

BAŽANT
POSTGRADUATE CONFERENCE
2022

Proceedings of Abstracts



INSTITUTE OF CHEMICAL PROCESS FUNDAMENTALS OF THE CAS

Prague, 13th-14th June, 2022

Bažant Postgraduate Conference 2022

Proceedings of Abstracts

Prague, 13th–14th June, 2022

Editor © Magdalena Bendová and Zdeněk Wagner, 2022

Published: Institute of Chemical Process Fundamentals of the CAS, v. v. i.
Prague 2022

CONTENTS

Chiral membrane prepared by electrostatic modification of ion-exchange membrane <i>Ing. Jan Čížek</i>	5
Removal of PFASs from sewage sludge by pyrolysis <i>Ing. Matěj Hušek</i>	6
Application of hydrodynamic cavitation in brewing <i>Ing. Jiří Štěřba</i>	8
Analysis of textile waste streams in the Czech Republic <i>Ing. Anastasia Shtukaturova</i>	9
Multiplication of urea sites—impact on binding phosphates <i>Ing. Karolína Salvadori</i>	11
A seven-years based characterization of aerosol light scattering properties at Central European rural site: Variability and source apportionment <i>Mgr. Lenka Suchánková</i>	13
Vertical distribution of black carbon (BC) <i>Kajal Julaha, MSc.</i>	15
Continuous production of 1-methyl-10 α -methoxydihydrolysergic acid methyl ester via microreactors <i>Mgr. Natalie Jaklová</i>	17
Use of photoautotrophic microorganisms in bioremediation of surface waters <i>Mgr. Petra Mušálková</i>	19
Synthesis of biobased ionic liquids from the choline for lignin derivatization <i>Mahasoa-Salina Souvenir Zafindrajaona, MSc.</i>	21
Experimental study of bubble dynamics in aqueous solutions of simple alcohols: CFD validation data <i>Ing. Jakub Crha</i>	23
Continuous electrocoagulation of <i>Chlorella vulgaris</i> in a novel channel-flow reactor <i>Ing. Simona Lucáková</i>	25
What happens to microplastics in nature <i>Ing. Markéta Spáčilová</i>	27
Slit geometry microreactor for light induced photocatalysis with graphite carbon nitride thin films <i>Susmita Dolai, MSc.</i>	29

The study on stability of ionanofluids; change in heat capacity of ionanofluids over a long period of time	
<i>Nirmal Parmar, MSc.</i>	31
Tetracycline degradation using catalysts of platinum coated over CeO ₂ and CeO ₂ ZrO ₂	
<i>Mahdi Bourassi, MSc.</i>	33
Ambient organic aerosol origin at rural background site in the Czech Republic	
<i>Mgr. Radek Lhotka</i>	35
NMR-based metabolomic analysis of blood plasma as a pancreatic cancer diagnostic tool	
<i>Ing. Lenka Michálková</i>	37
Utilization of solid sorbents for high temperature removal of halogenated compounds from pyrolysis of waste plastic	
<i>Ing. Vít Šrámek</i>	39
Adaptive synthesis of functional amphiphilic dendrons for drug nanocarrier assembly	
<i>Ing. Anonín Edr</i>	41
Deoxyfluorinated <i>N</i> -acetyllactosamines as carbohydrate-based probes for human galectins	
<i>Ing. Martin Kurfiřt</i>	43
Hybrid organometallic galectin inhibitors	
<i>Ing. et Ing. Vojtěch Hamala</i>	45

Chiral membrane prepared by electrostatic modification of ion-exchange membrane

Student: Ing. Jan Čížek

Supervisor: Ing. Pavel Izák, Ph.D., DSc.

Supervising Expert: Doc. Ing. Zdeněk Slouka, Ph.D.

Many chiral drugs and food supplements were developed and are still sold as racemic mixtures of both enantiomers. However, human metabolism is a complicated set of biochemical reactions involving many chiral recognition sites, which recognize only one of the two enantiomers found in racemic drugs, while the other one is found to be inactive or even toxic. Therefore, it is very important to use enantiomerically pure drugs to avoid undesired side effects caused by administration of racemic mixtures. Yet, the enantioseparation of racemic substances on larger than laboratory scale has been a difficult challenge and membrane technology is a promising candidate to overcome this issue.

To separate enantiomers using membranes, a special type of membrane with immobilized chiral recognition sites (chiral membrane) is required.¹ In this work, a simple and effective method for chiral membrane preparation is demonstrated, involving electrostatic interaction between negatively charged sulfobutylether- β -cyclodextrin (SBE- β -CD) as a chiral selector and a commercially available anion-exchange membrane.² The modified home-made chiral membrane was tested in diffusion cells to characterize its enantioselectivity towards D,L-Tryptophan. We demonstrated in our work that L-Tryptophan is preferentially absorbed into the membrane, while D-Tryptophan is transported through the membrane with enantiomeric excess exceeding 80%. To increase the permeation rate of the membrane, thinner ion-exchange membrane substrate with higher degree of swelling is proposed.

References

1. Kasal, P.; Michel, M.; Gaálová, J.; Cuřínová, P.; Izák, P.; Dian, J.; Jindřich, J. *Mater. Today Commun.* **2021**, *27*, 102234.
2. Kučerová, G.; Procházková, H.; Kalíková, K.; Tesařová, E. *J. Chromatograph. A* **2016**, *1467*, 356–362.

Removal of PFASs from sewage sludge by pyrolysis

Student: Ing. Matěj Hušek

Supervisor: Doc. Ing. Michael Pohořelý, Ph.D.

Per- and polyfluoroalkyl substances (PFASs) are widely used in industry (packaging, textile, electroplating, metallurgical or plastic industries) because of their valuable properties (low surface tension, nonflammability, hydrophobicity, oleophobicity, or good thermal conductivity).¹ In contrast to properties suitable for industry, PFASs have several adverse health effects (e.g. kidney cancer, sperm quality, or cholesterol level),² and their occurrence in nature is not desirable. The extensive use of PFASs is later reflected in their content in wastewater and subsequently in sewage sludge.³ Thus, agricultural sludge use should be replaced by thermal sludge treatment. Monoincineration is a well-known technology, in contrast to sludge pyrolysis, which still has some research gaps, especially in the field of the behaviour of organic pollutants, including PFASs.⁴ Our work aimed to describe PFASs behaviour at different pyrolysis temperatures (200 to 700 °C). We analysed 37 PFAS in sewage sludge samples and pyrolysis products. The temperature at which PFASs were removed from the sewage sludge at more than 99.0% was 400 °C, and at 600 °C, removal was more than 99.9%. As a result, it is recommended for commercial sludge pyrolysis units (larger volume, lower material homogeneity) that the process temperature be not lower than 600 °C. This recommendation is supported and demonstrated by the analyses of samples from the Bohuslavice Trutnov WWTP (CZE), where the sludge pyrolysis unit is in operation.

Acknowledgements

This work was supported by the Ministry of Agriculture of the Czech Republic – project QK21020022), Czech Academy of Sciences AV 21 – Sustainable energy, and Specific university research – grant No. A1_FTOP_2022_001 and No. A2_FTOP_2022_003. We also thank our colleagues from UCT Prague and IM CAS, who collaborated on this research.

References

1. Glüge, J.; Scheringer, M.; T. Cousins, I.; C. DeWitt, J.; Goldenman, G.; Herzke, D.; Lohmann, R.; A. Ng, C.; Trier, X.; Wang, Z. An Overview of the Uses of Per- and Polyfluoroalkyl Substances (PFAS). *Environ. Sci. Process. Impacts* **2020**, *22*(12), 2345–2373. <https://doi.org/10.1039/D0EM00291G>.
2. Fenton, S. E.; Ducatman, A.; Boobis, A.; DeWitt, J. C.; Lau, C.; Ng, C.; Smith, J. S.; Roberts, S. M. Per- and Polyfluoroalkyl Substance Toxicity and Human Health Review: Current State of Knowledge and Strategies for Informing Future Research. *Environ. Toxicol. Chem.* **2021**, *40*(3), 606–630. <https://doi.org/10.1002/etc.4890>.
3. Semerád, J.; Hatasová, N.; Grasserová, A.; Černá, T.; Filipová, A.; Hanč, A.; Innemanová, P.; Pivokonský, M.; Cajthaml, T. Screening for 32 Per- and Polyfluoroalkyl Substances (PFAS) Including GenX in Sludges from 43 WWTPs Located in the Czech Republic—Evaluation of Potential Accumulation in Vegetables after Application of Biosolids. *Chemosphere* **2020**, *261*, 128018. <https://doi.org/10.1016/j.chemosphere.2020.128018>.
4. Hušek, M.; Moško, J.; Pohořelý, M. Sewage Sludge Treatment Methods and P-Recovery Possibilities: Current State-of-the-Art. *J. Environ. Manag.* **2022**, *315*, 115090. // <https://doi.org/10.1016/j.jenvman.2022.115090>.

Application of hydrodynamic cavitation in brewing

Student: Ing. Jiří Štěřba

Supervisors: Prof. Ing. Tomáš Brányik, Ph.D., Ing. Miroslav Punčochář, DSc.

Supervising Expert: Ing. Lukáš Kulaviak, Ph.D.

The positive role of hydrodynamic cavitation (HC) is the object of study in the last two decades. HC phenomena involves the generation, growth, coalescence and subsequent implosive collapse of bubbles or cavities, occurring in few microseconds and releasing large magnitude of local pressure and temperature. Due to its very high oxidative capability in combination with mechanical shockwaves, HC process can disrupt the biological cells, destroy microorganisms, neutralize toxic chemicals or change molecule structures.

The aim of this work is to apply these advantages in the brewery industry. In the field of beer brewing, we would like to investigate several phenomena, such as the isomerization of bitter hop acids, the reduction of gluten concentration or the cell-walls breakdown.

The first step in the field of cavitation have been the construction of the experimental setup formed by the special jet and the pump control. Venturi jet system with special inclined tube have been chosen as the HC technique due to energy savings and robust design. The process of cavitation has been occurred and examined in more details. Hence the Venturi tube was installed in real scale brewery system.

Several experiments have been performed to confirm the positive effect of hydrodynamic cavitation on the isomerization of the hop bitter substances, and significant influence in gluten removal due to the cavitation. Furthermore, several parts of experimental brewery have been improved. The regulation of individual parameters affecting the performance of HC have been achieved due to equipment improvements.

Hydrodynamic cavitation is a very interesting phenomenon, which can find application not only in the process of beer brewing, but also in the entire food industry. It is important to investigate this phenomenon, to find the mechanism and to expand into new application.

Analysis of textile waste streams in the Czech Republic

Student: Ing. Anastasia Shtukaturova
Supervisor: Prof. Ing. Vladimír Kočí, Ph.D., MBA
Supervising Expert: Ing. Michal Šyc, Ph.D.

The constantly growing population and standard of living have, together with the phenomenon of fast fashion, caused a significant increase in textile consumption around the world. The textile industry consumes a large amount of natural resources, contributes to environmental pollution and produces greenhouse and waste gases. In 2020, the EU adopted the new Circular Economy Action Plan (CEAP) which principles have to be implemented into the legislation of each Member state for the transition to the circular economy where the recycling of all types of usable waste is maximized. In the Czech Republic, a new waste treatment law based on the CEAP appeared in 2020. The new waste treatment law determines important changes to existing collection and treatment methods of textile waste. As a basis for optimizing these processes, a material flow analysis (MFA) was created to determine the current state with textile waste streams in the Czech Republic. The results showed that the production of industrial textile waste was

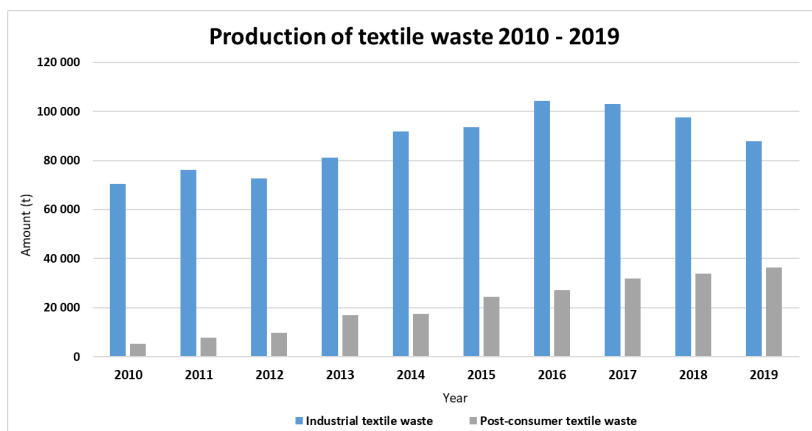


Figure 1: Development of textile waste production in years 2010–2019

70 405 tons in the year 2010 and 87 840 tons in the year 2019, so there is no significant increase for this type of textile waste. The production of textile waste from households was 37 393 tons in the year 2019 and, comparing to the year 2010, it is almost ten times higher (Fig.1). Moreover, the analysis of municipal solid waste (MSW) samples showed that they contained 5–7% of different types of used textiles which may be suitable for recycling. Surprisingly, according to MFA based on official data, more complex textile waste from households is mainly recycled while more homogenous industrial textile waste with a known composition is more often landfilled or incinerated. Our results confirm that the Czech Republic is not well prepared to fulfill the ambitious goals of the CEAP in respect to textile waste because of continually growing volumes of this type of the waste and hardly available official data about its production, lack of recycling technologies and obsolete waste collection system.

Multiplication of urea sites—impact on binding phosphates

Student: Ing. Karolína Salvadori

Supervisor: Ing. Petra Cuřínová, Ph.D.

Supervising Experts: Prof. Dr. RNDr. Pavel Matějka,

Prof. RNDr. Jiří Ludvík, CSc.

The formation of supramolecular complexes between ligands and negatively charged species is a fundamental process in nature. Consequently, the anion recognition, elimination, and sensing represent attractive research topics important in biological and environmental issues. Moreover, the above noticed topics also encroach on the development of new separation procedures, catalysis, or trace analysis.¹ Inspired by nature, supramolecular chemists have synthesized a variety of compounds with high binding constants to target anions.² However, systems offering their real-life application are still rare.

In our work, we focused on the synthesis of sensory groups based on urea structural motifs, suitable for binding phosphates. These units were tested for their selectivity and binding efficiency in HB competitive solvent (DMSO). Then, they were anchored on the dendritic carrier to improve their recycling, desirable for economic, and ecological reasons.³ As confirmed by spectroscopic studies in classical or competitive titration mode, the attachment to a carrier retains the superior efficiency of a monomer unit. Moreover, dendritic receptors with low dihydrogen phosphate loadings offer a cooperative complexation mode associated with a positive dendritic effect, which even amplifies the binding selectivity. At higher concentrations of dihydrogen phosphate, the dendritic branches act independently and the binding mode changes to a 1:1 anion:urea stoichiometry. For weaker complexes, with chloride, no effects similar to those observed for dihydrogen phosphate can be obtained (Fig. 1). It seems that chloride does not have a convenient shape and size for cooperative binding to dendritic receptors. Recycling of obtained dendritic receptors by complex dissociation and nanofiltration enables their repeatable use. According to all these findings, the anchoring seems to be favourable providing advantages for phosphate separation.

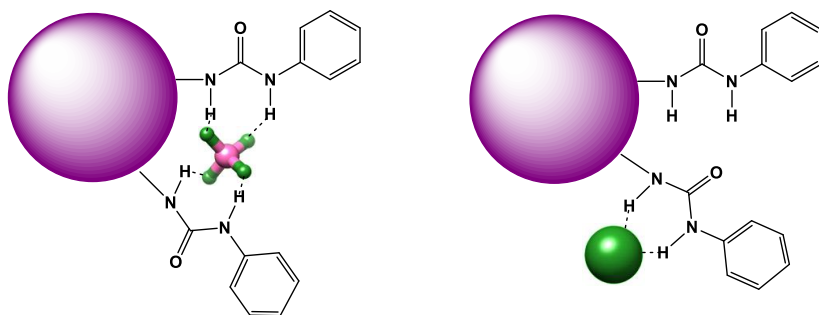


Fig. 1: Cooperative (dendrimer+ $\text{H}_2\text{PO}_4^{3-}$) vs. non-cooperative (dendrimer+ Cl^-) binding mode.

References

1. Sessler, J. L.; Gale, P. A.; Cho, W. Anion receptor chemistry; The Royal Society of Chemistry: UK, **2006**.
2. Busschaert, N.; Caltagirone, C.; Van Rossom, V.; Gale, P. A. Applications of supramolecular anion recognition. *Chem. Rev.* **2015**, *115*, 8038–8155.
3. Cuřínová, P.; Winkler, M.; Krupková, A.; Císařová, I.; Budka, J.; Wun, Ch. N.; Blechta, V.; Malý, M; Červenková Šťastná, L.; Sýkora, J.; Strašák, T. Transport of anions across the dialytic membrane induced by complexation toward dendritic receptors. *ACS Omega* **2021**, *6*, 15514–15522.

A seven-years based characterization of aerosol light scattering properties at Central European rural site: Variability and source apportionment

Student: Mgr. Lenka Suchánková

Supervisor: Prof. RNDr. Ivan Holoubek, CSc.

Supervising Expert: Ing. Vladimír Ždímal, Dr.

Atmospheric aerosols have a significant impact on the radiative forcing of Earth's climate, directly through the aerosol-radiation interactions (ARIs) i.e., scattering or absorption of incoming solar and outgoing infrared radiation, or indirectly through the aerosol-cloud interactions (ACIs).^{1,2} Although there are studies addressing aerosol impact on local climate,³⁻⁵ the information on long-term measurements at rural background site is missing. Such studies are important for understanding of local sources and long-range transport of both anthropogenic and natural aerosols. Therefore, we focused on temporal variations of the total light scattering (σ_{sp}) and backscattering (σ_{bsp}) coefficients and associated optical properties such as the Ångström exponent (SAE), backscattering ratio (b), and asymmetry factor (g) at a rural background site National Atmospheric Observatory Košetice (NAOK; 49°34'20.787"N, 15°4'48.155"E) in Central Europe. We measured σ_{sp} and σ_{bsp} at 5 min resolution at three wavelengths (450, 550, and 700 nm) using the Integrating Nephelometer TSI 3563 (PM10 inlet). Measurements were performed from 16 August 2012 to 31 December 2019. The analysis has been performed using R software version 4.1.0. The preliminary results show that the overall trend for both σ_{sp} and σ_{bsp} is downward from 2012-2019; the slope of the median trend line was $-2.50 \text{ Mm}^{-1}/\text{yr}$ and $-0.18 \text{ Mm}^{-1}/\text{yr}$ at 550 nm, respectively. SO_2 and NO_x concentrations were well correlated with σ_{sp} and σ_{bsp} throughout the period, confirming their contribution in the light-scattering enhancement. b had a positive slope of the median trend line ($0.012/\text{yr}$), indicating more efficient cooling effect alongside lower aerosol loading. Both σ_{sp} and σ_{bsp} reached higher values in the cold seasons (median, 46.8 and 5.9 Mm^{-1}) than in the summer (median, 25.4 and 4.1 Mm^{-1}). This phenomenon is probably related to the higher aerosol loading in winter due to higher energy consumption, poorer dispersion of pollutants, and lower planetary boundary

layer. Elevated SAE observed in summer indicates smaller particles and corresponds to secondary organic aerosol. On the other hand, decreased SAE during winter corresponds to bigger particles (higher atmospheric stability and thus aerosol aging).

In addition, the sources of scattering aerosols, chemical composition, meteorological conditions, particle size distribution, and radiative forcing will be further investigated at NAOK to better understand the direct effects of aerosols on local climate.

This work was supported by the Ministry of Education, Youth and Sports of CR within the CzeCOS program, grant number LM2018123 within the National Sustainability Program I (NPU I), grant number LO1415, European Regional Development Fund-Project ACTRIS-CZ LM201818122, ACTRIS IMP (www.actris.eu) which is supported by the European Commission under the Horizon 2020 – Research and Innovation Framework Programme, H2020-INFRADEV-2019-2, Grant Agreement number: 871115.

References

1. IPCC, 2013. Summary for Policymakers. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change; Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S. K., Boschung, J., A. Nauels, Y. X., Bex, V., Midgley, P. M., Eds.; **2013**
2. Ramanathan, V.; Crutzen, P. J.; Kiehl, J. T.; Rosenfeld, D. Atmosphere: Aerosols, Climate, and the Hydrological Cycle. *Science*. **2001**, *294* (5549), 2119–2124.
3. Delene, D. J.; Ogren, J. A. Variability of Aerosol Optical Properties at Four North American Surface Monitoring Sites. *J. Atmos. Sci.* **2002**, *59* (6), 1135–1150.
4. Luoma, K.; Virkkula, A.; Aalto, P.; Petäjä, T.; Kulmala, M. Over a 10-Year Record of Aerosol Optical Properties at SMEAR II. *Atmos. Chem. Phys.* **2019**, *19* (17), 11363–11382.
5. Pandolfi, M.; Alados-Arboledas, L.; Alastuey, A. et al. A European Aerosol Phenomenology - 6: Scattering Properties of Atmospheric Aerosol Particles from 28 ACTRIS Sites. *Atmos. Chem. Phys.* **2018**, *18* (11), 7877–7911.

Vertical distribution of black carbon (BC)

Student: Kajal Julaha, MSc.

Supervisor: Petr Pišoft, Ph.D.

Supervising Experts: RNDr. Naděžda Zíková, Ph.D.,

Ing. Vladimír Ždímal, Dr.

Introduction

Black Carbon (BC) is one of the leading contributors affecting our climate system.¹ Absorbing at all visible wavelengths results in a warmer environment² and thus has been considered the second most important contributor to global warming after carbon dioxide. The primary sources of BC aerosol are the incomplete combustion of fossil fuels and biomass burning. However, the composition of atmospheric aerosols varies with the height above the Earth's surface. Recent studies have shown significant uncertainties (about 25%) in model simulations of the vertical BC distribution, both on the regional and global levels.³ BC's vertical transport is suggested to be one area where the models still differ significantly,^{4,5} highlighting further investigation.

Methods

In the present study, we used an unmanned aerial vehicle (UAV)—Hexarotor UAV, M600, in cooperation with Czech Globe—Global Change Research Institute CAS. Compared to other land-based approaches or other aerial methods, it is found to be a versatile method for measurements. Micro-Aethalometer (AE51, AethLabs, San Francisco, CA), a portable handheld instrument, was used to measure eBC (equivalent black carbon) mass concentration. Measurements were performed on the flow rate of 150 ml/min with a time resolution of 1 sec. During the sampling campaign, eBC was simultaneously monitored every 1 min at 4 m above the ground with a multi-wavelength aethalometer (AE33, Magee Scientific, Berkeley, CA, USA). We measured the eBC using two mounting methods: 1- Inlets were mounted on the top of the drone. 2- Hanging the instruments below the drone using a 2.5 mm string. The measurements were found stable when inlets were mounted on the drone. The descent flights were not found reliable because of the downwash effect from drone wings.

Results and Discussion

The measured concentration from AE-33 was found to be lower at ground level (4 m) than the concentration measured by AE51 at 50 m. The measurements were taken during the daytime and strong vertical mixing inside the planetary boundary layer (PBL) led to aerosol particles being rapidly transported to the upper level. The eBC concentration did not vary much up to 70-180 m and showed a sudden high increase above 180 m. Such behavior can be due to lower noon-time PBL height because of the presence of cloud, as cloud suppresses the evolution of PBL. Further investigation and measurement campaigns can reveal more about the vertical behavior of the eBC concentration with PBL.

This work was supported by MEYS of the Czech Republic under grants ACTRIS-CZ LM2018122.

References

1. Altstädter, B.; Deetz, K.; Vogel, B. et al. *Atmosph. Chem. Phys.* **2020**, *20*, 7911–7928.
2. Koch, D.; Schulz, M.; Kinne, et al. *Atmosph. Chem. Phys.* **2009**, *9*, 9001–9026.
3. Koffi, B.; Schulz, M.; Bréon, et al. *J. Geophys. Res. Atmos.* **2012**, *117*.
4. Ramachandran, S.; Rajesh, T.A. *J. Geophys. Res. Atmos.* **2007**, *112*.
5. Schwarz, J.P.; Spackman, J.R.; Gao, R.S.; Watts, L.A.; Stier, P.; Schulz, M.; Davis, S.M.; Wofsy, S.C.; Fahey, D.W. *Geophys. Res. Lett.* **2010** *37*.

Continuous production of 1-methyl-10 α -methoxydihydrolysergic acid methyl ester via microreactors

Student: Mgr. Natalie Jaklová

Supervisor: Doc. Ing. Petr Klusovník, DSc.

Supervising Expert: Ing. Petr Stavárek, Ph.D.

The main topic of the contribution is the conversion of the batch N-alkylation reaction into a continuous regime. It is the reaction of 10 α -methoxydihydrolysergic acid methyl ester to 1-methyl-10 α -methoxydihydrolysergic acid methyl ester.¹ This reaction represents a one step in industrial synthesis of Nicergoline, a pharmaceutical used for example for senile dementia treatment.^{2,3} This methylation reaction is performed in two immiscible liquid phases. Phase transfer catalysis is used to increase the efficiency of the reaction, which allows the reaction to proceed in the entire volume of organic solvent, not only at the phase interface.^{4,5} The reaction is fast and has an exothermic character. The advantages of continuous arrangement are better control of the reaction, increased operational safety due to the handling of smaller volumes of reaction components, and simplification of the reaction procedure.^{6–8} The present contribution addresses the influence of reaction conditions on the course of the reaction in a microfluidic reactor. The feasibility of reaction in microchip reactor, optimization of reaction condition, the scaling-up and effect of sonication to selectivity and conversion of the reaction will be presented.

References

1. Cvak, L.; Stuchlik, J.; Cerny, A.; Krepelka, J.; Spacil, J. DI-HYDROLYSERGOL'S 1-ALKYLATED DERIVATIVES PREPARATION METHOD. CS234498B1, 1984.
2. Winblad, B.; Fioravanti, M.; Dolezal, T.; Logina, I.; Milanov, I. G.; Popescub, D. C.; Solomon, A. Therapeutic use of Nicergoline. *Clin. Drug Invest.* **2008**, 28(9), 533–552.
3. Böttiger, Y.; Dostert, P.; Benedetti, M. S.; Bani, M.; Fiorentini, F.; Casati, M.; Poggesti, I.; Alm, C.; Alvan, G.; Bertilsson, L. Involvement of CYP2D6 but not CYP2C19 in nicergoline metabolism in humans. *Br. J. Clin. Pharmacol.* **1996**, 42(6), 707–11.

4. Gordon, J. E.; Kutina, R. E. Theory of phase-transfer catalysis. *J. Am. Chem. Soc.* **1977**, *99*(12), 3903–3909.
5. Dehmlow, E. V. PHASE-TRANSFER CATALYZED 2-PHASE REACTIONS IN PREPARATIVE ORGANIC-CHEMISTRY. *Angew. Chem.-Int. Edit. Engl.* **1974**, *13*(3), 170–179.
6. Porta, R.; Benaglia, M.; Puglisi, A. Flow Chemistry: Recent Developments in the Synthesis of Pharmaceutical Products. *Org. Process Res. Dev.* **2016**, *20*(1), 2–25.
7. Baumann, M.; Moody, T. S.; Smyth, M.; Wharry, S. A Perspective on Continuous Flow Chemistry in the Pharmaceutical Industry. *Org. Process Res. Dev.* **2020**, *24*(10), 1802–1813.
8. Bojang, A. A.; Wu, H.-S. Design, Fundamental Principles of Fabrication and Applications of Microreactors. *Processes* **2020**, *8*(8), 891.

Use of photoautotrophic microorganisms in bioremediation of surface waters

Student: Mgr. Petra Mušálková
Supervisor: Ing. Irena Brányíková, Ph.D.

Water eutrophication is one of the current problems of water ecosystems (including waterbodies used for recreation and as potable water sources). Since the 1980s there is an increase of eutrophication due to human activity, pollution and increased usage of fertilization in agriculture. Nutrients such as different forms of nitrogen and phosphorus, enter the water environment in great amount, affecting the whole ecosystem. These excessive pools of nutrients are favorable for massive seasonal harmful cyanobacterial blooms. The negative consequences of which are production of toxins and depletion of oxygen, which is dangerous for human health and could eventually lead up to a total collapse of the ecosystem. Although there are several procedures on how to deal with water blooms, or to prevent them, these procedures are expensive, have limited efficiency, or they introduce chemicals in the ecosystem (i.e. dredging lake beds, coagulation, sonication, mixing, use of herbicide or metals, aeration etc.). The aim of my thesis is to develop an alternative method of removing this overplus of nutrients from surface waterbodies in a biological way, with the use of microalgae and cyanobacteria. The first main task is a construction of a floating open reactor, which would be placed on the eutrophic water surface, the design of the reactor will enable exchange of water between its inner volume and the bulk water. In this bioreactor, non-toxic, strictly filamentous cyanobacteria will be cultivated in order to uptake the available nutrients into biomass, making them unavailable for the harmful species. Afterwards, the obtained biomass will be harvested and used as a fertilizer in ecological agriculture. The second task is to get understand the mechanisms of nutrient, especially phosphorus, uptake in the selected appropriate species and make use of them in designing the method of surface water bioremediation.

My first experiments were carried out with the filamentous cyanobacteria *Tolypothrix tenuis*. During the batch cultivation experiments carried with suspended biomass, the time course of concentration of phosphorus in the cultivation medium, the concentration of the intracellular phosphorus and biomass production, were determined.

Preliminary results confirmed that *Tolypothrix tenuis* is capable of reducing of the phosphorus in a medium efficiently down to 0.02 mg/L which is generally considered as preventing harmful algal blooms. Additionally, the rate of the reduction was proportional to the concentration of *T. tenuis* biomass. To further increase the rate of nutrients removal, phosphorus starved cultures were prepared by cultivating *Tolypothrix tenuis* in a medium without phosphates for different time period. These cultures had lower content of intracellular phosphorus leading to a higher rate of phosphorus uptake from the medium. In the near future, the same experiments will be carried out in the prototypes of the floating bioreactors.

Synthesis of biobased ionic liquids from the choline for lignin derivatization

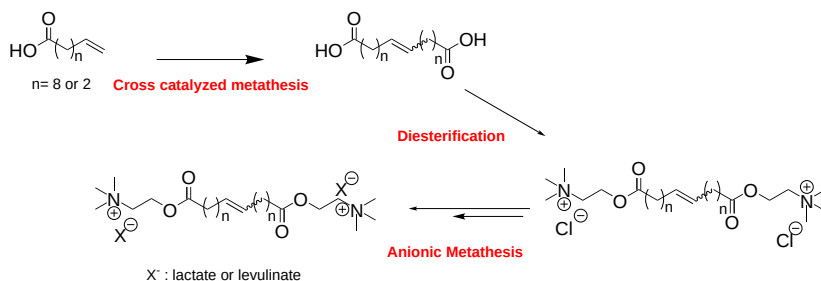
Student: Mahasoa-Salina Souvenir Zafindrajaona, MSc.

Supervisors: Prof. Sandrine Bouquillon, Ing. Magdalena Bendová, Ph.D.

Supervising Expert: Dr. Jean-Pierre Mbakidi

Lignin, the second most abundant biopolymer after cellulose, is a heteropolymer composed of three monomers linked via different bonds such as among other β -O-4 or carbon-carbon.¹ Its complex structure is a hindrance to its valorization. Despite this, the valorization of lignin is an issue for scientists and industries. Thanks to these major entities of which the lignin is composed and which represent a great interest for the chemical industry, it is therefore a real challenge to find a way to valorize it.² Indeed, for a few years, studies on the dissolution and the treatment of lignin have been developed to valorize this biopolymer. Scientists have used different ionic liquids or deep eutectic solvents as solvents. Generally, the cation that has been most studied in order to dissolve lignin is imidazolium modified by methyl, ethyl, allyl, butyl, hexyl or benzyl groups.³ However, these petroleum-based ionic liquids are very cyto- and eco-toxic,^{4,5} so other biobased and less ecotoxic ionic liquids have been used for lignin dissolution.⁶ For example, choline ester-based ionic liquids are used to dissolve lignin from Kraft pulp at 100 °C for 1 hour.⁷

In this context we want to develop new biobased bolaform ionic liquids based on choline ester with levulinate or lactate anions as associated anions (Scheme 1).



Scheme 1: Synthetic pathway used for the bolaform biosourced ILs

The presentation will be dedicated to the description of the syntheses and the characterization of the new bolaform ILs. The further work which will be realized in Prague will be also presented and discussed in relation to the lignin depolymerisation purpose.

References

1. Rakotoveloa, A.; Peruch, F.; Grelier, S., Edition TI, **2019**, Réf. IN235 V1
2. Xu, J.; Li, C.; Dai, L. ; Xu, C. ; Zhong, Y. ; Yu, Y. ; Si, Y. *Chem. Sus. Chem.* **2020**, *13*, 4284–4295
3. Mäki-Arvela, P. ; I. Anugwom, Virtanen,P. ; Sjöholm, R.; Mikkola., J.P. *Ind. Crop. Prod.* **2010**, *32*, 175–201.
4. Costa, S. P. F.; Azevedo, A. M. O. ; Pinto, P. C. A. G.; Saraiva, L. M. F. S. *Chem. Sus. Chem.* **2017**, *10*, 2321.
5. Garcia, M. T.; Gathergood, N; Scammells, P. J. *Green. Chem.* **2005**, *7*, 9–14
6. Mbakidi, J.P.; Barjhoux, I, Aguib, K.; Geffard, A; Rioult, D.; Palos Ladeiro, M.; Bouquillon, S. *ACS Sust. Chem. Eng.*, **2021**, *9*, 15427–15441
7. Mbakidi, J.P.; Kerkache, A.; Lazar ,F.; Bouquillon S. *J. Solut. Chem.* **2022**, *51*, 345–356.

Experimental study of bubble dynamics in aqueous solutions of simple alcohols: CFD validation data

Student: Ing. Jakub Crha

Supervisor: Dr. Ing. Pavlína Basařová

Supervising Expert: Doc. Ing. Marek Růžička, DSc.

Simple short-chain alcohols and their aqueous solutions are widely used in industrial, biological and pharmaceutical applications. The physico-chemical properties of these solutions, such as dynamic viscosity and surface tension, are highly affected by the complex structure of water-alcohol mixtures.¹ Dilute solutions of alcohols act as a strong surfactant that can immobilize the bubble surface and consequently affects bubble rising dynamics and shape deformations.²

The aim of this work was to obtain experimental values of terminal velocities and shape deformations for a wide range of bubble sizes and compare them with theoretically calculated values. These data were obtained for the whole concentration range of aqueous solutions of 1-propanol and ethanol and will be used for validation of CFD results in future work.

From the obtained results three distinctive regions were identified. In mixtures with very low alcohol content ($x_p, x_E \leq 0.005$) the molecules of alcohol behave as a surfactant and adsorb on the bubble surface. Depending on the bubble size, the surface is fully or partially immobilized. The transitional region ($0.005 \leq x_p \leq 0.07$ and $0.005 \leq x_E \leq 0.18$) is characterized by the shift from immobile surface to fully mobilized at higher alcohol concentrations. In the third region, where the concentration is above the critical aggregation concentration ($x_p \geq 0.07, x_E \geq 0.18$), the surface mobility of the bubble is not affected. However, the bubble terminal velocity reaches a minimum, which is caused by one of the anomalies of alcohol-water mixtures, an existence of the dynamic viscosity maximum of the solution. The addition of alcohol beyond this point results in the minor increase of the velocity, as the viscosity lowers to a value of pure liquid.

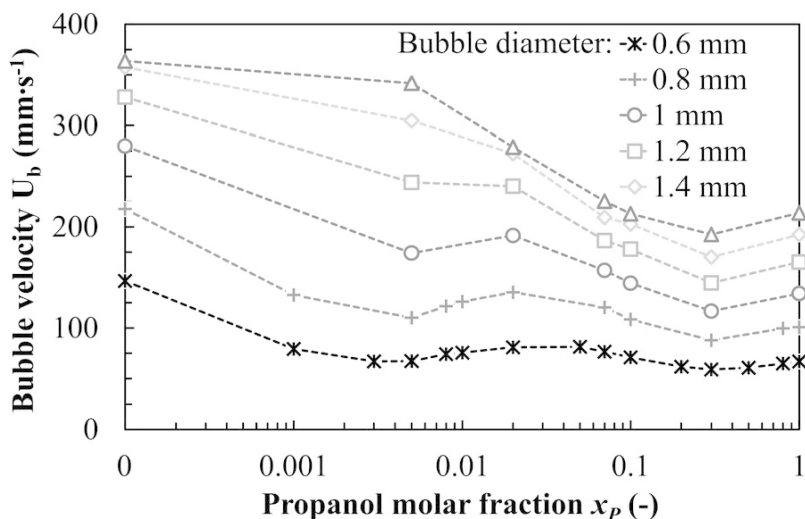


Figure 1: Effect of the propanol concentration on the bubble terminal velocity for different bubble diameters.

Acknowledgements:

This work was supported by a Czech Science Foundation (GACR) grant 19-09518S.

References

- Chodzińska, A.; Zdziennicka, A.; Jańczuk, B., Volumetric and Surface Properties of Short Chain Alcohols in Aqueous Solution-Air Systems at 293 K. *J. Solut. Chem.* **2012** 41(12), 2226–2245.
- Basařová, P.; Pišlová, J.; Mills, J.; Orvalho, S., Influence of molecular structure of alcohol-water mixtures on bubble behaviour and bubble surface mobility. *Chem. Eng. Sci.* **2018**, 192, 74-84.

Continuous electrocoagulation of *Chlorella vulgaris* in a novel channel-flow reactor

Student: Ing. Simona Lucáková

Supervisor: Prof. Ing. Tomáš Brányik, Ph.D.

Supervising Expert: Ing. Irena Brányiková, Ph.D.

Separation of microalgae cells from culture medium after cultivation (so called 'harvesting') is one of the most challenging steps in a large-scale autotrophic production of microalgae. Due to a very low concentration of cells in medium (usually in range 0.5–3 g/L),¹ small cell diameter (3–30 μm)¹ and low wet cell density (1030–1100 g/L),² low cost harvesting methods as sedimentation or filtration are inapplicable. Currently, the most common type of microalgae harvesting on industrial scale is centrifugation, although it is expensive due to high energy demands. Coagulation was proposed to be a suitable process for microalgae suspension pre-concentration prior to centrifugation in order to decrease the volume of suspension needs to be centrifuged. During coagulation, cells are induced to form large aggregates (flocs) with relatively high sedimentation velocity, which can be subsequently separated by gravity sedimentation, flotation or filtration. Various types of coagulation including inorganic and polymer chemical coagulation, autoaggregation, biocoagulation and electrocoagulation were tested during past few years for microalgae harvesting.

Electrocoagulation, a well-known process in industrial wastewater treatment, was proposed to be a promising technique for harvesting single-cell freshwater and saline water microalgal species. In our laboratory, we employed an electrocoagulation process with iron sacrificial anode leading to the separation of *Chlorella vulgaris* cells with high efficiency and at the same time acceptable low contamination of separated biomass by iron. Comparing to only centrifugation, the total energy costs of harvesting using electrocoagulation as a pre-concentration step prior to centrifugation were reduced by more than 80%. After extensive study of the influence of relevant process parameters such as pH, electric charge, temperature, agitation intensity, initial biomass concentration and residual salt concentration conducted in laboratory scale equipment, three bench-scale electrocoagulation devices were designed and tested. The best results (highest separation efficiency and lowest iron contamination) were obtained using continuous pneumat-

ically agitated channel flow reactor with submerged perforated plates. Subsequently, this device was scaled up from the working volume of 13 L to the working volume of 160 L. Final electrocoagulation device consisted from three functional domains (i) electrolyser, where the iron = coagulant dissolves into microalgal suspension, (ii) aggregator, where the microalgal cells form aggregates by appropriate mixing achieved by the flow of the suspension through the series of perforated plates and (iii) lamellar settler, where the aggregates sediment. The hydraulic characteristic of this reactor was determined to be a dispersed plug flow. Using this device, harvesting efficiency of *Chlorella vulgaris* higher than 85% was achieved while the iron content in the separated biomass was below the limit for potential food application. Thus, electrocoagulation was evaluated as a suitable and cost-effective method for harvesting of single cell microalgae for human consumption.

References

1. Christenson, L.; Sims, R. *Biotechnol. Adv.* **2011**, *29*, 686-702.
2. Al Hattab, M; Ghaly, A.; Hammouda, A. J. *Fundam. Renew. Ener. Appl.* **2015**, *5*, 1000154.

What happens to microplastics in nature

Student: Ing. Markéta Spáčilová

Supervisor: Ing. Olga Šolcová, CSc., DSc.

The ever-increasing amount of microplastics in water is a serious environmental problem. In addition, their detection is also complicated, so information about their quantity and types is rather missing. For this reason, it is necessary to obtain more information regarding their occurrence in the aquatic environment. However, to determine the microplastic amount in aqueous solution is far from easy and to distinguish between the individual types of microplastics is even more difficult, because the obtained data are skewed by their degradation in the environment. Degradation of microplastics can be caused, for example, by sunlight, abrasion, contact with chemicals, or a combination of these effects.

This work was focused on preparation of microplastic particles which correspond to microplastics in the environment. The five most used plastics (polyethylene, polyamide, polytetrafluoroethylene, polyethylene glycol terephthalate, and polystyrene) were used for preparation. Microplastics were prepared by grinding common used plastics to match the actual microplastics present in the environment as closely as possible. The shape and size of the prepared particles were obtained by scanning electron microscopy. Raman and infrared spectroscopy were used to characterize the microplastic structures. Simultaneously, methodology to determine the amount of microplastic particles in simulated water samples was developed. Furthermore, the effect of UV degradation by a medium-pressure mercury lamp and also the effect of abrasion on structure of microplastics was investigated on the prepared microplastics. The results provided information concerning changes of the spectra for the individual types of microplastics during the long-term exposure by UV radiation or abrasion. The knowledge from these experiments will lead to improved microplastic detection and their fate in real samples.

Acknowledgement

The Financial support of the Ministry of Industry and Trade of the Czech Republic in the TRIO program, the project No. FV40126: *“Advanced sorbents for the separation of microplastics and micropollutants from water”* is gratefully acknowledged.

Slit geometry microreactor for light induced photocatalysis with graphite carbon nitride thin films

Student: Susmita Dolai, MSc.

Supervisor: Doc. Dr. Ing. Petr Klusoň, DSc.

Supervising Expert: Ing. Petr Stavárek, Ph.D.

The rational synthesis of graphitic carbon nitride materials by supramolecular preorganization of monomers is a powerful tool for the design of their morphology, photophysical and catalytic activities. This work is based on facile and scalable approaches for the synthesis of ordered graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) materials with an excellent photoactivity, which consists of supramolecular interfacial preorganization of graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) monomers at the interface of two non-miscible solvents.¹ The development of microfluidic reactors for photocatalytic applications presents valuable advantages like simultaneous and fine control of light and fluids, large surface area-to volume ratio and uniform distribution of light onto the photocatalyst. Several groups have used microfluidic chips for enhanced chemical reaction performance. We have made a synergy of combining microfluidics and photocatalysis by using some nitrogen-based materials for photocatalytic reaction, to increase the rates and yields. As a proof of concept, we show different properties behaviour of the graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) materials before and after thermal condensation.^{2,3}

The advantages of this research, is the methods which are demonstrated through the tunable morphologies and surface area. The formation of new electronic junctions and high activity as a photocatalyst have been useful for hydrogen evolution and pollutant degradation of the graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) materials.^{4,5}

In summary, we have demonstrated a facile, controllable, scalable and efficient new method for synthesizing carbon nitride materials with morphology and optimizing their catalytic performance in microreactor and cuvette. History and different structures and classification of carbon nitride materials also properly explained in this review. Different organic pollutant degradation and hydrogen generation performance are shown for carbon nitride materials, as per as their catalytic activities and properties.

References

1. Dolai, S.; Bhunia, S.K.; Kluson, P.; Stavarek, P.; Pittermannova, A. Solvent-assisted synthesis of supramolecular-assembled graphitic carbon nitride for visible light induced hydrogen evolution - a review. *ChemCatChem* **2021**, *13*, 1-22.
2. Dolai, S.; Karjule, N.; Azoulay, A.; Barrio, J. Monomer sequence design at two solvent interface enables the synthesis of highly photoactive carbon nitride. *RSC Adv.* **2019**, *45*, 26091-26096.
3. Parmar, J.; Jang, S.; Soler, L.; Kim, D.P.; Sanchez, S. Visible light induced photocatalytic degradation of organic pollutants. *J. Photochem. Photobiol. C: Photochem. Rev* **2005**, *6*, 186
4. Dolai, S.; Barrio, B. J.; Peng, G.; Grafmüller, A.; Shalom, M. Tailoring carbon nitride properties and photoactivity by interfacial engineering of hydrogen-bonded frameworks. *Nanoscale* **2019**, *12*, 5564-5570.
5. Lui, W.; Zhang, Z.; Zhang, D.; Wang, R.; Zhang, Z.; Qiu, S. Synthesis of narrow-band curled carbon nitride nanosheets with high specific surface area for hydrogen evolution from water splitting by low temperature aqueous copolymerization to form copolymers. *RSC Adv.* **2020**, *10*, 28848-28855.

The study on stability of ionanofluids; change in heat capacity of ionanofluids over a long period of time

Student: Nirmal Parmar, MSc.

Supervisor: Ing. Magdalena Bendová, Ph.D.

Supervising Expert: Ing. Zdeněk Wagner, CSc.

Ionanofluids, ionic liquids containing dispersed nanoparticles, show fascinating thermophysical and electrochemical properties.¹ In the last decade, some research work reported on the study of thermophysical properties of multi wall carbon nanotubes (MWCNT) based ionanofluids.²⁻⁵ These works showed that, by adding well defined nanoparticles into ionic liquids, it is possible to tune or/and enhance their thermophysical properties and make them more suitable for electrical and thermal energy storage, and heat transfer applications.²

Ionanofluids samples have been prepared by adding 1% wt. MWCNT into a series of 1-alkyl-3-methylimidazolium bis(trifluoromethyl)sulfonyl imide ionic liquids $[C_n\text{mim}][\text{Tf}_2\text{N}]$ (here $n = 2, 4, 6, 8, 10$ and 12) to find if the heat capacity of the resulting ionanofluids will be increased or decreased with respect to the original pure ionic liquids. To prepare the samples of ionanofluids, mixing of ionic liquids $[C_n\text{mim}][\text{Tf}_2\text{N}]$ and MWCNTs was performed at 220 rpm, 1 mbar pressure and 50°C temperature for two hours on the Rotavapor R-300. A properly mixed solution was submerged for up to an hour for ultrasonic bath where it converted to viscous fluid or gel².

Nevertheless, the major missing topic in the literature was the study of dispersion stability of the ionanofluids. The stability of the ionanofluids is a basic but fundamental requirement to consider them as alternative energy storage materials. To the best of our knowledge for the very first time, the study was conducted on factors affecting the stability of the ionanofluids samples like; temperature, the concentration of nanoparticles, the size of a cation of ionic liquid and, aging over a long period of time. Moreover, the change in isobaric heat capacity was also measured for aged samples after long period of time (20 months) to study the variation in heat capacity due to aging.

Measurements of isobaric heat capacity were carried out as a function of temperature in range of 20°C to 70°C for base ionic liquids $[C_n\text{mim}][\text{Tf}_2\text{N}]$ and ionanofluids $[C_n\text{mim}][\text{Tf}_2\text{N}]$ dispersed with

MWCNT using a μ DSC 3 Evo Microcalorimeter manufactured by Setaram. The measured isobaric heat capacity data of new and aged ionanofluids samples were compared to that of the pure ionic liquid to study the change in isobaric heat capacity. Minor changes in isobaric heat capacity were noted in the studied temperature range for new and aged ionanofluid samples. Furthermore, these experimental isobaric heat capacity data have been assessed by nonstatistical methods of data analysis based on mathematical gnostics (MG). Based on the thermodynamics of data and on the theory of measurement, mathematical gnostics is a novel approach towards data uncertainty.⁷ MG marginal analysis was used to evaluate the interval of typical data and the tolerance interval for each measured data point. Moreover, a robust linear regression along a gnostic influence function was used to find the best curve fit for the measured data.

References

1. Fukushima, T.; Aida, T. *Chem. Eur. J.* **2007**, *13*, 5048-5058.
2. Parmar, N.; Bendová, M.; Wagner, Z.; Pěnkavová, V.; Douihri, I.; Jacquemin, J. *Ind. Eng. Chem. Res.* **2021**, *60*, 7714–7728.
3. Minea, A.A.; Murshed, S.M.S. *Renew. Sust. Energ. Rev.* **2018**, *91*, 584–599.
4. Oster, K.; Hardacre, C.; Jacquemin, J.; Ribeiro, A.P.C.; Elsinawi, A.; *J. Mol. Liq.* **2018**, *253*, 326–339.
5. Nieto de Castro, C.A.; Murshed, S.M.S.; Lourenco, M.J.V.; Santos, F.J.V.; Lopes, M.L.M.; Franca, J.M.P. *Int. J. Therm. Sci.* **2012**, *62*, 34–39.
6. Murshed, S.M.S.; Nieto de Castro, C.A.; Lourenco, M.J.V.; Franca, J.; Ribeiro, A.P.C.; Vieira, S.I.C.; Queiros, C.S., *Int. J. Phys. Math. Sci.* **2011**, *5(4)*, 579–582.
7. Wagner, Z.; Bendová, M.; Rotrekl, J.; Velisek, P.; Storch, J.; Uchtyl, P.; Setnickova, K.; Reznickova, J. *J. Solution Chem.* **2017**, *46*, 1836–1853.

Tetracycline degradation using catalysts of platinum coated over CeO₂ and CeO₂ZrO₂

Student: Mahdi Bourassi, MSc.

Supervisors: Doc. Ing. Petr Klusoň, DSc., Prof. Jacques Barbier

Supervising Experts: Prof. Gwendoline Lafaye,

Dr. Bertrand Gombert

Tetracycline (TET) is an oral antibiotic used for humans and animals. European chemical agency had reported TET to be toxic to aquatic life with long-lasting effects, suspected of damaging fertility or the embryos, may cause harm to breast-fed children, and causes skin irritation.¹ TET in the environment originates from leaking and incompletely treated wastewater loaded with pharmaceuticals, due to excessive production and use. TET risks are the deterioration of useful microorganisms and the gain of antibiotic resistance of harmful bacteria.² As a solution for the limited conventional wastewater treatment plants, catalytic wet air oxidation (CWAO) is one of the most efficient and complete pharmaceutical wastewater detoxification processes.³ This study focuses on TET (200 mg/L) degradation via CWAO using platinum coated over CeO₂ and CeO₂ZrO₂. Two different platinum loading at different temperatures were investigated. Catalytic experiments were followed by analyzing collected samples during running tests by HPLC-UV and TOC analysis for remaining TET and organic carbon quantification. Concerning catalysts characterization, fresh catalysts were analyzed using ICP for platinum quantification, specific surface characterization, temperature-programmed reduction, H₂ chemisorption to highlight metal dispersion, and oxygen storage capacity. Used catalysts were additionally analyzed using elemental analysis to quantify depositions over catalysts. Further analyses were performed on the best catalytic test like HPLC-MS for byproducts identification, *Vibrio fischeri* luminescence inhibition test, BOD, and BOD inhibition for toxicity evaluation. Material characterization showed that CeO₂ had the largest specific surface (144 m².g⁻¹) which stayed similar after Pt coating, even though, oxygen storage capacity increased after Pt coating and ZrO₂ doping (Pt/CeZr 188 μmol.g⁻¹). The most relevant catalytic test results showed that 1% Pt loading was much more efficient for TET degradation, due to higher metal dispersion than 2% loading. 1% Pt/CeZr reached 98% TOC

elimination with high CO₂ selectivity at 50°C atmospheric pressure. Moreover, both catalysts 1% Pt/CeZr and 1% Pt/Ce showed more than 86% TET and TOC elimination after a 3h test under room conditions. Used catalyst test revealed much slower TET degradation reaching 66% and 40% TET and TOC elimination. Used catalysts witnessed specific surface deterioration due to depositions over catalysts. Those depositions were the only deactivation agent for the catalysts. Toxicology evaluation showed that the catalyst test is efficient for water depollution.

References

1. Agency, E. C. Tetracycline. <https://echa.europa.eu/en/substance-information/-/substanceinfo/100.000.438> .
2. (a) Daghbir, R.; Drogui, P., Tetracycline antibiotics in the environment: a review. *Environ. Chem. Lett.* **2013**, *11*(3), 209–227; (b) Bungau, S.; Tit, D. M.; Behl, T.; Aleya, L.; Zaha, D. C., Aspects of excessive antibiotic consumption and environmental influences correlated with the occurrence of resistance to antimicrobial agents. *Curr. Opin. Environ. Sci. Health* **2021**, *19*, 100224.
3. Sushma; Kumari, M.; Saroha, A. K., Performance of various catalysts on treatment of refractory pollutants in industrial wastewater by catalytic wet air oxidation: A review. *J. Environ. Manag.* **2018**, *228*, 169–188.

Ambient organic aerosol origin at rural background site in the Czech Republic

Student: Mgr. Radek Lhotka

Supervisor: Ing. Jaroslav Schwarz, CSc.

Supervising Experts: RNDr. Petra Pokorná, Ph.D.,

Ing. Petr Vodička, Ph.D.

Introduction

Source apportionment of organic aerosols (OA) at background sites is one of the important tasks of the current air quality protection. OA are emitted directly from primary sources or formed in the atmosphere via the oxidation of gas-phase precursors with subsequent partitioning resulting in low-volatility products into the particle phase.³

Methods

The variability of OA sources and their origin during four measurement campaigns were studied at the rural background station National Atmospheric Observatory Košetice (NAOK) in the Czech Republic. Ambient aerosol measurements of non-refractory PM₁ (NR-PM₁) were performed using a Compact Time-of-Flight Aerosol Mass Spectrometer (C-ToF-AMS,²) from 8th January to 14th October 2019 with a 5-min time resolution. The C-ToF-AMS measurements were supplemented with 1-min equivalent black carbon (eBC) data by an aethalometer (Model AE33, Magee Scientific, Berkeley, CA), 1-hour boundary layer height (BLH) by satellite measurements (ERA hourly dataset provided by the Copernicus Climate Change Service), 72-h back-trajectories (GDAS 1°) for every hour by the Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPLIT) and 1-hour meteorology data. 30-min averages of NR-PM₁ were calculated from the 5-min data. A Positive Matrix Factorization (PMF) with multi-linear engine (ME-2) was applied to separate OA into different factors in terms of their mass spectra and time series. The Source Finder (SoFi¹) was used to run PMF and ME-2.

Results and discussion

During three seasons (winter, spring, and autumn), five OA factors and/or sources were identified namely hydrocarbon-like OA (HOA), biomass burning OA (BBOA), coal combustion OA (CCOA) and more and less oxidized OA (MO-OOA and LO-OOA). Four OA factors/sources were identified for the summer, HOA, BBOA, MO-OOA, and LO-OOA. Three of these factors represent primary sources (HOA, BBOA, and CCOA), the other two represent secondary/oxidized factors. The largest share of primary factors (29% of total OA concentrations) was found in winter, the lowest (20%) in summer. Since the aged primary OA becomes part of OOA and therefore, the percentage of primary factors cannot be directly related to the share of these emission sources in the overall immission budget. The concentrations of individual factors were significantly influenced by meteorological and dispersion conditions. The highest concentrations of primary factors were calculated for periods with low wind speed and low atmospheric boundary layer height.

This work was supported by MEYS of the Czech Republic under grant ACTRIS-CZ-LM2015037, ACTRIS-CZ LM2018122 and ACTRIS-CZ RI (CZ.02.1.01/0.0/0.0/16_013/0001315), and by the GACR under grant P209/19/06110Y.

References

1. Canonaco, F.; Crippa, M.; Slowik, J. G.; Baltensperger, U.; Prévôt, A. S. *Atmos. Meas. Tech.* **2013**, *6*, 3649–3661.
2. Drewnick, F.; Hings, S. S.; DeCarlo, P.; Jayne, J. T.; Gonin, M.; Fuhrer, K.; Worsnop, D. R. *Aerosol Science Tech.* **2005**, *39*, 637–658.
3. Kroll, J. H.; Seinfeld, J. H. *Atmos. Environ.* **2007**, *42*(16), 3593–3624.

NMR-based metabolomic analysis of blood plasma as a pancreatic cancer diagnostic tool

Student: Ing. Lenka Michálková

Supervisor: Prof. Ing. Vladimír Setnička, Ph.D.

Supervising Expert: Ing. Jan Sýkora, Ph.D.

Current diagnosis of pancreatic cancer (PC) is insufficient and mostly late due to asymptotic course and unspecific symptoms. Thus, the mortality rate is very high, only 5% of PC patients survive 5 years. However, the poor prognosis can be improved by early diagnosis. In this context, the relationship between PC and diabetes mellitus should be investigated, as diabetes or impaired glucose tolerance had been observed in 80% of PC patients.¹ Pancreatogenic diabetes (T3cDM) is a specific type of diabetes mellitus characterized with increased risk of PC development. Unfortunately, T3cDM is often misdiagnosed for the most prevalent type 2 diabetes mellitus (T2DM) because of similar development. T3cDM patients are associated with an up to 7-fold increased risk of PC development.¹ The crucial role of early PC diagnosis is the differentiation of T3cDM-T2DM among recent onset diabetes mellitus (RODM) patients. NMR-based metabolomics may help to solve this complicated problem of current clinical diagnosis.^{2,3}

In this work, ¹H NMR metabolomic analysis of blood plasma was used as an alternative diagnostic tool of PC. The concentration profile of 58 metabolites was used to discriminate PC patients from long-term T2DM patients and healthy controls. Based on successful discrimination, a specific biomarker panel of eight metabolites was proposed. Furthermore, a prediction model for the identification of risk individuals for PC development in RODM group was developed and the patients with increased risk of PC development were identified. Similar metabolic features with PC were observed in six of 59 RODM patients, and therefore their health conditions were re-examined. Our findings correlate with pathological changes or hereditary predisposition. Recent results also indicate subtle metabolic changes among individual PC clinical stages that could be used for their differentiation in future.

References

1. Pannala, R.; Basu, A.; Petersen, G. M.; Chari, S. T. *Lancet Oncol.* **2009**, *10*, 88-95.
2. Michálková, L.; Horník, Š.; Sýkora, J.; Habartová, L.; Setnička, V. *Analyst* **2018**, *143*, 5974-5978.
3. Michálková, L.; Horník, Š.; Sýkora, J.; Habartová, L.; Setnička, V.; Bunganič, B. *J. Proteome Res.* **2021**, *20*, 1744-1753.

Utilization of solid sorbents for high temperature removal of halogenated compounds from pyrolysis of waste plastic

Student: Ing. Vít Šrámek

Supervisor: Doc. Ing. Karel Cíahotný, CSc.

Supervising Expert: Doc. Ing. Michael Pohořelý, Ph.D.

Pyrolysis of waste plastics offers utilization of material that is not suitable for mechanical recycling process and is able to produce materials with higher added value. Other benefit of chemical recycling is the option to substitute current fossil feedstock in petrochemical industry or refineries.¹

Plastic materials can contain unwanted components and additives such as chlorine from PVC or bromine from flame retardants. These unwanted components or their parts can then transfer to final product (pyrolysis oil, gas), that could ultimately damage subsequent refinery technologies (e.g., catalysts damage, corrosion). Therefore, these halogenated compounds have to be reduced to very low concentration before utilization of the final product. Halogenated compounds are represented in the form of inorganic volatile substances (HCl, HBr) or halogenated organic compounds.^{1,2}

Possible way to remove halogenated compounds from pyrolysis gas before condensation is high temperature adsorption on solid sorbents.^{1,3}

This work focuses on high temperature removal of halogenated compounds in model mixture with hydrocarbons and other compounds. The study was performed in laboratory apparatus under controlled temperature and gaseous mixture composition. Solid sorbents for removal of halogenated compounds (HCl) from previous experiments⁴ are used in subsequent tests to estimate optimal conditions in the environment that is more similar to real application (water and hydrocarbon condensing phase). The results of the performed sorption experiments demonstrate the possibility of using some of the tested materials for the dehalogenation of pyrolysis gas. Particular sorbents show even better performance in presence of water vapor. Final purpose is to transfer laboratory results to the scale of pyrolysis unit operated by industrial partner.

Acknowledgements

This work was supported from Technology Agency of the Czech Republic – project FW01010158, AV 21 – Efficient energy transformation and storage, and from the grant of Specific University research – grant No A1_FTOP_2022_005.

References

1. Staf, M.; Šrámek, V.; Pohořelý, M. Halogenderiváty v pyrolyzovaných plastech. *Paliva* **2020**, *12*(4), 136–148.
2. Czégény, Zs.; Jakab, E.; Blazsó, M.; Bhaskar, T.; Sakata, Y. Thermal decomposition of polymer mixtures of PVC, PET and ABS containing brominated flame retardant: Formation of chlorinated and brominated organic compounds. *J. Anal. Appl. Pyrol.* **2012**, *96*, 69–77.
3. Blazsó, M.; Bozi, J. Catalytic Conversion of Thermal Decomposition Products of Halogen Containing Polymers Studied by Pyrolysis-GC-MS. *Curr. Anal. Chem.* **2011**, *7*, 110–116.
4. Šrámek V. High Temperature Removal of Halogenated Compounds from Pyrolysis of Waste Plastic Polymers. Bažant Postgraduate Conference 2021. Prague (CZ), 23.06.2021. In: Bendová, M., Wagner, Z., eds. Proceedings of Abstracts. Prague: Institute of Chemical Process Fundamentals of CAS, v. v. i., **2021**. 40–41.

Adaptive synthesis of functional amphiphilic dendrons for drug nanocarrier assembly

Student: Ing. Anonín Edr
Supervisor: Ing. Tomáš Strašák, PhD.

Drug nanocarriers such as liposomes or micelles are a quickly developing biochemical field. These supramolecular objects can potentially ensure drug's targeting, reduction of drug's side effects or increase of the drug's efficacy. In the recent decades, research has been focused on preparation of alternative amphiphilic building blocks leading to new nanocarriers with enhanced properties. Effort is made to obtain nanoparticles with optimal stability, lower cytotoxicity, higher selectivity *etc.* One of such alternative buildings blocks are amphiphilic dendrons, precisely defined molecules that contain one linear and one branched part. They are a broad research area with high potential.¹

In this work, an adaptive synthesis of new type of amphiphilic dendrons for nanocarrier purposes will be presented.² This methodology was applied in preparation of vast library of substrates (Figure 1). Firstly, it was applied in preparation of series of dendrons bearing different polar groups on their dendritic periphery (OH, COOMe, COOH, COO⁻, NH₂, NMe₂H⁺, PPh₃⁺). Secondly, it was applied in preparation of two series of ammonium resp. phosphonium dendrons carrying different number of lipophilic alkyl chains and different number of dendritic wedges. Physico-chemical studies of these two series will also be shown. And thirdly, the methodology was applied in preparation of unsymmetrical analogues of the previously mentioned dendrons with one alkyl chain, one polar dendritic wedge and one auxiliary molecule. If these analogues were added to the mixtures with symmetrical dendrons, the final nanoparticle would carry advantages of the auxiliary molecule, *e.g.*, fluorescence.

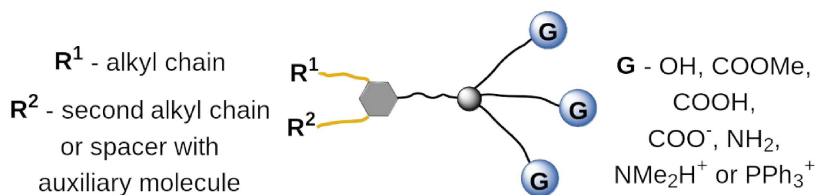


Figure 1: Schematic presentation of the prepared dendrons

References

1. Apartsin, E.; Caminade A.-M. Supramolecular Self-Associations of Amphiphilic Dendrons and Their Properties *Chem.-Eur. J.* **2021**, *27*, 17976.
2. Edr, A.; et al. Adaptive synthesis of functional amphiphilic dendrons as a novel approach to artificial supramolecular objects *Int. J. Mol. Sci.* **2022**, *23*, 2114.

Deoxyfluorinated *N*-acetylglucosamines as carbohydrate-based probes for human galectins

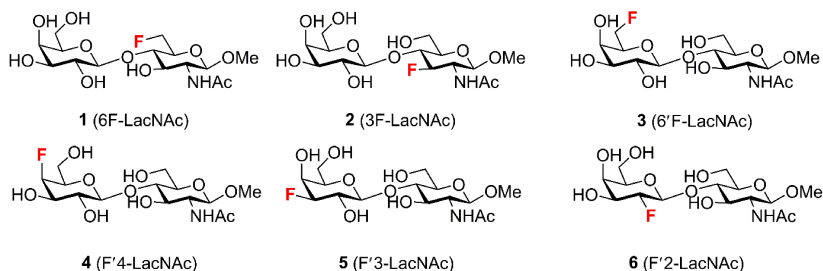
Student: Ing. Martin Kurfiřt

Supervisor: Mgr. Jindřich Karban Ph. D.

Supervising Expert: Prof. Cañada Vicinay Francisco Javier Ph. D.

Human galectins (hGals) are carbohydrate-binding proteins playing key roles in a plethora of physiological processes. They are able to modulate immune responses or neoplastic transformation processes via molecular recognition of galactoside-containing glycans.¹ Therefore, the development of their selective inhibitors has become a focus of pharmaceutical research. However, the preparation of inhibitors targeting individual hGals remains challenging as 12 hGals featuring similar substrate specificities have been identified. A deeper understanding of differences between individual hGals could facilitate the development of galectin inhibitors, and deoxyfluorinated carbohydrates are established tools capable of providing such valuable information.²

This work is focused on a detailed NMR investigation of human galectins via a complete series of mono-deoxyfluorinated *N*-acetylglucosamine probes 1–6, which were prepared previously in our laboratory.³ Advanced ¹⁹F NMR T₂-filter technique enabled the identification of hydroxyl groups essential for the interaction with various hGals, and permitted to compare hGals in terms of the importance of these key hydroxyl groups in the recognition events. Furthermore, the library was also investigated by various NMR techniques such as ¹⁹F EXSY, STD and ¹⁵N CSP to reveal the molecular origin of recognition events.



Support from MEYS (Project No. LTC20052 and LTC2007 2, COST Action CA18103 INNOGLY) and Czech Science Foundation (grant no. 20-01472S) is gratefully acknowledged. The authors also thank Jesús Jiménez-Barbero (CIC bioGUNE, Bilbao, Spain) and Roman Hrstka (RECAMO, Brno, The Czech Republic) for providing various human galectins.

References

1. Dings, R. P. M.; Miller, M. C.; Griffin, R. J.; Mayo, K. H. *Int. J. Mol. Sci.* **2018**, *19*, 905–926.
2. Linclau, B; Ardá, A.; Reichard, N.; Sollogoub, M.; Unione, L.; Vincent, S. P.; Jiménez-Barbero, J. *Chem. Soc. Rev. J.* **2020**, *49*, 3863–3888.
3. Kurfiřt, M.; Dračinský, M.; Červenková Štastná L., Cuřínová, P.; Hamala, V.; Hovorková, M.; Bojarová, P.; Karban, J. *Chem. Eur. J.* **2021**, *27*, 13040–13051.

Hybrid organometallic galectin inhibitors

Student: Ing. et Ing. Vojtěch Hamala

Supervisor: Ing. Tomáš Strašák, Ph.D.

Supervising Expert: Mgr. Jindřich Karban, Ph.D.

Galectins are lectin-type proteins defined by their sequence homology and the ability to bind β -galactosides. Human galectin-1 (Gal-1) and galectin-3 (Gal-3) are involved in tumor progression. Elevated Gal-1 levels are reported for many tumor tissues and Gal-1 contributes to tumor progression including cell migration and tumor immune escape. Gal-3 is characteristically overexpressed in many cancers and an elevated Gal-3 level is associated with increased invasiveness, metastatic spreading, immunosuppression and angiogenesis. Galectins are also implicated in progression of serious diseases other than cancer e.g., cardiovascular ones, diabetes mellitus, fibrosis, and others. These properties make galectins promising therapeutic targets.¹

Natural ligands of galectins include galactose, lactose, *N*-acetyl-lactosamine and their glycosylated and sulfated forms. Modifications of these carbohydrate ligands can create non-natural structures (or glycomimetics) with enhanced binding to galectins, thus acting as their potent inhibitors. The most common type of alternation is to introduce an aromatic substituent instead of carbohydrate hydroxyl which do not participate in the binding.

In this project, we replace the aromatic substituent with arene-containing organometallic structure – ferrocenes² and ruthenium arenes³ with known antitumor or antimetastatic properties. This creates a hybrid molecule, that acts both as a galectin inhibitor and a cytotoxic and/or antimetastatic agent. We have confirmed that both ferrocenes and ruthenium arenes moieties are viable bioisosteric replacement for planar arenes in the context of glycomimetic galectin inhibitors. Prepared organometallic inhibitors have a comparable or even better binding affinity to galectins than their nonmetallic counterparts. We have also established, that galactose bearing two ferrocenes moieties at positions C1 and C3 is selectively cytotoxic to resistant ovarian cancer cell line SK-OV-3 with about 100× higher cytotoxicity (expressed as IC₅₀) than currently used drug *cisplatin*.

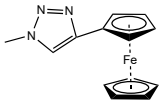
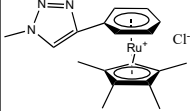
	R=	K_d (Gal-1) [μM]	K_d (Gal-3) [μM]
1	-OH	150	33
2		3.4	7.3
3		> 500	17.7

Figure 1: Structures of N-Acetyllactosamine (LacNAc) (1), 3'-LacNAc-ferrocene complex (2) and 3'-LacNAc-ruthenium-arene complex and their dissociation constants (K_d) to human Galectin 1 (Gal-1) and human Galectin 3 (Gal-3).

References

- Johhanes, L.; Jacob, H.; Leffler, J. *J. Cell. Sci.* **2018**, 131.
- Bartosik, M.; Koubková, L.; Karban, J.; Červenková Štastná, L.; Hořík, T.; Lamač, M.; Pinkas, J.; Hrstka, R. *Analyst*, **2015**, 140, 5864–5867.
- Lamač, M.; Horáček, M.; Červenková Štastná, L.; Karban, J.; Sommerová, L.; Skoupilová, H.; Hrstka, R.; Pinkas, J. *Appl. Organomet. Chem.*, **2020**, 34, 5318–5323.