
Synthesis and Characterisation of Carbon Materials

CLEANWATER Project Workshop – Book of Abstracts



June 24–25, 2024

MARIA CURIE-SKŁODOWSKA PRESS

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Welcome Remark

Dear Friends and Colleagues,

On behalf of the Organizing Committee, we warmly welcome you to take part in the CLEANWATER Project Workshop on “Synthesis and Characterisation of Carbon Materials”, which will be held on June 24-25, 2024 at the Maria Curie-Skłodowska University in Lublin with hybrid format.

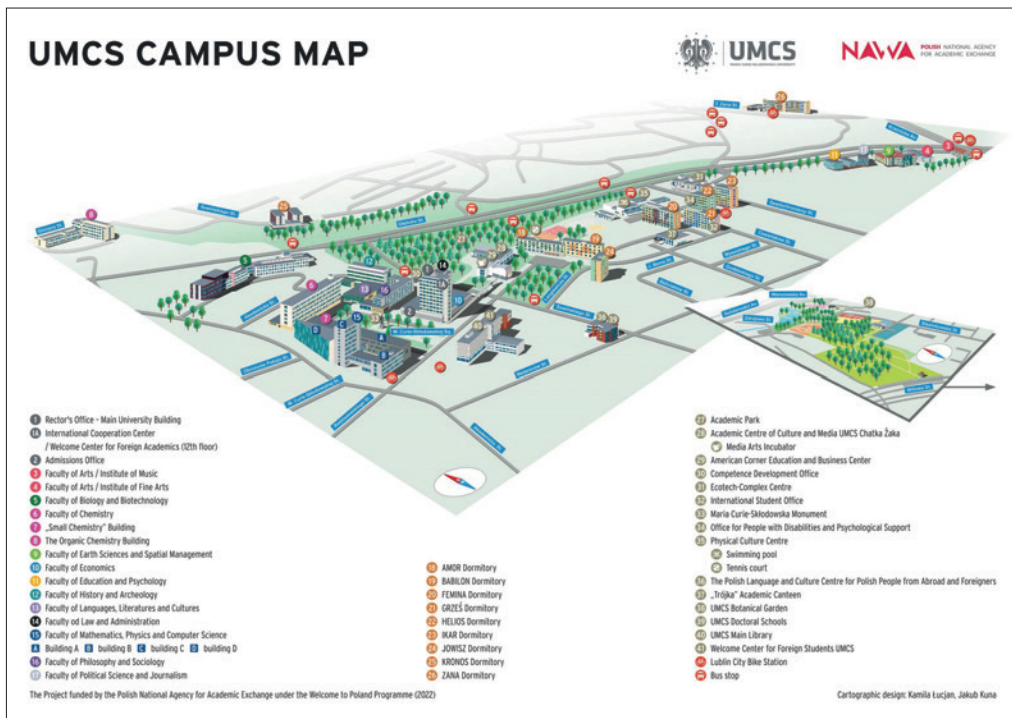
Workshop includes lectures delivered by outstanding scientists, as well as oral presentations and discussions. The main topic concerns the synthesis and characterisation of carbon materials. Scientific research regarding porous polymeric sorbents as well as catalyst, organometallic composites, plasma treatment and environmental protection cases were also welcome.

The workshop brings together scientists and specialists from universities, research institutes and non-academic institutions from all over the world. Project members at various stages of their scientific careers will share their exciting results and build new collaborations.

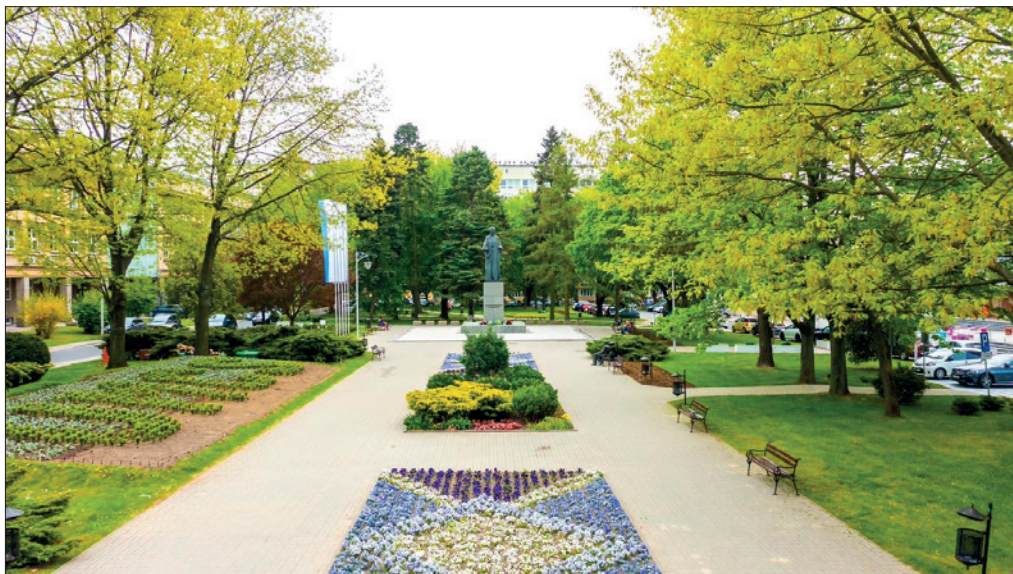
Participants’ great ideas and key discoveries will help develop novel aspects regarding the preparation and characterisation of various sorbents. Porous materials can be used for the efficient adsorption of heavy elements/metals including radionuclides, persistent organic pollutants and contaminants of emerging concern present in fresh water, as well as an enterosorbent compositions for health protection against chronic exposure of the population to the pollutants consumed with water and food intake

We hope you will join us and take part in a high interesting and engaging hybrid event. Your presence and deliberation will make this Workshop remarkably successful.

*Barbara Gawdzik
Przemysław Pączkowski*



Maria Curie-Skłodowska University (UMCS) Campus Map



Maria Curie-Skłodowska Monument (Maria Curie-Skłodowska Square)

LECTURES

Future of green hydrogen

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Currently, the dominant source of hydrogen production is natural gas (Fig. 1). It is responsible for approximately three quarters of the world's annual hydrogen production for own needs, amounting to approximately 70 million tonnes. This represents approximately 6% of global natural gas consumption.

Governments and companies are considering three main options to make the process cleaner. The first is „green hydrogen”, which uses water electrolysis powered by renewable energy. This would reduce emissions, but is still very expensive. The second option is the so-called „blue hydrogen”. It is made from natural gas, but the process produces greenhouse gases. Among others ExxonMobil and ENI (Ente Nazionale Idrocarburi – national hydrocarbon authority) are working on capturing CO₂ during this process, but the technology is still not refined and is expensive. The

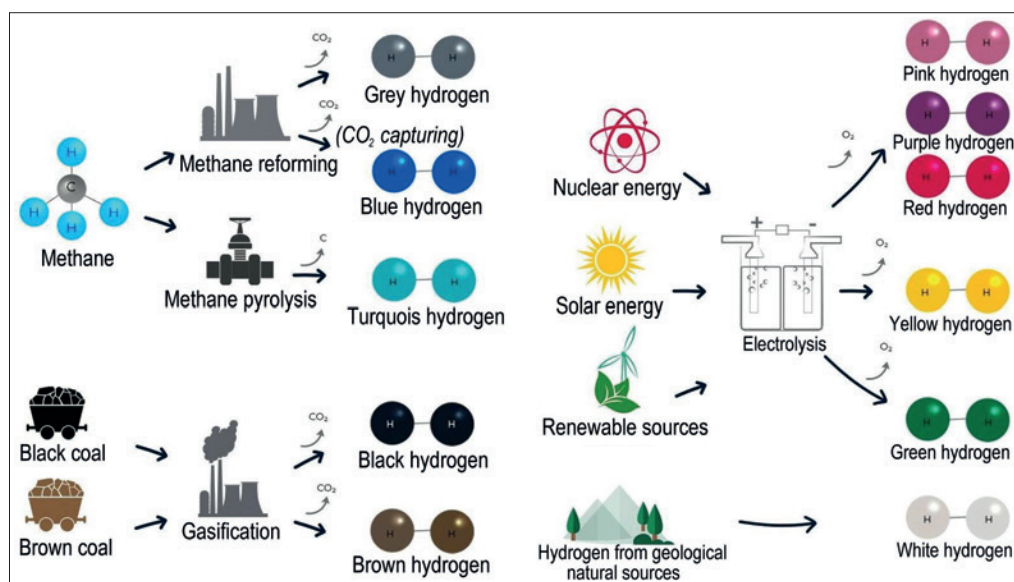


Fig. 1. Current directions for obtaining hydrogen.

third option is low-emission hydrogen produced by electrolysis, but using nuclear energy (so-called hydrogen: pink, purple, red). The main proponent of this method is China. However, nuclear energy is losing popularity in other parts of the world mainly due to public pressure.

Hydrogen production could increase to 300 million tonnes in 2050, with the majority of it being environmentally friendly, low-emission hydrogen. Currently, global production is approximately 115 million tons, of which hydrogen produced based on low-emission energy sources – the so-called blue or green hydrogen, constitutes less than 1%. The hydrogen market may almost triple by 2050 thanks to falling production costs, rising prices of CO₂ emission allowances and government subsidies for the implementation of hydrogen solutions. The price of blue and green hydrogen may fall, reaching as much as 1\$ per kg in the next 30 years (according to some sources, even 0.88\$/kg). However, on the other hand, the massive supply of hydrogen produced in the Russian Federation based on the natural gas deposits existing there may inhibit the development of green innovations in the production of this fuel on the European continent. Global electrolyzer capacity will need to increase 91 times by 2030 to meet demand. In the published EC report to the European Parliament and the Council on „Progress in competitiveness in clean energy technologies”, the production capacity of water electrolyzers in 2021 in Europe was estimated at 2.5 GW/year. Global production capacity was estimated at approximately 6–7 GW/year.

There is one significant bottleneck within hydrogen production technology. The use of platinum in currently used electrolyzers is unsustainable in the long term, not least because of the price. The carbon footprint of platinum mining and the low availability of the metal mean that the social and environmental consequences of its abundant use in fuel cells have drawn criticism.

After Russia's attack on Ukraine, the European Union, as part of the revision of its energy policy, significantly accelerated work on the development of green hydrogen. It is intended not only to replace some of the raw materials imported from the East, but also to constitute one of the key fuels for the energy transformation currently taking place and to be widely used in the future, among others. in transport, chemical industry and energy storage.

It is estimated that European countries will achieve a generation capacity of 40 GW of energy by 2040. In turn, according to the forecasts of the International Energy Agency (IEA), the production of green hydrogen in 2020 amounted to 0.2 million tonnes, but in 2040 it is expected to increase to 45 million tonnes per year (hydrogen is one of the leading energy storage options). The IEA predicts that by 2030, total industrial demand for hydrogen will increase by 44%, with clean, green hydrogen produced from renewable sources becoming increasingly important. However, on a global scale, it currently constitutes only about 5% of total production, and its production is still more expensive than obtaining it from fossil fuels.

Poland is currently the third producer of hydrogen in the European Union and the fifth in the world. Hydrogen is produced here in the natural gas reforming process or as part of the refining of crude oil. Poland produces over one megaton of gray hydrogen annually, obtained from natural gas (Fig. 2).

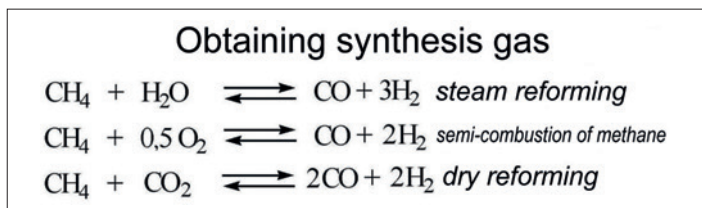


Fig. 2. Hydrogen from synthesis gas.

However, it should be noted that advanced work is underway in Poland to obtain green hydrogen using renewable energy sources.

Keywords: green hydrogen, environment

Organo-lanthanide adsorbents for the removal of geogenic pollutants from water

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The adsorption properties of organo-lanthanide adsorbents (synthesized with cerium, gadolinium, and ytterbium salts) for arsenic and fluoride removal were studied under batch adsorption conditions at 20, 30, and 40 °C and pH 7. The physicochemical properties of these adsorbents were determined by XRD, FTIR, SEM/EDX, N₂ physisorption and XPS analyses. The equilibrium adsorption data were correlated with statistical physics models, and the thermodynamic nature governing the adsorption process was elucidated via the estimation of adsorption energies related with pollutant-adsorbent interactions.

Keywords: adsorption, lanthanides, arsenic, fluoride

Acknowledgments: We acknowledge the support provided by the MatPore – Porous Materials National Laboratory.

Synergistic effect of acid blue dyes on cadmium removal from water using bone char

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Dyes and heavy metals in industrial wastewater are harmful to the environment and human health. Conventional wastewater treatment technologies (e.g., ion exchange, membrane technology, flocculation, and biological treatment) have inherent drawbacks to remove these pollutants. Adsorption is considered an attractive method for removing hazardous compounds from wastewater because of its numerous advantages such as easy operation, adaptability, low energy demand, high efficiency, and low operational cost. Therefore, advanced adsorbents have been developed to improve their capacity to selectively adsorb pollutants from wastewater [1,2]. In this context, adsorbents, such as bone char (BC), are mainly employed to remove inorganic and organic chemical compounds from aqueous solutions. BC is primarily composed of hydroxyapatite (HAP) $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$, carbon, and calcite [3,4], and its adsorption capacity is competitive for depolluting water containing various toxic compounds. In this study, multicomponent adsorption isotherms of Cd(II) in the presence of acid blue 29 (AB29), acid blue 80 (AB80) and acid blue 129 (AB129) were evaluated and analyzed. The adsorption capacities of Cd(II) by BC at 30 and 40 °C were 67, 82, 86, 110, 88, and 111 mg/g, and 94 and 102 mg/g for the Cd(II), Cd(II)-AB29, Cd(II)-AB80, and Cd(II)-AB129 systems, respectively. The experimental data showed that synergistic adsorption can occur for Cd removal in multicomponent solutions containing these dye molecules. Density functional theory (DFT) calculations were performed to investigate the interactions between the Cd(II) ions and the molecular structures of these anionic dyes. The calculated interaction energies indicated that the stability of the dye – cation complexes followed the trend: Cd(II)-AB29 > Cd(II)-AB80 > Cd(II)-AB129. The adsorption mechanism of these systems is discussed and explained with the aim of characterizing the removal performance of BC for the treatment of wastewater containing both dye molecules and metallic cations.

Keywords: Wastewater, heavy metals, acid blue dyes, bone char, adsorption, DFT calculations

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Conversion of biomass to porous carbon

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With a continuous increasing population in our changing world, there is the urgent need to transition from a fossil fuel-based society to more efficient and environmentally friendly technologies. In this regard, materials science plays a predominant role to achieve the design and synthesis of novel materials which should perform outstandingly (exceed existing technologies) but at the same time should be low cost, scalable, industrially attractive, and derived from renewable and abundant resources [1]. Porous carbon is one of the most versatile materials explored for the environmental remediation applications. Some of the advantages of porous carbon materials are their low density, large specific surface area, chemical stability, high thermal conductivity, high electrical conductivity, high mechanical strength. Initially the production of porous carbon was reduced to the use of precursors derived from fossil fuels such as coke, tar, or toxic organic chemicals which produced contaminant by-products and was not sustainable on the long term.

Marine biomass and biowaste from the food industry are among the non-traditional precursors of porous carbon production [2,3].

The carbon precursor potential of marine plant based ι-carrageenan and crab shell as well as spent coffee grounds biowaste will be exploited in this presentation. Beside the traditional physical and chemical activation processes hydrothermal conversion will be discussed as well. At this level the pore morphology and the carbon yield will be considered.

Keywords: non-traditional carbon precursor, marine biomass, food-industry biowaste, pyrolysis, activation, hydrothermal conversion

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Influence of carbonization temperature on structural and sorption properties of nanoporous hybrid carbons

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Porous carbons are widely used in many different fields including not only sorption techniques covering separation and purification processes, but also in storage and conversion of energy, catalysis biomedicine, microelectronics and other smart or intelligent systems [1–3]. Such a wide range of applications results from a number of advantages of these materials, including: high thermal and chemical stability, electrical conductivity and good biocompatibility. These features in combination with high mechanical strength and hydrophilicity of inorganic (e.g. silica, silicate) framework allow to obtain a huge variety of new interesting materials [4].

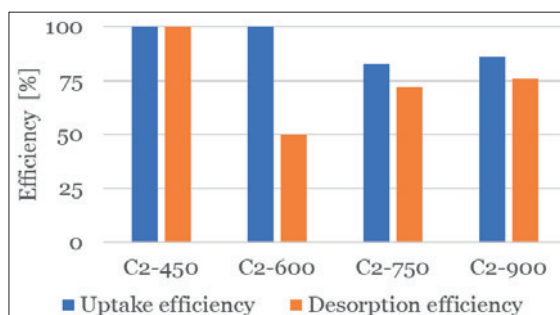
This work presents structural and chemical properties of four nanoporous hybrid carbons prepared by direct carbonization at 450, 600, 750 and 900°C of the terpolymeric precursor composed of methacrylamide, divinylbenzene and trimethoxyvinylsilane. Before thermal treatment the polymers were impregnated with sulfanilic acid (SA) to gain uniform porous structure. The resulting carbonized products were characterized by ATR, Raman, XPS, XRD methods as well as standard porosimetric measurements. Additionally sorption capacity and efficiency of the synthesized carbons were evaluated with stationary sorption experiments using ibuprofen as a testing adsorbate. Weighed amounts of the carbon samples were placed for 24 hours in aqueous solution of the drug (20 mg/L) then filtered off and 2,5 mL of methanol was added to elute adsorbed compound. Concentrations of ibuprofen both in aqueous and methanolic solutions were determined using HPLC system. Some of the obtained results are collected in Table 1.

Thermal treatment performed in the temperature range from 450 to 900 degrees, changed at intervals of 150 degrees allowed to analyse gradual, structural changes of the precursor during carbonization. The results collected with ATR, Raman, XPS and XRD methods showed changes taking place in the chemical structure of the prepared materials. As the carbonization temperature increased, the sp²/sp³ carbon ratio increased

Table 1. Chosen properties of the studied hybrid carbons.

Carbon	Carbonization temperature [°C]	sp ² /sp ³ [%]	O:Si *	A _{BET} * [m ² /g]	Q _A * [mg/g]	Q _D * [mg/g]
C2-450	450	1	2.00	387.4	7,95	7,95
C2-600	600	8	1.87	495.4	7,98	3,98
C2-750	750	33	2.29	377.9	6,63	5,78
C2-900	900	65	2.39	390.4	6,68	6,08

* A_{BET} – specific surface area; Q_A – Adsorbed quantity, Q_D – Desorbed quantity


Fig. 1. Efficiency of ibuprofen uptake from aqueous solution and desorption with methanol.

proving progressive ordering and aromatization of the organic matter. At the same time cyclic and symmetrical structures of silicates species turned to amorphous ones.

The obtained hybrid carbons had homogeneous bimodal porosity with pores widths of approximately 1 and 14–28 nm. Well-developed porous structure makes materials useful in purification and separation techniques. For this reason, the sorption properties of the prepared materials were tested in experiments simulating water purification from the popular and widely used non-steroidal anti-inflammatory drug – ibuprofen.

The results presented in Fig. 1 show the high efficiency of the studied hybrid carbons in removal of ibuprofen from water. Full regeneration of the sorbent was possible only in case of C2-450. Carbons C2-750 and C2-900, although a little less efficient in purification, could be regenerated with good performance and reused. Desorption from C2-600 was possible only in 50%, it meant that ibuprofen was partially irreversibly adsorbed on the surface of this carbon.

Keywords: hybrid carbon, porous carbon, carbonization, TGA-EGA, ATR, XPS

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Water treatment technologies: challenges and opportunities for PFAS removal

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According to the latest data published by the US EPA in February 2024, there are 42,293 active substances in its Toxic Substances Control Act Chemical Substance Inventory and about 2,000 new chemicals are introduced into commerce every year [1]. It is not possible to obtain adequate information on the occurrence, fate, toxicity and exposure levels of even a fraction of these new chemicals. Improved screening and analytical methods allow us to identify new contaminants of emerging concern (CECs), including endocrine disruptors, pesticides, pharmaceuticals and per- and polyfluoro-alkyl substances – PFAS, dubbed “forever chemicals” due to their exceptional resilience and pervasiveness. Recalcitrant to conventional waste and freshwater treatments as well as natural processes in the environment, these chemicals reach finished drinking water, posing threat to both aquatic life and human health. According to the Drinking Water Inspectorate (DWI-UK), there are about 5,000 PFAS currently in use [2]. What makes them ‘forever chemicals’? They: do not break down in the environment; can move through soils and contaminate drinking water sources; build up (bioaccumulate) in fish and wildlife. With growing evidence of ecotoxicity and potential impact on human health, the EU, UK and US have been considering tightening the legislation banning or restricting the use of PFAS and introducing stricter requirements for the maximum allowable concentrations (MAC) of these pollutants in water. To date, two PFAS – perfluorinated octanoic acid (PFOA) and perfluorooctanesulphonic acid (PFOS), are restricted through UK REACH (registration, evaluation, authorisation and restriction of chemicals) as POPs and the US Action Plan.

These two PFAS are most widely used and there is sufficient data regarding their environmental fate. They are used as salts of K^+ (PFOS) or NH_4^+ (PFOA) rather than acids. In this state they are not biodegradable, have long hydrolysis half-life (>41 y PFOS and > 92 y PFOA) and withstand photolysis (>3.7 y PFOS and >256 y PFOA),

which are common routes for the environmental degradation of organic pollutants. The information on the environmental fate of other PFAS is very limited, but it is clear that they also accumulate in the soil from which they leach back into the aqueous environment.

In 2021, DWI (UK) produced a list of 47 PFAS substances required for monitoring. A recent survey carried out by the Environment Agency (EA-UK) together with the Royal Society of Chemistry in 2022, showed that more than one third of samples from 31 wastewater treatment plants (WWTP) had PFOA and PFOS concentration exceeding the currently accepted safe threshold of 10 ng/L and in some cases even >100 ng/L after treatment [2]. Even more worrying and surprising was the fact that in most cases the PFAS concentration after WWTP passage was higher than before the treatment. At present no confirmed explanation for this observation has been proposed. It could be partly attributed to the uncertainty of the PFAS analysis at such low concentrations, however, an alternative suggestion that this increase could be attributed to the presence of some other undetected PFAS which were converted into PFOA and PFOS in the WWTP. Regardless of the real mechanism of this phenomenon, it confirms that the current treatment processes used in WWTPs are ineffective in PFAS removal. The latest analysis of the literature dedicated to the development and assessment of methods for water decontamination from PFAS carried out by the US EPA concluded that granulated and powdered activated carbon and anion exchange resins could remove PFAS, but their efficiency varied in a wide range from 10% to 99% depending on the PFAS structure and composition [1]. The key challenge is: what to do with the spent adsorbents/ion exchangers? They are quite expensive materials. To reduce their costs, they could be reused after regeneration. However, the regeneration by PFAS desorption creates more concentrated solutions of these chemicals which must be disposed of. Considering their environmental stability, PFAS would leach from landfill sites into the environment and the contamination recurs. The only truly efficient approach is to remove PFAS by destroying them and converting them ideally into the inorganic (mineral) products such as CO₂, water, fluoride anion, etc. If the complete mineralisation is not possible, the longer-chain PFAS should be broken down into shorter-chain products which are easier to remove by adsorption or ion exchange methods. The complete or partial destruction of PFAS could be achieved, at least in theory, using advanced oxidation processes (AOP). This approach showed some promising results particularly if two or more AOPs were combined, such as electrocoagulation, electrochemical processes, O₃ + H₂O₂ and UV + chemicals, but to date these results were limited to lab bench experiments and required special conditions (high pH, high energy consumption, etc.).

Recently, numerous publications reported high efficiency of atmospheric nonthermal plasma (ANTP) in water decontamination from organic contaminants. These publications are limited to small bench scale devices with serious scalability problems due to their 2-D design. Nevertheless, the „lightning in water” created by the electric discharge, which is essentially what the nonthermal plasma is, attracts attention as a potential solution for water decontamination from PFAS due to its strong oxidising potential and ability to break down chemical bonds thus destroying these persistent contaminants.

We designed a 3-D ANTP device which has an increased water throughput and is potentially scalable to treat high volumes of water. The first results of PFAS treatment with NTP showed its PFAS destruction efficiency over 70% determined for PFOA, perfluorobutane-sulphonic acid (PFBS) and perfluorononanoic acid (PFNA). These are promising results which indicate the good potential of the NTP technology for water decontamination from PFAS thus solving the problem of forever chemicals and their impact on the environment and health.

Keywords: PFAS, water treatment, atmospheric nonthermal plasma

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ORAL PRESENTATION

Valorization of olive mill wastewater for the development of carbon-based catalyst nanoparticles for hydrogen sulfide removal from industrial streams

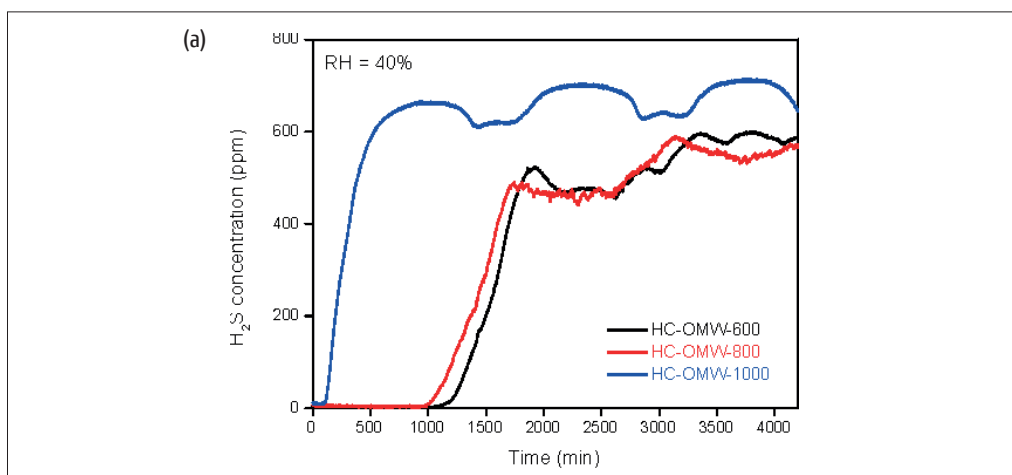
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Removal of hydrogen sulfide in industrial streams (e.g., coke production from sulfur-containing coal, manufacture of viscose rayon, among others) is critical to minimize emissions to the atmosphere, with the associated production of sulfur dioxide, sulfuric acid, and elemental sulfur. Actual environmental regulations are demanding novel and cost-effective technologies for the efficient capture and conversion of H_2S . Among these technologies (e.g., amine scrubbing), adsorption in the cavities of nanoporous solids (e.g., carbon materials) and the subsequent conversion on active metal sites constitute a promising alternative [1]. In this study, a series of Fe@carbon catalysts have been prepared from industrial residues (alpechin) through a hydrothermal metal-catalyzed carbonization (HTC) [2]. These materials constitute a step-stone in this application with removal efficiencies as high as 0.6 g H_2S /g catalyst, highly above any commercial adsorbent.



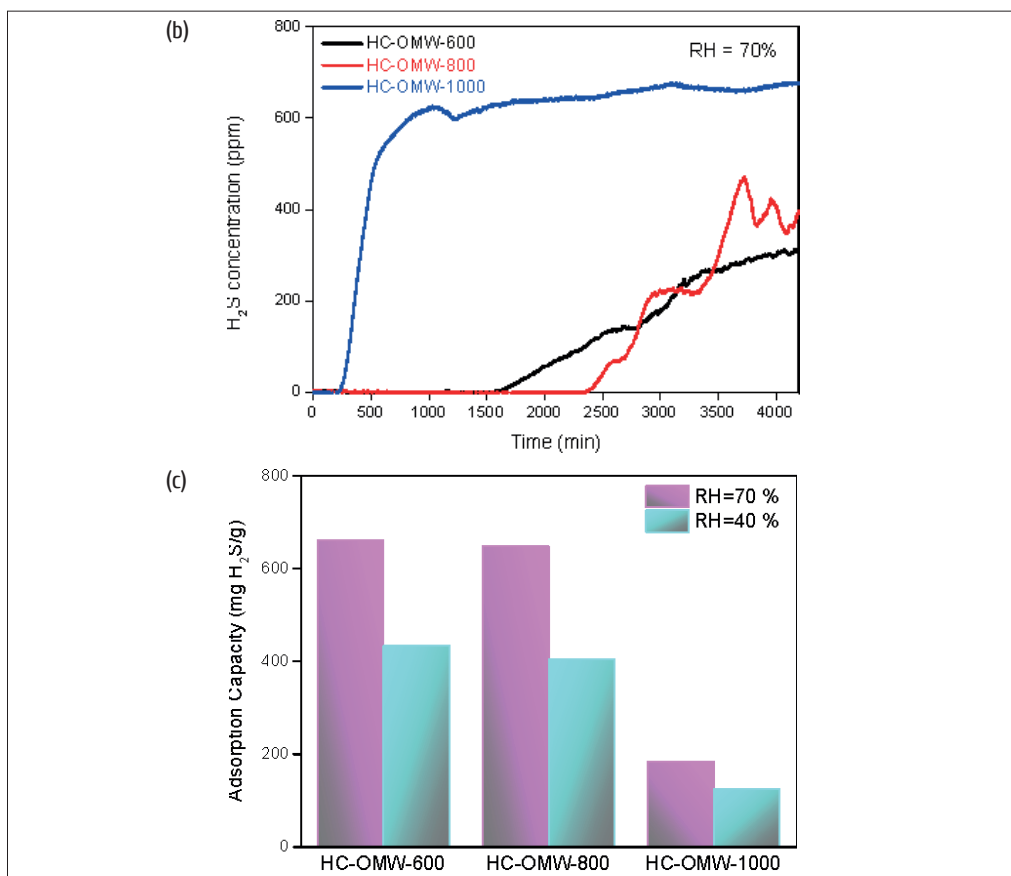


Fig. 1. H₂S breakthrough column experiments at 25°C for the different samples evaluated at two different humidity Ratios (a) 70%, (b) 40%, and (c) Summary of the adsorption/catalytic performance for all samples.

Table 1. Adsorption/catalytic performance of the different nanoparticles under different relative humidity conditions.

Sample	Adsorption/catalytic capacity [mg/g]	
	RH: 40%	RH: 70%
HC-OMW-600	434	661
HC-OMW-800	405	649
HC-OMW-1000	124	184

Keywords: hydrothermal carbonization, core-shell nanoparticles, Fe@C, H₂S

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Novel organometallic-based adsorbents for the sequestration of pharmaceutical compounds from water

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In this study, the effectiveness of three rare earth-based organometallic adsorbents, denoted as M-X (where X represents a rare earth element, i.e.: Ce, Gd, and Yb), in the removal of acetaminophen, diclofenac, and naproxen was investigated. The batch adsorption experiments were performed at pH 7 and 30 °C. The adsorbents were characterized using X-ray diffraction and Fourier-transform infrared spectroscopy. The adsorption capacities of acetaminophen, diclofenac, and naproxen using M-Ce, M-Gd, and M-Yb were 0.03-0.07, 0.14-0.46, and 0.03-0.42 mmol/g, respectively, suggesting that these adsorbents could be a promising alternative for the pharmaceutical removal from aqueous solutions. The adsorption efficiency of the adsorbents followed the trend: M-Yb > M-Gd >> M-Ce, underscoring the pivotal role of adsorbent properties in drug removal. X-ray diffractograms of all adsorbents exhibited well-defined diffraction peaks and highly crystalline structures [1–3]. Infrared spectra revealed the presence of absorption bands corresponding to hydroxyl and carboxylic groups, along with absorption bands associated with the vibration of the respective rare-earth elements (i.e., Ce-O, Gd-O, and Yb-O) [2–5].

Keywords: adsorption, organometallic-based adsorbents, emerging water pollutants

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Synthesis of a carbon-organometallic composite for fluoride adsorption from aqueous solution

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This study evaluated the fluoride adsorption performance of carbon-organometallic composites synthesized under different conditions. The carbon support was prepared via pyrolysis using *Jacaranda mimosifolia* biomass as the precursor. Subsequently, gadolinium ions were incorporated into the carbon matrix to obtain a carbon-organometallic adsorbent. Optimal synthesis conditions were found to enhance the fluoride adsorption capacity of the composites. The most effective adsorbent was chosen for adsorption equilibrium studies at pH 7 and 20–40 °C. The best composite was characterized before and after the adsorption process by FTIR, XRD, XPS, and SEM. The thermodynamic parameters of the adsorption process were estimated and the experimental data were correlated using statistical physics models. It is noteworthy that fluoride was selected as target pollutant because of the elevated levels observed in Aguascalientes, Mexico (ranging from 1.16 to 6.27 mg/L), which exceed the permissible limit (1.5 mg/L), affecting over 50% of the population with dental fluorosis [1–3].

Keywords: adsorption, carbon-organometallic composite, defluoridation

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Experimental study and modeling of the phenol adsorption process in aqueous solution using a Tetra Pak char

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In the present work, phenol adsorption using Tetra Pak char obtained via pyrolysis was studied. Adsorption isotherms and kinetics were obtained at different temperatures. The experimental isotherm and kinetic data were correlated using statistical physics models and the pore volume and surface diffusion (PVSD) model. The adsorbent was characterized before and after phenol adsorption using FTIR and XRD. Finally, phenol desorption was studied using an ethanol/water mixture. Phenol adsorption process was endothermic and the adsorption capacities ranged from 1.04 to 15.6 mg/g. The time required to reach equilibrium during the adsorption process was 10 h. A monolayer model with two energies showed better performance than the monolayer model with one energy in correlating the equilibrium data. PVSD model was suitable for correlating the kinetic data. Regeneration studies indicated that 11% phenol desorption yield was obtained using a 50% ethanol solution. Finally, the X-ray diffractograms indicated that the adsorbent was mainly composed of CaCO₃, and its crystallinity decreased after phenol adsorption. The main absorption bands identified in the FTIR spectra of the adsorbent were associated with O-H, C-H, and CO₃⁻² groups [1,2]. This adsorbent, derived from widely available urban waste, demonstrated competitive characteristics for the adsorption of phenol from aqueous solutions.

Keywords: adsorption, char, Tetra Pak, phenol, statistical physics, PVSM.

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Porous polymeric sorbents for water purification

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Polymeric materials, especially those of spherical in shape, have been utilized in numerous applications for decades. Numerous polymerization techniques are used to obtain polymeric sorbents with different grain sizes. Polymers in the form of porous or non-porous microspheres we can obtain by one of the heterogeneous polymerization: emulsion, suspension dispersion polymerization, membrane emulsification, or swelling and polymerization techniques.

Polymer materials, especially those with a spherical shape, have been used in numerous applications for decades. The obtained materials can be used in solid-phase

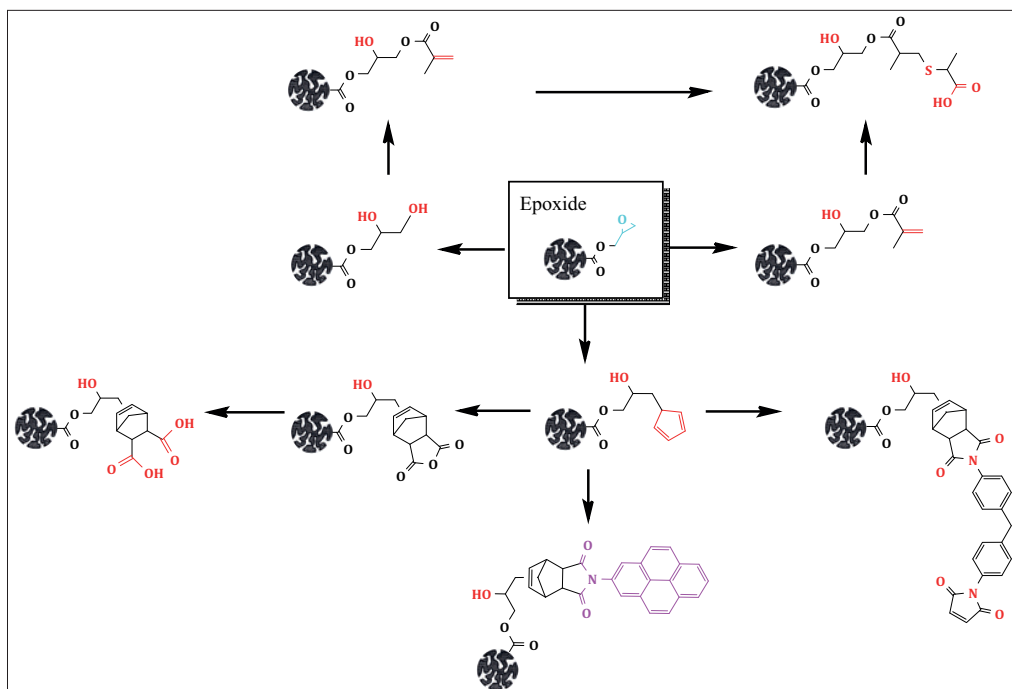


Fig. 1. General scheme of functionalization of polymer microspheres.

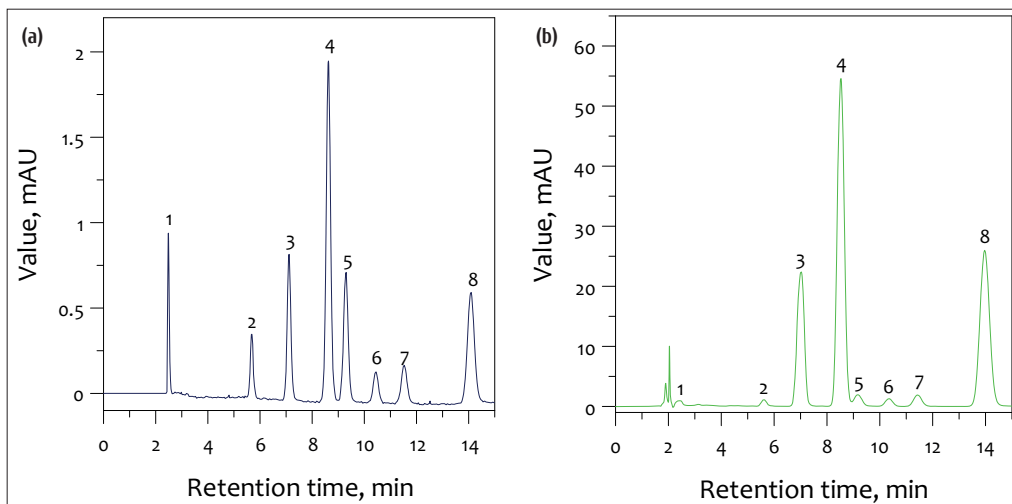


Fig. 2. Chromatograms of water sample before (a) and after (b) pre-concentration. 1: 4-hydroxyaniline; 2: aniline; 3: 4-nitroaniline; 4: 3-nitroaniline; 5: 2-methoxyaniline; 6: 2-methylaniline; 7: 3-methylaniline; 8: 2-nitroaniline.

extraction for the isolation of organic compounds from water and air and as stationary phases in high-performance liquid, supercritical fluid, ion-exchange and particle size exclusion chromatography [1–3].

In some applications, polymeric materials have a chemically modified surface. For this purpose, functional groups or unreacted double bonds present in the polymer structure are used. Such enormous possibilities are offered, for example, by the modification of polymer materials bearing pendant epoxy groups [3].

Epoxy groups in the structure of the material are highly reactive and undergo ring opening reactions, to which vic-diol groups were introduced in the hydrolysis process. The surface of the polymer microspheres was also decorated with amide, diene, vinyl, carboxyl and thioether moieties (Fig. 1.).

Modified polymer sorbents were used as stationary phases in the HPLC separation process of mixtures of various homologous series. Materials were also used in the SPE to pre-concentrate water samples of aniline and its derivatives (Fig. 2). Nitroanilines had the best sorption on the polymers containing carboxyl groups.

Porous polymers can act as precursors for the preparation of carbon sorbents [4]. An attempt to use these interesting starting materials with chemically modified surfaces will be made in subsequent studies. For this purpose, the carbonization process will be supported by microwaves.

Keywords: polymeric microsphere, porous structure, surface modification, functional groups, water purification

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Molecularly imprinted polymers – potential applications and limitations in the water purification process

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The specificity of interactions observed in biological systems, referring to the key and lock model proposed by Emil Fischer in 1894, became an inspiration to search for a method of producing synthetic (polymeric) materials characterized by a similar degree of selectivity. Molecularly imprinted polymers (MIPs) often referred to as “artificial” or “plastic” antibodies are obtained by creating three-dimensional polymer networks that have a memory of the shape and functional group positions of the template molecule. The resulting molecular imprinted polymers can selectively recognize and consequently retain the analyte used in the imprinting process. Molecular imprinting technology (MIT) was proposed by Polyakov in 1930 [1], introduced by Wulff and Sarhan in the early 1970s. The term “*imprinted polymer*” was first used by Mosbach in 1984 [2].

The specificity of the interaction of the MIP with molecules of one selected chemical substance is a consequence of the phenomenon of self-assembly during polymerization process. The concept behind the formation of the selective binding sites is schematically shown in Fig. 1. Occurrence of weak interactions between the molecules of the template molecule (a) and the functional monomer (b) leading to the formation of pre-polymerization complexes in the initial stage of polymerization (1). The pres-

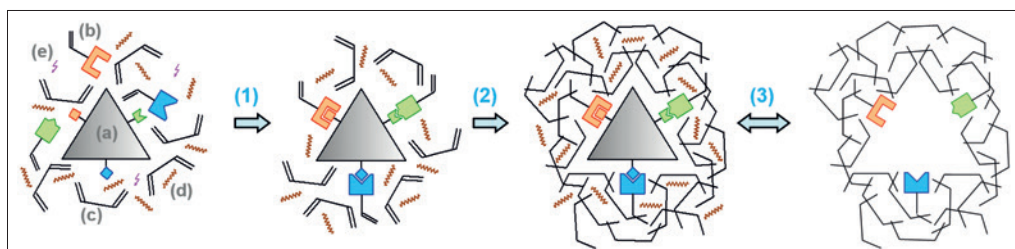


Fig. 1. Idea of the mechanism for the synthesis of molecularly imprinted polymers (generation of a molecular imprint in a polymer matrix).

ence of the cross-linking reagent (c) and the initiator (e) enables the polymerization reaction combined with cross-linking, i.e. the incorporation of functional monomer molecules bound to the template into the rigid, three-dimensional structure of the polymer (2), while the pore-forming solvent (d) ensures the proper porosity of the resulting product. After removing the template molecules (extraction), the resulting polymer matrix, thanks to areas capable of molecular recognition, has the ability to reversibly bind molecules of the compound used to create the molecular print (3) or its close structural analogue.

There are many parameters that determine the quality of the obtained sorbent and its future effectiveness. Critical parameters are: functional monomer, template, porogen (solvent), cross-linker, initiator and temperature. By modifying and optimizing the composition of the reaction mixture and the copolymerization conditions, it becomes possible to obtain MIPS showing selectivity towards many groups of chemical compounds (e.g. pharmaceuticals, food additives, explosives, pesticides) [3]. MIPS are promising materials that have many applications in chemical and biological fields, e.g. chromatography, solid phase extraction, sensor and catalysis. This type of polymeric sorbent can be also used for the determination and removal of pollutants from the wastewater and drink water [4,5].

Critical barriers and limitations to success of MIP application in wastewater treatment are limited life-span, instability under extreme conditions, increased costs and challenging adaptation to a large-scale level. In the face of the serious problem of water pollution, research on the search for substances that will make the analysis and removal of undesirable substances from water easier becomes advisable.

Keywords: molecularly imprinted polymers, polymeric sorbent, water

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Towards green water treatment of plastic degradation products

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The production of plastic is estimated at 400 million metric tonnes in 2022 [1]. Plastic degradation releases a myriad of products, some of which are detrimental to water quality. Bisphenols, perfluoroalkyls and plastic particles are among the most concerning environmental pollutants today. Microplastics refer to particles 0.1 μm–5 mm, and nanoplastics <0.1 μm [2]. We have explored and optimized the effectiveness of treatments targeting suspended solids: sand filtration and coagulation, flocculation and sedimentation [3] and have learnt about their limits and benefits. Our bench studies with sand filtration removed ~90% of polyester microfibres from grey water and the performance was heavily impacted by filtration flow rates. Hence, there is still release of microfibers. Will tertiary treatment with porous carbon materials perform better?

The treatment of water spiked with microplastic beads with optimized coagulation, flocculation and sedimentation steps was effective but microbeads <250 μm and those that had low density (such as polypropylene, polyethylene, polystyrene) remained at important proportions in water (~30–50% of the initial level) when being ~50 μm. From our studies with water treatments optimised to target microplastics, we conclude that new technologies and sorbents should focus on low density (<1 g/cm³) plastic particles and the “smaller” microplastics.

Keywords: microfibre, microplastic, sand filtration, coagulation.

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New phosphorus materials and metal complexes for catalytic applications

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We will give an overview on current projects of my team in catalyst and material development, hoping to initiate new collaborations and joint projects. Our work mainly focusses on group 15 (pnictogen) chemistry, and we are developing new molecular building blocks, metal complexes and inorganic materials:

1) **Weak interactions** are very important “glue forces” to produce new materials, and help designing new catalytic processes to convert simple building blocks into useful chemical products. We are investigating a “new” type of weak interactions, so-called pnictogen interactions and use simple molecular skeletons to build molecular cages containing phosphorus (P) and bismuth (Bi). In these cages we observe weak pnictogen interactions between P and Bi and for the first time we could verify these bonding forces using Nuclear Magnetic Resonance (NMR) Spectroscopy.

2) **Black phosphorus (bP)** is the most stable allotrope of phosphorus, and it exhibits a layered structure (similar to graphite). We have developed and improved the synthesis for bP and for its exfoliations to few-layer bP (phosphorene). The band gap of a bP composite depends on the number of layers and the properties can be further tuned by modification of the surface. In general, bP is an interesting (non-toxic) substrate material for metal nanoparticles and we are currently exploring the potential of Bi-doped bP in heterogeneous catalysis.

3) **The valorisation of glycerol** has gained significant recent attention as it is considered as an industrial waste product from biodiesel production. We are working on catalysts for the dehydrogenation reaction to convert glycerol into dihydroxyacetone, which is an important raw material for cosmetic products. Furthermore, this process generates hydrogen gas, which can either be used as fuel or be recycled in other chemical processes (*e.g.* hydrogenation reactions).

Keywords: weak interactions, pnictogen chemistry, glycerol valorisation, black phosphorus.

Acknowledgement: the 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. The Royal Society Exchange grant (IES\R3\223129) and Dr Baquero et al. (National University of Colombia).

Remediation of chlorinated hydrocarbons contamination in ground water

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The submitted paper is based on the geological task „Remediation of the environmental burden in the Bardejov area – former JAS company property”. The geological task was carried out within the framework of a strategic document with national reach „Environmental Quality Operational Program”, based on a public procurement, from which the contractor – the association GEO Slovakia-ENVIRONCENTRUM, was selected as the successful bidder.

In 2015, a survey revealed serious groundwater pollution by **aliphatic chlorinated hydrocarbons** in the area, and as part of pre-remediation work in 2021, the presence of an environmental risk from the spread of groundwater pollution was updated. The dominant pollutant was **tetrachloroethene (PCE)**. Furthermore, in the south-eastern part of the site, groundwater pollution was also formed by secondary products of the reductive dechlorination of aliphatic chlorinated hydrocarbons, namely **trichloroethene (TCE)** and **cis-1,2-dichloroethene (DCE)**.

One of the elements of the remediation works, due to the potential of additive supply of pollutants in the direction of groundwater flow from off-site sources, was the **construction of a protective remediation element – a geochemical reaction barrier (RB)** on the northern border of the JAS site. The task of RB is to reduce the concentration of the migrating priority pollutant – PCE and effective buffering of the environmental stressor in the long-term horizon. Contaminants passing reaction gates in the flowing groundwater are reduced and eliminated by exchangeable reaction fillings – a mixture of **activated Fe filings and zero-valent iron**.

In order to fulfil the objectives of the geological task, a combination of several remediation methods was used. Considering the acquired set of knowledge about the parameters of the affected components of the environment and about the pollutants themselves, the territory was divided into two areas in terms of the application of remedial methods. **Area I (PCE pollution)** represented the northern part of the

area, where the remediation method used for groundwater purification was reductive dechlorination in situ, without using the removal of the volatile part of the pollution on site. **Area II (PCE, TCE and cis-1,2-DCE pollution)** represented the southern part of the site, where groundwater remediation project was carried out in two phases. **The first phase was the oxic phase**, during which groundwater remediation involved pumping polluted groundwater from wells and subsequent cleaning in **stripping facility**, together with auxiliary methods of **airsparging/biosparging and venting/bioventing**. **The second phase was the anoxic phase**, when the oxygen supply in the saturation zone was limited a reducing agent was purposely applied for the use of processes of **reductive dehalogenation of aliphatic chlorinated hydrocarbons**.

In the northern part of the area (area I), a total of **151,300 liters of reducing agent** was infiltrated into the saturated zone of the rock environment with the help of a network of application wells. **Whey – milk serum (yellow-green liquid)**, which is obtained after removing casein from milk, was used as a **reducing agent**. Main remediation method in area II – the southern part of the area was **active pumping and subsequent treatment of groundwater in a stripping facility**. Remediation works were intensified based on the analysis of the obtained parameters. In the northern part of the area (area I), the process of **anoxic dechlorination** was fully manifested in the second half of the remediation period, when the concentrations of PCE (Fig. 1) in the groundwater in the treated area fell significantly below the level of the remediation target values. In the southern part of the area (area II) **remedial pumping** of groundwater led to elimination of pollution by releasing volatile substances.

A significant decrease in the intensity and lateral content of pollutants, manifested in the fulfilment of the target values, is evident in the entire area of the remediated territory. Considering set of works, obtained data, their analysis, synthesis and using it in risk analysis, we can conclude that the location in the current qualitative state

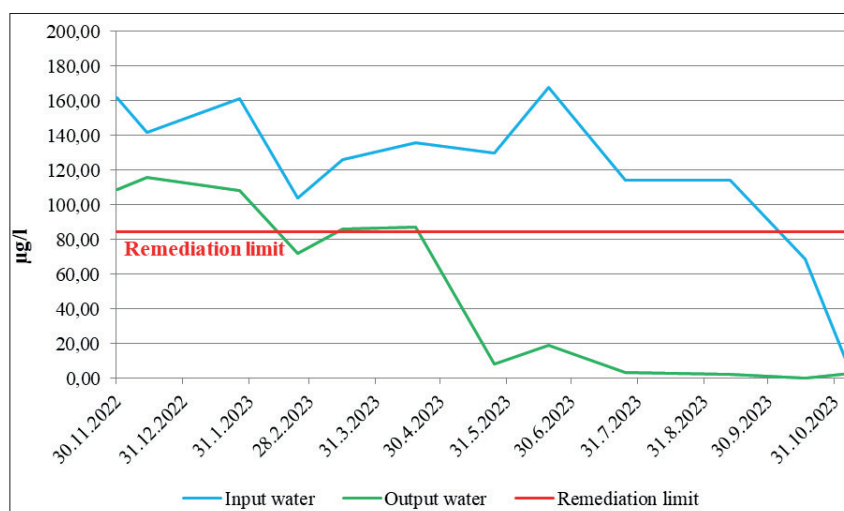


Fig. 1. Content of PCE in area I (north).

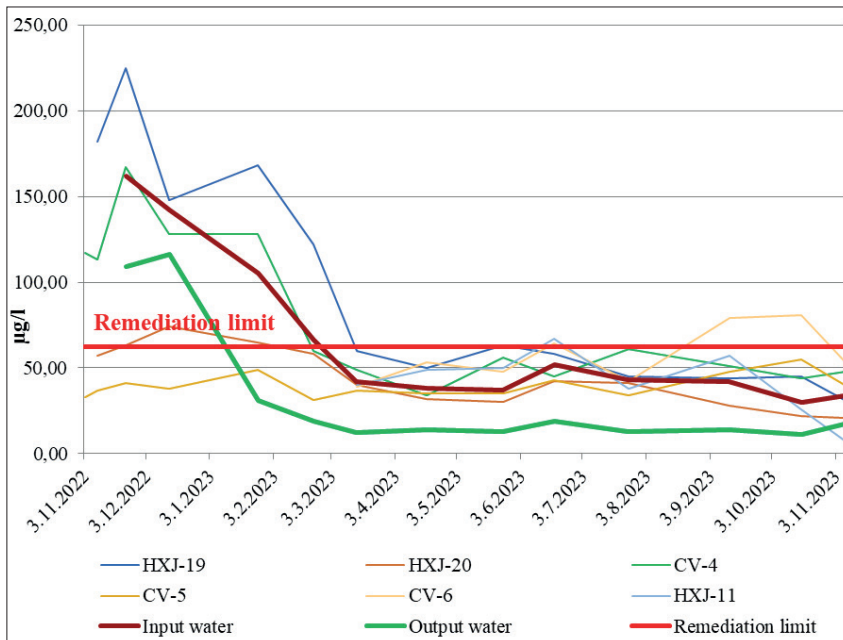


Fig. 2. Content of PCE in area II (south).

of the hydrosphere and with the existing usage does not represent an environmental or health risk.

Keywords: remediation, chlorinated hydrocarbons, pollution

Advanced silica-based carboxyl hybrids for the effective removal of Ni(II) and Mn(II) ions from aqueous media

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In response to the growing global problem of heavy metal contamination of water sources, this research focuses on the development of silica-based carboxyl hybrids aimed at removing such pollutants. Materials with carboxyl groups are effective in removing heavy metals from solutions due to their excellent ion exchange and complex-forming properties. Since they are both hydrogen-bond acceptors and donors, their tendency to bind with silanol groups on the silica surface can impede their efficiency in ion exchange processes. Consequently, this study presents an innovative solution: the introduction of additional phenyl ($-C_6H_5$) or methyl ($-CH_3$) groups onto the surface of silica. This modification aims to release carboxyl groups from their binding constraints, thereby increasing their availability for interaction with metal ions. This novel approach not only alleviates existing limitations, but also explores new avenues for enhancing the efficiency for the removal of heavy metals from aqueous environments. The schematic representation of the surface of silica materials with carboxyl and other hydrocarbon groups is shown in Figure 1.

Three hybrid materials were prepared via a one-pot sol-gel process. Tetraethyl orthosilicate (TEOS) was chosen as an inorganic precursor, as well as an organic component – carboxyethylsilanetriol disodium salt (CEST), along with

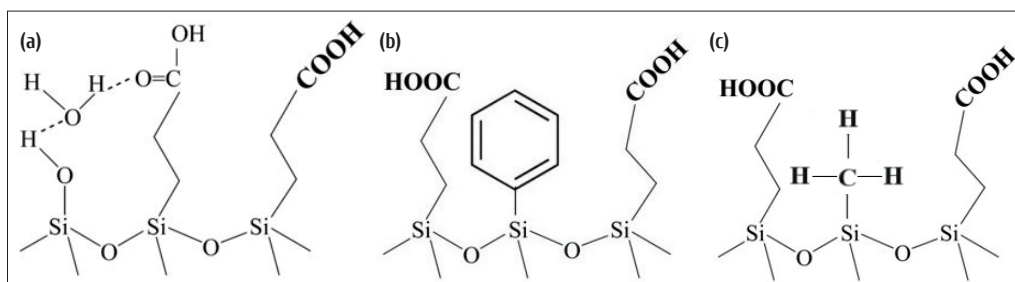


Fig. 1. Schematic representation the availability of functional groups on the surface of functionalised silica particles (a – silica/-COOH; b – silica/-COOH/- C_6H_5 , and c – silica/-COOH/- CH_3).

additional silanes: phenyltriethoxysilane (PhTES) and methyltriethoxysilane (MTES). The resulting hybrid composition are as follows: $\text{SiO}_2/\equiv\text{Si}(\text{CH}_2)_2\text{COOH}$ (silica/-COOH); $\text{SiO}_2/\equiv\text{Si}(\text{CH}_2)_2\text{COOH}/\equiv\text{SiC}_6\text{H}_5$ (silica/-COOH/- C_6H_5) and $\text{SiO}_2/\equiv\text{Si}(\text{CH}_2)_2\text{COOH}/\equiv\text{SiCH}_3$ (silica/-COOH/- CH_3).

According to SEM data and measurements from low-temperature nitrogen adsorption-desorption isotherms, the synthesized hybrid materials are non-porous spherical particles with an approximate size of 350–400 nm. Zeta potential measurements and titration data were conducted to evaluate the content and nature of surface functional groups of silica-based materials. The results showed the isoelectric point at pH 2.2–2.3 and the presence of acidic groups, where silica/-COOH – 6.0 mmol/g, silica/-COOH/- C_6H_5 – 5.0 mmol/g and silica/-COOH/- CH_3 – 3.0 mmol/g. Despite the use of the same TEOS/CEST ratio, additional silane incorporation with $-\text{C}_x\text{H}_y$ groups influenced the hydrolysis rate of CEST, resulting in variations in the amount of carboxyl groups present. According to the results, the hybrid materials were utilized for the removal of cationic heavy metals, specifically nickel(II) and manganese(II). Various experimental parameters were investigated to study adsorption, including pH, contact time, and initial concentration. For Ni(II) ions, the adsorption kinetics correlated well with the pseudo-second-order model. Analysis of the isotherm data shows that the Langmuir model ($R^2 = 0.99$) best-fit the data, revealing maximum adsorption capacities of Ni(II) ions on silica/-COOH is 75.9 mg/g, silica/-COOH/- C_6H_5 is 122.4 mg/g, and silica/-COOH/- CH_3 is 83.6 mg/g, at a pH of 6.8. The same parameters also apply to Mn(II) ions, with the maximum adsorption capacities on silica/-COOH is 72 mg/g, silica/-COOH/- C_6H_5 is 95.6 mg/g, and silica/-COOH/- CH_3 is 65 mg/g, at a pH of 7.1.

The regeneration process of spent sorbents was also investigated by conducting six consecutive cycles of adsorption-desorption of Ni(II) and Mn(II) ions on the sorbents using 1 M HCl as the desorption eluent. A gradual decrease in metals removal efficiency was observed with an increasing number of cycles, as depicted in Table 1. It was noted that cycles 1, 2, 3 for the Ni(II) ions and 1, 2 for the Mn(II) ions exhibited good recovery of both metal ions accumulated on the surface of the adsorbents.

Table 1. Desorption of Ni(II) and Mn(II) ions adsorbed on hybrid materials.

Sample	Desorption efficiently, %					
	I cycle	II cycle	III cycle	IV cycle	V cycle	VI cycle
	Ni(II) ions					
silica/-COOH	91.7	90.8	88.9	52.6	42.8	30.4
silica/-COOH/- C_6H_5	98.2	91.7	91.7	57	50.5	41.8
silica/-COOH/- CH_3	98	91.5	89.2	56.9	50.1	41.3
	Mn(II) ions					
silica/-COOH	85.3	83.2	56.2	30.1	18.6	9.2
silica/-COOH/- C_6H_5	90.2	88.9	60.4	35	22.4	12.2
silica/-COOH/- CH_3	88.3	87	58.1	32.4	20	10.1

Subsequently, following two-three cycles, the adsorption capacity of Ni(II) and Mn(II) ions on the adsorbent decreased by ~50%, and after 4, 5, 6 cycles, it was significantly reduced to 10% desorption. Consequently, after three cycles of use, the active sites on the adsorbents surface became saturated with adsorbed substances, reducing their ability for further metal adsorption from the solution.

Based on the results, it can be concluded that the introduction of additional hydrophobic groups indeed enhances the sorption capacity of the material. Even with a lower overall quantity of carboxyl groups, this contributes to greater accessibility of active sites for interaction with metals. Furthermore, these findings are corroborated during desorption. Over 4 cycles, the availability of groups for the material's reuse is maintained, indicating the stability and effectiveness of this synthetic approach for cleaning aqueous media from heavy metals.

Keywords: silica, hybrids, functional groups, adsorption, nickel(II) and manganese(II) ions, desorption

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Unlocking the potential of pine sawdust biochar for adsorption of Co(II) and Ni(II) ions and sustainable recycling for carbamazepine removal

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Eurostat's 2020 data reveals that the EU produced approximately 2.135 billion tonnes of waste, averaging 4.815 kg per capita. About 59.1% of this waste was recovered through recycling, backfilling, or energy-producing incineration, while 40.9% was disposed of through landfilling or non-energy producing incineration. The figures underline significant waste generation and recovery efforts within the EU. Further research emphasizes the importance of responsible waste management, particularly with pine-related waste, in environmental sustainability. Various studies explore the potential of pine waste in applications like odor control in waste treatment and as biochar for pollution control and water treatment, showing its utility in sustainable practices. Additionally, the treatment of persistent pollutants like carbamazepine using innovative photocatalytic methods highlights ongoing challenges and the need for effective environmental remediation strategies.

The study successfully showcases how waste from pine tree sawdust can be repurposed into a versatile biochar, serving as a tool for environmental clean-up efforts. Utilizing leftover plant materials from *Pinus sylvestris*, a sustainable form of biochar with superior qualities for adsorbing Cobalt(II) and Nickel(II) ions from water has been engineered.

The biochar's composition, architecture, and surface properties were thoroughly examined through a battery of physicochemical techniques including SEM, TEM, XRD, and FTIR spectroscopy. These investigations revealed the biochar's intricate structure and vast surface area, both essential to its remarkable ability to adsorb pollutants.

Additionally, the study tackles the pressing issue of managing pine waste by transforming it into a valuable resource for water purification methods. The biochars produced showcase outstanding capabilities for heavy metal ion adsorption and are also effective in breaking down stubborn pharmaceutical pollutants when exposed to UV light, thus offering a twofold strategy against water contamination.

The role of the biochar in the photocatalytic degradation of the drug carbamazepine was further explored. Findings indicated that the metal ions absorbed onto the biochar surface contribute to forming nickel hydroxide and cobalt phosphate. These substances play a crucial role in the photochemical degradation of organic compounds, suggesting that used biochars could be repurposed for photocatalytic uses.

The findings highlight the promise of pine sawdust-derived biochar in sustainable waste management. This approach effectively confronts pollution, addressing both toxic metal removal and organic pollutant breakdown in aquatic environments. Figure 1 presents all the transformations that pine-derived charcoal underwent, including cation adsorption and subsequent photocatalytic degradation of carbamazepine.

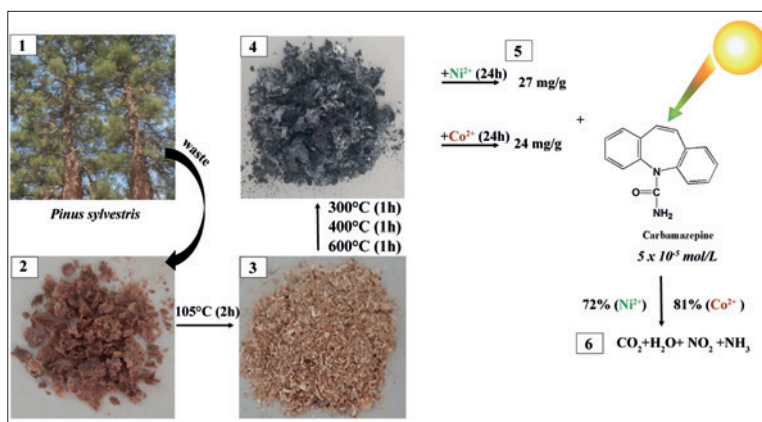


Fig. 1. Synthetic ways of obtaining biochar samples from *Pinus sylvestris* waste.

This field of study is still emerging and overlaps with multiple disciplines such as environmental engineering, chemistry, and materials science. It plays a crucial role in advancing green technologies for water purification, contributing to the overarching objective of sustainable development. As the world faces the twin challenges of environmental pollution and the demand for sustainable practices, the investigation of these innovative technologies grows increasingly important.

In conclusion, our research underlines the need to develop economical, sustainable, and effective waste treatment and environmental conservation techniques. It advocates for the transformation of biomass waste into valuable substances for environmental cleanup, in line with worldwide sustainability objectives.

Keywords: sustainable material, pine waste biochar, cobalt(II) ions, nickel(II) ions, photocatalysis, carbamazepine removal

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Use of plasma to clean NPP wastewater from organic substances, including oil products

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Radiation, the phenomena of cavitation and radiolysis, combined with high-energy impulse discharges, contribute to the destruction of intermolecular and interatomic bonds of organic substances dissolved in water. The use of a plasma chemical method with the use of a sorbent developed by us (smectites modified with humic substances) makes it possible to effectively purify trapped water containing inorganic radicals, non-polar organic substances, and heavy metals. When an electric pulse passes through an aqueous dispersion containing nanoparticles of smectites modified with humic acids, graphite-like structures are formed (Fig. 1), the elementary packets

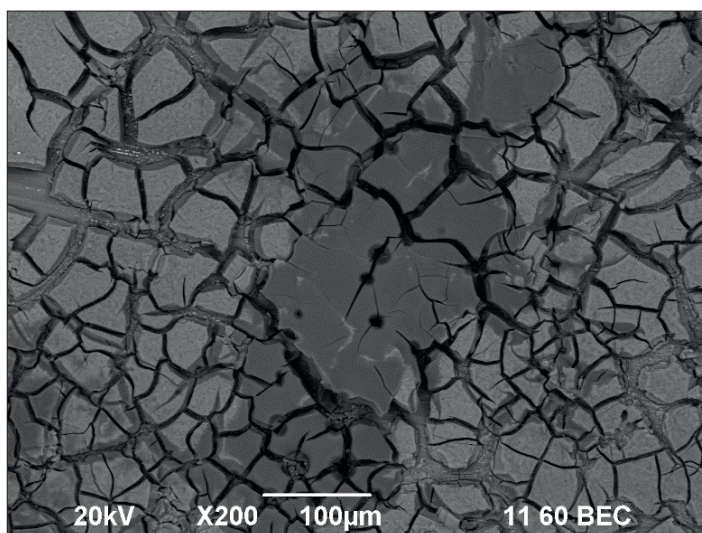


Fig. 1. SEM image of the film obtained after drying the dispersion.

of which are similar in structure to graphene, which causes the increased affinity of the sorbent activated in this way to nonpolar organic substances (petroleum products).

The use of a complex sorption-plasma-chemical method allows to reduce the rate of chemical absorption of oxygen by 10–15 times.

Keywords: plasma, organic substances, NPP effluents

Complex plasma-chemical cleaning of radioactively contaminated soil

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A comprehensive method for cleaning radioactively contaminated soil has been developed, including plasma-chemical treatment of the soil-water suspension, followed by separation of decontaminated soil and separation of the resulting supernatant into purified water and radioactive sludge, subject to compaction and burial.

When a high-voltage electric discharge passes through a “soil-water” suspension, conditions arise under which soil aggregates are dispersed, the bonds of the mineral matrix with radionuclides are destroyed, which migrate from the surface of soil minerals into the dispersion medium, which is accompanied by the enrichment of the aqueous phase with radionuclides.

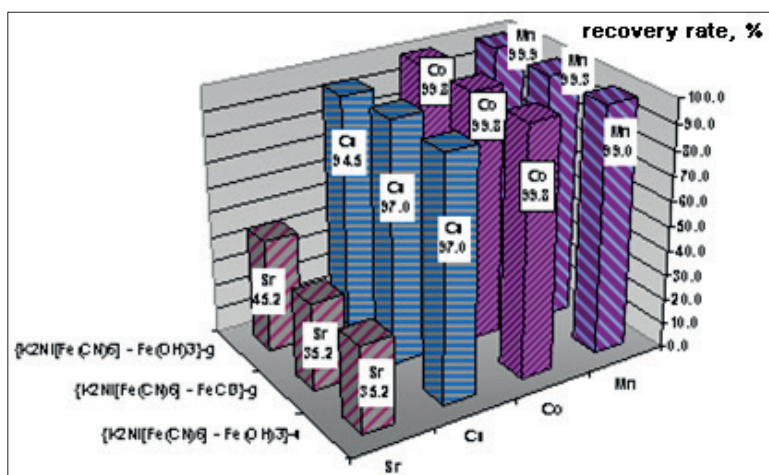


Fig. 1. The degree of extraction (%) of radionuclides from liquid radioactive waste by a complex sorbent based on micro- and nanoparticles of iron hydroxide modified with nickel-potassium ferrocyanides.

For effective sedimentation of a highly dispersed solid phase, the principle of heterocoagulation is used, which prevents the migration of radionuclides into the dispersion medium, using a positively charged colloid of iron (III) hydroxide as a coagulant. To decontaminate the liquid phase, we used a complex sorbent developed by us based on micro- and nanoparticles of iron hydroxide modified with nickel-potassium ferrocyanides, with the additional use of highly dispersed layered aluminosilicates.

The proposed method makes it possible to obtain purified soil and purified water (Fig. 1), which can be used in the technological process of soil purification. The purified soil can be used in soil rehabilitation processes. Radioactive sludge is suitable for further compaction and long-term storage in special radioactive waste storage facilities.

Keywords: plasma chemistry, complex sorbent, soil

Application of activated carbon in water treatment: radionuclides and microplastics removal

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Activated carbon has emerged as a valuable tool in water treatment due to its exceptional adsorption properties. This study focuses on the application of activated carbon for the removal of radionuclides and microplastics from water sources. Radionuclides, especially radioactive iodine, pose serious health risks when present in drinking water, while microplastics have become a pervasive environmental concern. Activated carbon offers an effective solution for mitigating these contaminants, with its high surface area and porous structure enabling the adsorption of both radionuclides and microplastics. In this study, for the first time, a series of activated carbons were obtained based on walnut shells, which underwent chemical activation with KOH and were modified with nitrogen groups due to the hydrothermal introduction of urea into the structure of the activated carbon. Nitrogen doping was carried out to introduce positively charged active sites. The sorption capacity of the sorbent was 459.42 mg I⁻ per gram of composite with an initial iodide ion concentration of 100 mg/l. The sorption capacity of the WN KOH composite without modification with nitrogen groups was 432.5 mg/g with an initial iodide ion concentration of 100 mg/l.

Keywords: activated carbon, radionuclides, microplastic, adsorption

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