18th INTERNATIONAL
SCIENTIFIC CONFERENCE

"EcoBalt 2013"

EcoBalt 2013

Vilnius, Lithuania ● October 25 - 27

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CONFERENCE PROGRAM

Friday (25th October)
Language: English
Venue: Hall of Lithuanian Academy of Sciences, Gedimino pr. 3, Vilnius
Chairmans: prof. Aivaras Kareiva, prof. Valdemaras Razumas, prof. Arturs Viksna

TIME	PRESENTER	INSTITUTION	TITLE OF THE LECTURE
8.30 – 10.00	Registration of the participants		
10.00– 10.15	Prof. **Valdemaras Razumas**	President of Lithuanian Academy of Science, Lithuania	Welcome speech and introduction to the conference EcoBalt 2013
10.15– 10.45	Prof. **Arturs Viksna**	University of Latvia, Riga, Latvia	Historical overview of the conferences EcoBalt
10.45 – 11.30	Prof. **Ewa Bulska**	Warsaw University, Poland	**Topic**: **Analytical Chemistry** Analytical Strategy Towards Investigation of Elements Bio-transformation in Plants via Speciation Studies
11.30 – 12.00	Coffee break		
12.00 – 12.45	Dr. **Thierry Toupance**	University of Bordeaux 1, France	**Topic**: **Functional Inorganic Materials** New Approaches towards Organic-Inorganic Hybrid and Nanostructured Metal Oxide Materials for Gas Sensing, Photovoltaic and Photocatalysis Applications
12.45 – 13.30	Prof. **Maarit Karppinen**	Aalto University School of Science and Technology, Finland	**Topic**: **Green Chemistry** Oxide Energy Materials for Future Sustainable Technologies
13.30 – 15.00	Lunch break (not provided by the organizers)		

15.00 – 15.45	Dr. **David J. Payne**	Imperial College London, United Kingdom	**Topic**: **Sustainable Chemistry and Materials** High-pressure photoelectron spectroscopy: new research opportunities in clean energy materials
15.45 – 16.30	Prof. **Viktor Kanicky**	Masaryk University, Czech Republic	**Topic**: **Environmental Chemistry** Laser-Assisted Plasma Spectrometry in Elemental Mapping
16.30 – 17.15	Dr. **Birutė Railienė**	Wroblewski Library of the Lithuanian Academy of Sciences, Lithuania	**Historical lecture:** **Paul Walden** (1863-1957, 150 year aniversary)
18.00 – 22.00	Welcome Party		

Saturday (26th October)
Language: English
Venue: Faculty of Chemistry, Vilnius University, Naugarduko st. 24, Vilnius
Chairmans: prof. Aivaras Kareiva, prof. Valdemaras Razumas, prof. Arturs Viksna

TIME	PRESENTER	INSTITUTION	TITLE OF THE LECTURE
8.00 – 9.00	Hanging of the posters		
9.00 – 9.30	Dr. **Vladimir Sivakov**	Institute of Photonic Technology, Dept. "Semiconductor Nanostructures", Germany	Novel Discovery of Silicon
9.30 – 10.00	Prof. **Stefan Lis**	Department of Rare Earths, Faculty of Chemistry, Adam. Mickiewicz University, Poland	Synthesis Strategy, Spectroscopic Properties and Functionalization of Inorganic Nanoluminophors doped with Lanthanide(III) Ions
10.00 – 10.30	PhD student **Juris Burlakovs**	University of Latvia, Latvia	Physical-Chemical Properties of Clay Modified with Hydroxyapatite

10.30 – 11.10	Dr. **Thomas Luxbacher**		Nanostructure and surface characterization: New insights using SAXS and streaming potential analysis
11.10 – 11.30	Coffee break		
11.30 – 12.00	Prof. **Gunnar Svensson**	Dep. Materials and Environmental Chemistry, Stockolm University, Sweden	Searching for New Perovskite Related Materials for Use in SOFC:S
12.00 – 12.30	Prof. **Andres Öpik**	Faculty of Chemical and Materials Technology, Tallinn University of Technology, Estonia	Higher Education in Sustainable Energetics in Estonia
12.30 – 13.30	Lunch break (not provided by the organizers)		
13.30 – 15.30	Poster session		
15.30 – ...	Excursion		

Sunday (27th October)
Language: English
Venue: Faculty of Chemistry, Vilnius University, Naugarduko st. 24, Vilnius
Chairmans: prof. Aivaras Kareiva, prof. Valdemaras Razumas, prof. Arturs Viksna

TIME	EVENT
10.00 – 11.00	Discussions and concluding remarks
11.00 – ...	Excursion

LECTURES

ANALYTIC STRATEGY TOWARDS INVESTIGATION OF ELEMENTS BIO-TRANSFORMATION IN PLANTS VIA SPECIATION STUDIES

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Several plants exhibits the ability to accumulate various compounds, those considered as essential for living organism or those known as toxic. Therefore a lot of attention is focused on the investigation of the process ongoing in plants tissues and cells when they are exposed to the enhanced amounts of chemical species in environment. Several analytical scenarios were tested towards investigation of the elements bio-transformation via examination of the presence of specific compounds in plants tissues. The investigation of two example elements (i) selenium and (ii) zinc will be discussed.

In the case of selenium, the aim of the study was to identify its compounds in onions (*Allium cepa* L.) grown hydroponically and in particular understanding the processes of its biotransformation in plants exposed to selenium compounds. The Allium Test allowed to evaluate the impact of inorganic ions on the growth of onion roots and the mitotic activity in apical meristem of plant roots. High-performance liquid chromatography (HPLC), coupled to an inductively coupled plasma mass spectrometry (ICPMS), was used to identify chemical forms of selenium (selenium speciation). XANES was used for in-vivo studies of the presence of selenium species. It will be demonstrated that selenium have the ability of biotransformation of inorganic forms of selenium from soil into the antitumor, organic forms – selenoaminoacids (in particular Se-methylselenocysteine), which are most beneficial for humans, may play an important role in the prevention of cancer.

In the case of zinc the aim was to optimize the analytical procedure enables the investigation of zinc speciation in plants exposed to the industrial contamination. The experiments were performed for *Plantago lanceolata* which is well adopted to unfavorable environmental conditions of mining dump. Its important features are the ability to accumulate zinc and the developed mechanisms protecting plants from harmful environmental influence. Therefore these plants are attractive objects of research related to remediation processes. Plants were grown under hydroponics conditions than a part of floral material was digested in liquid nitrogen and used for speciation investigation. For this purpose the HPLC ICP MS was used and the experimental conditions for various chromatography separation was optimized. The analytical scenario for speciation studies was developed toward the evaluation of the bio-mechanism which enable plants to adapt for unfavorable environmental conditions.

NEW APPROACHES TOWARDS ORGANIC-INORGANIC HYBRID AND NANOSTRUCTURED METAL OXIDE MATERIALS FOR GAS SENSING, PHOTOVOLTAIC AND PHOTOCATALYSIS APPLICATIONS

T. Toupance
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Combining at the nanometer scale semi-conducting metal oxide as tin dioxide (SnO_2) or titanium dioxide (TiO_2) with organic functionalities gives rise to functional hybrid materials with promising applications in various fields such as catalysis, sensing, opto-electronics and energy conversion. The fine control of the interface between the organic and the inorganic networks constitutes a key requirement to reach good stabilities and reproducible properties. In this context, we aim at developing organic-inorganic hybrid systems based on semi-conducting metal oxides, in which strong covalent or iono-covalent linkages exist between both networks, to obtain new functional materials.
First of all, an original molecular route towards functional organotin-[1] and titanium-based[2] hybrid materials will be first described along with some promising properties in the field of gas sensing.[3] In a second part, different approaches developed in the field of dye-sensitized solar cells (DSCs) will be reported, in particular new porous SnO_2 photoanodes for efficient and stable DSCs,[4] the low-temperature processing of metal oxide photoanodes for flexible devices[5] and original organic dyes compatible with various redox mediator or hole transporter.[6] Finally, the concept of heterojunction metal oxide nanocatalysts will be introduced and exemplified in the case of the SnO_2-ZnO, TiO_2-RuO_2 and ZnO-RuO_2 systems.[7]

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OXIDE ENERGY MATERIALS FOR FUTURE SUSTAINABLE TECHNOLOGIES

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On-demand-designed oxide materials are anticipated to play important roles in a variety of next-generation sustainable energy technologies, such as superconductors, thermoelectrics, fuel cells and batteries. Here in this lecture, I will discuss our recent efforts in the field of oxide energy materials, the focus being in oxide thermoelectrics. Thermoelectric devices are capable of transforming various forms of waste heat directly into electric power and can – in principle – improve the energy efficiency of any system or application in which unwanted heat is produced. An efficient thermoelectric material should play a dual role, being concomitantly both a good electrical conductor and a poor thermal conductor, and the difficulty lies in the fact that these two requirements are difficult to be achieved at the same time. Nanostructuring provides us with a potential tool to block heat conduction without affecting electrical conductivity. An exciting new idea currently explored by us is to deposit superlattices where single layers of organic molecules (*e.g.* hydroquinone) are regularly inserted within an inorganic thermoelectric oxide matrix (*e.g.* Al-doped ZnO) employing the ALD (atomic layer deposition) thin-film technique.

HIGH-PRESSURE PHOTOELECTRON SPECTROSCOPY: NEW RESEARCH OPPORTUNITIES IN CLEAN ENERGY MATERIALS

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Photoelectron spectroscopy (PES) is perhaps the most direct probe of electronic structure available to the physical scientist, as well as an invaluable tool for elucidating bulk and surface chemical composition. It is commonplace to use PES for the characterization of samples held in high or ultra-high vacuum (HV, UHV), yet what is gained in understanding the fundamental surface physics of a material, is lost when this knowledge needs to be transferred to the material operating in real-world conditions. This so-called "pressure-gap" has been the focus of intense technological development over the last 40 years, culminating in the latest generation of HiPPES instruments. The majority of recent HiPPES research falls within three main research themes: catalysis [1], energy materials [2] and environmental chemistry [3].

A recent $1.8m award by the EPSRC (UK) to the group has enabled the design and commissioning of a laboratory-based HiPPES instrument (the most advanced worldwide) based in the Department of Materials, Imperial College London. This instrument, built by VG Scienta Ltd (UK/Sweden), consists of monochromated Al Kα and VUV photon sources, a high-pressure electron energy analyser (HiPP-2), and a unique high-pressure sample environment (gas-cell) enabling the instrument to operate in UHV and high-pressure without compromising the performance of either. The instrument will underpin the research of the group as well enabling potential collaboration with researchers worldwide.

The focus of the group's work is to understand the electronic structure of materials using advanced x-ray spectroscopy techniques including XPS, UPS, HAXPES, XES/XAS and HiPPES. The materials range from transparent conducting oxides (TCOs) [4-5] to solar energy conversion based-upon post-transition metal oxides [6]. These are grown via a number of techniques, from traditional solid-state chemistry to UHV-based physical deposition methods.

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LASER-ASSISTED PLASMA SPECTROMETRY IN ELEMENTAL MAPPING

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Laser-assisted plasma spectrometry techniques are useful for direct analysis of solids if spatially resolved information is required. Elemental imaging and local analysis may provide significant information on technological materials, biological tissues, geological materials and archaeological findings.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) represents efficient analytical tool for these purposes and is frequently combined with physical methods of surface analysis and imaging. Laser-induced breakdown spectroscopy (LIBS) represents less expensive alternative for elemental mapping but exhibits higher limits of detection in comparison with LA-ICP-MS.

LA-ICP-MS is employed in our laboratory for study of biominerals (recent urinary stones, fossil teeth and bones from archaelogical excavations), moreover, our attention is paid to soft biological tissues. Selected elemental ratios and elemental contents may yield information on diet and mobility/migration of prehistoric animals or humans. LA-ICP-MS application in biomedical research, e.g. imaging of tumor tissues *via* distribution of Cu and Zn bound to proteins, may bring information important for a better understanding of processes in living organisms, which might be helpful in medical treatment. Concerning technological samples, LA-ICP-MS is applied to quantitative elemental 2D-mapping for the description of compositional changes on nickel-based alloys for nuclear industry throughout the depth of the corrosion-affected layer formed by the action of the molten mixture of LiF and NaF at high temperature. Elemental mapping of selected samples was performed also with LIBS.

Presented topics constitute applications, investigation of fundamental processes responsible for influence on quality of analytical results, preparation of matrix matched calibration standards, and development of appropriate calibration procedures.

Acknowledgment

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HISTORY OF CHEMISTRY FROM SCIENTOMETRICAL VIEW – IN THE WORKS OF PAUL WALDEN

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Paul Walden (1863–1957), the famous chemist of Latvian background, director of Riga Polytechnic, later – a rector, member of St. Petersburg Academy of Sciences where he headed the chemical laboratory, the founder and first president of the Chemical Society of Riga Polytechnic, member of numerous international chemical societies and academies is also known for his achievements in the history of chemistry.

During the second Mendeleev's meeting of chemists in St. Petersburg (1911) P. Walden presented a paper on the history of chemistry in Russia. The survey was performed using the bibliometrical methods to analyse the published historical works and started a new discipline – scientometrics. It was first ever attempt to analyse the input of scholars of Russian empire to the development of chemistry, based on the statistics of published works. In the survey P. Walden also advocated the importance of biographical heritage of chemistry, he insisted on the importance to document the past to foster the future of chemistry.

The paper will present more detailed picture of Paul Walden's scientific biography and main ideas suggested for the history of chemistry commemorating his 150th anniversary.

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NOVEL DISCOVERY OF SILICON

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In spite of almost 15 years of intense research on the formation and studies of semiconductor nanowires, several of the expected, significant, breakthroughs have been reached due to the influence of the nanowires structure. Semiconductor nanowires have been attracting large interest as a very promising approach toward post CMOS nano-electronics, for photonic, for energy and life science, as well as for fundamental materials science and physics studies. This is because NWs offer bottom-up or top-down self-assembly of ordered one – dimensional nanostructures, creation of new combinations of hetero-junctions with sharp interfaces, including materials with large lattice mismatch, and the ability to grow semiconductor nanowires on silicon and further integration in silicon technology. The silicon based technologies are certainly favored because of material abundance and non-toxicity at a high level of materials control and understanding together with a huge industrial infrastructure to account for low production/processing costs and high production yields. This paper comprises a comprehensive review of new observation in silicon material grown by top-down or bottom-up technologies which can be useful for the future optoelectronic applications, especially in energy and biotechnology sector. Our society is strongly relying on oil for primary energy consumption. Solar energy is the field of technology and research related to the application of solar devices for energy generation by converting solar energy directly into electricity or to support hydrogen generation. Solar devices based on silicon nanowire arrays have emerged as promising candidates for solar energy harvesting. Silicon nanowires are expected to possess significantly different optical properties from their bulk-length counterparts because they are smaller than the wavelength of visible light. The enhancement of intensities of Raman scattering and photoluminescence signals with silicon nanowires in comparison with bulk-like single crystalline silicon was studied. The observed enhancement in PL and Raman can be explained by the partial light localization in the investigated samples by an increase of the lifetime of photons in silicon nanowire that can useful for the new type laser development with low generation thresholds. Excitons luminescence was observed in aqueous suspensions of SiNWs. Our experiment indicates that SiNWs could penetrate into the cells via an endocytosis mechanism that makes such structures very promising for the luminescent labeling on living cells, so-called bio-imaging. While recent advances have been impressive, cost, durability, and performance remain as key challenges to silicon nanowire based devices. We showed that silicon nanowires with different morphologies and geometries with unique optical and electrical properties can be successfully and easily produced by top-down technology. We anticipate that the concepts presented here will also be highly relevant to the development of future, more efficient single- or multi-junction devices.

SYNTHESIS STRATEGY, SPECTROSCOPIC PROPERTIES AND FUNCTIONALIZATION OF INORGANIC NANOLUMINOPHORS DOPED WITH LANTHANIDE(III) IONS

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Luminescence properties of lanthanide(III) ions, Ln(III), characterised by very narrow emission bands and a long decay time, are important tools in the study of photophysical and coordination aspects of lanthanide compounds [1]. Nanocrystalline inorganic matrices, based on fluorides, oxyfluorides, oxides, borates, vanadates and phosphates doped with luminescent Ln(III) ions, synthesized with the use of various methods, are discussed concerning their structure, morphology and photophyscial properties [2-6]. Surface functionalized core/shell nanoparticles with a luminescent core were obtained in Stöber synthesis. Crystal structures of the prepared materials are confirmed using IR, XRD, TEM, Raman spectroscopy and EDX analysis. Morphology of nanocrystals, obtained by various synthesis methods, is examined with the use of TEM images and calculations based on Scherrer equation.

Spectroscopic properties of the obtained luminophors [2,3], up-convering luminophors [5], and bifunctional nanostructures of core/shell type hybrid nanoparticles [4,6], with different concentrations of the doped Ln(III) ions, were characterized. Based on registered excitation and emission spectra, measured emission lifetimes, quantum efficiency, calculated values of Judd-Ofelt intensity parameters and chromaticity coordinates luminescent properties of the nanolumionophores were compared. Investigated inorganic matrices are effective host materials for the Ln(III) ions, resulting in the intensive luminescence even with a very low concentration of the emitter. The upconverted nanophosphors and surface functionalized core/shell type nanoparticles and can be utilized in many novel applications, e.g. as bio-imaging, intelligent bio-sensors, tracing techniques, etc. Obtained products characterized by exceptional luminescence properties and chromaticity coordinates have nanosized dimensions, chemical and physical stability and therefore, can be considered as promising inorganic phosphors.

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PHYSICAL-CHEMICAL PROPERTIES OF CLAY MODIFIED WITH HYDROXYAPATITE

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Contamination with heavy metals in soils is a major problem in former industrial, military territories as well as areas with high natural pollution level. Soil amendments often are used to improve agricultural properties, but also those can be applied for remediation of contaminated soils. Clays are crystalline-hydrated alumosilicate minerals characterized by cage-like structure with high internal and external surface areas [1]. Adsorption of pollutants by zeolites is considered as an effective method for heavy metal ions immobilization due to its cost effectiveness and high efficiency [2]. The use of clay as an efficient adsorbent to remove heavy metal cations from aqueous solution has gained great attention in recent years due to their high cation adsorption capacity and low cost [3]. Natural clays have a comparatively lower adsorption capacity than modified clays whose research is promoted broadly. Clay ion exchange capacity plays a great role in various processes, however, for Latvia the most important are those related to soil fertility and environmental pollution problems. Ion exchange capacity of clays from Latvia is an important parameter for description of sorption processes [4]. In this study clay was modified by using calcium chloride and potassium dihydrogenphosphate in different proportions of Ca/P molar ratio. Modified clays were prepared and characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, field emission scanning electron microscopy (FE-SEM), BET surface analysis, but cation exchange capacity was determined by methylene blue method. Adsorption of lead (II) on raw and modified clays was investigated by using batch kinetic experiments and compared.

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NANOSTRUCTURE AND SURFACE CHARACTERIZATION: NEW INSIGHTS USING SAXS AND STREAMING POTENTIAL ANALYSIS

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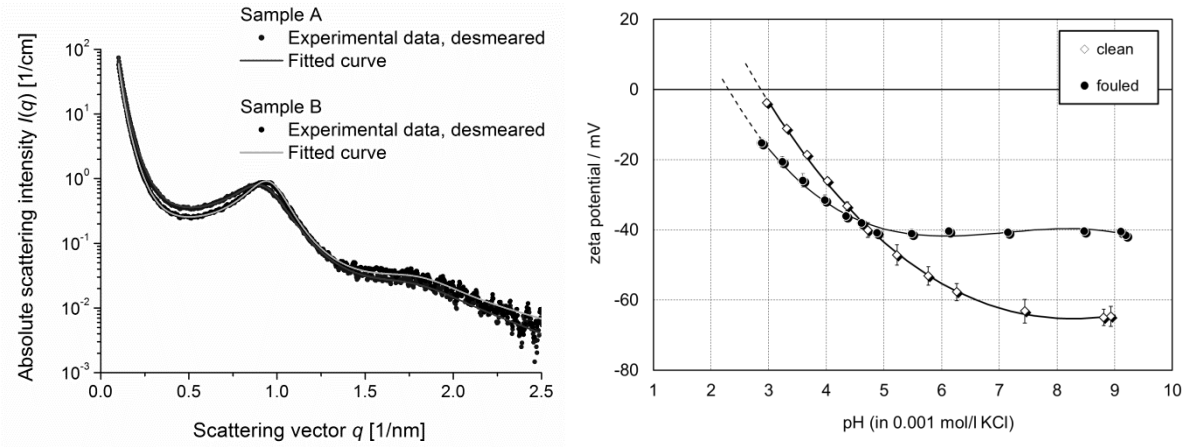
Two evolving methods for material characterization will be presented. Small angle X-ray scattering (SAXS) is commonly known for the analysis of particle size and shape in colloid systems such as particle dispersions, emulsions, but also porous materials. SAXS is sensitive for size analysis in the range of 1 to 100 nm.
The measurement of streaming potential is used to assess the zeta potential at the interface between a macroscopic solid and a surrounding aqueous solution. While the zeta potential is widely used to study the stability of colloidal dispersions, the streaming potential enables the application of the zeta potential principle to solid surfaces.

In this contribution we report the use of the SAXS method for the characterization of mesoporous material. The rather new development of GI-SAXS (grazing incidence small angle X-ray scattering) enables the structure analysis on solid surfaces and the characterization of thin-film coatings.

The solid surface zeta potential is mainly used as the indicator for surface charge and the isoelectric point, which help to estimate the interaction of solids with surrounding aqueous media. Compounds dissolved in water may adsorb on the material surface and alter the surface charge. Such changes are detected by the analysis of the zeta potential, which makes the streaming potential method suitable for the characterization of liquid-on-solid surface adsorption processes.

Results for SAXS analysis of a porous particle dispersion and for zeta potential analysis of clean and fouled polymer membranes for nanofiltration are shown below as representative examples.



Left: SAXS curve for porous particles in dispersion providing information about pore diameter (sample A: 2.65 nm, sample B: 2.64 nm), separation between pores (A: 3.71 nm, B: 3.45 nm) and pore volume fraction (A: 0.38, B: 0.43).
Right: pH dependence of zeta potential for clean and fouled thin-film composite membrane for nanofiltration showing the shift in surface charge and isoelectric point (clean: IEP 2.9, fouled: IEP 2.3) upon membrane fouling.

SEARCHING FOR NEW PEROVSKITE RELATED MATERIALS FOR USE IN SOFC:S

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Fuel cells are one alternative for efficient converting chemical energy in to electrical one. Solid oxide fuel cells have some advantages compared to other fuel cells due to their rather large flexibility in possible fuels; e.g. hydrocarbons. SOFC operate at elevated temperatures, T = 700-1000°C, which place high demands on the electrode, electrolyte and interconnector materials. They should all have good transport properties electronic and or ionic and the electrod materials good catalytic activities. The materials that fulfill these criterias should be chemcially stable at the redox and temperature conditions used and have matching thermal expansion behaviours.
There is an intensive search for new and better materials. Many new compounds are prepared although in most cases their performance are inferior to those existing. However, their study can give the fundamental understanding needed to prepare a superior material.

We will report about our search for new materials in perovskite related systems like $La_2Co_{1+x}(Mg_xTi_{1-x})O_6$, [1,2] $Sr_xY_{1-x}FeO_{3-\delta}$, [3] $Sr_2Ga_{1-x}M_{1+x}O_5$, M = Sc, [4] In and $Sr_{4-x}Y_xFe_{1.25}Ni_{0.75}O_{7-d}$. A focus will be put on synthesis, structure and transport properites.

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HIGHER EDUCATION IN SUSTAINABLE ENERGETICS IN ESTONIA

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Energy production, storage and security are key problems for mankind for the future. A new boundary condition for energy use is in the fact that energy is becoming more and more a major cost factor for all players in the energy business due to increased world-wide consumption on the one and due to needs to restrict the production of green- house gases on the other side. All it rises up a new need for people educated to deal with minimizing the energy input as well as with optimizing the conversion and production of energy developed.
The main aim of the Joint Master Curriculum of Tallinn University of Technology and of the University of Tartu is to educate engineers able to solve or minimize problems connected with the utilization, the conversion, transport and storage of energy. The curriculum provides education in alternative energy materials science and engineering with a strong technology component. The curriculum offers an integrated approach towards current and long term materials and energetics issues, focusing on technologies and concepts in sustainable development of industrial production and use of energy. The education is aimed at: n engineers leaving the academic environment to solve energy connected problems for consumers, buildings construction, energy consuming and providing industry, planning institutions, governments etc. As changes in the overall energy situation and as a result in economic developments are accelerating, education of such engineers requires curricula providing a broad spectrum of knowledge**.** In situations of high competitiveness the existence of modern technology is important, but the importance of flexibility, competence and management skills is becoming even more valuable. Additionally scientists are educated who will continue their studies in a PhD programme. Development of scientific fundamentals for efficient use of renewable energy technologies as well as negative consequences for the environment and an efficient use of capital is here the main goal.
The Curriculum is organized in accordance with the requirements of Tallinn University of Technology and of the University of Tartu as well as with the regulation proposed in the Bologna process of the European Union. The curriculum consist of a general part for all students providing the basics of sustainable development, energetics and, depending on the educational background of the students Engineering for scientists of Science for engineers courses. The students have to decide for one of the two specialities i.e. **Materials (**materials for energy saving, conversion, transport and storage; environmental protection) for those aiming at a scientific career, and **Processes** (Biomass Utilization, Buildings Engineering and Industrial Processes, environmental protection) for those planning to finish their higher education with this master degree. An important part of the education is the practical training in research laboratories or in industry. At the beginning of the first term students together with the program director will choose a project topic called “Research Project” and at the end of the fourth term the project end with the Master Thesis.

POSTER PRESENTATIONS

ANALYTICAL CHEMISTRY

COMPARISON OF SERS AND SPR IMMUNOSENSORS DESIGN AGAINST BOVINE LEUKEMIA VIRUS

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Keywords: SERS, SPR, immunosensors, oriented immobilization

Recently, the European Economic Community declared most of its member states as free of enzootic bovine leucosis. However, BLV is still widely disseminated in USA [1], Argentina [2], Japan [3] and other regions of the world. BLV is one of the most common infectious viruses of cattle and is endemic in many dairy herds; therefore, the control and eradication programs based on early detection of infected cattle and subsequent culling face a major economic task.

Current detection methods, e.g. immunoperoxidase assay [4], immunobloting etc. are still not routinely used in diagnosis, because they are not as easy to perform on the large numbers of samples as laboratories seek for commercial testing. In the future it is expected that the traditional methods give way to higher performance and much quicker methods such as immunosensors.

The efficiency of immunosensor strongly depends on the amount of immobilised antibodies, their orientation on the surface and remaining antigen binding properties [5]. The application of smaller and well-oriented antibody fragments as bioreceptor molecules influences the final immunosensor signal. The aim of this study was to develop an indirect, less time consuming and easy-to-use method for the detection of bovine leukemia virus antigen *gp*51 using SERS-based sandwich immunoassay and SPR-based immunosensing formats. The sensitivity of the developed SERS-based immunoassay was investigated and the LOD and LOQ of the proposed method for bovine leukemia virus antigen *gp*51 detection were found to be 0.95 µg mL^{-1} and 3.14 µg mL^{-1}, respectively. Recoveries of the proposed method in real samples were in the range of 85.5 – 100 % [6]. In the case of SPR detection method The developed immunosensor offered the limit of detection (LOD) as low as 0.0028 mg/mL, while the limit of quantification was as low as 0.0092 mg/mL with very good repeatability during the three detection–regeneration cycles (1-4 %) [7]. These methods were successfully applied for the detection of *gp*51 in milk samples in a rapid, reliable and selective manner.

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COMPARISON OF METHODS FOR DETERMINATION OF MERCURY IN WASTEWATER AND SLUDGE FROM WASTEWATER TREATMENT PLANT BTP "DAUGAVGRIVA"

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The biological wastewater treatment in Riga city takes place in biologic wastewater treatment plant (BTP) "Daugavgriva". The plant started its work in 1991 and it was projected to purify 350 000 m^3 of wastewater per day.

Wastewater biological treatment is carried out through the worldwide used technologies (anaerobic - anoxic - aerobic treatment). Wastewater flows into the anaerobic zone of aeration tank, where it is mixed and held with activated sludge for a certain time. Then wastewater is transferred to the anoxic zone, where it is also held for a certain time. After that, water is transferred to aerobic zone, which is intensively fed with oxygen and mixed with activated sludge.

Every year in Latvia have been produced approximately 23 000 t of wastewater sludge. BTP "Daugavgriva" produces about 6 000 t of sludge every year. About 8 000 t of wastewater sludge is used for land fertilization and therefore it is important that concentrations of heavy metals and other pollutants in sludge should be as low as possible.

Due to its high toxicity mercury is one of the heavy metals which concentration must be determined in sludge. In addition, both inorganic as well as organic forms of mercury are poisonous. Poisoning can result from mercury vapor inhalation, mercury ingestion and through the absorption through the skin. Industrial wastewater may contain significant amounts of mercury. By discharging wastewaters into the rivers, lakes or other watercourse, the mercury by aquatic organisms and vegetation can be converted to its most poisonous form – methyl mercury.

Most common method for determination of mercury is cold vapor method. The method is based on the reduction of mercury ions to atomic mercury as reducing agent using sodium borohydride or tin (II) chloride. Formed atomic vapor of mercury is then guided to the measuring cell of AAS.

Due to high volatility of mercury sample preparation for mercury analyses must be done in closed system and very often it is needed to use some kind of mercury vapor absorber.

Evaluation and comparison of conventional wet digestion and microwave assisted digestion for sample preparation for mercury determination and also cold vapor generation as reducing agent using sodium borohydride and tin (II) chloride methods for the determination of mercury in crude, treated wastewater and also sludge has been made.

GOLD NANOPARTICLE MULTILAYERS FORMATION BY LAYER-BY-LAYER DEPOSITION TECHNIQUE

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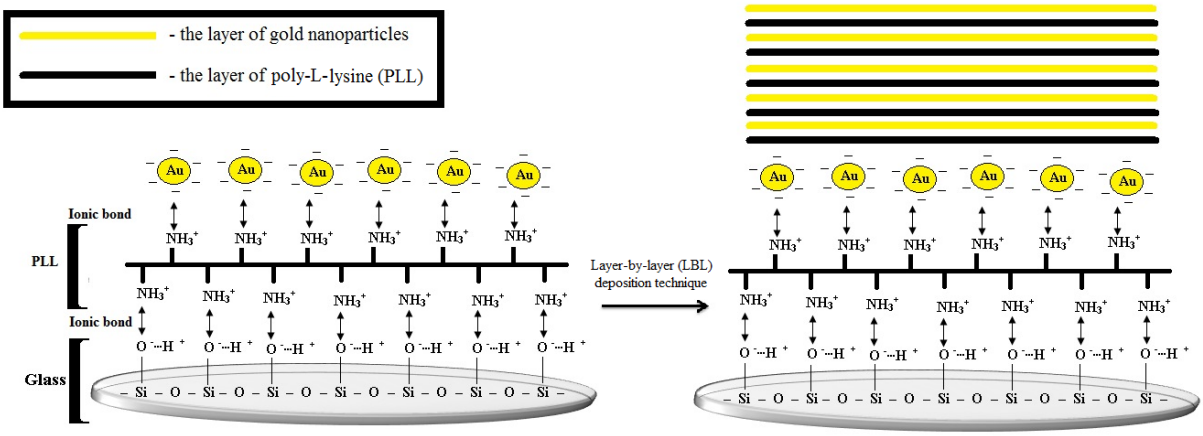
In this study, multilayer films composed of gold nanoparticles and polymer poly-L-lysine (PLL) through a layer-by-layer (LBL) deposition technique were described. For this purpose gold nanoparticles of 13 nm were synthesised. Au-NPs layers were prepared on glass chip using poly-L-lysine, which was used to attach gold nanoparticles on glass surface. The chemical growth of Au-NPs layers was performed. The deposition process and the formed multilayer nanoparticle films were characterized by means of absorption measurements by UV-VIS-spectrometer (Lambda 25 UV/VIS spectrometer, from PerkinElmer Inc., USA), measurements were made in spectral range between 300 nm to 900 nm. Atomic Force Microscope Catalyst from Veeco Instruments Inc., (Santa Barbara, USA) was used to evaluate size, shape, and height of prepared samples. Contact mode was chosen for all measurements. RTESP (Phosphorus doped Si) and NP (non-conductive Silicon Nitride) tips were used. The M-2000X type from J.A. Woollam Co., Inc., (Linkoln, NE, USA) spectroscopic ellipsometer was used for the determination of ellipsmometric parameters ψ (Psi) and Δ (Delta) and layer thickness parameter. Measurements were performed at spectral range from 210 nm to 1000 nm.

Spectrophotometric evaluation of Au-NPs-based layered structures showed that Au-NPs-related peak of absorption band depends on the number of deposited Au-NPs layers. Therefore it could be concluded that Au-NPs aggregation processes changes optical and morphological nanoparticle geometry therefore surface plasmon absorption occurs as an integrated transverse and longitudinal dipole polarization.



UV TITRATION OF Hg(II) IN FENTON REAGENT SOLUTION

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There are number of methods for treating of waste containing mercury: thermal/chemical, solidification/stabilization technologies. An oxidation-based decontamination of Hg involves the transformation of toxic species (Hg° or Hg_2^{2+}) into less harmful (Hg^{2+}) and becomes an important method [1]. Research of the past decade have focused on Hg oxidation using Fenton's reagent which refers to the strongly promoted oxidation reaction in acidic media using hydrogen peroxide (H_2O_2) by the presence of the ferrous ion (Fe^{2+}) [2]. To date a variety of methods have been developed for the quantitative Hg analysis. Nevertheless the demand of analytical method for simple, accurate and particularly suitable for the direct analysis of mercury ions in the homogenic systems under the low pH values is still relevant. In this abstract, we describe application of UV titration method for Hg^{2+} determination in Fenton's reagent solution as more accurate and sensitive than simple titrimetry (end-point detection by naked-eye or photocolorimetrically). Simple complexometric titration of mercury(II) solution is based on the use of Fe^{3+} ions as indicator (red $Fe(NCS)^{2+}$ complex ion appears). The titration in Fenton system could be applicable only after H_2O_2 decomposition.

We performed UV/VIS titration of standard Hg^{2+}(constant conc. at 10^{-4} M level) : Fe^{3+}(constant conc. at 10^{-5} M level) : SCN^-(varied conc. at 10^{-4} M level) solutions, acidified with H_2SO_4. The response at 450 nm identified by other researchers [3], is assigned to $Fe(NCS)^{2+}$ complex. This response in our experiments is at the noise level and cannot be analyzed. However we found clear and intense peak in the range of 216–219 nm which intensity increases with added amount of SCN^- ion. The intensity of this response is more than 300 times higher compared with response at 450 nm. Six calibration curves were obtained at six different wavelengths in the range of 215–225 nm. The highest regression coefficient is at 215 nm (figure) and is the most appropriate. The photocolorimetrically obtained calibration curves at 450 nm was noninterpretable at investigated relatively low concentrations.

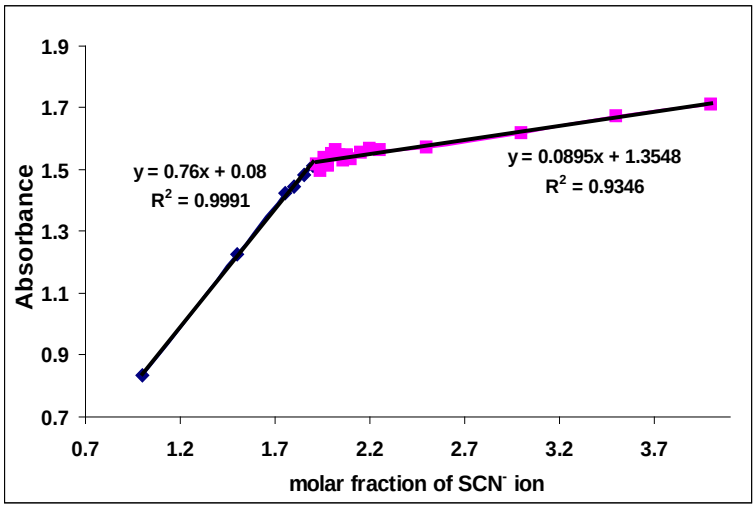

Figure. Absorbance dependence on the molar ratio of SCN^- in Hg^{2+} : SCN^- : Fe^{3+} solutions at 215 nm

These results justified the use of response at ~215–220 nm for further method application.

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APPLICATION OF ION EXCHANGE RESIN IN THE CHARACTERIZATION OF FAST PYROLYSIS LIQUIDS

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INTRODUCTION

Since cellulose and hemicellulose along with lignin are the main components of plant matter, fast pyrolysis of wood yields a complex mixture of products, among which sugars and anhydrosugars are one of the most abundant and valuable components. Because of the presence of high molecular compounds, this sugar mixture of pyrolysis products has proven to be difficult to analyse. In this study, research has been done to improve the characterization of pyrolysis liquids by sample separation on an ion exchange resin [1].

EXPERIMENTAL METHODS

The experiments were performed at room temperature. The chromatographic system consisted of a glass column, filled with FINEX WAC resin in Na+ form. H_2O/EtOH (4:1) was used as the mobile phase. Sugars and anhydrosugars were determined iodometrically [2].

RESULTS AND DISCUSSION

Separation of a standart sample (levoglucosan + glucose + cellobiose), has shown that levoglucosan or 1,6-β-D-glucopyranose is more strongly retained on a weak acid cation exchange resin column than glucose. Due to size exclusion mechanisms, cellobiose is eluted very fast. Figure 1 shows a chromatogram of a real fast pyrolysis liquid sample.

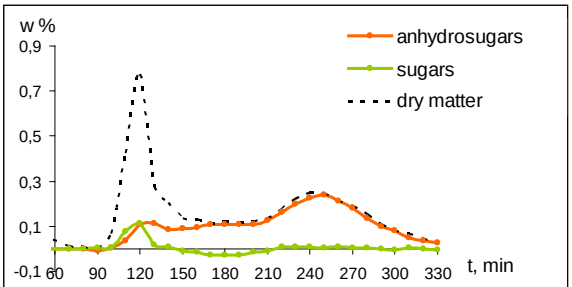

Fig. 1. A chromatogram of a pyrolysis liquid sample

The chromatogram shows that there are mostly disaccharides present in the sample (90-130 min), the correlation between sugars and anhydrosugars corresponds to that, which was determined iodometrically before the sample was separated on the column. Levoglucosan builds up the major part of anhydrosugars (210-300 min), but there are other anhydrosugars present – probably cellobiosan at 100-140 min. Negative sugar values indicate that dianhydroglucose is eluted at 140-210 min.

CONCLUSION

Fast pyrolysis product sample separation on a WAC exchange column benefits the characterization of sugar, anhydrosugar and their oligomer content in the sample.

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COMPARISON OF ELECTROLUMINESCENCE SIGNAL OF RUTHENIUM CHELATE, LUMINOL AND N-(4-AMINOBUTHYL)-N-ETHYL-ISOLUMINOL

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Ruthenium chelate tris(2,2'-bipirydine)dichlorruthenium(II)hexahydrate has received much attention for its cation optical and electrochemical properties. This perspective compound has been suggested for use in bio-diagnostics and production of OLED and dye-sensitized solar cells [1]. Another group of organic compounds that have electroluminescence (EL) properties are luminol and its derivatives. They have been used in affinity assays for determining protein concentrations [2]. In this work the electroluminescence properties of three compounds: Ruthenium complex, luminol and ABEI (N-(4-aminobuthyl)-N-ethyl-isoluminol) were investigated.

The experiments were performed using homemade system, containing spectrophotometer and potentiostat – galvanostat. The EL signal was collected in liquid form the bottom of the glass via optical fiber. First the emission spectra for each compound were analyzed to determine the optimal EL wavelength for the further investigations. The surface EL reaction was determined using spinning gold electrode as a working electrode. The critical concentration of the investigated compounds for EL was determined using cyclic voltamperometry. Electrochemical parameters were optimized for the experiment: this included the selection of the reaction potential (the experiments were performed using chrono charge – discharge function in the range of 1V – 1,7V); the optimization of the solution's pH value (the borate buffer was adjusted in the range of pH 7 – 12). All results were analyzed and compared.

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SIMULTANEOUS DETERMINATION OF BENZODIAZEPINES IN BIOLOGICAL MATRICES USING MIXED-MODE CATION-EXCHANGE POLYMERIC SORBENT AND FAST GAS CHROMATOGRAPHY-NEGATIVE-ION CHEMICAL IONIZATION MASS SPECTROMETRY

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Benzodiazepines belong to a group of substances known for their sedative and hypnotic properties [1]. Researchers are making great efforts to develop rapid, accurate, precise and sensitive methods for the determination of benzodiazepines and their metabolites in real samples [1,2].

Gas chromatography combined with negative-ion chemical ionization mass spectrometry (GC/NICI-MS) improves the sensitivity and specificity of simultaneous determination of 15 benzodiazepines in whole blood, significantly exceeding these parameters achieved by traditional electron impact ionization mass spectrometric detection [3,4]. A mixed-mode cation-exchange polymeric sorbent (Oasis MCX) was used for solid phase extraction of biological samples. The use of extraction solvents for the elution of the adsorbed analytes, washing steps for eliminating interferences in the column, and, finally, sample pretreatment at different pH values were optimized. To the best of our knowledge, this method has been used for the first time for the optimization of sample preparation at pH 1.0. A derivatization step using different silylation reagents, duration, and temperature was investigated. This method is the fastest among the others reported up to now. Under the optimized GC conditions derivatives of analytes were completely separated within 3.9 min, as shown in Figure 1. Sensitive and specific NICI-MS detection combined with fast GC resulted in sharp and symmetric peak shape of the target analyte, while maintaining sufficient resolution.

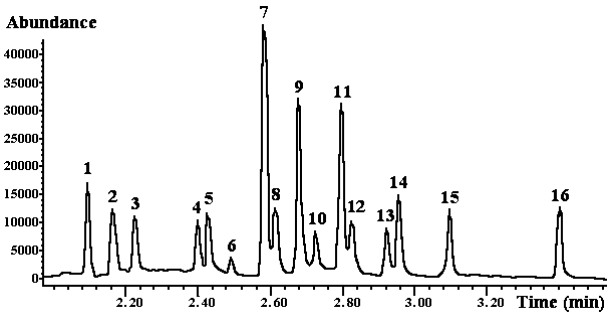

Figure 1. Chromatogram of whole blood sample at pH 1.0 spiked with 20 ng mL^{-1} of benzodiazepines. The peak numbering refers to: (1) internal standard; (2) diazepam; (3) nordiazepam; (4) midazolam; (5) flunitrazepam; (6) bromazepam; (7) oxazepam; (8) nitrazepam; (9) temazepam; (10) 7-aminoclonazepam; (11) lorazepam; (12) clonazepam; (13) alprazolam; (14) α-OH-midazolam; (15) triazolam; (16) α-OH-alprazolam.

The developed method provides significant advantages in comparison with other previously published methods [2-5]. Obtained results show, that the developed GC/NICI-MS method is effective, accurate, precise, sensitive and selective. The fully validated method has been applied for the quantification of several benzodiazepines in real blood samples.

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COMPARISON OF DIFFERENT ANTIBODY IMMOBILIZATION TECHNIQUES ON THE EFFICIENCY OF THE IMMUNOSENSOR FOR HUMAN GROWTH HORMONE DETECTION

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Immunosensor is an analytical sensor consisting of immune system molecules employed as specific capture ligands and a coupled signal transducer converting the physicochemical changes of the ligands upon the affinity interactions with an analyte to a signal proportional to analyte concentration. Characteristics of an immunosensor are primarily influenced by the quantity, remaining activity and orientation of the capture ligands after the immobilization procedure [1-2].

In this study the impact of three different antibody immobilization techniques on the efficiency of the surface plasmon resonance (SPR) based immunosensor for human growth hormone (hGH) detection have been compared. In a random immobilization approach, antibodies against human growth hormone (anti-hGH) were covalently immobilized on the self-assembled monolayer of 11-mercaptoundecanoic acid (11-MUR SAM) modified SPR sensor surface. In contrast, a site-directed approach was based on oriented immobilization via affinity interactions between anti-hGH and a protein G monolayer previously formed on 11-MUR SAM modified SPR sensor surface. Since protein G specifically binds the Fc region of anti-hGH, the interaction between these molecules results in a recognition layer of directed anti-hGH alignment. The main disadvantage of this antibody immobilization technique is the reversibility of affinity interactions between both protein G/anti-hGH and anti-hGH/hGH. Firstly, as the protein G/anti-hGH system is based on weak interactions, it exhibits antibody leakage thus preventing the exact evaluation of the sensing surface and its analytical characteristics. Futhermore, in order to develop a multiple use immunosensor, anti-hGH/hGH complex must be dissociated by the use of regeneration solutions, which, in turn, also affect the interactions between protein G/anti-hGH disassembling the anti-hGH layer. In order to avoid these problems a bifunctional covalent cross-linking agent dimethylpimelimidate hydrochloride (DMP) was used for attachment of anti-hGH to protein G layer.

The three aforementioned systems were exposed to hGH samples of the same concentration. The most significant SPR response was registered after the oriented anti-hGH immobilization via affinity interactions between the anti-hGH and protein G. However, this system proved to be very unstable as rapid and continuous dissociation of anti-hGH from the sensing surface was observed. After the DMP cross-linking, the SPR response to hGH decreased slightly, however, still outweighing the response of anti-hGH after the random immobilization. The decrease of the SPR response was most likely influenced by the attachment of DMP to some antigen binding sites of anti-hGH. Nevertheless, cross-linking enabled the development of a multiple use immunosensor exhibiting good sensitivity and reproducibility.

Acknowledgements
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SYNTHESIS OF GOLD – POLYPYRROLE NANOCOMPOSITES

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Nanocomposites of conducting polymers and metal nanoparticles have received a considerable attention due to their potential possibilities to create suitable materials for electrocatalysis, chemical sensors, and microelectronic devices [1-3]. In comparison with nanocomposites constructed by insulating polymers, conducting polymers can serve as a novel electroactive relay among these metal nanoparticles (NPs) in the nanocomposites matrix [5, 6]. Therefore, the fabrication of novel nanocomposites based on metal NPs and conducting polymers would provide various interesting characteristics and new features in nano-technological applications.

The seed-mediated approach has become increasingly popular recently in the production of ordered morphologies of gold nanoparticles (AuNPs) in aqueous solutions [6]. In a seed-growth method, small metal NPs are prepared first and later used as seeds (nucleation centers) for a systematic growth of large sized NPs. The size distribution (typically 10–15%) in the range of 5 – 40 nm was successfully controlled by manipulating the ratio of seed to metal salt [7]. Size and shape of NPs are generally controlled by external influence factors such as reaction temperature, time and precursor or surfactant concentration.

In this work, we report the single-step synthesis of gold – polypyrrole (Au-PPy) core–shell particles by using tetrachlorauric acid ($HAuCl_4$) as an oxidant at room temperature for the first time. Firstly the AuNP seeds were grown followed by the seed-mediated growth of gold nanoparticles. Then the polymer layer was polymerized giving the core-shell nanoparticles.

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SYNTHESIS AND APPLICATION OF GRAPHENE OXIDE FOR RADIONUCLIDES REMOVAL FROM CONTAMINATED SOLUTIONS

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Numerous studies have been performed in order to identify new materials that can reduce the costs associated with waste disposal and minimize the contamination risk of the environment during processing and disposal of the radioactive waste. This issue is an especially hot topic nowadays in Lithuania due to the decommissioning of the Ignalina Nuclear Power Plant.
The application of synthetic materials for the removal of harmful radionuclides from the bulk waste solution can be one of the possible solutions, since they are distinguished for high efficiency, ionizing radiation resistance, their thermal stability and compatibility with the final waste forms. Recent studies have shown the high efficiency of graphene oxide (GO) for rapid removal of some of the most toxic long-lived radionuclides from contaminated solutions [1]. It was reported that GO is more effective in removal of transuranium elements from simulated nuclear waste solutions than other routinely used sorbents such as bentonite clays and activated carbon.
During the last ten years, many studies related to the chemical modification of GO and its synthesis were carried out. The variety of modified structures was used as polymer composites and received wide application in nano-technology and biomedical practice [2]. It has been found that GO has excellent electrical, mechanical, thermal properties and its synthesis or modification is quite simple.
The main purpose of this study was synthesis of GO using improved methods and its application for removal radionuclides from contaminated solutions.
GO was synthesised using methods described in literature [3]. The obtained GO was identified using FTIR, V/UV spectroscopy and applied for sorption of ^{137}Cs, ^{241}Am, ^{239,240}Pu as well as Ni and Co. During the sorption process the cation/GO coagulation and the formation of nano-particle aggregates of GO sheets were observed.

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Pu OXIDATION STATE TRANSFORMATION BY NATURAL CLAY AND THEIR VARIOUS COMPONENTS

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Natural clay minerals are often used as engineered barriers for retardation migration of radionuclides from a repository of radioactive waste. The complex composition of natural minerals can be considered as their advantage since radionuclides with a wide range of chemical properties can find appropriate sorption sites on their surfaces. However, sorption processes are rather complicated in these heterogeneous systems for this reason migration of radionuclides can be affected by different factors, e.g. type of mineral, pH and redox potential. Recent studies have shown that data on association of plutonium with geological materials are rather contradictory. On the other hand, various microorganisms common in nature may also result in changes of the Pu oxidation state. The importance of biotic processes affecting the redox speciation of radionuclides has been discussed in recent publications. It has been shown that there are at least three types of processes that can influence mobility of Pu: biotransformation, biosorption/bioaccumulation and degradation or synthesis of organic ligands that change the solubility of radionuclides.

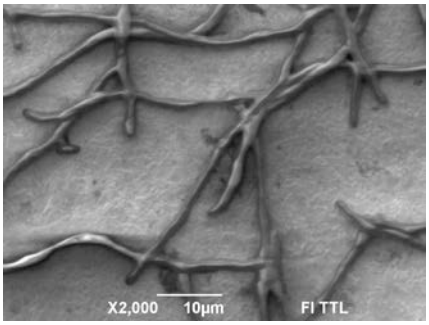

Fig 1. SEM image of Penicillium chrysogenum 21RM used in sorption experiments.

The main purpose of this study was to estimate the Pu oxidation state distribution affected by Šaltiškiai clay as well as iron oxides and microorganisms naturally present in the clay. The fungi (*Trichoderma* sp. M-1, *Penicillium sp.*14 M and *Penicillium chrysogenum* 21RM) and gram-negative bacterium isolated from groundwater and the Triassic clay selected as an engineered barrier for a cement (concrete) based near-surface low and intermediate level radioactive waste repository was used in sorption experiments under aerobic conditions.

Clay samples with different amounts and compositions of iron oxides in their coatings as well as synthetic magnetite, goethite and hematite were used in sorption experiments. The composition of clay mineral coatings and their leaching during the SE procedures were investigated by means of the Mössbauer spectroscopy and X-ray diffraction.

Pu (IV), (V) or (VI) was added to achieve their initial concentration of $3\cdot10^{-10}$ mol·L^{-1} in 0.154 mol/L NaCl. Solids and biomass were separated by centrifugation at 6000xg after desired time. Pu activity concentrations were measured by alpha spectrometry. The oxidation state distribution analysis was performed using thenoyltrifluoroacetone (TTA), bis(2-ethylhexyl) hydrogen phosphate (HEDHP) and 1,3-diphenyl-1,3-propanedione (DBM) solvent extraction and Pu(III, IV), Pu(V), Pu(VI), Pu(IV) and Pu(IV polymeric) were separated.

The maximum of Pu biosorption to bacterium and fungi was observed at pH ~7 and 4, respectively. In the liquid phase (LP) plutonium oxidation state distribution was found to be as follows: Pu(IV) - 36%, Pu(IV-polymeric) - 58%, Pu(V) - 2% and Pu(VI) - 4%. The reduction of Pu(IV) and Pu(V) by natural clay containing iron-bearing minerals was found.

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DISPERSIVE LIQUID-LIQUID MICROEXTRACTION OF METHYLTIN COMPOUNDS

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Methyltin compounds are mostly used as stabilizing additives in polyvinyl chloride plastics [1], may originate from the biomethylation of inorganic precursors [2]. Methylated tin is much more toxic than inorganic tin, so methylation of inorganic tin in the environment can seriously affect both human and environmental health. Moreover, toxicity of methyltin compounds is strongly dependent on the species. Thus, the development of accurate and sensitive analytical methods for determination of methyltin species is of special importance.
For speciation analysis, gas chromatography is the preferred technique. As mono-, di- and trimethyltin compounds present in the environment are in the ionized form, they need to be derivatized before gas chromatographic analysis to obtain their volatile and thermostabile forms. In the literature, several derivatization strategies for organotin compounds are described. The most commonly used derivatization reactions are formation of hydrides using sodium borohydride, formation of ethyl derivatives using sodium tetraethylborate ($NaBEt_4$) and formation of methyl or phenyl derivatives using Grignard reagents [3].
Since environmental concentrations of methyltins are low, prior to the gas chromatographic determination a preconcentration step is required. In recent years, preconcentration techniques using miniaturized versions of liquid phase extraction are gaining a growing interest. One of them, dispersive liquid-liquid microextraction, has been applied for butyltin and phenyltin compounds extraction from water samples [4, 5].
In this work, dispersive liquid-liquid microextraction technique for methyltin compounds was elaborated. Prior to the extraction, a derivatization step using ethylation with $NaBEt_4$ was applied. The derivatization conditions were optimized. After the extraction, methyltin compounds were determined using capillary gas chromatography with mass spectrometric detection. The precision, linearity, detection limits of the suggested methyltin extraction and determination method were determined.

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SCANNING ELECTROCHEMICAL MICROSCOPY ANALYSIS IN FEEDBACK MODE OF IMMOBILIZED GLUCOSE OXIDASE

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Scanning Electrochemical Microscopy (SECM) is the promising tool for investigate chemical reactivity, electric conductivity, and enzymatic activity [1] of various surfaces, like as glass, metal, polymer, biological material [2] and liquids. For SECM measurements, typical three-electrode electrochemical cell is used with platinum ultramicroelectrode (UME), 10 µm diameter as working electrode, which is moved in x and y directions in the vicinity of the enzyme substrate. Two main modes of operation – generation-collection (GC) and feedback mode can be applied for the investigation of enzyme surface, but the better resolution can be achieved in feedback mode. The activity of enzyme glucose oxidase immobilized by glutaraldehyde has been imaged in earlier studies [3], where the feedback mode for such measurements was applied with low concentrations of glucose and mediator in buffer. In this research, the approach curves were registered from 0 to 250 $mmol \cdot L^{-1}$ glucose concentrations in buffer and $[Fe_3(CN)_6]^{3-}$ /$[Fe_3(CN)_6]^{4-}$ red-ox couple was applied as mediator in order to find the best possible image resolution. For the determination of UME distance from enzyme surface, feedback mode is used, and for imaging GC mode was used. The very low quantity of glucose oxidase 1mg/mL 0.5 µL drop was immobilized on the plastic surface in order to get advanced measurements range of current signal. We concluded that the sensitivity of measurement is highest if using 90 $mmol \cdot L^{-1}$ of glucose and 48 $mmol \cdot L^{-1}$ of $[Fe_3(CN)_6]^{4-}$ with current ranging from 90 nA to 1.3 µA.

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ENVIRONMENTAL CHEMISTRY

FREE RADICALS OF AIRBORNE PARTICULATE MATTER

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Burning of various combustibles, such as candles, diesel or kerosene, produce much fine solid airborne particulate matter. Particles with different sizes have different penetration efficiencies into a human respiration system. The fine particles have more harmful impact to the human health than coarse particles. Particulate matter of combustible burning contains active products of termodestruction process – free radicals ($\dot{C}H$; $\dot{C}H_2$; $\dot{C}H_3$; $\dot{C}HO$; $\dot{C}_2$; $\dot{C}H\dot{C}H$ and other [1]), which increase health risk. Airborne particulate matter from atmosphere of city contains free radicals, too [2]. Radicals of particles may react between together, as the result particles may stick together by radical mechanism and grow up in size.

In this research solid particles from burning of various combustibles were collected on the filters in a burning chamber and collected from atmosphere of city of Riga by dichotomous impactor. Free radicals of particulate matter were detected by electron paramagnetic resonance (EPR). Samples were placed in flat dismountable cell WG 806-B-Q. EPR spectra were recorded using an EMX-plus EPR spectrometer (Bruker, Germany). Reference marker ER 4119HS-2100 (g-factor 1.9800, radical concentration $1.15 \cdot 10^{-3}$ %) was used for quantitative EPR.

EPR spectrum of particulate matter is shown in the Figure 1. At g-factor 1.9800 was the signal of EPR reference marker. There no signal at organic region in the spectrum of blank cell. When blank filter was placed in the cell, there was signal of organic free radicals at g-factor 2.003. Intensity of signal of organic radicals was not changed after filter exposure in the burning chamber with combustible burning. The signal of organic radicals at g-factor 2.003 had more intensity in the spectrum of filter with particulate matter then signal of blank filter. That is analysed particulate matter contains more organic free radicals, and its concentration is about $1 \cdot 10^{-4}$ %.

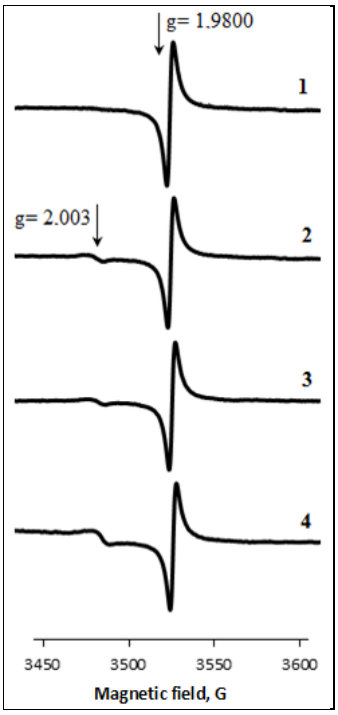

Fig.1. EPR spectra of reference marker (1), blank filter before (2) and after (3) exposure in the burning chamber, and after sampling of particulate matter (4)

When sample of particulate matter was carbonized in a nitrogen flow at 450 ^{o}C, obtained concentration of radicals was more higher than concentration of sample before treatment and it was higher than concentration of sample heated in an oxygen flow. Inert environment (deficiency of oxygen) with high temperature contributes formation of free radicals in large quantities.

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PHYSICAL PARAMETERS OF AGGREGATES USED AS A DRAINAGE IN GREEN ROOF CONSTRUCTION

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During the progressive development of the cities we are losing natural areas available for infiltration. Thus why, green roof over the garage, terrace or roof of the building become more and more interesting solution [3]. One of the key elements of green roof construction is a drainage layer. In addition to the water drainage capacity, this layer should also have a possibility to be a reservoir of the moisture necessary for plant growth [1]. An additional feature of this layer is to create space for the penetration of roots. The thickness of the drainage layer ranges on average from 5 to 10 cm. The aim of this study was to determine the physical properties of aggregates: LECA (lightweight expanded clay aggregate), chalcedony and washed gravel, typically used as a drainage layer in green roofs.
Determination of physical properties of aggregates was carried out in accordance with the following standards: grain composition PN EN 933-1:2012, absorption PN EN 1097-6:2002, bulk density PN EN 1097-3:2002.
Bulk density of LECA and chalcedony amounted 1.1 kg m^{-3} and were lower than bulk density of washed gravel (1.5 kg m^{-3}). Particle size of tested materials were: 16-32 mm for washed gravel, 8-16 mm for LECA and 8-16 mm for chalcedony. The homogeneity of grains were high, with uniformity coefficient amounted U = 2.4 for LECA and U = 2.0 for chalcedony. The resulting values determine the aggregate as uniform [2].
The best water absorption (15%) was observed for LECA, followed by chalcedony (14%) and the lowest in case of washed gravel (1%). However, it should be noted that maximum water retention can be reached only once at the beginning of operation, because only in the initial phase aggregates are gradually giving maximum water absorption. Relative humidity of dry matter in relation to the optimal moisture content of aggregates was 2.6% for LECA, 1.9% for chalcedony and 0.3% for washed gravel. All of the tested aggregates are resistant to frost (water absorption higher than 1%).
Performed studies shown, that the best values of physical parameters characterizing LECA. The material is light, frost-proof and has the highest water absorption and as a additional benefit it is resistant to mold and mildew.

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COLONIZATION OF CERAMIC SUPPORTS BY ARTIFICIAL BACTERIAL ASSOCIATIONS

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Bacterial adhesion is a common ecological feature. Surface adhesion and colonization is a survival strategy employed by virtually all bacteria and refined over millions of years [1]. The study and application of adhesion have taken great importance for biotechnology as one of the methods of cell immobilization. Investigations show that porous ceramic carriers can be used in wastewater treatment [2], in environmental bioremediation [3, 4], in biogas and bio-hydrogen production bioreactors [5] and other biotechnological applications.

The objective of this work was to evaluate suitability of Devonian clay granules as a support for immobilization of multi-species artificial bacterial associations.

Ceramic granules from Latvian Devonian clay deposit were sintered at 1100 °C and characterized in the Institute of Silicate Materials, Riga Technical University. The diameter of granules was 1.2 cm and the bulk density was 1.33 g cm^{-3}. Bacterial adhesion on ceramic granules was studied under anaerobic and aerobic conditions.

Anaerobic experiments were performed in serum bottles with a volume of 30 ml. Suspension of fresh bacteria was prepared and added to the bottles containing sterilized granules and nutrient medium up to the concentration of 10^8 CFU/ml. Argon gas bubbling through the media was used to sustain anaerobic environment. Incubation was carried out at 37 °C. After two weeks, the incubation liquid and rinsed granules were subjected to microbiological analyses. The results were expressed as CFU per millilitre of suspension or per gram of dry ceramic granules for bacteria recovered from granules.

Aerobic nitrifying association containing *Nitrosomonas* sp. and *Nitrobacter* sp., was tested in the column experiment. Activity of free and adhered bacteria was compared by enzyme activity and plating method.

The results showed that ceramic materials could serve as supports for bacteria. However, the difference was found between composition of species on the ceramic and in the suspension. Ceramic supports favour certain species and thereby select and modify the composition of microbial populations. We assume that this applies to both natural and artificial microbial associations.

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TREATMENT OF PHOSPHOROUS- AND NITROGEN-CONTAINING SYNTHETIC WASTEWATERS IN THE CASCADE OF CERAMICS-PACKED COLUMNS

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Eutrophication of water is a global environmental problem due to disposal of nutrients (N and P) directly from wastewater plants or indirectly from agriculture runoff and leaching from sludge deposited in landfill and fields [1]. Removal of phosphorous and nitrogen from wastewaters depends on pH, COD, magnesium, calcium, and potassium, incubation time, temperature, excessive aeration, etc. [1].

The aim of this study was to evaluate an efficiency of microorganisms attached on the ceramic beads, for removing of nitrogen and phosphorous from wastewater. Ceramic beads were prepared from Devonian clay by plastic shaping and fired in the laboratory furnance. Our previous study showed an appropriateness of this clay as a raw material for carrier for biofilm formation [2]. Dried pellets were put in the furnace at temperature 1100°C with holding time 20 min. Afterwards pellets were taken out of the furnace and air-cooled. Porosity of ceramics pellets 19.8 %, surface area 5.23 m^2/g, which was determined by mercury porosimetry.

The laboratory-scale model system with seven columns was established for synthetic wastewater treatment. All columns were packed with identical ceramic beads. The columns differed by microbial consortium inoculated, as well as aeration conditions. In particular, each column was designated for the separate process, i.e., nitrification, denitrification and phosphorous accumulation. First, the synthetic wastewater, which contained both, nitrogen and phosphorous compounds, was applied to each column with retention time 3 days and longer. The second stage of the experiment was aimed at treating the synthetic wastewater in the cascade of columns, i.e., wastewater was added to “the nitrification column” under aerobic conditions with nitrifying bacteria consortium, followed by “denitrifying and P-accumulating column” under microaerophilic conditions with *Pseudomonas fluorescens* PS AM11, etc.

The process was studied during the experiment via testing of inlet and outlet wastewater. After the experiment, ceramic beads were evaluated for their integrity and other physico-chemical properties, as well as activity of microorganisms attached onto the surface. Additionally ceramic beads were tested in vegetation experiment in the context of alternative fertilization tools.

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EVALUATION OF THE CHANGES MADE BY GASIFICATION-BIOCHAR IN PEAT SOIL

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Gasification-biochar (Bc-G) system represents one of the sources of biochars applied for agricultural uses. The coupling of energy production from gasification technology and the application of the resulting biochar as soil amendment could serve as a new solution in the competing demand for food and bioenergy [1]. Biochar used in this study was obtained from hard wood by gasification and characterized in terms of component and elemental composition. Our previous results demonstrated a stimulating effect of this Bc-G to pea *Pisum sativum* in loamy sand soil and cucumber *Cucumis sativus* in peat soil at comparatively low application rate [2].

The aim of this experiment was to study the physico-chemical and biological changes occurred in peat soil with addition of Bc-G in concentrations of 2; 4; 6; and 10 g/L. The presence of Bc-G in concentration of 2 and 4 g/L stimulated the growth of *Cucumis sativus* during 12 days experiment. In particular, dry weight of roots and aboveground part was higher in the set with 2 g Bc-G/L up to 30% and 16%, respectively, as compared to unamended soil. The similar effect was shown also for the set with 4 g Bc-G/L. Some inhibition of plant growth was detected in the presence of 6 g Bc-G/L comparing with unamended soil.

To reveal the mechanisms of the processes initiated by Bc-G addition in peat soil, the model experiments were performed with emphasis on liming effect, leaching, microbial respiration, etc. All these changes are supposed to occur in soil in Bc-G concentration-dependent manner. At the same time, the shift in physico-chemical and biological properties of soil due to biochar amendment is dependent on soil type. The results obtained for peat soil were compared with those for loamy sand soil.

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COMPARATIVE STUDY OF AMMONIUM BIODEGRADATION IN BIOFILTRATION COLUMNS USING DIFFERENT OPERATING AND FEEDING MODES

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In recent years, the use of inert packing materials has become prevalent. Porous ceramic beads have been shown to be an appropriate packing material for biofilters due to their high gas and liquid film mass transfer coefficients [14]. In a previous study [15], we tested six inorganic materials, including naturally occurring minerals and rocks, and found that ceramic beads showed significantly higher attachment capacity ($p<0.01$) for the nitrifying consortium of *Pseudomonas* sp., *Nitrosomonas* sp., *Nitrobacter* sp., and *Sarcina* sp. (PNNS). The use of inorganic carriers, however, should be accompanied by added nutrients that will support the targeted biological processes, including the growth of microorganisms, the formation of biofilm, and biodegradation. The stimulation of these processes is a key factor in noticeably enhancing biofiltration efficiency.
Laboratory-scale submerged solid state and biotrickling systems were developed to study the process of ammonium biodegradation. Three organic amendments, molasses, humic acid extract, and malt extract, were used for bead pretreatment. Molasses significantly enhanced ($p<0.05$) the process of bacteria attachment onto the ceramic carrier and further ammonium removal from the bulk liquid media. The addition of 0.45% fructose to the column significantly enhanced ammonium oxidation, as demonstrated by more rapid formation of nitrites in the medium when compared to the sets without sugars. The results of this study are to be incorporated in a larger-scale test of a biofiltration column using wastewater from a fish processing factory.

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RESEARCH ON HIGH PARTICLE POLLUTION EPISODES AND AEROSOL FORMATION CHEMISTRY IN RIGA CENTER

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Riga City Council is managing three air quality monitoring stations - two traffic stations in City Centre and one industrial station in the Sarkandaugava region. Traffic is largest air polluter in Riga, giving about 65-80% according to CO, NO_x, PM_{10} long-term monitoring results [1]. On 2004 Riga started to realize Air Quality Action Plan (2004- 2009), were most of planned activities were realized successively, but NO_2 and PM_{10} exceedance remained. Second Air Quality Action Plan is accepted in 2011. Nevertheless due to non-compliance with air quality standards, Latvia has received the European Commission's formal notice of the infringement procedure (Case No. 2008/2195) on 2010, 2012 which indicates that the submitted air quality assessments of the 2007-2011 shows that the agglomeration of Riga has exceeded the threshold for human health for particulate matter PM_{10} - the annual limit value and the daily limit.

It is important to evaluate pollution sources and reasons in connection with actual local meteorological parameters. From different particulate matter (PM) in air only aerosols will be evaluated in this research. Atmospheric aerosols are very small (up to 0.1 microns) particles in atmosphere, and can be in solid or liquid state, or a mixture of both as well, and can contain a wide range of components, but most are believed to be mainly composed of an inorganic part, an organic part and associated water [2]. PM_{10} monitoring data from Kr.Valdemara Street air monitoring station in Riga centre for 2009-2012 shows characteristic case situations with very high PM_{10} concentrations (Fig.1) which are analyzed in relation to the particular weather conditions.

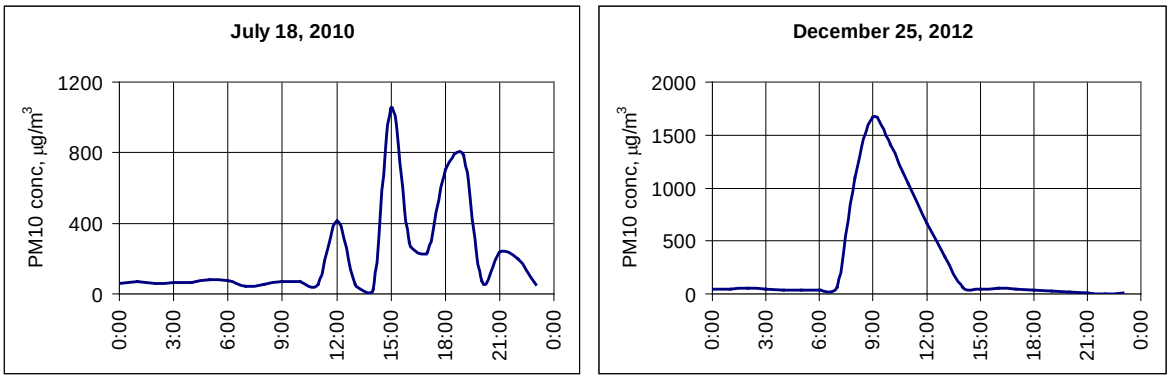

Figure 1. PM_{10} high concentration level episodes in Riga center (data from air monitoring station on Kr. Valdemara Street 18, Riga City Council).

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REMOVAL OF HEAVY METALS FROM CONTAMINATED SOILS BY ELEKTROKINETIC REMEDIATION

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Heavy metals as well as other pollutants are widespread and creating deleterious impact to the environment and human health. There are different *in situ* and *ex situ* technologies of immobilization and removal of contaminants and electrokinetic remediation is one of such technology as well [1;4;5]. It can be applied for treatment of wide areas, e.g. former industrial and military firing-grounds. Technology is applicable to water soluble contaminants at sites with homogeneous soils that are fine-grained and exhibit both high permeability and high moisture contents [2]. Electrokinetic technology is potentially effective in both the saturated and unsaturated zone and applicable in soils of low hydraulic conductivity, particularly with high clay content and can treat both organic and inorganic contaminants. Applicability limitations of electrokinetic technology include low target and high non-target ion concentration and large quantities of iron or iron oxides. Applied electric field during technology application is promoting three interfering processes: electroosmosis, electromigration and electrophoresis - all of which is removing heavy metals from soils, mine tailings, and waste sludges. As fluid flow occurs due to an applied electric field, appropriate placement of electrodes would direct the fluid flow in a controlled manner [3].
Pilot scale experiments were applied to test the efficiency of electrokinetic removal of contaminants from soil by application of low voltage DC. Experimental results show that use of DC power can be the solution for treatment of heavy metal contaminated soils. Batch scale experiments were done by using clayey soil with known physical mechanical properties, which is spiked with known amount oh heavy metals. Electric force was varied by changing its parameters. Article represents efficiency of electrokinetic method for heavy metals removal from contaminated soil and is modeling the behavior of those elements in the electric field.

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EXPERIMENTAL INVESTIGATION OF A FILTER WITH PLANT SORBENTS FOR RUNOFF CLEANING FROM PETROLEUM PRODUCTS

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Petroleum products concentration in the runoff collected from highways and motorways usually reaches about 50 mg/l (in exceptional cases even higher oil concentrations, reaching 400 mg/l, may be observed) [6]. Considering negative road runoff effect on aquatic ecosystems, it is clear that discharge of such runoff into surface water bodies is dangerous, as oil concentration often exceeds the allowable 7 mg/l limit by ten times. Road runoff produced from petrol stations and car parking areas is usually treated by settlement tanks and filters that may be coalescing and sorption [5-6]. Currently more and more publications are about the using of natural organic sorbents for runoff treatment, as they are more acceptable than synthetic sorbents from the environmental point of view [1-4, 7]. The aim of this study was to investigate the abilities of plant sorbents – *Schoenoplectus lacustris* and *Typha angustifolia* – growing on the lakesides to absorb oil from runoff when it flows through filters filled with these materials. The filtration equipment was installed in the laboratory at the Department of Water Management of Vilnius Gediminas Technical University. Road runoff or tap water (with inserted petroleum) was poured into the tank (1) and the pump carried it to the tank (2), where a stable liquid capacity, ensuring steady flow velocity in the pipe with 3° slope, was maintained. Diesel from the vessel was inserted by peristaltic pump into the running liquid at the rate which allowed reaching initial oil concentration before the sieve in the end of the pipe, where samples were taken. Afterwards, road runoff or tap water with initial oil concentration was provided at equal load through the sieve to the filter column. The water was filtrated through 10 or 20 cm height filler (*Schoenoplectus lacustris, Typha angustifolia* chopped into 0,5–1,5 cm pieces) layer, as these height values are usually used in oil separators. The quantitative gravimetric determination of petroleum products in the runoff was made by the chemists of Vilniaus kolegija/university of Applied Science. The importance of this work is due to high runoff filtering rate (~10 m/h) and high oil concentrations in the runoff (50–230 mg/l) used in the experiment. In these cases the use of sorbents is limited. *Schoenoplectus lacustris* and *Typha angustifolia* fillers are quite efficient (90–93 %) in oil removal from runoff at 10 m/h filtering rate.

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CHEMICAL COMPOSITION OF COMMON LIME LEAVES AS BIOINDICATORS IN THE STREET GREENERY

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Popular taxon used in the street greenery not only in Riga, but also in Northern, Eastern and Central Europe is common lime - *Tilia x vulgaris* H. A topical problem in Riga, as well as worldwide is development of leaf necrosis caused by de-icing salt accumulation in trees and further tree decay. The visual diagnostic of tree condition is relatively low cost and fast method, but there has been scarce information on the concentrations and ratios of plant 12 essential nutrients in lime leaves with different intensity of leaf necrosis. Therefore, the aim of the research was to evaluate the chemical composition of *Tilia x vulgaris* leaves and its relationship with different intensity of leaf necrosis in the street greenery of Riga.

The investigation was done for 27 street trees, as well as 3 trees in a park (a background level) in the centre of Riga. Leaf samples were taken from street tree leaves just reaching maturity and before leaf yellowing from different branches of trees along roadside three times during the vegetation season of 2005 (June, July and August) and two times in 2007 (June and August). Along with leaf sampling, an assessment of intensity of leaf necrosis (0 %, 1-5 %, 6-20 %, 21-50 %, 51-50 %) was done, as well as evaluation of crown defoliation at the end of summer 2007. The levels of Ca, Mg, Fe, Cu, Zn and Mn were determined by AAS, those of N, P, Mo, B by colorimetry, and S by turbidimetry, K and Na by flame photometer, Cl^- concentrations - by $AgNO_3$ titration.

The investigation demonstrated that the status of tree crowns was characterized as damaged at the end of summer, in general. Mainly 26-40 % premature leaf loss, which corresponded to the third class of defoliation, was observed for the lime trees in the street greenery (for 42.31 % of the all studied trees) at the end of summer 2007.

The most marked decrease of the essential nutrient concentrations with the increase of intensity of leaf necrosis was stated for K. The average concentration of K in the lime leaves of the street greenery with no signs of necrosis was 1.45±0.07 % (1.12±0.07 % in the park), whereas in the most damaged leaves (the intensity of necrosis >51 %) was on average three times lower. A small tendency the concentration of elements in the lime leaves to decrease with the increase of leaf necrosis was observed also for P (from 0.29±0.02 % in the healthy leaves to 0.19±0.01 % in the lime leaves with >51 % necrosis), as well as for S (from 0.19±0.02 % in the healthy leaves to 0.14±0.01 % in the leaves with >51 % necrosis).

The results demonstrated a close correlation between the intensity of leaf necrosis and the concentration of Na and Cl^- in the lime leaves. The concentration of Na in the healthy lime leaves in the street greenery was on average 0.07±0.01 % and for Cl^- - 0.39±0.03 % (in the park: 0.02±0.01 % Na, 0.11±0.01 % Cl^-), but in the most damaged lime leaves (the intensity of necrosis >51 %) were 0.99±0.13 % and 1.41±0.25 %, respectfully.

The most marked decrease of element concentration ratios with the increase of intensity of leaf necrosis were found for K/Mg, K/Ca, P/Mg, all macronutrients in relation to Na, as well as S/Cl^- and P/Cl^-. A tendency for macronutrients – N, P, K, Ca and Mg – concentration in relation to Na to reduce in lime leaves with necrosis was stated. The more intensive was development of leaf necrosis the higher was N/K, N/P, as well as Ca/Mg and Fe/Mn ratio.

The results demonstrated that the visual diagnostic method for common lime trees in urban conditions could be used only for forecasting the concentration Na, Cl^- and, probably, K.

NEW METHOD OF GLYCERIC AND LACTIC ACID PRODUCTION BY CATALYTIC OXIDATION OF GLYCEROL. NEW METHOD OF CATALYST SYNTHESIS WITH ENHANCED ACTIVITY AND SELECTIVITY

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Demand for energy continues to grow worldwide; and with it the so-called "greenhouse gas" emissions continue to increase, causing dangerous climate change. In order to mitigate the climate change effect the whole set of measures is worked out; these include energy saving and renewable energy resources proportion increasing activities, including the use of bio-fuel. European biodiesel production capacity is estimated around 22 million m^3 per year.

Rapeseed oil, which is the feedstock for biodiesel manufacturing, cannot be fully converted to biodiesel due to the forming of glycerol as the by-product. Given the volume of biodiesel manufacturing, the amount of glycerol obtained as the process's by-product increases correspondingly, and that significantly lowers its market price and forces to look for a new, alternative ways of its application. Intensive research related to glycerol alternative utilization options has been performed for many years.

Glycerol liquid phase catalytic oxidation with molecular oxygen is one of the most promising methods for glycerol utilization. Oxidation of glycerol with molecular oxygen in the presence of a heterogeneous catalyst makes it possible to get a number of important and valuable compounds that are either end-products or feedstock in various organic synthesis processes. New, simple and cost-effective methods of glyceric and lactic acid selective synthesis by oxidation of glycerol with air or molecular oxygen in the presence of palladium and platinum catalysts are developed in this work. These methods are environmentally friendly, as oxygen is the most "green" oxidizer possible, and the only glycerol oxidation by-product is water. The new, extraction-pyrolytic, method of supported catalysts synthesis is worked out. This method allows obtaining catalysts that are more active and selective than those catalysts that are synthesized by conventional methods. It is possible to reach 72-78% yield by glyceric acid with full glycerol conversion, oxidizing glycerol in the presence of 1.25-2.5%Pd/Al_2O_3 catalyst using the developed methods. This result is 8% higher compared to other published reports. The yield of 54% by lactic acid with glycerol conversion ratio 86% is reached in the presence of 1.25%Pt/Y_2O_3 catalyst. Previously the best yield by lactic acid found in publications was 10% with glycerol conversion ratio 70%. The developed methods of glyceric and lactic acid obtaining, as well as the new catalyst synthesis methods, are patented in both EU [1] and Latvia [2] and can be applied for glyceric and lactic acid production in an industrial scale. The developed catalyst synthesis method provides a way for nanostructured palladium and platinum efficient catalysts synthesis.

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POROUS CERAMIC PELLETS FROM LATVIAN CLAYS

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Porous clay ceramics are low-cost materials with wide range of applications. Their properties such as porosity, specific surface, mechanical strength, thermal insulation allow them to be used as sorbent, building materials, insulation materials [1]. These properties depend on raw material characteristics and composition, shaping, thermal treatment [2-3].

Clays from 4 deposits were investigated – Planci, Progress, Laza and Liepa. These deposits offer Devonian and Quaternary clays with different mineral compositions. There are added some additives to observe their influence on materials porosity and specific surface area. As additives are used saw dust, straw, TiO_2. Pellets are sintered at 4 temperatures.

Main clay mineral in all of investigated clays is illite. Progress and Laza contain calcite. During sintering different mineralogical reactions take place. In this process in calcareous clays forms anorthite as a main mineral and traces of calcium oxide are detected. In non-calcareous forms spinel and hematite gives the specific color of ceramic. Traces of calcium oxide are responsible for high pH of water after immersing pellets. All samples of Progress and Laza show pH in range 9,8 – 10,7 for the sintering temperature range 700 – 900 °C. At higher sintering temperature all CaO is bounded in structure of anorthite. pH for non-calcareous clay ceramics is 6,2 – 7,5 for all sintering temperatures.

The highest porosity and specific surface area is shown by calcareous clay pellets. The porosity shown by investigated pellets mostly is in range from 15 to 25 % through all temperatures with slight decrease at 1050 °C. At the same time specific surface area is much higher at 700 and 800 °C and varies from 9,5 to 30 m^2/g. With higher temperatures sharp decrease can be observed and the shown specific surface area for all pellets drops below 4 m^2/g at 1050 °C. Such results are easily explainable with fusion of small pores during sintering at high temperatures still keeping high porosity but reducing specific surface area.

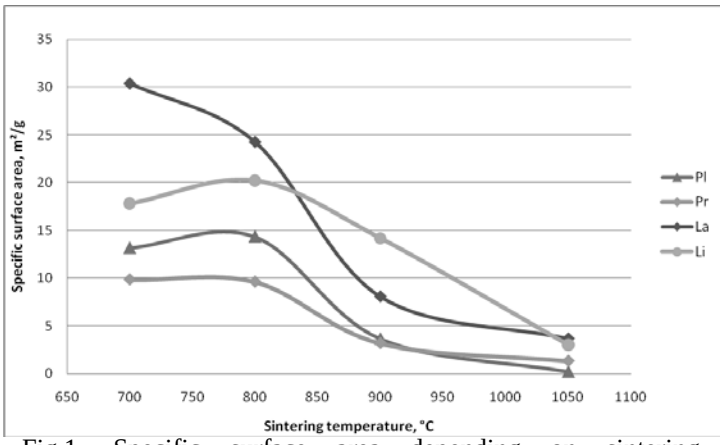

Fig.1. Specific surface area depending on sintering temperature. Pl – Planci, Pr – Progress, La – Laza, Li – Liepa

The sorption properties and their changes during three weeks time were tested for all pellets. In most cases was detected especially high sorption of iodine – 12,7 mg/g (100%). Lower sorption capacity was shown by pellets sintered at 1050 °C (8,2 – 11,2 mg/g) and pellets with TiO_2 addition. Regarding to sorption of dichromate ions results are spread in wider range (2,7 – 11,1 mg/g) and highest sorption capacity is shown by pellets sintered at 800 °C and higher porosity. Such sorption level is below 14,5 % of initial amount in solution.

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HUMIC SUBSTANCES AS SORBENTS FOR REMOVAL OF METALS

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Humic substances (HS) are the major group of refractory substances, produced in the process of biomass degradation and a substantial component of natural organic matter in soils, sediments, and waters [1]. Humic substances significantly affect metal speciation forms in soil and groundwater [2] and thus play an important role in the binding and transport of metal ions in the aqueous environment. Therefore, the presence of humic substances can strongly influence the fate of metal ions and potentially impact on the remediation of water or soil polluted with heavy metals and radionuclides. Pollution with heavy metals is of great concern because of their toxic effect on plants, animals and human beings, therefore, effective removal methods for heavy metal ions are important. Natural organic material based sorbents include peat moss, straw, hay, sawdust, ground corncobs, feathers, and other readily available carbon-based products. Biosorbents are cheaper, more effective alternatives for the removal of metallic elements, especially heavy metals from aqueous solution. Peat is natural organic, low-cost sorbent, which after use can be disposed with incineration. The chemical and heat treatment of peat can be used for extraction of humic acids, alcohols, activated charcoal, wax, fodder yeast. Due to a large number of functional groups, peat humic substances can be used as sorbent for binding of different metals, where the efficiency of binding depends on their origin.

The aim of the research is to investigate the possibilities to use humic substances for heavy metal sorption and compare the sorption efficiency of different origin humic substances. Three different (raised bog peat, fen peat, lake sapropel) HS samples have been tested as sorbents for the removal of zinc, iron, copper, boron, molybdenum, using fluorescence spectroscopy.

The sorption experiments of different source HS using metals indicated that sorption onto peat HS from raised bog is much higher in comparison with HS from other sources, indicating the importance of HS origin towards capacity of heavy metal sorption. The sorption capacity of metals onto different humic substances is influenced by physical and chemical properties of HS and depends on the oxygen-containing functional groups in HS.

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A CHEMICAL CONTENT ASSESSMENT OF NEEDLES FROM A DAMAGED SPRUCE STAND (*PICEA ABIES* (L.) H. KARST.) AFTER TREATMENT OF POTASSIUM CONTAINING FERTILISER IN 2010

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In 2010 a severe damages (yellowing needles, drying tree tops) was observed in spruce (*Picea abies* (L.) H. Karst.) stands in forests on drained organic soils managed by company "Rīgas meži" and JSC "Latvijas Valsts meži", in the result of which the trees were dying. A substantial amount of spruce bud scale *(Physokermes piceae)* was found to be present within the affected stands. A spruce bud scale typically settles on already damaged trees, and thus one is led to assume that the said pest complex represents another growth condition change-related factor [1]. In 2010, a negative correlation was found between the intensity of damage and potassium content in the soils in the studies conducted by the Latvia State Forest Research Institute "Silava" [2]. Potassium is a significant nutrient for trees, deficiency of which may reduce the frost and drought resistance qualities of a tree plan, thus weakening the stand and exposing it to a pest invasion.

In order to evaluate the extent of fertilisation usage opportunities in terms of forest stand recovery, a fertilisation trail was implemented in 2011 by JSC "Latvijas Valsts meži" at the Klives site of Zemgale forestry, in which a fresh damage resultant of bud scale invasion was found. The fertilizer was inserted into soil in June 2011 using 9 sample plots. Wood ash (dose 2,5 tonnas ha^{-1}) and potassium containing mineral fertilizer (K_2SO_4; dose 145 kg ha^{-1}) were used for the purpose of fertilisation.

In order to evaluate the influence of potassium containing fertiliser and wood ashes on the recovery of trees, samples of spruce needles were collected from one of the plots where the fertiliser tests were carried out. 36 samples of spruce needles from 9 sample trees were analysed within the study (1 to 4 year-old spruce needles). The spruce needle samples were washed with chloroform, dried and mineralised by employing a microwave technique in the presence of concentrated nitric acid. The total content of biogenic elements was determined in the prepared nitric acid extracts of spruce needle samples by using the methods of flame photometry (K), flame absorption spectroscopy (Ca, Mg, Mn) and photometry (P).

The obtained results show that the needle content of K, Ca, Mg and P in the sample trees of the fertilised sample plots is elevated not only in the first-year needles, but also in older needles. A higher content of Mn has been determined in the needles of the control trees of control sample plots. The content of P and K is higher in the first-year needles. As the age of the needles increased, the content of K and P featured a decreasing trend. Older needles had higher content of Mn and Ca. As the age of the needles increased, the content of Ca and Mn featured an increasing trend.

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TIO_2 NANOSTRUCTURES PRODUCED USING VARIOUS POLYMERIC MATRICES

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Titanium oxide (TiO_2) due to its unique physical and chemical properties is widely used for antimicrobial film applications [1,2]. On the other hand, the physical-chemical interactions between a coating and environmental materials is strongly influenced by a variation in film properties such as surface topography, pore size and crystal structure [3].
In this work we aimed to obtain various TiO_2 nanostructures. Nano-TiO_2 (Degussa P-25 and anatase) powders and various co-polymers were used as precursors to prepare TiO_2-polymer hybrid material gels which were further employed to fabricate coatings by a dip-coating technique. Techniques such as DLS, FE-SEM/EDX and XRD were used to investigate a particle size of formed TiO_2-polymer hybrid materials as well as morphological and structural features of the resulting TiO_2 films. The relationship between solution parameters, particle size, sintering conditions and obtained material properties will be presented and discussed. The development of coatings will be addressed.

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REMOVAL EFFICIENCY OF ANIONIC DYE AND COPPER(II) FROM AQUEOUS SOLUTIONS BY ACTIVATED CARBON: EFFECT OF TEMPERATURE AND SOLUTION COMPOSITION

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Colour removal from effluent is one of the most difficult requirements faced by various industries [1]. The most efficient and cost effective method of removal of dyes from aqueous effluents is the adsorption process. Wastewater from textile and dyeing industries contains not only dye materials, but also other pollutants, such as heavy metals [2, 3]. Removing of heavy metals ions from sewages, before their release to the environment, is a key problem of modern wastewater treatment. This work is devoted to the removal of copper(II) and commercial anionic dye Lanasyn Navy M-DNL (LN) from aqueous solutions by activated carbon Norit PK 1-3. Removal efficiency of LN dye and Cu(II) was investigated in the single and binary adsorption systems. To determine removal process and properties, the effects of various operating parameters, initial concentration of Cu(II) ions (1-5 mM), contact time (5-180 min) and temperature (293-333 K) were investigated in a batch adsorption technique. The time profiles for 0.05 mM LN dye and Cu(II) have been obtained using 4.0 g of activated carbon per liter of the solution. The composition of the solution plays an important role in the evolution of solution pH during removal process. The solution pH increased from its initial value of 5.0 to 5.3-6.4 in single Cu(II) and binary adsorption systems whereas the final solution pH increased up to 7.9 in single LN dye adsorption system. The increase can cause several additional reactions, such as surface precipitation [4]. Due to these reactions, the Cu(II) and LN dye uptake process is therefore accelerated. Adsorption kinetic studies demonstrated that the solution temperature played an important role. The presence of copper(II) resulted in about 15-20 % increase in removal efficiency of LN dye at higher temperature of 40 or 60 °C whilst a slight decrease in dye adsorption capacity from binary solutions at 20 °C temperature was observed. The copper adsorption rate increases when the temperature is higher. For Cu(II) concentration of 1 mM, the increase of solution temperature from 20 to 60 °C leads to the increase of adsorption rate from $1.1 \cdot 10^{-5}$ to $3.5 \cdot 10^{-5}$ $Mmin^{-1}$. The presence of LN dye in the solution results in slightly lower adsorption rate but it does not hinder the copper(II) removal significantly. Probably, the positively charged Cu(II) ions and negatively charged anionic dye particles do not compete toward the same sites of carbon surface. The adsorption kinetics revealed that in 3 h the Cu(II) ion uptake reaches nearly 90 %, when the initial concentration of metal ions is 1 mM whilst the activated carbon is able to adsorb only about 50 % of initial amounts of Cu(II) in the respective time when the initial concentration of metal ions was increased from 1 to 4 mM. The investigated process allows removing LN dye with higher removal efficiency and, at the same time, removes Cu(II) ions.

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USE OF SOLAR ENERGY FOR BIODEGRADATION OF OIL PRODUCTS

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Solving the problem of sustainable development, currently there exist two important approaches: applying of biological methods in environmental protection and alternative energy sources application. Time is a limiting factor that prevents the efficient use of a biological treatment method, as the biodegradation of oil products is largely dependent on the season of the year and takes place during the warm season, when microorganisms are active decomposers [1-3]. Degradation of oil and oil products in the temperate climate takes about 10 months. In order to implement bioremediation technologies, temperature control could be one of the operating factors. This study sought to integrate alternative energy sources into traditional biological treatment and thus guarantee the functioning of this advanced method at any temperature conditions. During the experiment, a possibility was tested to use solar water heating system in the biological treatment of oil products from soil. In order to carry out the experiment a solar water heating systems was designed, the main device whereof was a collector of solar energy. This system was made from recycled metal and waste construction materials. The change in diesel fuel and fuel oil concentrations in soil was tested during warm and cold seasons of the year. The concentration of oil products in soil is tested with gas chromatograph SHIMADZU GC-2010 (ISO 16703:2004 standard).

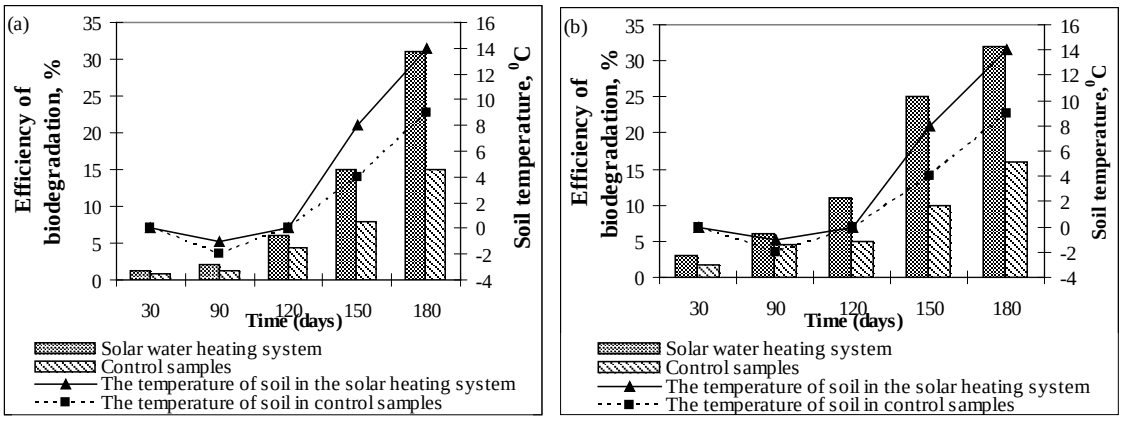

Fig. 1 Efficiency of biodegradation of oil products and changes of soil temperature in time: a) fuel oil; b) diesel fuel

To summarize the results we can state, that the outcome of biological treatment of samples using solar-based heating system during cold and warm seasons was better in both cases of pollutants. Heat produced by solar collector intensified the process of degradation of pollutants: in samples with solar-based water heating system, the diesel fuel removal level reached 59 %, in case of fuel oil - 46 %, and in control samples it was 32 % for diesel fuel and 26% for fuel oil. According to the results, the suggested technology allows to reduce the time-span and expenses related to treatment as well as extends the sphere of alternative energy application.

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ARSENIC, ANTIMONY AND TELLURIUM REMOVAL USING Fe-MODIFIED BIOMATERIALS

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Environment pollution with V and VI group metalloids (As, Sb, Te) is one of the research direction that extensively has been investigated during last decades [1-6].
Arsenic is well known, naturally occurring element that is mobilized in natural water systems through the range of anthropogenic as well as natural sources [1]. Antimony, like arsenic, is present in the environment as a result of natural and human activities. Its chemical and toxicological properties are similar to arsenic. The antimony concentration in unpolluted waters is low, while in polluted areas – close to anthropogenic sources – the concentration can be up to 100 times higher in comparison to natural levels [3]. Although tellurium is found in low abundances in the Earth crust, its toxicity can induce local environmental problems. Like it is for other metalloids, the toxicity of tellurium is dependent on its chemical form and oxidation state [6].
The aim of this study was to investigate and compare Fe-modified biomaterial application possibilities for metalloid sorption, to reduce their concentration and obtain new effective and perspective sorbents.
The present work investigates the sorption of metalloids – As (V), Sb (V), and Te (VI) – on unmodified materials (peat, humic acid) as well as Fe-modified biomaterials (Fe-modified peat, shingles, moss, straw, canes, and sand) using batch tests. Sorption was studied as a function of initial metalloid concentration, pH, and temperature.
Fe-modified peat is the best sorbent for As (V), Sb (V), and Te (VI). It can sorb up to 98 % of As (V) and Te (VI) and up to 95% of Sb (V). The sorption capacities for arsenic and tellurium are similar, but it is much higher for antimony. Fe-modified moss and Fe-modified shingles can effectively sorb all the studied metalloids (As, Sb, Te), although other sorbents, like Fe-modified straw and Fe-modified canes, can also be used in areas where metalloid concentrations are low.
The best sorption conditions are in the pH interval 6.5 – 7.5 for As (V) and Sb (V), while pH 7 – 9 is the most appropriate interval for Te (VI) removal.
The impact of temperature on the metalloid sorption capacity of Fe-modified peat was tested at four temperatures: 275 K, 283 K, 298 K, and 313 K, and the sorption capacity increased with increase in temperature for all of the studied metalloids. The calculated thermodynamic parameters suggest that the sorption process is of a spontaneous nature and endothermic.

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VISCOSIMETRIC MEASUREMENTS FOR THE DEVELOPMENT OF A PROTOCOL FOR OPTIMAL FLOCCULANTS USED IN THE TREATMENT OF WASTE WATER

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Different chemical and natural reagents can be added to the waste water cleanup process to improve settling. Depending on the chemistry of the wastewater treated, and the compounds to be removed from the solution, coagulants such as inorganic salts or polymeric flocculants (polyacrylamides, polyelectrolytes) can be widely used. Polymer flocculants create large aggregate particles (flocks) and settle quickly [1]. It is well known that the dosage of flocculants is critical - too low an addition will not improve the settling rate, while too much an addition reduces the compressibility of the sludge bed – however, many other technological parameters are also most essential[2].

Despite the fact that the handling of chemical substances is regulated by EU legislation, it is not possible for consumers to have access to the kind of information concerning flocculants used in treatment processes, which would allow for their full effective use. Many of the important characteristics of flocculants that are useful and needed for specialists are not actually shown or listed in certificates or relevant chemical documentation. Given that flocculants are used not only in the treatment of waste water, but also in the treatment of drinking water, it is important and necessary to have information available on the technical characteristics of flocculants.

Most of the available studies have been carried out in concentrations and conditions which are far removed from real waste water treatment station work conditions. The primary objective of this study is to perform systematic intrinsic viscosity measurements using two different methods on some (3) commercial anionic polyacrylamide flocculants in dilute solutions (concentration ranges from 0,002% - 0,2%). The aim of the study is to understand the behavior of the flocculants under different physico chemical conditions: temperature, electrolyte presence and a time dependent alteration of the solution's intrinsic viscosity, according to a real wastewater treatment regime. Measurements were made using a rotational viscometer. For all the flocculants that were investigated, viscosity increases with the increase of flocculant concentration in the water (behavior that is typical for Non-Newtonian fluids). It has been determined by experiments, that an important role is played by the speed (which is different for each flocculant) at which the growth or reduction of viscosity takes place, as the viscometer cylinder changes (or increases) its' number of rotations per minute.

It was found that the properties of anionic polymers were strongly dependent on the presence of the type of salt and metal value. The intrinsic viscosity decreased in the presence of the salts, due to shielding of the negatively charged carboxylic group. A systematic study of the effect of temperature was also carried out. It was established from aging studies, that anionic flocculants have time dependent alterations of the solution viscosity. The results obtained can serve to optimize the working conditions of a waste water treatment plant working with flocculants. The results of the study can also serve as guidelines to choose and test new flocculants.

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ARE GREEN ROOFS SUSTAINABLE SOLUTION TO ENVIRONMENTAL PROBLEMS?

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Green roofs are one of the method of recovering green space in urban areas. One of the benefits of their implementation is rain water retention, resulting in delaying of the runoff. Green roofs are the engineered constructions, consist of different layers: hydroisolation, drainage, geomembrane, substrate and plant cover. Two of them: substrate and drainage layer can bring or solve environmental problems, as a result of the type of material which is used in their construction.

Green roofs can be a source of phosphorus in runoff [1,3,5]. The main source of P leaching is plant substrate, and factors influencing the load of phosphorus in runoff are: used plants, roof age and the type of roof maintenance [1,4]. Substrate is an artificial medium which substitutes natural soil for plant growth. It usually consists on mixture of mineral (eg. sand, gravel aggregate, debris) and organic particles (eg. bark, peat, compost). The share of compost in substrate mass can vary from few to several dozen percent, however big share of compost can cause negative effect eg. decomposition of organic material and self-consolidation of soil [2,4].

The main hypothesis of presented study is, that negative effect of phosphorus leaching from green roof substrate can be leveled by implementation of P-reactive material in drainage layer. Different materials, typically used for drainage layer construction, and some alternative P-reactive materials were tested as a potential drainage medium as well as a P-trap. Materials used in the study are Pollytag, LECA (lightweight expanded clay aggregate), chalcedony, serpentynite and AAC (autoclaved aerated concrete).

Based on performed study it can be stated that some of tested materials can be effective as a P-trap for substrate leachate. Physical and chemical characteristic of materials were used as a base for choosing the best media for drainage layer, and their efficiency has been confirmed in column experiment. It was proved, that properly chosen material for drainage layer construction can level negative effect of substrate leachate on green roof runoff quality.

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SORPTION OF METALLIC ELEMENTS ONTO FEN PEAT

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Water plays an important role in life biogeochemical cycles and in human developments. Regrettably but increasing environmental pollution is of major concern nowadays. Pollution from industrial wastewater is one of the most urgent environmental problems particularly in developing countries. To promote sustainable environment high on agenda is to limit heavy metal contamination which exists in wastewaters of metal plating facilities, tanneries and of many other industries. Some of the most dangerous heavy metals are chromium, iron, lead and mercury. Heavy metals are not biodegradable and they are tended to accumulate in living organisms which causes variety of disorders and diseases, such as peripheral neuropathy, multiple sclerosis, cancer and others. Hence, there is an urgent need to find possibilities to treat wastewaters before they are discharged into the water bodies. The most popular methods in decontamination of waste water are coagulation, membrane separation, oxidation and other physic-chemical methods, but, however, these methods are expensive, have many technical constrains and handling as well as disposal problems, so there is an urgent need to find universal, cost effective and simple operable method in treatment of waste water – not only in decontamination of industrial waters, but also in decontamination of any waste material which might end up into water. One of these effective methods is usage of biosorbents. Several currently used biosorbents/adsorbents have proven their effectiveness – peat moss, seaweeds, bacteria, wool, rice, etc. Actually, usage of peat and peat products in adsorption/biosorption of heavy metals could be technically feasible and economically viable method, because it is low cost organic material which requires little processing and is abundant in nature. During the centuries peat due to its characteristics has been used as filtration/sorption material for variety of liquids, gases and odours. Peat has great importance as biosorbent in uptake of contaminants in wastewaters. Mostly raised bog peat and products of its modification are used; hence fen peat perspectives as sorbent are not fully evaluated. In this study by increasing the concentration of analytical solution we have examined sorption abilities of several types of unmodified fresh fen peat samples. We have tested sorption of Ca, Mg, K, Na, Pb and Cr onto fen peat and looked how it affects metallic elements which are already in peat, for instance, how absorbance of lead ions affects concentration of calcium or magnesium in peat sample. Fen peat due to its variable botanical composition and complex properties has huge variability as biosorbent, for instance, under equal conditions; wood-sedge fen peat would have higher lead absorption capacity than wood fen peat, etc.

FRACTIONATION OF KRAFT LIGNIN FROM HARDWOOD FOR ITS VALORIZATION AS ANTIOXIDANT

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Lignin is a major constituent in structural cell walls of all higher vascular land plants and it serves to protect plants against chemical, biological and mechanical stresses. In industrial scale lignin is obtained as a by-product from the plant chemical processing. Antioxidant properties of lignins are well documented. However, technical lignins contain admixtures, which decrease their efficiency as antioxidants by changing solubility and diluting the reactive phenolic groups. Polymeric antioxidants due to their higher compatibility with polymeric systems, low volatility and lesser toxicity often can be successfully applied, when the employment of low molecular antioxidants is inefficient. The aim of the present work was to reduce the heterogeneity of an innovative kraft lignin produced in pulp-and-paper industry in order to improve its potential as antioxidant. With this aim, hardwood kraft lignin isolated according to the *LignoBoost* process (Innventia AB Sweden), was fractionated by sequential extraction with organic solvents of increasing polarity: dichloromethane, n-propanol, methanol.

After fractionation of the parent lignin four fractions, differed by composition, polydispersity, molecular mass and functional groups content, were obtained: 23,1% CF1 – (CH_2Cl_2 soluble fraction), 48,3% CF2 – (C_3H_7OH soluble fraction), 9,2% CF3 – (CH_3OH soluble fraction) and 19,3% CF4 – (fraction insoluble in the organic solvents used).

Lignin and its fractions obtained were analyzed using SEC (for molar mass distribution), Py-GC/MS (for composition and lignin structure), wet chemistry analysis (for functionality). Antioxidant activity of lignin samples were evaluated using tests on scavenging of radical cation of 2,2'-azino-bis(3-ethylbenzothiazoline)-6-sulphonic acid ($ABTS^{\bullet+}$), free radical 1,1-diphenyl-2-picrylhydrazyl ($DPPH^{\bullet}$), superoxide radical anion ($O_2^{\bullet-}$) and ORAC assay as well. Water-soluble derivative of E vitamin Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) was used as a reference antioxidant. Radical scavenging activity was expressed by IC_{50} – the concentration of antioxidant required to reduce the initial concentration of the radicals on 50% (Table 1)

Table 1. Antioxidant activity of hardwood lignin and their chemical fractions

IC_{50}, mg/L	Parent lignin	CF 1	CF 2	CF 3	CF 4	Trolox
$ABTS^{\bullet+}$	4,8	4,0	3,7	4,2	6,4	4,1
$DPPH^{\bullet}$	15,0	17,6	11,3	12,0	17,4	4,7
$O_2^{\bullet-}$	36,9	59,7	30,4	39,5	44,9	17,7

The results obtained show that solvent fractionation of technical kraft lignin can be considered as prospective tool for obtaining efficient antioxidants for stabilizing of various systems. The radical scavenging capacities in $ABTS^{\bullet+}$, $DPPH^{\bullet+}$ and $O_2^{\bullet-}$ tests of the fractions soluble in n-propanol and methanol were close to Trolox and higher in comparison with parent lignin. The dichloromethane-soluble fraction demonstrated good potential as antioxidant for vegetable oil. The methanol- and propanol-soluble fractions demonstrate high antioxidant activity in the test with model polyurethane films.

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INFLUENCE OF THE THERMAL AND IRRADIATION TREATMENT ON THE SORPTION PROPERTIES OF CERAMIC PELLETS

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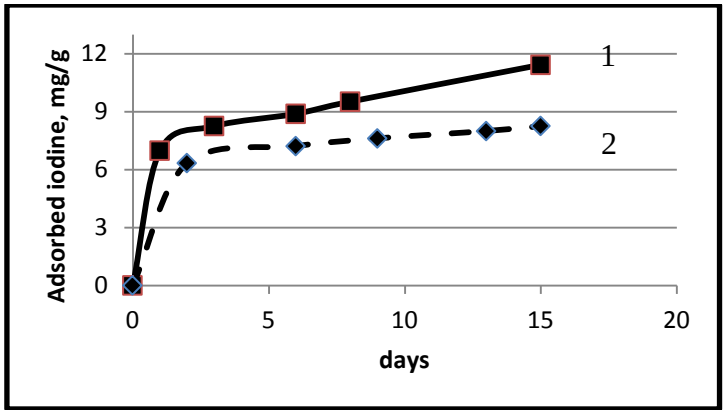
A porous clay ceramic appropriate some sorption properties and may be used in the water purification technologies. In the current work Devonian clay of Latvia is used. Chemical composition of Devonian clay deposit Kuprava (wt %) SiO_2 – 48.16; Al_2O_3 - 16.99; Fe_2O_3 - 8.44; TiO_2 - 0.91; CaO – 3.29; MgO – 4.35; Na_2O – 0.20; K_2O – 4.83, ignition loss at 1000˚C 12.68%. The main mineral in the used clay is hydromica. The other minerals are quartz, calcite, dolomite and potassium feldspar. Thermal analysis of this clay shows the decomposition of illite (516˚C), dolomite (615˚C) and calcite (676˚C) and formation of hematite at temperature 983˚C. These conclusions are grounded with results of x-Ray analysis. In accordance with results of thermal analysis dried clay pellets are sintered in temperature range 700 - 1050˚C. The pH of water immersion of sintered pellets is determined. The water immersion of pellets sintered at temperature 800 and 900˚C are given alkaline medium. Part of sintered pellets is irradiate with β-rays with intensity 5 MGy The sorption ability of iodine (substance with molecular bonding) is determined depending on the sorption time for both irradiated and non-irradiated pellets. Investigations show dependence of sorption ability on the sintering temperature of pellets. Sorption ability decreases by rise of sintering temperature. Determination of pore size distribution, porosity and specific surface area by mercury porosimetry is indicative on decrease of porosity and specific surface area by rise of sintering temperature. A porosity decreases from 16.94 % to 1.56 % and specific surface area from 28.94 to 1.25 m^2/g by increasing of the temperature range 700 - 1050˚C.
Sorption ability of irradiated pellets increases in comparison with non-irradiated pellets. Influence of sintering temperature on the sorption ability of irradiated pellets is similar. Difference of sorption ability non-irradiated and irradiated pellets decreases by rise of sintering temperature. Sorption ability of non-irradiated and irradiated pellets is shown in fig.



Sorption ability of ceramic pellets sintered at temperature 700˚C: 1 – irradiated pellets; 2 – non-irradiated pellets.

PREPARATION AND PROPERTIES OF BIODIESEL FROM CHICKEN FATS

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The most promising alternative to fossil fuel is biodiesel that is mainly produced by transesterification reaction with methanol in the presence of homogeneous alkaline catalysts such as NaOH, KOH and $NaOCH_3$. The world's largest proportion of biodiesel is derived from edible vegetable oils as raw materials. For instance, the major raw materials for biodiesel production in Asia and U.S. are, respectively, palm oil and soybean oil [1]. While in the EU most widely applied biodiesel raw material is rapeseed oil. It is mainly due to the favourable climate conditions for seed growing [2]. It is also possible to produce biodiesel using animal fats as raw material. Thereby it is possible to utilize waste generated from food processing industry and reduce cost of biodiesel production [3]. In this study FAME (fatty acid methyl esters) obtaining process from chicken fats was investigated and also the most important quality parameters for raw material and FAME were determined.

Chicken fat used in experiments was obtained from local meat processing company. Acid value (0.98 mg KOH/g) and saponification value (181.5 mg KOH/g) of this raw material were determined in accordance with EN 14104 and EN ISO 3657 standard. $NaOCH_3$ and methanol of purity >98% (purchased from *Sigma - Aldrich Chemie Gmbh*) were used in experiments.

Transesterification reaction was performed at 70°C with a reaction time of 1 h by using 4 moles of methanol to 1 mole of chicken fat and 0.8% $NaOCH_3$. In such conditions it was possible to obtain 394.8g of FAME from 450.0g chicken fat, which is equal to 87.3% of outcome and 97.2% of ester content. The resulting FAME quality parameters (ester content, viscosity, density, carbon residue, flash point, water content, acid value, total contamination, iodine value, monoglyceride, diglyceride and triglyceride content, free glycerol, total glycerol) met the requirements of the EN 14214 standard. Furthermore, the heat of combustion of obtained FAME (39.93 MJ/kg) was determined (according to EN ISO 1928 standard). It is approximately 11.3% lower than the heat of combustion of the category C summer diesel fuel (~ 45.0 MJ/kg), but ~ 7.9% higher than the heat of combustion of the rapeseed oil methyl esters (~ 37.0 MJ/kg). Determined according to EN ISO 116 standard cold filter plugging point (CFPP, 5°C) of the obtained biodiesel is 10°C and 15°C higher than this characteristic of the summer diesel category C (-5°C) and RME (-10°C) respectively.

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DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS IN WATER COLUMN

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The Baltic Sea is one of the most intensely trafficked marine areas in the world [1]. This heavy traffic occurs in narrow straits and shallow waters, making the Baltic Sea a difficult area for navigation, with an increased risk of shipping incidents. Some of the environmental consequences of the extensive shipping are illegal and accidental discharge of oil. Oil spilled deliberately or during accidents may destroy important marine and coastal habitats [1]. Oil spills cause extensive damage to marine life, terrestrial life, human health, and natural resources [2]. A large number of oil compounds are known to cause hazardous effects in aquatic organisms. Many contaminants exert their effects via genotoxic and metabolically toxic mechanisms, simultaneously causing carcinogenesis, embryotoxicity and inflict long term damage to organisms [3].

The distribution of oil spilled on the sea surface occurs under the influence of gravitation forces. It is controlled by oil viscosity and the surface tension of water. Only ten minutes after a spill of 1 ton of oil, the oil can disperse over a radius of 50 m, forming a slick 10-mm thick [4]. Physical/mechanical methods are the primary response options for oil spill clean up, but the crude oil recovery is only about 10–15% [5]. Only a few studies have dealt with the distribution of PAHs in Baltic Sea water [6]. In particular, there is a lack of information on the levels and behavior of PAHs in the deep water. Therefore, we need to know how fast and which oil hydrocarbons begin to diverge from the spilled oil film and move through water column.

The distribution of aliphatic and polycyclic aromatic hydrocarbons was researched *in vitro* experiment in water column (1 m height and 0.2 m diameter). Samples were taken at three depths and determined by gas chromatograph Shimadzu GC-2010 plus. After two weeks low molecular weight polycyclic hydrocarbons Naph, Phe, Antr were diverged from oil slick in water column. High molecular weight polycyclic hydrocarbons were not detected during the experiment.

The influence of the environmental conditions on the distribution of PAHs was assessed using canonical correspondence analysis (CCA). Based on CCA analysis environmental characteristics explained 54% of PAH concentration in water depth. Statistically significant environmental factors were TOC ($F=93.2$, $p=0.001$), time ($F=57.2$, $p=0.001$) and temperature ($F=18.9$, $p=0.001$), pH ($F=16.1$, $p=0.001$). The positive correlation was observed between temperature and Naph, between Naph and TOC, a negative correlation - between Naph and time. Phe negatively correlated with temperature and TOC and positively correlated with time. Between Antr and pH and between Antr and depth was found a positive correlation, between Antr and dissolved oxygen was observed negative correlation.

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HYDROTREATING OF WHEAT STRAW IN TOLUENE AND ETHANOL

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Biomass is considered to be the most reliable alternative energy source in future due to its renewability and potentially near to zero emission. The production of liquid fuels from biomass is particularly attractive and promising because of the abundance of raw materials and lower greenhouse gas emissions comparing with those of the combustion of fossil fuels [1, 2]. Pyrolysis and gasification require high operating temperatures (500 – 1000 °C) which can lead to cross-linking reactions between unsaturated compounds, yielding a tar which is difficult further to process. Less energy is required for the solvolysis/liquefaction reactions which can be carried out at relatively low temperatures (200 – 300 °C) and with lower tar yield [3].

In the present work, wheat straw was hydroliquefied at temperature 300 °C for 4h in the presence of ethanol or toluene in order to obtain the bio-components for fuel purposes.

Experiments were performed in 100 mL batch reactor, equipped with a magnetic stirrer and a temperature controller, under initial cold hydrogen pressure 40 bar. Typically 2 g of straw and 0.1 g of catalyst (66% Ni/SiO_2-Al_2O_3) was dispersed in 15 g of solvent. After experiment the liquid phase was separated by filtration and further distilled to remove the solvent. The reaction product (oil) was analyzed by gas chromatography-mass spectroscopy. The compounds that compose the majority (up to 70%) of obtained oil are given in Table 1.

Table 1 - Composition of oil

R. time, min.	Compound	With toluene, %	With ethanol, %
9.440	1-butanol	-	4.82
11.008	1,2-ethenediol	-	9.49
11.762	1,2-propanediol	-	10.00
12.488	1-hydroxy-2-butanone	-	9.97
13.898	1,2-butanediol	8.33	12.43
14.980	2-furanmethanol, tetrahydro-	35.33	21.69
15.846	butyrolactone	11.87	1.94
16.820	cyclopentane-1,2-diol	4.02	-
19.658	2-furanmethanol, tetrahydro-, acetate	8.39	-

The main compounds of oil obtained in both solvents are tetrahydrofuran-2-methanol, 1,2-butanediol and butyrolactone. These compounds were produced during the liquefaction of cellulose and hemicellulose of wheat straw. Clearly, the ethanol favours the decomposition of bigger molecules to short-chain alcohols such as 1-butanol, 1,2-propanediol and 1,2-ethanediol. Toluene contributes to the production of furans and other cyclic compounds. The light fractions distilled together with solvent contain 1-propanol, 2-methyl-cyclopentanone, acetic acid and ethyl acetate.

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CHEMICAL CHARACTERISTICS OF HIGHBUSH BLUEBERRY PEAT AND MINERAL SOILS IN LATVIA, 2011-2012

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Although highbush blueberry (*Vaccinium corumbosum* L.), native to North America, have not been cultivated on a large scale in Latvia (~ 200 ha), blueberries have a great potential to become commercially important and biologically valuable small fruit crop with a high market demand, processing and export possibilities. Blueberries are distinguished among fruit crops in that they thrive on acid peat or sandy mineral soil, preferable in the 4 to 5 pH range. Consequently, appropriate site selection, soil pH amendment and maintenance are critical for successful blueberry cultivation.

In Latvia highbush blueberries are cultivated in extracted raised bogs on bare sphagnum peat, as well as on mineral soils with high organic matter content. The chemical composition of soil is one of the most important factors for a normal plant growth and development. While blueberries require low fertility level for proper growth and yield, the specific acid growth conditions can cause significant nutrient availability problems. Therefore blueberries need special fertilizer rates, types and timings due to acidic growth conditions and nature of blueberry physiology. Knowledge concerning the optimization of mineral nutrition of blueberry crop in Latvia especially in two completely different growing medium – mineral soil and peat soil is still incomplete. The main aim of the research was to find out the nutrient status of blueberry crop cultivated in mineral and peat soils in Latvia to evaluate actual fertilization practices, revealed main problems and peculiarities.

Together 40 peat and soil samples from different blueberry producing sites, established in the extracted raised bogs and mineral soils, were collected during 2011–2012 and analyzed on plant available nutrients (N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu, Mo, B), as well as soil pH and electrical conductivity (EC). In general, the chemical results of blueberry soils demonstrated a high heterogeneity in nutrient concentrations for both substrata. The highest concentration range in mineral soils was found for S and Mn, but the lowest – for N and Fe. For the peat soils, the highest concentration variance was found for Mg and Cu, the lowest – for N, Mo and B. Statistically significant differences were found between mean nutrient concentrations in diverse blueberry growing medium. Significantly higher mean concentration of P, K, Fe, Mn and Mo was found in the mineral soils.

Serious imbalance in highbush blueberry providing with the essential mineral nutrients was found for producing plantings of Latvia over the study period of 2011-2012. Our results suggest that only about 50 % of nutrient indices were in optimal range for both mineral and peat soils. Whereas, the percentage of indices in deficient range was significantly higher for the blueberries in peat soils (45%) to compare with the mineral soils (30%). The research revealed seriously decreased levels of N, S, Cu and B in the vast majority of samples. In addition, deficiency of Zn was found for mineral soils, but Mo – in peat soils. Corresponding to the low level of nutrients in the growing medium, 55 % of the soil samples and 75% of the peat samples had a less than optimal soil EC. Therefore corrections of nutrient disorders must be done to avoid reductions in growth and yield of blueberry plantings in Latvia.

SORPTION OF PHARMACEUTICALLY ACTIVE COMPOUNDS IN ENRICHED SMECTITE CLAYS

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World's pharmaceutical industry is increasing as well as production of waste by it. It is recognized that pharmaceutically active compounds (PhACs) reach the environment and can be considered as the environmental pollution [1]. Therefore there is a need to develop a new, efficient and inexpensive method for treatment of industrial wastewater. In this case smectite clay minerals can be a potential solution for ground water and wastewater treatment, because of their high specific surface area, colloidal size, large cation exchange capacity and propensity for intercalating organic compounds [2].

Triassic clays of the Baltic region contain a large amount of different matrix minerals (quartz, carbonates, etc.) and low content of smectite minerals (20 – 40%). It is possible to remove most of the non-clay minerals from the raw clay samples by the procedure of the clay enrichment [3]. The procedure allows extracting up to 70% of the smectite, increasing its cation exchange capacity (CEC) from 0,3mmol/g to 0,7mmol/g (determined by methylene blue method) [4]. Proposed method [3] of the enrichment provides enough clay material for researches.

In this study the sorption process of some PhACs (xylazine hydrochloride, imatinib mesylate, arbidole hydrochloride, antazoline phosphate) in enriched clays was investigated. The sorption of these PhACs is based on the cation exchange mechanism, where inorganic ions, neutralizing negative charge of the clay minerals, are replaced by organic cations. Sorption of the monovalent xylazine hydrochloride is lower than CEC of the smectite (0,7mmol/g). Sorption of the imatinib cation is low due to the large size of the molecule and its ability for multi protonation.

Changes in the clay structure were characterized by using thermogravimetry, X-ray diffractometry and X-ray fluorescence spectrometry.

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AMMONIUM IONS REMOVAL FROM REJECTED WASTEWATER USING NATURAL ZEOLITE

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Rejected wastewater from the centrifugation of digested sludge can contain ammonium ions concentrations till 1400 mg/L. These loads are usually returned to the intake of wastewater treatment plants (WWTP) without additional treatment and can interrupt biological wastewater and/or sludge treatment processes, e.g. phosphorus and nitrogen removal [5]. A previous study that included few water treatment plants throughout the Lithuania reported that some of advanced treatment (e.g. membranes) dealing with high ammonium concentrations levels in biological treatment system can have impact on the presence of different nitrogen compounds e.g. nitrates and nitrites [7].

This article is dealing with the use of naturally obtained sorbent, zeolite, as an ion exchange in batch and column tests procedure for ammonium removal from rejected wastewater. Laboratory scale research performed at Vilnius WWTP, the biggest sludge digesting works in Lithuania. During the experiment, the constant initial concentration of solution was established by using a mixture of rejected wastewater from Vilnius sludge treatment plant with high ammonium ions concentrations from the centrifugation of digested sludge. The novelty of this research was concentrated on rejected wastewater from the centrifugation of digested sludge related to highest obtained ammonium ions concentrations.

Since sorption properties of zeolite in groundwater and wastewater treatment systems is well documented [1, 2, 3, 4, 6, 8], this research study was carried out with different zeolite particle sizes of 0.8–1.6 mm and 1.6-2.5 mm in laboratory scaled column test. Retention time was evaluated using filtration rate and dependencies on quantities.

Comparison of the results showed that the highest removal of ammonium from rejected wastewater was obtained by using the finest particle size zeolite. The removal efficiency was 70-92% for 1.0-1.6 mm particle size zeolite packed in laboratory scaled columns. The highest ammonium removal efficiency (till 99 %) was achieved by using 0.8–1.6 mm particle sized zeolite.

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COMPARATIVE STUDY ON IRON MICROBIAL REDUCTION

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In Latvia 73% of deviations of drinking water quality are associated with increased iron concentration, the threshold value (0.2 mg/l) is exceeded in more than 30% of all water samples [1]. This is caused by a high Fe^{2+} content in groundwater. It is hyphotised that reduction of the trivalent iron from mineral phases of the Fe-oxyhydroxides that are common secondary minerals in most of the sediments in Latvia is an important source of the dissolved iron in groundwater.

Fe-reducing bacteria have been identified as important geochemical agents with the ability to influence metal and metalloid mobility in aqueous environments [2]. Bacterial reduction of structural Fe^{3+} has been documented for a variety of clay minerals, and the process is dominated by the activity of facultative and obligate anaerobic microorganisms [3]. Although significant research has examined microbial communities associated with aquifer and other higher-permeability geologic units, the characterization of microorganisms associated with clay deposits and other low-porosity sediments and soils has received much less attention to date [2,4].

The aim of this study is to characterise the ability of soil bacteria to mobilise iron found in mineral phases in soils where reducing conditions are developed due to permanent saturation with groundwater (*gleysols*, FAO soil classification).

Sandy sediments rich in detrital organic matter with visible traces of iron reduction were collected at depth 0.9 – 1 m from three locations near Lake Ķīšezers and Lake Jugla, Latvia for Fe^{3+} reduction activity under different incubation conditions. 100 ml incubation medium contained 60 g sample (dry weight 24÷25%) and liquid phase. Four types of "slurry" system were tested, i.e., i) intact sample in synthetic medium with pH 5.7; ii) intact sample in synthetic medium with pH 3.0; iii) intact sample in distilled water with pH 6; iv) autoclaved sample in distilled water with pH 6. The sets were incubated in 120 mL polypropylene vials sealed with lead, at 20 °C without agitation during 21 days. Initial number of aerobic mesophilic microorganisms in the samples Ķīšezezers 1 (KP), Ķīšezezers 2 (KO) and Jugla (J) was 7.68×10^5 cfu/gdw; 7.20×10^5 cfu/gdw and 4.24×10^5 cfu/gdw, respectively. The number of colonies grown under anaerobic conditions was one order lower, as compared to aerobically cultivated samples. The response of microorganisms to the different incubation conditions was tested in dynamics by their enzyme activity. Physico-chemical changes were detected during 21 days experiment. In particular, content of Fe^{2} and Fe_{tot}, redox and pH were determined.

Further model experiments with 5 samples and microorganisms isolated from different geological conditions will expand the knowledge on clay mineral-metal adsorption mechanisms and microbial controls on metal mobility in the environment.

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SOCIO-ECONOMIC ANALYSIS OF WATER DISINFECTION WITH ELECTROLYSIS IN LATVIA

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Drinking water disinfection is necessary in order to minimize multiplication of microorganisms in engineering water supply systems and to eliminate the possibility of human infection, which could lead not only to deterioration of the public health and working abilities but, consequently, to significant economic losses. This is a serious problem in developed countries and partially in Latvia too, as significant number of people consume low-quality water from individual wells and have no access to the centralized water supply systems. By improving microbiologic quality of drinking water in de-centralized water supply systems, number of infections caused by poor water quality will be significantly decreased. Electrochemical water treatment is a perspective method for obtaining high-quality water, as during the water electrolysis, disinfectant substances are formed which destroy microorganisms and decrease their ability to multiply [1]. Applying titanium oxide (TiO_{2-x}) ceramic electrodes, an effective non-reagent electrochemical water disinfection method was developed at Riga Technical University which can be used on local water collection venues, in emergency situations and for water preparation for specific applications.

The following influences on the electrolysis process were investigated: current intensity; concentration of chloride ions in the solution; flow regime and other ions impact on the changes of the extracted chlorine. It was found that while using the TiO_{2-x} electrodes, even minor chlorine ions concentration (7–9 mg/L) in the water during electrolysis can ensure a sufficiently high water disinfection efficiency with a lasting exposure. Based on the experimental data, a principle scheme of a continuous operation water disinfection device is developed. In order to develop this device a socio-economic analysis in Latvia was performed in situation when no water purification activities were conducted, which is a typical situation for Latvian citizen's individual water supply systems.

Device cost is assessed as 150 LVL for a unit (VAT excluded), its service time is 15 years, and it is considered that all the devices will be sold during the first 5 years. Base year is 2013. Data is taken from main macroeconomic indicators and economic forecasts publicly available by the Ministry of Finance [2]. State social discount rate for the next 15 years is 5.5%. GDP growth [2] in comparative prices was used for numeric data prediction. Development costs of device were accounted. Installation of electrolytic device brings 492, 868 LVL benefit to state due to productivity growth and 40,317,191 LVL from device sales. Device production costs are 32,253,753 LVL. Dividing total earnings and costs brings a positive 1.26 large benefits and expense ratio. Installation of devices in households without centralized water supply over 15 years would bring both increased productivity to the state and profit for the device manufacturer.

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EVALUATION OF NATURAL RADIOACTIVITY IN BUILDING MATERIALS AND CLAY CERAMICS

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Building materials are a significant source of indoor gamma-ray exposure for the population due to activity of natural radionuclides K-40 and Th-232, U-238 (Ra-226) decay chain products. As yet, Latvia is one of a few EU countries in which no one has performed comprehensive measurements of natural radionuclide contents in these materials [1-2].
The aim of present work was to perform measurements of natural radionuclides in various types of building materials used in Latvia in order to establish their conformity with the Cabinet of Ministers regulations No.149 (adopted on 09.04.2002). These regulations set the maximal allowed limit for K-40 and Th-232, U-238 (Ra-226) decay chain product activity in building materials and construction elements. The most attention in this presentation is given to materials produced in Latvia.
The concentrations of K-40 and Th-232, U-238 gamma radioactivity in different building material samples (bricks, cement, concrete, natural stones, etc.) were determined in the energy range from 50 to 2000 keV using the high resolution HPGe gamma-spectrometers Ortec and Canberra. Uncertainty of measurements was within the range of 3–10 %, the minimal detectable activity – 0.3 Bq/kg for the one litre volume sample.
Results of our measurements have shown that the concentration of natural radionuclides in granite, and some sorts of ceramsite and fireproof bricks exceeds the limits allowed by regulations. High contents of Th-232, U-238 has been found also in clay. With regards to obtained results, we have undertaken a systematic study of natural radionuclide (K-40, Ra-226, Th-232, U-238) contents in clay based building materials produced by different firms in different years.
Natural radionuclide content in building materials is compared between different EU countries. For some of analysed materials the activity concentration index I is determined. Material usage safety requirements provision that this index should be lower or equal to one unit.
The credibility of obtained results is ensured by the quality assurance and control according to the main requirements of ISO/IEC 17025:2008 standard.

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COMPARISON OF DIFFERENT SOLVENTS AND EXTRACTION METHODS FOR ISOLATION OF PINOSYLVINS FROM SCOTS PINE

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Scots pine (*Pinus Sylvestris L.*) is one of the most important tree species in the Latvian economic. Approximately the content of pinosylvins in the pine wood is about 0.01-1 % (w/w). Generally, pinosylvins possess potent anti-fungal activity against a wide assortment of fungi and is secreted in situations in which the tree is susceptible to infection by fungal agents. Pinosylvins are structurally similar to the anti-cancer stilbene resveratrol. It may be assumed that this structural similarity has also to be accompaned by anticancer activity. The bioactivities of pinosylvins make them exceptionally interesting as active compounds with many potentially beneficial effects. However, their availability has been a bottleneck preventing proper studies of their effects and potential applications. Therefore, at present, the isolation of pinosylvins from different sources is actual. The aim of the present research was to determine best method for extraction of pinosylvins, comparison of solvents of different polarity (ethylacetate, acetone, and ethanol) and efficiency of traditional Soxhlet method with new ones proposed for reducing the amount of solvents, operation time and the cost of the procedure. Pine trees were felled from wet forest in the South - East part of Latvia in November 2011. The samples of heartwood and sapwood were separated from 5-10 cm thick dick of the stem and grounded using Retsch equipment. The lipophilic compounds were removing from wood by hexane extraction before isolation of pinosylvins. Sequential extraction was carried out in an ASE apparatus (ASE 350, Dionex Corp.), FBE apparatus (fexIKA 200) and Soxhlet apparatus (Gerhardt, 250mL). Pinosylvin (PS) and pinosylvin monomethyl ether (PMME) were analysed by high-performance liquid chromatography (HPLC-DAD) on Zorbax C18 column.

The data obtained have shown that ethanol is more efficient than acetone and ethyl acetate for extraction of pinosylvins (Table 1). Moreover 60% aqueous ethanol was found more prospective for isolation of pinosylvins and its derivatives. The yield of PS and PMME achieved 0.40% PS and 0.63% PMME.

Table 1. Yield (% o.d. wood) of PS and PMME from heartwood obtained with FBE extraction

Solvents	Yield of extracts	PS	PMME
Hexane	6.50	0	0
Ethyl acetate	1.66	0.21	0.31
Ethanol (96%)	1.25	0.38	0.36
Acetone	1.11	0.36	0.39

The comparison of extraction methods has indicated that ASE is more preferable than other two extraction methods, due to higher yield of PS and PMME. Pinosylvins content and yield of extractions from heartwood were much higher (5 times) than for sapwood. The results of investigation have shown that the pine wood is a prospective resource for production of valuable stilbenoids – pinosylvins.

Acknowledgement. The research leading to these results has received finding from the WOODWISDOM –NET Research programme, which is transnational R and D programme jointly funded by national funding organization with the framework of the ERA-NET WOODWISDOM-NET and the financial support from the Latvian National Programme is gratefully acknowledged.

INFLUENCE OF UV−C EXPOSURE ON THE OXIDATIVE DEGRADATION OF POLYPROPYLENE SAMPLES

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Wide varieties of plastics absorb solar ultraviolet (UV) radiation and undergo photolytic and photo-oxidative reactions that result in degradation of these materials [1]. This type of degradation is the principal component of environmental ageing of plastics. The absorbed UV light leads to the generation of free radicals. An auto-oxidation process then occurs which leads to eventual disintegration of the plastic. Photo-degradation affects physical and optical properties of the plastic, such as colouring effect, decrease of molar mass, occurrence of cracks on the surface, it loses plasticity, elasticity and strength [2, 3].

Objective of this work was to study the kinetics of photo-oxidative degradation of the isotactic polypropylene (PP) samples with thickness of 0.5 mm, under experimental conditions when wave length of UV radiation is 254 nm, energetic lightness 54 W/m^2, temperature of the samples 39°C. Exposure time of samples lasted up to 370 hours. Measurements were carried out on average every 24 hours. Thickness of PP samples and strength by stretching were measured. Magnetic characteristics were tested by measuring the inductance of the circuit made of two inductance coils with PP sample between them. The level of oxidation of the samples was tested by recording IR spectra with Nicolet IR 100 FTIR spectrometer after different exposure time. Absorbance was determined at 3410, 1713 and 1640 cm^{-1} peaks, which correspond to the absorption of peroxide, carbonyl and vinyl groups, respectively.

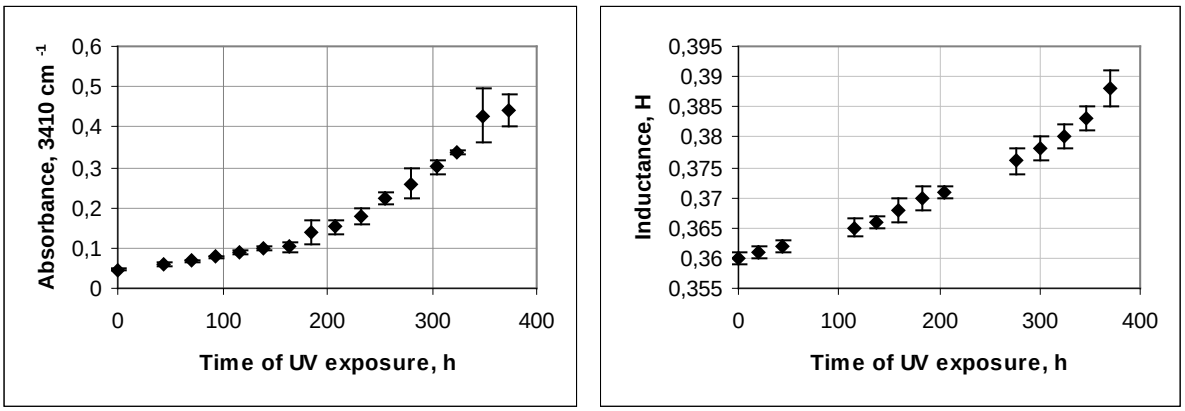

Fig 1. Dependence of PP absorbance at 3410 cm^{-1} and inductance on UV exposure time

The study revealed that radiation of high energy UV photons UV (E=470 kJ/mol), when direct photolysis of PP is possible, gives rise to fast oxidation of PP and groups of peroxides and carbonyls are formed in the polymer chains. Measuring of the inductance demonstrated that free radicals are formed in the course of the process. Up to 160 hours of exposure, thickness of the samples is constant; however, throughout longer time of UV exposure the samples gradually become thinner. Simultaneously, elasticity of the samples decreases. The cracks are formed on the surface of the samples.

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EVALUATION OF BIOTECHNOLOGICAL POTENTIAL OF CULTURE *PSEUDOMONAS FLUORESCENS* AM-PS11 TO MODIFY PROPERTIES OF LATVIAN DEVONIAN AND QUATERNARY CLAY

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Bacteria play an important role in determining the properties and behavior of clay minerals in natural environments and such interactions have a great potential for biotechnologies. Previous studies have suggested that some microorganisms found in clays secrete polysacharides, which could be as cross-bridge to aggregate the clay particles and promote increased plasticity [1-3]. Clay improvement by these bacteria was attributed mainly to mucilaginous exopolysaccharides produced during growth [4-5].

In this work an interaction of *Pseudomonas fluorescens* AM-PS11 with three different illite clay types (from Laza, Nicgale and Kuprava deposits, Latvia) and the influence of bacterial exopolysaccharides (EPS) on plasticity of these clay was studied.

Clay suspensions were incubated at 28 ^{o}C for 48h and after that at 37 ^{o}C for 24h to determine the influence of clay on bacterial growth and synthesis of EPS. Suspensions were tested for the number of colony forming units and carbohydrate concentration. Besides, plasticity number by Atterberg of treated clay was determined. The results showed that the Quaternary clay from Nicgale and Laza deposits stimulated bacterial growth and synthesis of EPS better than Devonian clay from Kuprava clay deposit. Plasticity of clay Laza and Nicgale increased with the amount of bacterial EPS synthesized and was for 1.25-1.30 times greater than without bacteria influence.

It was concluded that incubation of several Latvian clays with *P. fluorescens* AM-PS11 stimulated bacterial growth and synthesis of EPS thus resulted in an increase of clay plasticity.

Further experiments will be focused on the effect of other microorganisms and extended aging times on the reologycal properties of illite clays.

Acknowledgements. This study was financed by the State Research program Nr. 2010.10-4/VPP-5 NatRes, subprojects V7884 and Y3-26493.

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CHANGES IN CHEMICAL CONTENT OF FOREST LITTERFALL DURING THE FOUR YEAR PERIOD IN THE LATVIAN LEVEL II FOREST MONITORING PLOT

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In 1985, due to the forest health and its vitality decline, a two–level system of International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP-Forests) was established. The Level I monitoring plots provide general information about forest health. However, more intensive observations and analysis, along with quantitative analysis of the litterfall chemical content, are held in the Level II monitoring plots [1, 2]. Litterfall constitutes an important nutrient feedback to the soil and may provide essential information as a phenological indicator of the effects of climate change on forests [1]. In this study the changes in litterfall biomass and its chemical composition, as well as the changes in its input into the Scots pine (*Pinus sylvestris L.*) stand soil were investigated in order to indicate the present Latvian forest ecosystem condition. The research was carried out during 2009-2012 years in the Latvian Level II monitoring plot, which is situated in Valgunde parish of the Jelgava municipality.

In 2011 and 2012 years, the total annual litterfall production in the Latvian Level II monitoring plot decreased significantly compared to the previous years. However, during that period the biomass distribution of different litterfall fractions remained stable. Thus, pine needles provided the main part of litterfall, meanwhile wood fraction represented the second, and fruit bodies – the third highest proportion of annual litterfall production (respectively 45-55 %, 30-40 % and 10-15 % from total litterfall biomass).

The litterfall quantitative element analysis showed that higher concentrations of the nutrient such as Ca, K, Mg and Mn were observed in pine needles meanwhile trace element (Al, Ba, Cr, Cd, Co, Cr, Fe, Ni, Pb, Sr, Zn) concentrations were significantly higher in wood fraction. However, the main source of macro- and microelement input into the pine stand soil was the needle fraction, due to its higher biomass quantity compared with other litterfall fractions.

During 2009-2012 years the average annual quantities of macro- and microelement that transferred to the forest floor via litterfall fell significantly as a result of the lost of biomass in the wood fraction. The exception was manganese, which input into the soil remained stable due to its substantially higher concentration in pine needles as well as because of needle biomass stability during the four-year period.

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RESEARCH ON INDUSTRIAL AIR POLLUTION RISK ANALYSIS, CASE STUDY: OIL TERMINAL LTD „OVI RIGA”

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Industrial risk analyses and management are the main focus points in this research. Every industrial activity involves certain risks and threats. Modeling of possible industrial disaster risks, including all possible catastrophe scripts, predicting environmental consequences - are the main parameters to help understand the threats of industrial activity.
The aim of this case study is to evaluate the likelihood of industrial accidents and the consequences of the oil terminal LTD "OVI RIGA" (located close to Riga city center) with particular focus on 3 main scenarios – evaporation of volatile organic compounds, heat wave damage in case of product burning and overpressure in case of explosion. All scenarios have been evaluated only for discharge in atmosphere, soil and water environments are neglected. Mathematical modelling has been performed by software ALOHA. Additionally, possibilities of DOMINO effects or scenarios have been evaluated. All products are grouped in 5 categories depending on volatility (see table 1).

Main products and amounts handled/planned to handle in the oil terminal LTD "OVI RIGA"

Table 1

Group	Name	Product	Amount, t/yr
A	Diesels	Gas oil	15000
		Marked gas oil	5000
		Fuel oil	15000
		Petrolatum	100
B	Base oil	Base oil	90000
C	Heavy oils	Coal tar	120000
		KORB	200
		Heavy fuel oil	10000
		Paraffin	200
D	Solvents	Antiseptic GTK	1000
		Nefras	400
		Neonol	60
		Xylene	500
		Solvent	5000
E	Light oils	Aviation gasoline	1500
		K10	60000

In this study the risk chart includes environmental damage, person damage and property risks. LTD “OVI RIGA” is not legally considered to be an object of the high risk (according to the National Civil Defense Plan, approved with amendments 07/12/2013.), therefore has been assumed that consequences of industrial accident are small, so no risk assessments were formally written.

FUNCTIONAL INORGANIC MATERIALS

A METASTABLE PHASE PATHWAY FOR FORMING NANOSIZED β-TRICALCIUM PHOSPHATE

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The combination of metastable phases and apatite defect states offer alternative pathways towards more stable phases. Instead of growing crystals, it may be possible to utilize the amorphous phase transition to calcium deficient hydroxyapatite for further transformation to beta tricalcium phosphate.

Amorphous calcium phosphate ($Ca_xH_y(PO_4)_z \cdot nH_2O$, n=3–4.5) is an intermediate phase in the preparation of several CaPs. ACP is present in many biomaterials and preparations. ACP is found in several composite materials used in odontology as a remineralising phase for enamel and its inclusion in toothpaste formulations as a remineralising agent for early carious lesions [1].

CDHAp (calcium-deficient hydroxyapatite, $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$ ($0<x< 1$)) can be easily prepared by simultaneous addition of calcium- and orthophosphate-containing solutions into boiling water, followed by boiling the suspension for several hours. During this time, the initially precipitated ACP is restructured and transformed into CDHAp. Therefore, there are many similarities in the structure, properties and application between the precipitated in alkaline solutions (pH > 8) ACP and CDHAp [2].

ATCP is converted into CDHAp in aqueous media. This reaction has been studied in different temperatures. Some common features can be distinguished: an induction period is generally observed during which the amorphous state is preserved; crystallisation then occurs rather rapidly and follows a sigmoid evolution [3,4].

The objective is to determine a) the conditions for producing calcium deficient hydroxyapatite with different degrees of structural order and b) the characteristics of the beta tricalcium phosphate formed after heat treatment.

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SYNTHESIS AND PSEUDOCAPACITIVE BEHAVIOUR OF POROUS COBALT HYDROXIDE FILMS ON STAINLESS STEEL MESH

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Supercapacitors, also known as electrochemical capacitors, are considered as one of the potential energy storage systems in addition to batteries [1]. Due to the greater surface area (up to 2500 m^2 g^{-1}) and less distance between electrodes (around 0.1 nm) supercapacitors are able to store much greater amount of energy. They are distinguished by much longer cycle life (~10^6 cycles) and shorter period of charge accumulation (~0.6 s) comparing with electrochemical batteries or fuel cells [2, 3]. Supercapacitors are already used in lightweight electronic fuses, heavy and public transport, automotive, motor racings, complementing batteries and etc. [4, 5]. Ruthenium oxide, active carbon and conducting polymers are generally used as materials for supercapacitators. However, metal oxides are considered as the most promising materials. Among them cobalt oxide compounds are great candidates due to their layered structure with large interlayer spacing.

The aim of the present work was to study the structure and pseudocapacitive properties of cobalt hydroxide films deposited on stainless steel mesh.

The formation of cobalt hydroxide films was performed under galvanostatic conditions using 0.05 M $Co(CH_3COO)_2$ + 0.1 M KNO_3 electrolyte. $Co(OH)_2$ films were structurally characterized by X-ray diffraction and X-ray photoelectron spectroscopy, Fourrier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and thermal analysis (TG–DSC). The measurements of pseudocapacitance were performed by cyclic voltammetry using 0.1 M NaOH aqueous solutions. The electrochemical measurements revealed the high charging-discharging stability of the prepared β-$Co(OH)_2$ films (Fig.). The highest specific capacitance was estimated to be 945 F g^{-1}.

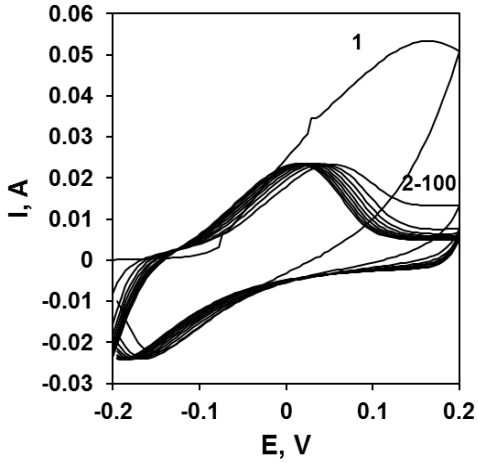

Fig. Cyclic voltammograms of β-$Co(OH)_2$ films on stainless steel mesh in 0.1 M NaOH solution at various cycles. The potencial scan rate 20 mV s^{-1}

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SYNTHESIS OF UPCONVERTING $NaYF_4$ NANOPARTICLES VIA THERMAL DECOMPOSITION OF LANTHANIDE TRIFLUOROACETATE PRECURSORS

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Upconversion is an optical process that involves the conversion of lower-energy photons into higher-energy photons. The main difference between upconversion nanoparticles and other nanomaterials is that they can emit visible light with near infrared excitation. The near infrared irradiation leads to low autofluorescence, less scattering, low absorption and deep penetration in biological samples [1]. The synthesis using the thermal decomposition of metal trifluoroacetates is widely used to prepare oleate capped lanthanide-doped upconverting $NaYF_4$:Er^{3+}/Yb^{3+} nanoparticles (Ln-UCNPs). X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) was used to characterize the UCNPs. The influence of reaction temperature, time, dopant concentration and ratio of initial reagents on the size and crystal phase purity of the as-prepared nanocrystals will be discussed.

In figure 1 is plotted the XRD patterns of $NaYF_4$. It is clearly visible that diffraction peaks of the two samples can be assigned for a pure hexagonal (β-) phase (space group $P6_3/m$), which coincides well with the literature values (JCPDS No. 16-0334).

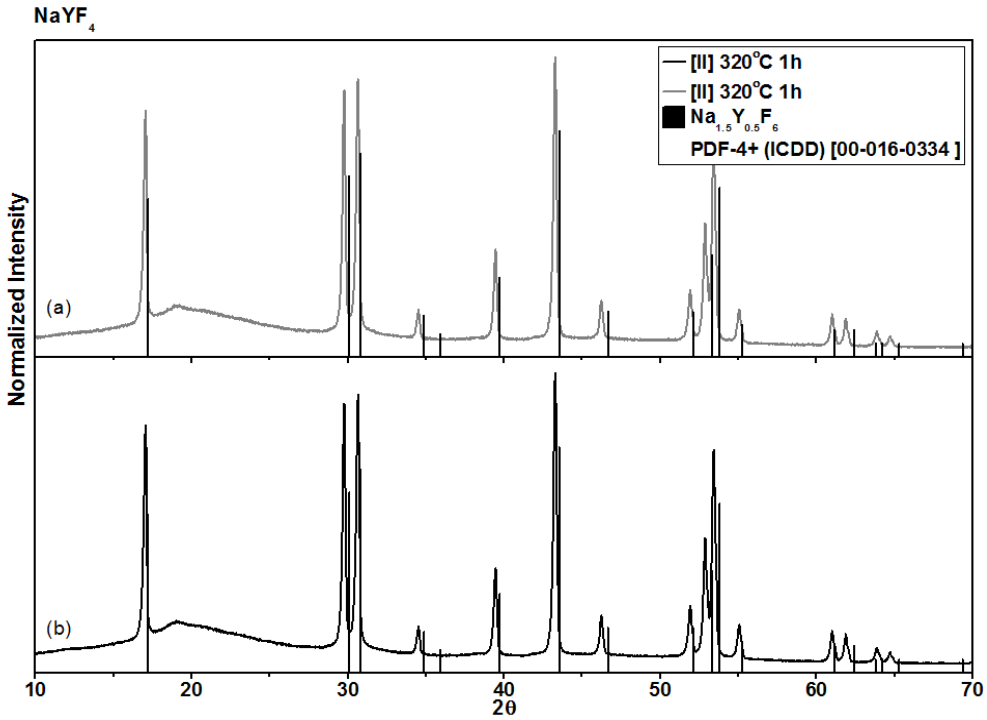

Figure 1. The XRD patterns of the as-prepared $NaYF_4$ products: (a) 5 mmol $NaYF_4$ and (b) 2,5 mmol $NaYF_4$, and the standard data of hexagonal β-$NaYF_4$ (JCPDS 16-0334) is given as a reference.

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CHARACTERIZATION OF $Gd_3Ga_5O_{12}$, $Gd_3Sc_2Ga_3O_{12}$, $Y_3Ga_5O_{12}$ and $Lu_3Ga_5O_{12}$ GARNETS DOPED WITH Cr^{3+} METAL IONS SYNTHESIZED VIA SOL-GEL COMBUSTION METHOD

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One of the most important families of hosts for luminescent dopants are garnet crystal structure materials, because of their many favourable chemical and physical properties [1]. The best known laser active compound is yttrium aluminium garnet ($Y_3Al_5O_{12}$, YAG) doped with Nd^{3+} [2]. Depending on the strength of the crystal field garnet phosphors exhibit luminescence in the red or far-red spectral region if doped with chromium. When the crystal field is strong like in YAG, luminescence occurs due to the $^2E \rightarrow {}^4A_2$ transition, which peaks at around 700 nm [3]. Substituting Al by Ga results in a weaker crystal field and in this case luminescence originates from the $^4T_2 \rightarrow {}^4A_2$ transition, which is characterized by a broad band peaking at around 720 nm [3]. This is the reason why gallium garnets are suitable to be far-red light emitting diodes, when blue inorganic GaN LED is been used for excitation. Far-red phosphors are still not enough investigated as this light area is one of the most important four light areas for plants growing [4]. Sol-gel synthesis method was chosen because of well-known advantages, such as a low sintering temperature (1000 °C) of garnet samples, an excellent homogeneity and control of stoichiometry [5]. This study deals with sol-gel combustion synthesis and characterization of $Gd_3Ga_5O_{12}$ (GGG), $Gd_3Sc_2Ga_3O_{12}$ (GSGG), $Y_3Ga_5O_{12}$ (YGG) and $Lu_3Ga_5O_{12}$ (LGG) garnets doped with different concentrations of Cr^{3+}.
Sol-gel combustion method has been developed for the preparation of doped with different concentrations of Cr^{3+} garnet structure compounds. GGG doped with 5 mol% of Cr^{3+} metal ions, GSGG - 8 mol% of Cr^{3+}, YGG - 8 mol% of Cr^{3+} and LGG - 3 mol% of Cr^{3+} were synthesized using high purity Gd_2O_3, Sc_2O_3, Y_2O_3, Ga_2O_3, Lu_2O_3, $Cr(NO_3)_3 \cdot 9H_2O$ as starting materials and $NH_2C(CH_2OH)_3$ both as complexing agent and fuel for self-burning reactions. Cr^{3+} concentrations for a doping were chosen because of earlier studies. The products after combustion reaction were preheated at 800 °C and finally sintered at 1000 °C, 1300 °C, 1400 °C and 1500 °C in air. The synthesis products were characterized employing XRD, SEM, and EDX analysis methods.

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CALCIUM COMPOUNDS FOR PAPER DEACIDIFICATION

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Documents, books and artworks from paper are slowly degrading due to the inherent ageing of the cellulose substrate or the technological errors of the past (acid paper, iron gall ink). Aqueous deacidification is the most widespread chemical treatment in paper conservation. The main stabilization procedure of damaged documents – deacidification process. Aqueous solutions of calcium and magnesium compounds have been widely used for many decades, and nanoparticles of calcium hydroxide just started to be used for wall painting conservation. Smaller size of particles should ensure greater penetration efficacy in panted surface layer, so same have to be with paper fibres.

The object of study was to get suspension of nano-$Ca(OH)_2$ particles suitable for paper deacidification. According sol-gel method prepared solution was tested and compered with currently widely used deacidification methods – commercial Bookkeper and $Ca(OH)_2$ prepared by Barrow method.

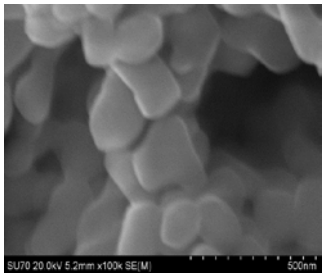

Fig. 1. a.SEM picture of prepared $Ca(OH)_2$ particles;

Suspensions of obtained particles were used for cotton paper treatment. Samples aged in heat of 90 ^{0}C for 512 h. The pH values and alkaline reserve results of treated paper showed that synthesized nano-$Ca(OH)_2$ compound with stabilization of gelatin are more effective for paper conservation than Bookkeeper or commercial $Ca(OH)_2$. Using stabilized nanoparticles after accelerated ageing pH value of treated paper decrease 0.79 of value, alkali reserve - 0.08, and using Bookeeper respectively – 1.51 and 0.24 of value, for $Ca(OH)_2$ – 1.69 and 0.18. Strength tests confirmed that paper treated with nano-$Ca(OH)_2$ was more stable.

The results of IR spectroscopic analysis showed that all deacidification systems reduce the formation of the acidic species on paper.

EXPLORING ZINC INCORPORATION IN APATITE FOR ORTHOPEDICS AND DENTISTRY

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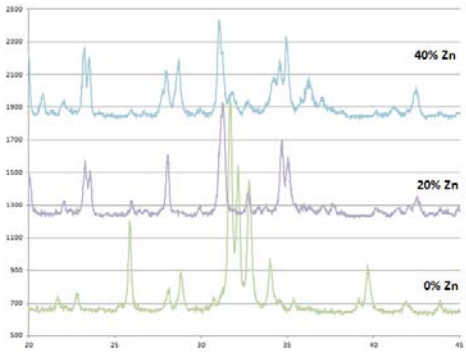
Zinc as the most abundant trace metal in bone minerals, is an essential element that has effects on bone formation as well as inhibitory effects on bone resorbtion. Inclusion of zinc in apatites is not completely understood due to complexes in solution preventing the incorporation or the inclusion of defects. Some work has shown zinc addition by alternative synthesis routes, but the level of incorporation has not been reassessed. This work uses a newly developed approach whereby zinc is included in an amorphous phase and subsequently crystallized. Different phosphate reactants (ammonium, sodium or potassium phosphates) were mixed together with calcium salts (calcium nitrate, calcium chloride or calcium acetate) and the pH level adjusted (with ammonia, NaOH or KOH) to investigate the ease of forming an amorphous phase and the inclusion of zinc. X-ray diffraction revealed that all reactants showed a tendency to form an amorphous phase, supporting the requirement of a high pH to prevent crystallization. X-ray fluorescence showed higher inclusion in the absence of ammonia. Potassium phosphate led to the highest zinc incorporation, accompanied by simultaneous inclusion of potassium. Crystallization at 700 ^{o}C indicated that zinc levels close to 20% replacement of calcium were the highest possible before the onset of tricalcium phosphate formation. FTIR-DRIFT showed a change in bonding conditions at higher zinc concentrations. This work shows the importance of reactants for including zinc, the larger zinc inclusion accompanied by potassium and zinc levels that can maintain the apatite structure.



XRD-spectra. HA parameters with an increase of expected Zn content in the absence of ammonia.

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SYNTHESIS AND PHOTOLUMINESCENCE IN $NaLaF_4:Eu^{3+}$ MATERIAL

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It is known that most of the fluoride and complex fluoride materials have relatively high chemical stability, moreover, these materials have small phonon energy which suppresses the rate of nonradiative transitions. These properties make fluorides very attractive as host materials for optically active trivalent rare-earth ions. Numerous studies on optical properties of fluoride and complex fluoride materials have been conducted for several decades, however not much information can be found about processes in europium doped $NaLaF_4$ material.

One of the most important problems of fluorides is oxygen-related defects which emerge as result of synthesis of the material. The presence of oxygen defects in fluorides may have negative effect on photoluminescence intensity and the quantum yield [1, 2].

In this work $NaLaF_4:Eu^{3+}$ samples with different Eu^{3+} concentrations were synthesized by solid-state reaction. The synthesis was performed using different annealing temperatures and atmospheres (air or fluorine). For these samples photoluminescence spectra, excitation spectra, luminescence decay kinetics and X-ray diffraction patterns were measured.

From the analysis of the obtained experimental data conclusions about composition and optical properties of the material were made. Optical transitions and cross-relaxation processes in the activator system as well as formation of oxygen related defects and their impact on material optical properties are discussed.

This research is a part of extensive studies of different rare-earth doped and codoped $NaLaF_4$ materials, their synthesis, optical properties and possible applications [3, 4].

The financial support of VPP IMIS is greatly acknowledged.

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IRON-DOPED/SUBSTITUTED CALCIUM HYDROXYAPATITE FROM SEASHELLS: SYNTHESIS AND CHARACTERIZATION

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Bioactive materials are currently at the leading edge of regenerative medicine research due to the predictable need for bone tissue regeneration as an effective way to improve the current medical practice of bone replacement.

To date the role of iron in bone accumulation has received little attention, however, a few studies have previously shown that iron restriction might have an inhibitory effect on the mineralization of osteoblasts *in vitro.* Moreover, experimental evidence suggests that there may be some positive association between iron metabolism and the *in vitro* proliferation of bone or non-bone cell lines [1-3].

Considering the importance of having pure and non-toxic calcium hydroxyapatite for a number of biomedical applications, and the significant role of iron in bone regeneration and remodeling, this study aimed to synthesize Fe-doped/substituted calcium hydroxyapatite via sol-gel combustion method employing *Macoma balthica* (*L.*) sea shells as the precursor of calcium.

The developed apatite was characterized applying the following analytical techniques: Fourier transform infrared spectroscopy (FTIR), X-ray diffraction analysis (XRD), energy-dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM).

Observed data were in good agreement with the standard values for calcium hydroxyapatite, which indicated successful formation of the Fe-doped/substituted calcium hydroxyapatite. The magnetic behaviour and iron Mössbauer spectroscopy will be used to give added information on nanoscaled Fe-doped/substituted hydroxyapatite powders. The other physical properties of synthesized products will be also studied.

Acknowledgment
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PREPARATION OF INDIUM-TIN OXIDE NANOPARTICLES AND THEIR INTERACTION WITH PHOTOCONDUCTING POLYMERIC GEL

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Indium tin oxide (ITO) is widely used for optoelectronic applications [1]. However, it has several drawbacks such as brittleness of ITO films, and scarce supply and high cost of indium. On the other hand, in the development of the optoelectronic devices organic molecules play significant role [2, 3], but properties such as conductivity and transparency have still to be balanced in these materials.
In this work we designed a new inorganic-organic hybrid material (IOHM) composed of ITO nanoparticles and photoconductive polymeric gel, based on the pyridine molecule (poly(4-vinyl pyridine)) aiming to enhance conductivity of the polymeric gel and reduce brittleness of ITO film. Several IOHM preparation approaches were used. TG, XHR-SEM/EDX, ICP-OES, XRD, AFM and C-AFM were used for the characterization of ITO, IOHM and to investigate an interaction between ITO and photoconductive polymeric gel. The new reactions for the further research will be proposed.

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PHASE EQUILIBRIUM AT POTASSIUM CHLORIDE AND AMMONIUM DIHYDROGEN PHOSPHATE SOLUTIONS

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Potassium chloride is one of the most common potassium fertilizer. This advantage of potassium chloride is high chloride concentrations and it prevents fertilization of some crops: grapes, hops, tobacco, many vegetables, especially flowers. For fertilize of this plants is needed chlorine-free potassium fertilizers as such potassium nitrate, potassium sulfate, potassium phosphate.

Great interest of potassium phosphate is using for greenhouse crop production, because the great concentration of potassium and phosphorus, but they are limited by expensive techniques and expensive chlorine-free material.

The aim - to investigate potassium chloride and ammonium dihydrogen phosphate interactions in aqueous solutions. As well as to determination the conditions of formation solid phase of potassium dihydrogen phosphate.

Potassium chloride and ammonium dihydrogen phosphate conversion reaction was studied by determining of liquid and solid phase in equilibrium isomolar series solutions. The salt water solution prepared by dissolving the starting material - potassium chloride and ammonium dihydrogen phosphate - at ratio of 1:0, 0.8:0.2, 0.6:0.4, 0.5:0.5, 0.4:0.6, 0.2:0.8, 0:1. Total number of moles is equal 5.5. A solid and liquid phase was analysed after keeping 5 h duration in isothermal conditions at 40 °C temperature. Equilibrium solid phase was filtered and dried.

Liquid and solid phase was studied by standart chemical analysis methods:

a) ammoniacal of nitrogen (NH_4) content - by the Kjeldahl method [1 – 3];
b) phosphorus (P_2O_5) content - photocolorimetrical method (after converting to P) [1, 3, 4];
c) potassium (K_2O) content - the critical solution method (after converting to K) [2 – 5];
d) chlorine (Cl^-) content – potentiometrically using a silver nitrate [2, 6].

The results show that the liquid phase composition is very different depending on the starting materials. Content nitrogen varies from 2.57 to up 2.98 %, as well as phosphorus from 0.46 to up 2.83%, potassium from 4.76 to up 22.04%, and chlorine – from 3.62 to up 13.39 %. Solid phase composition varies as follows: nitrogen - from 1.82 to up 10.29 %, phosphorus - from 21.50 to up 25.99 %, potassium - from 7.83 to up 64.87 %, and chlorine – from 0.85 to up 3.25 %.

The results shows that the largest concentrations of potassium at solid phase was obtainal when ratio of potassium chloride and ammonium dihydrogen phosphate was equal 0.8:0.2.

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PROBING THE EASE OF ANION EXCHANGE IN BONE MINERAL

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Bone mineral is easily modifed due to the defects and substitutions in the apatite lattice, but can the ease of processability be extended to non-physiological conditions. Anions in the hydroxyl column are the most mobile. The objective is to see if changes can be made to the hydroxyl concentration and whether a replacement with carbonate or peroxy ions is possible. Bone mineral was formed by heating cattle bone to remove the organic fraction. This allowed work on just the apatite structure. The apatite lattice was confirmed by X-ray diffraction and then processed in an atmosphere containing steam, steam and peroxy ions or steam and carbonate ions. Thermally processed bone was characterized with X-ray diffraction for the structure, FTIR for bonding and UV-VIS spectroscopy for the peroxy ions. Results will be discussed in reference to hydroxyapatite to show the ability of calcium deficient apatite to be modified in the anion content related to species occupying the hydroxyl column.

NANOSILICA COATINGS MADE BY SOL-GEL AND CHEMICAL NANOTECHNOLOGY

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Today the sol-gel technology expands rapidly and many new products are appearing in the market, especially since the advent of hybrid and nanocomposite materials. Most of the products are coatings which are developed to exhibit several functional properties using precursor solutions and easy and fast processing. Inorganic-organic hybrid coatings by sol-gel process are very suitable for fighting corrosion. Inorganic sols in hybrid coatings not only increase adhesion by forming chemical bonds between metals and hybrid coatings, but also improve comprehensive performances of polymer in the coatings. The effect of UV-curing time on the mechanism of interaction between the various precursor phases in a novel sol-gel-derived organic-inorganic hybrid coating material and the resulting mechanical and thermal properties of this material when coated onto substrates in thin film form have been examined using a variety of chemical and physical characterisation methods. Thin films have wide applications in the area of optics and photonics. Conventional thin film processing is usually followed for deposition, but the sol-gel route is unique as it can be applied very easily in a cost effective way on desired substrates of any shape for specific applications.

The main aim of the present study was to synthesize nanostructured silica coatings modified with hexamethyldisilazane (HMDS) on different substrates (glass, quartz and KDP crystal) using sol–gel processing by dip-coating technique. The precursor of SiO_2 colloidal sol was prepared by the base (NH_3) catalyzed hydrolysis of tetraethylorthosilicate (TEOS, $C_8H_{20}O_4Si$, ≥98 %). The schematic presentation of modification reaction of nanosilica with HMDS is shown in Fig. 1.

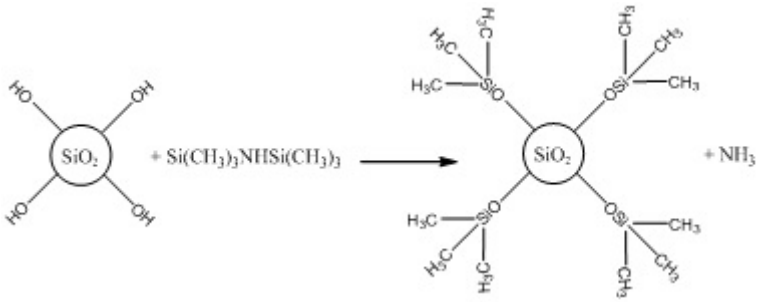

Fig. 1. Modification of nanosilica with HMDS.

It was determined that the modification of nanosilica coatings with HMDS reduced the reflection from the surface, and the obtained value of contact angle (164.98^o) showed high hydrophobicity of the modified surface.

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STUDIES OF THE POZZOLANIC ACTIVITY OF SOME NATURAL MINERALS AND INDUSTRIAL WASTE

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The application of supplementary cementitious materials or pozzolanic additives in the production of concrete could be based on several considerations, e.g., aimed to improve or alter some properties of concrete, to reduce the expenses for raw materials, to diminish the consumption of Portland cement and thus the emition of CO_2, which occurs during production of cement clinker. The basis of the use of pozzolanic materials in partial substitution for clinker in Portland cement is the ability of the alkaline medium produced by the hydrating cement to break down the silica or the alumina-silica networks in the particles they contain to form C-S-H (calcium silicate hydrate) [1].
In order to evaluate the pozzolanic activity of thermally treated clays (calcinated kaolinite and Devonian clay of Latvian origin) as well as waste product – coal ash (altogether called as micro additives), the research work has been carried out analysing their different properties: specific surface area (BET), surface morphology (SEM), particle size distribution (measured by zeta potential), chemical composition (content of reactive SiO_2 and R_2O_3), as well the pozzolanic ability or lime-combining capacity in the reaction with $Ca(OH)_2$. Obtained results indicated that the fineness of particles is of great significance in lime – pozzolana reaction, more reactive are micro additives with larger specific surface. However this assumption is valid to some optimal level of fineness, as further grinding of particles is not giving satisfactory results and indicates that during grinding the particles are forming agglomerates which should be dispersed in a solution for better reaction with lime. It also could be concluded that the selected micro additives improves the mechanical properties of concrete matured 28 days, working both as micro filler as well the additive for binder.

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PREPARATION AND MICROSTRUCTURES OF ALUMINA-NICKEL COMPOSITE COATINGS SHAPED BY ELECTROPHORETIC DEPOSITION

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Over the last decade ceramic-metal composite coating production has been of increased interest, due to its mechanical, optical and electrical properties. One of cermets applications is in solar thermal collectors as absorber because of the composites ability to be permeable for IS region but absorb visible light region [1].

Among all traditional deposition methods electrophoresis has the advantages of obtaining coatings with homogenous surface, complex geometry and advanced component variety [2]. One of important factors influencing EPD is the dielectric constant of non-aqueous liquid media that for optimal results must be in the range of 12-25. For propanol-2 the relative dielectric constant is 20 [3]. The ratio of Al_2O_3:Ni powders in suspension was 70:30 in order to produce ceramic-rich coating and the applied working potential was in the range of 20 – 100 V. After deposition the coating on stainless steal electrode was dried for 24 h and sintered at 1350 °C for 2 h [2].

Phases of obtained alumina-nickel coatings were characterized by X-ray diffraction. Microstructures of cermet samples were analyzed using scanning electron microscopy. The thickness of coatings was measured using profilometer.

In summary, relatively thick composite alumina-nickel coatings were successfully deposited by EPD followed by sintering. Ni nanoparticles were evenly distributed in Al_2O_3 matrix. The Ni particles embedded in ceramic matrix composite microstructure and the preparation method may find a wide range of application.

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QUATERNARY AMMONIUM COMPOUNDS AS BIOCIDES FOR PAPER DOCUMENTS CONSERVATION

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The microbiological contamination problem may occur when the document repositories, reading rooms or other spaces premises failure to comply the proper hygiene norms and storage microclimate, so resulted in favourable condition of moisture and temperature for bacteria and fungi growth. Climate control, frequent cleaning and monitoring of the objects are the most important prevention measures which reduce fungal growth and spreading intensity [1, 2]. For disinfection of a fungal damage a limited physical and chemical methods are used. Chemical treatments include liquid biocides and fumigation with gases. For preserving practice the most commonly used materials are derivatives of phenol, formaldehyde, gas of ethylene oxide. Recently the most promising biocide materials are quaternary ammonium compounds used for medical, pharmaceutical and other fields. The aim of this work is to study the possible application of quaternary ammonium salts: *Bromosept 50* and *P-3 Triquart AB* for paper restoration process.

Bromosept 50 and *P-3 Triquart AB* have been investigated as biocides for paper document treatment. The most prevalent types of paper deplete microorganisms are the following: *Aspergillus clavatus Desm,·Penicillium Paneum Frisvald,·Ulocladium chartarum Preuss.* The filter paper samples were immersed in black or brown historical ink solution [3]. The negligible changes on paper acidity and optical properties were observed after treatment inked samples with biocides solution (1%). The fungi growth was tested on 5 and 10 day, images of *Penicillium paneum Frisvald* fungi damaged samples after 10 days are presented in Figure 1.

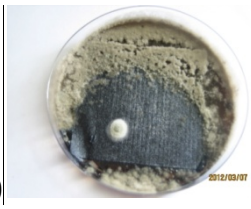
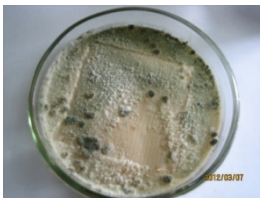
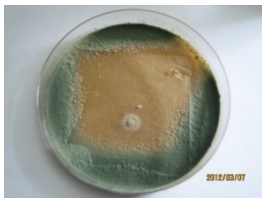
a)  b)  c)  d) 

Fig. 1. *Penicillium paneum Frisvald* fungi growth on treated paper samples with: (a) black ink, (b) black ink and *Bromosept 50* 1% aqueous solution; (c) brown ink, (d) brown ink on paper treated and *Bromosept 50*.

Biocide *Bromosept 50* and *P-3 Triquart AB* were investigated for the antifungal activity against fungi: *Aspergillus clavatus Desm,·Penicillium Paneum Frisvald·Ulocladium chartarum Preuss.* The results indicated that the antifungal activity of biocide is different, depending on fungi type, used concentration, ink and paper composition.

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ACQUISITION OF INDUSTRIAL WASTE CONTAINING POROUS GRANULES AND THEIR SORPTION PROPERTIES

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Several innovative suggestions on how industrial wastes could be utilized in new products have been presented in the literature, mainly focused to elaboration of dense glass-ceramic materials. The production of porous granules by thermal treatment–using different Latvian industrial waste (aluminum scrap metal processing wastes, metallurgical slag, cut glass waste, sewage sludge) and raw mineral materials (clay), could be one of the possibilities to recycle waste. In the given work three mixtures from mentioned industrial waste and limeless clay were studied. In order to produce porous granules, raw materials were sieved through a mesh size from 0.5 till 2.5 mm, covered with titanium oxide and treated thermally in temperature range from 1080 till 1160°C.

Obtained results confirm that porous granules were possible to acquire. Three different granular compositions were obtained and properties of which were investigated. The density of porous granules is from 1.18 g/ cm^3 till 2.2 g/cm^3, water uptake from 20% till 33% and porosity from 31% till 59%.

The experiments using water solution with various chemical compositions in order to detect the sorption properties of produced waste mixtures containing granule were performed. Results show the decrease of iron compounds content during treatment of granule with iron containing water solution. The optimal composition, showing the best sorption properties, was developed from mixtures containing 50 – 80 (wt.%) clay as a matrix material, 10 – 60 (wt.%) sewage sludge as well as 10 – 30 (wt.%) of waste glass. Obtained materials could be used as iron sorbent material in water purification process.

The results obtained means that along with dense glass-ceramic materials produced from industrial waste it is possible to make also porous granular materials. New produced porous granular materials perform the good sorption properties and they could be used in the water purification instead of natural mineral materials.

Acknowledgement
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SYNTHESIS AND SURFACE MODIFICATION OF $NaYF_4$ NANOPARTICLES DOPED WITH RARE EARTH METALS

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In recent years studies on lanthanide-doped upconverting nanoparticles (UCNP) have been attracting more and more attention due to their unique properties and advantages over most commonly used fluorescent probe. Having longer detection times, being nontoxic and biocompatible, UCNP have major advantages in terms of use in biomedicine [1, 2]. Thermal decomposition in organic solvent is one of most common route of synthesis for upconverting $NaYF_4$:Yb^{3+}, Er^{3+} nanoparticles. However, UCNP provided by this method are hydrophobic, non-biocompatible, thus requires surface modification.

In a typical synthesis procedure [3], dried lanthanide precursors ($RE(CF_3COO)_3$, RE= Y, Yb, Er) and 2.5 mmol CF_3COONa were added along with 7.5 ml each of oleic acid and 1-octadecene and mixed at 150°C under vacuum. Solution was slowly added to a mixture of 12.5 ml oleic acid and 12.5 ml 1-octadecene at elevated temperature and maintained for 1 h. The resulting product was dried and investigated with SEM, TEM, XRD, FTIR. X-ray diffraction patterns and SEM reveals that by increasing reaction temperature more efficient, polidisperse hexagonal β- $NaYF_4$ particles were acquired. In order to convert hydrophobic UCNP into hydrophilic ones modifications were performed by adding phospholipids [4] (DSPE-PEG-COOH) into UCNP-chloroform solution or removing oleic acid ligand from the surface. TEM analysis of aqueous solutions shows that surface properties of $NaYF_4$:20% Yb, 2% Er nanoparticles has changed (Fig. 1).

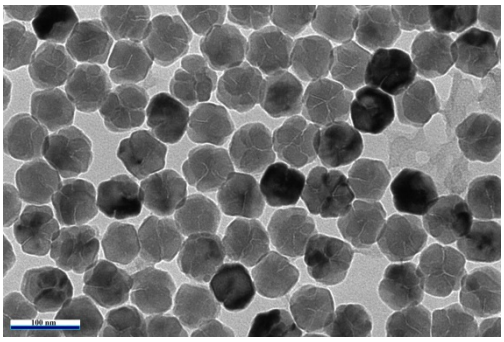
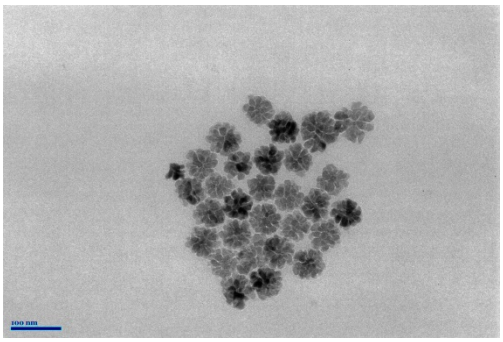
a)  b) 

Fig. 1 TEM images of $NaYF_4$:20% Yb, 2% Er a) before modification, b) DSPE-PEG-COOH coated

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SYNTHESIS AND INVESTIGATION OF DIFFERENT STRONTIUM ALUMINATES

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Despite large similarities with their closely related calcium counterparts, strontium aluminates have received much less interest. Beside their potential as refractory oxides in the steel industry and binder materials in the cement industry, they are of interest in materials science because of their use as long-duration photoluminescence or thermoluminescence pigments [1]. Most of the literature deals with the strong green emission (~530 nm) of Eu^{2+} in stoichiometric $SrAl_2O_4$ with monoclinic structure [2], although there are more possible strontium aluminates phases. There are four stable double oxides, namely $Sr_3Al_2O_6$, $SrAl_2O_4$, $SrAl_4O_7$ and $SrAl_{12}O_{19}$ [1]. Moreover, there are more strontium aluminates phases described in the literature, such as $Sr_4Al_2O_7$, $Sr_4Al_{14}O_{25}$, $Sr_{12}Al_{14}O_{33}$ and $Sr_{10}Al_6O_{19}$ [1, 3].
During this work, sol-gel synthesis was applied in order to obtain $SrAl_2O_4$, $Sr_3Al_2O_6$ and $SrAl_{12}O_{19}$ samples. Rietveld analysis of XRD data revealed that monophasic $SrAl_2O_4$ and $SrAl_{12}O_{19}$ samples were prepared, however, synthesis of $Sr_3Al_2O_6$ sample resulted in the mixture of different phases, although $Sr_3Al_2O_6$ phase was dominant. Optical properties of cerium doped strontium aluminate samples were investigated.
Single phase $Sr_4Al_{14}O_{25}$ compound was successfully synthesized by conventional solid state reaction method. The samples of $Sr_4Al_{14}O_{25}$ with partial Sr^{2+} substitution by Ca^{2+} and Ba^{2+} were also prepared. The X-ray powder diffraction patterns have been refined using Rietveld method.

Acknowledgement
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PECULIARITY OF THE USAGE OF RED OCHRE FOR THE PREPARATION OF CERAMIC GLAZES

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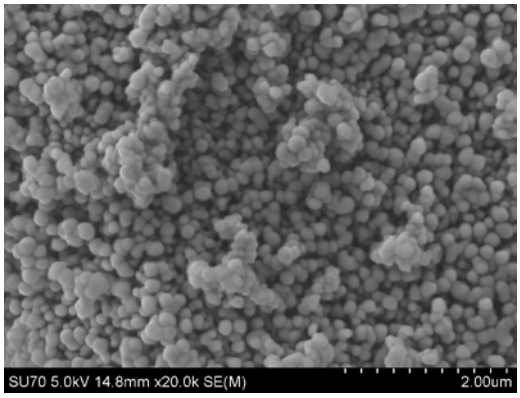
Synthetic and inorganic pigments are widely used in ceramics industry as colour agents for glazes and pottery [1]. Despite the fact that there is a huge variety of colorific inorganic materials, the producers are still interested in creation of pigments with new properties [2]. The pigments of high stability, intense tonality, which fulfil economical and ecological requirements, are important for the producers, investigators and users of the pigments [3].
In this study, synthetic red ochres were synthesized using sol-gel technique in the temperature range of 500-1000 °C. Interestingly, all produced pigments were different in colour from red to purple. It was estimated by X-ray diffraction analysis (XRD) that single-phase iron (III) oxide pigments were synthesized in whole temperature range. It was demonstrated that the colour of red ochre could be slightly controlled by annealing temperature.
Scanning electron microscopy (SEM) was used to evaluate the morphology of the pigments. Fig. 1 shows the micrographs of red ochre pigments, synthesized at 500 °C (a) and 1000 °C (b) temperatures.

a) 

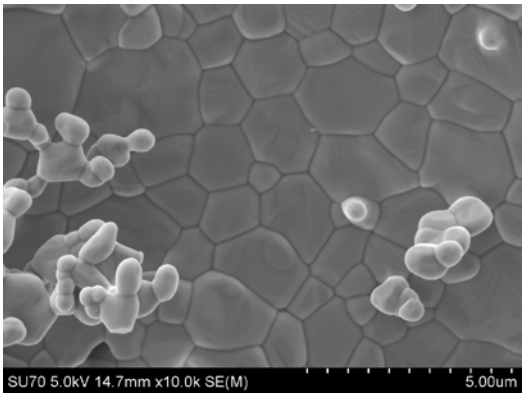
b) 

Fig. 1. SEM micrographs of red ochre pigments synthesized at 500 °C (a) and 1000 °C (b).

As seen from Fig. 1, the particle size and shape are changing by changing annealing temperature. These observations let us to conclude, that particle size and shape influence the colour of red ochre pigment.
Synthesized iron (III) oxide pigments were used for the preparation of ceramic glazes. High quality glazes were obtained at 1000 °C using sol-gel derived Fe_2O_3 pigments.

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PHOTOACTIVITY AND STABILITY OF A COBALT-BASED OXYGEN EVOLVING CATALYST ON A WO_3 PHOTOANODE

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Recently, several simple techniques for the production of cobalt-based (denoted as Co–Pi) oxygen evolving catalyst (OEC) were reported which mainly focuses on electrochemical [1] or photochemical deposition [2] routes in the aqueous neutral phosphate medium containing Co^{2+} ions. If this Co–Pi OEC is deposited on an n-type semiconductor electrode, the photogenerated holes can be directly used to evolve O_2, and photogenerated electrons can be used for the photoreduction reactions [2, 3], which is relevant to developing a photoelectrochemical method for the generation of hydrogen and oxygen from aqueous solutions.

The aim of this work was to modify tungsten trioxide (WO_3) coatings on AISI 304 stainless steel with cobalt-based OEC and to study their structure and photoelectrocatalytic activity in aqueous solutions.

WO_3 coatings on stainless steel were prepared by electrochemical deposition using peroxy–tungstic acid solutions. A photoelectrochemical quartz cell was employed with AISI 304 stainless steel as a working electrode, Ag, AgCl│KCl(sat) as a reference electrode and platinum wire as a counter electrode. As-prepared photoanodes were rinsed and then annealed at 400 °C for 1h in air. Co–Pi OEC layer was photochemically deposited onto WO_3 electrodes by placing them in a 0.1M phosphate buffer (pH 7) containing 0.5 mM $Co(NO_3)_2$ and then irradiated for various periods of time with a 400 W high pressure metal halogen lamp.

The experimental results show that Co–Pi OEC layer catalyzes the evolution of oxygen by shifting the onset potential to the positive direction by approximately 600 mV (Fig. 1). It also improves the photocurrent of WO_3 electrode if photochemical deposition of Co–Pi OEC layer lasts for 10–30 min (Fig. 2). The structure and photoelectrochemical stability of as-prepared photocatalysts were also investigated.

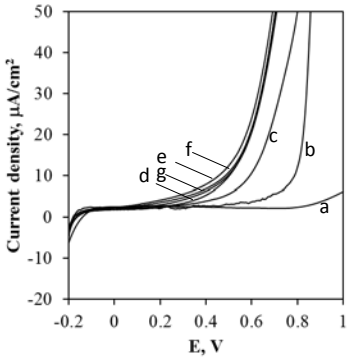

Fig. 1. Characteristic voltammograms in the dark of bare WO_3 electrode (a) and WO_3 electrode coated with Co–Pi OEC for 10, 20, 30, 40, 50 and 60 min (b–g, respectively). Potential scan rate 10 mV/s, 0.1M phosphate buffer (pH 7)

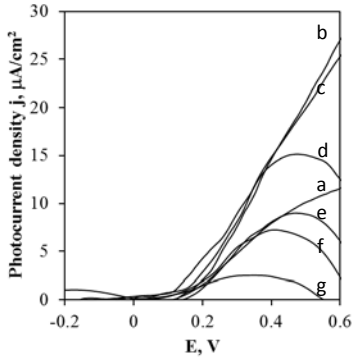

Fig. 2. Photocurrent density of bare WO_3 electrode (a) and WO_3 electrode coated with Co–Pi OEC for 10, 20, 30, 40, 50 and 60 min (b–g, respectively)

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ONIC LIQUID BASED SYNTHESIS OF LUMINESCENT NANOCRYSTALS AND THEIR STUDY BY MEANS OF ULTRAVIOLET EXITATION SPECTROSCOPY

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In present work we have summarized results for several types of luminescence nanoparticles (rare earth doped $LaPO_4$, $CaMoO_4$, CaF_2, etc.) having a high practical as phosphors and scintillators for scientific, industrial and increasingly medical purposes, and as dosimeter materials. All nanocrystals in the current study have been produced by means of the microwave-assited synthesis in ionic liquids. This synthesis method allows the efficient control of nanoparticles size, their morphology and impurity level [1-3]. The luminescence emission and excitation measurements were carried out under pulsed synchrotron radiation (3.6 – 40 eV) emitted from DORIS III storage ring on the SUPERLUMI station of HASYLAB at DESY (Hamburg, Germany). Special attention was paid to the vacuum ultraviolet spectral range, which is not reachable in standard commercial spectrometers and “in house” equipment. Peculiarities in emission and excitation spectra of luminescent nanoparticles as well as the influence of surface states on luminescence properties of nanoparticle will be demonstrated and discussed.

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PRODUCTION OF SILICA – SILVER NANOPRISMS COMPOSITES FOR FURTHER APPLICATION TO LASER SYSTEMS

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Noble metal nanoparticles chemistry is a domain in rapid expansion, as those objects lead to interesting applications in various fields. Two-dimensional assemblies of metal nanoparticles can be applied in catalysis, photonics, electronics, and biological sensing [1]. Silver nanoprisms (AgNp) may have high intensity surface Plasmon resonance (SPR) in longer wavelengths (500 – 1200 nm) due to their anisotropic shape [2]. As known, AgNp's have high non-linear index (non-linear refractive index, named Kerr effect) when SPR peak matches incident light wavelength. These features make AgNp's perfect for application on near-infrared (NIR) optical fiber communications [3]. Due to thermal, chemical stability and low light absorbance in NIR region silicon dioxide can be ideal matrix for AgNp's.
In this study AgNp-silica composites where made by self-assemblied nanoparticles on silica coated-modified surface. Nanoparticles where synthesized via seed-mediated method [2]. Monodisperse AgNp's are ~50 nm length, few nanometers thick and have SPR peak at 800 nm. Colloidal silica was made by Stober method, glass substrates where coated using dip-coating technique and different silanes ((3-Aminopropyl)triethoxysilane APTES, (3-Mercaptopropyl)trimethoxysilane MPTS, [3-(2-Aminoethylamino)propyl]trimethoxysilane, AEAPTS) where used for modification of silica surface. Modified silica coatings were kept in Ag nanoprisms colloidal solution for 1 week. Silica/Ag nanoprisms coatings were investigated by FT-IR, SEM, EDS, DLS, water contact angle methods.

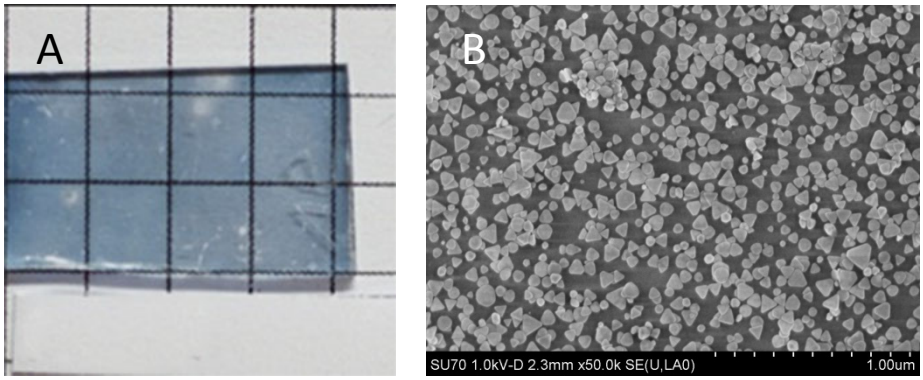

Fig. 1. Silica-Silver composite coating: A – photo image of coating; B – SEM image

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LOW FREQUENCY NOISE CHARACTERISTICS OF $BaTiO_3$ COMPOSITES AT PHASE TRANSITION

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Composite ferroelectromagnetic materials have recently stimulated much scientific and technological interest as coexistence of magnetic and electric subsystems allows for an additional degree of freedom in the design of actuators, transducers, and storage devices, high quality resonators and capacitors [1, 2]. High dielectric constant, low capacitor tolerance, good processibility and low cost are required for the composite materials on purpose to employ them in practice. New materials require comprehensive study of their physical characteristics. Investigation of low frequency noise characteristics is well known as very sensitive method to clear up a nature of physical processes in materials and devices [3]. In this work we present detailed low frequency noise characteristic investigation of $CoFe_2O_4$-$BaTiO_3$ and $BaTiO_3$-$NiFe_2O_4$ ceramic composites. Aim of the study was to find out noise characteristics of the composites in the phase transition region, to clear up physical processes that take part during the transition.

Low frequency (20 Hz – 20 kHz) noise characteristics (current fluctuation spectral density) were measured under continuous wave operation in temperature range from 230 K to 370 K. Noise measurements were performed in a specially shielded room (Faraday cage) in order to avoid interfering effects from electrical network and communication systems.

The investigation results show that at particular temperatures noise signal turns to random telegraph (RT) noise. In temperature range where RT noise is not observed noise spectrum has $1/f$ type that is characteristic for many materials and devices and caused by superposition of many physical processes with widely distributes relaxation times. RT noise was observed as sharp noise intensity peaks at 279,4 K, 300,0 K and 311,0 K temperatures. The spectra of observed RT noise have peak in frequency range (0,1 – 1) kHz, therefore characteristic relaxation time of the observed processes ranges from 0,1 ms to 1 ms. The origin of RT noise could be ferroelectric Barkhausen noise.

The temperatures where RT noise peaks were observed get under the broad maximum of dielectric permittivity that was observed for the investigated composites around 300 K (pure $BaTiO_3$ has phase transition at 287 K). Therefore we conclude that phase transition in the investigated materials goes through three separate stages instead of the smeared out one. And sensitive low frequency noise characteristic investigation enables to segregate these stages.

Aknowledgement
The study was funded from the European Community's social foundation under Grant Agreement No. VP1-3.1-ŠMM-08-K-01-004/KS-120000-1756.

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SYNTHESIS OF SODIUM YTTRIUM FLUORIDES VIA CO – PRECIPITATION AND HYDROTHERMAL METHODS

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Colloidal inorganic crystals has great fundamental and technical interest due to their unique properties which are dependent on crystal size and shape [1]. Resent publications have reported that colloidal $NaYF_4$ hosts in either α- or β-phase doped with RE (RE = Er, Yb, Ho or Tm) are the best candidates for biological applications. High-quality cubic (α-phase) and hexagonal (β-phase) $NaYF_4$ particle size are dependent on the nucleation rate, which, in turn, is influenced by the reagents concentration, molar ratio and choice of ligand. The phase transformation from cubic to hexagonal is sensitive to reaction time, temperature and reactant concentration [2].

$NaYF_4$ samples were synthesized using co – precipitation and hydrothermal methods. All samples were analyzed using X-Ray diffraction (XRD), scanning electron microscopy (SEM) and infrared spectroscopy (FT-IR) methods. By tuning the ratio of Na/Y/F, solvent composition, reaction temperature and time, it was successfully synthesized cubic (α-phase) and hexagonal (β-phase) $NaYF_4$ particles (structure shown in figure 1) of different size and shape. The influence of fluorine concentration, synthesis temperature and surfactant nature on final product is discussed.

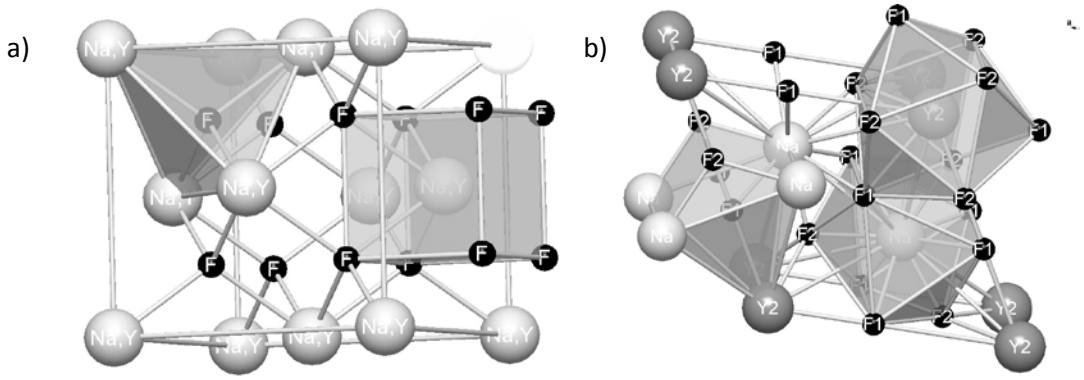

Figure 1. structure of $NaYF_4$ crystal a) cubic (α-phase), b) hexagonal (β-phase)

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NEUTRON DIFFRACTION STUDY AND LUMINESCENCE PROPERTIES OF $Y_3(Al,In)_5O_{12}$:1%Eu AND $Y_3(Ga,In)_5O_{12}$:1%Eu COMPOUNDS

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Inorganic materials doped with Eu^{3+} are successfully employed as orange/red emitting phosphors. These compounds are important components in light-emitting diodes, fluorescence lamps, cathode ray tubes, field emission displays, electroluminescence displays and plasma display panels [1-4].

Yttrium aluminium and yttrium gallium garnets ($Y_3Al_5O_{12}$ (YAG) and $Y_3Ga_5O_{12}$ (YGG), respectively) are widely used as core host materials in luminescence, while yttrium indium garnet ($Y_3In_5O_{12}$) is not obtained at the same conditions. The chemical composition and structure of the host materials influence the optical properties of such materials. Therefore, in the present work the matrices of YAG and YGG are modified by substituting aluminium or gallium with indium. The modified matrices are doped with 1% Eu.

The sol–gel route has been successfully used to obtain pure $Y_3(Al,In)_5O_{12}$:Eu and $Y_3(Ga,In)_5O_{12}$:Eu powders. X-ray and neutron diffraction were used for phase identification and refinement of the crystal structures. Moreover, these techniques helped to clarify the preferred positions of Al^{3+}/Ga^{3+} and In^{3+} ions in the tetrahedral and octahedral sites in the crystal lattice. The luminescence properties of the synthesized samples were characterized by VUV and UV/Vis spectroscopy, showing dominant emission of $^5D_0 \rightarrow {}^7F_4$ transitions (680–720 nm wavelength range) under 160 nm wavelength excitation. Finally, the slight change of the optical properties of Eu^{3+} in the different mixed-metal garnet matrices is explained in combination with the diffraction results.

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PREPARATION OF SILVER-CONTAINING HYDROXYAPATITE USING A SOL-GEL PROCESS

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Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is the most promising material in medical applications such as implants, coatings, prostheses because of its biocompatibility, bioactivity, and osteoconductivity. It is known that implant infections are associated with biofilm formation, and bacterial cells growing within the biofilm exhibit increased resistance to antibacterial agents [1]. Silver has a broad spectrum of activity against viruses, bacteria, fungi. The use of silver has recently become one of the preferred methods to protect biomaterials from bacterial adhesion [2]. Studies have shown that Ag^+ ions are able to penetrate the bacterial cell wall and cause DNA to transform to a condensed form which reacts with thiol group proteins resulting in cell death. The higher the level of silver incorporated into a material, the better the antimicrobial effect, but it comes at the cost of increasing cytotoxicity. Optimization of the Ag concentration is critical to guarantee an optimum antibactericidial effect without citotoxity [3]. Various methods, such as ion exchange, plasma spraying, sol–gel technology, Ag doping using a blasting process, ion beam-assisted deposition, micro-arc oxidation, magnetron sputtering and microwave processing technique have been used to dope Ag or Ag ions into the CHA lattice. The substitution of Ag^+ (1.28 A˚) ions takes place for Ca^{2+} (0.99 A˚) preferentially in the Ca(1) site of CHA, and this leads to an increase in the lattice parameters linearly with the amount of silver added [4].

Silver substituted (1, 5 and 10 mol%) hydroxyapatite samples were synthesized by sol-gel method. Calcium acetate monohydrate, $Ca(CH_3COO)_2{\cdot}H_2O$, silver nitrate and diammonium hydrogen phosphate, $(NH_4)_2HPO_4$, were selected as Ca/Ag and P sources, respectively, in mole ratio 1.67. Firstly, calcium acetate monohydrate was dissolved in 50 ml of distilled water when aqueous solution of silver nitrate added and stirred for 30 min. In order to obtain water-soluble calcium complexes, EDTA or DCTA were dissolved in distilled water, deprotonated with ammonia, and afterwards added to the initial solution. The resulting mixture with pH 10, was stirred for 1 h. Then an aqueous solution of $(NH_4)_2HPO_4$ was added and stirred for 10 h at 70-80°C. Finally, after slow evaporation under continuous stirring the Ca–P–O sols turned into transparent gels. The oven dried (100°C) gel powders were ground in an agate mortar, calcined at 800°C for 5 h heating rate 1°C min^{-1}, and twice at 1000°C temperature for 5 or 24 hours in air. CHA-Ag powders were analyzed by X-ray diffraction and FTIR methods. The microstructure of silver-containing hydroxyapatites were characterized using scanning electron microscopy.

Acknowledgements
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PHOTOELECTROCHEMICAL PROPERTIES OF ZnO FILMS MODIFIED BY COBALT-BASED CATALYST

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Zinc oxide (ZnO) is an important semiconducting material in various industrial applications [1]. In order to improve the photoelectrocatalytic properties of ZnO, the efforts are focused on its modification with transition metals, such as Fe, Cr or Co. Recently, Nocera and coworkers [2–4] have developed a water oxidation electrocatalyst containing cobalt phosphate complex, termed CoPi.

The aim of this work was to study electrochemical behaviour of nanoparticulate ZnO coatings modified with photochemically-deposited cobalt phosphate catalyst.

ZnO coatings on stainless steel were prepared by using electrophoretic deposition (EPD). AISI 304 type stainless steel plates were used as a support. A suspension for EPD was prepared by dispersing ZnO in methanol. EPD synthesis was performed under constant voltage (30 V), the deposition time being 10 minutes. All samples were thermally treated in air at 673K for 1 hour. Photochemical deposition of Co-based catalyst on ZnO surface was carried out by immersing electrode in 0.5 mM $Co(NO_3)_2$ and 0.1 M potassium phosphate electrolyte (pH 7). The electrochemical measurements where performed with a computer-controlled Autolab PGSTAT12 potentiostat/galvanostat. Ag, AgCl | KCl(sat) was used as a reference electrode and a platinum wire as a counter electrode. 0.1 M potassium phosphate solution (pH 11.5) was used as a supporting electrolyte.

It was established that the observed currents in the dark increased in the presence of CoPi catalyst, the highest current value is when CoPi deposition time is 30 min. The photocurrent density tends to decrease by increasing the amount of Co-based catalyst. The structure, morphology and photoelectrochemical properties of the prepared coatings were studied too.

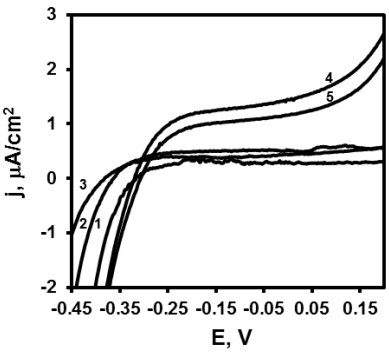

Figure 1. Characteristic voltamperograms of ZnO electrode in the dark in 0.1 M phosphate buffer (pH 11.5): 1 – without CoPi catalyst, 2 – after 10 min of CoPi photodeposition, 3 – 20 min, 4 – 30 min, 5 – 35 min. V= 10 mV· s^{-1}

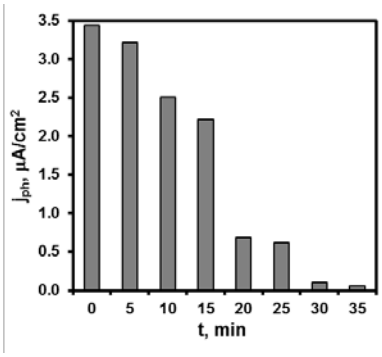

Figure 2. Photocurrent j_{ph} dependence on CoPi photodeposition time

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TOTAL OXIDATION OF TOLUENE OVER CuO-CeO_2/NaX ADSORBENT-CATALYST

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Catalytic oxidation is the most convenient and effective process for decontamination of volatile organic compounds (VOCs) [1]. This process can be carried out under different conditions: stationary process or by less abundant cost-effective adsorptive-catalytic technique. Adsorbent-catalyst is a material representing adsorptive and catalytic properties in a heterogeneous system [2, 3]. The second type of catalytic process consists of two steps: the first step is the adsorption of VOCs from the flow, the second - thermal regeneration of adsorbent-catalyst and catalytic oxidation of VOCs. Effective operation of adsorbent-catalyst depends on appropriate support selection and active component.

CuO-CeO_2/NaX adsorbent catalyst was used for toluene oxidation. Catalytic oxidation was performed in a fixed-bed reaction system. Custom-made quartz reactor was loaded with 40 g of catalyst. Adsorption of toluene and catalytic oxidation were performed at a gas hourly space velocity (GHSV) of 3100 h^{-1}.

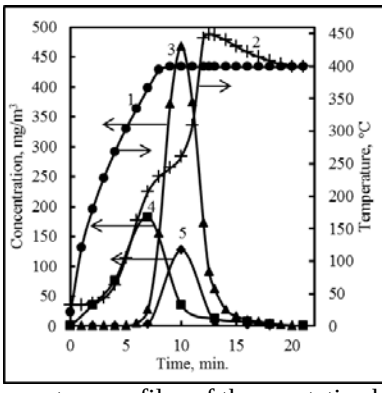

Fig. 1. Temperature profiles of thermostatic chamber (1) and reactor (2); concentrations of desorbed toluene (4) and formed carbon monoxide (3) and benzene (5).

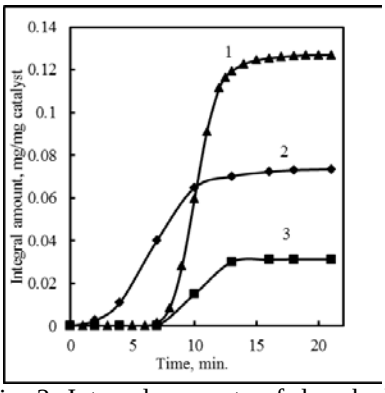

Fig. 2. Integral amounts of desorbed toluene (2) and formed carbon monoxide (1) and benzene (3).

Firstly, adsorbent-catalyst was saturated with 6 mg/g of toluene. Breakthrough of toluene was checked and was not observed after adsorption stage. Fig. 1 represents temperature profiles of thermostatic chamber and reactor, concentrations of desorbed toluene and formed CO and benzene during catalytic oxidation stage. As seen from reactor temperature profile, “light-off” occurred at ~250 °C. Integral amounts of desorbed toluene and formed CO and benzene are shown in Fig. 2. 98.8% conversion of toluene was reached during catalytic oxidation stage. Since undesired product was formed (benzene), overall efficiency of VOC oxidation was 98.3%. Compared to stationary process, the advantage of such catalytic oxidation method is that low concentration VOCs can be adsorbed from the effluent gas stream for a long period of time and oxidized within a relatively short period of time, resulting in lower energy consumption.

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UV-VIS SPECTROSCOPICAL INVESTIGATIONS OF THE YSZ THIN FILMS ON CORUNDUM, SILICON AND SILICA SUBSTRATES

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Zirconium oxide (ZrO_2) is one of the industrially most important ceramic material [1] that finds wide applications in thermal barrier coating [2], clinical application [3], oxygen sensor [4] and electrolyte in solid fuel cell (SOFC) [5]. Unfortunately, at room temperature stable only monoclinic phase of ZrO_2, which is not suitable because of volume expansion during the transformation from tetragonal to monoclinic phase. The stabilization of ZrO_2 high-temperature phases: (1170 ºC) tetragonal and (2300 ºC) cubic, respectively, can be successfully perform by doping with different oxides including Y_2O_3, La_2O_3, Gd_2O_3, CaO, Sc_2O_3, In_2O_3 and etc. Usually, stabilized zirconia has superior mechanical, thermal, and optical properties comparing with room-temperature stable monoclinic phase. Moreover, in order to achieve the best utilization of this kind of materials in the electrochemical devices such as SOFCs and gas sensors, a strong demand for clarifying the source of the size dependence is emerging [6]. The reducing of YSZ operating temperature is closely related with the particle size of the synthesized material. As the grain size is reduced from micrometer to nanometer, the defect properties (defect formation, lattice defect and band structures) are considered to play an essential role in defining the ionic and electronic conduction in the nanometer regime [7].

The preparation and characterization of the YSZ thin films on different substrates, which were produced by so-called aqueous sol-gel synthesis, are reported. This sol-gel method is based on the complexation with citric acid, acetylacetone, 2-propanol and 1,2-propanediol of the metal nitrate salts dissolved in aqueous solution, producing a final compound as thin layers on Al_2O_3, Si and SiO_2 substrates at relatively low temperatures comparing with solid state reaction. Moreover, in this study we compared the optical properties of obtained films prepared by sol-gel synthesis method using both dip- and spin coating techniques. All as prepared YSZ thin layers on different substrates were dried at 400 ºC temperature on hot-plate and afterwards repeatedly calcined at 800 ºC for 1 hour in air atmosphere after each coating procedure and characterized by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) and UV-Vis spectroscopy. XRD data exhibited that at 800 °C temperature nano-sized $Y_{0.2}Zr_{0.8}O_2$ thin films with cubic (Fm-3m) crystal structure have formed. The morphological features of obtained coatings investigated by SEM confirmed the nanosized surface of YSZ coatings. The optical reflection (UV-vis) measurements of sol-gel derived specimens let us to conclude that the preparation technique of the synthesized thin film significantly influences the optical properties of produced YSZ surfaces.

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GREEN CHEMISTRY

ADSORPTION AND DESORPTION FROM MESOPOROUS CARBONACEOUS MATERIALS

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Chemical contamination of water is a growing concern due to the negative environmental impact of chemicals and deterioration of water quality, which leads to demanding purification. Activated carbons are commonly used to remove contaminants from water for potable applications. However, regeneration of activated carbons is energy intensive and results in the destruction of adsorbed valuable chemicals. Desorption could recover activated carbons and chemicals; however, it is rarely considered in the scientific literature and it is rarely successful.

A new class of carbonaceous porous materials - Starbons® - was developed in the Green Chemistry Centre of Excellence at the University of York and available from Starbon® Technologies.[1] The material can be produced from renewable and widely available polysaccharides, such as starch, alginic acid and pectin. The characteristic trait of Starbons® is their mesoporosity, high pore volume and tunability (through carbonization temperature) of the surface chemistry. This corresponds to faster adsorption diffusion rates and potential for selective adsorption. Since physical adsorption is reversible and is in equilibrium with desorption, greater pore volume also offers increased desorption diffusion rate.

Table 1. Physical properties of various Starbons and a representative activated carbon

ID	BET Surface Area, m^2/g	Total pore volume, cm^3/g	Mesopore volume, cm^3/g	Micropore volume, cm^3/g
Activated carbon	921	0.52	**0.12**	0.40
1 Alginic Acid Starbon®, 800 °C	565	1.89	**1.72**	0.17
2 Alginic Acid Starbon®, 800 °C	565	1.62	**1.46**	0.16
3 Alginic Acid Starbon®, 800 °C	428	0.97	**0.86**	0.11
Starch Starbon®	535	0.75	**0.53**	0.22

Previously, Starbons® showed an advantage over activated carbons in adsorption of some textile dyes.[2] Mesoporosity was demonstrated to be the key to improved adsorption capacity and rate.

A range of Starbons® was tested for adsorption and desorption of a range of aminophenols, which are common industrial pollutants. Starbons® demonstrated improved desorption over activated carbons. Although mesoporosity was not found to play a key role in adsorption of smaller molecules, it was observed that materials with a greater pore volume have greater desorption potential. This could be crucial for a low-energy, non-thermal regeneration of the adsorbent, which enables chemical recovery as well.

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ONE-POT SYNTHESIS OF SOME THIAZOLE AND AMINOTHIAZOLE COMPOUNDS USING TETRABUTYLAMMONIUM SALT AS A CATALYST

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Thiazole and its derivatives play a vital role in nature. For example, the thiazolium ring present in vitamin B1 serves as an electron sink and its coenzyme form is important for the decarboxylation of α-keto acids. This heterocyclic system has found broad applications in drug development for the treatment of allergies, inflammation, hypertension, schizophrenia, bacterial and HIV infections [1]. A tetrahydrothiazole also appears in the skeleton of penicillin which is one of the first and most important broad spectrum antibiotics. Aminothiazoles are known to be ligands of estrogen receptors as well as a novel class of adenosine receptor antagonists [2-3]. In view of the emerging importance of thiazoles and their derivatives, several methods for their synthesis were developed using various catalysts [4-8] conditions and strategies [9]. However, many of these reported methods suffer from drawbacks such as harsh reaction conditions, unsatisfactory yields, prolonged reaction time, tedious workup procedures and use of expensive catalysts. Therefore, the development of efficient and environmental friendly green chemical processes is a major challenge for chemists in organic synthesis.

A convenient method for the synthesis of thiazoles and aminothiazoles by treatment of phenacyl bromides with thioamides/thiourea in the presence of tetrabutylammonium hexafluorophosphate (Bu_4NBF_4) at room temperature was developed. The products having high yields were formed rapidly (within 18 min). The method is simple, rapid and practical, generating thiazole derivatives in excellent isolated yields. The structures of the newly synthesized products were identified by FT-IR, ^{1}H NMR, ^{13}C NMR spectroscopy and elemental analysis data.

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MODIFICATION OF THE SMECTITE CLAYS BY QUATERNARY AMMONIUM HALIDES

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Raw smectite clays from the Baltic deposits contain significant amounts of quartz, feldspar and carbonates (sometimes up to 50%), and the low clay mineral – smectite (less than 30-40%). These matrix minerals decrease the quality and influence physical properties of the smectite, but can be removed by procedure of clay enrichment [1]. Purified smectite clays have high cation exchange capacity (CEC), high surface areas and fine swelling properties therefore smectites are extensively used as raw material for organoclay production.

Chemically modified smectite clays are called organoclays. The chemical modification or organophilisation of the smectite clays is based on replacing the calcium or sodium ions in the interlayer space of the clay mineral to organic cations, that results in hydrophobic material. Such hydrophobic materials have found wide applications as adsorbents of various organic pollutants, as components in the synthesis of clay-based polymer nanocomposites and rheological control agents. Potentially organoclays can be used for production of antibacterial materials and coatings, and as reagents or catalysts in organic synthesis [2, 3].

There are different ways to modify layered clay minerals, but the most used methods are: cation exchange reaction in aqueous solution or in organic solvent (acetone, THF, ethanol, etc.) and the solid-state reaction [4].

The solid-state reaction between the smectite clay samples from Vadakste (Latvia), Šaltiškių deposit (Lithuania) and different quaternary ammonium halides resulted in organoclays – hydrophobic brown gels with crystalline structure. Octadecyl trimethylammonium – ODTMA, dioctadecyl dimethylammonium – DODMA, trioctadecyl methylammonium – TOMA halides were used for smectite clay modification. Molecules of organic compounds were intercalated into dry smectite samples without additional use of solvent [5]. The absence of solvent in the process of preparation is environment-friendly and makes the organophilisation more suitable for industrialization.

Intercalation of quaternary ammonium halides between layers of the smectite not only changed the clays' surface properties from hydrophilic to hydrophobic, but also greatly increased the basal spacing of the layers. X-ray powder diffraction patterns (Bruker D8 Advance diffractometer) for smectite clay and obtained organoclay approves a shift of the characteristic sodium smectite reflection at $2\theta=7.0$ (14 Å) to $2\theta=2.2$ for smectite modified with octadecyl trimethylammonium bromide (42 Å).

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METHANE DECOMPOSITION OVER METAL/ACTIVATED CARBON CATALYSTS AS A PRO-ECOLOGICAL WAY OF HYDROGEN OBTAINING

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High environment contamination and a growing shortage of natural resources prompt to search for alternative energy carriers/sources. Use of hydrogen can be one of the promising solutions. Conventional methods of hydrogen production are based on steam methane reforming, carbon gasification or partial oxidation of refinery residues [1]. However, these technologies have many limitations e.g. carbon dioxide formation. Therefore the new methods of hydrogen production are searched for. The catalytic methane decomposition seems to be an interesting and pro-ecological technology as pure hydrogen and carbon are the only products of this reaction. The process can be carried out over different catalytic systems such as metals or activated carbons [2-4]. We decided to combine the good catalytic properties of the above mentioned catalysts and applied the new catalytic system (i.e. metal/activated carbon). To the best of our knowledge, there are only a few papers about the application of these types of catalysts in the methane decomposition process. This fact prompted us to undertake research in this area.

The activated carbon (AC), used as a support for metallic phase, was prepared from ash wood. The raw material was ground and then chemically activated with solid potassium hydroxide at 800°C for 45 min. The activated carbon obtained was impregnated with the aqueous solution of the Ag, Cu or Ni nitrates for 24 h. The impregnated samples were heated at 460°C for 1 h and then contacted with hydrogen at the same temperature for 2 h. The final catalysts included 1, 5, 10 or 20% of metal phase. The methane decomposition reaction was carried out in a fixed-bed reactor using 50 mg of the catalyst. Three temperatures were applied: 750, 850 or 950°C. The process ran 4 h. The post-reaction gases were analysed chromatographically using TCD detector.

It was found that the catalytic activity of the prepared samples increases with the increase of temperature of the process. Unfortunately, in all cases rapid decrease in the activity of the catalytic systems with the time on stream is observed. This phenomenon is a consequence of the carbonaceous deposit formation from methane and blocking of the pores/active centres of the catalysts applied. The deactivation occurs quickly, especially at the highest temperature. The Ag/AC and Cu/AC systems show the lower catalytic performance than the activated carbon alone (AC) examined as a catalyst. The Ni/AC systems were more active in the reaction than the AC and generally, the higher the metal content, the better catalytic performance of the catalysts tested.

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SURFACE PROPERTIES OF SODA LIGNIN OBTAINED FROM ASPEN WOOD BY-PRODUCT

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Chips, bark and sawdust are formed as a result during wood processing and are mainly used for energy needs. At the same time, these by-products can serve as feedstock for obtaining technical lignin, which is often used for stabilisation and dispergation of various colloidal systems, including for drilling muds for oil exploitation. The last application is important due to the possible oil explorations in the Baltic Sea shelf of the Latvia's economic zone. Early [1], lignin obtained under laboratory conditions from aspen sawdust by soda delignification process was characterised by a chemical composition. In this work, its surface-active properties in aqueous solutions such as a surface tension at the air-water interface and a surface pressure (π-A) were measured using a tensiometer “Kruss K100” and a KSV NIMA Langmuir Trough. A size and zeta potential of lignin particles were found by a dynamic light scattering using a Malvern Nanosizer NZ. It was shown that soda lignin is a surface active substance. Its molecules can adsorb at the water-air interface and build up a surface film. The surface activity of the obtained lignin grows with falling the solution pH values. Simultaneously, with decreasing pH, the average sizes of aspen lignin particles in the aqueous solutions increase from 260 nm to 340 nm, but the values of zeta potential decrease from –25.7 mv to -18.6 mv, respectively. This reflects the increase in the hydrophobicity of the lignin macromolecules due to the decreasing of ionization of their phenol hydroxyl and carboxyl groups. The enhanced hydrophobicity of the soda lignin is manifested by the growth of the surface pressure at the air-water interface from 24 mN m^{-1} at pH 12,8 to 40 mN m^{-1} at pH 8.0 and can be associated with the formation of a more rigid lignin’s film due to strengthening its molecules interaction at the interface. The study of the soda lignin as a stabiliser of the “rapeseed oil-in-water” emulsion shows that it behaves according to water phase pH values and its content in emulsion. With growing the pH value of the lignin water phase, the colloidal stability of the emulsion towards creaming remarkably enhances. This may indicate the prevailed electrostatic mechanism in the O/W emulsion stabilization by the aspen soda lignin.

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SIMULTANEOUS STYRENE AND ANILINE OBTAINING VIA ETHYLBENZENE DEHYDROGENATION/NITROBENZENE HYDROGENATION OVER ACTIVATED CARBON SUPPORTED METAL OXIDE CATALYSTS

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Ethylbenzene dehydrogenation reaction leads to obtaining styrene – a valuable compound used for production of important polymer and co-polymers (such as ABS, SAN, SBR). The process is endothermic and requires a high temperature (above 600°C). Additionally, during the reaction different by-products could be formed. These compounds have a negative impact on the environment and on purity of the main product [1]. Because of the limitations of the process the alternative method of styrene production is searched for. Use of an oxidising agent, introduced into the reaction system, can be an interesting idea. As the oxidiser nitrobenzene could be applied. Its use guarantees that the ethylbenzene dehydrogenation could be carried out in a lower temperature. Moreover, in the coupled process other important product can be created (aniline). This compound is widely used in pharmaceutical industry, construction and automotive industry [2]. The main aim of this study was the application of different activated carbon supported metal oxide catalysts in the ethylbenzene dehydrogenation coupled with nitrobenzene hydrogenation. The present work fits perfectly in the idea of green chemistry (e.g. energy saving).

The activated carbon prepared from waste poly(ethylene terephtalate) (used bottles) by chemical activation with solid KOH was used as a support for different metal oxides. The catalysts were obtained using the incipient wetness method. First, the activated carbon was impregnated with the aqueous solution of $Fe(NO_3)_3$ or $Co(NO_3)_2$. Also NH_4VO_3 dissolved in aqueous solution of oxalic acid was used. The impregnated materials were calcined at a temperature of 460°C and then contacted with air at 250°C. The final catalysts included 1, 5, 10 or 20% of metal oxide phase. The ethylbenzene dehydrogenation reaction in the presence of nitrobenzene was carried out at 400°C for 4 h. The post-reaction mixture was collected every 12 min and analyzed using gas chromatograph equipped with FID.

All the catalysts obtained were active in the reaction tested and two main products (styrene and aniline) were formed. However, the catalytic activity of all samples prepared decreased rapidly with the time of the process. It is probably a consequence of catalyst's pore/active sites blocking by the carbonaceous deposit created from reagents (probably both the substrates and the products). It was found that, generally, the higher content of metal oxide in the catalytic system, the worse the catalytic performance of the catalysts used. Among the systems tested the 1% Co_3O_4/AC sample showed the highest activity towards the desired products.

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ORGANIC-INORGANIC NANOCOMPOSITES FOR FUEL CELLS AND SOLAR COLLECTORS

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Nowadays organic-inorganic nanocomposites attract great attention for their unique properties due to combining inorganic and organic constituents. In particular, they may be used as membranes in fuel cells; organic-inorganic materials can be applicated for obtaining thermoabsorbing coatings for solar collectors as well [1-5]. Sol-gel seems to be suitable technique for formation nanostructure of organic-inorganic composite materials.

Synthesis of nanocomposite organic-inorganic thin films was conducted via radical photoinitiated polymerization of acrylamide, acrylonitrile and 3-sulphopropylacrylate potassium salt. The reaction was carried out in thin films using UV irradiation. The intensity of irradiation was 14 W/m^2. Content of comonomer containing sulphogroups (3-sulphopropylacrylate potassium salt) was varied in the range 5 – 20 % w. of the total comonomer mixture. Cross-linker *N,N'* - methylenebisacrylamide was used to form networked structure of copolymer. Sol-gel system (tetraethoxysilane-ethanol-water in appropriate proportions) was added to the mixture of comonomers. The content of sol-gel system in compositions was 5 – 20 % w. Proton conductivity of synthesized films was measured by impedance spectrometry using impedance spectrometer “AUTOLAB” (Ecochem, Holland) with FRA program. Specific proton conductivity of organic-inorganic films at 35°C was found to be ~ 10^{-4} Sm/cm.

Some types of spectral-selective composite coatings for solar collectors were synthesized using sol-gel method. The coatings contain carbon nanoparticles dispersed in dielectric SiO_2 or NiO matrices. Comparative investigations of the synthesized coatings with the sample from SunSelect (Germany) were conducted. SunSelect coatings are widely used for production of solar collectors; however, they are prepared by expensive technology – vacuum evaporation.

Experimental results of measurements of investigated samples temperature at irradiating them with intensity of 1000 W/m^2 indicate that synthesized coatings are of the same effectiveness of solar energy absorption as the known analogue and can be used as selective coatings for solar collectors. The composition and the method of preparing of the sample with the best characteristics may be regarded as prospective for further improvement.

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COMPARISON OF CHEMICAL AND ENZYMATIC SYTHESIZED POLYPYRROLE NANOPARTICLES

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The polymer nanoparticles are now widely used in various experimental fields like electronics, photonics, sensors, medicine, biology and biotechnology, also pollution and environmental control [1, 2]. Synthesis of the polymers could be achieved using various techniques: solvent evaporation, salting-out, dialysis, supercritical fluid technology, micro-emulsion, mini-emulsion, chemical synthesis and enzymatic synthesis [3]. In this work the comparison of two polypyrrole synthesis techniques such as chemical and enzymatic is presented.

Polypyrrole is widely used in many fields due to its thermal and mechanical stability, biocompatibility, chemical inertness and limited permeability [4]. This polymer could be synthesized using mild conditions (neutral pH and water environment), thus enzymatic synthesis could be implemented [5].

Synthesis of polypyrrole was carried out using two techniques at various concentration of monomer. Chemical synthesis was executed using hydrogen peroxide as an oxidator. During the enzymatic synthesis Glucose oxidase (from *Aspergillus niger*) and the substrate glucose were used to obtain the same initiator of the polymerization – hydrogen peroxide [6]. Both reactions were performed in phosphate buffer at pH 6.0 due to further application of formed polymeric nanoparticles for the investigation of toxicity toward cells. The growth of the polymeric particles was evaluated using Dynamic Light Scattering (Malvern Zetasizer, England). In addition the polymerization reaction was registered by the spectrophotometer, the formation of peak at λ = 460 nm was registered. The obtained results suggest that the polymerization rate of enzymatic synthesis occurred faster than in chemical polymerization. This could be due to local increase of the hydrogen peroxide concentration and decrease of pH near to enzyme.

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BIODIESEL PRODUCTION VIA TRANSESTERIFICATION OF RAPESEED OIL WITH METHANOL OVER SULFONATED ACTIVATED CARBON CATALYSTS

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Diesel engines have many advantages compared with gasoline ones, such as high efficiency, low fuel consumption per unit distance or less carbon dioxide production. More and more restrictive law on environmental protection has caused growing interest in biodiesel fuel application in the diesel engines. Biodiesel can be obtained in the vegetable oil transesterification process using acidic or basic catalytic systems, both homogeneous and heterogeneous. The application of the latter ones provides some benefits e.g. simplified separation of the reaction products and the catalyst [1]. Among heterogeneous catalytic systems the activated carbons seem to be an interesting concept as they are rather cheap (can be produced from waste materials) and can be easily modified. The present work is focused on the use of the activated carbon-based solid acid catalysts, prepared in different ways, in the transesterification of rapeseed oil with methanol.

The initial activated carbon (AW) was obtained by physical activation of the ash wood with carbon dioxide. In order to introduce strong acidic sites on the carbon surface different modifications were applied – sulfonation with concentrated or fuming sulphuric acid at 140ºC for various times (5, 10 or 20 h) or the reaction of brominated AW with sodium sulfide and subsequent oxidation of the product with 30% solution of hydrogen peroxide at 30 or 60ºC. The catalysts obtained were characterized using different methods (e.g. elemental analysis, potentiometric titration). The process of rapeseed oil transesterification with methanol was carried out at relatively high temperature and under moderate pressure (130ºC, 13 atm.) for 24 h. During the reaction four samples of post-reaction mixture were collected. For comparison purposes, the reaction studied was also performed using the commercial catalyst (Amberlyst-15). The content of fatty acid methyl esters (FAME) was determined using gas chromatography.

All the activated carbons prepared were active in the reaction tested. In all cases, the content of methyl esters formed increased gradually with the time of the process, reaching the highest values after 24 h of the reaction. However, the catalytic activity of the samples examined varied significantly. The worst results were obtained for carbon modified with sodium sulfide and subsequently oxidised with hydrogen peroxide - these catalysts had the lowest density of $–SO_3H$ groups. Carbons treated with fuming sulphuric acid exhibited higher activity in reaction studied (the content of FAME reached 14.4% after 24 h for carbon modified for 10 hours). The best results were obtained for activated carbons sulfonated with conc. H_2SO_4 (more than 40% of methyl esters in the post-reaction mixture). This is a consequence of high content of sulfonic groups on the surface of these catalysts.

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CHARACTERISATION OF ACID/BASE PROPERTIES OF SULFONATED ACTIVATED CARBONS BY ISOPROPANOL DECOMPOSITION REACTION

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Homogeneous catalysts, such as H_2SO_4 or NaOH, play a very important role in fuels production or obtaining different chemical compounds [1]. Unfortunately, there is a problem with separation of products and catalyst which causes increasing of the costs of the process. A solution of those problems could be the application of heterogeneous catalysts, e.g. modified activated carbons. In comparison with the conventional catalysts, carbon materials have many advantages, which allow to classify these materials as environmentally friendly. These advantages include: low production costs (they could be obtained from waste materials), easy utilization, high thermal stability and good resistance to poisoning. In addition, activated carbons can be relatively easily modified. There are several methods for the introduction of acidic (e.g. –COOH or $–SO_3H$) or basic (e.g. $–NH_2$) functional groups on carbon catalyst surface [2]. In this paper different methods of modified activated carbons obtaining were used. Active sites created were characterised based on the test reaction – isopropanol decomposition.

The initial activated carbon was prepared from ash wood by carbonisation and subsequent activation with carbon dioxide. The product obtained was then modified using different methods such as: sulfonation with concentrated sulphuric acid (95%) at 140ºC for 20 h or at 180ºC for 5h, sulfonation with fuming sulphuric acid (20% SO_3) at 140ºC for different times (5, 10 or 20 h), reaction of brominated carbon with sodium sulphide and subsequent oxidation of the product with hydrogen peroxide at 30 or 60ºC. Isopropanol decomposition reaction (involved five injections of the substrate) was carried out in a glass reactor connected with a chromatographic system equipped with a FID detector. Temperature of the process was 180ºC. For comparison purposes, the reaction studied was also performed using the commercial catalyst (Amberlyst-15) or the activated carbon with basic character of its surface. According to the results of the test reaction, the kind of activated carbon modification has a significant impact on the surface character of the samples prepared. In most cases the main reaction is isopropanol dehydration towards propene, which confirms the presence of acidic centres on the catalyst's surface. The activated carbon modified with conc. H_2SO_4 at higher temperature shows, similar to Amberlyst-15, the highest activity towards propene formation. This is due to the high concentration of acidic groups on the catalysts surface. The initial activated carbon shows certain activity towards acetone formation, which indicates the presence of some amount of basic centres. As expected, the carbon modified with amine catalyse mainly acetone production.

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SUSTAINABLE CHEMISTRY AND MATERIALS

DEVELOPMENT OF SOL-GEL PROCESSING ROUTE FOR THE CONSERVATION OF STEEL

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Corrosion inhibitors, polymer and synthetic wax coatings are used for the conservation of historical iron, copper, copper alloys, steel and other metal objects. H*owever, these coatings do not provide successful preservation of these objects for a longer time*. Therefore, scientists have attempted to establish new methods for the conservation of metals'. Investigations are essentially focused on the developing of better quality, faster, long–term, anticorrosion preservation methods that could be applied in conservation and restoration of metals.

The sol–gel method is one of the most prospective and newest techniques that have been applied for conservation of glass, mosaics and other cultural heritage objects, but information about the use of this technique for metal preservation is not sufficiently explored [1-5]. Various different coatings can be formed by using sol-gel method: hydrophobic, anticorrosion, protective and other. Sol-gel protective coatings have shown great chemical stability, oxidation control and enhanced corrosion resistance for metal substrates. Moreover, the sol–gel method is an environmentally friendly technique for the protection of surface and had showed the potential for the replacement of toxic pre-treatments and coatings which have traditionally been used for increasing corrosion resistance of metals.

In the present study, methyl–modified silica coatings were structured on the surface of steel. The main purpose of these coatings is to protect the steel-based artefacts from adverse influence of environment. The surface morphology changes of coated, uncoated and photochemically aged specimens were investigated by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The hydrophobicity was evaluated by contact angle measurements. Corrosion parameters were evaluated by polarization curves.

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ELECTROSPINNING OF CELLULOSE ACETATE FIBERS FROM TERNARY SOLVENT SYSTEM

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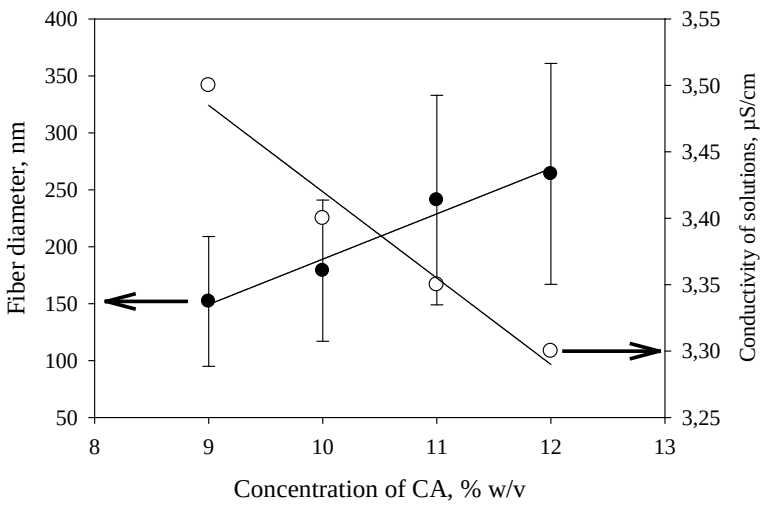
Cellulose acetate (CA) is the most abundant natural polymer, possessing a polyfunctional macromolecular structure and an environmentally benign nature [1]. Consequently, application of electrospinning could be seen as an attractive technique for CA fibers fabrication. However, weak solubility of CA in traditional single solvent and binary solvent systems makes it not suitable for formation of uniform fibers [2].
Authors of the study developed a new ternary solvent system for continuous (without needle clogging) electrospinning of uniform CA fibers. CA fibers with average diameters below 300 nm were electrospun from the ternary solvent system consisting of acetone/dichloromethane (DCM)/*N*,*N*-dimethylformamide (DMF) at ratio of 2/1/1 (v/v/v), while other proportions of this solvent system were not suitable to produce fibers. The morphology and diameter of electrospun CA fibers were highly dependent on the concentration of CA solution. The figure presents relationships between CA solution concentration and average diameter of the fibers as well as relationship between solution concentration and electric conductivity of the solution.



Smooth fibers with the mean diameter of 241±92 nm were obtained with the solvent system containing more than 11% (w/v) of CA. High porosity and interconnectivity of CA fibers provide prerequisites for new technical applications of electrospun fibrous materials. Filtering applications [3], improved catalytic separation efficiency and smart textiles with improved functionality these are only several areas of potential applications. At the same time limited use of toxic substances will help to ensure development of environment-friendly industrial processes.

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LATVIAN CLAY RESOURCES FOR LOW TEMPERATURE ALKALINE ACTIVATION

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The clay is one of the most abundant local mineral resources in Latvia, chiefly, the illite clays of Devonian bedrocks and Quaternary glacigenic clayey sediments [1]. The systematic large-scale exploration and prospecting of clay deposits in Latvia in the period of the fifties up to the eighties of the 20th century was done together with the integrated mineralogical investigations of the clayey deposits of various geological ages [1-3]. The composition and correlation of ceramic properties of various types of local clays were investigated profoundly and data with certain limitations are useful for implementation of new ceramic materials even nowadays [1].

Elaboration of ceramic building materials from local clay raw material by the mean of low-temperature (20-100^{0}C) alkali activation is considered as a perspective alternative production technology ensuring 50% up to 85% energy consumption and 2 times lower CO_2 emission compare to the traditional technologies [4]. The reaction of a solid hydrous aluminosilicates with an aqueous alkali hydroxide or silicate solution produces a synthetic alkali aluminosilicate material generically called a ‘geopolymer’ [5]. These materials can provide comparable performance to traditional ceramic materials [6]. The original raw material used for alkali activation is metakaolinite, however other aluminosilicate precursors, including natural minerals, have also been the subject of investigation [6].

In Latvia the most abundant clay raw material is illite clays that traditionally have been used for the production of building ceramic. The laboratory test scale results show good potential of illite clays for alkali activation [7] with reasoning that the compressive strength of obtained material predominantly depends on the clay’s composition and alkaline solution concentration while only secondary - on treatment temperatures.

The current paper study Latvian clay deposits of various geological ages in order to confirm the adequacy of the raw material for low-temperature alkali activation. Study includes the estimation of the adequate clay resources, sampling of the raw material from the commercial beds, analyses of mineralogy (by x-ray diffraction) and chemical composition (according to LVS EN 196-2:2005 [8]).

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COMPOSITE SPEEK POLYMER MEMBRANES WITH ACIDIC IONIC LIQUIDS FOR MEDIUM TEMPERATURE FUEL CELLS

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In alternative energy devices the medium temperature polymer electrolyte membrane (PEM) fuel cells are of growing importance. Ionic liquids [1] are suitable components for polymer membranes due to higher temperature (100-200°C) and electrochemical stability.
Acidic ionic liquids synthesized and examined in this paper include 3-(1-pyridinio)-1-propanesulfonate [PyPS] hydrogen sulfate (1a), dihydrogen phosphate (1b) and p-toluenesulfonate (1c), 3-(1-methyl-3-imidazolio)-1-propane¬sulfonate [MeImPS] hydrogen sulfate (2a), dihydrogen phosphate (2b) and p-toluenesulfonate (2c) as well as 3-(1-butyl-3-imidazolio)-1-propane¬sulfonate [BuImPS] hydrogen sulfate (3a), dihydrogen phosphate (3b) and p-toluenesulfonate (3c) [2]. Composites with SPEEK membranes were obtained by casting and impregnation. Structures of ionic liquids obtained in this work have been determined by ^{1}H NMR and XRD, but water content by Karl Fischer method. Thermal stability of ionic liquids and membranes was controlled by thermogravimetry analysis. Conductivity was obtained from impedance measurements using Autolab set-up in temperature range 20-120°C.

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ELECTROCATALYTIC ACTIVITY OF PLATINIZED Ti ELECTRODES FOR CYANIDE ELECTROOXIDATION

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Cyanide solutions used in industry are harmful not only to humans but also to other living organisms. Cyanide solutions may not be disposed to the environment, especially at high cyanide concentration levels. One of the environmentally friendly ways to utilize cyanide solutions is an electrochemical oxydation. Ti anodes covered with Pt nanolayers could replace commonly used metal Pt electrodes for the cyanide ions oxidation. This allows to significantly reduce costs associated with neutralization of the cyanide waste. The main goal of this work was to investigate electrocatalytic activity of platinized Ti electrodes and to determine possible activity changes of Pt coatings during the electrochemical oxydation of cyanide ions.

In our experiments, Ti electrodes were electrochemically covered by different amounts of Pt using the hexachlorplatinic acid electrolyte. The current density was 1.5 mA cm^{-2} and the time of electrolysis was calculated according to thickness of Pt. The morphology of Ti electrodes with 200 nm, 500 nm and 1000 nm thickness Pt coatings were investigated using SEM. It was determined that the spherical shape platinum crystallites form on Ti electrode surface and their density increases as the thickness of Pt layer increases. Elemental composition in chosen areas revealed that electrode surface structure consists of 20-30 % Pt particles, when coating thickness is 200 nm and 50-70 % when coating thickness is 500 nm. At 1000 nm of calculated thickness, 90 % of electrode surface are covered by the Pt particles.

Electrocatalytic activity of platinized Ti electrodes was investigated using 0.1 M KCN solution. During the electrolysis of cyanide solution, cyanide ions concentration was measured every 1 hour. Total electrolysis time was 5 hours. It was found that cyanide electrooxydation proceeds slowly on Ti anode covered with 200 nm thickness of Pt layer. If Pt layer thickness is 500 nm or more, concentration of cyanide ions decays much faster. Moreover, the process speed is almost independent on further increase in thickness of the Pt coating. After 5 h of anodic oxydation of cyanide ions surfaces of used electrodes were once again interrogated by the SEM method. It was found that Pt nanocrystals still are visible on the electrode surface but the surface coverage by Pt particles decreases. Extending the electrolysis time from 5 h to 50 h, increases the rate of degradation of the Pt-coated Ti electrode. In particular, for 200 nm Pt layer electrode it has been found by the SEM that Pt coating was almost completely lost from the electrode surface (only 1 – 3 % left). The oxidation of cyanide still can be accomplished after 50 h of electrolysis if 500 nm or 1000 nm thickness of Pt layer covered Ti anodes are used; however, the rate of electrooxidation is much slower. SEM data analysis revealed that the remaining of Pt particles on the electrode surface occupies just 6 to 7 % of all surface area.

So, we conclude that extending the electrochemical oxidation time of cyanide diminishes electrocatalytic activity of platinized Ti electrodes due to the decrease of the number of Pt crystallites on the electrode surface. Lost of Pt coating is likely associated with the growth of TiO_2 film layer on Ti surface that inevitably occurs during the anodic polarization of electrode.

POLYOXOMETALLATE CATALYZED OXIDATIVE MODIFICATION OF LIGNIN AS A FAVORABLE PRE-TREATMENT FOR COPOLYMERIZATION WITH PROPYLENE OXIDE FOR POLYURETHANES PRODUCTION

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In the present work lignin, extracted from wheat straw in organic acid media (product of a novel biomass refinery technology developed at CIMV, France), was subjected to oxidative modification. The regimes of oxidative modification catalyzed by $[PMo_{12}O_{40}]^{3-}$ (POM) increasing content of lignin hydroxyl groups, in particular carboxyl groups (more than twice) and not accompanied by degradation of the lignin polymeric structure have been developed earlier (EcoBalt 2012). Such oxidizing of lignin before its oxypropylation can be considered as a favorable pretreatment stage of lignin because increasing the amount of reactive sites able to copolymerization with propylene oxide.

The modification was performed using as reoxidant for POM (1) oxygen of air or (2) H_2O_2 under moderate conditions: pressure of 1 bar and temperatures of 90^0C (O_2 reoxidant) and 50^0C (H_2O_2 reoxidant). The effect of the oxidative treatment on the lignin functionality and structure was evaluated using Py-GC/MS, solid state ^{13}C NMR and chemical analysis.

It was established that use of the H_2O_2 reoxidant in the process of lignin oxidation was more promising in comparison with the O_2, because it allowed to increase the content of targeted hydroxyl groups, at significantly lower demand of POM (approximately by 25 times) and temperature of the process (50^oC against 90^oC).

The oxypropylation of the parent and oxidized lignins with propylene oxide (PO) was studied in high pressure Parr reactor using KOH as a catalyst. It was shown that oxypropylation of lignin pre-oxidized in the system POM/H_2O_2 proceeded in the similar manner as the parent lignin but the rate of the process was some lower due to the presence of higher amount of -COOH groups with lower nucleofility. Oxypropylation of lignin oxidized in the system POM/O_2 proceeded dramatically slower and was characterized by high residual pressure of non-reacted PO, and high amount of solids fraction (~30%) in reaction products. This can be explained by the neutralization of alkali catalyst by $[PMo_{12}O_{40}]^{3-}$ presented in the lignin oxidized by POM/O_2 as an admixture. Therefore, the method of lignin pre-oxidation in the system POM/H_2O_2 was chosen in order to obtain polyols for polyurethanes (PU) production.

The composition of polyols obtained from the parent and oxidized lignins, their functional characteristics and reactivity with isocyanate were studied. Both the parent lignin and oxidized lignin based polyols were applied in composition of cross linked PU elastomers. The tensile and thermal properties of PU obtained were measured and compared.

The results obtained have shown that the oxidative modification by POM/H_2O_2 can be considered as an approach to lignins upgrading for production of high reactive lignopolyols suitable in the field of polyurethane chemistry.

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EVALUATION OF ANTIBACTERIAL AND FUNGICIDE ACTIVITY OF COTTON TEXTILE TREATED VIA SOL-GEL METHOD

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Development of functional textiles based only on natural raw materials is related to many more difficulties because natural fibres have their own unchangeable inherent characteristic features, like shape, linear density, and surface structure, but application of natural fibres for advanced functional clothing and materials allows to obtain green, safe and healthy products, environmentally and human friendly [1].

The present paper describes the deposition of zinc oxide thin-coatings by the sol-gel method on cotton textile substrates. Sol-gel method has been extensively used in order to synthesize inorganic materials, because the sol-gel method is simple, low cost and large area coating method [2;3]. Zinc oxide ir classified as non-toxic material [4; 5] and ZnO have been shown to be useful antibacterial and fungicide agent when used as a surface coating on materials and textiles [5; 6]. The cotton fabric was dipped in the nanosol solution prepared with 5% and 7.5% zinc acetate dihydrate concentration after treatment samples were dried at 90°C for 10 minutes then subjected to different thermal post-treatment temperatures (120°C, 140°C and 160°C for 2 minutes). Comparison of coatings antibacterial and fungicide properties of samples treated with nanosol prepared using different zinc acetate dihydrate concentrations and different thermal post-treatments was made. Analyses based on the SEM show that obtained textile coatings are distributed evenly, not only on surface of yarns but in the depth of textile material as well, and are resistant to exploitation processes.

Antimicrobial activity of tested cotton textile substrates was compared using a parallel streak method using bacteria, yeasts and filamentous fungus as test organisms [7]. Incubated plates were examined for interruption of growth along the streaks of inoculum. Strong inhibition of microbial growth was detected for all cotton textile samples treated via sol-gel method.

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EFFECT OF CU-FUNCTIONALIZED COTTON PREPARED BY VACUUM EVAPORATION TECHNIQUE TO VIABILITY OF MICROORGANISMS

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The present paper describes the vacuum evaporation process of the copper coating on cotton textile substrates with low-pressure air plasma pre-treatment and without. Advantages of vacuum evaporation are high purity films deposited from high-purity source material and it is the lease expensive of the physical vapor deposition processes [1]. Short time of deposition (1-3 seconds) in vacuum chamber is sufficient to get a thin copper coating without destruction of substrate from natural fibres, during the process, the typical textile properties (softness, flexibility, surface relief and texture) were not influenced.

The recognition that copper has potent antibacterial properties followed and was well established in laboratory studies [2,3]. The fungicidal properties of copper were demonstrated in controlled laboratory studies starting in the early 1950s and since then copper and copper compounds have been shown to effectively kill a wide range of yeast and fungi [2; 4]. Copper is considered safe to humans, as demonstrated by the widespread and prolonged use of copper intrauterine devices by women [5].

Antimicrobial properties of samples coated at different time (1, 2 and 3 seconds) and with or without plasma pre-treatment was compared. Scanning electron microscopy (SEM) has been used to examine the nature of the surface modification after textile coating and laundering tests.

Cotton substrates were tested for their influence on the growth of *Pseudomonas fluorescens*, *Saccharomyces cerevisiae* and *Trichoderma viride*, using a parallel streak method. The results of 24h growth of microorganisms in the presence of cotton samples indicated that the Cu-functionalized cotton prepared by vacuum evaporation technique, did not inhibit the growth of microorganisms tested in this study.

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CATALYTIC PROPERTIES OF UREASE IMMOBILIZED ON VARIOUS POLYSILOXANE CARRIERS

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The hydrolytic variant of sol-gel method [1] is widely used in the design of the polysiloxane materials functionalized by various groups including complexing ones [2]. Recently this method calls emphasis of researchers. This is due to the possibility of applying multicomponent systems during an one-step synthesis of and to create various types of materials (powders (including consisting of submicron- and nanospheres), monolith, film coatings, etc.) [3]. Furthermore, it is possible to embed various objects in the matrix formed during the hydrolytic polycondensation reaction including biological objects. This direction has recently developed the most intense.

Our attention was drawn to the use of an enzyme such as urease as a biocatalyst in the hydrolysis of urea. Usually, enzymes fixed on the surface of various carriers to increase their resistance and prolongation. In recent years considerable attention among carriers involve hybrid organic-inorganic matrix based on silicon dioxide. Most suitable for their synthesis is a sol-gel method.

In this report we consider the catalytic activity of urease, attached in various ways to the carriers (adsorption, covalent binding, inclusion) obtained by the sol-gel method. Among them were used as follows: functionalized xerogels and mesoporous silicas obtained by template method [4]; functionalized spherical submicron- and nanoparticles of silica; magnetically sensitive particles containing a polysiloxane layer on their surface with functional groups [5]. As functional groups are used ones to easily form a hydrogen bond (for example, amine and thiol). In addition, alkyl radicals also applied to influence on the degree of hydrophobicity of carriers surface. The covalent immobilization of urease was performed using aldehydes (in the case of amino groups) or Ellman's reagent (in the case of thiol groups). Based on the analysis of experimental data we made conclusions about the factors that affect the activity of the enzyme fixed and the retention of its activity.

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INDEX OF AUTHORS

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W

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