Workshop on Methods of Water Pollution Control

Book of Abstracts

CLEANWATER

3–4 December, 2024
Košice, Slovakia

Workshop topics:

- **Removal of heavy metals, metalloids, radionuclides and persistent organic pollutants from water**
- **Determination of toxic components by analytical techniques**
- **Degradation of toxic organic substances**
- **Novel sorbents, nanosorbents, enterosorbents & activated carbons**
- **Advanced oxidation processes**
- **Non-thermal plasma technologies**
- **Photochemical oxidation**
- **Electrochemical oxidation**

Venue: Research centre PROMATECH, Slovak Academy of Sciences, Kosice, Slovakia

Chair: Ing. Lucia Ivaničová, PhD.

Editors: Ing. Slavomír Hredzák, PhD.,
MVDr. Daniel Kupka, PhD.

Reviewers: All abstracts went through an anonymous review process.

ISBN 978-80-89883-17-2

CLEANWATER

Scientific and Organizing Committee:

Prof. Joaquin Silvestre-Albero, PhD.

Ing. Lucia Ivaničová, PhD.

Ing. Katarína Hreus, PhD.

MVDr. Daniel Kupka, PhD.

Mgr. Olha Semeshko, PhD., DrSc.

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Ing. Dominika Marcin Behunová, PhD.

Ing. Peter Sekula, PhD.

The workshop is organized within the Maria Skłodowska-Curie Actions: Staff Exchanges Grant Agreement 101131382 “Multifunctional sustainable adsorbents for water treatment assisted with plasma technologies and for health protection from xenobiotics” (CLEANWATER).

Welcome Remark

Dear Colleagues, Friends and Guests,

We are pleased to welcome all participants to the workshop on the topic "Methods of Water Pollution Control." This event is taking place on December 3-4, 2024, at the Institute of Geotechnics of the Slovak Academy of Sciences in Košice and is available in a hybrid (online and offline) format.

This workshop is conducted as a part of the CLEANWATER project, which aims to develop versatile sorbents by combining safe and effective materials such as activated carbons, biochars, and natural polymers. These sorbents are designed to remove multiple contaminants from drinking water in a single step, potentially using cold plasma technology to further break down harmful substances. This approach promises to significantly enhance water purification efficiency by integrating two processes to remove multiple types of contaminants in a single step. Additionally, the project investigates adapting these sorbents to be biocompatible, allowing them to be used as dietary supplements to help eliminate toxins from the human body.

The workshop features oral presentations, short communications, and discussions focused on diverse methods of controlling water pollution. Topics include scientific advancements in porous polymeric sorbents, catalytic materials, organometallic composites, plasma treatments, and various applications in environmental protection. We hope that this event brings together experts, researchers, and participants from various fields, fostering meaningful discussions and collaborations to address pressing water pollution issues.

We are delighted to have you here and wish everyone a productive and enriching experience as a part of the proceedings of the CLEANWATER project.

Sincerely,

IGT CleanWater Team

Progress in the synthesis and characterisation of heteroatom doped carbon xerogels

Kata Lipták[1,2], Anna Bulátkó[1], Krisztina László[1]*
[1]Department of Physical Chemistry and Materials Science, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Műegyetem rkp. 3., Budapest, 1111, Hungary
[2]Institute of Materials and Environmental Chemistry, HUN-REN Research Centre for Natural Sciences, Magyar Tudósok körútja 2, H-1117 Budapest, Hungary
**Corresponding Author: laszlo.krisztina@vbk.bme.hu*

Resorcinol-formaldehyde polymer based carbon gels represent a versatile group of carbon materials for various green applications including electrode materials, gas storage or water treatment. The advantage of their sol-gel synthesis method is that both the morphology and the chemistry of such materials can be tuned in the various stages of the manufacturing process.

Using a co-monomer already in the gelation period allows the introduction of heteroatoms. With the addition of urea or thiourea N single and N, S double doped carbon xerogel series were synthesized in aqueous medium [1, 2]. The morphology of the carbons was characterized by scanning electron microscopy and low temperature nitrogen adsorption. The chemical features were studied by elemental analysis, XPS and TG/MS.

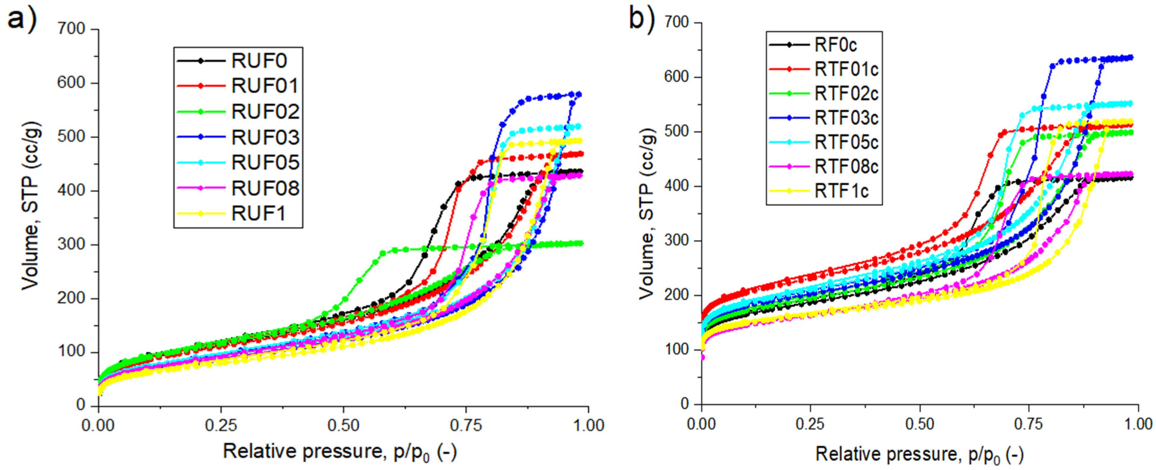


Fig. 1. Low temperature nitrogen adsorption isotherms of the urea (a) and thiourea (b) doped carbon xerogels.

N_2 adsorption-desorption measurements showed that carbon xerogels with high specific surface area and well-developed micro- and mesoporosity were produced (Figure 1). As an effect of the additional N or N and S, the S_{BET} slightly decreased with increasing degree of doping. Studies on the chemical composition revealed a rising tendency in the N-content through both series. SEM/EDXS and TG/MS but not XPS confirmed the presence of sulfur.

Water adsorption isotherms corroborated the enhanced hydrophilicity of the doped samples. Electrical conductivity tests revealed a link between the specific conductivity and pore volume of the samples. This relationship seemed to be more significant as the degree of doping.

Keywords: *carbon xerogel, heteroatom, N-doping, N, S-dual doping*

References

[1] Tran Hoang Thanh Truc: Synthesis and characterization of resorcinol-urea-formaldehyde carbon xerogels. MSc thesis, 2024 Budapest.
[2] K. Lipták, Zs. Czégény, M. Mohai, P. Németh, Á. Szegedi, T. H. T. Truc, A. Tompos, K. László: N-doped and N, S-dual doped resorcinol-formaldehyde carbon xerogels for fuel cell application. 11th Torunian Carbon Symposium, Torun, Poland, 15-18 September 2024.

Acknowledgments: *This work is part of the HORIZON-MSCA-2022-SE-01-01 project CLEANWATER (#101131382), as well as the TKP-6-6/PALY-2021 and RRF-2.3.1-21-2022-00009 projects. Project no. TKP-6-6/PALY-2021 has been implemented with the support provided by the Ministry of Culture and Innovation of Hungary from the National Research, Development and Innovation Fund, financed under the TKP2021-NVA funding scheme.*

Advanced remediation technology for decontamination of mine effluents followed by metallic critical raw materials recovery

M. Vaclavikova*, K. Hreus, L. Ivanicova, S. Dolinska, J. Hroncova, D. Kupka
Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, Kosice, 04001, Slovakia
**Corresponding Author: vaclavik@saske.sk*

The old dumps, tailings ponds, and mine effluents from abandoned mine sites can have a significant negative impact on the environment and surrounding local communities. Conversely, if managed effectively, they present significant opportunities, including those contributing to the circular economy, minimising environmental impacts, and creating additional value from waste as potential secondary resources of critical raw materials (CRM). The complex solution for the cleanup of the environmental burdens is in the integrated approach that includes removal of toxic metals, and recovery of metallic CRM, involving combination of advanced biotechnological and chemical techniques.

Former metal mining activities in the Spiš-Gemer Ore Mountains region in Slovakia have left a legacy of numerous old, closed (poly)metallic mines after the mining industry started to decline in the 1990s. The abandoned mine sites are represented by flooded mine workings, waste-rock piles, tailing impoundments, waste dumps with much seepage, leachates, and mine drainage effluents. The most important source of Fe-ore in the Spiš-Gemer Ore Mountains was the Nižná Slaná mine deposit, consisting of metasomatic siderite with elevated Mn content and undesirable impurities of As, S, Pb and Zn in the form of oxides, sulphides, sulphates and sulphosalts. In February 2022, asudden major outbreak of mine waters from the abandoned flooded mine in Nižná Slaná caused an ecological disaster on the Slaná River. High-concentrated mine-impacted effluents transported huge amounts of metals and metalloids directly to the river stream – effluent of Mg-sulphate type with a high dissolved Fe concentration and high total mineralization of 53 g/L. The high Fe content resulted in a significant red coloration of the river visible several tens of km downstream and contamination even crossed the borders to Hungary. The permissible limits for pollution of surface water in the Slaná River have been exceeded heavily and adversely affected the living quality of the river [1, 2].

The complex treatment technology for the cleanup of Nižná Slaná mine effluents with parallel recovery of metallic CRM was designed. It combines co-precipitation and sorption steps, followed by a purification and recovery system based on membrane, resin and composite adsorbents to recover high-value constituents (Ni, Co, Mn, Mg) in a high-quality form and purify water from other toxic elements (As). The proposed innovative methodology of the sequential treatment chains aims to meet the ‘green technology’ principle by minimising the use of chemicals, which is opposite to commonly applied (waste)water treatment technologies.

Keywords: *mine impacted water, water treatment, metallic CRM recovery*

References

[1] J. Zeman, D. Kupka, Z. Bártová, L. Hagarová: Chemism of mine effluent from the Gabriela Shaft in Nizna Slana and proposal for its treatment, Proceedings of Geochémia (2022) 118.

[2] D. Kupka, Z. Bártová, L. Hagarová, J. Hroncová, E. Mačingová, M. Stahorský, M. Bačik, P. Sekula: Ecological disaster on the Slaná River – Geochemistry of mine waters and the remediation procedures, Proceedings of Situation in Ecologically Loaded Regions of Slovakia and Central Europe (2022) 4.

Acknowledgments: *Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V03-00083.*

Pristine and Schiff base-surface-modified MIL-101(Fe)-NH_2 for water remediation: Kinetic, thermodynamic and thermoporometry approach

Ľ. Zauška[1], T. Zelenka[2], G. Zelenková[2] and M. Almáši[1]*
[1]*Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Safarik University, Moyzesova 11, Kosice, 04001, Slovak Republic (lubos.zauska@student.upjs.sk)*
[2]*Department of Chemistry, Faculty of Science, University of Ostrava, 30. dubna 22, Ostrava, 70200, Czech Republic (tomas.zelenka@osu.cz; gabriela.zelenkova@osu.cz)*
**Corresponding Author: miroslav.almasi@upjs.sk*

Cobalt(II) ions and Congo red dye are significant water pollutants with adverse environmental and health effects. Co(II) cation, a heavy metal, is toxic to aquatic life and humans when present in excess, while Congo red, a synthetic azo dye, is carcinogenic and resistant to degradation. Effective removal of these contaminants is essential for maintaining water quality. Porous materials, such as metal-organic frameworks, activated carbon, and zeolites, have gained attention due to their high surface area, tunable pore sizes, and adsorption capabilities. These materials can efficiently adsorb the mentioned pollutants, offering sustainable solutions for water treatment and pollution mitigation [1].

This study investigates the adsorption kinetics Co(II) ions and Congo red using surface-modified MIL-101(Fe)-NH_2 [2]. The material's large surface area and dual pore structure enhance adsorption performance, making it suitable for environmental applications. The MIL-101(Fe)-NH_2 material was synthesized and further modified with 2-pyridinecarboxaldehyde to create MIL-101(Fe)-Pyr with the aim of enhancing the adsorption properties (see Fig. 1). Characterization techniques, including FTIR, TG/DTA, ss-NMR, nitrogen adsorption/desorption measurements, thermoporometry [3] and PXRD, confirmed the structural integrity and functionalization of the materials. Kinetic studies revealed that MIL-101(Fe)-Pyr demonstrated superior adsorption capacity and faster kinetics for Co(II) ions compared to pristine MIL-101(Fe)-NH_2. The adsorption mechanisms were analyzed using pseudo-first-order, pseudo-second-order, and Elovich models. The pseudo-second-order model provided the best fit for both Co(II) and Congo red adsorption. Boyd's diffusion model indicated that external diffusion is a significant rate-controlling step. The adsorption isotherms were fitted with the Freundlich and Langmuir models, and the thermodynamics of the adsorption processes were also studied. The adsorption mechanism of the selected pollutants was proposed, and the stability and reusability of the materials were investigated. The study concludes that surface modifications enhance the material's adsorption properties, making MIL-101(Fe)-Pyr a promising adsorbent for removing pollutants from aqueous environments.

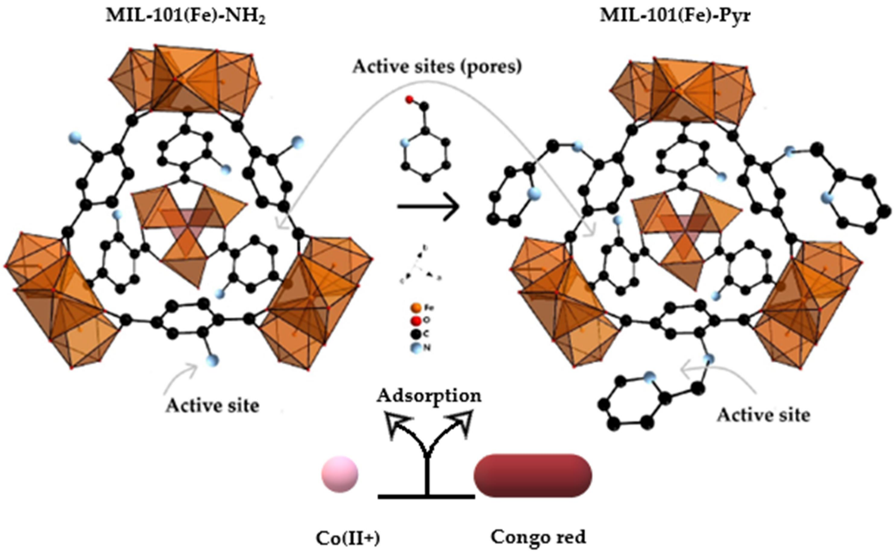


Fig. 1. Supertetrahedral cage in MIL-101(Fe)-NH$_2$ showing the post-synthetic modification process with active adsorption sites and pollutants used for water remediation.

Keywords: *metal-organic frameworks, MIL-101(Fe)-NH$_2$, heavy metal ions, azo dyes, kinetics, thermodynamics, thermoporometry*

References

[1] Y. Song, J. Phipps, C. Zhu, S. Ma, Angewandte Chemie, 135 (2023) e202216724.

[2] Ľ. Zauška, P. Pillárová, E. Kinnertová, J. Bednarčík, V. Hornebecq, M. Almáši, Microporous and Mesoporous Materials, (2025) under review.

[3] G. Zelenková, T. Zelenka, M. Almáši, Journal of Thermal Analysis and Calorimetry, (2024) in press.

Acknowledgments: *This work was supported by APVV project no. SK-CZ-RD-21-0068 and LUASK22049 (INTER-EXCELLENCE II, MŠMT).*

Microwave-assisted preparation of activated carbons from lignosulfonates and their use in the preconcentration of pesticides from water by the SPE method

Przemysław Pączkowski* and Barbara Gawdzik
Department of Polymer Chemistry, Institute of Chemical Sciences, Faculty of Chemistry,
Maria Curie-Skłodowska University, Gliniana 33, Lublin, 20-614, Poland
**Corresponding Author: przemyslaw.paczkowski@umcs.pl*

Pesticides are an important class of environmental pollutants [1]. These compounds often detected in plant foods, including fruits and vegetables, soil and in waste water are introduced into the environment by various agricultural treatments. Commonly used pesticides include chlorpropham, chlorsulfuron, and methyl thiophanate.

In this paper four carbon sorbents derived from commercially available lignosulfonate are presented. These materials were obtained by carbonization and activation under microwave influence. This process was conducted with the presence of phosphoric acid as an activator [2].

Depending on the irradiation time (from 2 to 10 min), carbon sorbents were obtained with significantly different porous structure and different chemical structure. Despite the increasing share of micropores in the structure, they can be classified as mesoporous carbons. As the carbonization time increased, graphitization progressed but a large number of heteroatoms still remained in the structure. The carbon sorbents obtained in this way were tested for their application in pesticides preconcentration from water using the SPE method.

For the sorbent obtained by 2 min irradiation in microwave reactor recoveries for 100 mL preconcentrated chlorpropham and methyl tiophanate reach 100 % (Fig. 1). Recovery for chlorosulfuron 84% and decreased rapidly. On carbon derived from lignosufonate irradiated 3 min relationships between sample volume and recovery have similar courses but recovery of none of the studied compounds reach 100 %. For the sorbent obtained during 5 min carbonization in microwave reactor, the recoveries of the studied pesticides decrease. For 100 mL, they slightly exceed 70%. The change in the course of the curve for chlorpropham, for which the recovery is the highest in the range of 200-400 mL, is worth noting. Father changes in the nature of interactions between the tested compounds and the sorbent surface can be observed by analyzing the course of the dependence of recovery on the sample volume for the sorbent obtained during 10 min of irradiation in a microwave reactor. In this case, the recoveries of chlorpropham are still the highest, compared to chlorsulfuron and methyl thiophanate, which means that this compound has the greatest affinity for the sorbent. The weakest interactions with the sorbent surface indicates methyl tiophanate.

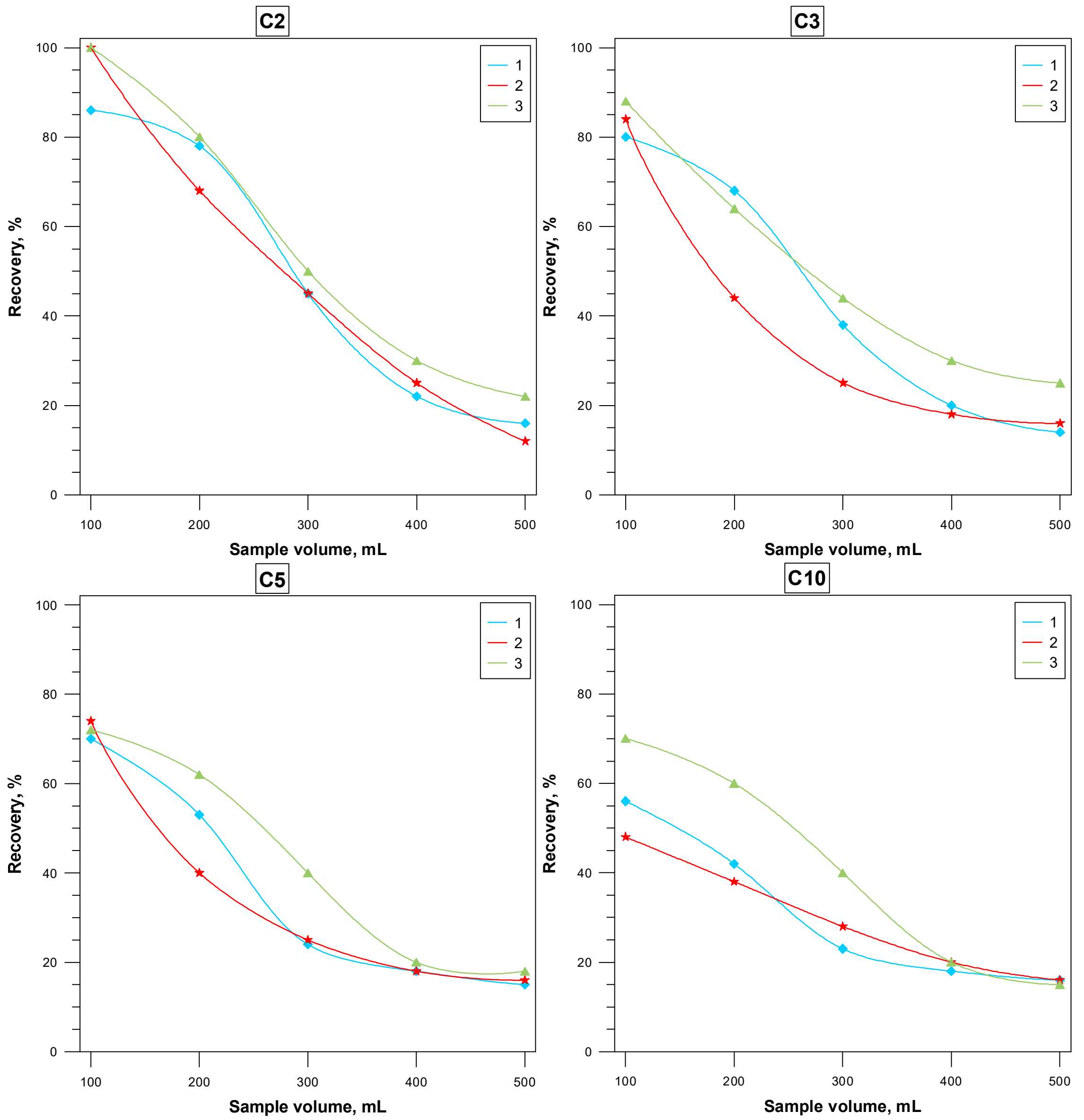


Fig. 1. Relationship between recoveries and sample volumes. 1 - chlorpropham, 2 - chlorsulfuron, 3 - methyl thiophanate.

Keywords: *solid-phase extraction, pesticides, carbon sorbents, environmental analysis*

References

[1] Y. Syrgabek, M. Alimzhanova, Foods, 11 (2022) 1623.
[2] A.M. Puziy, O.I. Poddubnaya, B. Gawdzik, J.M.D. Tascon, Carbon, 157 (2020) 796.

Acknowledgments: *This work has been supported by Horizon-Europe project 101131382 CLEANWATER.*

Assessment of the efficiency of slow filtration

Ulan Zhantikeyev, Shynggyskhan Sultakhan, Seitkhan Azat*
Satbayev University, Satbyaev 22, Almaty, 050013, Kazakhstan
**Corresponding Author: s.azat@satbayev.university*

Providing safe drinking water in developing countries is a pressing global issue and a priority within the UN Sustainable Development Goals. One of the most effective and affordable ways to address this need is by promoting slow sand filtration (SSF) [1]. This review highlights the capability of SSFs to deliver safe drinking water to rural communities lacking centralized water treatment.

A key advantage of SSFs for less-developed regions lies in their role as biological filters. In areas where surface and shallow groundwater sources are often contaminated by domestic wastewater, SSFs are particularly beneficial. They reduce microbial contamination—like viruses, bacteria, and parasites—that are common in polluted waters around urban and settlement areas. The warm climates and nutrient availability typical in many developing regions support rapid microbial growth, which, in turn, enhances the natural predation and efficiency of SSFs in removing pathogens [2].

However, certain factors can hinder SSF performance, such as low water temperatures, inconsistent flow rates, reduced sand depth, immature filters, and modifications to filter media [3]. To optimize SSF use in developing countries, further research is necessary to address these challenges and improve microbial removal under varying environmental conditions.

Keywords: *slow sand filtration, water treatment, microbial contaminants*

References

[1] K. Abdiyev et al., Water (Switzerland), 15 (2023) 2007.
[2] A. A. Melloul, K. Flata, S. El Fadeli, A. El Abbassi, A. Pineau, and Y. Barkouch, Desalination Water Treat, 315 (2023)280.
[3] S. Verma, A. Daverey, and A. Sharma, Environmental Technology Reviews, 6 (2017) 47.

Acknowledgments: *Marie Skłodowska-Curie Actions Staff Exchanges project 101131382 "Multifunctional sustainable adsorbents for water treatment assisted with plasma technologies and for health protection from xenobiotics" – CLEANWATER funded by the European Union under Horizon-Europe Programme and Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP23489574).*

Scientific basis for plasma-chemical treatment of low and intermediate activity radioactive waters

Yu.L. Zabulonov*, S.G. Guzii, O.V. Pugach, A.I. Voznyshchyk, D.G. Tutskyi
State Institution "The Institute of Environmental Geochemistry" of National Academy of Sciences of Ukraine, Akademika Palladina Ave 34A, Kyiv, 02000, Ukraine
**Corresponding Author: 1952zyl@gmail.com*

For the first time worldwide, we have established the scientific foundation for a unique and innovative plasma-chemical technology, PlASMA-SORB [1], for liquid radioactive waste treatment. This technology is based on a synergistic interplay of physical processes: quasi-stationary bulk microbubble plasma, acoustic-vortex aeration, hydrodynamic cavitation, and plasma electrolysis (Fig. 1).

The latter destroys persistent organic compounds with the simultaneous synthesis of nanosorbents with high sorption efficiency of cesium, strontium, europium and americium [2-5]. These physical effects are implemented in the equipment of the first radioactive water treatment module. As a result, the initial activity of water decreases from 10^7 Bq/dm^3 for cesium-137 to 10^2-10^4 Bq/dm^3, for strontium-90 from 10^6 Bq/dm^3 to 10^2-10^3 Bq/dm^3, and for transuranium - to complete purification.

The second module uses a purely sorption purification mechanism, namely, the passage of water through a column filled with a mixture of zeolite and porous aluminosilicate powder of the heulandite-clinoptilolite type. After that, the water passes through an ultramembrane and we get pure water at the outlet.

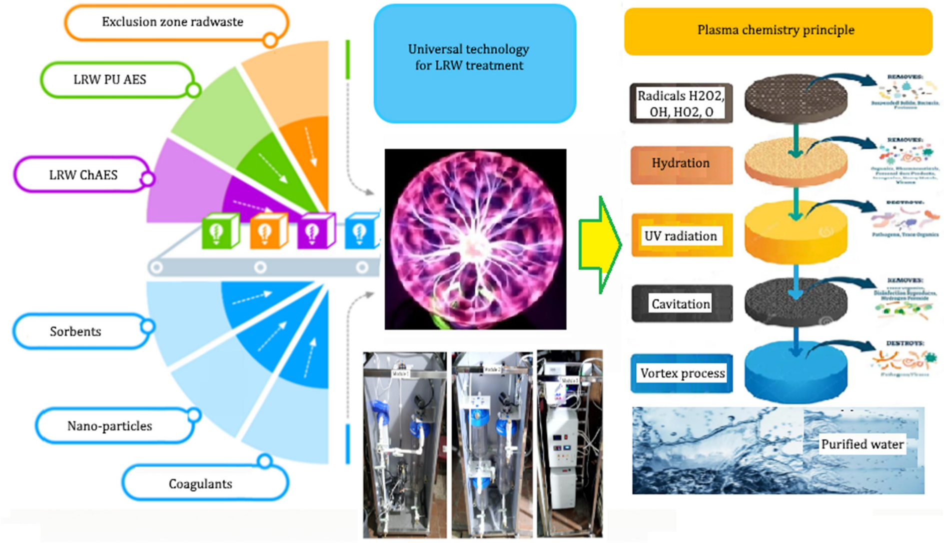


Fig. 1. Block diagram of the universal technology for liquid radioactive waste treatment of the PLASMA-SORB technology.

As a result, the water activity decreases from 10^2-10^4 Bq/dm^3 for cesium-137 to 0-2 Bq/dm^3, and for strontium-90 from 10^2-10^3 Bq/dm^3 to 0-2 Bq/dm^3. The third module contains control devices for modules one and two with control of the cleaning process. The authors have determined the optimal duration of plasma-chemical electrolysis in conjunction with the ionic transfer of radionuclides on the surface of iron nanoparticles and sorbents, which contributes to the complete purification of water.

Spent sorbents from module 1 and a mixture of zeolite and porous aluminium silicate powder are automatically fed to the conditioning (evaporation) shop for further compaction into matrices based on alkaline cements or geocements [6].

Thanks to numerous scientific and experimental works to optimise the above processes, as well as the development of plasma technologies, we have managed to implement the treatment of industrial and naturally polluted water in a single technological cycle.

In-situ studies on real radwaste from the Chornobyl Shelter and radwaste from the South Ukrainian NPP showed high efficiency of the developed multi-stage method for their treatment (99.9%).

The PlASMA-SORB technology has a high economic effect and its implementation will have a major positive impact on the environment by reducing the volume of storage facilities, significantly reducing electricity consumption and time for cleaning the ladder water, which will improve the environmental safety of the entire nuclear fuel cycle.

The high relevance of this technology in the context of military aggression will significantly reduce the number of facilities with a high potential radiation and environmental hazard.

Keywords: *electrolysis, liquid radioactive waste, radionuclides, plasma chemistry, purification*

References

[1] Yu.L. Zabulonov, S.G. Guzii, Algorithm of liquid radioactive waste treatment using elements of plasma-sorb technology. XII Scientific Conference ‘Scientific Results 2023’, Collection of Scientific Proceedings, Kharkiv, Technological Centre, 2023, p. 95.
[2] Yu.L. Zabulonov, et al., Mineralogical Journal, 43 (2021) 74.
[3] S. Guzii, et al., Material Sci & Eng., 8 (2024) 15.
[4] Yu. Zabulonov, et al., New sorbents and their application for deactivation of liquid radioactive waste, Lecture Notes in Civil Engineering, 469 LNCE, 2024, pp. 126–136.
[5] S. Guzii, et al., Problems of Atomic Science and Technology, 4 (2024) 84.
[6] S. Guzii, Solid State Phenomena, 364 (2024) 113.

Acknowledgments: *The work was carried out within the framework of the EURAD-2 project and was co-funded by the European Union under Grant Agreement No 101166718.*

Adsorption of arsenic from mine water by magnetic biochar

Anton Zubrik*, Eva Mačingová, Slavomír Hredzák and Marek Matik
Institute of Geotechnics SAS, Watsonova 45, Kosice, 04001, Slovak Republic
**Corresponding Author: zubant@saske.sk*

Arsenic is a highly toxic mobile pollutant. Chronic arsenic exposure causes severe health manifestations including different forms of cancers. The World Health Organization, as well as Slovak legislation (Decree MoH SR No 247/2017 Coll.) has set the maximum levels for arsenic in drinking water at 0.01 mg/L. Arsenic is persistent pollutant, which cannot be destroyed, but its negative impact can be reduced by immobilization. Adsorption is one of the frequently used procedures to remove toxic pollutants from wastewater. Synthesis of new efficient adsorbent with high value of adsorption capacity is still hot topic of many researcher activities. Therefore, the low cost carbonaceous materials such as waste biomass, biochars with developed pore structure are frequently synthesized and tested for removal of inorganic (heavy metals/metalloids) and organic (PAHs, pesticides, dyes,) contaminates.

In Slovakia, arsenic contamination is a significant problem due to the rich mining and industrial history and natural occurrence. For example, Zlatá Idka village, situated in the eastern part of the Spiš-Gemer Ore Mts., is distinctive by intensive mining and ore processing activity. Between the 14th and 19th centuries, As bearing Au–Ag–Sb ores were here exploited. Geochemical analyses indicate high pollution of the surrounding environment by As and Sb [1]. Our research examined the effectiveness of magnetic biochar as an adsorbent for arsenic in mine water flowing from the Hauser adit, the deepest horizontal adit of the Zlatá Idka ore district.

Magnetic biochar (MWchar-Mag) was prepared as described by Zubrik et al. [2]. Magnetic adsorbent contains maghemite nano-particles with superparamagnetic properties. It is easy to remove it from aqueous solution by external magnetic field. The equilibrium adsorption tests were carried out under batch conditions. The metal quantity in the mine water was determined by AAS, ICP-MS and ion chromatography (IC). Chemical analysis of water from Hauser adit is highlighted in Table 1.

Table 1: Chemical analysis of waste water from Hauser adit. Sampling April 22, 2024.

	pH	**Mn [µg/L]**	**Fe [µg/L]**	**Ba [µg/L]**	**Sb [µg/L]**	**As [µg/L]**	**Ni [µg/L]**
Method	-	AAS	AAS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
Value	6.9	425	1428	2.5	0.6	201.2	1.2
	Zn [µg/L]	**Cu [µg/L]**	**Pb [µg/L]**	**Cr [µg/L]**	**Co [µg/L]**	**Li [µg/L]**	**Na [µg/L]**
Method	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	IC	IC
Value	21.7	1.6	0.8	0.2	0.7	12.4	5334
	NH_4^+ [µg/L]	**K [µg/L]**	**Mg [µg/L]**	**Ca [µg/L]**	**F^- [µg/L]**	**Cl^- [µg/L]**	**SO_4^{2-} [µg/L]**
Method	IC	IC	IC	IC	IC	IC	IC
Value	34.6	864	12140	21880	119	1033	31334

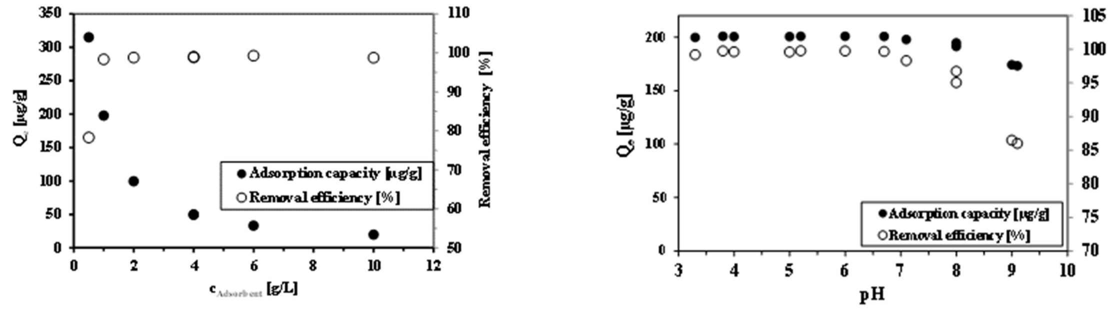


Fig. 1. The effect of adsorbent dosage (left side) and pH (right side) on arsenic removal from mine water (c(As^{5+}) = 201.2 μg/L). Conditions at adsorbent dosage test: c(MWchar-Mag) = 0.5-10 g/L; 24 h, RT, pH = 7.3 (no pH modification). Conditions at pH influence test: c(MWchar-Mag) = 1 g/L; 24 h, RT, pH adjustment with HNO_3 and NaOH.

The magnetic carbon composites are promising adsorbents towards wastewaters contained oxyanions. In our previous work [2], we found that MWchar-Mag is an excellent adsorbent of arsenic from model solution (Q_m = 24.9 mg/g; pH = 3.8). Therefore, we decided to test it as an adsorbent of arsenic from real wastewater. The effect of adsorbent dosage and pH influence were investigated in order to remove arsenic from real water (Fig. 1). The findings verify the excellent performance of the magnetic adsorbent on arsenic anion. Removal efficiency reaches 100% in the adsorbent concentration range of 1-10 g/L. The pH monitored after adsorption is neutral demonstrating the pH buffering effect of wastewater. In the case of pH influence tests, removal effectiveness reduces when pH increases above 8. In the acidic environment, removal efficacy was 100%. Note that model experiments are frequently performed at ideal conditions. The sorption of metal runs in deionised water at ideal pH, without any additional influences. Therefore high value of maximum adsorption capacity can be reached. However, the effects of competing ions, ionic strength, pH, and selectivity for other elements are phenomena that significantly impact the adsorption process in real wastewater.

Keywords: *magnetic biochar, mine water, arsenic adsorption*

References

[1] Rapant, S.; et al., Environmental Geology, 51 (2006) 387.
[2] Zubrik, A.; et al., Chem. Eng. Process., 178 (2022) 109016.

Acknowledgments: *This work has been supported by VEGA 2/0116/23, VEGA 2/0138/24, VEGA 2/0108/23, APVV-20-0140 projects.*

Intensification of the adsorption process of heavy metals using synthesized graphene oxide

A.P. Melchor-Durán[1], M.R. Moreno-Virgen[1]*, A. Bonilla-Petriciolet[1], H.E. Reynel-Ávila[1,2], E. Lucio Ortiz[1], O.F. González-Vázquez[1]

[1]Tecnológico Nacional de México - Instituto Tecnológico de Aguascalientes, Av. Adolfo López Mateos #1801 Ote. Fracc. Bona Gens, C.P. 20255 Aguascalientes, Ags., México

[2]Conahcyt, Av. de los Insurgentes Sur 1582, Crédito Constructor, Benito Juárez, 03940 Ciudad de México, CDMX, México

**Corresponding Author: ma_rosario.mv@aguascalientes.tecnm.mx*

This study investigated the adsorption properties of graphene oxide in a magnetic-assisted adsorber for the depollution of water containing heavy metals. Two samples of graphene oxide with different surface chemistry were synthetized and assessed using the magnetic-assisted adsorption systems. One graphene oxide sample exhibited a dual magnetic behavior presenting both diamagnetic and ferromagnetic phases, while the other graphene oxide was diamagnetic. The adsorption properties of these graphene oxide samples for removing Pb^{2+} and Cu^{2+} were tested and compared with and without a magnetic field exposure.

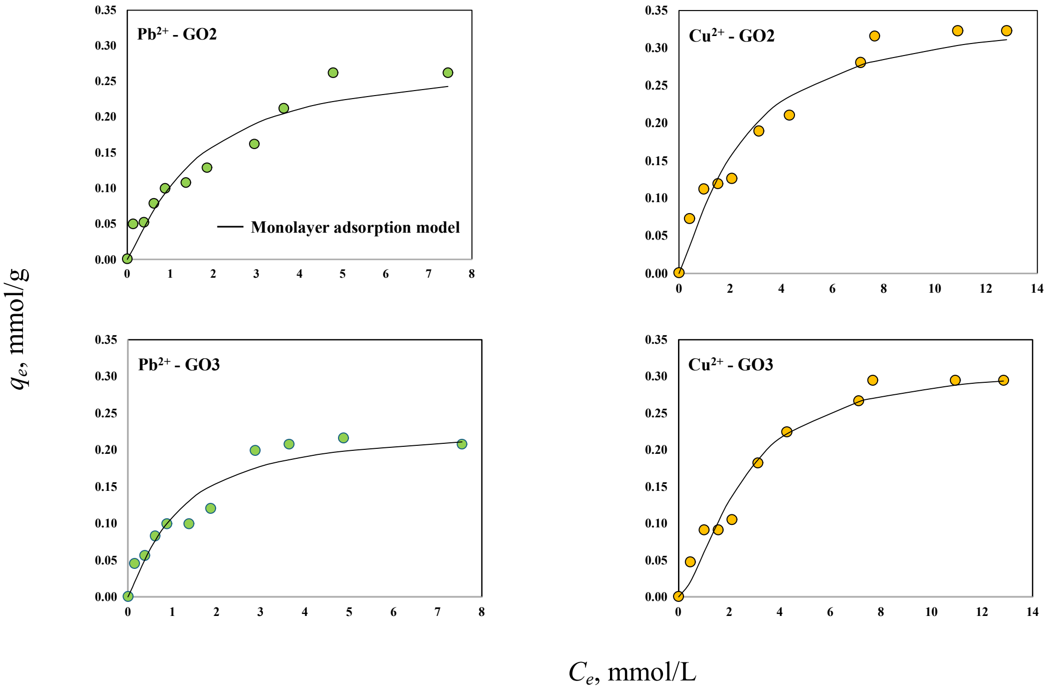


Fig. 1. Experimental isotherms for the magnetic-assisted adsorption of Pb^{2+} and Cu^{2+} using GO samples at pH 5 and 30 °C.

The results showed that the Pb^{2+} removal increased using both graphene oxide samples in the magnetic-assisted configuration, while Cu^{2+} adsorption was less sensitive to the application of the magnetic field (see Figure 1).

Keywords: *carbon-based adsorbent, environmental depollution, intensified water treatment*

References

[1] O.F. González Vázquez, M.R. Moreno Virgen, M.S. Esparza González, V. Hernández Montoya, R. Tovar Gómez, C. J. Durán Valle, Industrial & Engineering Chemistry Research, 59 (2020) 13820.

Acknowledgments: *Tecnológico Nacional de México (TecNM) and the MatPore – Porous Materials National Laboratory.*

The promising application of silica/pectin hybrid material as sorbent for the removal of lead(II) ions from aqueous solutions

V.Kyshkarova[1]*, Y. Boyko[2], V. Tomina[2], M. Vaclavikova[1] and I. Melnyk[1]
[1]Institute of Geotechnics SAS, Watsonova 45, Kosice, 04001, Slovak Republic
[2]Chuiko Institute of Surface Chemistry NASU, Oleha Mudraka 17, Kyiv, 03164, Ukraine
**Corresponding Author: kyshkarova@saske.sk*

With industrial pollution on the rise and heavy metals becoming increasingly prevalent in water systems, finding effective adsorbents for their removal is critical. Heavy metals, such as lead(II), cadmium(II), and mercury(II), not only negatively impact the environment but also pose a serious threat to human health, as they can accumulate in the body and cause various chronic diseases [1]. Therefore, it is necessary to develop inexpensive, environmentally friendly, and highly efficient water treatment materials. In this study, a hybrid material combining the properties of inorganic (silica) and organic (pectin) components was selected. Silica (SiO_2) exhibits a high specific surface area and stability. Meanwhile, pectin (Pec) is a natural, biodegradable polysaccharide containing numerous functional groups capable of binding with metal ions [2]. The combination of these two materials enables the creation of an effective and environmentally friendly adsorbent for the removal of heavy metals from water systems.

A one-step sol-gel method was employed to prepare the SiO_2/Pec hybrid material. This approach allows for the production of homogeneous materials with precise control over particle size and morphology by systematically adjusting reaction parameters. Tetraethoxysilane (TEOS) was used as the silica source. TEOS underwent hydrolysis with an HCl catalyst at 70-80°C, and the solution was stirred until it appeared homogeneous and transparent. Pectin was then added, serving as both a functionalizing and gelling agent. Gel formation was completed within 24 h after the addition of powdered pectin. The resulting gel was washed, oven-dried at 60°C for 24 hours, and vacuum-dried at 80°C for 5 hours. The composition and structure of the obtained hybrid material is presented in Table 1.

he next step was to use the hybrid material for the removal of heavy metals from model solutions. Lead was chosen for removal due to pectin's selective interaction with lead ions, forming stable complexes that enhance adsorption efficiency, as supported by the literature [3]. This makes the hybrid material particularly promising for water purification from this hazardous pollutant. Parameters such as pH, contact time, and initial metal concentration were studied.

Table 1. The composition of synthesized SiO_2/Pec hybrid.

Sample	ω (pectin), %	Elemental analysis data, %		pI	C_{-COOH}, mmol/g	S_{sp}, m^2/g	V_s, cm^3/g	d, nm
		C, %	H, %					
SiO_2/Pec	28	12.7	3.0	1.7	1.0	280	0.2	3.4

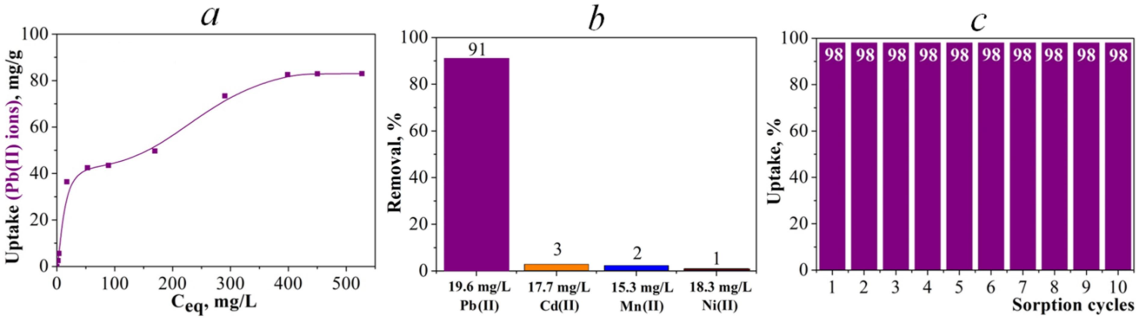


Fig. 1. Experimental Pb(II) ions adsorption isotherm (a); selective adsorption study (b); and adsorption of Pb(II) from a mixture of metal ions without regeneration by the SiO_2/Pec hybrid (c).

The results showed that the maximum adsorption capacity of the hybrid material was 83 mg/g (Fig. 1a) at pH 4 and a contact time of 5 hours. Moreover, the hybrid material demonstrated excellent selective removal of Pb(II) ions with an efficiency up to 91% (Fig. 1b) from model solution with Cd(II), Mn(II), Ni(II), and Pb(II) ions at pH 4.

The hybrid material was also tested under real conditions using tap water. The experimental results demonstrated its high efficiency over 10 cycles of use, it removed up to 98% of lead(II) ions at a concentration of 5 µg/L with a contact time of 5 hours for each cycle (Fig. 1c). These results confirm both the effectiveness of the developed adsorbent and its practical applicability for purifying drinking water from hazardous heavy metals.

In conclusion, the SiO_2/Pec hybrid material demonstrated a high adsorption capacity for lead, making it a promising solution for water purification. The synthesis process is straightforward, and both components are environmentally friendly. Furthermore, the material's reusability enhances its practicality for long-term use. These qualities suggest that this hybrid material could be a significant addition to water supply systems, ensuring the removal of hazardous heavy metals and contributing to water safety.

Keywords: *silica, pectin, composite, lead(II) adsorption, selective adsorption, sorbent reuse*

References

[1] C. Zamora-Ledezma, et al., Environmental technology and innovation, 22 (2021) 101504.
[2] R. Wang, R. Liang, et al., Trends in food science and technology, 91 (2019) 319.
[3] V. Dronnet, et al., Carbohydrate Polymers, 30 (1996) 253.

Acknowledgments: *Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V04-00700. This work was supported by the VEGA 2/0138/24 project.*

Disinfection of drinking water using cold discharge plasma

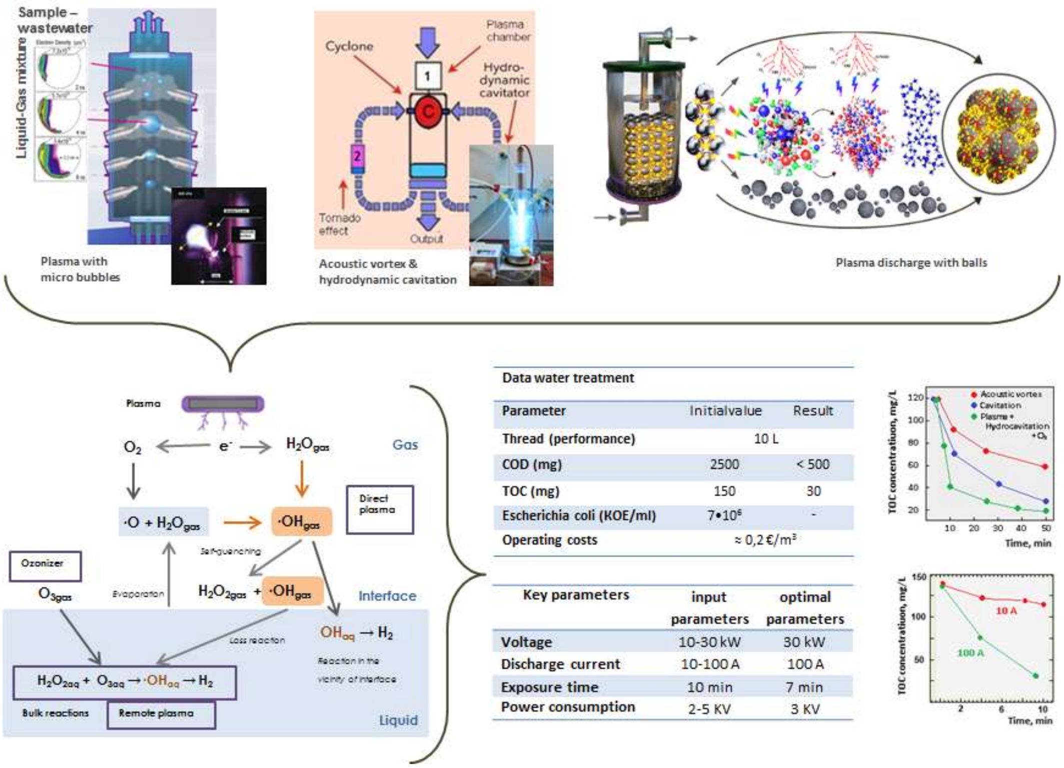
Yu.L. Zabulonov[1]*, L.A Bulavin[2], O.M. Arkhypenko[1], L.A. Odukalets[1],
M.A. Stokolos[1], V.A. Nikolenko[1]
[1]State Institution "The Institute of Environmental Geochemistry" of National Academy of Sciences of Ukraine, Akademika Palladina Ave 34A, Kyiv, 02000, Ukraine
[2]Taras Shevchenko National University of Kyiv, Volodymyrska 60, Kyiv, 01033, Ukraine
**Corresponding Author: 1952zyl@gmail.com*

The current tense sanitary and epidemiological situation in the world is caused not only by the high concentration of pathogenic bacteria, viruses and parasites found in drinking water, but also by a number of factors, including a decrease in the effectiveness of classic chlorine-containing disinfectants used to disinfect water. This is due to the intensive spread of chlorine-resistant forms of pathogenic microorganisms, the acceleration of their evolution with the formation of more resistant strains. The mass spread of chlorine-resistant microorganisms causes the extensive development of disinfection systems. Most of the leading companies in the creation of water treatment systems are trying to solve the problem by using increasingly toxic, expensive and harmful in all respects disinfectants.

Therefore, the development of innovative approaches and systems that use new physical, chemical and technological processes that guarantee effective disinfection of natural and waste water from a wide range of microorganisms, pathogenic bacteria, viruses and parasites is an extremely relevant area of research.

The team has developed a fundamentally new reagent-free method that is more effective than disinfection of drinking water with such oxidizers as ozonation, ultraviolet irradiation, hydrogen peroxide. It is based on the creation of low-temperature plasma in a liquid using a pulsed electric discharge. Numerous experiments were conducted on disinfection of water that was contaminated with Escherichia coli (*E. coli*). For this, a laboratory setup with a specialized disinfection reactor was used in which a heterogeneous water-air environment was formed, using an ejector with electrodes inserted into it, to which pulses of electric current are supplied. The discharges in the mixture initiate a whole range of various physical and chemical phenomena, such as a strong electric field, intense ultraviolet radiation, shock waves of excess pressure and especially the formation of various highly active chemical substances, such as radicals (OH•, H•, O•) and molecules (H_2O_2, H_2, O_2, O_3) (Fig. 1). The initial concentration of E. coli in the studied water corresponded to $3.4 \cdot 10^6$ CFU/cm^3.

Water treatment for 1 minute reduced the concentration of E. coli to 5.2 CFU/cm^3, i.e. the treated water corresponded to the indicators of practically pure water. The experiments proved the effectiveness of the low-temperature plasma water treatment technology with a concentration of bacteria significantly exceeding the maximum permissible levels.



Data water treatment

Parameter	Initialvalue	Result
Thread (performance)	10 L	
COD (mg)	2500	< 500
TOC (mg)	150	30
Escherichia coli (KOE/ml)	$7 \cdot 10^6$	-
Operating costs	≈ 0,2 €/m³	

Key parameters	input parameters	optimal parameters
Voltage	10-30 kW	30 kW
Discharge current	10-100 A	100 A
Exposure time	10 min	7 min
Power consumption	2-5 KV	3 KV

Fig. 1. Physicochemical processes in plasma.

Keywords: *cold plasma, drinking water, disinfection*

References

[1] V. Bereka, I. Boshko, I. Kondratenko, Yu. Zabulonov, D. Charny, Yu. Onanko, A. Marynin and V. Krasnoholovets, Journal of Environmental Engineering and Science, 3 (2020) 92.

[2] Yu.L. Zabulonov, D.V. Charniy, L.A. Odukalets, D.A. Yaroschuk, O.V. Pugach, O.M. Arkhypenko, N.M. Chernova, Geochemistry of technogenesis, 5 (2021) 71.

[3] D.V. Charny, O.M. Arkhypenko, M.A. Stokolos, A.V. Pugach, Advanced disinfection technology, Modern scientific research: achievements, innovations and development prospects. Proceedings of XIV International Scientific and Practical Conference Berlin, Germany, 17-19 July 2022.

[4] Yu.L. Zabulonov, D.V. Charniy, L.A. Odukalets, O.M. Arkhypenko, A.V. Pugach, M.A. Stokolos, I.V. Tishchenko, Geohìm. tehnology, 3 (2020) 143.

Toxic metals adsorption on different activated carbons derived from agricultural wastes

I. Ceban (Ginsari)*, R. Nastas, T. Lupascu
Institute of Chemistry of Moldova State University, Academiei 3,
Chisinau, MD-2028, Republic of Moldova
**Corresponding Author: irina.ginsari@outlook.com*

Numerous studies have shown that toxic metals, such as lead, cadmium, cobalt, and strontium, are poisonous to plants, aquatic life, and humans, accumulating in organisms and causing severe health issues. With the rise in nuclear reactors, radioactive metals like cesium and cobalt pose additional threats through ionizing radiation, further damaging DNA and proteins. Activated carbon is widely used to remove toxic metals from water via adsorption, influenced by different factors, such as pH, temperature, and surface chemistry [1]. Low-cost activated carbons from agro-based materials, like walnut shells and apple wood, have proven effective in metal ions removal [2].

In this study, concentrated nitric acid and mixture of nitric acid/urea were used as oxidizing agents to modify activated carbons surface, enhancing their metal adsorption properties. Kinetic (pseudo-first-order, pseudo-second-order and intraparticle diffusion models) and isotherm (Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin–Pyzhev) models result indicate that the modified activated carbons, efficiently adsorb Co(II), Cs(I), Hg(II), Pb(II), Cd(II) and Sr(II) ions, additionally explaining the adsorption behavior and mechanisms. Comparative analysis of activated carbons adsorption capacity for metal ions shows higher values for cobalt, lead, cadmium and strontium (Figure 1).

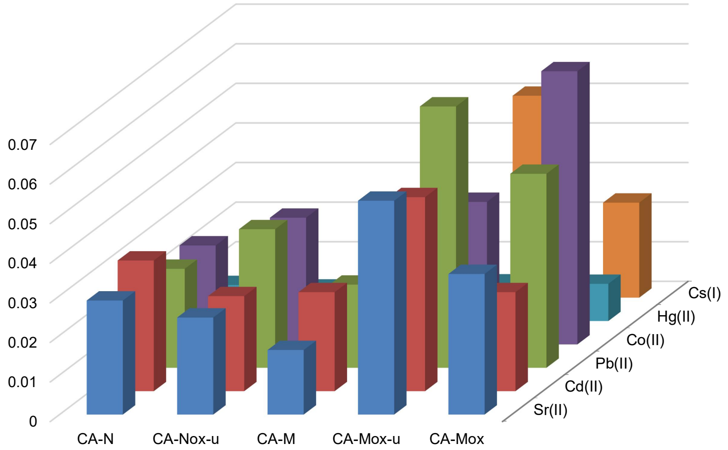


Fig. 1. Adsorption capacity (a, mmol/g) of activated carbons for metal ions at pH 4 [3].

By summarizing the obtained results, the adsorption mechanisms of toxic metal ions on activated carbons were proposed. The investigations highlight the important role of the solution pH, of the activated carbons functional groups and the pHpzc value for the adsorption process of cobalt(II) and pH, the adsorption of strontium(II) and cobalt(II) ions occurs via different mechanisms.

Keywords: *activated carbons, modification, adsorption, heavy metal ions*

References

[1] P.B. Tchounwou, C.G. Yedjou, A.K. Patlolla, D.J. Sutton, Molecular, Clinical and Environmental Toxicology, 3 (2012) 133.
[2] S. Mikhalovsky, O. Voytko, V. Demchenko, P. Demchenko, Chemistry Journal of Moldova, 16 (2021) 9.
[3] R. Nastas, I. Ginsari, T. Lupascu, Abstract book, International Conference Achievements and Perspectives of Modern Chemistry, Chisinau, Republic of Moldova, 2019, p. 183.

Acknowledgments: *The presentation is supported by HE MSCA-RISE-2022-SE-01/ CLEANWATER Project (grant no. 101131382).*

Tendency and current progress in sustainable technologies of solid/liquid waste valorization: Waste-based adsorbents for H_2S removal

M.Abid[1]*, A. Fullana[2], M. Martinez-Escandell[1], J. Silvestre-Albero[1]
[1]Advanced Materials Lab, Inorganic Chemistry Department, University of Alicante, Ap. 99, Alicante, E-03080, Spain
[2]Chemical Engineering Department, University of Alicante, San Vicente del Raspeig, Ap. 99, Alicante, E-03080, Spain
**Corresponding Author: abidmeriem095@gmail.com*

In the search for a suitable adsorbent for any type of pollutant gas removal, preference is always given to the ones having a greater capacity for adsorbate, stability under the operating parameters, and separation selectivity for a single gas or a mixture of gases. Lately, waste material utilization as adsorbents is gaining popularity due to its abundant availability and yet to be fully exploited. Moreover, this strategy obviously involves environmental benefits whereby emphasis was placed on waste minimization, recovery, and reuse. Various types of waste materials were tested as adsorbents for H_2S removal, porous carbon materials are the most efficient and eco-friendly material with low cost for that purpose. [1]

Gas-phase desulfurization on carbon materials is an important process attracting the attention of scientists and engineers. When involving physical adsorption, reactive adsorption, and catalytic oxidation combined, the process is considered as energy-efficient. Recent developments in materials science directed the attention of researchers to inorganic phases which react with H_2S and participate in its oxidation to elemental sulfur. The present study aims to obtain a carbon material from liquid/ solid wastes able to efficiently remove hydrogen sulfide from an industrial gas stream under ambient conditions [2].

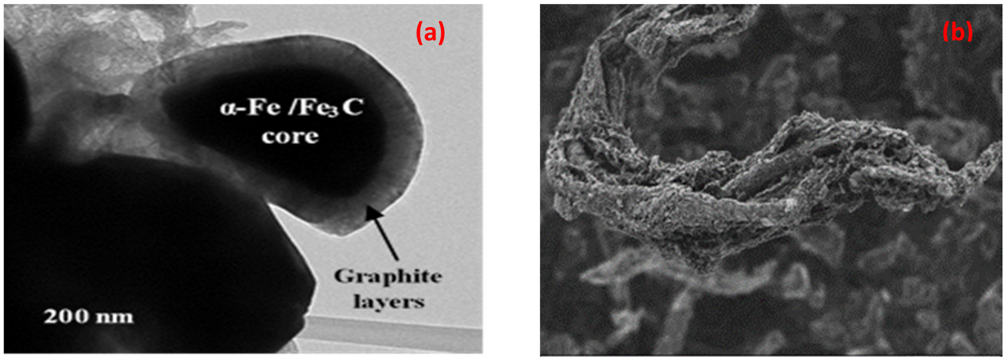


Fig. 1. The morphology structure of the synthesized carbon particles (a) olive mill wastewater-derived carbon material, (b) footwear waste residue-based activated carbon material.

Keywords: *olive mill waste water, footwear residue, hydrogen sulfide, carbon material*

References

[1] M. Shah, M. Tsapatsis, J.I. Siepmann, Chemical Reviews, 117 (2017) 9755.

[2] C. Yang, G. Falco, M. Florent, T.J. Bandosz, Journal of Hazardous Materials, 437 (2022) 129414.

Acknowledgments:

This work was supported by HORIZON-MSCA-2022-SE-01 (CLEANWATER - 101131382) project.

Authors acknowledge financial support from MINECO (Project PID2022 142960OB-C21) and Conselleria de Innovación, Universidades, Ciencia y Sociedad Digital (Project CIPROM/2021/022).

Magnetic particles with polysiloxane shell and silver nanoparticles as potential sensor for detecting Tuberculosis DNA

N. Chechitko[1], M. Galaburda[2], A. Pawlik[2], M. Osińska-Jaroszuk[2], G. Janusz[2] and I. Melnyk[1]*
[1]*Institute of Geotechnics SAS, Watsonova 45, Kosice, 04001, Slovak Republic*
[2]*Maria Curie-Sklodowska University, Maria Curie-Skłodowska 3, Lublin, 20-031, Poland*
**Corresponding Author: melnyk@saske.sk*

Tuberculosis (TB) remains a major challenge for global health, causing millions of infections and deaths annually. Despite advancements in medical science, the detection and diagnosis of TB—particularly in developing nations—are hindered by the lack of affordable, accurate, and rapid diagnostic tools. Traditional methods, such as sputum culture and chest X-rays, are often slow, require advanced laboratory facilities, or lack the necessary sensitivity and specificity. This underscores the urgent need for innovative diagnostic solutions that are efficient and practical for widespread use in resource-limited settings.

Magnetic particle-based detection methods have emerged as a promising advancement in the fight against tuberculosis. These techniques employ magnetic particles coated with silver and gold nanoparticles, significantly enhancing the sensitivity and specificity of TB detection. The unique properties of silver and gold nanoparticles, such as their strong optical signals and ability to specifically bind to TB bacteria, make them ideal for rapid, point-of-care diagnostic tests. By simplifying the detection process and delivering swift results, these innovative methods have the potential to transform TB diagnosis, enabling earlier treatment, curbing disease transmission, and ultimately saving lives. The development and adoption of magnetic particle-based TB detection techniques are thus crucial to advancing global efforts to control the disease.

Magnetic particles coated with polysiloxane shells bearing thiourea groups and decorated with silver nanoparticles hold significant potential for biomedical applications, particularly for detecting tuberculosis DNA. In this study, we developed magnetic nanoparticles functionalized with a polysiloxane layer incorporating thiourea groups [1]. These groups provide sites for further modification and enhance binding properties. Silver nanoparticles were immobilized on the surface of these magnetic particles, adding functional properties such as improved sensitivity [2].

The synthesized particles were characterized using various techniques, including scanning and transmission electron microscopy, Fourier-transform infrared spectroscopy, N_2 adsorption-desorption, elemental analysis, thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and zeta-potential measurements [1], to confirm successful coating and decoration. These composite particles demonstrated promising physical and chemical properties, making them suitable candidates for developing DNA detection systems targeting Mycobacterium tuberculosis and other biosensing applications.

This study explores the potential of these particles for detecting tuberculosis DNA, focusing on their magnetic responsiveness, surface functionality, and interaction with specific biomolecules. The results showed that the amount of adsorbed silver ions was 29 mg/g, and after reduction, silver nanoparticles with a size of 5 nm were formed on the surface of the magnetic particles with a polysiloxane shell. These nanoparticles were evenly distributed across the surface. Furthermore, nanocomposites were tested to bind the Alexa-labelled DNA probe (5’-Thiol- TTT TTT TTT TTT TTT ACC GTT ATA TAT AAG TAA TCC CAA TTA TAA GGT AAA TGT ATA TGC TG - Alexa 594- 3’). The results showed that the sample with Ag NPs provided the largest fluorescence signal, generating a value of approximately 210,000 compared to 80,000 for free DNA probes, suggesting a 2.6-time increase in fluorescence. The enhancement effect for the DNA probe not chemically bonded to the nanoparticles (control 1; 165,000 RFU) is lower than for the chemically bonded DNA (228,000 RFU), but higher than for the DNA alone (control 2; 107,000 RFU), demonstrating that there is an effect on the level of fluorescence when the fluorophore-labelled DNA probes are chemically bonded to the surface of the nanoparticle.

These findings suggest that these magnetic composites could serve as a foundation for creating sensitive and selective DNA-based diagnostic tools for infectious diseases, paving the way for advanced biosensor technologies in clinical diagnostics.

Keywords: *magnetite/silica composite, thiourea groups, Ag nanoparticles, fluorescence sensors*

References

[1] Melnyk, I.V. et al., Applied Surface Science, 609 (2023) 155253.
[2] Melnyk, I.V., et al., Applied Nanoscience, 9 (2019) 683.

Acknowledgments: *Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V04-00708.*

Preparation of SiO_2 from talc and its functionalization by *n*-phenylaminomethyltriethoxysilane for water treatment

K. Simanová* and I. Melnyk
Institute of Geotechnics SAS, Watsonova 45, Kosice, 04001, Slovak Republic
**Corresponding Author: simanova@saske.sk*

The aim of this work was the preparation of silica from available SiO_2-rich minerals, followed by subsequent surface modification of the prepared silica using suitable silanes containing both hydrophilic (NH_2) and hydrophobic (C_xH_y) groups to create effective and inexpensive adsorbents for wastewater treatment from inorganic and organic pollutants. In the first stage of the presented work, a mineral called talc ($Mg_3Si_4O_{10}(OH)_2$) from a deposit located near the village of Gemerská Poloma in the district of Rožňava in the Košice Region was chosen as a source of SiO_2 for the preparation of silica particles. The theoretical composition of the used talc was 63% SiO_2, 32% MgO, and 5% H_2O. By determining the composition of the real talc sample, it was found that in addition to silica, magnesium oxide, and water, talc also contained various impurities, mainly iron and aluminum oxides. Therefore, to obtain pure silica, a multi-step treatment was chosen, in which magnesium compounds and most of the impurities were removed.

In the first step, the talc was ground into particles of size ≤ 100 µm and then underwent heat treatment. The activated talc powder was subsequently used to prepare silica using a two-step synthesis. The first step was acidic leaching using hydrochloric acid. This step was performed to remove impurities and metal cations from the material. The second step was basic leaching with sodium hydroxide, followed by re-precipitation of SiO_2 by neutralization with an acidic solution. The prepared silica was characterized by infrared spectroscopy, powder X-ray diffraction analysis, and the percentage composition, structural and adsorption properties of the individual samples were also determined. Infrared spectroscopy confirmed the presence of vibrations characteristic of Si-O-Si bonds for all samples at around 1100 cm^{-1} (ν(Si-O-Si)), 600 cm^{-1}, and 500 cm^{-1} (δ(Si-O-Si)). The amorphous structure of the samples was determined by PXRD analysis, where the presence of sharp signals indicated impurities. Diffractograms showed that the number of these signals decreased through treatment, which confirmed the purification of silica from the used talc. The percentage composition of the samples was determined by atomic absorption spectroscopy, which confirmed the results from PXRD analysis. The percentage volume of used silica increased from 53.5% to 65.2%, while the percentage volumes of impurities significantly decreased. Sorption measurements of the individual samples showed an increase in specific surface area from 19 m^2/g to 77 m^2/g, pore volume from 0.066 cm^3/g to 0.620 cm^3/g, and pore size from 3.4 nm to 9.8 nm during the silica preparation process.

The second stage of the presented work involved the preparation of the adsorbents by surface modification of the prepared silica powder. *N*-phenylaminomethyltriethoxysilane was used as a coupling agent. The modification took place in an EtOH/H_2O solution with NH_4OH as a catalyst, with various wt.% of the coupling silane used (6, 12, and 18%) based on the literature. The prepared samples were characterized by various physicochemical methods. The presence of functional groups from the coupling silane was determined by infrared spectroscopy (Fig. 1) and CHNS analysis, and structural and adsorption properties were also determined. After characterization, the samples will be used for research in the adsorption of heavy metals from wastewater [1-3].

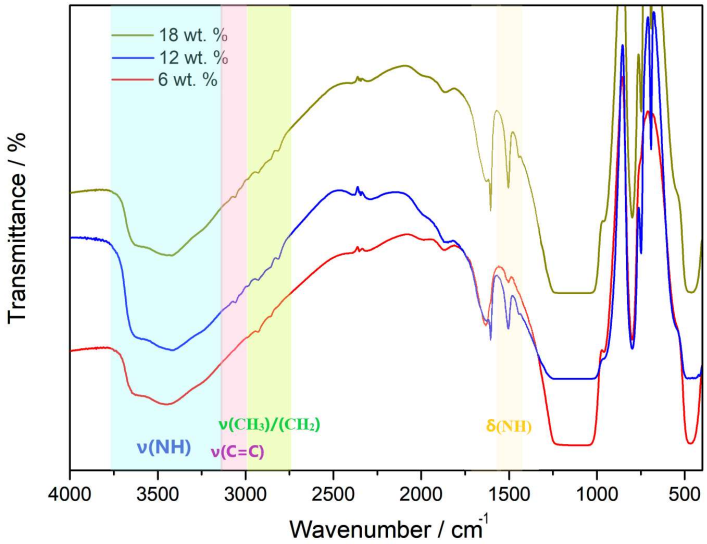


Fig. 1. IR spectra for the silica modified samples with different % of coupling silane.

Keywords: *silica, modification, adsorbents, water treatment*

References

[1] K. Taeho, et al., Colloids and Surfaces A: Physicochemical and Engineering Aspects, 501 (2016) 24.

[2] M. Kamali, et al., Green energy and technology: Advanced wastewater treatment technologies for the removal of pharmaceutically active compounds, Publisher: Springer Nature Switzerland AG, Switzerland, 2023, 26.

[3] K. Simanová, I. Melnyk, Metalurgia Junior 2024, Publisher: Technical University of Košice, Košice, Slovak Republic, 2024, 182.

Acknowledgments: *This work was supported by the VEGA 2/0138/24, the Recovery and Resilience Plan for Slovakia 09I03-03-V02-00029 projects.*

Structural peculiarities of organosilicas with diethylenetriamine functional groups as sorption materials

V. Tomina[1]*, N. Stoliarchuk[1], M. Fizer[2], D. Marcin Behunova[3], O. Semeshko[3], and I. Melnyk[3]
[1]*Chuiko Institute of Surface Chemistry NASU, Oleha Mudraka 17, Kyiv, 03164, Ukraine*
[2]*University of Nevada, 1664 N. Virginia Street, Reno, NV 89557, USA*
[3]*Institute of Geotechnics SAS, Watsonova 45, Košice, 04001, Slovak Republic*
**Corresponding Author: w.w.tomina@gmail.com*

Sol-gel derived amino-silica materials have been widely researched as adsorbents for water purification from various pollutants, especially heavy metal and rare-earth elements ions. The main factors determining their sorption behaviour are the porous structure and the content, accessibility and arrangement of the functional groups [1]. Therefore, in order to increase the number of the surface adsorption centres, we decided to use silane with diethylenetriamine functions, N1-(3-trimethoxysilylpropyl)diethylenetriamine(TMPET), as a source of amino groups to be attached onto the particles. Thus, three types of materials were synthesized via the co-condensation of TMPET with either of the structuring agents: tetraethyl orthosilicate (TEOS); 1,2-bis(triethoxysilyl)ethane (BTESE); or 1,4-bis(triethoxysilyl)benzene (BTESB) applying the technique described earlier in [2], see Table 1. These silica materials were analyzed with a range of methods, including analysis on CHNS elements, SEM, FTIR and UV-Vis spectroscopy in solid state, N_2 adsorption and desorption isotherms measurements, studying adsorption capability to metal ions of Cu(II) and Ni(II).

As was anticipated, in a row of samples of the same type, with an increase in the fraction of structuring agent in the reaction medium, the specific surface area (S_{BET}) of the derived sorbent increases, while the content of functional groups (C_{NNN}) decreases.

Table 1. Characteristics of the synthesized diethylenetriamine-silicas.

Sample	Ratio of silanes	C_{NNN} mmol/g	S_{BET} m^2/g	Cu^{2+} uptake			Ni^{2+} uptake		
				SSC, mmol/g	K_d, cm^3/g	K_β	SSC, mmol/g	K_d, cm^3/g	K_β
SiO_2/NNN	6/1 (TEOS/TMPET)	1.5	294	1.32	3317	2.16	0.80	1694	2.16
E/NNN2	2/1 (BTESE/TMPET)	1.9	3	1.86	2212	2.45	0.31	616	3.00
E/NNN4	4/1 (BTESE/TMPET)	1.3	239	1.47	4502	2.13	0.68	877	2.77
B/NNN1	1/1 (BTESB/TMPET)	2.3	2	1.47	1300	2.49	0.30	311	3.24
B/NNN2	2/1 (BTESB/TMPET)	1.5	397	0.70	357	2.89	0.97	760	2.81
B/NNN4	4/1 (BTESB/TMPET)	1.4	438	0.69	612	3.10	0.34	346	3.23

K_d stands for distribution coefficient, K_β - binding constant with N-active site

To assess the features of location and reactivity of functional groups, copper(II) and nickel(II) ions adsorption studies were conducted by batch method in static conditions. Analyzing heavy metal ions uptake, the higher the C_{NNN}, the higher SSC(Cu^{2+}); however, no such dependency is observed for Ni^{2+}. Comparing the K_d values, majority of the samples have a better affinity for Cu(II) rather than Ni(II) ions, with E/NNN4 as the most selective. The exception is phenylene-bridged material B/NNN2, favouring Ni^{2+}, which demonstrated SSC(Ni^{2+}) = 0.97 mmol/g. Such behaviour may be connected with its higher hydrophobicity compared to the other samples.

According to the complexes structure calculations (see K_β values in Table 1), each of the Cu^{2+} (or Ni^{2+}) ions appears to coordinate with 2÷3 active N-containing sites on the surface. These calculations correlate with the UV-Vis spectra of the samples also indicating the engagement of 2 or 3 nitrogen atoms from amines in the coordination spheres of copper(II) ions [3]. Taking, into consideration, that the materials were functionalized with diethylenetriamine functions, the ratio of Metal(II) ion : Ligand on the surface of each of the samples is 1 : 1. Other free slots in the surface complex appear to be occupied by water molecules. It also should be mentioned, that and intence absorption band in the FTIR spectra of all the Cu^{2+}(Ni^{2+}) samples from the NO^{3-} ions suggests their involvement in the surface complex.

Summarizing, the properties of organosilicas with diethylenetriamine functional groups largely depend on the synthetic conditions, namely the reagents ratio. Identification of the metal ions complexes on the surface of the silica is important both for the characterization of the sorbents and for the evaluation of potential possibilities of their application.

Keywords: *organosilica, (propyl)diethylenetriamine groups, sorbents, copper(II) ions, nickel(II) ions*

References

[1] I.V. Melnyk, V.V. Tomina, N.V. Stolyarchuk, M. Václavíková, Nanoscience and Nanotechnology in Security and Protection against CBRN Threats. NATO Science for Peace and Security Series B: Physics and Biophysics. Springer: Dordrecht, 2020, 67-73.

[2] V. Tomina, N. Stolyarchuk, E. Dutková, J. Briančin, O. Semeshko, I. Melnyk, Proceedings of the XXXIII Scientific Symposium with International Participation 'Situation in ecologically loaded regions of Slovakia and Central Europe', 24-25 October, 2024, Hradok, Slovakia, pp. 209-215.

[3] I.V. Melnyk, V.V. Tomina, N.V. Stolyarchuk, G.A. Seisenbaeva, V.G. Kessler, Journal of Molecular Liquids, 336 (2021) 116301.

Acknowledgments: *Current research is financially supported by Visegrad Scholarship ID#52410608, VEGA 2/0138/24, and HORIZON-MSCA-2022-SE-01 (CLEANWATER - 101131382) projects.*

Recent developments in photocatalytic water pollution control technology: Hetero-nanostructured g-C_3N_4@$CuFe_2O_4$ nanoparticles for organic Dye treatment

M. Abid[1]*, L. Zauška[2], M. Almáši[2], J. Silvestre-Albero[1]
[1]Advanced Materials Lab, Inorganic Chemistry Department, University of Alicante, Ap. 99, E-03080, Alicante, Spain
[2]Department of Inorganic Chemistry, Faculty of Science, P. J. Šafárik University, Moyzesova 11, Košice, 04101, Slovak Republic
**Corresponding Author: abidmeriem095@gmail.com*

Water contamination by dyes is a major global issue, posing serious threats to aquatic life and, indirectly, to the broader ecosystem and human health. The use of reactive dyes has risen across various industries, necessitating effective removal methods. Advanced oxidation technologies (AOTs), particularly photocatalytic degradation, have emerged as efficient solutions. Unlike conventional methods (e.g., adsorption, chemical coagulation), which transfer dyes from liquid to solid phase, photocatalysis breaks down pollutants almost entirely, avoiding secondary pollution and providing a more eco-friendly approach [1]. Nanoparticles (NPs) are currently extensively utilized in various fields, such as medicine, solar energy, water treatment, and pollution detection. Recently, graphitic carbon nitride has been a research hot pot in the removal of water contaminants due to its outstanding properties like nontoxicity, low cost, facile synthesis, good stability, and visible-light absorption band-gap (2.73 eV) [2]. So far, the combination of ferrite and carbon-based nanomaterials as catalysts for the degradation of organic pollutant compounds has been rarely reported.

A new type of g-C_3N_4/$CuFe_2O_4$ composite photocatalyst has been prepared by a facile synthesis approach using the wet impregnation method followed by the calcination process.

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In comparison to other catalysts within the same domain (water media), the g-C_3N_4/$CuFe_2O_4$ heterostructure synthesized in this study demonstrated exceptional catalytic activity in the photodegradation of blue methylene. These findings could serve as a foundation for the development of highly effective photocatalytic degradation methods that may be employed in the future for the removal of hazardous dyes from contaminated water.

Keywords: *water contamination, photocatalytic degradation, reactive dyes, graphitic carbon nitride (g-C_3N_4), g-C_3N_4/$CuFe_2O_4$ composite*

References

[1] B. Palanivel, et al., Materials Science in Semiconductor Processing, 100 (2019) 87.
[2] F.W. Owa, Int. Lett. Nat. Sci, 8 (2014) 1.

Acknowledgments:

This work was supported by HORIZON-MSCA-2022-SE-01 (CLEANWATER - 101131382) project.

Authors acknowledge financial support from MINECO (Project PID2022 142960OB-C21) and Conselleria de Innovación, Universidades, Ciencia y Sociedad Digital (Project CIPROM/2021/022).

This work was supported by APVV SK-CZ RD 21-0068.

Photocatalytic degradation of Imidacloprid pesticide using graphite/TiO_2 hybrid nanocomposites

S.J. Segovia-Sandoval and J. Silvestre-Albero
Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica-Instituto Universitario de Materiales, Universidad de Alicante, Ap. 99, E-03080, Alicante, Spain
**Corresponding Author: sonia.segovia@ua.es*

In recent decades, the presence of emerging pollutants (EPs) in aquatic environments has become a global concern. These pollutants include pesticides, pharmaceuticals and personal care products (PPCPs), endocrine-disrupting chemicals (EDCs), and others. They are commonly detected in wastewater, surface water, groundwater, and even drinking water at alarming concentrations, posing significant risks to human health and aquatic ecosystems [1]. As a result, developing effective technologies to remove EPs from water is essential. Among the alternative approaches, photocatalysis not only degrades chemically stable and non-biodegradable organic pollutants but also efficiently breaks down trace organic contaminants.

Titanium dioxide (TiO_2) is perhaps the most commonly used photocatalyst. Its advantages include high stability, low cost, chemical and biological inertness, and ease of production. However, its limitations—such as its ability to absorb light only in the UV region and the rapid recombination of photo-generated electron-hole (e^-/h^+) pairs— have driven significant efforts to develop more efficient photocatalysts. In this context, combining TiO_2 with graphene or graphene derivatives has gained attention. These materials exhibit broad absorption in the visible light spectrum, high surface area, excellent stability, high electrical conductivity, and superior charge mobility. This combination is expected to enhance the photocatalytic activity of the newly developed hybrid nanocomposites. Graphene (or its derivatives) acts as an electron sink, extending the lifetime of photogenerated charges and thereby reducing recombination [2]. The main goal of this study was to evaluate the photocatalytic performance of graphite (G)/TiO_2 hybrid nanocomposites (ratios of 1:4 and 1:9), synthesized via an impregnation method, in degrading the pesticide imidacloprid, chosen as a representative emerging pollutant. In the second stage, graphene functionalized with 2.5% and 5% oxygen will also be used to impregnate TiO_2.and these composites will be tested against other concerning pollutants, such as antibiotics in different water matrices.

Batch photocatalytic experiments were performed in a 200 mL glass beaker containing 100 ML of IMI solution (15 mg/L, pH7) and a photocatalyst loading of 0.25g/L. The suspension was magnetically stirred and kept in the dark for 60 min to achieve adsorption equilibrium. The photocatalytic reaction was then initiated by continuously irradiating the suspension with UV light using a custom-built photoreactor at room temperature. Aliquots of 1 mL were collected every 60 min over a 6-hour period, filtered with a syringe filter (PES, 0.45 m), and analyzed by a UV-Vis spectrophotometer.

Fig. 1 shows the degradation percentage ($\%X_{IMI}$) of IMI using Graphite, TiO_2, and G/TiO_2 nanocomposites with ratios 1:4 and 1:9. Among the tested materials, the G/TiO_2 (1:4)

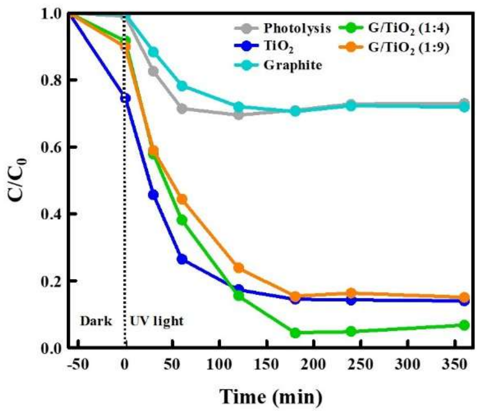


Fig. 1. IMI photocatalytic degradation using G, TiO_2, G/TiO_2 hybrid nanocomposites with different ratios (1:4, 1:9 wt.%) and photolysis test.

Table 1. The initial concentration (C_0), the adsorption (%Ads_{IMI}) and degradation (%X_{IMI}), percentage of IMI, the second-order rate constant (k_2), the determination coefficient (R^2).

PC (m = 25 mg)	**C_0 (mg/L)**	**%Ads $_{IMI}$ t = 60 min**	**%X $_{IMI}$ t = 360 min**	**K_2 * 10^{-2} (L mg^{-1} min^{-1})**	**R^2**
Photolysis	15.79	0.99	28.33	0.3408	0.7622
Graphite	15.81	0.34	29.20	0.2377	0.8299
TiO_2	14.72	25.33	81.22	2.4533	0.9937
G/TiO_2 (1:4)	12.23	8.41	95.05	2.8612	0.9791
G/TiO_2/G (1:9)	15.31	10.16	83.17	1.9161	0.9940

composite demonstrated the highest performance, achieving 95% degradation (%X_{IMI}) in 180 min, compared to 81% for TiO_2 and 83% for G/TiO_2 (1:9). Furthermore, the k_2 value of G/TiO_2 (1:4) was 1.17-fold and 1.49-fold higher than those of TiO_2 and G/TiO_2 (1:9), respectively. G acts as an electron bridge, promoting the separation of photogenerated charges and enhancing the photocatalytic degradation of IMI. Table 1 summarizes the %X_{IMI}, the k_2 constants of the second-order kinetic model, and the determination coefficient (R^2) for the photocatalytic experiments using the prepared nanocomposites.

Keywords: *pesticide, graphite, TiO_2, photodegradation*

References

[1] Zhao, L., Deng, J., et al., Science of the Total Environment, 627 (2018) 1253.
[2] Luna-Sanguino, G., et al., Science of the Total Environment, 737 (2020) 140286.

Acknowledgments: *The author thanks the support of the HORIZON-MSCA-2022-SE-01 project "CLEANWATER" (Grant Agreement 101131382).*

Photodegradation of ofloxacin over ZnO-based nanocatalysts under visible and UV irradiation

O. Makota[1,2]* and I. Melnyk[1]
[1]*Institute of Geotechnics of the Slovak Academy of Sciences, Watsonova 45, Košice, 04001, Slovak Republic,*
[2]*Institute of Chemistry and Chemical Technologies, Lviv Polytechnic National University, Stepana Bandery 12, Lviv, 79013, Ukraine*
**Corresponding Author: makota@saske.sk*

Safe and clean water is vital for human survival. However, urbanization and population growth have led to the widespread use of pharmaceuticals, especially antibiotics, resulting in significant environmental pollution. Ofloxacin belongs to a widely available class of quinolone antibiotics with a high and broad spectrum of antibacterial activity and is commonly used in the treatment of various diseases. On the other hand, ofloxacin is a weakly metabolized antibiotic with genotoxic effects. Photocatalysis is an effective and "green" method for wastewater purification. Among the various catalysts used in this process, nanocatalysts based on the semiconductor zinc oxide (ZnO) are considered highly promising due to their simple preparation, high photosensitivity, good chemical stability, low cost, and environmental friendliness.

In this work, ZnO was synthesized by the homogeneous precipitation method. Magnetic properties and visible light photocatalytic ability were introduced to ZnO by combining it with magnetite (Fe_3O_4) and the narrow band gap semiconductor $Bi_2O_{2.7}$, forming double (Fe_3O_4@ZnO) and ternary (Fe_3O_4@ZnO@$Bi_2O_{2.7}$) composites. The structures of the prepared samples were studied using XRD, SEM, XPS, zeta potential measurements, and low-temperature nitrogen adsorption/desorption techniques.

The synthesized samples were tested as photocatalysts for the photodegradation of ofloxacin under UV and visible light irradiation (Fig. 1). It was established that uncatalyzed photodegradation and adsorption did not occur, indicating the high stability of the pollutant under UV irradiation and allowing the exclusion of ofloxacin adsorption by the synthesized samples from the degradation process.

The photocatalytic removal of the pollutant was found to proceed more than twice as fast under UV irradiation compared to visible light treatment. The catalytic activities of ZnO and Fe_3O_4@ZnO were similar in the removal of ofloxacin under visible irradiation, while under UV irradiation all samples exhibited similar and very high efficiency. Fe_3O_4@ZnO@$Bi_2O_{2.7}$ demonstrated the highest performance in ofloxacin photodegradation under visible light, whereas ZnO showed the best results under UV treatment. The degradation efficiency reached up to 100%, 94%, and 96% under UV treatment and 35%, 32%, and 45% under visible light irradiation for 4 hours for ZnO, Fe_3O_4@ZnO, and Fe_3O_4@ZnO@$Bi_2O_{2.7}$, respectively. It was shown that the photocatalytic degradation of ofloxacin under visible and UV treatment can be well described by the pseudo-first-order kinetic model.

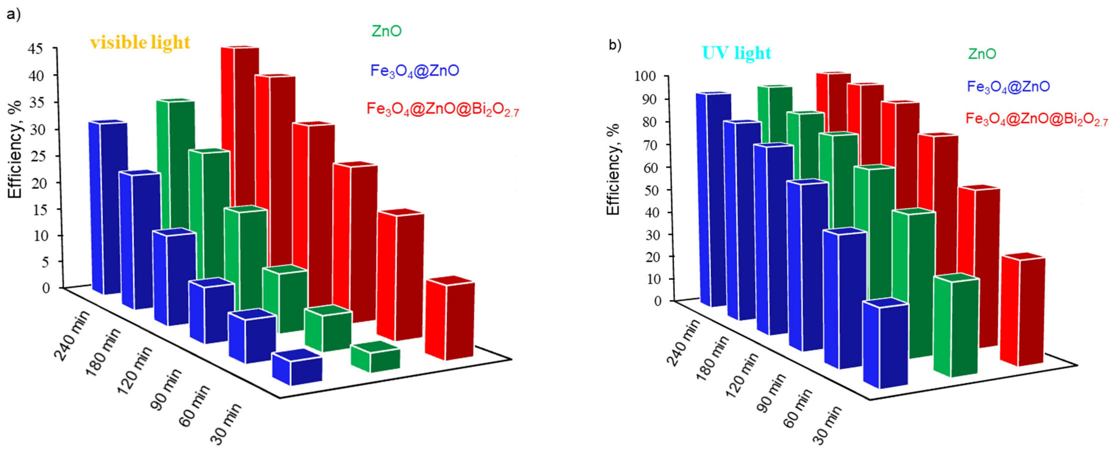


Fig. 1. The percentage of photocatalytic degradation efficiency of ofloxacin over ZnO, Fe_3O_4@ZnO and Fe_3O_4@ZnO@$Bi_2O_{2.7}$ photocatalysts under visible (a) and UV (b) irradiation.

Therefore, all synthesized samples exhibited excellent photocatalytic performance for ofloxacin removal under UV.

Keywords: *ZnO, photocatalysis, ofloxacin, visible and UV irradiation*

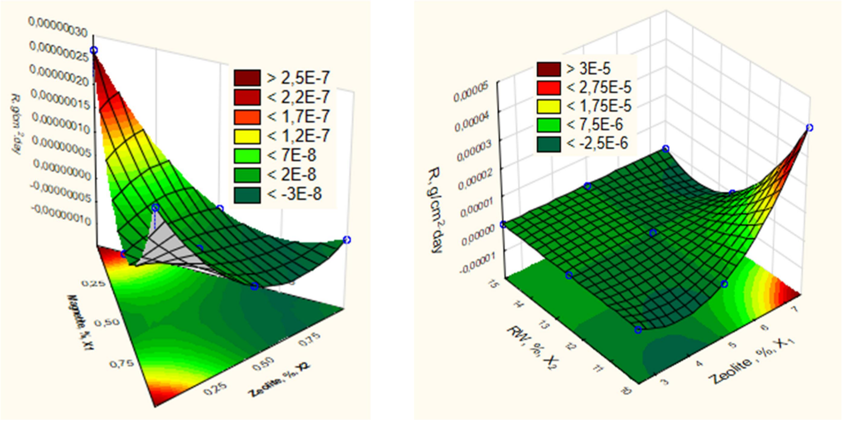
Acknowledgments: *This research was funded by the EU's NextGenerationEU through the Recovery and Resilience Plan for Slovakia under project number 09I03-03-V01-00108, as well as by the VEGA 2/0108/23, VEGA 2/0138/24 projects.*

Immobilisation of treatment products of radiation contaminated water with alkaline binder compounds

S.G. Guzii
State Institution "The Institute of Environmental Geochemistry" of National Academy of Sciences of Ukraine, Akademika Palladina Ave 34A, Kyiv, 02000, Ukraine
**Corresponding Author: sguziy2@gmail.com*

Water is one of the most precious resources on our planet, essential for sustaining life and ecosystems. However, with increasing pollution and growing demand, the importance of effective water treatment of wastewater and radiation contaminated water cannot be overstated. In addition to the treatment itself, it is also important to dispose of water treatment products to prevent their proliferation and pollution of the environment.

The current practice of liquid radioactive waste management is to store solid and vaporised radioactive waste in special storage facilities at NPP sites and can be consider only as a temporary measure. Unfortunately, most of the currently available projects and programmes mainly envisage engineering methods of safe conditioning and disposal, which cannot be recognise as reliable even for the next 100 years of storage. This is due to the fact the existing methods of radioactive waste management we based on its compaction in cement or bitumen matrix, which, due to their nature, are incompatible with liquid radioactive waste and only provide for its physical binding.



a b

Fig. 1. Isoparametric diagrams of leaching rates of compositions based on alkaline cement (a) and geocement (b) depending on the amount of additives and leaching time.

A fundamentally new approach to solving this problem they propose based on the creation of a mineral-like durable matrix due to the chemical binding of radionuclides in its composition. Such matrices include advanced alkali-activated binding systems, namely alkaline cements and geocements (geopolymers), in the structure of which hazardous elements we blocked not only mechanically, but also mainly due to adsorption and chemical binding. Below are the data on the chemical resistance of composites based on alkaline cement and geocement matrices (Fig. 1, a, b), obtained by the method of long-term chemical leaching.

Alkaline cement-based compounds include magnetite and zeolite additives in addition to the vaporised radioactive waste. Compounds based on geocement include γ-weakening additives (WNi, $MoSi_2$, B_4C), zeolite and radioactive waste. The leaching rate of the first type of compounds at 270 days is 2.55-2.69 E-7 $g/cm^2 \cdot day$; the second type of compounds at 28 days is 4E-5 $g/cm^2 \cdot day$ [1, 2].

The difference in the leaching rates depending on the term they explained by the differences in the composition of cement new growths. For example, in alkaline cement, the predominant formations we represented by low-base calcium hydrosilicates, tobermorytes, pectolites, and a small amount of zeolite-like hydroalumina phases $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot H_2O$ [3]. These phases, except for hydroalumino silicate, have a low sorption capacity. In geocement, the new formations are represented by a mixture of heulandite-clinoptilolite-mordenite phases $Na_2O \cdot Al_2O_3 \cdot (6\text{-}8)SiO_2 \cdot (15\text{-}17.5)H_2O$, which have a high sorption capacity. Radionuclides present in such a matrix are reliably and mechanically blocked in micropores due to its high density and impermeability, partially ‘locked’ (packed) in a three-dimensional lattice due to the energy unsaturation of the zeolite structure sorption binding and partially bound due to their inclusion in the above-mentioned zeolite-like formations chemical binding [4]. Such compounds are characterised by extremely low solubility and chemical stability in time.

Keywords: *alkaline binder, compound, immobilisation, leaching rate, radioactive waste*

References

[1] S. Guzii, B. Zlobenko, Application of alkali-activated cements for immobilization of dry low-level radioactive waste containing copper ferrocyanide, proceedings of the 7th annual conference Technology transfer: fundamental principles and innovative technical solutions, 2023, pp. 3–8.

[2] S. Guzii, Solid State Phenomena, 364 (2024) 113.

[3] S. Guzii, The use of alkaline slag-portland cement matrices for immobilisation of low-active water treatment products, Problems of decommissioning of nuclear power facilities and Environmental Restoration (INUDECO 24): Proceedings of the IX International Conference (24-26 April 2024, Slavutych), Chernihiv: National University of Chernihiv Polytechnic, pp. 40-50.

[4] D.W. Breck, Zeolite Molecular Sieves. Structure, chemistry and use, John Wiley&Sons, New York, London, Sydney, Toronto, 1974, 781 p.

Acknowledgments: *The work carried out within the framework of the EURAD-2 project and was co-funded by the European Union under Grant Agreement No 101166718.*

Adsorption of hexavalent chromium cations on copolymers of divinylbenzene and maleimide anhydride

M. Parcheta and M. Sobiesiak
Maria Curie-Skłodowska University, Department of Polymer Chemistry,
Maria Curie-Skłodowska 3, Lublin, 20-031, Poland
**Corresponding Authors: monika.parcheta@umcs.mail.com,*
magdalena.sobiesiak@mail.umcs.com

Chromium is a metal that occurs in small amounts in nature, most often in the form associated with other metals - mainly iron. Chromium in the third oxidation state is the most stable form of this element in the environment and biological systems. Chromium in the +I, +IV and +V oxidation states occurs rarely in nature. Chromium compounds in the VI oxidation state are strong oxidants. The most abundant chromium mineral is chromite: $FeCr_2O_4$, in which chromium takes on the third oxidation state. Chromite is a mineral found in Zimbabwe, Russia, Turkey, Iran. Approximately 95% of chromium resources are located in southern Africa. Chromium is used in the metallurgical industry, in the production of steel and iron alloys, in the production of fire-resistant materials, the chemical industry in such industrial processes as leather tanning, ore refining, wood preservation or galvanization. Cr (III) is an essential trace element in the human body. In combination with some enzymes, it participates in the processing of sugars, fats and proteins. Water-soluble Cr (III) compounds can irritate the eyes and skin, which is related to their acidic nature. It has been proven that Cr III does not have carcinogenic properties for humans and animals, unlike Cr (VI) [1]. Cr (VI) as a component of leather clothing can cause allergic reactions, e.g. skin rashes, inhalation of Cr (VI) fumes can result in nosebleeds. Other ailments caused by exposure to Cr (VI) include stomach ulcers, weakening of the immune system, breathing problems, kidney and liver damage, changes in genetic material or lung cancer. The World Health Organization recommends that the maximum permissible concentration of Cr (VI) in drinking water should not exceed 0.05 mg/L of total chromium [2].

The article discusses the sorption capacity of divinylbenzene (DVB) and maleic anhydride (MA) copolymers for hexavalent chromium. DVB and MA copolymers were obtained by block polymerization in monomer molar ratios of 1:1, 1:2 and 2:1, in a mixture of decanol and benzyl alcohol as pore-forming diluents, mixed together in a volume ratio of 1:3. The sorption process was carried out using stationary and dynamic sorption methods. In the stationary sorption method, aqueous solutions of Cr (VI) with a concentration of 10-80 mg/L were used for the tests, while in the dynamic method, the samples were concentrated with an aqueous solution of Cr (VI) with a concentration of 1 mg/L. In Fig. 1 the Langmuir isotherms for Cr (VI) removal on studied copolymers are presented.

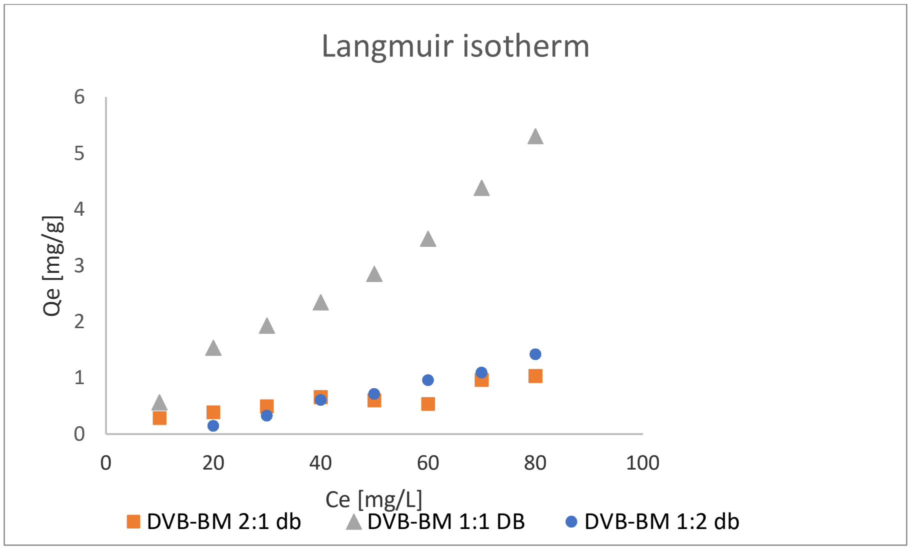


Fig.1. Langmuir sorption isotherms for Cr (VI) removal on studied copolymers.

The chromium content in the solution was determined by the spectrophotometric method, and the changes in Cr (VI) concentration in the tested solutions were assessed based on the calibration curve (356 nm). The stationary sorption results were presented in the form of adsorption isotherms including the Langmuir and Freundlich models, while the results of the dynamic method were presented in the form of column breakthrough curves.

Regardless of the sorption method used, the best ability to remove Cr (VI) from aqueous solution was demonstrated by the DVB-BM 1:1 copolymer. In the dynamic approach, the total mass of Cr (VI) retained on the bed was 0.23 mg/g. DVB-MA copolymers in the monomer molar ratio of 1:2 and 2:1, respectively, showed similar Cr (VI) sorption capacities of 0.13 and 0.14 mg/g, respectively.

Keywords: *DVB, maleimide anhydride, chromium, dynamic sorption, Langmuir, Freundlich*

References

[1] A. Zaidi, P. A. Vani, M. S. Khan, Toxicity of Heavy Metals to Legumes and Bioremediation, ISBN 978-3-7091-0729-4, Springer-Verlag Wien, 2012, 64.

[2] R. Rakhunde, L. Deshpande, H. D. Juneja, Critical Reviews in Environmental Science and Technology, 42:7 (2012) 777.

Acknowledgments: *This work was financially supported by Project: 101131382 – Cleanwater in the frame of Horizon MSCA -2022-SE-01 program.*

Ecotoxicity assessment of graphene oxides using aquatic test organisms from hierarchical trophic levels to evaluate their potential environmental risk

Mónika Molnár[1]*, Imre Németh[1], Anna Bulátkó[2], Emese Vaszita[1], Krisztina László[2]
[1] Department of Applied Biotechnology and Food Science, Budapest University of Technology and Economics, Műegyetem rkp. 3., Budapest, 1111, Hungary
[2]Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, Műegyetem rkp. 3., Budapest, 1111, Hungary
**Corresponding Author: molnar.monika@vbk.bme.hu*

Despite more than ten years of research on the ecotoxicity of graphene oxide nanomaterials (nGOs), numerous reports concluded that environmental risk assessment studies of graphene-based materials were still very limited. The results of these studies demonstrated that the ecotoxicity assessments conducted among various nGOs are based mainly on selected single-species tests, while their effects at the community level are understudied [1]. The objective of this complex research [2] was twofold: first, to examine the toxicity of two GO types from different graphite precursors (AF 96/97 and PM 995) on various test organisms from diverse trophic levels in aquatic environments, including microorganisms, microbial communities, protozoa, nematodes, and plants. Secondly, to compare the impacts of nGO and establish the effective concentration values for each test organism aiming to develop initial PNEC values that aid in the primary risk characterisation of the tested nGOs.

The ecotoxicity and the mechanism of nGO-mediated toxicity were evaluated by various methods. Different test systems were applied with distinct test organisms from several trophic levels to measure the toxicity of GO nanoparticles. Besides, a systematic study was performed to determine the influence of GOs on the metabolic activity and functional diversity of freshwater microbial community of Lake Balaton.

The concentration- and time-dependent effects of graphene oxides was assessed and evaluated at all levels of the ecotoxicity test systems. Comprehensive concentration-response analysis was carried out to determine the effective concentration values (EC_{20}, EC_{50}) causing 20 and 50% inhibition on the observed endpoint. Table 1 provides a summary of the EC_{20} values for both GO suspensions across all test systems and endpoints, with data presented for different contact times. The EC_{20} values indicate the presence of more toxic effects in red (and its shades), while green (and its shades) indicate lower ecotoxicity. Our results showed that 0.004 mg/L nGO concentration had a significant negative effect on the growth and enzymatic activity of *Tetrahymena pyriformis* after 24 hours. Therefore, the smallest EC_{20} values were calculated for this protozoon, which indicates that *T. pyriformis* was the most sensitive among the applied test organisms. The Predicted No Effect Concentrations (PNECs) were determined from the EC values (EC_{20}) and were used to calculate risk characterization ratios for aquatic ecosystems.

Table 1. EC_{20} values [mg/L] of the tested GO suspensions for the examined test organisms.

Examined endpoint of the test	**Incubation time**	**AF 96/97**	**PM 995**
		EC_{20} [mg/L]	EC_{20} [mg/L]
Escherichia coli enzyme activity	24 h	3.97	2.57
Aliivibrio fischeri bioluminescence intensity	30 min	5.86	5.06
	120 min	4.01	4.40
Aliivibrio fischeri enzyme activity	120 min	22.86	16.13
Tetrahymena pyriformis reproduction	24 h	0.008	0.033
	48 h	0.011	0.004
Tetrahymena pyriformis enzyme activity	24 h	0.038	0.020
	48 h	0.014	0.004
Panagrellus redivivus mortality	24 h	79.74	217.56
	72 h	56.09	11.33
Sinapis alba root length	72 h	76.71	40.73
Sinapis alba shoot length	72 h	380.13	554.01
Triticum aestivum root length	72 h	224.78	392.53
Triticum aestivum shoot length	72 h	223.98	203.49

The PNEC values for GO AF 96/97 and GO PM 995 were estimated as 8 ng/L and 4 ng/L, respectively. The level of the potential environmental risk can be characterized by the risk characterization ratio (RCR), which is the quotient (RCR=PEC/PNEC) of the predicted environmental concentration (PEC) and the predicted no effect concentration (PNEC), which probably does not affect the ecosystem adversely. To determine the PEC value, the environmental concentrations based on the literature were considered.

The results obtained have clearly demonstrated that the reliable characterisation of the effect of GO NMs on the aquatic ecosystem requires a complex ecotoxicity test-battery including organisms from different trophic levels and with various exposure routes.

Even after applying the worst-case scenario approach, the tested GO NMs pose no environmental risk.

Keywords: *ecotoxicity, environmental risk assessment, graphene oxide, nanomaterials, predicted no effect concentration*

References

[1] A.N. Ghulam, et al., Journal of Functional Biomaterials, 13 (2022) 77.

[2] I. Németh, K. László, A. Bulátkó, E. Vaszita, M. Molnár, Nanomaterials, 13 (2023) 2858.

Acknowledgments: *This research was supported by the Hungarian National Scientific Research Programmes (NRDI K128410 and K143571) and the Hungarian National Research, Development and Innovation Office Fund in the frame of the TKP2021-EGA-02. This work is part of the HORIZON-MSCA-2022-SE-01-01 project CLEANWATER (#101131382).*

Targeted photoluminescent detection of doxycycline in wastewater using silica-lanthanide nanoprobes

O. Semeshko[1,2]* and I. Melnyk[1]
[1]*Institute of Geotechnics SAS, Watsonova 45, Košice, 04001, Slovak Republic*
[2]*Kherson National Technical University, Instytutska 11, Khmelnytskyi, 29016, Ukraine*
**Corresponding Author: semeshko@saske.sk*

Monitoring the presence of antibiotics in aquatic ecosystems is a crucial task in modern ecology and public health, as the excessive accumulation of these substances can lead to the development of microbial resistance and negatively affect biodiversity. A particular threat comes from antibiotic residues in wastewater, which can enter natural water bodies. Notably, the tetracycline antibiotic doxycycline has been reported to be present in the environment, with significant amounts originating from hospitals and households due to its widespread use in treating COVID-19 globally in recent years. Therefore, the detection of antibiotics, particularly doxycycline, in water is currently a significant scientific challenge.

This study presents the development of a sensor for detecting doxycycline, based on a silica-containing adsorbent with sorbed europium ions. To enhance the sensor's signal and improve its sensitivity for detecting the antibiotic, cerium and lanthanum ions, derived from used batteries, were simultaneously adsorbed. The use of secondary sources of rare-earth elements not only reduces the cost of sensor production but also contributes to environmentally safe waste management. The synthesis of silica adsorbents using silica obtained from minerals is another important ecological aspect of this technology. Thus, the proposed approach combines eco-friendly waste utilization with an efficient method for controlling antibiotic pollution in water, making it promising for further development in environmental monitoring.

A bifunctional adsorbent based on silica nanoparticles obtained from mineral and silanes with diamine and phenyl groups was synthesized. Investigations into the morphology, structure, chemical composition, and electrical properties of the synthesized adsorbent confirmed that the functionalized silica particles have a size of 50-60 nm, exhibit a non-porous structure (although, due to the packing of equally sized particles, they have a large sorptive volume), and possess diamine and phenyl groups on their surface. The presence of lanthanide ions on the surface of the sample after adsorption from a ternary ion mixture has been confirmed through ICP-MS method, EDXS analysis and XPS spectroscopy. Considering the pH value of the solution during ion sorption (6.5), where lanthanides are present in solution as ions, it is hypothesized that lanthanides are sorbed in the form of ions with a valence of III due to complex formation with the amino groups of the adsorbent.

Subsequently, photoluminescent (PL) spectra of the suspension containing lanthanide ions were recorded in the presence of doxycycline at excitation wavelengths characteristic of each lanthanide ion. La(III) does not exhibit photoluminescence due to the absence of f-f transitions. At an excitation wavelength of λ_{ex} = 264 nm, typical for cerium ions, no enhancement of photoluminescence was observed. However, at an excitation wavelength of

λ_{ex} = 396 nm, characteristic of Eu(III) ions, narrow intense bands and an increase in photoluminescence intensity from 3735 to 143,867 arbitrary units at the emission wavelength of λ_{em} = 616 nm were observed, indicating an "antenna" luminescence response. It is worth noting that at the excitation wavelength of λ_{ex} = 396 nm, the silica-containing fragments of the synthesized adsorbent did not affect photoluminescence. Therefore, it is clear that the obtained materials can be used as sensors for detecting doxycycline.

It was established that the highest photoluminescence intensity values were observed under the following conditions for sensor use in suspensions: pH = 8-9 (natural pH of the suspension), ionic strength created by 0.05 M KCl, contact time limited to 3 hours, and a suspension concentration of 0.1 g/L. When examining the effect of doxycycline concentration on the sensor's photoluminescence response, it was found that the sensor demonstrated a linear response to doxycycline in the concentration range of 0.005–10.0 µM, with a correlation coefficient $R^2 = 0.9993$. The detection limit for doxycycline was 0.15 µM (0.07 mg/L), and the quantification limit was 0.44 µM (0.2 mg/L), indicating that the suspension can be used as a highly sensitive tool for detecting doxycycline in aqueous solutions. Studies on the influence of known concentrations of substances and ions that may be present in hospital wastewater demonstrated the selectivity of the suspension for doxycycline.

The obtained photoluminescence spectra of systems containing individual lanthanide ions and their binary combinations, as well as solutions of lanthanide salts at concentrations equivalent to those during sorption, allow for the following conclusions. The high sensitivity in the photoluminescent detection of doxycycline using the silica matrix with adsorbed La, Ce, and Eu ions is due to the luminescent response of Eu(III) to doxycycline via the "antenna effect" and intermolecular energy transfer from La(III) to neighboring Eu(III) ions, as well as electron transfer between Ce(III) and Eu(III) ions. Additionally, the synthesized silica with diamine and phenyl groups serves as a matrix for lanthanide immobilization, prevents the quenching of Eu(III) luminescence, and can enhance photoluminescence through π-conjugation of phenyl groups.

Thus, an effective and eco-friendly sensor for monitoring doxycycline in aquatic environments has been developed, based on a silica matrix with adsorbed La, Ce, and Eu ions, which is characterized by high stability, sensitivity, and selectivity.

Keywords: *silica particles; ethylenediamine groups; phenyl groups; rare earth ions adsorption; doxycycline sensing*

Acknowledgments: *Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V01-00098, and supported by VEGA 2/0138/24.*

Radon in drinking water

P. Addonizio, G. Buccheri*, R. Crisci and F. Di Guida
INAIL UOT CVR Napoli - Complesso INAIL, Edificio 11, Napoli, 80143, Italy
**Corresponding Author: g.buccheri@inail.it*

It is known that radioactive elements can be also found in drinking water. Presence of radon in drinking water can gradually cause severe diseases.

Radon is a radioactive noble gas, naturally existing as three isotopes: ^{222}Rn, ^{220}Rn, ^{219}Rn. ^{222}Rn is the most common radiogenic isotope of radon, derives from the natural radioactive decay of uranium, and it is almost ubiquitous in rocks, soil and water. It is abundant above all in volcanic areas. As a gas, radon can easily migrate through air and pores, and dissolve in groundwater [1]. In Italy, the percentage of water demands supplied by groundwater is about 91% [2].

While using tap water or during a shower, radon can enter the human body by ingestion or by inhalation: in fact, radon dissolved in water may be released into indoor air [3] and inhaled. While in contact with body tissues, ^{222}Rn can decay to other radioisotopes, releasing α particles that can cause biological damages to human tissues. Radon percentage in drinking water, that is released into indoor air, can be highly variable according to local conditions: total consumption of water, volume of the interior areas and their ventilation rate. Higher radon doses by inhalation may concern workers in water supplies [4].

The International Agency for Research on Cancer (IARC) included radon in the group 1 as a carcinogenic agent [5]. The World Health Organization (WHO) recognized radon as the second cause of lung cancer after smoking, and also set the radon guideline value for drinking water at 100 Bq/l [6]. In Italy, the Legislative Decree 15/02/2016 n. 28 and the Ministerial Decree 02/08/2017 adopted the Council Directive 2013/51/EURATOM, and rule about protection of people health against radioactive substances in water for human consumption.

Fig. 1. Alphaguard DF2000 equipment to measure radon concentration in water samples.

Table 1. Average ^{222}Rn in water samples from the investigated areas.

Area	^{222}Rn in water sample (Bq/l)
Napoli	1.74
Vesuvian villages	5.12
Santa Maria a Vico	2.25
Montesano sulla Marcellana	6.45

This abstract reports the first results of a research activity about radon content in some drinking waters, that INAIL is carrying out in Campania (Italy). INAIL is the Italian Workers' Compensation Authority, and its activity is also focused on evaluation and management of risks for workers' health, according to current laws.

Water samples have been collected both from some areas with volcanic substratum and from some other areas with calcareous substratum. The ^{222}Rn measurement equipment has consisted of an active mobile radonometer Alphaguard DF 2000 (Bertin), used in connection with its own AquaKIT accessory (Fig.1). Duration of measurements has been set at 30 minutes.

Results show that radon concentrations in the analyzed water samples do not exceed values that are provided by the Italian Legislative Decree 15/02/2016 n. 28 (Table 1).

Keywords: *radon, water, cancer*

References

[1] A. Iannone, S. Albanese, A. Guarino, M. Ambrosino, G. Germano, G. De Tullio, D. Cicchella, Journal of Hazardous Materials, 470 (2024) 134229.

[2] I. S. Zektser, L. G. Everett, Groundwater Resources of the World and Their Use, UNESCO: 2004.

[3] UNSCEAR, Sources and effects of ionizing radiation. Report to the general assembly, United Nations: New York, 2000.

[4] G. Cinelli, M. De Cort, T. Tollefsen, European Atlas of Natural Radiation, Publication Office of the European Union: Luxembourg, 2019.

[5] International Agency for Research on Cancer (IARC). Man-made mineral fibres and radon. IARC Monographs on the evaluation of carcinogenic risks to humans, Vol. 43, IARC: Lyon, 1988.

[6] World health organization guidelines for drinking water quality. Third edition, incorporating first and second addenda, Vol. 1, WHO Press: Geneva, Switzerland, 2008.

New cold plasma water treatment device for the removal of persistent contaminants

M. J. Illsley[1], Y. L. Zabulonov[2], and S. V. Mikhalovsky[1]
[1]*Anamad Ltd., Brighton & Hove, BN3 7GS, UK*
[2]*IGNS, Academician Palladin Ave 34a, Kyiv, 03142, Ukraine*
**Corresponding Author: matt.illsley@gmail.com*

The authors have installed a novel flow through plasma water treatment system (Fig 1) at Anamad in the UK and are replicating the results generated in our batch plasma reactor. Our experiments demonstrate the removal of pharmaceuticals, dyes, and plasticisers (Table 1).

Fig. 1. flow-through laboratory non-thermal plasma system.

Table 1. Energy required to remove persistent pollutants from water.

Pollutant	Type of pollutant	Energy required to reduce pollutant an order of magnitude (EEO), kWh/m^3
DNT	Polymer intermediate, POP	4.2
DDT	Pesticide, POP	3.8
EDTA	Chelator	1.5
Chloroform	Solvent	1
HCB	Fungicide, POP	0.49
TDA	Polymer intermediate, POP	0.87
Paracetamol	Pharmaceutical	2.5
Diclofenac	Pharmaceutical	3.8
Bisphenol A	Plasticiser, endocrine disrupter	4
Metaldehyde	Molluscicide	3
Propyzamide	Pesticide, POP	2
PFAS (PFOA+PFNA+PFBS+PFBA)	Forever chemicals	3
E. coli	Bacteria	0.07

Non-thermal plasma (NTP) is proving to be a cost-effective tool in the in situ destruction of persistent and difficult pollutants in flowing water, using only electricity, and without intervention of the user. We are investigating the use of NTP for the removal of PFAS, a growing issue in water treatment throughout the EU [1].

Keywords: *non-thermal plasma, decontamination, flow through reactor*

References

[1] S.Barisci, R.Suri, Water Sci.Technol., 84 (2021) 3442.

Acknowledgements: *we thank the support of Prof Zabulonov's Team at IGNS and funding from the Ofwat Water Discovery Challenge and EU Cleanwater (UKRI Guarantee: EP/Y037154/1).*

Workshop on Methods of Water Pollution Control

3–4 December, 2024
Košice, Slovakia

Book of abstracts

ISBN 978-80-89883-17-2

a member of Association of Slovak Scientific and Technological Societies
a basic unit at the Institute of Geotechnics SAS, Košice, 2024
Institute of Geotechnics SAS, Košice

Press: Institute of Geotechnics SAS