### MACROSCOPIC AND MICROSCOPIC PROPERTIES OF SOME SURFACTANTS AND BIOSURFACTANTS

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The adsorption and micellization of surfactants occur due to asymmetric structure of their molecules. The surfactant molecule can be divided into two parts hydrophobic (tail) and hydrophilic (head) [1]. Such type of molecules structure causes that surfactant surface tension depends on the molecules orientation toward the air phase [2]. If they are oriented by tail toward air then the surface tension results only from the Lifshitz-van der Waals intermolecular interactions and its value should be close to surface tension of hydrocarbon being a tail of surfactant. In the case when the surfactant molecules are oriented by head toward air phase the surface tension results from the Lifshitz-van der Waals and Lewis acid-base intermolecular interactions. The values of the surface tension of tail and head (macroscopic property) as well as the size of the particular parts of the molecule (microscopic property) decide about surfactant tendency to adsorb at the water-air and solid-water interfaces and to form the micelles at the concentration called critical micelle concentration (CMC). It should be remembered that the adsorption of surfactants at the water-air, solid-air and solid-water decides about the wettability of the solid surface. The studies of the adsorption, aggregation and wetting properties of the surfactants based on the surface tension of solid, head and tail of the surfactant, aqueous solution of surfactant with regards to the size of the surfactants molecule is difficult to find in the literature. Therefore the purpose of our studies was to establish the correlation between these properties and Gibbs free energy of interactions of surfactants molecules through the water phase and interactions with solid surface through this phase basing on the surface tension of water, solid [3], head and tail of surfactants [3] as well as the size of their molecules. For this studies the rhamnolipid (RL), surfactin (SF), *n*-octyl- $\beta$ -Dglucopyranoside (OGP), n-dodecyl-\beta-D-glucopyranoside (DDGP), n-dodecyl-\beta-Dmaltoside (DM), sucrose monodecanoate (SMD), sucrose monododecanoate (SML), Tween 20 (T20), Tween 60 (T60) and Tween 80 (T80) as well as polytetrafluoroethylene (PTFE), polyethylene (PE), poly(methyl methacrylate) (PMMA), polyamide (nylon 6) and quartz were chosen. The surfactant tendency to adsorb at the water-air interface was analyzed on the basis of the changes of the water-tail interface tension to the tail surface tension at the assumption that the water-head interface tension is constant during surfactants adsorption. In turn the adsorption of surfactants at the polymer-water and quartz-water interfaces and the micelle formation were analyzed on the basis of the interactions of surfactant molecules with solid surface and interactions of their molecules through the water phase. For the determination of the interactions of the surfactants molecule with solid surface through the water phase the new equation was proposed. This equation has the form [4]:

 $\Delta G_{\text{int}} = -N \left[ \left( \gamma_{WT} + \gamma_{WS} - \gamma_{ST} \right) S_T^1 + \left( \gamma_{WH} + \gamma_{WS} - \gamma_{SH} \right) S_H^1 \right]$ (1)

where  $\Delta G_{int}$  is the Gibbs free energy of interactions of the surfactants molecules with solid surface through the water phase, N is the Avogadro number,  $\gamma_{WT}$  is the water-tail interface tension,  $\gamma_{WS}$  is the solid-water interface tension,  $\gamma_{ST}$  is the solid-tail interface tension,  $\gamma_{WH}$  is the water-head interface tension,  $\gamma_{SH}$  is the solid-head interface tension,  $S_T^1$  is the contactable area of tail and  $S_H^1$  is contactable area of head.

The results obtained from this analysis were compared to Gibbs free energy of surfactants adsorption at the water-air and solid-water interfaces as well as Gibbs free energy of the micellization. From our studies it results among many things that:

The Gibbs standard free energy of adsorption of surfactant at the water-air interface can be predicted on the basis of the surface tension of surfactant tail, the water-tail interface tension as well the surfactant tail contactable area with water molecules. These predicted values are close to the literature data for monorhamnolipid and sucrose ester surfactants obtained applying different methods.

There is the relation between the surfactants molecule interactions through the water phase with the solid surface and the standard Gibbs free energy of adsorption at the solid-water interface. The best agreement between the standard Gibbs free energy of adsorption and the interactions is observed for the all studied surfactants at the PTFE/PE-water interface.

The standard Gibbs free energy of micellization can be predicted based on the surface tension of surfactants tail and head and its components and parameters.

The partial molar volume of surfactant in the monomeric and aggregation forms can be predicted from the size of the molecule calculated from bonds length, the angle between them and the average distance between the surfactants and water molecules as well as between the surfactants molecules.

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## THE INFLUENCE OF STATIC MAGNETIC FIELD ON EVAPORATION RATE AND SURFACE TENSION OF WATER

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Water is the most important substance in nature. Our life and activity cannot function without water. However, lack of potable water is well known problem that appears in many regions. Therefore, water treatment and purification processes are very important. The magnetic water (MF) treatment has been investigated for over 50 years, however there is still no full mechanism explaining this phenomenon. Most of the papers dealing with the magnetic water treatment are actually related to the chemical substances dissolved in water and less related to the properties of water itself. Since 1990s, the effect of magnetic fields on the structure and the physicochemical properties of liquid water has been also studied. However, the results of these studies are often contradictory [1,2].

In this study the neodymium ring magnets (0.5-0.65 T) were used in experiments of magnetic field (MF) effects on water evaporation rate and surface tension which were carried out at room temperatures (22–24°C). For water evaporation experiments one ring magnet 86 x 58 x 35 mm and for the surface tension experiments three neodymium magnets  $101 \times 60 \times 30$  mm were used.

It was found that the external magnetic field enhanced evaporation rates in a time period of several days or weeks and the evaporated amounts depended also on the direction of the magnetic field. The water surface tension decrease by 2.11 mN/m was observed after 60 min of MF treatment. It was also shown that after removing the external magnetic field, the surface tension value increases slowly over time period. However, after 1 hour it was still lower than 72.30 mN/m which was measured for untreated water. It confirmed the so called 'memory effect'. For both measurements the reproducibility of the experiments was high.

The obtained results were published in Colloids Interfaces 2018, 2(4), 68.

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## THEORETICAL MODELING OF THE SURFACE-CONFINED SELF-ASSEMBLY OF FUNCTIONAL TETRAPOD MOLECULES

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Self-assembly of functional molecules on solid substrates has recently attracted special attention as a versatile method for the fabrication of low dimensional nanostructures with tailorable properties. In our studies, using theoretical modeling, we demonstrated how the architecture of 2D molecular assemblies can be predicted based on individual properties of elementary building blocks at play. To that end a model star-shaped tetratopic molecule was used and its self-assembly on a (111) surface is simulated using the lattice Monte Carlo method. Several test cases were studied in which the molecule comprised terminal arm centers providing interactions with differently encoded directionality. Our theoretical results showed that manipulation of the interaction directions can be an effective way to direct the self-assembly towards extended periodic superstructures (2D crystals) as well as to create assemblies characterized by a lower degree of order, including glassy overlayers and quasi one-dimensional molecular connections. The obtained structures were described and classified with respect to their main geometric parameters.[1] A small library of the tetratopic molecules and the corresponding superstructures was built to categorize the structure-property relationship in the modeled systems. The results of our simulations can be helpful to 2D crystal engineering and surface-confined polymerization techniques as they give hints on how to functionalize tetrapod organic building blocks which would be able to create superstructures with predefined spatial organization and range of order.

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## 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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Fossil fuels, which are an indispensable source of energy in our daily lives, are causing serious environmental problems, such as emission of carbon dioxide and air pollutants, and are a depleting non-renewable energy source. Hydrogen has been considered an ideal candidate as an alternative energy source because it can be used to generate electricity in fuel cells with high efficiency and is environmentally friendly. As a feedstock for the production of hydrogen, alcohols are very promising candidates because they are readily decomposed in the presence of water, to generate a hydrogen-rich mixture at a relatively low temperature. The steam reforming of ethanol (SRE) is of particular interest because ethanol, obtained by the fermentation of biomass, has advantages from the environmental point of view. Cobalt and nickel are widely recognized for their catalytic activity in SRE reaction. These metallic phases favouring C–C bond and O–H bonds rupture, and C–O bonds generation. Also, they acting as oxygen carriers and are therefore used in chemical looping and autothermal reforming. However, the deactivation due to deposition of carbonaceous species on cobalt and nickel-based catalysts have promoted the development of different methods of synthesis, catalyst composition, incorporation of promoters, etc. in order to diminish such limitations. The addition of basic oxides (e.g. MgO, La2O3) can decrease the coke deposition rates through gasification of carbon; for example lanthanide oxide can facilitate the removal of coke deposits (formed in SRE) on the catalytic surface though formation of carbonate species which decompose readily during reaction [1-4]. Therefore, the aim of this work was to study effect of lanthanum promotion on the catalyst performance in SRE reaction and to verify its influence on activity, selectivity and coking of the cobalt- and nickel-based catalysts.

Catalysts were synthesized via co-impregnation method with the application of citric acid in order to increase dispersion of the cobalt active phase using aqueous solutions of cobalt nitrate or nickel nitrate and lanthanum nitrate. Ceria (Sigma, pore volume = 0.14 mL/g, average pore diameter = 14 nm, SBET = $42.5 \text{ m}^2/\text{g}$ ) was used as the catalytic support. The best preference to use in SRE process at H2O/EtOH=12/1 demonstrates Co-0.1La/CeO2 among studied cobalt-based catalysts and Ni-0.1La/CeO2 among studied nickel-based catalysts. The most advantageous temperature for this catalyst for hydrogen-rich gas production is 500 °C for Co-0.1La/CeO2 and 460 °C for Ni-0.1La/CeO2.

	Cobalt content (wt.%)	Lanthanum content (wt.%)	Sbet (m²/g)	Co crystallite size (nm)
Co/CeO <sub>2</sub>	7.67	-	34.2	19.2
Co-0.1La/CeO <sub>2</sub>	7.64	2.00	38.9	10.8
Co-0.5La/CeO2	7.36	8.50	33.1	6.0
Co-La/CeO <sub>2</sub>	8.19	20.00	27.6	7.5
Ni/CeO <sub>2</sub>	9.09	-	39.8	6.7
Ni-0.1La/CeO <sub>2</sub>	9.19	2.50	42.0	11.1
Ni-0.5La/CeO <sub>2</sub>	8.84	10.00	32.9	5.4
Ni-La/CeO <sub>2</sub>	7.58	17.00	24.1	5.1

Table 1. Physicochemical properties of catalysts.



Fig. 1. Effect of (A) La/Co and (B) La/Ni molar ratio on the catalytic properties ceriasupported catalysts in the steam reforming of ethanol at 420°C (TOS=21 hours).



Fig. 2. Effect of time-on-stream on ethanol conversion and selectivity over (A) Co-0.1La/CeO2 at 500°C and (A) Ni-0.1La/CeO2 at 460°C under SRE conditions.

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### REGULATION OF THE NUMBER OF ACTIVE SITES AND THEIR REACTIVITY USING THE COMPOSITION OF COBALT-MANGANESE OXIDE CATALYSTS FOR METHANE OXIDATION

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Complete catalytic oxidation is primarily a process of obtaining energy from natural gas in an environmentally friendly manner, of which a highly active and stable catalytic system is a key component. Mainly, catalysts based on noble metals such as palladium and platinum are recommended, because demonstrate the best properties. However, according to the literature [1], cobalt-manganese oxides can be the alternative to noble metals, because demonstrate comparable activity and their cost of production will be significantly lower. Therefore, this catalytic material was the subject of studying.

The cobalt-manganese catalysts were prepared from an aqueous solution of the mixture containing proper amounts of cobalt acetate and manganese acetate by a precipitation method. The obtained catalyst precursors were calcined at 400°C.

The cobalt and manganese content in the catalysts was determined by the X-ray fluorescence (XRF) method. The total BET surface area of the catalysts was measured by low-temperature nitrogen adsorption. The phase composition of the obtained catalysts was determined by means of X-ray diffraction (XRD).

The activity of cobalt-manganese catalysts were tested in a fixed-bed quartz reactor placed inside an electric furnace with a temperature control system. The reaction mixture contained methane, oxygen and inert gases (helium and argon). The composition of the post-reaction mixture was analysed by a quadruple mass spectrometer.

The SSITKA experiment was carried out by the switch from the mixture contained  ${}^{12}CH_4$ , oxygen, argon and helium to the mixture contained  ${}^{13}CH_4$ , oxygen, krypton and helium. In order to calculate the average surface life-time of methane, carbon dioxide and methane oxidation intermediates leading to the formation of carbon dioxide, areas between the curve of argon and the curve of suitable components ( ${}^{12}CH_4$  or  ${}^{12}CO_2$ ) were taken into account.

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

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 $CO_2$  is commonly perceived as greenhouse gas. The utilization of captured  $CO_2$  to the valuable chemical products is a great environmental challenge. One of the most promising methods is conversion of  $CO_2$  to methane. Hydrogen for this process can be produced by water electrolysis using renewable energy. Biogas and landfill gas contain in average from 50 to 75 vol. % of  $CH_4$  and from 25 to 50 vol. %  $CO_2$ . Production of biomethane by the conversion of  $CO_2$  in biogas stream may lead to the increase of the heating value, improve the overall sustainability of biogas plants and waste management systems.

The aim of the studies was determination of the influence of catalysts composition on the activity, selectivity and durability of catalysts in the  $CO_2$  methanation reaction.

Nickel catalysts based on different supports, such as CeO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> were prepared by the impregnation method. The catalysts were modified by the introduction of selected promoters. The catalysts were studied by means of numerous experimental techniques, including X-ray diffraction, nitrogen adsorption-desorption, electron microscopy, temperature programmed reduction and desorption of hydrogen. The reaction mechanism over catalysts of different composition was studied by means of *in-situ* Diffuse-Reflectance Fourier Transform Infrared and Raman spectroscopy. The activity and selectivity of catalysts was determined in a wide range of temperatures (200-600°C). Durability studies, coking and poisoning resistance of catalysts in the presence of the traces of H<sub>2</sub>S were performed under different reaction conditions using model reaction mixtures.

It was found that the activity of catalysts and resistance for sulphur poisoning depends on the nature of support and nickel loading. Selected catalysts were used for development of microchannel reactors and tested under high pressure conditions in the CO<sub>2</sub> methanation reaction by the project partner at ICT-IMM Fraunhofer in Mainz (Germany).

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## SORPTION OF SELECTED RADIONUCLIDES ON THE NATURAL LOW – COST MATERIALS

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The growing problem related to inorganic and organic pollutants of water sources provide an great interest in methods allowing the removal of the abovementioned groups of chemical compounds [1, 2]. The strontium and caesium isotopes of anthropogenic origin should be included to the most hazardous substances undoubtedly, mainly due to the high environmental mobility and negative impact of the emitted radiation on the living organisms.

Primary objective of this project was to determine the sorption mechanism of the selected Sr or Cs radionuclides on the so called low - cost adsorbents. Two artificial origin isotopes emitting the gamma radiation were used (Sr-85 and Cs-137). They are present in the environment as a result of atmospheric nuclear weapon tests and also pose a potential, serious threat in the case of nuclear power plant accidents [3, 4]. In the studies a waste raw materials from plants cultivated on a large scale in the Lublin region were applied as an adsorbents (e.g. hops (Humulus Lupulus) after supercritical extraction with carbon dioxide). The mentioned solids were obtained due to cooperation with Supercritical Extraction Department, Fertilizer Research Institute, Puławy, Poland [5, 6] It is worth noting that these materials are characterized by a complex structure depending both on the plant occurrence place as well as on the technological processing of the starting raw material. This means that biosorbents are an innovative, but not fully characterized and known class of solids. An undoubted advantages of these materials are their abundance, high availability and low price. Nevertheless, because of the size of the crops as well as ecological considerations, it is necessary to find a proper management of the generated wastes [7]. These activities are consistent with the principles of green chemistry. It should be noted that the planned physicochemical measurements allow to determine the surface properties of the selected materials, which is the crucial issue in the adsorption mechanism researches context. It is assumed that the metal ions binding to the biosorbents surface may be related to the occurrence of several processes such as ion exchange, specific adsorption or complex bonding formation. Therefore, application of the various measurement methods allows to determination of the most probable adsorption mechanism. For this reason this research problem perfectly fits in the trend associated with radioecology.

As a interfering substances the surface active agents of different chemical nature were chosen: anionic sodium dodecyl sulphate (SDS), cationic hexadecyltrimethylammonium bromide (CTAB) and nonionic Triton X-100. All surfactants have important practical significance, which means that despite the treatment of municipal and industrial wastewater, these substances can enter

groundwater. Although, the concern at the artificial radionuclide distribution, according to the author's best knowledge there is no scientific information concerning the influence of the surfactants on the strontium and caesium isotopes removal from the aqueous solutions.

It was decided to use several different research methods. First of all, the physicochemical properties of the applied solids were investigated using the particle size distribution measurements (dynamic light scattering), the solid charge density (potentiometric titration), the electrophoretic mobility tests as well as the Boehm titration technique for the determination of the solid surface active groups amounts. Next step involves defining the model system and interactions occurring in it – sorption of the Sr or Cs isotope on the adsorbent surface in the absence and presence of the surface active agents. These data allow to properly describe the mechanisms of radionuclide binding in the studied systems. The last stage included the problems related to the impact of the surface active agents on the Sr (or Cs) radionuclide sorption. The method used for the determination of the surfactant adsorption is UV-Vis spectrometry. Simultaneously, the amount of the removal radioisotope was measured using the gamma radiation spectrometry.

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### EFFECT OF CNT ADDITION ON PHOTOCATALYTIC PROPERTIES OF TiO<sub>2</sub> IN THE REMOVAL OF PHARMACEUTICALS FROM WATER AND WASTEWATER

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Nowadays the increasing concern of new emerging pollutants including pharmaceuticals and personal care products (PPCPs) results in numerous studies confirming PPCPs occurrence in different matrices [1]. Among different classification, paracetamol (Acetaminophen or APAP) is often listed [2]. APAP is the most commonly detected wastewater contaminant (together with caffeine and ibuprofen). Caffeine (CAF) is well known marker of the domestic wastewater contamination in surface waters [3]. Caffeine is often used as a stimulant and component of drugs and dietary supplements. PPCPs presence in the wastewater effluent have confirmed that existing wastewater treatment methods are not effective in PPCPs removal. Recently, Advanced Oxidation Processes (AOPs) have been tested intensively and have been proven to remove most of the PPCPs completely or to the lowest acceptable level at least.

The application of photocatalysis can be recommended as the promising method of PPCPs removal from water and wastewater. The high photocatalytic activity, low price, easy maintenance, make  $TiO_2$  the mostly tested photocatalyst.  $TiO_2$ , however, requires UV irradiation. In order to obtain photocatalytically active materials under visible light (Vis) irradiation,  $TiO_2$  is combined with a material reducing the band gap energy of  $TiO_2$ . Carbon doping of  $TiO_2$  reduces band-gap energy, charge carrier recombination and increases surface area for target pollutants adsorption [5].

The studies of photocatalytic removal of APAP from water [6] confirmed that tested nanocomposites were very effective and enabled to reduce APAP concentration by up to  $81.6\pm0.6\%$ . The high resistance of CAF to Vis photocatalytic decomposition was noted: the only reduced CAF concentration (29.4±2.7%) was observed for 60 minutes irradiation of CAF using CNT1 nanocomposite. The highest removal of APAP in the presence of CAF, (47.6±2.4%), was observed using CNT1, nanocomposite that contained 0.15wt% of MWCNT and possessed moderate surface area (383.4±11.5 m<sup>2</sup>·g<sup>-1</sup>), pore diameter (3.1±0.1), but the lowest anatase crystal size (5.04 nm) and the highest Eg (3.22 eV).



Fig. 1. Changes of CAF and APAP concentration after dark adsorption and 60 min of Vis irradiation; [CAF], [APAP]=10 mg·L<sup>-1</sup>, [CNT]=0.5 g·L<sup>-1</sup>, Vis  $\lambda$ =550 nm, CAF+APAP - describes removal of CAF and APAP without nanocomposites, CNT – removal of CAF and APAP with respective nanocomposite.

Although photocatalytic methods have been proven to be very effective in APAP removal, the application of tested nanocomposites, effective under Vis irradiation, was not justified economically. The kinetics of CAF and APAP photocatalytic degradation and mineralization proceeded according to a pseudo-first-order reaction model and APAP k<sub>DOC</sub> in the presence of CAF was reduced up to 4 times. The photocatalytic APAP removal over MWCNT-TiO<sub>2</sub>-SiO<sub>2</sub> proceeded via photo generated holes and, in lower extend, •OH radicals. The photocatalytically treated model water containing APAP and CAF was not toxic to *Vibrio fischeri*.

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### EFFECT OF BIOCHAR AGING ON THEIR PROPERTIES AND INTERACTION WITH ORGANIC AND INORGANIC CONTAMINANTS IN CONTEXT OF THEIR TOXICITY

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Biochar (charcoal-like product) is a carbon-rich material obtained by pyrolysis, i.e. thermal degradation carried out in the temperature range from 300°C to 700°C under conditions of limited oxygen access or under anaerobic conditions, of biomass and more recently waste. This material can be used for soil fertilization, rehabilitation or remediation. Biochars may however contain hazardous contaminants which call into question their common use. These contaminants immediately after the production process are strongly bound to biochar. However, biochar after application to soil is exposed to action of a range of environmental factors (variable temperature, humidity, oxygen access) and to microbial activity. They can lead to changes in its structure, which are usually termed as aging. This can result in the release of contaminants primarily strongly bound to biochar, thus not bioavailable for organisms. When released to soil, these contaminants may, on the one hand, be taken up by plants, which in effect may lead to contamination of animal feed. On the other hand, they may be leached from the soils leading to contamination of aquatic ecosystems. This issue is particularly important in the case of biochar derived from waste materials (e.g. sewage sludge) that contain a range of various contaminants.

The aim of the research is to determine the persistence of biochar-contaminant interactions as affected by simulated biochar aging processes in the context of their impact on the ecotoxicological properties of biochars. Two different groups of biochars obtained in our laboratory in three temperatures (500°C, 600°C and 700°C), i.e. biochars made from organic municipal waste (two different sewage sludges) and biochars made from biomass (willow shoots) were used for studies. They were characterized in terms of their composition and physicochemical and surface properties with using advanced analytical methods (mainly <sup>13</sup>C NMR and FTIR spectroscopy, XPS, SEM, CHN analysis), subjected to ecotoxicological evaluation with respect to various groups of organisms and analyzed for contaminants (total and bioavailable) content. Polycyclic aromatic hydrocarbons (16 PAHs from the US EPA list) and polybrominated diphenyl ethers (7 out of 209 known congeners of PBDEs used as a flame retardants), classified as persistent organic contaminants, as well as heavy metals (Pb, Cd, Cr, Zn, Ni and Cu) were selected for the studies. The selection of contaminants was made based on the available literature data concerning the commonness of their occurrence in biochar, plant biomass and sewage sludge as well as based on applicable legislation. Previous studies show that heavy metals come from the material that was used for biochar production, whereas PAHs are formed additionally during pyrolysis.

Therefore, even biochars obtained from materials not containing PAHs, like for example plant biomass, will be contaminated by these compounds. Both PAHs and heavy metals have toxic, mutagenic and cancerogenic properties.

Obtained biochars and soils amended with selected biochars were subjected to the following types of aging (in laboratory conditions) for a period of 12 months:

- Chemical (continuous action of different temperatures: -20°C, 4°C, 20°C, 60°C and 90°C). Application of high temperatures, i.e. 60°C and 90°C, will allowed chemical processes occurring in the materials to be accelerated, which will enable us to track long-term changes taking place in these materials.
- Physical (alternately action of extreme temperatures, i.e. -20°C and 20°C, at one week intervals to lead to fragmentation of biochar particles).
- Biological (the action of a mixture of bacterial inoculum in the presence of nutrient solution).
- Enzymatic (the oxidation with horseradish peroxidase).

The changes in the biochar structure during aging will be confronted with changes in the content of the selected compounds and the results of ecotoxicological tests to determine the risk for various groups of organisms associated with the presence of these compounds in biochars, particularly when their availability increases as a result of aging of these materials. In turn, aging of biochar-amended soils will allow to determine the effect of type of soil, feedstock type and biochar production temperature as well as environmental conditions on the persistence of contaminants introduced into soils with biochar.

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### THE IMPACT OF THE AGING PROCESS AND THE PRESENCE OF ORGANIC AND INORGANIC CONTAMINANTS ON THE ECOTOXICITY OF MICROPLASTICS

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Civilisation development has caused a notable increase in the global production of plastics. In 1950 it amounted to 1.5 million tons, recently global production of plastics has exceeded 322 million tons annually. While some waste plastics is subjected to recycling processes, the rest is stored at landfills, where proceeds a slow degradation processes. However, despite attempts postconsumer waste management of plastics much of it gets into the environment, in particular for natural waters, where they undergo various physico-chemical processes leading to their partial decomposition and interact with other contaminants present in the water. As a result of these processes micro- and nano-plastics are often formed. The composition of micro- and nano-plastics and a large surface to volume ratio allow sorption of contaminants both organic and inorganic on their surface making them even more dangerous for the aquatic fauna, compared with plastics did not contain the contaminants adsorbed on the surface. Numerous studies have demonstrated that even small organisms are able to accumulate waste plastics. In conjunction with data on sorption of organic and inorganic contaminants on the surface of the plastics must be concluded that often accumulate in biota are contaminated particles of plastics.

It is therefore necessary to determine to what extent the plastics are degraded in the environment depending on different conditions. In addition, an important aspect is to quantify the ability to accumulate contaminants by degraded plastics. Another object of this project is to determine the sorption capacity and the binding strength of plastics waste previously subjected to different types of aging in respect of organic contaminants (PAHs) and inorganic (heavy metal ions). In addition to determining the sorption of contaminants by plastics subjected to various processes of "aging" under study it planned to carry out ecotoxicological tests providing information about the direct effect of the test materials on living organisms. Important stage of the project is to determine the degree of desorption of contaminants by means of simulating gastric fluid.

It will test plastics, which, according to literature data, get the largest amount of an aqueous medium and have different structure, e.g. polypropylene (PP) and high density polyethylene (HDPE) which crystalline structure and poly(vinyl chloride) (PVC) characterized by amorphous structure. Plastics will be subject to conditions simulating aging processes occurring in the environment, ie. the photoand thermooxidation, the aging under controlled conditions in the laboratory in the waters coming from reservoirs with different physicochemical characteristics. Then testing of adsorption abilities of plastics in respect to selected compounds of PAHs and heavy metals will be performed. The choice of contaminants will depend on the results of the first stage of research on contaminated plastics collected from the environment. In addition to direct sorption studies in order to understand the mechanisms of binding pollution by plastics of varying severity degree of aging

research will be conducted plastic surfaces in order to obtain complete information about the mechanism of binding pollution by selected materials (SEM/TEM, FTIR). In the last stage it is planned to assess risk based on ecotoxicological tests using *Daphnia magna* invertebrates, *Vibrio fischeri* bacteria (Microtox®) and algae *Pseudokirchneriella subcapitata CCAP 278/4*. In addition, to determine the potential transfer of contaminants from plastic organisms will be carried out kinetics of desorption from the surface of the plastics using the simulant gastric fluid and determining its impurities.

Undertaken research interests due to its innovative nature is of great importance both cognitive and practical. Led multifaceted, combining elements of materials chemistry, surface chemistry, analytical chemistry and environmental chemistry, will make a realistic assessment of the risks associated with the impact of pollution from post-consumer waste plastics. Particularly valuable will be the information obtained from desorption studies are to fully define the impact of plastics on living organisms.

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#### LONG-TERM EFFECT OF MOISTURE ON COPPER FRACTIONATION IN DIFFERENT SOILS

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The growing production and use of nano-products result in increasing proliferation of nanoparticles (NPs) in the environment, including soils. NPs, due to their size, are characterized by different properties compared to their bulk counterparts. Therefore, processes such as dissolution, aggregation or adsorption may differ from those of larger particles, and that in turn may have a bearing on their mobility, bioavailability and toxicity [1]. In the case of metal-based NPs their, toxicity is caused primarily by ions of metals released from NPs and therefore estimation of the fate of metals in soils is an important issue. In the case of heavy metals, apart from the total metal content, assessment of the concentration metals bound to various soil fractions is especially important [1]. For this purpose sequential analysis is often applied, as it allows the determination of the content of ion-exchangeable metals (F1), bound to carbonates (F2), Fe-Mn oxides (F3), organic matter (F4) and residual fraction (F5) [2]. Changing environmental conditions can lead to changes in metal partitioning, and metal fractions believed to be stable and bioavailable may liberate metals that can contribute to the unstable fractions [3].

The objective of the study presented here was to estimate Cu fractionation in different soils at various moisture content (30, 50, 80% of water holding capacity) after treatment with CuO nanoparticles. To determine the effect of aging on the distribution of Cu soil samples were incubated for 1 day, 3 and 24 months.

The time of incubation of samples with NPs had an impact on Cu fractionation in all of the soils, but the character of changes in Cu distribution was related to the type of soil and its moisture content (Fig. 1). In all the soils, the level of the bioavailable fractions (F1, F2) increased. In soils with a 50% moisture level, an increase of the content of these fractions with the passage of time was found (Fig. 1B, E, H). After 24 months it was 18.3-20.6%. In the most and least moist soils, after the period of 3 months the highest levels of fractions F1 and F2 was noted (17.5-22.3%) (Fig. 1C, F, I). Subsequently, after 24 months there was a decrease in the content of these fractions (14.3-16.7.3%), though their level was higher than after 1 day (5-8.5%). The content of fraction F3 increased with the passage of time in all soils irrespective of their moisture content, attaining the level of 16-26.3 % after 24 months. Higher levels of this fraction were noted in soils SL2 and SL3 with the lowest moisture (Fig. 1A, D, G). The content of Cu fraction bound to organic matter decreased over time, after 2 years attaining the level of 32.1-44.3%, i.e. below that after 1-day incubation (44-65.2%). The content of fraction F5 increased slightly after 24 months in soils SL2 and SL3, by 1.1-4.3%. A more pronounced increase of the content of this fraction, by about o 8%, was observed in soil SL1 (Fig. 1A, B, C).

The results of the study provided significant information on metal

distribution in soils with various properties, treated with NPs, and on their changes under the effect of various moisture conditions over a long period of incubation. The study confirms the need for analysis of the content of all fractions of metals, not only the bioavailable ones, as due to changes in environmental conditions metal transfer can take place within the individual fractions.



Fig. 1. Effect of aging on Cu fractionation in soils with different moisture level after treatment of nano-CuO (at 10 mg kg<sup>-1</sup>).

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## EFFECT OF WATER AND WASTEWATER TREATMENT ON THE PROPERTIES OF ENGINEERED NANOMATERIALS (ENMs) IN CONTEXT OF THEIR FATE, TOXICITY AND INTERACTION WITH OTHER CONTAMINANTS (SAFEnano)

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Our latest studies [1-2] showed that under the influence of  $UV/H_2O_2$  carbon nanotubes (CNTs) undergo changes that affect their properties. These changes may affect CNTs fate and distribution (adsorption capacity, toxicity, bioavailability, bioaccumulation, etc) in the environment. In view of the above information it is necessary to undertake research on the effect of water treatment processes on the properties of other engineered nanomaterials (ENMs), especially nanocomposites and nanohybrids [3,4].

Modification of the ENMs properties under the influence of advanced methods of water and wastewater treatment ( $H_2O_2$ , UV,  $H_2O_2/UV$ ) were carried out in the photochemical reactor. The studies were conducted using different ENMs in distilled water. Several different nanohybrids and nanocoated carbon nanoparticles were selected. Overall 10 different materials were investigated compared to seven tentatively planned. Following materials were investigated: (1) carbon nanotubes with different coatings - CNT-Zn, CNT-Cu; (2) graphene – graphene nanoplatelets (with different surface area and functionalization - 50-80, 120-150 and 300 m2/g, hydrocarbon functionalized and polycarboxylate functionalized), (3) nanohybrids (NHs) - graphene nanoplatelets-carbon nanotube hybrid, graphene nanoplatelets-Zn hybrid, graphene nanoplatelets-Cu hybrid. The selection of these materials was based on their potential production and possibility of water contamination, thus affecting human health. Different methods were used for ENMs characterization before and after treatment: elemental analysis (C, H, N), surface area (S<sub>BET</sub>, pore volume, micropore volume and surface area, average pore width), FTIR and Raman Spectroscopy.

The results showed that effect of treatment on physico-chemical properties of ENMs depended on method of treatment and material tested. In the case of graphene nanoplatelets (GNPs) with various surface area, UV,  $H_2O_2$  and  $H_2O_2/UV$  treatment, only slightly affected this parameter. However, in the case of functionalized graphene nanoplatelets increasing of the surface area after  $H_2O_2/UV$  treatment of hydrocarbon functionalized GNPs was observed (Fig. 1). All treatments affected polycarboxylate functionalized GNPs increasing surface area significantly. In the case of different nanohybrids and metal functionalized carbon nanotubes significant increase of surface area was observed after UV,  $H_2O_2$  and  $H_2O_2/UV$  treatment. Generally, UV and  $H_2O_2$  treatment of ENMs decreased the carbon content in these materials and increased the other elements which was confirmed by FTIR spectra. However, there were some exceptions, where increase

of C was observed (for example  $UV/H_2O_2$  treated polycarboxylate graphene nanoplatelets).



Fig. 1.  $N_2$  adsorption-desorption isotherms of studied non-treated (GPhob, GPhyl) and treated (H2O2, UV, UV/H2O2) graphene nanoplatelets (GNPs). GPhob – hydrocarbon functionalized (hydrophobic) and GPhyl – polycarboxylate functionalized (hydrophilic)

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## **BENZOPHOSPHOLAN-3-ONES – SYNTHESIS AND APPLICATION IN COUPLING REACTIONS**

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In last years, synthesis of hetererocyclic phosphorus compounds with potentially useful physicochemical properties has been atracted interest of chemists [1-4]. A special place among these compounds hold benzophospholene derivatives due to the phosphorus atom present in the heterocycle structure in connection with the conjugated system. These properties can be additionally modified by oxidation (O, S), complexation (eg BH<sub>3</sub>, metal atoms) or quaternization of the phosphorus atom [5]. Therefore, phosphorus heterocyclic compounds can be a new alternative to the optoelectronic materials used so far. Bearing that all in mind the main goal of the project is to recognize the possibility of the synthesis of 3-arylbenzophospholene derivatives by coupling with vinyl triflates with arenes.

Herein we want to report the synthesis of benzophospholan-3-one **1**, its transformation into the appropriate trilate and preliminary attempts of coupling with arene derivatives.



Scheme 1. Synthesis of benzophospholan-3-one 1.

First, secondary phosphine oxide was obtained starting from methyldiphenylphosphine oxide via P-Ph cleavage in liquid ammonia in the presence of Na (Scheme 1, a) [6]. In the next step, Ullman-type coupling of methylphenylphosphine oxide with methyl o-iodobenzoate afforded a precursor of **1** (Scheme 1, b) [7] which was further subjected to cyclisation in the presence of base resulting in desired benzophospholan-3-on **1** with moderate yield (Scheme 1, c).



Scheme 2. Attempts for synthesis of triflate 2.

Then, attention was paid on the synthesis of triflate 2 (Scheme 2). It was found that the best base for this transformation was DIPEA which led to complete conversion of 1 and afforded the desired product in up to 75% yield.



Scheme 3. Attempted synthesis of 3-arylbenzophospholene via coupling of trilates with arene devivatives.

Finally, triflate 2 was subjected to a very few coupling reactions with arylboronic acid using standard catalysts. However, till now all trials failed to give the desired compound 3.

To summarize, I have presented the synthesis of benzophospholan-3-on 1 and its transformation to the corresponding triflate 2 with good yields. Synthesis of larger library of benzophospholan-3-one analogues and further optimization of the synthesis of 3 are underway in our laboratory.

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## THE COMBINATION OF ACHIRAL CROSS-COUPLING REACTION OF >P(O)H COMPOUNDS WITH CYCLIC VINYL ESTERS AND ASYMMETRIC CONJUGATE ADDITION AS THE SOURCE OF CHIRAL 1,2-BIS(FUNCTIONALIZED) CYCLOHEXANES FOR APPLICATION IN ORGANIC

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The synthesis of enantiopure compounds has been one of the major challenges in organic chemistry since its very beginning as a discipline of science. The most versatile approach towards stereoselective synthesis is transition-metal catalysis. The modification of chiral metal catalysts is mainly focused on the development of ligands with specific electronic and steric properties, especially useful are ligand scaffolds that allow for easy tuning of structural features.

Among chiral ligands organophosphorus compounds constitute one of the major classes with wide application in asymmetric catalysis. These mainly include *P*-chiral and *C*-chiral bidentate diphosphines with diverse hydrocarbon linkers between two phosphinyl groups. An underutilized group of chiral phosphine ligands are 1,2-bis(functionalized)cycloalkanes. The application of metal catalysts with ligands of this type has been pioneered by the group of Knochel with their results on asymmetric hydrogenation of dehydroamino acids<sup>1</sup> and asymmetric hydroboration of styrenes<sup>2</sup>. At present there exists no method for the synthesis of 1,2-bis(functionalized)cycloalkanes that would not require an enantiopure starting material.

In the method proposed by our group 1,2-bis(functionalized)cycloalkanes may potentially be accessed via the combination of C-P cross-coupling between cycloalkenyl (pseudo)halides and >P(O)H compounds and asymmetric conjugate addition of heteroatom- or carbon-based nucleophiles to thus obtained vinylic organophosphorus compounds. The sequence of these two reactions may possibly be catalyzed by a single catalyst (Fig. 1). Cycloalkenyl (pseudo)halides are conveniently prepared from commercially available cycloalkanones.



Fig. 1. Combination of cross-coupling and conjugate addition

Preliminary results show that copper(I) salts in the presence of lithium salt additives and diamine ligands may be used as catalysts for the cross-coupling of cycloalkenyl bromides with secondary phosphine oxides. The same catalytic system trasforms cyclohexenyl tosylate to the corresponding  $\alpha$ -phosphoryl cyclohexanone (Fig. 2).



Fig. 2. Cu-catalyzed C-P cross-coupling of cycloalkenyl (pseudo)halides

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#### **RP-HPLC-HRMS ANALYSIS OF PHOSPHINE-BORANES**

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The presence of weak phosphorus-boron bond frequently rises the problem of the complete analysis of phosphine–boranes especially when the data are collected during the preparation of the manuscript for publication. Contrary to NMR which is regarded as non-destructive analytical method, the MS analysis, and especially the coupled LC–MS or GC–MS techniques, cause predominantly the cleavage of P–B bond leading to the corresponding free phosphines during measurement. The latter may undergo oxidation affording the completely different compound which enters the mass analysis. As a consequence, additional statement should be included and the presence of other molecular ions should be pointed out.

The analogous problem is associated with the identity confirmation which is usually associated with either elemental analysis or high resolution mass spectrometry. Many phosphine–boranes exist as oils which strongly influences results reliability using elemental analysis. Therefore, HRMS technique should be the method of choice for identity confirmation for these compounds.

Herein, we would like to discuss the results concerning the HRMS analysis of a set of structurally different phosphine–boranes using RP–HPLC–HRMS technique along with some interesting consequences associated with the discussed observations.

All phosphine–boranes were submitted to HRMS analysis using RP–HPLC–HRMS technique. Samples were dissolved in MeOH and subjected to HPLC analysis with 5% or 30% MeCN in water as eluent in an isocratic mode followed by HRMS analysis with ESI mode and IT–TOF mass peak analysis. For better ionization of the analyzed compounds, formic acid as added to each solvent (1mL/L). The analysis of each compound shows an interesting feature which is described in detail for diphenylmethylphosphine–borane as depicted in Figure 1.



Figure 1

The results presented in Figure 1 show that none of the mass peaks found for phosphine–borane is of M+H–type. The mass peak closest to the molecular mass of was m/z = 213.1001 which corresponds to the molecular peak of Ph<sub>2</sub>MeP(BH<sub>2</sub>) cation I (Figure 1b). This peak, however, was weak compared to the other peaks found in the spectrum. The most intensive peak was found at m/z = 427.2091, which corresponds to III, an adduct of the starting phosphine–borane and Ph<sub>2</sub>MeP(BH<sub>2</sub>) cation (Figure 1d).

It appeared that most of phosphine-boranes tested underwent similar ionization mode which also points towards a very interesting reactivity of these species. This topic is currently underway in our laboratory.

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### STEREOSELCTIVE CATALYTIC WITTIG REACTION IN THE PRESENCE OF PHOSPHETANE OXIDE

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For over 50 years, the preferred method used in the synthesis of alkenes was the Wittig reaction. The reaction proceeds via condensation of phosphine ylide with the aldehyde or ketone to the corresponding alkene and phosphine oxide as byproduct, which is usually difficult to separate from the desired reaction products and economically unviable. As an effort to address this concern, O'Brien et al. reported in 2009 the first catalytic Wittig reaction (CWR), which relied on an organosilane to chemoselectively reduce a five-member ring phospholane oxide [1]. As it turned out, catalytic Wittig's reactions were most effective at elevated temperatures and in the presence of phospholane oxides, which were easily reduced in the catalytic cycle due to the high stress in the five-membered ring. Fundamentally, the challenge in the development of CWR is the chemoselective reduction of P=O bond at room temperature. The employment of four-membered phosphetane oxides was more promising as ring strain is known to significantly aid the ease of P=O bond reduction and have not yet been used in the catalytic version of Wittig reaction. For practical reasons, McBride approach has been applied by us for the synthesis of phospethane oxides from commercially available olefins and chlorophosphine [2].



Fig	1
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Subsequently, attempts in application of four-membered phosphine oxides in catalytic Wittig reaction were undertaken. We chose the reaction of benzaldehyde with methyl bromoacetate as a model reaction to test a catalytic CWR process. Reactions were performed in the presence of 5 mol% phosphetane oxide 1 (Fig. 1) as precatalyst loading and 1.5 equiv. of DIPEA for the selective deprotonation of the phosphonium salt. Employing the same reasoning silane was used in 1.5 equiv.. Satisfyingly, phosphetane oxide promoted catalytic process at room temperature resulting in high conversions of the substrates in all cases along with good E diastereoselectivity.

⇒ Ĵ	5% fosfetan <b>1</b> 5% RPhCOOH		$\square$
Ϋ́, Η	1.25M BrCH <sub>2</sub> CO <sub>2</sub> Me 1.5M PhSiH <sub>3</sub> / <i>i</i> -Pr <sub>2</sub> NEt tp., 12 godz.	E/Z	

Lp.	RPhCOOH		Conversion [%] <sup>a</sup>	$E/Z^{a}$
1	-	toluene	43	67:33
2	-	AcOEt	63 (51)	70:30
4	C <sub>6</sub> H <sub>5</sub> COOH	AcOEt	89 (80)	71:29
5	4-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> COOH	AcOEt	94 (85)	71:29
6	3,5-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> COOH	AcOEt	88 (80)	63:37

<sup>a</sup> GC-MS, (isolated yield)

#### Table 1

Addition of a catalytic amount of an aryl carboxylic acid notably enhanced phosphine oxide reduction. To check this, reductions in the presence of series of arylcarboxylic acids with different  $pK_a$  values were screened and 4-nitrobenzoic acid yielded the greatest enhancement in CWR (Table 1). In the following optimization step, an assessment of precatalyst was performed. However, the use of more substituted cyclic phosphetane oxide **2** (Fig. 1) led to an insignificant variation in yield, but gave enhanced diastereoselectivity. Subsequently, substrate evaluation was undertaken by utilizing aliphatic and aryl aldehydes in combination with organohalides containing ylide-stabilizing ester, nitrile, ketyl moieties. All attempts led to the formation of olefins in good yields. The use of electron-deficient benzyl bromides afforded stilbene derivatives with moderate yields in an unselective manner.

In conclusion, we have developed mild catalytic Wittig reaction by utilizing an organosilane that chemoselectively reduces phosphetane oxide precatalyst to a phosphetane.

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### CYCLIC AMINOALCOHOLS AS CHIRAL AUXILIARIES IN THE SYNTHESIS OF ENANTIOMERICALLY PURE P-STEREOGENIC PHOSPHINES AND THEIR DERIVATIVES

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Constant demand for enantiomerically pure phosphines is one of strongest driving forces in a field of organophosphorous compounds. Although many methods of the synthesis of P-chiral compounds have been published most of them have limitations that strongly narrows the scope to some specific scaffolds.

Simple synthetic strategy allowed us to obtain diastereomerically pure oxazaphospholidine boranes with moderate yields (scheme 1, table 1).

Scheme 1



Nr.	R =	Yield
3a	<i>o-</i> Tol	45
3b	<i>p</i> -Tol	100
3c	<i>o</i> -An	40
3d	<i>1</i> -Nph	14
3e	<i>t-</i> Bu	5
3f	1-Ad	5
3g	<i>c</i> -Hex	36
3h	<i>c</i> -Pent	100
3i	Mes	0

Simplicity and ease of the synthesis is the basic principle of this project, thus the synthetic route follows a well-known path with nucleophilic insertion of first substituent, transesterification (or chlorination) and second nucleophilic substitution inserting second fragment as the main synthetic steps [1]. Several analogs were reacted with methyllithium affording products without loss of optical purity (scheme 2, table 2).

Table 1



Table	2
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Nr.	R =	Yield	
5b	<i>p-</i> Tol	67	
5c	<i>o</i> -An	0	
5d	1-Nph	14	
5e	<i>t</i> -Bu	0	
5g	<i>c</i> -Hex	34	
5h	<i>c</i> -Pent	47	

The obtained compounds were examined towards the formation of chiral tertiary phosphine-boranes. Following the established synthetic route allowed us to obtain opposite enantiomers of chiral phosphines with only 80% ee which requires further investigation to increase optical purity (scheme 3).





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## SELF-ORGANIZATION OF NANOPARTICLES WITH MODIFIED SURFACES

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The aim of our work is to study the behavior of hairy particles on solid substrates [1]. A particle is modeled as a spherical core with attached one chain. The particle (core) has the diameter  $\sigma_c$ . Each chain consists of M tangentially jointed spherical segments of identical diameters  $\sigma_s$ . The first segment of a tether is permanently connected to the core. All species interact via Lennard-Jones potential

$$u^{(kl)} = \begin{cases} 4\varepsilon_{kl} [(\sigma_{kl}/r)^{12} - (\sigma_{kl}/r)^6] & r < r_{cut}^{(kl)} \\ 0 & \text{otherwise} \end{cases},$$
(1)

where r is the distance between interacting spheres,  $r_{cut}^{(kl)}$  denotes the cutoff distance, and  $\varepsilon_{kl}$  is the parameter characterizing interactions between species k and l.

The core-surface and the segment-surface potentials are given by

$$v_k(z) = \begin{cases} \varepsilon^{(k)} \left[ \frac{2}{15} (\sigma_k/r)^9 - (\sigma_k/r)^3 \right] & r < r_{cut}^{(k)} \\ 0 & \text{otherwise} \end{cases},$$
(2)

or

$$\nu_k(z) = \begin{cases} \infty & r < 0.5\sigma_k \\ 0 & \text{otherwise} \end{cases}$$
(3)

depending on the assumed model. In the above, r is the distance from the surface,  $r_{cut}^{(k)}$  denotes the cutoff distance, and  $\varepsilon^{(k)}$  is the parameter characterizing interactions of species k with the surface (k = c, s).

Molecular dynamics simulations have been carried out using the LAMMPS package [2, 3].

To study the behavior of mono-tethered nanospheres near a solid surface, we have conducted a series of simulations for two models of the system. In these models the substrate has different affinity for cores and for segments: (i) the substrate attracts cores but is neutral to segments (the AC-surface), and inversely, (ii) the substrate attracts segments and remains neutral to cores (the AS-surface). We have modeled the 'neutral' surface using the purely repulsive hard-wall potential (eqn (3)) for cores (the AS-model) or for segments (the AC-model).

Most simulations have been carried out for nanoparticle diameter  $\sigma_c = 4\sigma$  and attractive interactions between segments (model P1). We have performed calculations for two tether lengths: M = 6 and M = 12. The total density of nanoparticles has been varied from  $\rho_t^* = 0.01$  to  $\rho_t^* = 0.4$ . We have also performed some simulations for systems with purely repulsive interactions between nanoparticles (model P0).



Fig.1. Fragments of vertical sections of snapshots of surface films formed by mono-tethered nanoparticles for M = 12 at  $r_t^* = 0.1$  on the AC-surface (left panel) and on the AS-surface (right panel), and for: purely repulsive segment–segment interactions (model P0 – upper panels) and attractive segment–segment interactions (model P1 – lower panels). The cores are red, while the segments are blue [1].

The surface layers for the models P0 and P1 ont the AC-surface are compared in the left panel of Fig. 1. We show here fragments of vertical sections of the corresponding snapshots. In the case of repulsive segment–segment interactions (P0) one sees two sharply distinguished layers. The first layer is built of cores. The second one, located farther away from the wall, contains segments. However, for attractive interactions between segments (P1) the 'mixed' film is formed on the surface. The adsorbed aggregates are well visible.

The morphologies of surface films on the AS-surface are shown in the right panel. In the case of purely repulsive interactions between segments one sees here a monolayer of particles. The surface film has an 'inverted structure' as compared with that obtained for the AC-surface. The first layer consists of segments, while the second is built of cores. In the case of attractive segment–segment interactions the surface film is built of clusters of particles. It is interesting that these aggregates are different from those found on the AC-surface. They are similar to a 'cut orange' with the 'open' side lying on the wall.

Concluding, we have proved that the solid surface affects strongly the behavior of mono-tethered particles and that surface films of various morphologies are formed depending on the properties of the substrate.

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## CHITOSAN-SILVER BIOCOMPOSITES AS NEW MEMBRANE SYSTEMS IN ADSORPTION OF BIOLOGICALLY ACTIVE COMPOUNDS

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Nanocomposites are one of the type of nanotechnology products with a constantly growing importance, mainly due to the possibility of modifying and adapting properties to specific applications. Biocomposites create a new generation of multi-element materials. A lot of effort is given to the development of sustainable and environmentally friendly methods of obtaining and processing nanocomposites. One of the concepts concerns the production of nanocomposites from natural biopolymers, with the hope that in specific applications they can replace traditional materials, including synthetic polymers.

The current state of knowledge in the field of bio- and nanocomposites allows to obtain them in various morphological forms and with different compositions. Nevertheless, the implemented projects often based on synthetic polymers. The incompleteness of knowledge about biopolymer multiphase systems enforces undertaking research to learn and describe new properties of nanocomposites and to specify the relationships between particular elements. The chitosan as an example of a natural polymer is one of the basic components of the biocomposites and due to its importance, it is the protagonist of this story. Chitosan can be used in medicine, cosmetology, horticulture, and agriculture (chitosan has a positive effect on plant infections and diseases caused by fungal activity). The most important features are non-toxicity, biocompatibility with the human body, biodegradability, and ease of modification. A very attractive form of chitosan are fibers with nanometer dimensions (so-called chitosan nanofibers). However, there is a necessity to control the preparation procedure and optimize the parameters during this process. The specific surface properties of materials made from chitosan can be responsible for selective and efficient adsorption (specific trapping) of biological compounds, e.g. cholesterol. The studies performed in this area confirmed their usefulness and the possibility of applying as membrane systems. A new issue was the idea of incorporating metallic nanoparticles (e.g. silver nanoparticles) onto the surface of nanofibers.

Chitosan (CS) nanofibers were synthesized by electrospinning technique for obtaining porous 3D nanofiber matrix and the silver nanoparticles were deposited. In this work, the chitosan phase was applied as polymeric matric and silver nanoparticles as reinforcement. Silver nanoparticles in the form of well-dispersed metallic phase were embedded in CS nanofibers by two ways using silver precursor (diamminesilver(I) complex  $[Ag(NH_3)_2]^+$ ). The proposed approach aims to use the natural reducing properties of chitosan and generates ultra-small sizes of metallic crystallites. In this work, the special attention was paid to the structure

characterization by X-ray diffraction methods. Materials were examined with X-ray diffraction (XRD), Small angle X-ray scattering (SAXS) and compared with Scanning Electron Microscope (SEM).

A new aspect was also the phenomenon of the reduction of metallic precursors through by the matrix material. When biopolymers are applied as the supports, the usage of an external reducing agent is avoided. In such procedure, the metallic ions can be reduced during adsorption directly on the surface by the organic functional groups located in the polymer structure. In view of the above, the behavior of silver ions in relation to the chitosan matrix was investigated. It turned out that the silver nanophase formed on polymeric fibers exhibit extremely small sizes (2-6 nm), definitely smaller than those obtained according to standard procedure outside the biopolymer system and deposited on the surface of the matrix (~ 20 nm). In-situ reduction procedure of silver ions by chitosan fibers was confirmed indeed. In both cases, the distribution of silver nanoparticles on the biopolymer matrix was also surprisingly uniform. The transfer of the research from the experimental to the practical sphere is often associated with the specific biological properties of new materials.

Applications in medicine, food industry, and agriculture are conditioned by specific biological activity, which is determined by antimicrobial (antimicrobial and antifungal) activity, thermal and hydrothermal stability as well as synergism or interaction between active components. The application of the biocomposites modified by silver nanoparticles gives the opportunity to reduce the negative effects such as limiting the amount of using the chemotherapeutic agents. All those remarks suggest that the potential application of the resulting nanomaterials should be described taking into account their biostatics. Such activity of proposed biomaterials was confirmed in this work.

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### ACTIVE CARBONS FROM AGRICULTURAL WASTES FOR ADSORPTION OF ORGANIC POLLUTIONS

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Currently, the most popular active carbons are produced from fossil coals and wood because of simplicity of developing porous structure. Commercial active carbons are relatively expensive, thus more and more attempts are being made to use new raw materials and biomass as precursors.

In this work a series of active carbons from agricultural wastes by two various methods: chemical and physical activation were obtained. Preparation of sample Ac\_Ar was as follows: a residue material after the supercritical extraction of strawberry seeds was subjected to chemical activation by acetic acid impregnation. Than the sample was dried and subjected to pyrolysis at 600°C (2 hrs) under argon. For a series of active carbons from Pistachio shells the pyrolysis process was carried out at 400°C (1 hour) under carbon dioxide. Then, the char was subjected to physical activation at 800°C under carbon dioxide for 1 hour – sample CD\_1h. The same preparation procedure was applied to other active carbons changing: time of activation process to 3 hours – sample CD\_3h; time and activation atmosphere: simultaneous activation using carbon dioxide and steam for 1 hour – ST\_CD\_1h; or 3 hours – ST\_CD\_3h. Part of the sample CD\_1h was additionally subjected to activation by microwave in a reactor for 1 hour – CD\_MV\_1h or 1.5 hour – CD\_MV\_1.5h.

The porosity of active carbons was characterized by low-temperature nitrogen adsorption/desorption (Table 1). The sample Ac\_Ar is characterized by the lowest specific surface area as well as total and micropore volume. It is supposed that a biochemical composition of precursor (relatively high percentage of inorganics) results in the poor structural parameters and significant amount of ash in the final product. It was confirmed by thermogravimetric analysis (TGA) in synthetic air atmosphere which revealed significant residual mass of raw precursor. A series of active carbons obtained from Pistachio shells shows well developed porosity with differentiated share of micro- and mesopores. In the case of two samples the preparation was carried out with simultaneous application of carbon dioxide and steam as activation agents; materials with predominant mesoporous structure and well developed specific surface area were obtained. These characteristics of adsorbents are particularly desirable from the point of view of environment protection because enable adsorption of organic pollutants of small and large molecular sizes in multicomponent systems. Therefore the adsorption studies on removing model adsorbates with the differentiated molecular sizes belonging to the group of herbicides (MCPA) and dyes (crystal violet) on active carbon ST\_CD\_3h were performed.

In Figure 1 comparison of MCPA and crystal violet adsorption isotherms (A) and the concentration profiles (B) from one-component and bi-component solutions (with 10:1 MCPA/CV w/w in initial solutions) on ST\_CD\_3h are presented. Only a slight influence of the dye presence on herbicide adsorption and herbicide presence on dye adsorption was found. It suggests that both adsorbates compete to various adsorption sites of adsorbent. The large crystal violet molecules are adsorbed in mesopores, while the small MCPA molecules fill mainly micropores. Similarly, only slight effect of a competing substance on the herbicide adsorption rate was noted. However, in the case of the crystal violet adsorption, the presence of herbicide with much higher concentration compering to dye, causes more distinct effect on the adsorption kinetics. It is due to higher number of herbicide molecules hindering dye diffusion in solution and adsorption space of the active carbon. Analyzing the adsorption isotherms along with the kinetic dependencies from one-and two-component solutions of both substances, we can state the partially independent adsorption process by filling pores of other sizes.

Activate carbon	$S_{BET}$	$S_{ext}$	$V_t$	$V_{mic}$	$D_{mo}$	$pH_{pzc}$
Ac_Ar	243	84	0.12	0.07	1.05	9.7
CD_1h	599	114	0.27	0.20	0.50	11.4
CD_3h	556	116	0.28	0.18	0.55	11.1
ST_CD_1h	587	166	0.37	0.17	0.69	11
ST_CD_3h	669	247	0.52	0.17	1.50	10.4
CD_MV_1h	646	164	0.30	0.19	0.55	9.9
<u>CD_MV_1.5h</u>	685	104	0.35	0.24	0.59	9.5

Table 1. The values of parameters characterizing porous structure of adsorbents.



Fig. 1. Comparison of MCPA and crystal violet (CV) adsorption isotherms (A) and concentration profiles (B) from one-component and bi-component solutions on ST\_CD\_3h.

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