor of Environmental Geology in the Sfax National School of Engineers at the University of Sfax, Tunisia. He holds a B.Eng. in Georesources and Environment (1998) from the University of Sfax (Tunisia) and an M.Sc. degree and a Ph.D. degree in Georesources and Environment (2004) from Hokkaido University (Japan). He joined Venture Business Laboratory (VBL) at Akita University, Japan (2005–2006), as a researcher focusing on refining and recycling technologies for the recovery of rare elements from natural and secondary sources. On his return to Tunisia, he worked at the University of Gabes from 2006 to 2011, where he contributed to the elaboration of teaching programs at the Higher Institute of Water Sciences and Technologies of Gabes. Since 2011, he has joined the Sfax National School of Engineers. There, he has also been involved in various research projects related to Environmental Geology and Environmental Geotechnics. Dr. Kallel has co-organized many prestigious workshops, seminars, and international conferences. In 2016, Dr. Kallel joined the *Arabian Journal of Geosciences* (Springer) and the *Euro-Mediterranean Journal for Environmental Integration* (Springer) as Chief Editor and Managing Editor, respectively.



**Jesús Rodrigo-Comino** a graduate in Geography, currently works as an Assistant Professor at the University of Granada and was included for the second time in the World's Top 2% Scientists ranking by Stanford University. He got a Master in Territorial Planning and Geographic Information Systems (2013) at the University of Málaga/Granada, whose final work was divided into three national publications and a monograph. During his predoc stage, he obtained three scholarships for doctoral studies: DAAD (German Academic Exchange Service), La Caixa Foundation, and FPU (Ministry of Education, Spain). During this period, he completed his first doctoral thesis in Geography between the University of Trier (Germany—2 years) and Malaga (2 years) in 2018: “Actual Geomorphological Processes in Sloping Vineyards. A Comparison Between Ruwer-Mosel Valley (Trier, Germany) and Montes de Málaga (Málaga, Spain)”. In 2023, he defended his second doctorate in engineering in Geomatics and Topography at the Polytechnic University of Valencia. His research career consists of four complete monographs (Nova, Springer, etc.) and some edited books (Elsevier, CRC, Nova),

>200 indexed publications in Scopus and WoS, leading international collaborations with research teams over the world. He is a regular reviewer in more than 150 indexed international journals, a member of two doctoral theses committees, and an evaluator of projects for the Ministries of Science of Chile, Peru, the United States, Serbia, Switzerland, Kazakhstan or Poland, and postgraduate scholarships for DAAD. He has organized several international scientific meetings and congresses (for example COST Actions, Biohydrology, and Fire in the Earth), sessions at international conferences (EGU, TerraEnvision, Conference of the Arabian Journal of Geosciences, etc.), oral presentations, and conference master classes (Germany, Bulgaria, Norway, Algeria, etc.). He is Editor-in-chief of the indexed journal (Scopus and ESCI; Q2) *Air Soil and Water Research* (SAGE) and *Euro-Mediterranean Journal for Environmental Integration* (Springer). In addition, he was Associate Editor at *Scientific Reports* (Nature) and *Hydrological Science Journal* (Taylor & Francis) and continues in the *Arabian Journal of Geosciences* (Springer), and *Journal of Mountain Science* (Springer). He has participated as a researcher in R+D+I projects on social issues related to housing or the census, or transfer and knowledge at a European level, such as the INTERREG Smart-Light HUB project (light pollution) or COST FIRElinks (fires). He has been invited to give lectures on agriculture, sustainable management, and erosion. He has supervised five final degree projects and three master's degrees. He has taught regulated and certified teaching at the Universities of Granada, Valencia, Málaga, León, Oviedo, Trier (in German), Quito (Ecuador), and La Habana (Cuba) on geopolitics, geomorphology, Geographic Information Systems, remote sensing, and statistical techniques. He managed some international (FIRElinks COST Action), national (BBVA Foundation), and regional projects and supervised two Ph.D. theses.



**Mario Parise** Graduated with honors in Geology at the Faculty of Sciences of the University Federico II, Naples, Italy. Since 1990, he has developed research mainly into the geological and geomorphological analysis of slope movements, namely with the identification of the areas susceptible to different types of slope movement (from debris flows, to deep-seated gravitational slope deformations, to general mass wasting processes) by means of stereoscopic interpretations of aerial photographs and field surveys. Particular focus is given to multi-temporal analysis, aimed at understanding the likely evolution of slopes, even in relationship with anthropogenic activities, and/or as a consequence of specific triggering events (rainfall, earthquakes, etc.). For several sites in southern Italy, he has outlined a framework of the influence of weathering in the predisposition of slope movements. He has also contributed to the analysis of rapid landslides (debris avalanches, rock avalanches) in different geological settings in Italy and abroad, and to studying the occurrence of debris flows and erosional processes in areas recently affected by wildfires. He has

studied various landslides in Italy and the USA, and within this research activity he has developed an expertise in the recognition and investigation of slope failures, production of thematic maps, and also collaborating in the interpretation of monitoring data and in slope stability analyses. In addition, since 2002 he is working in the field of karst research, focusing on the evaluation of the natural and anthropogenic hazards occurring in karst territories, with particular regard to sinkholes and to underground instability and failures. This research is carried out also thanks to the caving activity in which he is active since 1998. He is the author of over one hundred papers published on international journals and proceedings of international conferences. He has given several presentations in international symposium and workshops. He has acted as Guest Editor in 10 special issues for ISI international journals, and has published three books with the Geological Society of London. He is a Member of the Editorial Board of *Natural Hazards and Earth System Sciences*, *Journal of Mountain Sciences*, *Carbonates and Evaporites*, *Natural Hazards*, *Bulletin of Engineering Geology and the Environment*, *Opera Ipoega*, and *Journal of Cave and Karst Studies*.



**Dr. Rahim Barzegar** is a Postdoctoral Fellow in the Department of Bioresource Engineering at McGill University in Canada. Before joining McGill in 2019, he obtained a Ph.D. and M.Sc. in Hydrogeology and a B.Sc. in Geology from the University of Tabriz, Iran. He has worked as a postdoctoral researcher in joint projects at the University of Tabriz in Iran and Wilfrid Laurier University in Canada. His main research focuses on the exploration of new methods in machine learning- and deep learning-based hydrological modeling. His other research activities also revolve around time series analysis, water quality assessment, water resources management, and climate change impacts on water resources. Dr. Barzegar also acts as an Associate Editor for the *Arabian Journal of Geosciences* (Springer publication), *Earth Science Informatics Journal* (Springer publication), *Communications Earth and Environment* (Nature publication), and Topic Editor for *Water Journal* (MDPI).



**Prof. Dr. Zeynal Abiddin Ergüler** is a Full Professor at the Geological Engineering department at Kutahya Dumlupinar University (Turkey). Dr. Erguler holds a B.Sc. (1998), an M.Sc. (2001), and a Ph.D. degree (2007) in Geological Engineering from Hacettepe University (Turkey). His research interests mainly focus on rock mechanics, engineering geology, environmental geology, and soil mechanics. His current investigation is to understand and model the thermo-hydro-mechanical behavior of shale rocks in the area of shale gas production. In addition to performing many types of research and industry-funded projects, he has also taught and supervised undergraduate and graduate students. In 2017, Dr. Erguler joined the *Arabian Journal of Geosciences* (AJGS) as an Editor responsible for evaluating submissions in the fields of rock mechanics, engineering geology, environmental geology, and soil mechanics.



**Nabil Khelifi** undertook fellowships at the System for Analysis, Research and Training (START) in 2005 and the German Academic Exchange Service (DAAD), as part of my Ph.D. studies in Marine Geosciences at the University of Kiel in Germany (2006–2010). After my Ph.D., I received a research grant from the German Science Foundation (DFG) to conduct research projects at the GEOMAR Ocean Research Centre in Kiel on oceanography and climate reconstructions in the North Atlantic and the Mediterranean (2010–2013). My research findings have been presented at international conferences and published in esteemed journals. From 2009 to 2013, I co-organized with my Kiel colleagues two workshops on the Pliocene climate at the University of Bordeaux, France (2009), and the University of Bristol, UK (2013), funded by the European Science Foundation (ESF). In late 2013, I received the Swiss Government Excellence Scholarship to pursue my postdoctoral research career. In 2014, I joined Springer (now Springer Nature) in Heidelberg, Germany, as an Editor, and was promoted to Senior Editor in 2017 responsible for developing their publishing program in the Middle East and Africa, which consists of managing 20 journals and two book series. From 2015 to 2022, I was active in educational seminars for authors, reviewers, and editors to help improve publication output and quality. In 2015, I was also a visiting lecturer at King Saud University, KSA, and University of Sfax, Tunisia, where I gave lectures on publishing techniques. Recently, I launched two international conferences (more details at [www.emcei.net](http://www.emcei.net) and [www.medgu.org](http://www.medgu.org)) aiming at promoting two journals that I was managing at Springer. In 2016, I was awarded the Africa Green Future Leadership Award for my promotion of publications from Africa. In 2020, I received the Saudi Society for Geosciences Award.



**Prof. Imran Ali** is a world-recognized academician and researcher. He completed his Ph.D. at the Indian Institute of Technology Roorkee, Roorkee, India. Professor Ali is known globally due to his great contribution to pharmaceutical analysis by chromatography and capillary electrophoresis, the development of anticancer drugs, nanotechnology for water treatment, and water splitting for hydrogen green fuel generation. He has published more than 500 papers in reputed journals including papers in *Nature* and *Chemical Reviews* of more than 72 impact factors. He has also written six books published by Marcel Dekker, Inc., USA; Taylor & Francis, USA; John Wiley and Sons, USA; John Wiley and Sons, UK; Elsevier, The Netherlands; and Springer, Germany. His total citation is 35,500 with an h-index of 102 and an i10-index of 323. He is a member of various scientific societies globally. He is Editor-in-Chief of 02, Editor of 03, Associate Editor of 06 journals, and is on the editorial board of 40 journals.

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## Environmental Earth Sciences



# Removal of Pb(II), Cu(II), and Cd(II) from Aqueous Solution by Alginate-Immobilized Aquatic Weed *M. spicatum*

Jelena Milojković, Zorica Lopičić, Marija Mihajlović, Milan Kragović, Biljana Gligorijević, Tatjana Vojvodić, and Jelena Avdalović

## Abstract

Biosorption is evolving as a potential alternative to the existing conventional technologies for the removal and/or recovery of pollutants from aqueous solutions. The present work investigates the possible application of waste biomass *Myriophyllum spicatum* (Ms) in removing contaminants, evaluating equilibrium through isotherms of selected heavy metals: lead, copper, and cadmium. As a heavy metal biosorbent, Ms was immobilized in alginate beads (Ms: Alginate 2:1). Applied biosorbent, MsA, was characterized by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) and Fourier transform infrared spectroscopy (FT-IR). Experimental results were fitted (non-linear) by six isotherm models: Langmuir, Freundlich, Sips, Redlich and Peterson, Toth, and Temkin. For lead(II) ion removal, fitting follows the following sequence,  $F \approx R-P > S > To > L > Te$ , while for copper(II) and cadmium(II) ions are as follows:  $R-P > To \approx Te \approx L > S > F$  and  $R-P > L > To > S > F > Te$ , respectively. TOC analyses revealed that *M. spicatum* releases 35.04 mg/L of total organic content while immobilized sample, MsA, only 6.81 mg/L. Finally, this biosorbent was tested on

a sample of real wastewater from a coal-fired thermal power plant complex TPP Kostolac (operated by PE “Electric Power Industry of Serbia”). The results indicate that using immobilized aquatic weed *M. spicatum* as a biosorbent has a high potential for heavy metal wastewater treatment applications.

## Keywords

Biosorption · Heavy metals · Aquatic weed · Immobilization · Wastewater

## 1 Introduction

*Myriophyllum spicatum* L. is a submerged aquatic weed found in at least 57 countries. Therefore, this weed is native to Europe, Asia, and North Africa but is also a major aquatic invader across most of North America (Couch et al., 1985). This weed has been classified as a Category 1 weed due to its widespread negative effects on the environment around the world (Martin & Coetzee, 2014). *M. spicatum* fits the criteria for a prospective biosorbent because of its natural abundance, high availability, and non-toxic nature (Milojković et al., 2019). In our earlier investigations, we also showed good performance of *M. spicatum* immobilized in alginate beads (MsA) for the removal of Pb (Milojković et al., 2019), Cu (Milojković et al., 2019), and Cd (Milojković et al., 2016) ions from single-component aqueous solutions.

This study aims to continue previous research and investigate the possible application of alginate-immobilized aquatic weed *M. spicatum* in removing Pb, Cu, and Cd ions from multimetal aqueous solutions.

J. Milojković (✉) · Z. Lopičić · M. Mihajlović  
Institute for Technology of Nuclear and Other Mineral Raw  
Materials, 86 Franchet d'Esperey, Belgrade, Serbia  
e-mail: j.milojkovic@itnms.ac.rs

M. Kragović  
“Vinča” Institute of Nuclear Sciences, National Institute of the  
Republic of Serbia, University of Belgrade, 22-24 Mike Petrovića  
Alasa, 11351 Belgrade, Serbia

B. Gligorijević · T. Vojvodić  
PE “Electric Power Industry of Serbia”, Branch TE-KO Kostolac,  
Nikole Tesle 5-7, Kostolac, Serbia

J. Avdalović  
Institute of Chemistry, Technology and Metallurgy, Department of  
Chemistry, University of Belgrade, Studentski Trg 14-16, Belgrade,  
Serbia

## 2 Materials and Methods

*M. spicatum* used to prepare beads MsA originates from Sava Lake (Belgrade, Serbia). *M. spicatum* was immobilized in alginate beads (Ms: Alginate=2:1), and beads were made according to the method (Yan & Viraraghavan, 2001).

Scanning Electron Microscopy—Energy Dispersive X-Ray Spectroscopy (SEM–EDX) analysis was performed on MsA before and after the biosorption of heavy metals using JEOL JSM 6460 model. The release of organic carbon was determined by measuring the TOC by Analytik Jena, TOC/TN Analyzer (Multi N/C 2100S). In addition, infrared spectroscopy analysis (FT-IR) was performed on a Thermo Scientific Nicolet iS50 FT-IR spectrometer in transmission mode with 256 scans over a range 4000–400  $\text{cm}^{-1}$ .

The adsorption of the Pb(II), Cu(II), and Cd(II) was studied at pH 5.0 in the concentration range 0.2–6 mmol/L (for each heavy metal) as batch biosorption tests with two g/L MsA. After 24 h, heavy metal concentrations were determined on an atomic absorption spectrometer Perking Elmer Analyst 300. In addition, Langmuir, Freundlich, Sips, Redlich and Peterson, Toth, and Temkin adsorption isotherms were used to fit experimental results. Evaluation of isotherm was made using OriginPro 2021 software.

To determine the effectiveness of the MsA in real wastewater samples, this biosorbent was tested on wastewater samples from the coal-fired thermal power plant complex-TPP Kostolac (PE “Electric Power Industry of Serbia”, Branch TE-KO Kostolac).

## 3 Results and Discussion

### 3.1 MsA Characterization

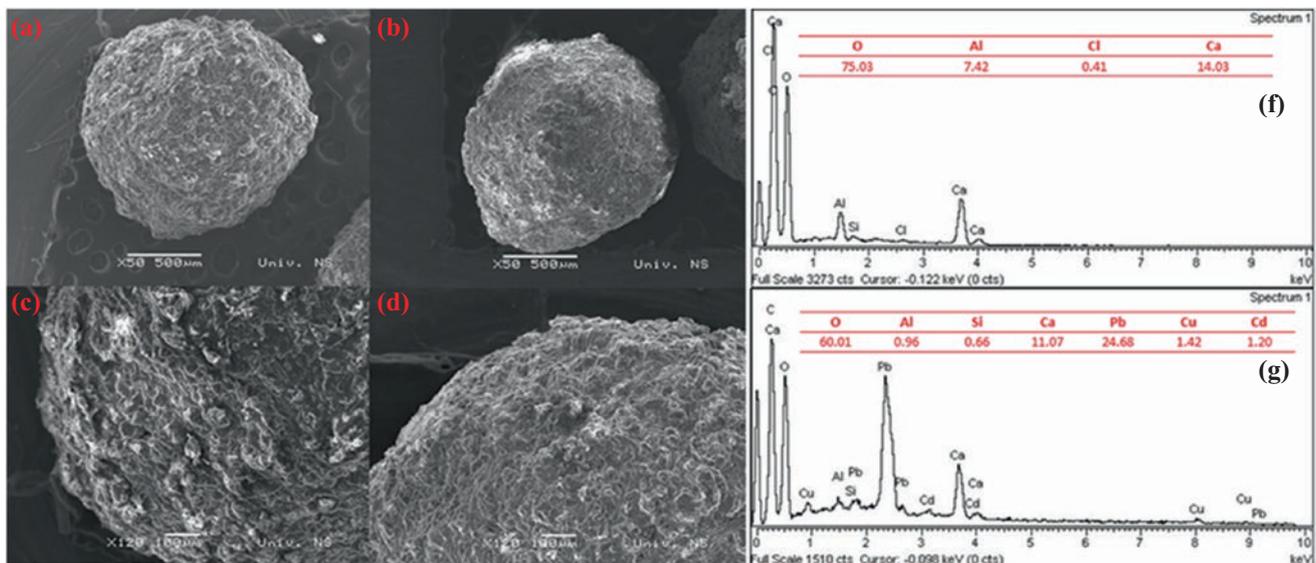
The presence of calcium in studied samples could explain the white areas visible on micrographs (Dibdiakova et al., 2015). Granule MsA is ovoid and spherical with rough, uneven edges (Fig. 1a, b). Different porosity is visibly stratified. Macro pores are made up of complex layers, and tiny balls are bonded to the surface of MsA. After biosorption of heavy metals, porosity exists (Fig. 1b) but is not as plain as in granules. EDX confirmed the infiltration of examined heavy metals. After sorption, reduced peaks of Ca, as well as new peaks of Pb(II) Cu(II), and Cd(II), are observed (Fig. 1g) compared to the starting MsA material (Fig. 1f).

TOC analysis showed that MsA releases only 6.81 mg/L of total organic content.

FT-IR showed that carbonyl, carboxyl, and hydroxyl groups are likely involved in the biosorption of detected heavy metals by MsA. Identified chemically active groups are components of polysaccharides, cellulose, hemicellulose, lignin, and proteins, which can be found in aquatic weed *M. spicatum* (Dibdiakova et al., 2015).

### 3.2 Heavy Metal Adsorption Study

During the biosorption process, the highest removal was obtained for lead ions with a maximum capacity of 0.530 mmol/g, while for copper 0.255 mmol/g, and the



**Fig. 1** SEM micrographs of MsA: before biosorption 50× **a** and **c** 120× magnification; after biosorption 50× **b** and **d** 120× magnification; **f** EDX before biosorption and **g** EDX after biosorption

**Table 1** Parameters of isotherms obtained for heavy metal ion removal by MsA

Isotherm	Parameters	Pb(II)	Cu(II)	Cd(II)
Langmuir (L)	$q_m$ (mmol/g)	0.479	0.251	0.130
	$K_T$ (L/mg)	32.166	21.739	121.559
	$R^2$	0.89641	<b>0.97392</b>	<b>0.86253</b>
Freundlich (F)	$K_f$	0.618	0.268	0.134
	$n$	3.337	2.354	8.308
	$R^2$	<b>0.97939</b>	0.90042	0.52145
Sips (S)	$q_m$	5.470	0.666	0.078
	$K_S$ (L/g)	0.144	0.681	3.909
	$n_S$	0.368	0.426	0.332
	$R^2$	0.96457	0.94488	0.79875
Redlich and Peterson (R-P)	$k_{RP}$ (L/g)	105.235	7.512	10.825
	$a_{RP}$ (L/mg)	174.659	29.165	87.716
	$b_{RP}$	0.736	0.918	1.081
	$q_m$ (mmol/g)	0.602	0.258	0.123
	$R^2$	<b>0.97790</b>	<b>0.98053</b>	<b>0.88843</b>
Toth (To)	$q_m$ (mmol/g)	1.620	0.278	0.127
	$K_T$ (mg/L) <sup>Th</sup>	0.234	0.087	8.125
	$T_h$	0.208	0.697	1.674
	$R^2$	0.95469	<b>0.97661</b>	0.85988
Temkin (Te)	$b_T$ (J/mol)	89,265.475	57,675.715	477,630.489
	$A_T$ (L/mg)	921,277.849	405.437	6.386
	$R^2$	0.56652	<b>0.97495</b>	0.43264

lowest for cadmium, 0.144 mmol/g. For lower initial heavy metal concentrations (2.5 mM), the removal efficiency was 90–100%, while for the highest concentrations (6 mM), MsA adsorbed 72% of lead, 39% of copper, and 14% of cadmium.

To get more information about the removal mechanism, Langmuir, Freundlich, Sips, Redlich and Peterson, and Toth and Temkin models were used to fit experimental results, and characteristic parameters are given in Table 1.

The affinity of MsA for binding heavy metal ions changes in the following order Pb>Cu>Cd. It is common for all three heavy metals that Redlich and Peterson isotherm is one of the best-describing models for their removal from solutions. According to this model, the maximal adsorption capacities of the MsA for lead, copper, and cadmium ions were 0.602, 0.258, and 0.123 mmol/g, respectively, which is in good agreement with ex12%). Lead ions removal was best described by Redlich and Peterson and Freundlich, while copper and cadmium ions removal were best described by Redlich and Peterson and Langmuir model. This suggests that for active centers in internal channels and cavities of MsA materials that are more difficult to access, there was direct competition between these heavy metals. Due to the higher affinity of the biosorbent for lead, copper and cadmium ions were displaced from these hard-to-reach places, so they were mainly bound only to surface-active centers. In contrast, lead ions were bound to the surface and in larger quantities to harder-to-reach centers.

The advantages of immobilization of *M. spicatum* were proven through TOC analysis because it was shown that immobilized biomass releases (6.81 mg/L) 5 times less organic matter compared to the biomass of this water weed (35.04 mg/L) during the treatment of water with the tested heavy metals.

MsA beads showed an excellent percentage of heavy metal removal from an actual sample of wastewater (TPP Kostolac). Chromium was removed in the highest percentage 75%, copper and zinc were released in the same amount 50%, Cd 30.8%, and then other heavy metals: Ni (20%), Pb (7.14%), Fe (5.12%), and Mn (4.45%).

## 4 Conclusions

Subsequent conversion of plant biomasses into animal feed, biochar, adsorbent, fertilizer, and bioenergy production materials may support a circular economy approach (Kurniawan et al., 2021). It is demonstrated that this water weed can be applied sustainably as alginate granules because it is easy to cut and collect, with no need for additional energy for drying, solving some potential ecological problems and low cost (Milojković et al., 2018).

The application of aquatic weed *M. spicatum* may support a circular economy approach because it is something that would be discarded as waste, and that would have to be

removed, disposed on landfills, and/or burnt; by its application described in this study, it is re-valued as biosorbent for Pb(II), Cu(II), and Cd(II) removal.

**Acknowledgements** These results are part of the projects supported by the Ministry of Education, Science and Technological Development (contract number 451-03-9/2021-14/200023) and Innovation Fund (project PoC5099) of the Republic of Serbia. Jelena Milojković is grateful to the public company “Ada Ciganlija” (Belgrade, Serbia) for providing samples of the aquatic weed *M. spicatum*. In addition, the authors are grateful to TE-KO Kostolac (TPP Kostolac) for making and enabling research on real wastewater samples.

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