HIGH SURFACE AREA ELECTRODE MATERIALS PREPARED WITH THE USE OF A REVERSIBLY DEPOSITED MEDIATOR METAL IN THE STRIPPING ANALYSIS OF METAL IONS

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The general objective of the project is to develop methodology for the fabrication of high surface area electrode materials with the use of a reversibly deposited mediator metal as a new way to improve the performance of the metal film electrodes and their application for the stripping analysis of trace concentrations of metal ions.

Firstly, we have reported the utilization of screen-printed carbon electrode as the support for an in situ plated lead film electrode prepared with the use of a reversibly deposited mediator. The investigated electrode was tested as a sensor for the anodic stripping voltammetric determination of Cd(II) traces. The obtained detection limit of Cd(II) is equal to 6.6×10^{-9} mol L^{-1} (the deposition time of 185 s). The presented procedure was successfully applied to cadmium determination in Bystrzyca River water samples. Secondly, in-situ deposited bismuth films that have been plated with the use of a zinc mediator on either self-produced or commercially available screen-printed carbon electrodes are assessed for their potential as Cd(II) and Pb(II) determinates, and as for being cheap and environmentally friendly alternatives to mercury and other bismuth-covered electrodes. The obtained detection limits for Cd(II) and Pb(II) are 1.35×10^{-9} and 1.41×10^{-10} mol L^{-1} (the deposition time of 190 s), respectively. The proposed voltammetric procedure was applied for the simultaneous determination without a preliminary mineralization step of Cd(II) and Pb(II) in certified reference material, as well as in sea and river water samples. Thirdly, in order to improve the sensitivity of U(VI) determination at an in situ plated lead film electrode a reversibly deposited mediator was applied. A very low detection limit (2.9×10^{-11} mol L^{-1}) for accumulation time of 180 s was achieved due to application of a zinc mediator in the step of lead film electrode preparation.

INVESTIGATION OF IMPLANTS IN ASPECT OF THEIR ADHESION TO BIOLOGICAL MATERIALS: SURFACE MODIFICATION OF TI-4AL-6V

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Due to prolongation of life span, the demands for safe and long-enduring medical implants are growing. Surface characteristics, i.e. surface composition, surface topography, surface roughness and surface free energy play of important role in determining the biological response to the implanted materials. This information may help develop materials that can be biocompatible and successfully incorporated in the surrounding tissue.

The cell membrane is considered to be the best surface for smooth interactions with biological components. The major components of biological membranes are phospholipids, which form bilayers in natural cell membranes. In fluid-mosaic model, phosphorylcholine lipids, such as phosphatidylcholines, are usually located in the outer leaflet. Hence using phosphorylcholine containing lipids as the surface modifier, to cover the implant materials could be promising tools to improve the implants properties.

Based on the above information, the investigation of implants was implemented through the surface modification of Ti-6Al-4V which is the most widely used metal for implants. In our research, the surface properties of bare Ti-6Al-4V alloy with different roughness [1], DPPC deposited plate via different methods [2], and model biostability study of DPPC films [3, 4] were investigated. The surface property involves two aspects; surface topography and surface free energy. The surface topography was obtained using the surface profilometer and AFM. The surface free energy was calculated by the Lifshitz-van der Waals/Acid Base (LWAB) and Contact Angle Hysteresis (CAH) approaches. Besides, the work of adhesion of both polar and apolar liquids was also determined to acquire knowledge about the adhesion strength.

Finally, model tests of biostability were conducted using four different liquids, i.e. water, PBS (phosphate-buffered saline), SBF (simulated body fluid) and 1% Triton X-100 aqueous solution. For probe control of shaking (20 rpm), temperature (37°C) and time (2h), a shaker (KS 4000 ic control, IKA) were applied for these biostability tests. The biostability tests of films prepared by LB/LS and by spreading techniques were conducted and a similar trend in the biostability changes was found. The modified surface of Ti-6Al-4V plates with the DPPC layers could be applied in water because the layer shows a relatively good stability under this condition. Despite similar London dispersion interactions of the samples, after the contact with the PBS and SBF solutions their ions greatly influenced the surface

free energy by changing its polar electron donor component, which indicates significant increase in the hydrogen bonding. The most drastic changes were observed for the layers treated with Triton X-100, where in the case of DPPC monolayer it would be completely removed from the surface. The changes in topography were also reflected in the apparent surface free energy which was the largest after the Triton treatment.

In the case of SBF, two series of experiments were performed. In one series the DPPC monolayer and bilayer samples deposited by the LB/LS method on Ti-6Al-4V after their preparation were kept overnight in vacuum desiccators, further denoted as "dry". In the other series, the DPPC layers were immersed into the solution immediately after their preparation. No drastic differences have been observed between the 'wet' and 'dry' DPPC layers.

References:
[1] Y. Yan, E. Chibowski, A. Szcześ, *Mater. Sci. Eng. C,* **70** (2017) 207.
[2] Y.D. Yan, E. Chibowski, A. Szcześ, *Colloid Surface A,* **510** (2016) 135.
[3] E. Chibowski, Y. Yan, A. Szcześ, *Colloid Surface A*, (2016), DOI: 10.1016/j.colsurfa.2016.06.036
[4] Y. Yan, A. Szczes, E. Chibowski, *Surface Innov.* (2016), DOI: 10.1680/jsuin.16.00012.

USEFULNESS OF NEW WATER SURFACE TENSION COMPONENTS FOR PREDICTION OF SURFACTANTS WETTING PROPERTIES

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In literature it is possible to find many studies dealing with wetting properties of aqueous solutions of different kinds of surfactants in the hydrophobic solid-surfactant solution-air system. The visual measure of wetting properties is the contact angle of the liquid on the solid surface. According to van Oss et al. [1] in the case of the hydrophobic solids whose surface tension results only from the Lifshitz-van der Waals intermolecular interactions the contact angle (θ) of the liquid or solution should be calculated from the following equation [1]:

$$\cos\theta = -1 + \frac{2\sqrt{\gamma_S \gamma_L^{LW}}}{\gamma_L} \tag{1}$$

where γ_S is the surface tension of solid, γ_L is the surface tension of liquid and γ_L^{LW} is the Lifshitz-van der Waals component of the liquid surface tension. Indeed, equation (1) can be used for the solid-liquid drop-air system if the vapour of liquids does not influence on the value of solid surface tension.

Polytetrafluoroethylene (PTFE) is the most representative hydrophobic solid. However, in the literature it is possible to find different values of PTFE surface tension depending on the method used for its determination as well as the kind of liquids the contact angle values of which were considered. The value of PTFE surface tension obtained from the contact angle for water is considerably different than that determined using the contact angle of apolar liquids. It seems that this difference results from the fact that the Lifshitz-van der Waals component of the water surface tension was determined from the water-*n*-alkane interfacial tension in contrast to other liquids for which this component was determined from the contact angle on the model solids. Therefore, the aim of our studies was to determine new values of water surface tension components and establish their application for prediction of wetting properties of surfactants in the hydrophobic solid-solution drop-air system. Thus firstly the surface tension of PTFE was determined from the contact angle of homologous series of *n*-alkanes. It proved that there is a linear dependence between $\cos\theta$ and $1/\sqrt{\gamma_L}$. Taking into account the slope of this dependence the PTFE surface tension was determined as equal to 20.24 mN/m. Next using the measured θ for water on the PTFE surface equal to 111.1° the Lifshitz-van der Waals component of its surface tension was calculated from Eq. (1). This value is equal to 26.85 mN/m. Thus the calculated acid-base component is equal to 45.95 mN/m [2,3]. Taking into account the values of Lifshitz-van der

Waals component of water surface tension determined by Fowkes as the dispersion one equal to 21.8 mN/m and that obtained by us equal to 26.85 mN/m the contact angle of aqueous solutions of many surfactants on the PTFE surface was calculated from Eq. (1) and compared to those measured. In Figs. 1a and 1b the contact angle for the aqueous solution of rhamnolipid (RL), *n*-octyl-β-D-glucopiranoside (OGP), sodium dodecyl sulfate (SDDS) and Triton X-100 (TX-100) measured [2-4] and calculated from Eq. (1) is presented.
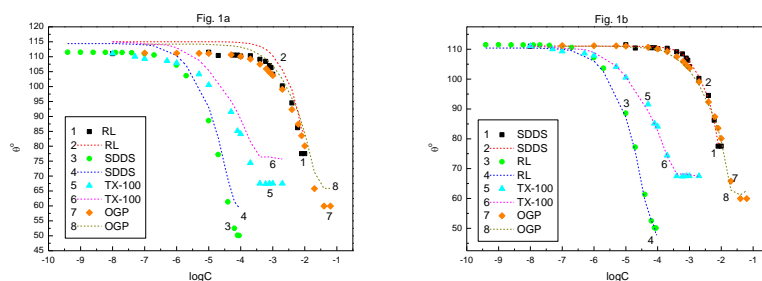

Fig. 1. A plot of measured (points) and calculated from Eq. (1) (lines) contact angle (θ) vs. the logarithm of surfactant concentration; a) values calculated using $\gamma_W^{LW} = 21.8$ mN/m and b) $\gamma_W^{LW} = 26.85$ mN/m.

It proved that if for calculations of contact angle the value of the Lifshitz-van der Waals component of water surface tension equal to 26.85 mN/m and the surface tension of aqueous solutions of surfactants were applied good agreement between the measured and calculated values of contact angle was obtained. However, it was assumed that surfactants influence only on the acid-base component of water surface tension It is more real if the Lifshitz-van der Waals component of water surface tension is assumed to be equal to 26.85 mN/m because the surface tension of surfactants oriented by the hydrophobic group toward the air phase is close to this value. It is interesting that the adhesion work of surfactants solution to the PTFE surface calculated from the geometric mean of the Lifshitz-van der Waals component of water equal to 26.85 mN/m and the surface tension of PTFE equal to 20.24 mN/m is very close to the adhesion work determined from the relationship between the adhesion and surface tension of aqueous solution of surfactants [3, 5].

References:
[1] J.M. Rosen, *Surfactants and Interfacial Phenomena*, Wiley-Interscience, New York, 2004.
[2] D. Mańko, A. Zdziennicka, J. Krawczyk, B. Jańczuk, *Colloids Surf. A*, **506** (2016) 409.
[3] D. Mańko, A. Zdziennicka, B. Jańczuk, *Appl. Surf. Sci,,* **120** (2017) 117.
[4] K. Szymczyk, A. Zdziennicka, J. Krawczyk, B. Jańczuk, *Colloids Surf. A*, **402** (2012) 132.
[5] K. Szymczyk, A. Zdziennicka, J. Krawczyk, B. Jańczuk, *Colloids Surf. A*, **402** (2012) 139.

FLOCCULATING PROPERTIES OF EXOPOLYTMER R-202 EXTRACTED FROM BACTERIAL STRAINS *RHODOCOCCUS RHODOCHROUS*

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Nowadays flocculants are widely applied in different industrial processes such as drinking water purification, wastewater treatment, and downstream processes in biotechnology [1,2]. Due to their effectiveness and low cost chemically synthetic flocculants play dominant roles. However, most of the synthetic flocculants are hazardous to human health. Hence, microbial-produced bioflocculants have attracted greater and greater scientific and technical attention because they are biodegradable and nontoxic. Their degradation intermediates are not secondary pollutants. Furthermore, these natural occurring and environment-friendly flocculants can be produced uniformly and reliably by fermentation processes [2]. Bioflocculants are kinds of extracellular biopolymer containing glycoprotein, polysaccharide, protein, cellulose, lipid, glycolipid and nucleic acid. Among others, bacteria are some microorganisms that have been reported to produce bioflocculants [2].

The characterisation and flocculation behaviour of exopolymer R-202 produced by *Rhodococcus rhodochrous* were investigated. It was found that the water-soluble fraction of this polymer with the molecular weight of about 1.3×10^3 kDa included 62.86% of polysaccharide and 10.36% of protein. The studied bacterial bioflocculant is the negatively charged macromolecule, and the addition of divalent cations could enhance its flocculating activity.
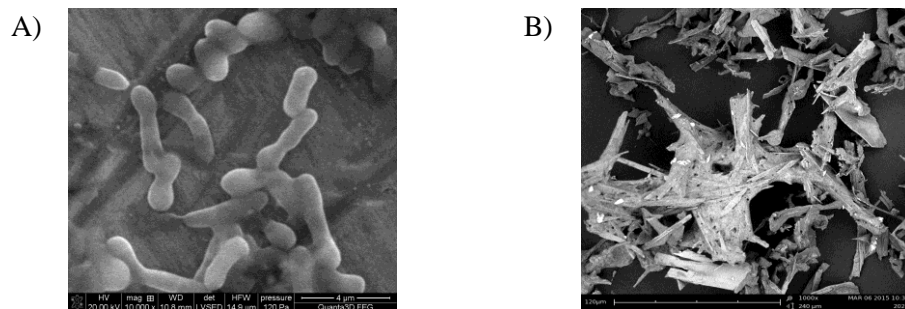
A)

B)

Fig. 1. SEM images of: A) *R. rhodochrous* cells and, B) water-soluble exopolymer of *R. rhodochrous*.

The flocculating activity was measured using the kaolin suspension and the basic flocculation parameters of exopolymer were established.
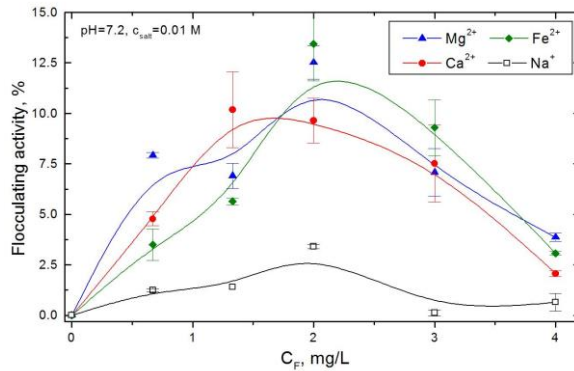

Fig. 2. Effect of the water-soluble fraction of R-202 concentration on the flocculating activity in the presence of cations (Na^+, Ca^{2+}, Mg^{2+}, Fe^{2+}). The final concentrations and parameters: kaolin clay 0.4 g/L, (C_F) 2 mg/L, metal ions concentration (C_{Me}) 10 mM, pH 7.2, temperature 25°C.

The highest flocculating activity of the water-soluble fraction of exopolymer R-202 was observed at a dosage of 2 mg/L, a pH value 7.2 and in the presence of 10 mM solutions of salts (NaCl, $CaCl_2$, $MgCl_2$ or $FeCl_2$). This effect depended on the type of ions and increased in the order - $Na^+ < Ca^{2+} < Mg^{2+} < Fe^{2+}$.
The obtained results will be published in a paper that follows.

References:
[1] Z. Li, S. Zhong, H.Y.Lei, Q.Yu, H.L. Li, *Bioresource Technol.,* **100** (2009) 3650.
[2] J. He, J. Zou, Z. Shao, J.Zhang , Z. Liu, Z. Yu, *World J. Microb. Biot.,* **26** (2010) 1135.

COMPUTER SIMULATIONS OF THE SELF-ASSEMBLY OF FUNCTIONAL ORGANIC MOLECULES ON SOLID SURFACES

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We demonstrated how fine tuning of directional intermolecular interactions which are encoded in a simple organic building block allows for the creation of surface-confined assemblies with largely diversified morphology. To that end the self-assembly of a model tripod-shaped molecule adsorbed on a triangular lattice was simulated using the canonical ensemble Monte Carlo method. The simulations were performed for flat, rigid building blocks built of four discrete segments (core plus three arm segments) and equipped with adjustable peripheral interaction centers providing directional intermolecular bonds. The simulated results revealed that changes in the directionality of interactions imposed on the centers are responsible for the emergence of different molecular structures including ordered porous networks, chain and ladder structures and chiral patterns [1]. The obtained assemblies were analyzed and classified with respect to their structural and energetic properties. Moreover, our simulations embraced enantiopure adsorbed systems, racemic overlayers as well as non-racemic mixtures and they are performed for two C_3-symmetric tectons differing in size [2]. The simulated results, including structural and thermodynamic characteristics, demonstrate that the pattern formation in the modeled systems is highly sensitive to the composition of the adsorbed overlayer, leading to a cascade of coexisting phases with scalable properties.

Our theoretical investigations showed that small changes in the position of the outer interaction centers in a tripod functional molecule can have dramatic effect on the morphology of the resulting 2D structures. On the other hand, these findings can be helpful in predicting the self-assembly of organic tripod molecules with the different interaction patterns discussed in this study. This information, can be relevant, for example, to synthetic chemists seeking for an optimal building block able to self-assembly into a 2D superstructure with predefined properties.

References:
[1] P. Szabelski, W. Rżysko, D. Nieckarz, *J. Phys. Chem. C*, **120** (2016) 13139.
[2] W. Rżysko, D. Nieckarz, P. Szabelski, *J. Phys. Chem. C*, **121** (2017) 410.

TWO-DIMENSIONAL MOLECULAR NETWORKS: THEORY AND COMPUTER SIMULATIONS

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The essential feature of modern structured adsorbents is the ability to selectively trap a wide class of guest molecules, especially those which are chiral and whose enantiomers need to be separated in an efficient way. An interesting example of systems with potential (enantio)selective adsorption behaviour are two-dimensional molecular networks, obtained by adsorption and self-assembly of organic (i.e. star-shaped) molecules on solid surfaces. The void spaces in 2D molecular arrays can be filled with foreign molecules having desired biological, chemical or magnetic properties, making them valuable materials for separation and catalytic purposes.

We used Monte Carlo simulation method combined with the coarse-grained representation of input molecules [1] to explore the effect of surface coverage and temperature [2] on the morphology of the resulting adsorbed overlayers comprising cross-shaped molecules. Next, we employed the model calculations and Monte Carlo method in grand-canonical ensemble to probe the ability of the nanostructured surfaces to trap chiral and achiral guest molecules differing in size and shape [3]. Specifically, we focused on calculating the selectivity of adsorption of enantiomeric pairs on these substrates.

The obtained results demonstrate how the individual properties of the cross-shaped building-block are related to specific adsorption properties of the corresponding 2D porous networks. The findings from our theoretical work can be helpful in designing the molecular guest-host systems for separation and catalytic purposes.

References:
[1] A. Kasperski, P. Szabelski, *Surf. Sci.,* **629** (2014) 57.
[2] A. Kasperski, P. Szabelski, *Appl. Surf. Sci.,* **391** (2017) 12.
[3] A. Kasperski, W. Rżysko, P. Szabelski, *Appl. Surf. Sci.,* **389** (2016) 378.

FUNCTIONALIZED NANOPOROUS SILICA MATERIALS: SYNTHESIS, CHARACTERIZATION AND APPLICATION IN SORPTION AND IMMOBILIZATION OF BIOMOLECULES

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Adsorption is commonly utilized and one of the most convenient techniques to remove impurities from the aqueous phase. Its effective implementation is inextricably linked with the development of new groups of sorbents expanding the area of its traditional uses. Despite the rapid development of this field of knowledge, there is still a demand for development of new adsorbents with controlled porosity and well-defined functionality surface.

Removal of pharmaceuticals by adsorption is one of the most promising techniques, due to its convenience once applied into current water treatment processes. So far, the removal of pharmaceuticals can be achieved by adsorption using activated carbon. Although, activated carbon displayed efficient removal for a number of pharmaceuticals, an inefficient removal for pharmaceuticals which are either electrically charged or hydrophilic has been observed. The working capacity of activated carbon greatly decreases in the presence of natural organic matter. Furthermore, regeneration of adsorbents is questionable. Mesoporous silica such as MCM-41, MCM-48, SBA-15 can be a promising adsorbent owing to its novel structure that comprises uniform ordered structure, high pore volume, and high surface area (up to 1000 $m^2 g^{-1}$).

Therefore, in the frame of this project, various types of functionalized silica nanoporous material of a predetermined porosity, morphology and surface chemistry were synthesized and tested as effective sorbents biomolecules from the aqueous phase. These groups of nanoporous silica materials are:
- Ordered Mesoporous Silicas (OMS),
- Meso-Cellular Foams (MCF),
- Amorphous Silica Xerogels (ASX),
- Porous Silica Nanotubes (PSN).

Particular attention was focused on multi-functionalization i.e. using more than one monomer bearing functional group to synthesize above-mentioned materials via sol-gel co-condensation route.

Structure and chemical composition of the obtained porous materials were investigated by wide range of complementary instrumental methods (including SEM, TEM, FTIR, NMR, XRD, XPS, EDS, elemental analysis, nitrogen sorption) to determine the effect of synthesis conditions for forming a porous structure and arrangement of the final material, as well as their surface chemistry, particular emphasis was placed on the description of the porous structure and chemistry surface, as the two most important factors influencing the adsorption process.

The resulting materials have been tested as sorbents of model biomolecules, including pharmaceuticals, amino acids and proteins. Particularly with regard to pharmaceuticals, the results are of very high importance due to the fact that increasing the presence of non-biodegradable drugs in waters and wastewaters, causes the necessity of development of effective methods for the removal of these compounds as well as their metabolites of the water environment.
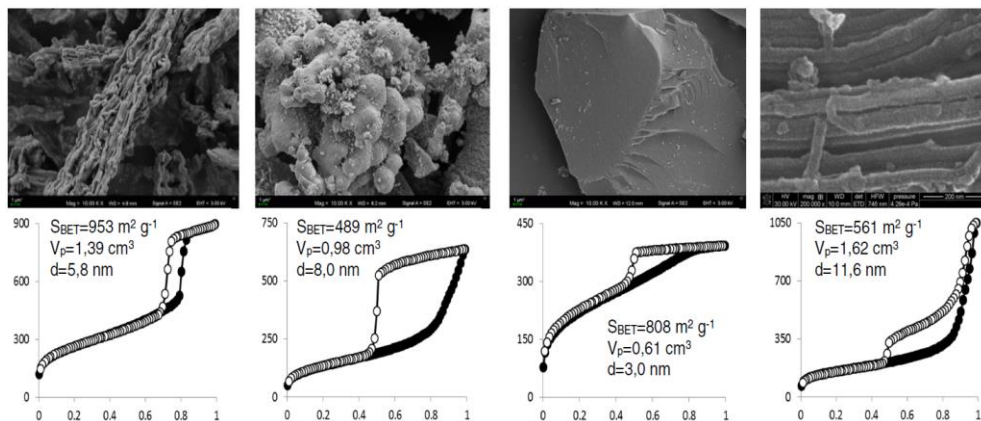

Fig. 1. SEM images and nitrogen sorption isotherms of the exemplary materials from each group (from the left: OMS, MCF, ASX and PSN, respectively)

Some of the materials synthesized using multi-functionalization approach had shown very good uptake of pharmaceuticals (e.g. diclofenac, ibuprofen, naproxen) from aqueous phase; some of them have reached the sorption capacity of more than 1000 mg g^{-1} with respect to drugs such as diclofenac or ibuprofen.

The proposed project have let for the creation and acquisition of unique skills related to the synthesis of many types of nanoporous silica materials with tailored porosity, morphology and surface chemistry and their application as efficient sorbents of biomolecules. Many research lines are planned to be continued in the future.

Acknowledgement

DEVELOPMENT OF A PORTABLE INTERNAL REFORMING METHANOL HIGH TEMPERATURE PEM FUEL CELL SYSTEM

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The changes in the morphology of the catalyst used in a long-term tests of the IRMFC (Internal Reforming Methanol Fuel Cell) were characterized by the electron microscope FEI Titan G2 60-300 kV, equipped with analytical tools – electron diffraction and EDS (Energy Dispersive X -Ray Spectroscopy). Microscopic studies of the catalyst were carried out at an accelerating voltage of the electron beam equal to 300 kV. The elements mapping was carried out in the STEM mode by collecting the EDS spectrum of each of the corresponding pixels in the map. For comparison the fresh catalyst (in the oxide form) was used. All catalyst samples were in the form used in the fuel cell, i.e. it contained also some amount of conductive carbon.

In all catalyst samples the main components were evenly distributed in the forms of nano-crystallites. The crystallites size distribution is shown in Fig. 1. It was found that in the used catalyst some new larger crystallites appeared as well as the share of the smallest increased.
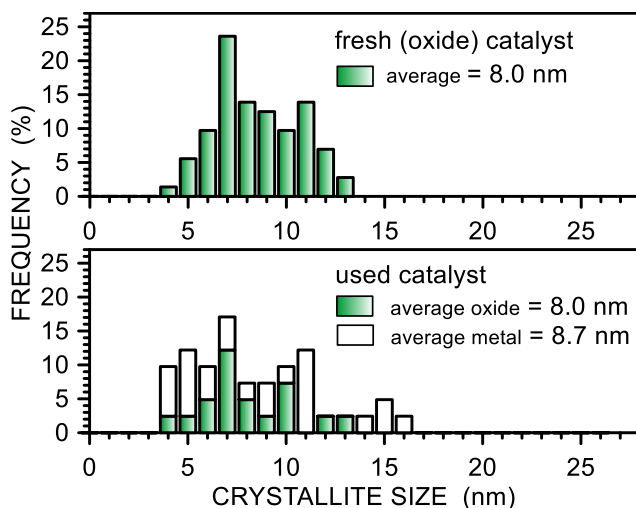

Fig. 1. Crystallites size distribution in fresh and used catalyst samples.

REGULATION OF MECHANISM OF THE ETHANOL CONVERSION IN PRESENCE OF WATER BY THE SIZE OF NANOPARTICLES OF AN ACTIVE PHASE OF METAL OXIDE CATALYSTS

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As it was mentioned by Bond in the introduction to his monograph "in order to understand catalysis phenomenon an understanding in three classical domains of chemistry is necessary. Catalysts are the most often inorganic substances which preparation requires the knowledge about inorganic chemistry. Catalytic reactions are very often organic reactions, so familiarity with reactivity of organic particles is useful. Whereas physical chemistry methods are used to study these reactions. Finally, industrial using of catalysis requires the knowledge about a chemical engineering and deep penetration in substance properties." And despite passage of 40 years from the time of an edition this monography, catalysis is still fascinating and it remains phenomenon which is still not investigated and known up to the end because of its complexity. And there are still found its new applications in new processes and equipments. Simultaneously, a progress of new physicochemical methods of catalytic materials investigation and possibility their versatile characterization through penetration inside a catalyst structure give a chance to better understanding of catalysis phenomenon and rules of catalysts performance in given process as well as the mechanism of their deactivation. What is also important, application of characterization methods currently available allows to get an answer to the question how a catalyst which will be suitable to a given process should "looks". So not only is choice of optimum composition possible but also there is a possibility of investigation and control with different physicochemical properties of catalyst in aim of preparation of catalyst which will be active and stable and will make that the reaction will be highly selective to desired products. As there is indicated by experience and mentioned by Bond [1] 40 years ago only understanding of physicochemical properties of catalyst allows to design suitable inorganic nanomaterial which will find an application in organic reaction. Therefore, an idea of this project arose on the base of experience of scientist investigating catalysis phenomenon from the beginning of its discovery by Berlioz and on the base of possibility of modern techniques. Simultaneously, an aspect of demand of contemporary world which copes with problem of decreasing of fossil fuels and increasing of a renewable energy demand was taken into consideration. The project concerning works on finding correlation between a size of nanoparticles of active phase of catalyst and its catalytic properties in conversion ethanol with water process. The results of these studies could contribute to getting an answer how obtain new catalytic materials which probably can find significant application in hydrogen production - the lightest and simplest fuel that can be used for transportation, heating, and power generation in places where it is difficult to use

electricity.

The aim of this work was to study the physical and chemical properties of the cobalt catalysts and comparison under identical conditions the performance of this catalyst with different contents of coablt and cerium in the SRE process.

Two catalysts were prepared by the co-precipitation method from aqueous solutions Characterization of the catalyst was done with XRF and low-temperature nitrogen adsorption. Physicochemical properties of catalysts are presented in Table 1.

Table 1. Physicochemical properties of catalysts.

	A	**B**	**C**
Cobalt content (wt.%)	28,5	20,7	15,2
Cerium content (wt.%)	46,0	54,7	63,1
Molar ratio Co:Ce	1,48:1,00	1,00:1,21	1,00:1,74
S_{BET} (m^2/g)	79,6	77,4	66,5
Pore volume (mL/g)	0,26	0,17	0,30
Average pore diameter (nm)	14,5	10,1	19,6

The reaction of ethanol conversion was carried out under atmospheric pressure in a fixed-bed continuous-flow quartz reactor over the catalyst (0.1 g, 0.15-0.3 mm) reduced *in situ* with hydrogen at 500°C for 1 hour, prior to the reaction. The aqueous solution of ethanol (H_2O/ethanol=12/1) was supplied to an evaporator (150°C) and the reactant vapours, without diluting with any inert gas, and were fed to the reactor at a flow rate of 100 mL×min^{-1}. The catalytic performance was tested in the temperature range of 420°C.
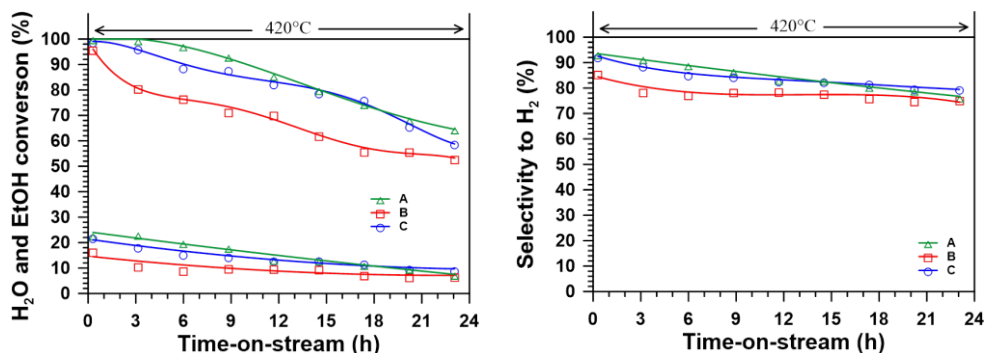

Fig. 1. Effect of the reaction temperature on ethanol and water conversion and selectivity to products over A, B and C catalysts under SRE conditions.

Steam reforming of ethanol (EtOH/H2O =1/12) over catalyst showed the best catalytic performance in this process indicates rhe catalyst A containing the highest molar ratio cobalt to cerium.

References:

[1] G.C. Bond, "*Heterogeneous catalysis: Principles and applications*", Oxford University Press 1974.

(Grant SONATA)

DEVELOPMENT OF AN INNOVATIVE CONCEPT FOR CARBON DIOXIDE UTILIZATION AS SIDE STREAM OF INTEGRATED BIOREFINERY CONCEPTS (ICOCAD)

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Carbon dioxide is emitted to the atmosphere during processing and combustion and fossil fuels. It is also formed in numerous industrial processes of raw materials conversion and biomass transformations. CO_2 is commonly perceived as the main agent which influence the greenhouse effect. Hence CO_2 capture and/or its utilization is a great environmental and technological challenge. The utilization of CO_2 by the direct transformation into the fuels, such as methane, methanol, dimethyl ether or polymers creates a high value added products. An application of hydrogen from renewable low-costs sources may bring additional benefits. Hydrogen production by water electrolysis, powered by near-by wind or solar farms may reduce the problems of power peaks in the power grid when wind or solar irradiation are available extensively.

The project aims at the development of innovative catalysts and the application of innovative reactor concepts for the methanation of carbon dioxide preferably from bio-refinery and biogas process streams. The project is conducted within ERANET Bioenergy programme by the international project consortium: Fraunhofer ICT-IMM Mainz (Germany), UMCS Lublin (Poland) and Konsun Sp. z o.o. Rybnik (Poland). The overall duration of the project was chosen to be 36 months.

The activity of UMCS in the first year of the project was focused on the catalyst development, conducted within parallel and consecutive Tasks: Catalyst design, Catalyst preparation and characterization, and Catalyst Screening. The main objective was development and characterization of durable, poisoning and coking resistant catalyst based on non-noble transition metals for carbon dioxide methanation. A series of nickel catalysts of different metal loading with different supports and modifiers, such as ceria, zirconia, alumina and silica were prepared, characterized by physical and chemical methods, and tested in the CO_2 methanation reaction in the wide range of temperatures. It was found that catalytic activity and selectivity can be tailored by suitable metal loading, reduction conditions in relation to the support composition.

EFFECT OF SURFACTANT ADDITION ON THE ADSORPTION MECHANISM OF ANIONIC POLYACRYLAMIDE AT THE NANOZIRCONIA – AQUEOUS SOLUTION INTERFACE

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Polyacrylamides – PAMs (especially ionic) are widely used in many fields of human activity. Their good water solubility, non-toxicity, relatively low price and biodegradability are the main reasons of PAM practical usage. The most important PAM application is flocculation process in wastewater purification technology. Other applications include: enhanced oil recovery (due to high viscosity of PAM solution), control of rain and wind erosion of agricultural soils (improvement of soil consistency, reduction of sediments transport), as well as fertilizers in gardening (improvement of plants vigour and colour, reduction of water consumption, elimination of disease). Many of above mentioned applications of polyacrylamide requires its adsorption on the solid surface. Adsorption occurs commonly in many areas of human life – biological, environmental and industrial. The ability of the polymeric chains to assume a huge number of the conformations at the solid – liquid interface makes that the adsorption process of macromolecular compounds is extremely complicated and dependent on many factors.

The main purpose of study was determination of adsorption mechanism of anionic polyacrylamide on the surface of zirconium(IV) oxide (which particles are characterized by mean size equal to 100 nm) in the anionic surfactant (sodium dodecyl sulfate, SDS) presence. Surfactant molecules and polymer chains can form various types of complexes and can compete for surface active sites of the solid. As a result, the modification of adsorption properties of the metal oxide – polymer – surfactant system can be obtained. Two anionic polyacrylamide samples differing in the content of carboxyl groups (5 and 50%) and weight average molecular weight (11 000 000 – 15 500 000 Da) were applied in experiments. PAM functional groups undergo dissociation with the increasing pH, resulting in negative charge of polyacrylamide macromolecules. Dissociation of the polymer anionic groups at pH 3 is at the level of 16.6-20.1%, whereas practically the total ionization of carboxyl groups in the PAM macromolecules occurs at pH 6 and 9 (99.5-99.9%).

All measurements were made in the solution pH range 3-9 at 25° C. Sodium chloride (NaCl) of the concentration 0.01 mole/dm^3 was used as the supporting electrolyte.

The structure of PAM-SDS layer formed on the nanozirconia surface was described basing on the following parameters: PAM adsorbed amounts - spectrophotometry method, solid surface charge density in the polymer (surfactant) presence - potentiometric titrations and zeta potential of colloidal particles covered with polyacrylamide (sodium dodecyl sulfate) – Doppler laser electrophoresis.

The pH$_{pzc}$ (pzc – point of zero charge) of ZrO$_2$ is about 6. Therefore, surface of the zirconium(IV) oxide is positively charged at pH values lower than 6. In turn, the solid surface charge assumes negative values at pH higher than 6. The addition of anionic surfactant influences considerably the adsorption behaviour of anionic polyacrylamide on the nanozirconia surface and SDS effect depends on the solution pH value. For both examined polymer samples the SDS addition causes about twofold increase of polymer adsorption at pH 3 and small decrease of adsorption level at pH 6 and 9. The hydrophobic interactions between the carbon chain of the polymer and hydrocarbon tails of the SDS molecules are the main reason of significant PAM adsorption decrease at pH 3. Under such conditions the minimal dissociation of anionic polyacrylamide occurs and the polymer-surfactant complexes formation is facilitated. The more probable structure of these complexes is following: the negatively charged hydrophilic heads of SDS molecules are directed towards the solution, whereas hydrophobic tails are connected with main carbon chain of the polymer. This increases considerably the affinity of PAM-SDS complexes for the positively charged zirconia surface. As a consequence, the surface aggregates at the nanozirconia-solution interface can be formed and polymer adsorption increases considerably (in the SDS presence).

On the other hand, due to the total dissociation of anionic polymer (lack of attractive interactions between adsorbing PAM and zirconia surface) the possibility of polymer-surfactant complexes formation is significantly reduced at pH 6 and 9. The observed slight decrease in polymer adsorption after the surfactant addition is probably caused by the competitive adsorption of polymeric chains and SDS molecules (both negatively charged). The obtained results suggest that the anionic surfactant is preferentially adsorbed on the solid surface under such pH conditions.

Proposed adsorption mechanism of anionic polyacrylamide in the SDS presence was confirmed by the specific changes of the solid surface charge density and zeta potential of nanozirconia particles.

DIFFERENT CHAIN TRANSFER AGENTS IN POLYMER TECHNOLOGY FOR POLYMER OPTICAL FIBERS

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Optical polymers are useful material instead of silica glass with many properties for short haul communications such as lower cost, larger core-diameter and, easy handling, low weight, multiplexing capabilities. PMMA is a preferred polymer to manufacturing optical fibers and for applications with better elastic limit (10%) according to silica (1-3%) and can stand up to 30% strains. Due to impurities and intrinsic absorption caused by C-H bonds, PMMA is not favorable material according to silica in long distance applications.

In polymer optical fiber technology, polymers should have proper molecular weight (M_w) and also have good transparency to enable the light to propagate inside the fiber. In order to control M_w and M_w distribution of polymer and also for degree of functionalization, radical chain transfer reactions are suitable for producing polymers. For this purpose, mechanism and kinetic of chain transfer agents were investigated by many researchers. Additionally, chain transfer agents have also effect on structure of polymer which causes to changes heating resistance.

Thiols derivatives are commonly used as a CTA due to weakness of S-H bonds. For vinyl monomers, e.g. methyl methacrylate and styrene, thiols are effective CTA.

Controlled pseudo-living radical polymerization studies were done by Korolev et al. and Zaremskii et al. to obtain monodisperse polymers but because of reversible inhibition the polymerization rate is low. For producing polymer with narrow molecular weight distribution, Semchikov et al. used polyfunctional silicon hydrides to solve the problem. Instead of mercaptans which are well-known CTA, Bulgakova et al. used organohydrodisilanes which are more effective. In another study of Bulgakova et al., they employed silicon hydrides as CTA and compared the reactivity of silicon hydrides for M_w of styrene and methyl methacrylate. As a conclusion of this study, the reactivity of organosilicon hydrides is related with chemical structure of CTA and the activity of monomer.

Okay et al. employed IPA as chain transfer agent to control the average number of segments in a network chain. As concentration of IPA is increased, the chain length of the primary chains is decreased and they indicated that the average number of segments in a network chain is highly related with IPA concentration.

In this study, investigation of the effects on optical properties of PMMA bulk polymer samples to use in optical fibers technology by comparing different structured CTAs was studied. For this purpose, molecular weight, transmission and

refractive index of bulk samples were measured and also scattering which was done by green laser was observed.

Same concentration of different CTAs caused to have varied M_w of polymer samples due to their different reactivity during polymerization. By comparison with commercial PMMA for drawing optical fiber, although IPA is not suitable CTA due to high M_w of samples, it can be produced proper preform with n-BMC and PMDS. Scattering is related with concentration of CTA but only for n-BMC. As decreasing the concentration of CTA M_w of sample is increased and it affect the scattering. For other CTAs, it can be considered that they have no effect on scattering. Further studies can be done with higher concentration of CTAs to see the effect on scattering but it will decrease the M_w and affect drawing process. No regular effect of CTA was observed in transmission results for samples which were produced with different concentration of CTA. There is no effect of CTA on refractive by changing the concentration of CTA but different type of CTAs changes the refractive index because of having different M_w which means also different molecular size. Polymer produced by purified PMDS is useful among other CTAs used in this study for producing optical fiber. They have better properties in M_w and scattering results. It is hard to compare by transmission results.
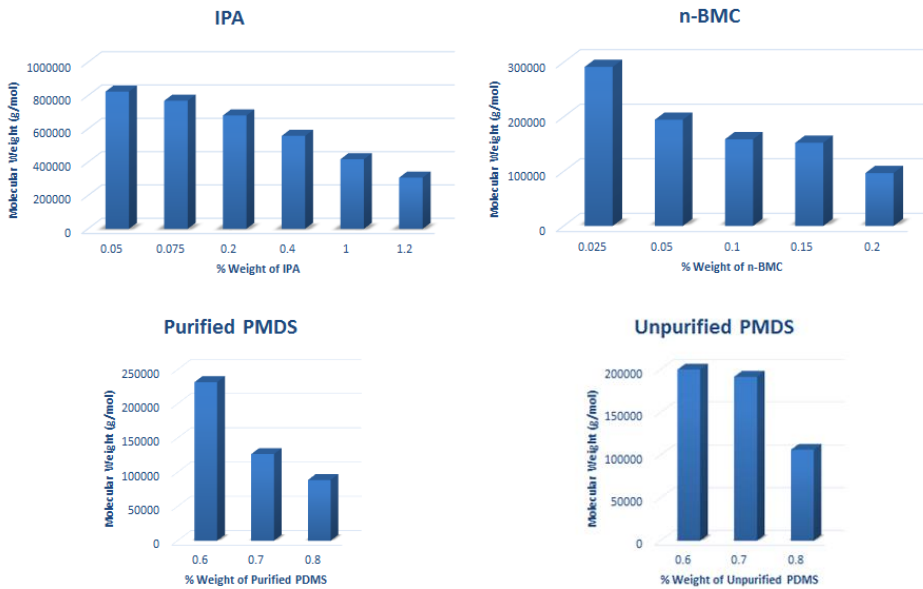

Fig.1. Molecular weights of sample with different concentration of CTAs.

(TRIPOD)

ACTIVATED BIOCHARS REDUCE THE EXPOSURE OF POLYCYCLIC AROMATIC HYDROCARBONS IN INDUSTRIALLY CONTAMINATED SOILS

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Contamination of the environment with polycyclic aromatic hydrocarbons (PAHs) is a threat to human health and may have a negative effect on other living organisms. These compounds are toxic, mutagenic, carcinogenic and highly stabile in the environment. The addition of a strong adsorbent to soil reduces the bioavailability of contaminants as well as the toxicity and bioaccumulation by living organisms [1]. The effectiveness immobilising organic contaminants using activated carbon (AC) has been confirmed in relation to sediments, soils and sewage sludge [2,3]. More recently, biochar has become a common tool for immobilisation. However, biochar is less effective than AC in immobilising contaminants. To increase the efficiency of contaminant binding by biochar, an alternative method of biochar activation that leads to an increase in surface area is proposed. Herein, we improve the biochar by subjection to a range of activation techniques using microwaves (MW), carbon dioxide (CO_2) or superheated steam (H_2O). To test their effectiveness, the untreated and activated biochars were added at 5% w/w into three different industrially contaminated soils sampled from areas around a coal plant (KOK and KB) and a bitumen processing plant (POPI).

The surface area (SSA) of biochar subjected to the activation techniques increased significantly. The SSA of the original biochar was 11 m^2/g, while those of the activated biochars was 443 m^2/g (MW), 512 m^2/g (CO_2) and 841 m^2/g (H_2O). The addition of activated biochar reduced the freely dissolved PAHs (C_{free}) in the KOK and POPI soils by up to 86% (from 153 to 22 ng/L and from 172 to 24 ng/L, respectively) and in the KB soil by up to 70% (from 52 to 16 ng/L) compared to the untreated soils (Fig. 1). Even more pronounced reductions were observed in the concentration of bioaccessible PAHs (C_{bioacc}). The activated biochars reduced C_{bioacc} in all soils by almost 100% (from 1.39 to 0.03 for KOK, from 1.92 to 0.01 for POPI and from 1.16 to 0.04 mg/kg for KB) compared with the untreated soil (Fig. 2).

This research shows that biochar activation by different methods leads to significant enhancements in contaminant binding and thus is a promising method for increasing the potential use of biochar in soil remediation.
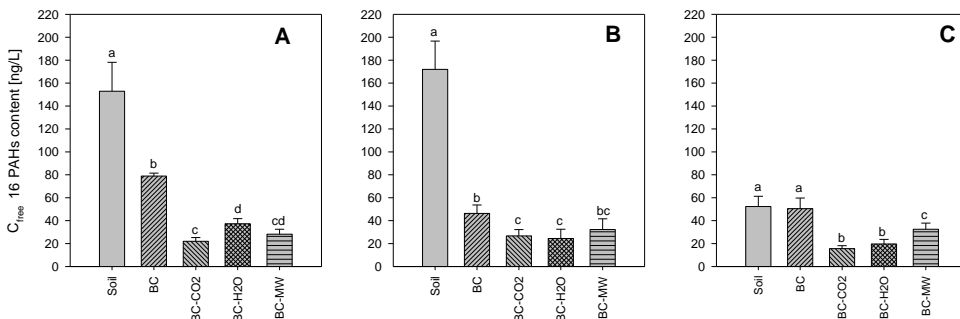
Fig. 1. C_{free} concentrations of 16 PAHs [ng/L] in control soils (A-KOK, B-POPI, C-KB) and amended by biochar activated by CO_2, H_2O and MW, determined by polyoxymethylene. SD – standard deviation n=3. Different letters mean statistically significant differences (P≤0.05).
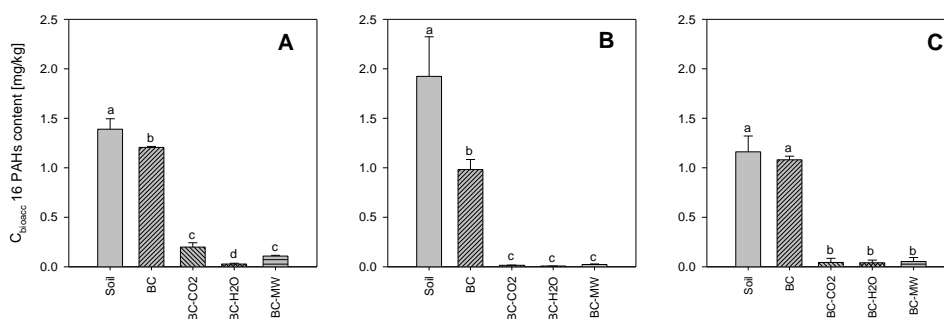

Fig. 2. C_{bioacc} concentrations of 16 PAHs [mg/kg] in control soils (A-KOK, B-POPI, C-KB) and amended by biochar BC activated by CO_2, H_2O and microwaves, determined by silicon rods. SD – standard deviation n=3. Different letters mean statistically significant differences (P≤0.05).

The most cost-effective method of activation (by microwaves) led to highly efficient contaminant immobilisation, which is strong evidence of the utility of this method for activating biochar. The high effectiveness of the analysed biochar activation methods was related to an improvement in the sorption properties of the biochars (specific surface area, micropore surface and volume) compared with non-activated biochar. The effectiveness of the particular biochars in the immobilisation of PAHs depended also on the type of soil.

References:
[1] U. Ghosh, R.G. Luthy, G. Cornelissen, D. Werner, C.A. Menzie, *Environ. Sci. Technol.*, **45** (2011) 1163–1168.
[2] M. Kołtowski, I. Hilber, T.D. Bucheli, P. Oleszczuk, *Environ. Sci. Pollut. Res.,* **23** (2016) 11058–11068.
[3] P. Oleszczuk, A. Zielińska, G. Cornelissen, *Bioresour. Technol.,* **156** (2014) 139–145.

ADDITION OF BIOCHAR TO SEWAGE SLUDGE DECREASES FREELY DISSOLVED PAHs CONTENT AND TOXICITY OF SEWAGE SLUDGE-AMENDED SOIL

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After application of sewage sludge to soils, there is a risk that contaminants that are contained in the sewage sludge can be taken up by organisms and plants, but also leached from such sewage sludge-amended soils to surface and groundwaters [1]. Due to their mutagenic and carcinogenic nature, PAHs require special attention. Efforts should therefore be made to minimize the risk associated with their presence in the environment. Our most recent research [2,3] has revealed that the addition of carbon adsorbents (activated carbon, biochar) to sewage sludge reduces the bioaccessible fraction of PAHs in the sewage sludge. Immobilization of bioaccessible fraction of PAHs reduces the uptake of contaminants by organisms [4]. This example shows that adding biochar (BC) to sewage sludge can be an effective tool in reducing the bioaccessibility and mobility of organic contaminants during application of sewage sludges to soils.

The aim of this study was to determine the total and freely dissolved (C_{free}) PAHs in soil to which a biochar-containing sewage sludge had been added. The effect of biochar type and biochar production temperature on the immobilization of Cfree PAHs was investigated. The study also investigated the effect of biochar on the toxicity of the sewage sludge added to the soils towards organisms representing various trophic groups: plants, bacteria and arthropods.

The freely dissolved PAH concentration (C_{free}) was determined by passive sampling using polyoxymethylene (POM). Total and freely dissolved PAH concentration was monitored at the beginning of the experiment and after 90 days of aging of the sewage sludge with the biochar and soil. Apart from chemical evaluation, the effect of biochar addition on the toxicity of the tested materials on bacteria - *Vibrio fischeri* (Microtox®), plants - *Lepidium sativum* (Phytotestkit F, Phytotoxkit F), and Collembola - *Folsomia candida* (Collembolan test) was evaluated. The addition of biochar to the sewage sludge decreased the content of C_{free} PAHs. A reduction from 11 to 43% of sewage sludge toxicity or positive effects on plants expressed by root growth stimulation from 6 to 25% to the control was also found. The range of reduction of C_{free} PAHs and toxicity was dependent on the type of biochar. After 90 days of incubation of the biochars with the sewage sludge in the soil, C_{free} PAHs and toxicity were found to further decrease compared to the soil with sewage sludge alone.
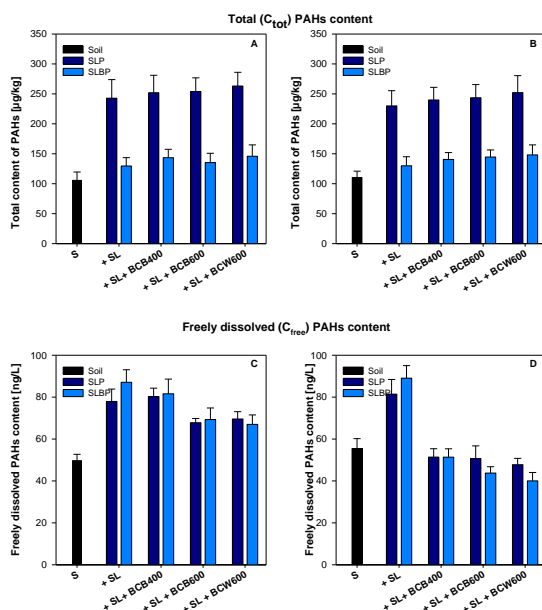
Fig. 1. The total (µg/kg) (A, B) and freely dissolved PAHs content (ng/L) (C, D) in soil, sewage sludge-amended soil and sewage sludge/biochar-amended soil at the beginning of the experiment (A, C) and after 90-days of aging (B, D). S – soil, SLP – sewage sludge from Przemyśl, SLBP – sewage sludge from Biała Podlaska, BCB – solid residues from biogas production at 400°C (BCB400) and 600°C (BCB600) and from willow produced at 600°C (BCW600).

The present study showed that the addition of biochar to sewage sludge and subsequently to soil has an effect on reducing C_{free} PAHs and significantly reduces the toxicity of sewage sludge relative to the soil mixture with sewage sludge alone. This effect is substantially enhanced with the passage of time. Soil amendment with sewage sludge containing biochar with a relatively low surface area can become an efficient method which not only leads to a reduction in the spread of contaminants in the environment, but which also allows the problem related to environmental use of sewage sludge to be solved.

References:

[1] N.A. Suciu, L. Lamastra, M. Trevisan, *Waste Manag.,* **41** (2015) 119–127.
[2] P. Oleszczuk, A. Zielińska, G. Cornelissen, *Bioresour. Technol.,* **156** (2014) 139–145.
[3] P. Oleszczuk, S.E. Hale, J. Lehmann, G. Cornelissen, *Bioresour. Technol.,* **111** (2012) 84–91.
[4] M. Waqas, S. Khan, H. Qing, B.J. Reid, C. Chao, *Chemosphere*, **105** (2014) 53–61.

BIOAVAILABILITY AND BIOACCUMULATION OF CUO NANOPARTICLES IN SOILS

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In the face of intensive development of nanotechnology, apart from benefits new challenges and problems appear. Growing production and exploitation of nanoproducts determines the spread of nanoparticles (NPs) in the environment, including soils. Thanks to their "nano" size they can penetrate into the organisms more easily. As a result of the activity of ions released from NPs as well as production of reactive forms of oxygen they can cause damage to cells or whole organs. Toxicity of NPs in various matrixes, including soils, was the subject of many studies [1–4]. Due to the richness of different components, soil can immobilize NPs as a result of various processes, making them unavailable to living organisms [5]. On the other hand, however, this increases the retention time of NPs in soil as compared with other matrixes (for instance in waters), which forces the need for learning the fate of NPs in soils. Heterogeneity of soil components determines different durability of connections with NPs, which may then determine their mobility and bioavailability, and in the final effect, their toxicity and bioaccumulation [3].

The study included performing chemical analyses and ecotoxicological test. CuO nanoparticles was used. Apart from NPs, CuO was applied in the form of macroparticles and soluble salts, in order to compare the effects induced by oxides with different particle sizes and solubility. Soils (SL1 and SL2) with different physic-chemical properties served as matrixes to the study. The evaluation of NPs fate in soils included the speciation analysis and the study of bioaccumulation using red Californian worm, *Eisenia fetida*. The speciation analysis, which allows distinguishing 5 metal fractions (exchangeable (F1), carbonate (F2), bound to iron and manganese oxides (F3), organic (F4) and residual (F5)) characterizing by varied durability, was conducted.

The participation of each fraction of Cu in soils was presented in the Figure 1. In control sample with soil SL1, the F5 and F4 fractions had the biggest shares (44.3 and 27.1%, respectively) in the speciation of Cu, whereas the parts of other fractions were around 10%. After treatment with nano- and bulk-CuO and $CuCl_2$, the speciation of Cu was different from control sample. In soil SL1 with nano-CuO and $CuCl_2$, the F1 fraction had the highest share in speciation (44.7 and 64.6%, respectively), while the part of the residual fraction was the smallest. The soil under bulk-CuO treatment characterised similar Cu speciation in comparison to control sample. Similarly to soil SL1, the highest share of F5 and F4 fraction was also observed in soil SL2. However, soil SL2 treated only with nano-CuO characterized the biggest share of F1 fraction, whereas in the amended soil with of bulk-CuO and
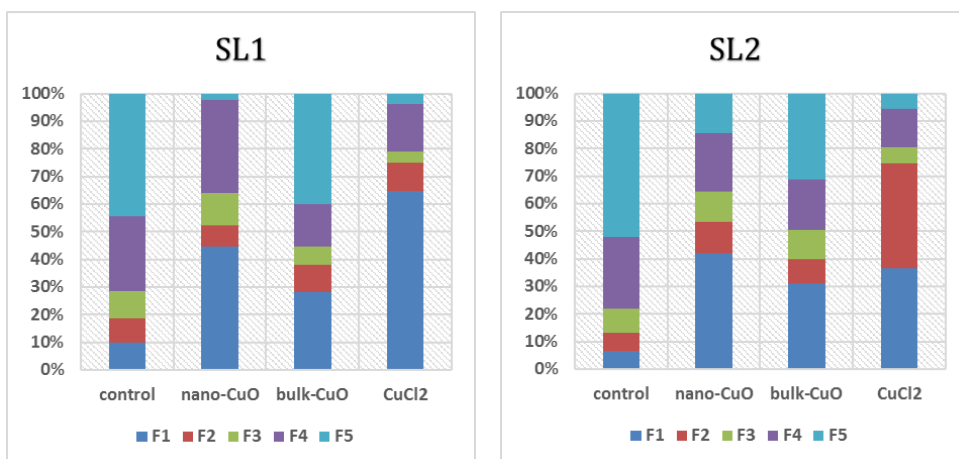
Fig. 1. Copper speciation of two soils (SL1 and SL2) untreated and treated with nano-CuO, bulk-CuO and CuCl₂.

CuCl$_2$, the fraction of F5 and F2 (respectively) had the biggest contribution in Cu speciation. The concentration of Cu in *E. fetida* from soil SL1 was almost on the same level (2.2-2.5 mg/kg), regardless of kind of treatment or without treatment. Opposite to soil SL1, *E. fetida* from soil SL2 characterised the higher concentration of Cu in case of organisms living in treated soil (2.6-3.9 mg/kg) in comparison to control sample (2.2 mg/kg).

The study provided the differences in Cu speciation in various soils, but the the potential bioavailable fraction of Cu have not correspond with Cu content in *E. fetida*. These discrepancies force the need for explaining of mechanisms and process occurring in the soil environment.

References:
[1] I. Jośko, P. Oleszczuk, B. Futa, The effect of inorganic nanoparticles (ZnO, Cr2O3, CuO and Ni) and their bulk counterparts on enzyme activities in different soils, *Geoderma,* **232–234** (2014) 528–537.
[2] I. Jośko, P. Oleszczuk, Influence of soil type and environmental conditions on ZnO, TiO2 and Ni nanoparticles phytotoxicity, *Chemosphere*, **92** (2013) 91–99.
[3] B. Pan, B. Xing, Applications and implications of manufactured nanoparticles in soils: a review, *Eur. J. Soil Sci.*, **63** (2012) 437–456.
[4] P. Wang, N.W. Menzies, E. Lombi, B.A. McKenna, B. Johannessen, C.J. Glover, P. Kappen, P.M. Kopittke, Fate of ZnO Nanoparticles in Soils and Cowpea (Vigna unguiculata), *Environ. Sci. Technol.,* **47** (2013) 13822–13830.
[5] J.L. Gardea-Torresdey, C.M. Rico, J.C. White, Trophic Transfer, Transformation, and Impact of Engineered Nanomaterials in Terrestrial Environments, *Environ. Sci. Technol.,* **48** (2014) 2526–2540.

SULFUR ATOM MIGRATION IN THIOLOALKYLPHOSPHINE OXIDES

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Tertiary phosphine sulfides are one of the classes of organophosphorus compounds possessing a phosphorus-sulfur double bond. They are somewhat analogous to the corresponding phosphine oxides but the chemical properties of both classes are quite different. Phosphine sulfides are in general lipophilic whereas phosphine oxides are usually polar compounds. Thiophosphoryl (P=S) group in phosphine sulfides can be easily removed in a stereospecific manner by a treatment with mild reducing agents (Ni Raney, n-Bu$_3$P) whereas phosphoryl group (P=O) in phosphine oxides requires the use of strong reducing agents like LiAlH$_4$ or SiHCl$_3$ and the stereoselectivity of this process is usually low. The mutual interconversion of these two classes of organophosphorus compounds requires the use of either sulfurating agents (P$_2$S$_5$ or Lawesson reagent) or two-step reduction-oxidation/sulfuration sequence.

During the course of our research topic concerning the synthesis of C-chiral organophosphorus compounds through desymmetrization of enantiotopic CH$_2$/CH$_3$ groups we were interested in the synthesis of cyclic P-stereogenic organophosphorus compounds using intramolecular electrophilic cyclization protocol (Scheme 1).

Scheme 1
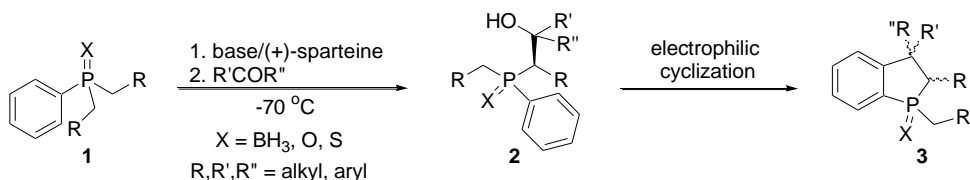
The initial optimization of the reaction[1] showed that β-hydroxyalkyl-phosphine oxides are the best substrates for this transformation. The use of the corresponding phosphine sulfides led to the formation of cyclic products but as phosphine oxides and not sulfides which suggests that in the case of phosphine sulfides hydrolysis of P=S bond takes place under the reaction conditions.

Unfortunately, attempted synthesis of non-racemic P-stereogenic β-hydroxyalkylphosphine oxides using sparteine methodology failed and therefore P-stereogenic phosphine sulfides were used as substrates for intramolecular

electrophilic cyclization. It was assumed that the conditions used for cyclization reaction (H_3PO_4, 170 °C) might be too harsh and therefore it was decided to use $AcOH/H_2SO_4$ mixture as a reaction media (Scheme 2).

Scheme 2
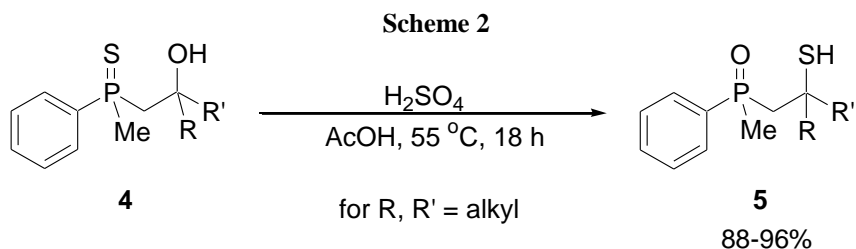
Surprisingly, the main products in every reaction of **4** derived from ketones were β-thioloalkylphosphine oxides **5**. These results suggest the rearrangement of substrates under the reaction conditions. Analogously, reactions of compounds **4** with $AlCl_3$ have been performed (Scheme 3).

Scheme 3
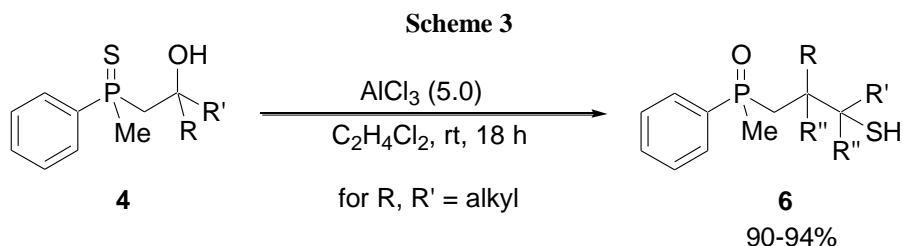
In this case, the products were γ-thioloalkylphosphine oxides **6**, which again could be obtained only through the rearrangement of the starting material.

Computational analysis has been applied for better understanding the mechanism of the observed rearrangements.[2] It turned out that rearrangement of **4** in $AcOH/H_2SO_4$ proceeds through the initial formation of the corresponding acetate ester followed by its protonation and AcOH elimination. The formed carbocation immediately undergoes intramolecular P-S bond formation. In the presence of $AlCl_3$ the reaction proceeds first through the formation of β,γ-alkenylphosphine sulfide which then coordinates the second $AlCl_3$ molecule. The formed complex undergoes intramolecular P-S bond formation with the γ carbon atom.

References:
[1] a) K. Włodarczyk and M. Stankevič, *Tetrahedron*, **72** (2016) 5074.
     b) K. Włodarczyk, P. Borowski, M. Drach, M. Stankevič, *Tetrahedron*, **73** (2017) 239.
[2] K. Włodarczyk, P. Borowski, M. Stankevič, *in preparation*.

NEW ELECTRON RICH WATER-SOLUBLE LIGANDS FOR CROSS-COUPLING REACTIONS

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The catalytic reactions are widely recognised as environmentally beneficial alternative to well defined classical industrial synthetic approaches based on utilisation of stoichiometric amounts of highly reactive organic substrates. They are also frequently considered as greener methods, especially in those cases where environmentally friendly solvents are used and mild reaction conditions are applied. Water is obviously one of the most safe and green solvents. Majority of cross-coupling reactions are conducted in organic solvents, in rare cases biphasic water-organic solvent system is used. It is well known that Suzuki-Miyaura coupling and many other transition metal mediated reactions tolerate aqueous medium [1] but usually poor solubility of substrates and catalysts forces chemists to apply the conventional conditions in reactions setup. There are many water soluble ligands known, nevertheless only in the rare cases the water-soluble phosphines possess sufficient level of electron density at phosphorus atom to form highly active catalysts for Suzuki-Miyaura coupling reactions. The straightforward approach to new electron-rich water-soluble ligands is presented herein.

Based on our previously reported approach [2, 3], the ligand core was prepared with consideration of the crucial features of efficient ligand designed to be used in the cross-coupling reactions (Figure 1). Such ligand must possess significant sterical hindrance around the highly electron rich phosphine function situated on a biaryl backbone at the position 2. The appropriate substituents have to protect positions 2` and 6` against *ortho*-palladation. The substituents G and EDG, are responsible for pushing the electron density through aromatic rings to phosphorus and next to metal atom.[4].

EDG = MeO, NMe_2 etc...
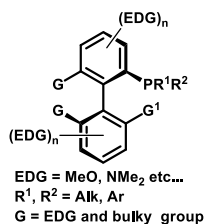R^1, R^2 = Alk, Ar
G = EDG and bulky group

Fig. 1. The ligand design.

To assure good solubility in water, some special functional groups could be incorporated into the ligand structure. Keeping in mind that new functionality should not decrease the electron density of the system and should not strongly

interact with transition metal the poly(ethylene glycol) group was selected as an optimal solution.

As a starting point in the synthesis, the structure of efficient ligand Sym-Phos [3] was selected. The oxygen atom at the position *ortho* to phosphorus group was deprotected in a reaction with trichlorosilane and the formed hydroxyphosphine oxide was subjected to the reaction with tosylated poly(ethylene glycol 900) monomethyl ether (Scheme 1).
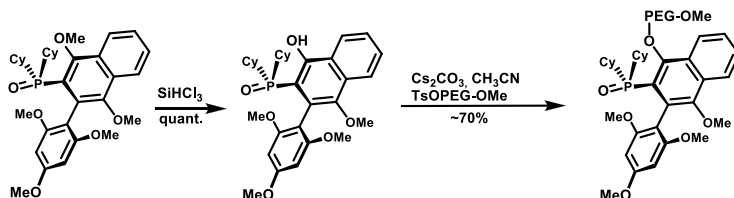
Scheme 1. Synthesis of the phosphine oxide.

Deoxygenation of phosphine oxide group situated in the position *ortho* to poly(ethylene glycol) tail is possible in dichlorodeoxygenation sequence followed by reduction of the formed chlorophosphonium salt with lithium aluminium hydride (Scheme 2).
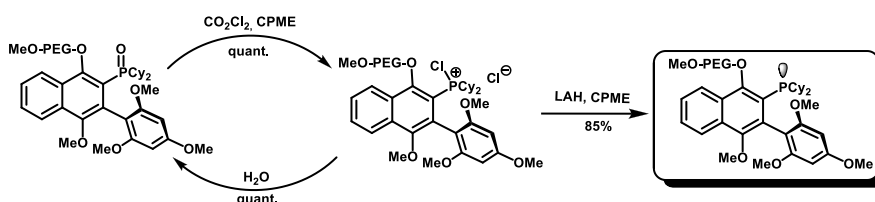
Scheme 2. Synthesis of the water-soluble ligand.

The ligand obtained using this methodology was well soluble in water. It was tested in the model Suzuki-Miyaura coupling reactions mediated by the corresponding phosphine-palladium complexes. The efficiency of the catalyst was confirmed by high yields of the coupling reactions products. It had been proven, that catalyst could be recovered by solid phase extraction, and reused for several times without significant loss of the yields of biaryl products.

References:
[1] O. Demchuk and R. Jasinski, *Phos. Sulf. Silicon. Relat. Elem.*, **191** (2016) 242.
[2] O. M. Demchuk, K. Kielar, K. M. Pietrusiewicz, *Pure Appl. Chem.,* **83** (2011) 633.
[3] O. M. Demchuk, Katarzyna Kapłon, Liliana Mazur, Dorota Strzelecka, K. Michał Pietrusiewicz, *Tetrahedron*, **72** (2016) 6668.
[4] O. M. Demchuk, D. Arlt, R. Jasiński, K. M. Pietrusiewicz, *J. Phys. Org. Chem.*, **25** (2012) 1006.

SELF-ORGANIZATION OF NANOPARTICLES WITH MODIFIED SURFACES

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AMPHIPHILIC JANUS DISKS AND SMALL MOLECULES IN TWO-DIMENSIONAL SYSTEMS

The theoretical modelling of the self-organization of Janus particles is a difficult task [1,2]. Janus particles have two hemispheres with dissimilar chemical or physical properties. Interactions between such particles depend not only on the separation of their centres but also on their orientations. The specific forces acting between Janus particles drive them to self-assemble into a large family of superstructures.

We consider a mixture of Janus disks and fluid molecules in a two dimensional system. A number of Janus particles (JPs) remains fixed while fluid molecules F can be exchanged with a reservoir. The Janus disks consist of two parts, one being attractive A and the other one being repulsive R. The total pair potential between particles k and l is a sum the hard sphere potential and an anisotropic contribution:

$$v_{kl} = v_{kl}^{hs} + v_{kl}^{an} \; (k,l = J,F).$$

The anisotropic interactions between two Janus particles are described as

$$v_{JJ}^{an} = v_{JJ}(r_{12})(\hat{\mathbf{u}}_1 - \hat{\mathbf{u}}_2) \cdot \hat{\mathbf{r}}_{21}$$

where $\mathbf{r}_1$, $\mathbf{r}_2$ characterize positions of both particles, $r_{12} = |\mathbf{r}_{12}| = |\mathbf{r}_1 - \mathbf{r}_2|$, $\hat{\mathbf{r}}_{21} = \mathbf{r}_{21}/|\mathbf{r}_{21}|$ and $\hat{\mathbf{u}}_1$, $\hat{\mathbf{u}}_1$ are unit vectors denoting orientations of particles. The vector $\hat{\mathbf{u}}_i$ points from the attractive A to repulsive R part of particle i ($i = 1.2$). In the case of interactions between a Janus particle and a fluid molecule the anisotropic part of the potential is given by

$$v_{JF}^{an} = v_{JF}(r_{JF})\hat{\mathbf{u}}_J \cdot \hat{\mathbf{r}}_{FJ}$$

while for fluid-fluid interactions $v_{JF}^{an} = v_{FF}$. We assume that $v_{kl}(r_{kl})$ is the square-well potential with range $\Delta_{kl} = 0.5\sigma_{kl}$, ($\sigma_{kl} = 0.5(\sigma_k + \sigma_l)$) and depth ε_{kl}.

The diameter of fluid molecule, $\sigma_F = \sigma$, provides the unit of length and the energy unit is $\varepsilon_{FF} = \varepsilon$. The Janus particle diameter is $\sigma_J = 4\sigma$ while the energy parameters are equal to $\varepsilon_{JJ} = \varepsilon_{FF} = \varepsilon$ and $\varepsilon_{JF} = 3\varepsilon$. The density of Janus particles remains equal to $\rho_J^* = 0.556$. We have carried out Monte Carlo simulations in grand canonical ensemble for different chemical potentials of the fluid (μ_F^*).

In the systems consisting exclusively the Janus particles and we have not observed the clustering. On the contrary, in their mixtures with fluid molecules we

have found an interesting co-assembly. Upon increasing fluid density the structure considerably changes. After insertion of a trace amount of fluid molecules we observe a dramatic change of the system behaviour. Chaotically distributed JPs transforms into a solid-like phase. The guest molecules are strongly attracted by the R-parts of JPs. They "adsorb" on these patches and act as linkers between JPs. In this way "mixed clusters" JP-F-JP are formed. The attractive patches of these aggregates are exposed to the outside. Interactions between the A-parts of "mixed clusters" cause the assembly into a striped structure (Fig. 1a). When the fluid density increases small molecules form films inside the "pores" built of JPs. Now, fluid molecules form flexible bands with JPs glued to them (Fig. 1b). The system transforms into a transient, gel-like structure. Janus particles form closed loops and rings. With a further increase of the density fluid only small clusters of IPs are formed.

It is interesting is that the presence of fluid molecules causes the bond switching between Janus particles. In the system without fluid molecules the AA-bonds are preferred. For extremely low fluid densities AA and RFR-bonds are formed with almost the same probabilities. However, for moderate fluid densities there are more $R-F-R$-bonds. In dense fluids, again, JPs are connected by A-patches. The similar bond switching caused by changes of temperature was observed in experiments [3].
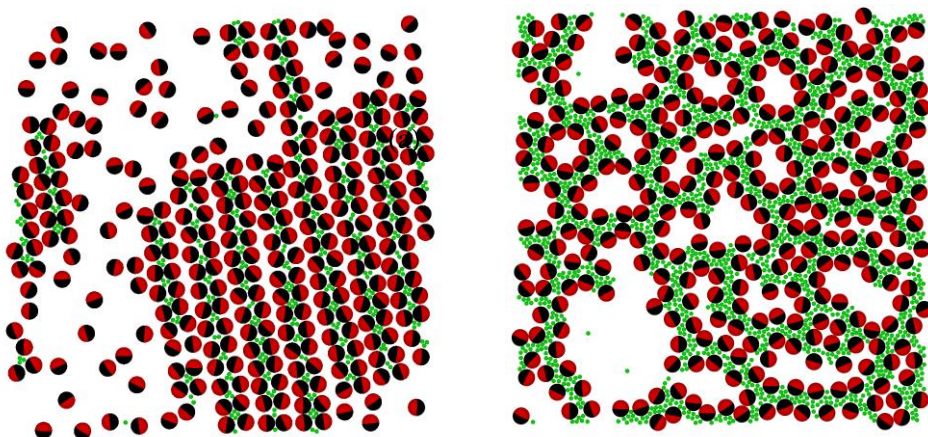

Fig.1. Snapshots obtained at $T^* = 0.7$ and (a) $\mu_F^* = -8.5$ (b) $\mu_F^* = -5.0$

References:
[1] A. B. Pawar and I. Kretzschmar, *Macromol. Rapid Commun.*, **31** (2010) 150.
[2] M. Borówko and W. Rżysko submitted article.
[3] C. Yu, J. Zhang, and S. Granick, *Angew. Chem. Int. Ed.*, **53** (2014) 4364.

Nanostructured Biocompatible/Bioactive Materials
NANOBIOMAT
EUROPEAN COMMUNITY'S SEVENTH FRAMEWORK PROGRAMME (FP-7-PEOPLE-2013-IRSES) UNDER A MARIE CURIE INTERNATIONAL RESEARCH STAFF EXCHANGE SCHEME, GRANT AGREEMENT NO PIRSES-GA-2013-612484

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Chitosan shows ability to bind dyes in aqueous environment because of its unique functional properties as polycationic biopolymer. However, it has low density, and is easily chemically and thermally decomposed. Preparation of chitosan-silica composites due to chitosan film formation, enable to obtain materials which exhibit characteristics of both organic polymer and silica. They are easily produced through sol-gel method or simple impregnation of silica from aqueous chitosan solution allowing incorporation of organic component into porous silica skeleton. These types of modifications let to improve the chemical and physical properties of final composite, because of higher chemical and mechanical stabilities of the system while preserving adsorption properties of chitosan macromolecules. Therefore, developed organic-inorganic composites can be used with satisfying efficiency as adsorbents in the liquid purification processes. One may expect homogeneous distribution of organic component particles in silica structure leading to strengthened interfacial interactions and better adsorptive behavior in various environmental conditions. In the present study, the chitosan-silica composites with the differentiated physicochemical properties were prepared via in situ sol-gel method (ChS1) or impregnation process (ChS2, ChS3) at room temperature. The structural, surface and morphology properties were investigated by using various techniques: elemental analysis, FTIR, SEM/EDX, adsorption/desorption of nitrogen, potentiometric titration. In order to verify applicability of chitosan-silica composites for removing anionic sulfonated azo dyes from aqueous solutions the equilibrium and kinetic adsorption experiments were carried out.

The obtained organic-inorganic composites are differentiated with regard to chemical composition (divergent amounts of chitosan: 16.7% for ChS1, 10% for ChS2 and 14.3% for ChS3), surface morphology (differentiated roughness,

heterogeneity: heterogeneous for ChS2, homogeneous for ChS3), grain size (0.2-0.5 mm for ChS2 and below 100 μm for ChS3), structural characteristics (ChS1 is microporous with the highest specific surface area, ChS2 and ChS3 are mesoporous with PSD maxima near 6 and 40 nm and lower specific surface areas), and acid/base properties (pH_{PZC} equal to 4.2, 5.7 and 6.0 for ChS1, ChS2 and ChS3, respectively). Due to its polycationic structure chitosan shows ability to adsorb dyes, however, the adsorption effectiveness of the obtained composites is differentiated due to their various physicochemical, surface and structure properties.

The influence of surface and structure characteristics of the composites on acid orange 8 adsorption from aqueous solutions was investigated and the following order of adsorption capacity changes was found: ChS3 : ChS2 : ChS1 = 3.5 : 2.9 : 1 Despite the largest content of chitosan for ChS1, its microporous structure is partly inaccessible for dye molecules, and its surface charge is too negative (electrostatic repulsion between adsorbent and adsorbate), which results in poor adsorption. ChS3 is the most efficient adsorbent because of high content of chitosan, less negative surface charge and wider pores. General negative correlation of dye uptake with solubility/hydrophobicity was observed for adsorption on ChS2. Some inconsistencies between the expected relation of solubility/hydrophobicity and adsorption is explained by presence of impurities which may compete to adsorption sites or change electrostatic interactions between dye and composite. Acid Red 88 shows the highest affinity to chitosan-silica composite which may be correlated with its high hydrophobicity, however, the weakest adsorption of OG and AR1 may be explained by their higher hydrophilicity. However, the other factors, like molecular size and functional groups, also determine the ability of dyes for adsorption on the chitosan-silica composites.

Kinetic measurements were also conducted to analyze dependencies between adsorption rate and properties of composites and dyes. Various equations and models were applied for analysis of experimental concentration profiles and basing on optimization results the multi-exponential equation was chosen for further data analysis. In the case of AO8 the adsorption rates were differentiated for three composites: for ChS3 50% of dye is removed from the solution after merely 5 min and almost 90% after 80 min, which correlates very well with composite structure (large pores). The slowest adsorption process controlled by a diffusion rate of dye molecules into the internal space of pore structure was found for microporous ChS1 (225 min halftime). In the case of composite ChS2 the adsorption rates for various dyes change in the following order determined by their adsorption halftimes: AO7 > OG > AR1 > AR88 > AO8 (half-times: 10.5 < 15.7 < 23.7 < 34.9 < 42.9 min). It may be correlated with chemical structures of dyes: AO7 with the lowest molecular weight and molecular dimension is adsorbed at the fastest rate, AR88 possessing two strongly adsorbed naphthalene rings is adsorbed at slower rate, adsorption of AO8 is the slowest (differences in adsorption rates for AO7 and AO8 may be also explained by presence of impurities).