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.

The utilization of bismuth film electrode plated in situ with the use of a zinc mediator as the sensor for the voltammetric Cr(VI) determination in the presence of diethylenetriaminepentaacetic acid and nitrate ions was confirmed. For 180 s accumulation time, very low limits of detection and quantification of Cr(VI) were obtained, with 5.8×10^{-14} and 1.9×10^{-13} mol L⁻¹, respectively. The proposed procedure was applied to determine Cr(VI) in the certified reference materials and in river water samples.

Additionally, a simple scheme for chromium speciation in natural water samples can be applied. Firstly, the determination of hexavalent chromium after 60 minutes delay from the moment of sample addition to the supporting electrolyte, and secondly, after UV-mineralization of the sample for 3 hours, determination of total chromium. The concentration of Cr(III) can be then calculated by subtraction of the hexavalent chromium concentration from total chromium concentration.

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THE INFLUENCE OF STATIC MAGNETIC FIELD ON ELECTRIC CONDUTIVITY OF WATER

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Water is one of the most important substances on the Globe and therefore our life and activity, as well as agriculture and industry, cannot function without water. Unfortunately many regions over the world feel lack of potable water and this problem will be increasing during coming years. On the other hand, industry consumes huge amounts of water which needs to be treated (softened) to avoid hard scale formation in various installations, especially those working at higher temperatures. Chemical water treatment involves not only high costs but also contamination of the natural environment. Therefore so called non-chemical methods of water treatment are of continuous interest of researches. Among the methods application of magnetic field is widely investigated for several decades and many companies offer so called magnetizers for applications both in industry and households.

The magnetic treatment has remained a controversial process for industrial and domestic water treatment for over 50 years. This type of physical treatment helps to prevent the use of chemicals such as polyphosphates or corrosive substances that are expensive and can be harmful for human life or disruptive to the environment.

A lot of studies on the mechanism dealing with magnetic water treatment have been conducted, especially in aspect of antiscaling and crystallisation [1-3]. Many of them are focused on the effects of magnetic fields on the ions in water and only a few works focus on the changes of water properties solely as caused by magnetic treatments. However, the magnetic treatment also has an impact on water molecules themselves.

The aim of this study was determination of the effects of:

- duration time of static magnetic field action,

- different water flow rates,

- temperature,

- and CO₂ saturation,

On the electric conductivity of water. Investigation of the effect of magnetic field time action was carried out using neodymium magnet of B = 0.27 T magnetic induction and magnetic stack (B = 15 mT).

The biggest magnetic field effect on water conductivity was observed at a flow rate equal to 180 ml/min. This effect depended on the duration time of static magnetic field action and decreases with the temperature increase. Moreover, CO_2 removal from the system by nitrogen flow caused the weakening of the magnetic effect.

Obtained results will be published in a paper that follows.

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COMPONENTS AND PARAMETERS OF MODEL LIQUIDS AND SOLIDS SURFACE TENSION AT DIFFERENT TEMPERATURES

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The wetting process occurs in numerous practical applications including everyday life. The main problem connected with this is prediction and finding the conditions under which complete spreading of solid by liquid takes place. To solve this problem the wetting process must be considered with regard to the surface tension of liquid and solid. In the literature there are many approaches dealing with the correlation between the contact angle in the three-phase systems and the liquid and solid surface tension. Among them that of van Oss et al. [1] based on the Lifshitz-van der Waals and acid-base components of liquids and solid surface tension as well as on the electron-acceptor and electron-donor parameters of acidbase component for the analysis of wetting process is the most frequently used. For this analysis the values of the components and parameters of the model liquids and solids should be known at different temperatures. Our previous studies [2] showed that there are considerable differences between the components and parameters of the model liquids surface tension determined by van Oss et al. and us. For this determination the liquid-liquid interfacial tension was applied. In turn, van Oss et al.[1] determined the components and parameters of model liquids from their contact angle on the model solids. For this determination they took into account the contact angle of water as the referee liquid and the Lifshitz van der component of its surface obtained by Fowkes [1] from the water-*n*-alkane interfacial tension which is equal to 21.8mN/m. It is easy to show that using this value for determination of hydrophobic solids surface tension a considerably different value is obtained in comparison to that from the contact angle of apolar liquids. Therefore the purpose of our studies was to determine the components and parameters of model liquids and solids surface tension based only on the contact angle measurements including water as the referee liquid at different temperatures. The first step of our studies was to determine the polytetrafluoroethylene (PTFE) surface tension which results only from the Lifshitz-van der Waals intermolecular interactions from the contact angle of several n-alkanes at 293, 303 and 313 K. The surface tension of PTFE was calculated from the equation [1]:

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

where γ_L is the liquid surface tension, θ is the contact angle, γ_S is the solid surface tension, the subscript LW refers to the Lifshitz-van der Waals component of liquid or solid surface tension. It appeared that the surface tension of PTFE is equal to 20.24 mN/m and practically does not depend on the temperature in the range from 293 to 313 K [3]. The second step of our studies was to determine the Lifshitz-van der Waals and acid-base components of several liquids surface tension from their contact angle on the PTFE surface taking into account the value of PTFE

surface tension equal to 20.24 mN/m. It proved that the calculated values of γ_L^{LW} for the studied liquids with the exception of water were the same as those determined by van Oss et al. [1]. Unfortunately, for water the γ_L^{LW} was equal to 26.85 mN/m [3]. This value is considerably higher than that determined from the water-n-alkane interface tension. Indeed the acid-base component of polar liquid is equal to the difference between γ_L and γ_L^{LW} . It should be emphasized that for such model bipolar liquids as water, glycerol, formamide and ethylene glycol, the values of γ_L^{LW} are almost constant in the temperature range from 293 to 313 K. The decrease of the surface tension results only from the decrease of the acid-base component of this tension [3]. The third step of or studies was to determine the electro-acceptor and electron-donor parameters of the acid-base component of glycerol, formamide and ethylene glycol. According to van Oss et al. [1] the values of these parameters for water were assumed to be equal at each temperature. For calculation of these parameters for bipolar model liquids the contact angle for the apolar liquid (diiodomethane, α -bromonaphthalene and others), water and a given polar liquid on polymethyl methacrylate (PMMA) was measured. PMMA. was treated as a monopolar solid. For calculations of the parameters of bipolar liquids there we applied the following equations [1]:

$$\gamma_W \left(\cos \theta_W + 1 \right) = 2\sqrt{\gamma_W^{LW} \gamma_S^{LW}} + 2\sqrt{\gamma_W^+ \gamma_S^-} + 2\sqrt{\gamma_W^- \gamma_S^+}$$
(2)

$$\gamma_P(\cos\theta_P + 1) = 2\sqrt{\gamma_P^{LW}\gamma_S^{LW}} + 2\sqrt{\gamma_P^+\gamma_S^-} + 2\sqrt{\gamma_P^-\gamma_S^+}$$
(3)

$$\gamma_A (\cos \theta_A + 1) = 2\sqrt{\gamma_A^{LW} \gamma_S^{LW}}$$
(4)

where W, P and A refer to the water, polar liquid for which parameters will be calculated and apolar liquid, respectively. It appeared that the values of the electron acceptor and electron-donor parameters of the model liquids surface tension depend on temperature and are different from those determined by van Oss et al. [1]. The last step of our studies was to determine the components and parameters of model solids using the contact angle values of one apolar and two polar liquids on a given solid and components and parameters of model liquid surface tension determined by us. [1]. The components and parameters of PE, PMMA and nylon 6 determined in such a way are somewhat different from those in the literature.

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SURFACE FREE ENERGY OF NATURAL AND SYTNTHETIC HYDROXYAPATITE DETERMINED BY THE THIN-LAYER WICKING METHOD

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Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HA) is a major component of vertebrate skeleton and teeth [1,2]. Hence it is often used in many biomedical applications as bone fillers, implant coatings and drug delivery systems. The use of HA as a bone substitute or replacement include complete or partial bone augmentation, filling bones and teeth or coating in orthopedics and dental implants.

In all these applications the interfacial phenomena such as: wetting by body fluids, adhesion to the natural bones, protein adhesion, and cell spreading play a crucial role.

In this study the thin layer wicking method was applied to estimate the surface free energy and its components for synthetic hydroxyapatite and natural sample obtained from pig bones.

The thin layer wicking method is based on a liquid penetration (wicking) into a solid thin porous layer deposited on a solid support and the solid surface free energy is determined using the Washburn's equation:

$$x^2 = \frac{RT}{2\eta} \Delta G$$

where: ΔG is the free energy (enthalpy) change of the system occuring during the wetting process when the solid-gas interface is replaced by the solid-liquid one.



Fig. 1. The total surface free energy and its components obtained using the thin layerwicking method for the synthetic and natural hydroxyapatite.

The total surface free energy values obtained using the thin layer-wicking method were similar and equal to 52.41 mJ/m² and 54.58 mJ/m², for the synthetic and natural HA, respectively. Greater differences appear for the electron acceptor (γ_s^+) and electron donor (γ_s^-) parameters which equal to 0.69 mJ/m² and 57.47 mJ/m² for the synthetic HA and 1.07 mJ/m² and 49.42 mJ/m² for the natural HA.

The obtained results indicate that the thin layer wicking method can be used to determine the surface free energy of powdered biological materials. Moreover, the synthetic HA possesses similar surface free energy to that obtained from pig bones.

Obtained results are published in Applied Surface Science 434 (2018) 1232-1238.

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2D SELF-ASSEMBLY OF TRIPOD MOLECULES WITH REDUCED SYMMETRY: MONTE CARLO MODELING

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On-surface self-assembly of organic building blocks is a promising method of creation of low dimensional structures with potential applications in nanotechnology and material engineering. An important factor which determines morphology of such 2D supramolecular assemblies is the geometry and functionality of a molecular building block at play. To identify this relationship we studied adsorbed systems in which tripod molecules with reduced symmetry interact via a short-range anisotropic pair potential. Accordingly, the self-assembly of a tripod molecule with one shortened/elongated arm, adsorbed on a triangular grid was modeled using the Monte Carlo simulation method. The asymmetric tripod tecton consisted of a few interconnected segments and it was equipped with terminal interaction centers (active segments) with differently assigned interaction directions. Our study focused on the effect of directionality of intermolecular interactions on the morphology of the resulting supramolecular 2D assemblies.

The calculations demonstrated that a suitable encoding of the interaction directions allows for the creation of largely diversified adsorbed structures including molecular ladders, strings, ribbons, aperiodic porous networks and dispersed aggregates.[1,2] Basic differences and similarities between the results simulated for the asymmetric molecules and their C_3 -symmetric counterparts were also discussed. The obtained findings can be helpful in designing new molecular tectons for controlled on-surface self-assembly and coupling reactions, as they provide useful information on the molecule-superstructure relation. This preliminary information can, for example, facilitate screening of molecular libraries to select an optimal molecule able to create low-dimensional structures with predefined properties

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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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The catalytic process of complete methane oxidation (flameless combustion) is the alternative to flame combustion, which creates significance amounts of nitrogen oxide. Moreover, this process can be used to methane oxidation from its lowconcentration mixtures, e.g. from coal mine post-ventilation air or from biogas formed at waste dumps during starting and final periods of their exploitation, when the concentration of methane is too small for its flame combustion.

Four different groups of materials (noble metals, oxides of transition metals, perovskites and hexaaluminates) are recommended as potential catalysts for the complete methane oxidation. It is well-known that palladium and platinum catalysts demonstrate the highest activity and good thermostability. 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. Nevertheless, the activity of cobalt-manganese oxide catalysts is very different and strongly depends on their chemical composition as well as phase composition and crystal structure. Thus, finding a correlation between these properties and the number and reactivity of active sites present on the catalyst surface during the course of methane oxidation will allow explaining and understanding differences in their catalytic abilities. For this purpose, among others, the steady state isotopic transient kinetic analysis SSITKA) will be employed. Moreover, cobalt-manganese oxide catalysts will be prepared by co-precipitation method and also analysed by the N₂ adsorption/desorption method, X-ray diffraction spectroscopy (XRD) and X-ray fluorescence spectroscopy (XRF).

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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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Global climate changes associated with the emission of greenhouse gases, and the reduction of natural fossil-fuel resources have attracted concern around the world. It is urgent to decrease the emission of greenhouse gases for environmental protection. Hydrogen is an ideal energy carrier and, when It is produced from sustainable energy sources, has a relatively low environmental impact. Among the possible methods of hydrogen production (reforming of hydrocarbons, electrolysis, photolytic and biological conversion, ethanol steam reforming (ESR) seems to be very attractive [1, 2].

The aim of this work was to study the performance of $Co-CeO_2$ catalysts in ethanol steam reforming for hydrogen production. 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.

-	
Co-Ce	1.5Co-Ce
22.4	29.2
53.1	45.6
1.00:1.00	1.53:1.00
108.1	107.3
0.15	0.21
7.76	9.70
	Co-Ce 22.4 53.1 1.00:1.00 108.1 0.15 7.76

Table 1. Physicochemical properties of catalysts.

BET surface area does not change with the increase of Co/Ce molar ratio from 1.00:1.00 to 1.53:1.00 and in the case of both studied catalysts a value of BET surface area is high in comparison with the BET surface area of cobalt catalysts supported on ceria. It means that an addition of small amount of hydrogen peroxide to aqueous solutions of salts during catalysts preparation allows to obtain catalyst with higher BET surface area in comparison with a total surface area of catalysts obtained by traditional co-precipitation method.

The reducibility of the Co-Ce catalysts increases with increase of Co/Ce molar ratio. A reduction of Co_3O_4 is a two-steps process which corresponds to the reduction of Co_3O_4 to CoO and then reduction of CoO to metallic cobalt.

Increasing the temperature from 420 to 540°C significantly improves longterm catalyst stability (EtOH:H2O=1:12, GHSV=60000 h⁻¹). The temperature of 540°C is not only sufficient for production of hydrogen-rich gas with only small amounts of by-products but also allows to obtain complete ethanol conversion. At this temperature, the SRE process is more efficient because of larger production of hydrogen. The stability of catalysts decreases with the increase of EtOH:H₂O molar ratio from 1:12 to 1:6.However, a decrease of GHSV parameter allow to maintain high ethanol conversion in SRE process for this molar ratio.



Fig. 1. Effect of Co/Ce molar ration on the catalytic properties Co-CeO₂ catalyst in the steam reforming of ethanol at 420°C (EtOH:H₂O=1:12, GHSV=60000 h^{-1}).



Fig. 2. Effect of Co/Ce molar ration on the catalytic properties Co-CeO₂ catalyst in the steam reforming of ethanol at 540°C (EtOH:H₂O=1:12, GHSV=60000 h^{-1}).

Temperature of 540°C is the most advantageous for ethanol conversion and hydrogen-rich gas production over Co-CeO₂ catalyst in SRE process for molar ratio of EtOH:H₂O=1:12 and GHSV=60000 h⁻¹. A decrease of GHSV parameter allow to maintain high ethanol conversion in SRE process for molar ratio of EtOH:H₂O=1:6.

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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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Carbon dioxide is commonly perceived as greenhouse gas. It is produced during combustion of fossil fuels and oxidative degradation of wastes. Moreover, it can be also formed as a by-product in the processing of biomass, e.g. during biogas and bioethanol production. Biogas contains in average from 40 to 75 % of CH₄ and from 25 to 50 % of CO₂. An effective utilization of waste CO₂ to methane may bring environmental and economic benefits.

The aim of the project is development of innovative catalysts and the application of novel reactor concepts for the methanation of CO_2 , 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) in the years 2016-2018.

The activity of UMCS in the second year of the project was focused on the catalyst development, durability and stability studies of catalysts. The main objective was development and characterization of durable, resistant for sulfur poisoning and coking catalyst, containing non-noble transition metals. The catalysts on different supports, including alumina, ceria, zirconia and silica, with introduction of modifiers were prepared and characterized by physical and chemical methods, including X-ray diffraction, FTIR, TEM, and tested using microactivity unit in CO_2 methanation reaction. The reaction was performed in the wide range of temperatures, composition of reaction mixture and different time-on-stream. It was found that catalytic activity and selectivity of catalysts can be improved by the use suitable metal loading, support composition, preparation method, and treatment conditions. The catalysts of best performance were selected and proposed to use in the fabrication of mini-plant reactor.

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STANDARD SINGLE MODE OPTICAL FIBERS WITH HIGH NUMERICAL APERTURE

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The main goal of the project is to develop a single-photon source of light using quantum dots. To ensure proper collection of the emitted light, it is necessary to create single-mode optical fibers with a large numerical aperture.

In the current period technology of highly GeO_2 doped fibers with NA> 0.4 was elabrated. Appropriate preforms were obtained using the MCVD method and the fibers were drawed on the glass optical fiber drawing tower.

The first attempts to obtain preforms for fibers with NA> 0.4 were made on the basis of the developed method in the previous period. They did not give a positive result. Although the preforms with numerical aperture NA = 0.4 obtained optical fibers, the cores of these fibers had an unstable diameter and uneven level of doping. In addition, during the collapse, so-called resonance bladders that deformed the core. In addition, some preforms, due to high stresses, burst during fabrication, measurement or preparation for fiber removal. The theoretical calculations made in WrUT allowed to optimize the preform project. According to the new design, the core consists of three areas with different degree of doping, which will allow reducing the stress at the core-coat boundary by 50-60%. On the basis of the developed design, several preforms were fabricated and their refractive index distribution profiles were measured. Profile measurements were repeated by rotating the preform by 90⁰. The obtained graphs were asymmetrical with respect to the axis of the preform, which indicated the high ellipticity of the cores. Figure 1a shows an example graph of the preform profile.

a)



Fig. 1. Refractive index profile (a) and SEM photo of cross section, (b) of first fabricated fiber

Optical fibers were drawed from the preforms. The photos taken with the electron microscope confirmed the high ellipticity of the cores of all extruded fiber sections. Figure 1b shows an example of a photo of the optical fiber core in which the ellipticity is 1.29. Unfortunately, such a large ellipticity disqualified the produced fibers. Therefore, in the next stage of the research, changes were made to some stages of the preform production. The stage in which the core ellipticity is most likely to be collapse. It consists in maximally raising the burner power (preform temperature about 1800^oC), reducing the pressure inside the tube by 3-4 mm H_2O and reducing the feed speed of the burner to 20-30 mm / min. The preform gradually reduces its diameter and after 3-4 such burner passes disappears the inner hole and the preform is a rod. Under such conditions, highly doped glass has a low viscosity. The mismatch of the rotational speed and feed of the burner causes local pre-heating of the preform, which results in the glass moving inside the tube and the core ellipse. Another important reason that can cause core ellipticity is the initial ellipticity of the tube, which increases throughout the process. Therefore, tubes with a minimum initial elliptity not exceeding 1.02 were selected for the production of further preforms.

In line with the optimized technique, new preforms were made. Optical insulation (5 layers) and three core areas with different concentrations of GeO₂ were embedded in them. During the collapse the pressure inside the preform was reduced only by 1-2 mm H₂O. The torch feed speed was from 80 to 100 mm / min. Rapid feed of the burner prevented local pre-heating of the preform. Pre-formed measurements were made for the refractive index distribution. The obtained profiles were symmetrical. There was also no difference in the measurements made after turning the preform by 90⁰. Figure 2a shows an example of the refractive index profile. Optical fibers were drawed from the preforms. The photos (figure 2b) taken with the electron microscope confirmed the high centricity of the cores of all extruded fiber sections.



Fig. 2. Refractive index profile (a) and SEM photo of cross section, (b) of fiber fabricated after process optimization.

(Projekt FI-SEQUR (NCBiR))

HELICAL MICROSTRUCTURED FIBERS FOR APPLICATIONS IN OPTICAL METROLOGY AND COMMUNICATION

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The principal goal of project is a full understanding of new wave phenomena arising as a result of helical twist of microstructured fibers of different types. The project combines two, until now almost independent, areas of research. The first one is related to microstructured fibers which have been investigated for almost 15 years, while the second one is connected with helical core fibers investigated since recently. The investigations of microstructured fibers are well advanced and have brought already many practical applications. Microstructured fibers are currently applied to supercontinuum generation in a broad spectral range. They enable light propagation in air core thanks to the effect of photonic bandgap which prompted applications of such structures in gas spectroscopy, make feasible single mode propagation in a broad spectra range, allow to increase a mode filed diameter while preserving single-mode propagation, make it possible to obtain record high birefringence, single polarization operation mode and are used in various sensing applications. Nonetheless, the investigations of microstructured fibers are still very intense and concentrate now on searching for structures and materials enabling for supercontinuum generation in other spectral ranges (for example in UV and MIR), searching for new nonlinear phenomena and their applications (like SC generation in all-normal dispersion regime) or novel sensing applications based on materials different than silica (for example polymer microstructured fibers).

Realization of this project will enhance a new research direction, which has already raised a significant interest among the leading research teams. This is confirmed by an increasing number of highly ranked publications devoted to this subject which in the present stage of development have predominantly a fundamental character. The results published so far point on high application potential of helical microstructured fibers. For example, it has been recently demonstrated in that by introducing high index inclusions in a direct neighborhood of centrally located step-index core and helical twist of such fiber it is possible to obtain single-mode propagation in the core of a record high diameter exceeding 50 μ m. It is expected that such fibers will find applications in future in high power fiber lasers technology. It was demonstrated experimentally that in twisted microstructured fiber with the core of threefold symmetry one may obtain a propagation of core modes with angular orbital momentum equal to 3. This phenomenon may find applications in future multichannel data transmission systems based on different spatial modes or in fiber laser technology for vortex beams generation. The area of research defined in this project is therefore very promising and will certainly bring in upcoming years many valuable publications as well as patents. The most important scientific result of the project will be identification and full understanding of new wave phenomena arising in helically twisted microstructured fibers with high potential for future applications. Additional outcomes of this project will be development of numerical tools for simulations of all relevant transmission and sensing parameters of helical microstructured fibers, development of technological processes for fabrication of helical microstructured fibers with predefined characteristics, methods of local twisting of microstructured fibers and development of experimental methods for characterization of helical microstructurded fibers. Moreover, it is expected that realization of this project will prompt further advances in the field of optical communication and metrology thus giving rise to future development of novel optoelectronic devices and components (for example new fibers for multichannel transmission based on vortex modes, lasers employing active helical microstructured fibers, passive optical components used in optical communications like couplers and filters, and sensors based on helical microstructured fibers for detecting various parameters) with improved characteristics.

In the first stage of realization of project two different dual core standard optical fibers were fabricated. The cores were manufactured with MCVD method. They are characterized with different GeO_2 concentration (3,1% and 6,8% respectively). Because the propagation conditions of light in individual cores should be the same, cores have different diameters. The core with a smaller GeO_2 concentration has a larger diameter and the core with a higher GeO_2 concentration has a smaller figure 1 presents the SEM photos of fabricated fibers.



Fig. 1. SEM photos of fabricated standard dual core optical fibers.

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OPTIMIZATION OF BULK PMMA POLIMERIZATION FOR POLYMER OPTICAL FIBERS TECHNOLOGY

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In optical fiber technology (glass and polymer) the main important point is attenuation which affects quality of the fiber. Therefore, many studies have been done in order to decrease attenuation such as reducing the impurities, fabricating fibers from different materials. Another reason which cause to increase the attenuation is inhomogeneity of structure of the optical fibers. Some parameters have key role in fabrication of optical fiber during drawing process such as diameter of preform, drawing tension, drawing speed. Fabrication process of optical fibers is very important for the quality of the fibers. Even in small changes of drawing process can affect the results of application of the optical fiber. The fibers drawn under different conditions cause to different results due to its mechanical and optical properties.

In the project production of PMMA bulk polymers were studied in order to optimize polymerization with different chain transfer agents. The molecular weight of polymer samples were adjusted by chain transfer agents which controls the length of polymer chains during the polymerization. The optical properties of these samples (scattering and transmission) were studied.

PMMA samples were produced via thermal bulk polymerization. Typically in this method, the monomer (MMA), initiator (BPO, 0.4%) and chain transfer agent (CTA) (IPA, nBMC or PMDS) were mixed in glass test tube and polymerized thermally. In order to compare the effect of the purification of PMDS, non-purified PMDS was also used as chain transfer agent.

In comparison of commercial PMMA for drawing optical fiber, IPA is not suitable CTA due to higher molecular weight of polymer samples. n-BMC and PMDS can be used as a CTA in order to fabricate polymer in proper molecular weight range. According to scattering results the polymer samples synthesized by n-BMC shows higher scattering than that of IPA and PMDS, due to S-C bonds which cause to increase the scattering strongly. The transmission results indicate that there is no effect of concentration of CTA on transmission clearly. Refractive index of PMMA samples was increased by increase of molecular weight of CTA.

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APPLICATION OF BIOCHAR TO SEWAGE SLUDGE REDUCES TOXICITY AND IMPROVE ORGANISMS GROWTH IN SEWAGE SLUDGE-AMENDED SOIL IN LONG TERM FIELD EXPERIMENT

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One of the new directions of agricultural management of sewage sludge is its use as a fertilizer in combination with carbon adsorbents (e.g. activated carbon or biochar). This win-win solution allows to utilize sewage sludge rich in organic matter and nutrients and, at the same time, reduce the mobility of contaminants due to their being bound by a carbon absorbent [1,2]. The benefits arising from the properties of biochar are an additional advantage of sewage sludge application in combination with biochar. Biochar has good fertilizing properties and, likewise sewage sludge, may beneficially affect the physical, chemical and biological properties of soils [3]. Our recent study also demonstrated [4] that despite of the PAHs immobilization in sewage sludge amended soil, biodegradation of PAHs occurs after usage of biochar. This is particularly beneficial because, contrary to appearances, after biochar application the persistence of PAHs in sewage sludgeamended soil does not increase.

The aim of the present study was to determine changes in the physicochemical properties and toxicity of soil amended with sewage sludge (10 t dw/ha) or sewage sludge (10 t dw/ha) with biochar addition (2.5, 5 or 10% of sewage sludge). The study was carried out as a field experiment over a period of 18 months. Samples for analysis were taken at the beginning of the experiment as well as after 6, 12 and 18 months. The study investigated toxicity of the unamended soil, sewage sludge-amended soil and sewage sludge-amended soil with biochar addition towards Folsomia candida (collembolan test) and *Lepidium sativum* (Phytotoxkit F). Moreover, toxicity of aqueous extracts obtained from the tested soils towards *Vibrio fischeri* (Microtox®) and *Lepidium sativum* (elongation test) was determined.

The study showed that addition of biochar to the sewage sludge and soil reduced leaching of nutrients (mainly phosphorus and potassium) from the amended soil. Biochar significantly reduced sewage sludge toxicity, exhibiting a stimulating effect on the tested organisms. The stimulating effect of biochar addition to the sewage sludge persisted throughout the entire experiment. Apart from the remediatory character of biochar, this is also evidence of its fertilizing character. In the tests with *L. sativum* (leachates and solid phase) and *V. fischeri* (leachates), increasing the rate of biochar in the sewage sludge increased root growth stimulation (*L. sativum*) and bacteria luminescence (*V. fischeri*). However, increasing biochar rate decreased *F. candida* reproduction stimulation, which could have been an effect of reduced nutrient bioavailability due to the biochar (Fig. 1).



Fig. 1. (A) *Folsomia candida* mortality and (B) inhibition of reproduction of *Folsomia candida* in soil amended with sewage sludge (S + SL) and soil with sewage sludge and different dose of biochar (S + SL + 2.5% BC, S + SL + 5% BC, S + SL + 10% BC) after 0, 6, 12 and 18 months. Error bars represent the standard deviation of the mean (n=3).

This study has shown that the use of sewage sludge with biochar may become not only an effective long-term method leading to reduced toxicity of sewage sludge, but also to increasing the fertilizing properties of sewage sludge. The positive effect of sewage sludge addition in combination with biochar to the soil was visible for the tested groups of organisms (plants, arthropods and bacteria) throughout the entire study period. Apart from a significant reduction in sewage sludge toxicity in the presence of biochar, beneficial changes in the soil's physicochemical parameters and long-term immobilization of nutrients were observed in this study. The higher nutrient content in the sewage sludge- and biochar-amended soil persisted longer than in the case when the soil was amended with sewage sludge alone. This allows us to presume that biochar may promote the prolongation of the beneficial fertilizing effect of sewage sludge. The percentage of biochar in sewage sludge is an important aspect that needs to be emphasized. The higher biochar rates had a more effective impact on plants, whereas the lower rates were more beneficial to arthropods.

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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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Behavior of engineered nanomaterials (ENMs) in the environment differs from the pathways observed for larger particles [1]. Due to the special properties of ENMs and a wide range of their applications, attempts are made to estimate the fate of ENMs in the environment and transformations during their use and storage [2]. The release of ENMs may occur during the use of materials containing nanoparticles, their processing or disposal and storage. It is assumed that the major part of ENMs gets into the environment with wastewater. During their transport and release into the environment, ENMs may undergo different transformations, e.g. oxidation and reduction, dissolution, adsorption, biotransformation, aggregation, and deposition [2]. Those transformations may lead to changes in the properties of ENMs. As released ENMs will firstly get into wastewaters, one can expect that they will be subject to various processes of transformation there. Moreover, ENMs are commonly produced with an organic capping agent or stabilizer. Moreover recent focus on material synthesis and development at the nano-scale shows a clear shift from single material processing toward hierarchical assemblages (nanohybrids). Transformations of the material (coated and nanohybrids) can therefore affect the core material, the capping agent, or both. While publications tracing the fate of ENMs during wastewater treatment appear more and more frequently [3-6] we currently lack sufficient knowledge of the types, rates, and extent of transformations expected for ENMs. By extension, we also fail to understand the impact of those transformations on the fate, transport, and toxicity of ENMs. To correctly forecast the environmental and human health risks associated with these materials, we must endeavor to broaden our knowledge of the transformations of ENMs.

The latest research shows [5,6] that in wastewater treatment plants certain ENMs may undergo the processes of sulfidation, which has a detoxifying effect on ENMs. However other research demonstrated [7] that sulphur and selenium in some metal sulphides and metal selenides (major components of quantum dots) are susceptible to oxidation that may release soluble toxic metal ions such as Cd. To date, studies on the impact of various processes on the transformation of ENMs are mainly focused on sulfidation. Broader description of the problem is not possible because other data does not exist in this area of research, especially when it comes to the transformation of nanoparticles in wastewater treatment plants. To our best knowledge the study will be the first in this area. Underestimation of the risk related to ENMs may create a serious threat to the environment. Our latest studies [8,9]

also demonstrated that under the effect of UV/H_2O_2 carbon nanotubes undergo degradation that changes their properties. In view of the above information it is necessary to undertake research on the effect of water treatment processes on the properties of ENMs. This will not only expand our current knowledge in this area, but it will also permit the identification of actual threats related with the use of ENMs. This in turn will permit the presentation of suitable solutions for the authorities responsible for environmental safety on Europe.

The primary aim of the present study will be to attempt to estimate what changes different ENMs (coated and nanohybrids) will undergo during water and wastewater treatment and how these changes will affect ENMs fate, toxicity and interaction with other contaminants. Specifically, I will:

1. Enhance our knowledge of the ENMs transformation during water and wastewater treatment (WP1).

2. Enhance our knowledge how ENMs transformation will affect their fate in the environment on the basis of laboratory and mesocosm experiments (WP2).

3. Enhance our knowledge about interaction between well-known contaminants and ENMs (WP3).

4. Perform risk assessment of ENMs in the context of their transformation (WP4).

The proposed approach will be the first which indicate how various water and wastewater treatment methods will influence the physicochemical and ecotoxicological properties of ENMs. Recognition of this problem has an extremely important aspect of cognition in a situation of increasing ENMs production. Acquired new knowledge on this topic will lead to a better understanding of the mechanisms and processes in the environment. The research will contribute to a broad base of knowledge that will be the basis for solving of known or expected future problems related to the use of ENMs.

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INFLUENCE OF THE ADDITION OF CNT ON PHOTOCATALYTIC PROPERTIES OF TiO₂ IN THE REMOVAL OF PHARMACEUTICALS FROM WATER AND WASTEWATER

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The problem of water and wastewater pollution is connected with the low susceptibility of target compounds to biodegradation [1]. Low efficiencies of pharmaceuticals and personal care products (PPCPs) removal from wastewater and the presence of PPCPs in water indicate that traditional wastewater treatment methods are inefficient in their removal [2]. Though different methods of PPCPs removal from water and wastewater are tested [3]. One of the promising methods that is able to remove PPCPs and decompose them into CO_2 and H_2O is photocatalysis [4]. Traditionally used TiO₂ is, however, activated only by UV. In order to increase TiO₂ activity in the visible light region (to reduce the size of Eg), TiO₂ must be modified. Carbon nanotubes (CNTs), both Single-walled Carbon Nanotubes (SWCNTs) and Multiwalled Carbon Nanotubes (MWCNTs) can be used for TiO₂ modification [5]. CNTs-doped TiO₂ possess increased adsorption capacity and reduced Eg [6].

During the studies 3 series of CNTs-doped TiO_2 photocatalysts containing 0.15-17.8wt% of CNTs were obtained and tested in PPCPs removal. For TiO_2 modification both SWCNTs (S-labelled photocatalysts), MWCNTs (CNT-labelled photocatalysts) and MWCNT-OH (CNTOH-labelled photocatalysts) were used. The photocatalysts were obtained by sol-gel method. Characterization of physicochemical properties of obtained photocatalysts was performed using Raman and UV-VIS/DRS spectroscopy, TEM, N₂ adsorption-desorption, XPS and XRD. The main properties of tested photocatalysts are presented in Table 1.



Fig. 1. The photocatalytic removal of acetaminophen (10 mg L^{-1}) under visible light irradiation using CNT-TiO₂ photocatalysts (0.5 g L^{-1}). Line represents the changes of acetaminophen concentration in time during 60 min of treatment.

As target pollutants carbamazepine (a psychotropic drug), acetaminophen and diclofenac (anti-inflammatory drugs) and caffeine (stimulant) were applied at concentration of 10 mg L⁻¹. Their photocatalytic removal was performed under visible light irradiation (550 nm) in photochemical reactor. The removal of pollutants was presented c/c_0 ratio (*c*- concentration at time *t*, c_0 - initial concentration of pollutants). The changes of TOC of wastewater were also measured. The mechanism of photocatalytic removal was proposed using *OH, O_2^{*-} and h⁺ radicals scavengers.

photocatalyst	$S_{BET} [m^2 g^{-1}]$	pore volume [cm ³ g ⁻¹]	pore size [nm]
CNT1	383	0.298	3.1
CNT5	421	0.284	2.7
CNT10	383	0.314	3.3
CNT20	349	0.359	4.1
CNT40	390	0.343	3.4
CNTOH1	403	0.317	3.0
CNTOH5	451	0.326	2.8
CNTOH10	415	0.323	3.0
CNTOH20	390	0.315	3.1
CNTOH40	437	0.370	3.3
SWCNT1	522	0.358	2.7
SWCNT5	438	0.297	2.7
SWCNT10	399	0.290	2.8
SWCNT20	368	0.270	2.8
SWCNT40	422	0.309	2.8

Table 1. The physicochemical properties of CNT-TiO₂/SiO₂ photocatalysts.

The greatest changes in wastewater quality were observed during first 20 min of photocatalytic treatment and application of CNT10 enabled to remove acetaminophen at least in 80% (Fig. 1). The highest impact in acetaminophen removal revealed *OH and O_2^{*} radicals.

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GREEN SYNTHESIS OF TETRAZOLOPYRIMIDINE DERIVATIVES

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Multicomponent reactions (MCRs) are ideal synthetic strategies based on green chemistry protocols to construct diverse molecular scaffolds starting from a few simple materials or intermediates. MCRs include various potentials such as intrinsic convergence, complexity-generating power, operational simplicity, resource and energy effectivity, atom-economy, sustainable technology and suitability for preparation of large chemical libraries of drug-like compounds. Substituted pyrimidines are very important biologically and pharmaceutically active agents in the medicinal chemistry and drug discovery processes. A few procedures have been reported in the literature for the synthesis of tetrazolo[1,5-a]pyrimidine derivatives [1].

In connection with our interest in design new efficient and green protocols of synthesis of new biologically active compounds we deside to combine the MCR aproach with ultrasonic irradiation activation and functionalized metal oxide magnetic nanoparticles (MNPs) catalysis which have attracted much attention of scientific and industrial researchers as an innocuous, green techniques for several chemical processes. The condition of such reactions are milder, more convenient, simple and easily controlled; while the MNP catalysts could be separated using an external magnet, they are reusable, highly activity but have a high degree of chemical stability in various organic solvents.

Herein, we reporting the sonochemical synthesis of tetrazolo[1,5-a]pyrimidines **5** via a one-pot 4-CR of 2-cyano-guanidine **1**, sodium azide (NaN₃) **2**, various aromatic aldehydes **3** and methyl or ethyl acetoacetate 4 in the presence of a catalytic amount of modified magnetic iron oxide nanoparticles (MNPs@NHC(O)CH₂CH₂PPh₂).



Fig. 1 Synthesis of tetrazolo[1,5-a]pyrimidines.

The synthesis of bare NMP, and MNP coated witch siloxane shell $MNP@NH_2$ were performed according to the modified previously reported procedures [2, 3]. The total amount of amino group was measured by acid-base titration as 0.48 mmol per 1 g of nanoparticles. At first, stepwise linker immobilization and diphenylphosphine functionalization of the silica-coated Fe₂O₃ nanoparticles (MNPs@NHC(O)CH₂CH₂PPh₂) as a heterogeneous MNC was readily accomplished.



Fig. 2 Synthesis of MNC.

The scope of the reaction was examined in synthesis of diversified tetrazolopyrimidines possessing EWD and EDG substituents.

R1	R ²	Time	Yield	R1	R ²	Time	Yield
		(min	(%)			(min	(%)
))	
C_6H_5	Me	15	89	$4-FC_6H_4$	Me	15	88
4- NO ₂ C ₆ H ₄	Me	20	82	$3-NO_2-4-HOC_6H_3$	Me	15	86
3- NO ₂ C ₆ H ₄	Me	15	84	$4-BrC_6H_4$	C_2H_5	15	90
3-CH ₃ OC ₆ H ₄	Me	20	80	3,4-(CH ₃ O) ₂ C ₆ H ₃	Me	20	85
2,4- Cl ₂ C ₆ H ₃	Me	20	83	4- MeC ₆ H ₄	Me	15	88
4- BrC ₆ H ₄	Me	20	82	$2,4-Cl_2C_6H_3$	C_2H_5	15	89
3- ClC ₆ H ₃	Me	15	90	3,4,5-	C_2H_5	20	81
				$(CH_3O)_3C_6H_2$			

Table 1. Synthesis of tetrazolopyrimidine derivatives.

In summary, tetrazolo[1,5-a]pyrimidine derivatives were synthesized by using 2cyano-guanidine, sodium azide, various aromatic aldehydes and methyl or ethyl acetoacetate under ultrasonic irradiation with a frequency of 40 kHz and power of 250 W in the presence of a catalytic amount of MNPs@NHC(O)CH₂CH₂PPh₂. The results indicated the scope and generality of the one-pot strategy with respect to various starting materials. This new, green and efficient MCR protocol for the preparation of synthetically, biologically, and pharmaceutically relevant tetrazolopyrimidine derivatives presents some important advantages such as simple and readily available precursors, easy workup procedure, reusability of the heterogeneous MNC, high atom economy, excellent yields and mild reaction conditions.

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INTRAMOLECULAR NUCLEOPHILIC SUBSTITUTION IN ω-HALOALKYLPHOSPHINE SULFIDES

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The modern organic synthesis is based largely on transition metal-catalyzed reactions where the use of ligands is crucial for the most effective and selective transformation of the substrates. One of the prominent class of ligands are phosphines, especially suitable for complexation of a set of very important transition metals like palladium, rhodium, iridium or copper. Among phosphine ligands those possessing cycloalkyl linker at phosphorus are intensively used as ligands, especially in C-C bond-forming reactions (Figure 1).

Figure 1



The synthesis of organophosphorus componds with cycloalkyl substituents at phosphorus is based mostly on a reaction of organometallic compounds with phosphorus electrophiles.[1] In the course of our research based on the synthesis of C-chiral diphosphine derivatives we were interested in the use of ω -haloalkylphosphine derivatives as electrophiles for the reaction with carbanions derived from organophosphorus compounds (Scheme 1).[2]



To our surprise, the expected product 6 was not detected in the reaction mixture. Instead, the formation of disubstituted cyclohexane 7 has been confirmed.

This result suggests, that ω -haloalkylphosphine derivatives may undergo cyclization through intramolecular nucleophilic substitution reaction.

In order to confirm this assumption, a set of ω -haloalkylphosphine derivatives has been prepared and subjected to the reaction with a base (Table 1).



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Nr	Alkylation				Cyclizatio	n
	Subst.	Dihalide	Product	Yield	Cycloalkane	Yield
1	8	Br(CH ₂) ₃ Cl	11a (n = 1)	77%	13a (n = 1)	25%
2	8	Br(CH ₂) ₄ Cl	11b (n = 2)	82%	13b (n = 2)	46%
3	8	Br(CH ₂) ₅ Cl	11c (n = 3)	67%	13c (n = 3)	58%
4	8	Br(CH ₂) ₆ Cl	11d (n = 4)	73%	13d (n = 4)	35%
5	10	Br(CH ₂) ₄ Cl	12a (n = 1)	85%	13a (n = 1)	64%
6	10	Br(CH ₂) ₅ Cl	12b (n = 2)	45%	13b (n = 2)	60%
7	10	Br(CH ₂) ₆ Cl	12c (n = 3)	37%	13c (n = 3)	65%
8	9	Br(CH ₂) ₆ Cl	12d (n = 4)	85%	13d (n = 4)	63%

It appeared that, indeed, both ω -haloalkylphosphine sulfides and boranes underwent intramolecular cyclization affording the corresponding cycloalkylphosphine derivatives in fair to good yields. Further development in this area included the application of the structurally different substrates and the stereochemical analysis of the developed transformation.

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ASYMMETRIC WITTIG REACTION CATALIZED FOUR MEMBER RING PHOSPHETANES

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For over 50 years, the preferred method used in the synthesis of alkenes was the Wittig reaction. In 2009, the first example of the synthesis of olefins catalyzed by phosphine oxides in a reducing silane environment was presented, which improved the economic aspect of the Wittig reaction and at the same time solved the problem of product purification.[1] As it turned out, catalytic Wittig's reactions (CWR) were most effective at elevated temperature and in the presence of phospholane oxides, which were easily reduced in the catalytic cycle of the reaction due to the high stress of the five-membered ring. (Figure 1).



Fig. 1

In contrast, phosphetane oxides belong to four-membered phosphorus ligands that can be readily prepared via McBride method[2] from commercially available olefins and have not yet been used in the catalytic version of the Wittig reaction. Therefore, it seems very reasonable to test the reactivity of the phosphetane oxides of the Wittig reaction due to the much higher stress of the four-membered ring than in phospholanes. It can be expected that the strain on the ring will significantly speed up the reaction and may allow the Wittig reaction to be carried out at room temperature and in the presence of mild reductive reagents such as borane derivatives (Figure 2).[3]



Fig. 2

This approach has been applied by us to the synthesis of phospethanes. Thus, according to McBride procedure, treatment of dichlorophenylphosphine with olefins formed cyclic phosphonium salt, which after hydrolysis gave phosphetane 1-oxides in high yields. In these reactions, addition of phosphenium ions to olefins

generate carbocationic intermediates that are prone to rearrangement. In case of the reaction of the (+)-camphene with PhPCl₂ the bridged bicyclic endo-isomer of phosphetane oxide was obtained in moderate yield.





We chose the reaction of benzaldehyde with methyl bromoacetate to form methyl phenylpropenoate as a model reaction to establish a CWR process. To ease integration in the final CWR, reductions were performed in the presence of base and a theoretical 10 mol% phosphetane oxide 2 as precatalyst loading. Employing the same reasoning the silane would represent 1.5 equivalents. This rationale led to the final conditions as depicted in Table 1 and the results were interesting. Satisfyingly, the phosphetane oxide promoted catalysis strategy was effectively adopted into the CWR resulting in a room temperature CWR with high conversion



of the aldehyde.

Base	Temp.	Time	Conversion	E/Z ratio	Yield[%]
Na ₂ CO ₃	rt	48h	0	-	-
Bu₃N	rt	30min	39.0	2.3:1	31.5
Bu₃N	rt	24h	90.0	2.9:1	64.1
Et₃N	rt	30min	41.4	4.4:1	34.1
Et₃N	rt	24h	96.7	5.8:1	61.7

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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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Enantiomerically pure phosphines are known as very effective ligands in asymmetric transition metal catalysis. Due to observable increase of the amount of chiral compounds produced by industry as well as the continuing improvement of the existing technological processes, the development of new methods of the synthesis of such compounds is one of the main targets in synthetic organic chemistry.

Our methodology is based on the application of several aminoalcohols as source of chirality for the synthesis of diastereomerically pure organophosphorus compounds. Thus, the synthesis of L-prolinol has been attempted first (Scheme 1).^[1]



Scheme 1

Phosphonous acid chloride bis(N,N-diethylamide) was chosen as the most favorable organophosphorus substrate. Simple synthesis allowed to obtain the desired compound (Scheme 2).^[2]



Scheme 2

Substitution of chlorine atom with organometallic reagent led to a series of phosphonous acid diamides (Scheme 3).



Scheme 3

Reaction of one of these compounds with L-prolinol followed by a protection of P(III) atom with borane led to the formation of oxazaphospholidine-boranes with moderate yields but with high diastereomeric purity (Scheme 5).



Scheme 4

Attempts towards the transformations of the obtained oxazaphospholidine derivatives into phosphines were taken through the cleavage of P-O bond with Grignard reagents. Up to now, all experiments failed to give any expected products.

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SELF-ORGANIZATION OF NANOPARTICLES WITH MODIFIED SURFACES

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In this year we have focused on the following problems:

- (i) Application od integral equation theory to describe the angular-dependent correlation functions of two-dimensional systems of nanoparticles with small ligands[1],
- (ii) Effective interactions between a pair of particles modified with tethered chains [2],
- (iii) Self-organisation of hairy disks at surfaces [3].

Here we briefly discuss the results of molecular dynamic simulation conducted for hairy disks in two-dimensional systems [3]. Nanoparticles are modeled as circular cores with three ligands attached to them The ligands are linear oligomers. Each chain is composed of M = 1,2,3,5,7,10 freely jointed segments, which are disks of the size σ . The diameter of the core is $\sigma_c = 3.5\sigma$. We consider two models of hairy nanoparticles. The first model involves particles with rigid geometry. In this case the grafting points are permanently fixed at vertices of an equilateral triangle inscribed into the circle of the radius $d = 2.00\sigma$. The angles between consecutive core-ligand bonds, ϕ , are equal to $2\pi/3$. According to the second model the grafted chains are mobile and they can slide over this circle.

All the entities (either cores or segments) interact via Lennard-Jones(12-6) potential. The cut-off distance is used to switch off attractive interactions. We assume that the core-core and segment-segment interactions are attractive whereas the core-segment interactions are repulsive. In this study the core-core energy parameter equals to $\varepsilon_{cr} = 9\varepsilon$.

We have shown that the morphology of a solid phase built of hairy disks depends either on the chain length or the chain mobility. For considered here disks decorated with monomers the impact of the ligand mobility is negligible. In case of the both model particles hexagonal structures of cores are observed. However, for longer tethers particles with fixed and mobile tethers assemble into completely different structures. Thus, the degree of ligand mobility decides the morphology of the system. In the case of disks with dimers we have found an amorphous solid phase for fixed ligands, and the lamellar phase for mobile chains. The similar lamellar structures have been observed for tethered trimers and pentamers. We have also seen a tendency to form a similar structure by disks with tethered mobile heptamers. However, the behavior of particles decorated with fixed ligands changes as the chain length increases. The cores of disks with tethered trimers lie on a honeycomb lattice (Fig. 1a), while for attached pentamers and heptamers the 'spaghetti-like' phases are formed (Fig. 1b).



Fig.1. Snapshots obtained for disks decorated with fixed (a) trimers and (a) pentamers [3]

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NANOSTRUCTURED BIOCOMPATIBLE/BIOACTIVE MATERIALS (NANOBIOMAT)

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The temperature dependences of sorption processes are of great importance in analysis of many natural systems which are subjected to strong temperature changes [1]. Temperatures of waters or wastewaters to be subjected to technological treatment processes can vary in a wide range, depending on seasonal and daily changes. Temperature is an important factor that could significantly change the effectiveness of sorption process.

Among the numerous techniques for dyes removal, adsorption shows good results as it can be used to remove different types of coloring materials. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents. In this work the synthesis of new adsorbent and investigation of its ability to remove dyes from water have been made. Chitosan-fumed silica adsorbent was obtained by using the method of impregnation of fumed silica [2]. The structure characteristics of the adsorbent were obtained from the lowtemperature adsorption/desorption isotherms of nitrogen and imaging by scanning electron microscopy (SEM). The adsorption isotherms of anionic dye, Acid Orange 8 (AO8) from aqueous solutions were measured over a wide range of solute concentrations and at different temperatures. The experimental equilibrium data were analyzed by the Generalized Langmuir (GL) equation taking into account the energetic heterogeneity of the adsorption system. The effect of temperature on dye uptake and adsorption rate was studied. The study of temperature effect on adsorption equilibrium and kinetics showed that the maximum adsorption capacity determined at 5°C was about one third higher than the value at 45°C. First-order equation, pseudo-first order equation, second-order equation, pseudo-second order equation, mixed 1,2-order equation and multi-exponential equation kinetics models were applied for kinetic analysis.

The analysis of measured concentration profiles indicates significant differences in rate of the adsorption process depending on temperature conditions. Adsorption rate strongly increases with temperature increase due to growing kinetic energy of adsorbate molecules. Moreover, in the initial part of kinetic curves linearity is kept as a result of fast process. Comparing kinetic data for the studied systems one can see that at extreme temperatures 5°C and 45°C times needed for decolorization efficiency of 50% and 75% differ nearly eight and seven times, respectively. For obtaining efficiency of 95% the difference of times is not so high and ranges about two times. In the temperature range 5 - 35°C one can find a linear time vs. temperature dependence for considered decolorization efficiencies. Especially, it is visible in the case of efficiency of 95%. Taking into account an industrial or environmental applications of chitosan-silica composite for removing of anionic dyes, the obtained results are very promising. Kinetics of the adsorption process is as important as capacity of adsorbent and may be treated as a critical factor determining usefulness of the method. In our experiment, the time 10 (at 45°C) and 20 minutes (at 25°C) is enough to achieve 50 % of dve removal. After six hours for the processes conducted at 35 and 45°C the adsorption equilibrium was achieved. On the contrary, for the process conducted at 5°C, the time of 20 h is too short to achieve the adsorption equilibrium. In all the studied systems the relative equilibrium concentration close to zero was reached. Analyzing adsorption profiles we can state that for all systems similar adsorption capacities were reached and any noticeable variation in values (3.3 % as results from calculations) are related with a specific behavior of systems at varioues temperatures or measurement errors. Fast kinetic in the range of temperaturs 25 - 45°C favors to use adsorption on these type of composites as a preliminary technique in wastewater treatment plant.

For each experimental system adsorption half-time t0.5, i.e. time required to adsorb half of aeq, was determined. The parameters for various terms of multiexponential equation were also obtained. All the obtained parameters were plotted as the spectra, each spectrum reflects shares of terms characterized by various rate coefficients. The broad distribution of kinetic constants with the highest term share about 0.5 to 0.6 was found, it means that the adsorption process proceeds in a few stages with different time constants. Faster kinetic processes with temperature increase correspond to the higher share of kinetic constants with higher magnitudes, as we can observe for 35 and 45°C. Differentiation in kinetic rate at various temperatures distinguish the studied systems into two groups related with the shapes of distribution of kinetic constants (at higher and lower temperature).

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