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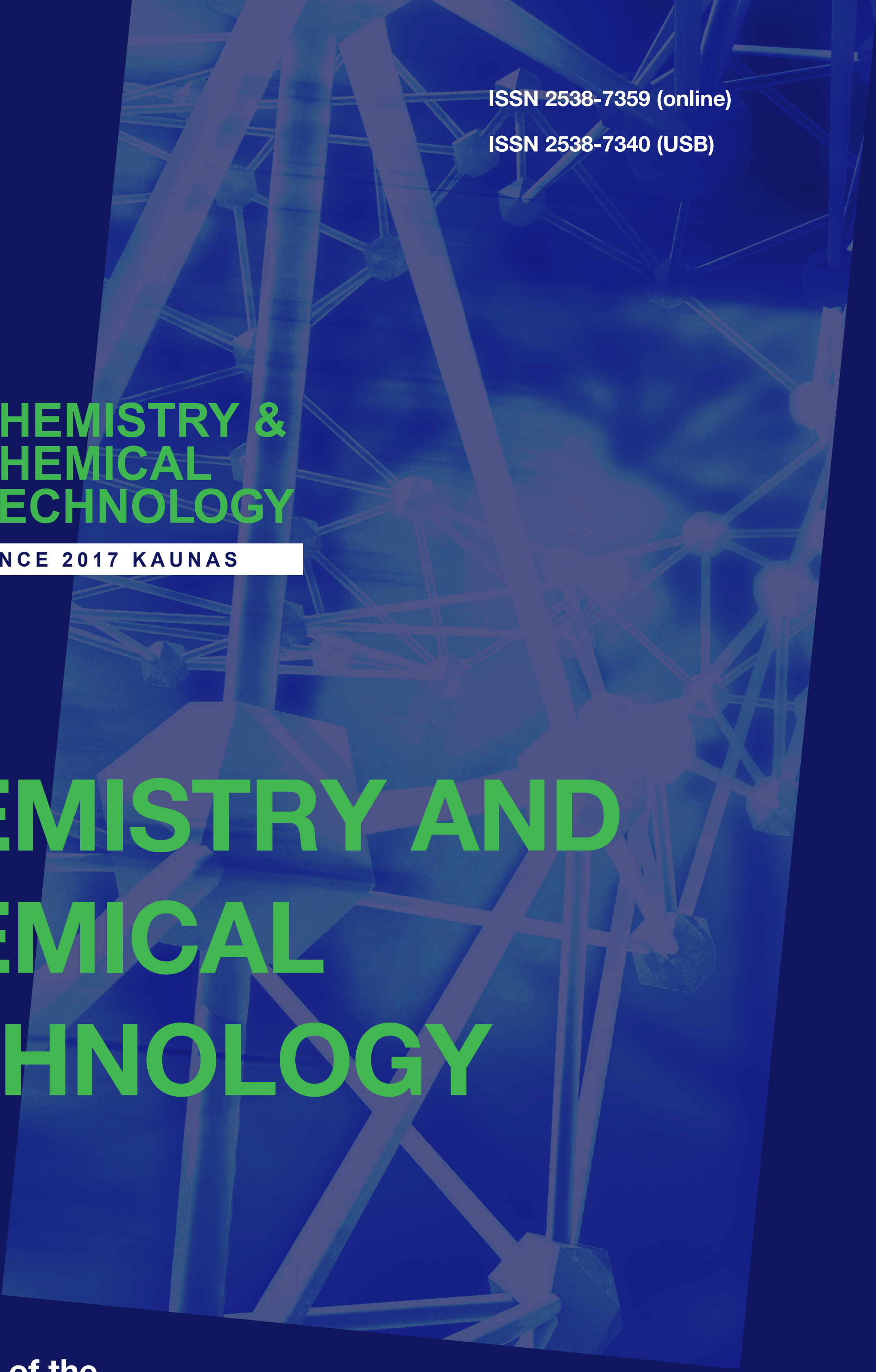

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CONTENT

Invited Lectures

PLASTICS – AGE-OLD AND BRAND-NEW

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Today, plastics are most common materials. They are companions of our daily life. Household, spare time and sport don‘t go without them, as well as large areas of medical, communication and traffic technology or that of aviation and space flight.

However, the contemporary consumable and high-tech plastics have an often not well-known, longstandig history. Interesting and exciting examples of age-old plastics, i.e. early organic polymeric materials, downwards to fossil biopolymers demonstrate their long existence and use.

This will be demonstrated with a special class of polymeric materials: the elastomers. Their more than 3600 years of development as important materials in precolumbian Mesoamerica, over the early semisynthetic rubber up to brand-new elastomers will be emphasised.

Some other fascinating modern polymeric materials will be shortly mentioned.

POLLUTION CONTROL USING GAS PHASE ADVANCED OXIDATION

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Gas-phase advanced oxidation (GPAO) is an emerging air cleaning technology based on the natural self-cleaning processes that occur in the Earth's atmosphere. The technology uses ozone, UV-C lamps and water vapor to generate gas-phase hydroxyl radicals that initiate oxidation of a wide range of pollutants. In this study four types of GPAO systems are presented: a laboratory scale prototype, a shipping container prototype, a modular prototype, and commercial scale GPAO installations. The GPAO systems treat volatile organic compounds, reduced sulfur compounds, amines, ozone, nitrogen oxides, particles and odor. The method is very effective at temperatures near ambient, in oxidising air streams and for pollution concentrations under 1000 ppm. Air residence time in the system and the rate of reaction of a given pollutant with hydroxyl radicals determine the removal efficiency. For gas phase compounds and odors including VOCs (e.g. C_6H_6 and C_3H_8) and reduced sulfur compounds (e.g. H_2S and CH_3SH), removal efficiencies exceed 80 %. The method is energy efficient relative to many established technologies and is applicable to pollutants emitted from diverse sources including food processing, foundries, water treatment, biofuel generation, and petrochemical industries. I will discuss application of the technology for reducing human exposure to pollution, including treatment of air in buildings and open urban spaces.

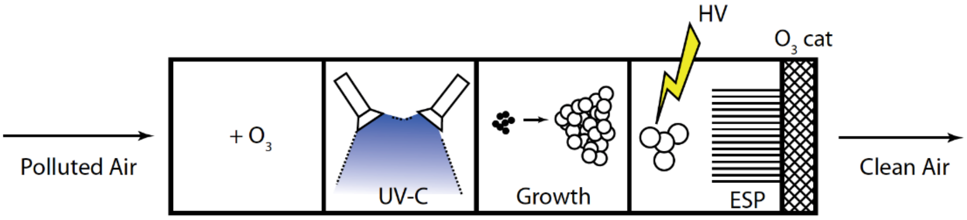

Fig. 1. Process diagram for Gas Phase Advanced Oxidation (GPAO). UV-C light is generated by a fluorescent lamp. High voltage (HV) charges particles that are removed by an electrostatic precipitator (ESP).

Fig. 2. The Infuser Climatic Gas Phase Advanced Oxidation system being tested at an iron foundry in Germany. The system was effective at destroying benzene, toluene, ethyl benzene and zylene (BTEX).

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GLUCOSINOLATES: FROM DAILY VEGETABLES TO THIOFUNCTIONAL CHEMISTRY

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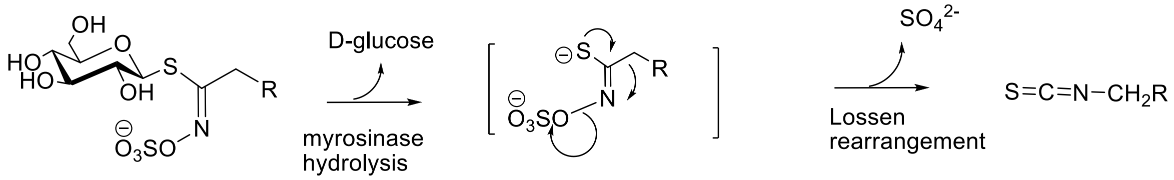
Keywords: *Vegetables, Brassicales, glucosinolates, isothiocyanates, thiofunctions.*

The botanical order Brassicales – which encompasses many of our daily vegetables – is strikingly chemo-characterized by the presence of thiosaccharidic secondary metabolites called glucosinolates [1, 2]. Those atypical anomeric thioesters display a remarkable structural homogeneity over three parts: a *β*-D-glucopyrano unit, a *NO*-sulfated anomeric *(Z)*-thiohydroximate functional group and a rather hydrophobic side chain, the constitution of which is the sole structural variant in Nature, according to plant species.

Associated in plants with an uncommon glucohydrolase – myrosinase (E.C.3.2.1.147) – glucosinolates usually operate like precursors to biologically active isothiocyanates:



Extraction of glucosinolates from appropriate vegetable sources can prove convenient in a number of cases to obtain pure compounds [3]. Nevertheless, the chemical synthesis approach has appeared to be a more efficient way to access most of glucosinolates – either natural or artificial. Diversified synthetic approaches of glucosinolates and tailor-made analogues - mainly targeting the myrosinase inhibition process – have been developed over the last decades [4].

In other respects, the discovery of several odd chemo-enzymatic transformations of glucosinolates have sparked off, in our laboratory, investigations on less common organic thiofunctionalities, such as cyclic thionocarbamates [5] and thio-imidate *N*-oxides [6].

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CAN GRAPHENE FEEL TASTE?

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Graphene, owing to its unique mechanical, thermal and electrical properties, finds more and more in various fields. One of the fastest growing graphene application fields is electrochemical sensing. A great number of papers was published in this field over the last decade. Nevertheless, this is still an attractive subject and new approaches are still discovered.

(Bio)sensors are already used in practical life for several decades. Electrochemical (bio)sensors are fast and reliable as well as cheap and they can be used for both disposable and long term operations. One of the fascinating applications is food analysis, so called “artificial tasting” of food, drinks and beverages.

Many papers report graphene employed in electrochemical sensing owing to its action as a signal amplifier via increase of electroactive area and as electrocatalyst which decreases activation energy of an electrochemical reaction. The main challenge is an immobilisation of graphene flakes on the electrode surface and an assurance of its stable response. For this purpose, polymer films are often used in a sensor development technology.

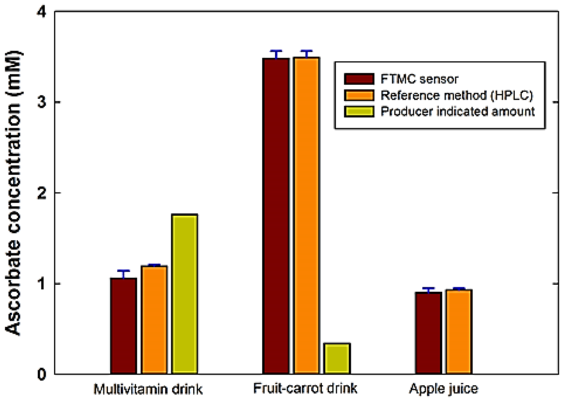

Fig. 1. Comparison of ascorbate sensor response with the reference (HPLC) method.

Ascorbate sensor was developed modifying the glassy carbon electrode with graphene-chitosan polymer film. The results showed that the sensitivity of the sensor was increasing with decrease in graphene load in the composite film. The highest response was obtained when 10 pg/mL of graphene was used. Such sensor was stable, reproducible, sensitive, and could “taste” ascorbate precisely. It was also applied to analysis of some natural samples such as soft drinks and juices. In order to evaluate its reliability, the reference analysis of the same samples was performed in other institution using chromatographic (HPLC) method. The response was in a good agreement with the graphene-based sensor as seen from Fig. 1. The deviation of the sensor response in the natural samples was up to 3 %.

The electrocatalytic activity of graphene was not satisfactory for the development of biosensors with oxyreductase enzymes. Therefore, additional natural mediators – some electropolymerised B_2 and B_9 vitamins were used to decrease an overpotential of the analyte response. Sensors for glucose, cholesterol, hypoxanthine, glutamate were developed and tested in natural samples as well as evaluated with the reference methods.

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Organic Chemistry and Technology

SYNTHESIS AND TRANSFORMATIONS OF 3-[(5-ACETYL-4-METHYLTHIAZOL-2-YL)(4-METHOXYPHENYL)AMINO]PROPANOIC ACID

I. Parašotas, E. Urbonavičiūtė, K. Anusevičius, I. Tumosienė, I. Jonuškienė, K. Kantminienė, R. Vaickelionienė, V. Mickevičius
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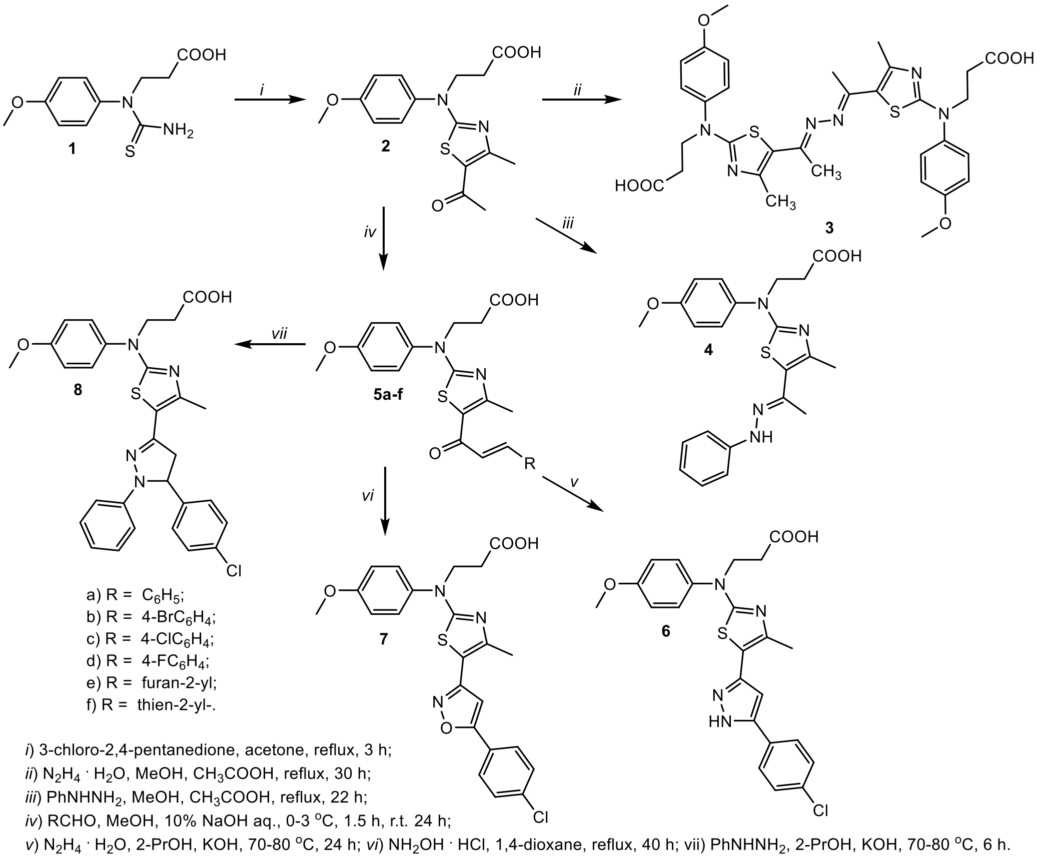
Thiazole derivatives play a crucial role in medical chemistry. They are associated with a broad spectrum of biological properties, such as anticonvulsant, antimicrobial, antituberculous, cytotoxic, anti-inflammatory, antioxidant activity, etc.

3-[(5-Acetyl-4-methylthiazol-2-yl)(4-methoxyphenyl)amino]propanoic acid (**2**) was synthesized from thioureido acid **1** and 3-chloropentane-2,4-dione in acetone at reflux temperature. Sodium acetate was used to convert the formed aminothiazolium chloride into the base. Reaction of thiazole **2** with hydrazine and phenylhydrazine in methanol in the presence of acetic acid as a catalyst resulted in formation of hydrazone type compounds **3** and **4**.



a) R = C_6H_5;
b) R = 4-BrC_6H_4;
c) R = 4-ClC_6H_4;
d) R = 4-FC_6H_4;
e) R = furan-2-yl;
f) R = thien-2-yl-.

i) 3-chloro-2,4-pentanedione, acetone, reflux, 3 h;
ii) $N_2H_4 \cdot H_2O$, MeOH, CH_3COOH, reflux, 30 h;
iii) $PhNHNH_2$, MeOH, CH_3COOH, reflux, 22 h;
iv) RCHO, MeOH, 10% NaOH aq., 0-3 °C, 1.5 h, r.t. 24 h;
v) $N_2H_4 \cdot H_2O$, 2-PrOH, KOH, 70-80 °C, 24 h; *vi*) $NH_2OH \cdot HCl$, 1,4-dioxane, reflux, 40 h; vii) $PhNHNH_2$, 2-PrOH, KOH, 70-80 °C, 6 h.

Scheme. Synthesis of 3-[(5-acetyl-4-methylthiazol-2-yl)(4-methoxyphenyl)amino]propanoic acid derivatives **2–8**

Chalcones **5a–f** were synthesized by *Claisen–Schmidt* condensation of acid **2** with various aromatic aldehydes in methanol and 10% aqueous sodium hydroxide solution. Heterocyclization reactions of trisubstituted thiazole **5c** bearing chalcone moiety with nitrogen nucleophiles, such as hydrazine, phenylhydrazine, and hydroxylamine, were investigated. Reaction of **5c** with hydrazine monohydrate in propan-2-ol in the presence of potassium hydroxide provided pyrazole derivative **6**, whereas isoxazole derivative **7** was prepared by refluxing **5c** with hydroxylamine hydrochloride in 1,4-dioxane in the absence of basic catalyst. Dihydropyrazole derivative **8** was synthesized from acid **2** and phenylhydrazine.

3-(1-(4-(PHENYLAMINO)PHENYL)THIOUREIDO)PROPANOIC ACID DERIVATIVES BEARING 1,3-THIAZOLE MOIETY

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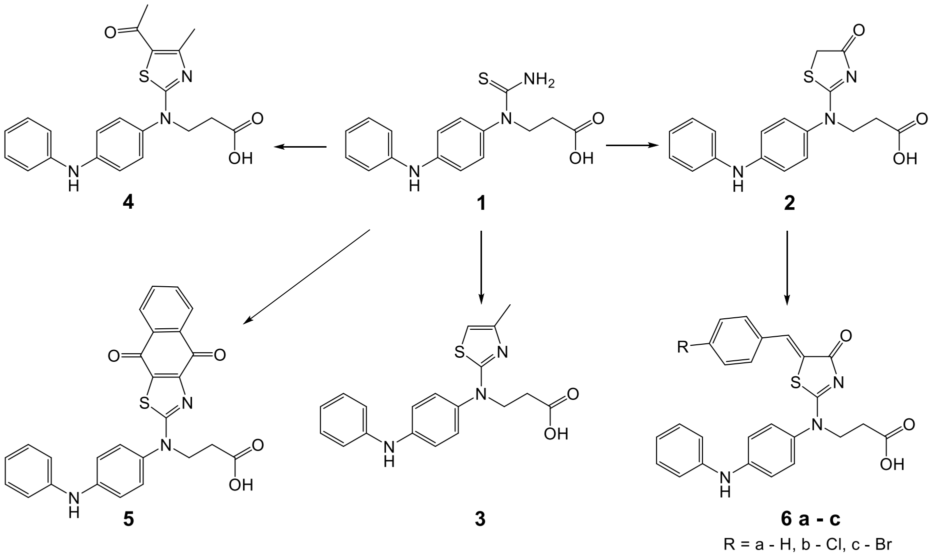
As an ongoing search of biologically active compounds, *Hanthsch* reactions of 3-(1-(4-(phenylamino)phenyl)thioureido)propanoic acid (**1**) with α-halocarbonylic compounds were investigated.

3-((4-Oxo-4,5-dihydrothiazol-2-yl)(4-(phenylamino)phenyl)amino)propanoic acid (**2**) was synthesized by treating thioureido acid **1** with chloroacetic acid in water in the presence of sodium acetate, whereas reaction of acid **1** with chloropropanone in acetone provided 3-((4-methylthiazol-2-yl)(4-(phenylamino)phenyl)amino)propanoic acid (**3**) in good yield. Reaction of thioureido acid **1** with 3-chloro-2,4-pentanedione in acetone gave 3-((5-acetyl-4-methylthiazol-2-yl)(4-(phenylamino)phenyl) amino)propanoic acid (**4**).



Scheme. Synthesis of 3-(1-(4-(phenylamino)phenyl)thioureido)propanoic acid acid derivatives

3-((4,9-Dioxo-4,9-dihydronaphtho[2,3-d]thiazol-2-yl)(4-(phenylamino)phenyl)amino)propanoic acid (**5**) was synthesized by the reaction of thioureido acid **1** with 2,3-dichloro-1,4-naphthoquinone in glacial acetic acid in the presence of sodium acetate. Condensation reaction of the formed 1,3-thiazole **2** with aromatic aldehydes in water in the presence of sodium carbonate provided compounds **6a-c**.

Structures of all synthesized compounds have been confirmed by ^{1}H NMR, ^{13}C NMR, and mass spectrometry data.

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SYNTHESIS OF NEW CONSTRAINED HETEROCYCLIC ANALOGUES OF 5-AMINOVALERIC ACID

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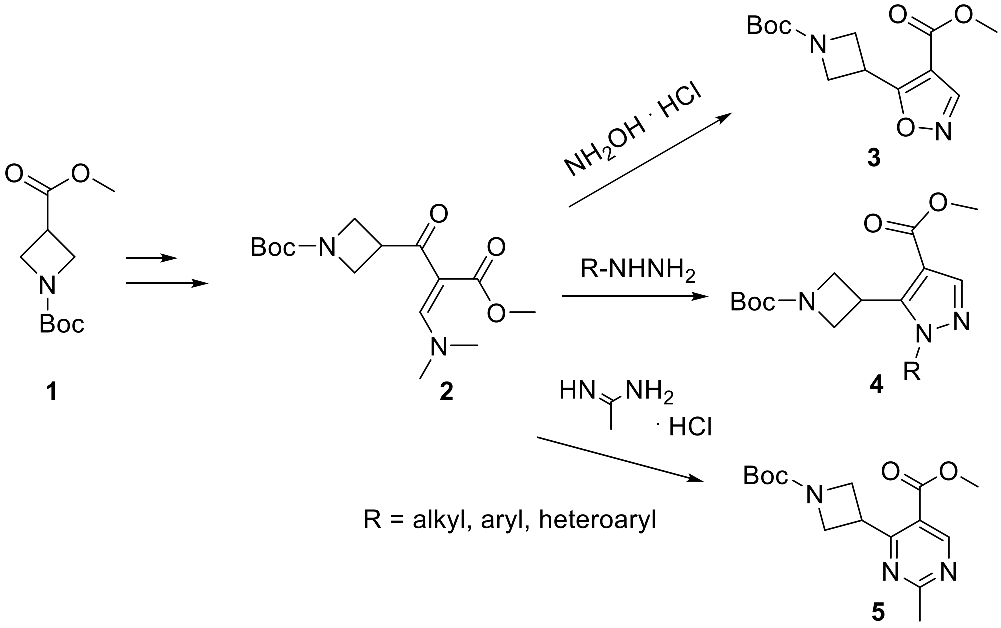
5-Aminovaleric (5-aminopentanoic acid) is a naturally occurring organic compound, which can be produced both endogenously or through bacterial catabolism of lysine. It is also believed that it acts as a methylene homologue of *γ*-aminobutyric acid (GABA) and functions as a weak GABA agonist [1,2]. It was shown recently that 5-aminovaleric acid suppresses the development of severe seizures related to neurological disorders such as epilepsy [3]. It is known that heterocyclic analogues of GABA are useful as agents in the treatment of epilepsy, depression, anxiety, panic, pain and other neuropathological disorders [4].

The aim of the present work was the construction of functionalized five-membered and six-membered aromatic heterocycles such as isoxazole, pyrazole and pyrimidine, respectively, bearing acid and amine functionalities *ortho*-positioned onto heterocyclic ring, as mimetics of 5-aminovaleric acid. The accomplished synthesis pathway is outlined below in Scheme 1. The target amino acid derivatives were prepared as *N*-Boc protected methyl esters.



Scheme 1. Synthesis of heterocyclic analogues of 5-aminovaleric acid.

The structure of the synthesized new heterocyclic compounds was confirmed by data of ^{1}H, ^{13}C and ^{15}N NMR spectroscopy and HRMS.

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SYNTHESIS OF METHYL 4-[(2*R*)- and (2*S*)-PYRROLIDIN-2-YL]-1,3-THIAZOLE]-5-CARBOXYLATES

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It is now widely acknowledged that the success of compounds through the drug discovery process is strongly associated with molecular and physical properties. In 2012, Nadin et al. challenged the synthetic community with the task of developing synthetic methodology that would be better suited to the preparation of lead-like molecules [1]. With this in mind, and building on Lipinski's rules, lead-oriented synthesis was defined with the following guidelines: molecular weight range of 200–350, molecules with chemically active, electrophilic or redox active functional groups should be avoided and molecules with a lower degree of aromatic character should be prioritised.

In the present work the synthesis of highly functionalized optically active thiazole derivatives was accomplished starting from commercially available *N*-Boc protected enantiopure *L*- and *D*-prolines. In the first stage of the synthesis, *L*- and *D*-prolines **1a** and **1b** were converted to the □-ketoesters **2a** and **2b**, respectively (*Scheme 1*). The obtained dicarbonyl compounds were treated with NBS, to afford the corresponding brominated derivatives **3a** and **3b**. Following reactions of the latter building blocks with thiourea, *N*-substituted thioureas and thioamides gave methyl thiazole-5-carboxylates **4a-7a** and **4b-7b**, respectively, which possessed chiral pyrolidine substitutents at C-4 of the thiazole ring.

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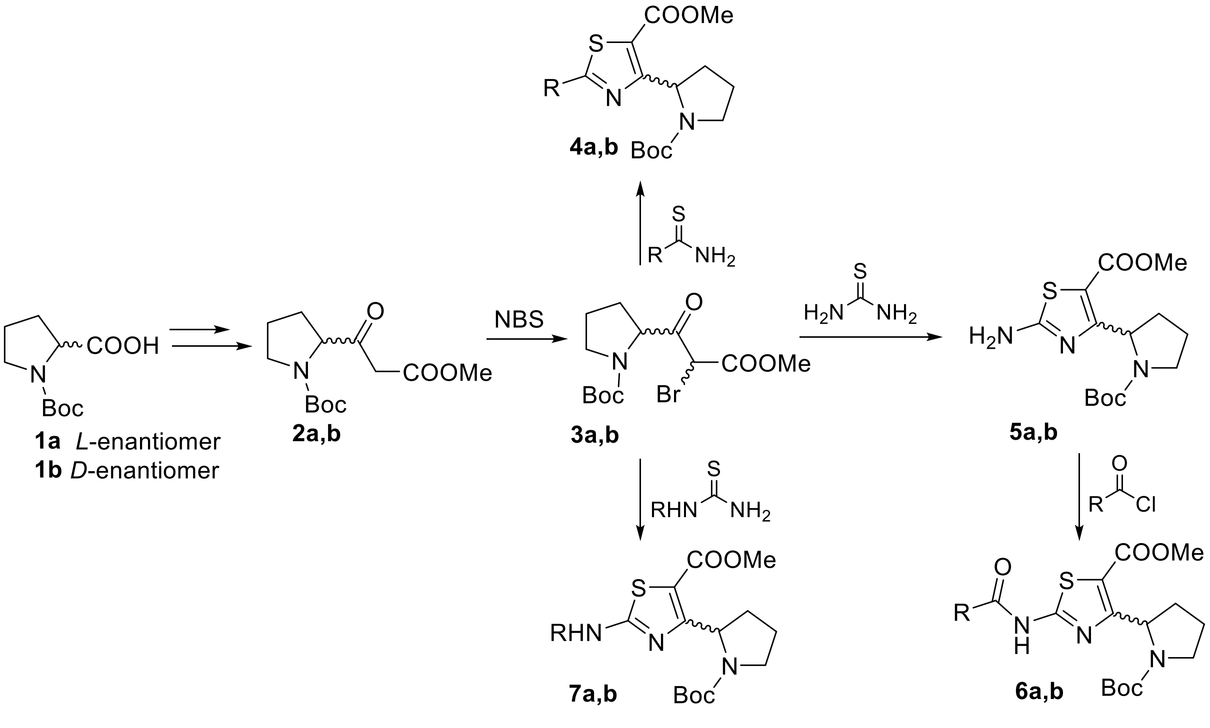

Scheme 1.

The structures of the isolated compounds were proved by means of mass spectrometry, IR and NMR spectroscopy.

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SYNTHESIS AND PROPERTIES OF 3-SUBSTITUTED 2-CYANO-2-PROPENOIC ACID DERIVASTIVES

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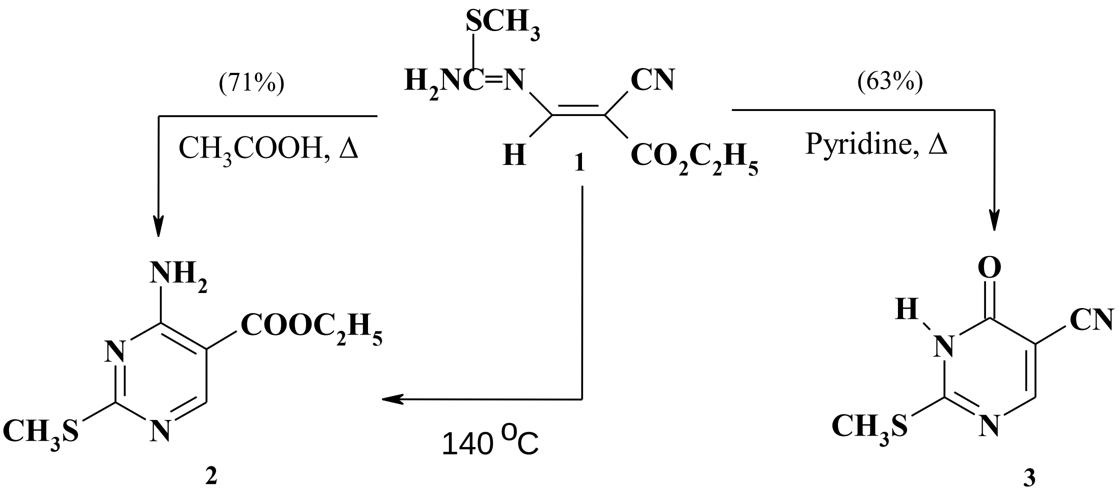
Substituted 2-cyano-2-propenoic acid derivatives have received a considerable attention because of their antiviral [1], anticancer [2] activities, as syntons of the druglike molecules in treatments for disorders of central nervous system [3] and the possibility of application in agrochemistry as herbicides [4]. On the other hand, condensation reaction of 3-alkoxy-2-cyano-2-propenoates with nucleophiles gives rise to a mixture of important products via two different ring closures [5].

(*E*)-2-Cyano-3-(*S*-methylisothioureido)-2-propenoic acid ethyl ester (**1**) was synthesized by reaction of (*E*)-2-cyano-3-ethoxy-2-propenoic acid ethyl ester with S-methylisothioureido sulphate. The cyclization of ester **1** has been studied. It was found that the reaction in boiling glacial acetic acid or without solvent at 140 °C led to formation of 4-amino-2-methylsulfanylpyrimidine-5-carboxylate (**2**), while ring closure in boiling pyridine gives rise to 2-methylsulfanyl-4-oxo-3,4-dihydropyrimidine-5-carbonitrile (**3**).



The treatment of ester **1** in aqueous alkaline media leads to a mixture of products **2**, **3** and ethyl (*Z*)- and (*E*)-2-cyano-3-ureido-2-propenoates [5].

The purity and structure of synthesised compounds were proved by TL chromatography, UV, IR, ^{1}H and ^{13}C NMR spectral data.

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NEUTRAL COLOR ELECTROCHROMIC DEVICE UTILIZING TRIPHENYLAMINE FUNCTIONALISED REDOX ACTIVE MATERIALS

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Electrochromism is a property of material to change color upon oxidation/reduction process. Market applications of devices utilizing electrochromic materials are very broad, including e.g. “smart windows” and display technologies [1].

In 1994 novel type of electrochromic device was developed by the group of D. Fitzmaurice, utilizing some features of the dye-sensitized solar cell [2]. In a typical device 4,4’-bipyridinium derivative (viologene), functionalized with different anchoring groups, forms monolayer on a mesoporous TiO_2 scaffold. Transparent electrode is placed on top of it, leaving small gap (~50-100 µm), which is further filled with liquid electrolyte. In order to compensate charges electrolyte contains ferrocene, which can be reversibly oxidized. Redox-active molecules from the field of the hole-transporting materials (HTMs) are known to change color upon oxidation [3], and thus can be used as an alternative to the ferrocene. Combination of viologene with such molecules would lead to the broad absorption over the whole visible range, resulting in transparent to neutral color device switching.

Two commercially available materials with reversible oxidation and intense color changes were tested in electrochromic devices, constructed following previously published procedure [4]. Spiro-OMeTAD, common HTM for the solar cell applications, upon oxidation changes color to brick-red[3]. V886, another HTM [5], synthesized in our group, changes color to intensive green-blue.

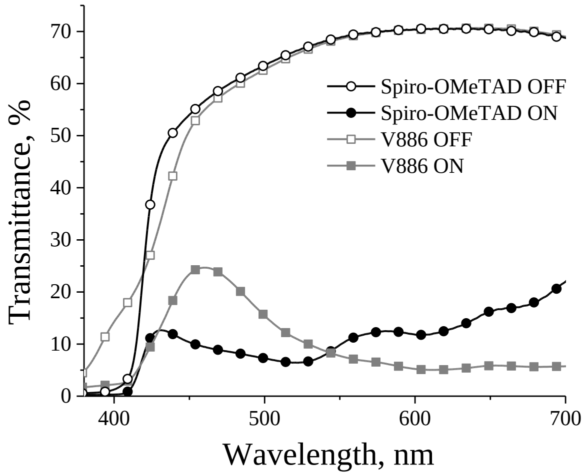

Fig. 1. UV−vis transmittance response of electrochromic devices containing Spiro-OMeTAD (black line, circles) or V886 (gray line, squares) at 0 V (OFF state) and 1.5 V (ON state).

As can be seen from the **Fig. 1.** by applying 1.5 V voltage, transparency is reduced over the whole visible spectrum range. Unfortunately, this change was found to be only partially reversible. Further optimization of device construction and/or structure of the molecules is crucial in order to get fully operational device.

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THIN FILM DEGRADATION TESTING OF LUBRICANTS FOR GAS GENERATOR, DIESEL ENGINE AND HYDRAULIC APPLICATIONS

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Lubricant stability is often tested at temperatures above those of normal operating regime to reduce testing durations. Increase in viscosity and acidity frequently constitutes a failing mark, although lubricant still remains liquid. Thus thin film tests gain popularity, because they can show the ability of a lubricant to remain liquid without decomposing into volatiles or polymerizing to solids [1].

Several commercial lubricants were obtained from BM Energy (Latvia) and CJC (Denmark), representing different manufacturers of diesel engine, gas generator and transmission lubricants. Thin film degradation was performed on low carbon steel coupons [1]. Films of initial 500 µm thickness were heated at 130 °C for up to 1815 hrs and then at 140 °C in a Memmert forced draft oven. From 3 to 5 coupons were used for each lubricant and periodically volatile emissions were measured gravimetrically. Typical plots for each lubricant appear in Fig. 1 (i). Time and Temperature Superposition (TTS) was utilized to normalize testing durations at 130 °C to those at 140 °C by applying van't Hoff's rule, i.e. doubling the duration with 10 °C drop in temperature [2], e.g.1815 hrs at 130 °C into 907.5 hrs at 140 °C.

When suspecting film solidification, the coupon was placed into a beaker with 20 mL of the same fresh lubricant and held for 180 min at 90 °C, stirring it several times. Afterwards the coupon was rinsed with heptane and dried. Most samples eventually produced insoluble residues when degreasing in chloroform for 180 min. Coupons were photographed before and after degreasing or heating.

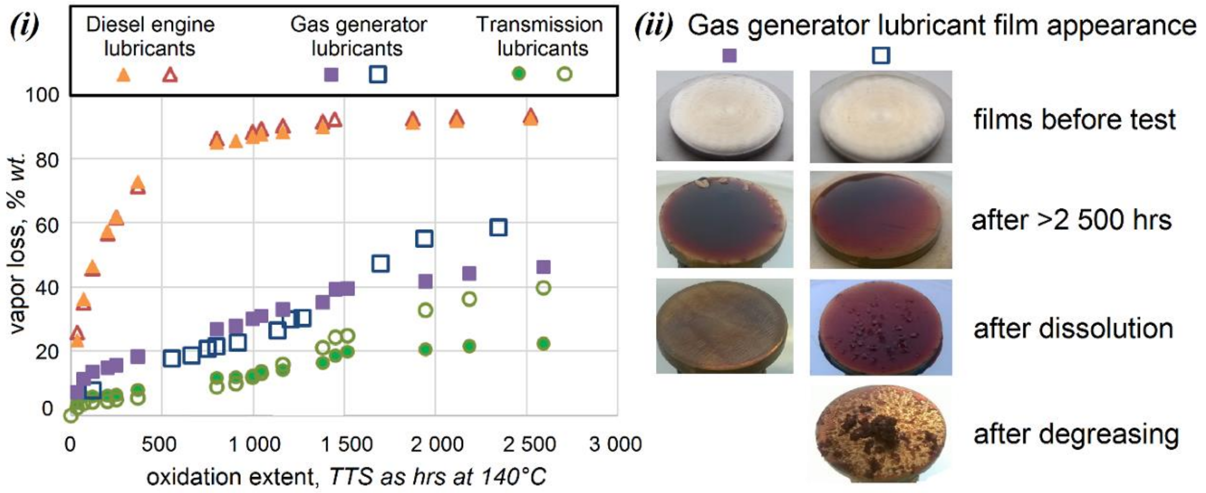

Fig. 1. (i) Volatile emissions from 500 µm lubricant films when heating at 130°C and 140°C, durations normalized by Time and Temperature Superposition (TTS) [2]. (ii) Appearance of representative coupons before and after heating and degreasing (just one sample was degreased) for the two tested gas generator lubricants.

Results show that commercial lubricants produce very different trends of volatile emissions and formation of residues insoluble in fresh oil. Lab observations are likely to relate to field performance.

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MANAGEMENT OF LNG AGEING PROCESS

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The popularity of natural gas is increasing in the world. Natural gas is liquefied below its boiling point (-161.5 °C) slightly above atmospheric pressure [1] to reduce its volume by a factor of 600 and transported as Liquefied Natural Gas (LNG) by sea, road and railway especially in places where is inconvenient to support natural gas through the pipelines to the grid. During transportation via storage, constituents, which have the lowest boiling points (nitrogen and methane), start to vaporize doe to the heat input entering from surrounding. The vaporization of methane and nitrogen causes changes of initial composition and properties of the LNG. This process of preferential vaporization is known as weathering or aging, when volatile components convert in gas statement and heavier components such as ethane, propane and other higher hydrocarbons remain in volume of LNG. This makes changes of properties such as gross calorific value, Wobbe index, density and could influence the price and quality of the gas [2].

To understand ageing process of LNG, the mathematical modeling of ageing was done. It was analyzed changes of initial LNG composition during storage and factors, which influence a major impact of ageing process. As validation of mathematical modeling selected data of three different periods obtained from historical Floating Storage Regasification Unit (FSRU) tanks measurement system. Polynomial trend equations were estimated to describe corresponding evaporation of methane and linear trend equations were estimated to describe corresponding evaporation of nitrogen and calculate what amount of methane and nitrogen evaporate per day. For the suitability of natural gas in different markets higher heating value and Wobbe index were calculated from LNG composition of selected data according standard ISO 697-1995. For calculated higher heating and Wobbe index values were made mathematical modeling to calculate every day changes. All models were tested using collected data to predict LNG properties changes following LNG storage for 60 days in FSRU if LNG is not out-off specification according industrial requirements.

Multiple regression model based on largest period of LNG storage was estimated to determine influence of vapor pressure of tank, volume changes, technological processes and LNG temperature of evaporation of methane and nitrogen. The statiscal analysis concerned multiple regression and t- test.

The functions corresponding evaporation of methane and nitrogen determined that methane evaporated intervals between 0.0002–0.0004 % per day, as well as nitrogen evaporated intervals between 0.007–0.0094 % per day. The results showed that evaporation of nitrogen limits evaporation of methane and resulting higher heating value and Wobbe index. Heating value increased intervals between 0.0099–0.0105 $MJ \cdot m^{-3}$ per day, Wobbe index increased intervals between 0.0087–0.00103 $MJ \cdot m^{-3}$ per day.

The influence of methane evaporation during LNG storage has a significant effect on LNG volume and LNG temperature ($p<0.05$) in FSRU tanks. The influence of nitrogen evaporation during LNG storage has a significant effect on LNG vapor pressure and LNG temperature ($p < 0.05$) in FSRU tanks.

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SYNTHESIS OF LANTHANIDE COMPLEXES WITH BICYCLIC OR PHENANTHROLINE LIGANDS AND INVESTIGATION OF THEIR PHOTOPHYSICAL PROPERTIES

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The unique chemistry of lanthanoids offers access to new complexes with unknown properties but this is coupled with significant synthetic challenges owing to the unpredictability of derivative formation [1]. The complexes of trivalent lanthanide ions, especially those with organic ligands exhibit a unique kind of luminescence.

In the present work, we were used for synthesis of complexes known and new ligands (Fig.1).

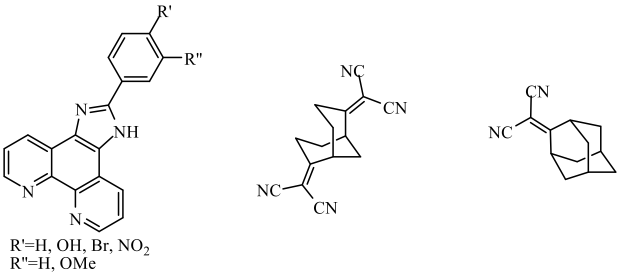

Fig. 1. Ligands

The lanthanide ions have high coordination numbers. Also, a complex containing lanthanide ion should be high thermodynamic stabile, coordination sphere saturated and kinetic inertness. So, we tested on various substrates proportions for the synthesis of our complexes.

Several new series of rare-earth complexes have been synthesized in two ways. The first is a classical method in which substrates are dissolved in a polar solvent. The reactions durations were 3-7 days in this method [2]. The second, reactions were carried out at microwave for 1-3 h. This method was very suitable for poorly soluble ligands.

We summarized data on the synthesis and photophysical properties of complexes and present the poster.

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MONOUNSATURATION EFFECTS ON LOW TEMPERATURE FLUIDITY OF ESTER DERIVATIVES

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Camelina and Crambe crops are potential sources for medium-chain fatty acids (MCFA) from C8 to C14, which represent an important feedstock for specialty oleochemicals. Their oils can also find utilization as lubricants after conversion into esters, if appropriate viscosity is achieved with good fluidity at low temperatures, usually measured as pour point. While MCFA esters might have fluidity problems, cis-double bonds can reduce pour pt. [1] The most abundant fatty acid (FA) in Camelina oil is gondoic (i.e. 11-eicosenoic a.), while Crambe oil contains up to 60 % erucic a. (i.e. 13-docosenoic a.). Initially dibasic esters with MCFA and oleic a. were synthesized, see Fig. 1, using a previously established method [2] with two major types of polyhydric alcohol derivatives: 1) H-containing β-carbon polyol with R=H in Fig. 1 and 2) tertiary β-carbon polyol. Additional branched moieties were also attached as R' for better fluidity. Kinematic viscosities were measured at 40 °C using Cannon-Fenske method (ASTM D455) and in some cases estimated from structural data. Pour pt. was measured under the same thermal cooling regime as in ASTM D97, just in smaller sample sizes.

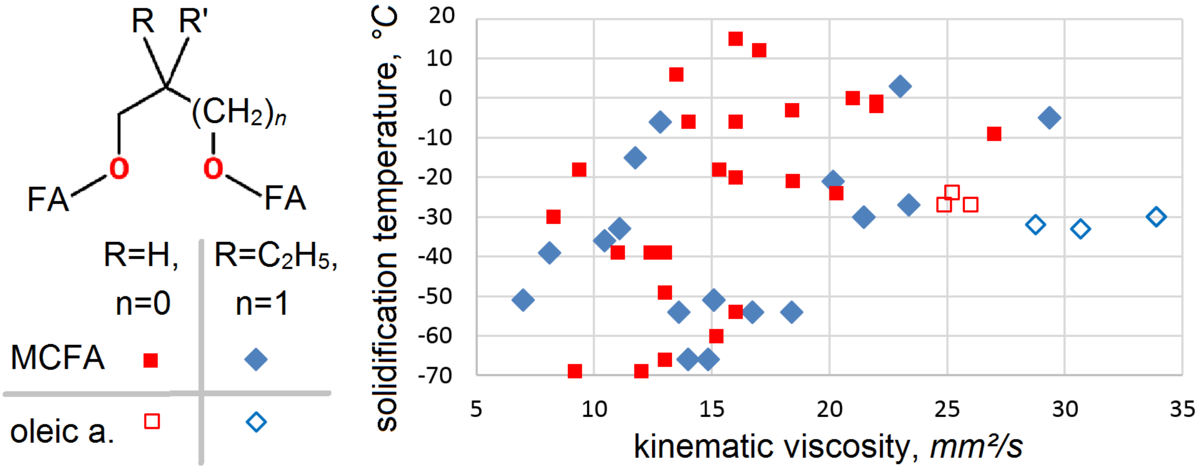

Fig. 1. Molecular structure of synthesized dibasic esters with various FA and R' (left). Their solidification temperatures (measured as pour points, °C) and kinematic viscosities, measured (or predicted) at 40°C (right).

Oleates clearly show that higher mol. weight increases viscosity. Since FA moieties were linear, MCFA esters with viscosities over 20 mm²/s could not retain fluidity at -30 °C. However, oleates approached 35 mm²/s viscosity with better pour pt. and showed a remarkable tendency to retain fluidity around -30 °C (with tertiary β-carbon) or -25 °C (when R=H) despite variation of R' moieties. Further synthesis with gondoic and erucic esters can give even more flexibility in achieving needed viscosities and lead to broader industrial viability of Camelina and Crambe crops.

Acknowledgment

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SYNTHESIS OF NEW HETEROCYCLIC ANALOGUES OF 4-AMINOBUTANOIC ACID (GABA) VIA SUZUKI-MIYAURA CROSS-COUPLING REACTION

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4-Aminobutanoic acid (γ-aminobutyric acid, GABA) is the major inhibitory neurotransmitter in the human central nervous system. It plays the principal role in reducing neuronal excitability throughout the nervous system [1]. It is well documented that GABA deficiency is associated with several neurological disorders such as Huntington's chorea, Parkinson's and Alzheimer's disease and other psychiatric disorders [2]. Over recent years, there has been increasing interest in the design and preparation of new synthetic GABA analogues, which can be considered as potential drugs in the treatment of neurodegenerative diseases. For example, (S)-Pregabalin, (S)-(+)-3-(aminomethyl)-5-methylhexanoic acid, marketed under the brand name Lyrica (Pfizer, Inc.) among others, is a medication used to treat epilepsy, neuropatic pain and anxiety disorder [3,4] while Vigabatrin, 4-aminohex-5-enoic acid, sold under the brand name Sabril (Lundbeck Inc.), is an antiepileptic drug [5].

Recently, several heterocyclic analogues of GABA, including 4-(aminomethyl)furan-2-carboxylic acid and 4-(aminomethyl)thiophene-2-carboxylic acid, have been synthesized and investigated as GABA aminotransferase enzyme inactivators [6]. In the present work new heterocyclic analogues of GABA, possessing azetidine ring as a carrier of amine functionality and the 4-substituted pyrazole ring in the side chain at C-3, were designed and synthesized.

The starting ester **1** was prepared by the Horner-Wadsworth-Emmons reaction from N-Boc-4-piperidinone **1**. Treatment of the α,β-unsaturated ester **1** with 4-bromopyrazole in the presence of DBU gave the aduct **2** in a good yield.

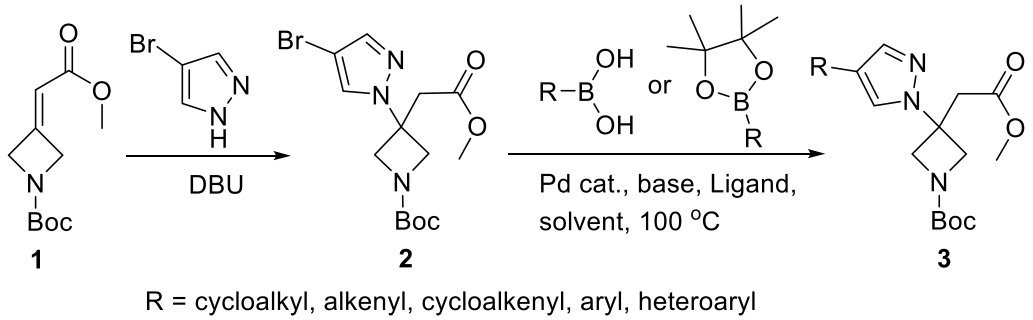

Fig. 1. Synthesis of new heterocyclic analogues of GABA

Suzuki-Miyaura couplings of the brominated substrate 2 and various cycloalkyl, alkenyl, cycloalkenyl and (het)arylboronic acids were carried out at 100 °C with 5 mol% Pd catalyst in the presence of base to afford heterocyclic GABA analogues **3** in N,O-protected forms in the moderate to good yields.

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SYNTHESIS AND INVESTIGATION OF 1-(4-ACETYLPHENYL)-5-OXOPYRROLIDINE-3-CARBOXYLIC ACID DERIVATIVES

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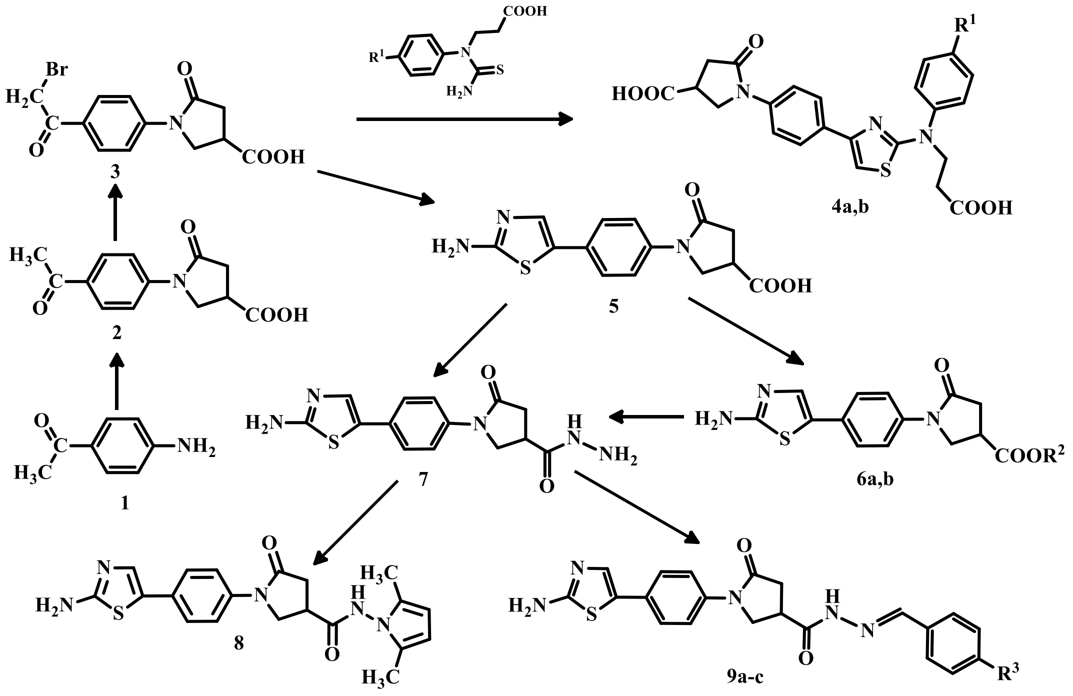
Thiazoles and their derivatives are appreciated for a wide range of biological activity, such as antibacterial [1], antitubercular [2], antiviral [3], anti-inflammatory [4], anticancer [5] and other. In this work synthesis of new potentially biologically active compounds, that have both – 5-oxopyrrolidine and thiazole heterocyclic fragments in their structure was performed using 4-aminoacetophenone (**1**) as a precursor.

Reaction of 4-aminoacetophenone (**1**) with itaconic acid in water provided oxopyrrolidine **2**, which was brominated with Br_2 in acetic acid at room temperature and resulted in formation of 1-[4-(bromoacetyl)phenyl]-5-oxopyrrolidine-3-carboxylic acid (**3**). The substituted thiazoles **4a,b** and **5** were synthesized from corresponding thioureido acid or thiourea and α-bromocarbonyl compound **2**. 5-Oxopyrrolidine-3-carboxylic acid (**5**) was converted to esters **6a,b**. The reaction of **6a,b** with hydrazine hydrate provided carbohydrazide **7**. Condensation reaction of **7** with 2,5-hexanedione resulted in the formation of *N*-substituted-2,5-dimethylpyrrole **8**. Hydrazones **9a-c** were synthesized in good yields (70-91 %) by reaction of hydrazide **7** with aromatic aldehydes in propan-2-ol at the reflux temperature.



4a: R^1 = CH_3; 4b: R^1 = Cl; 6a: R^2 = CH_3; 6b: R^2 = C_2H_5; 9a: R^3 = H; 9b: R^3 = Cl; 9c: R^3 = NO_2

The structures of synthesized compounds have been confirmed by the elemental analysis, ^1H, ^{13}C NMR, and IR spectroscopy.

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SYNTHESIS OF 4,5-DISUBSTITUTED-1,2,3-THIADIAZOLES

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Heat shock protein 90 (Hsp90) belongs to the family of chaperones; the main function of those is to fold other proteins. Recent data showed that the amount of this chaperone significantly increases in cancerous cells, therefore it was concluded that Hsp90 is necessary for the growth of malignant cells [1]. Moreover, the expression of large amounts of heat shock proteins accompanies parasite's adaptation in human host [2]. Treatment for these types of diseases is expected to be found by inhibiting the Hsp90 protein. The development of these synthetic drugs is advancing rapidly as some of the compounds are already enrolled in clinical trials.

Continuing the ongoing research [3, 4] on investigation of the Hsp90 inhibiting activity of synthetic compounds, a variety of 4,5-disubstituted-1,2,3-thiadiazoles were synthesized. The starting materials, 4-chloro- or 4-ethyl-1,3-benzenediols **1** were treated with arylacetic acids **2** in the presence of boron trifluoride diethyl etherate. Obtained ketones **3** were used in the following reaction to yield hydrazones **4**. The following treatment of compounds **4** with thionyl chloride led to formation of the desired 4,5-diaryl-1,2,3-thiadiazoles **5**.

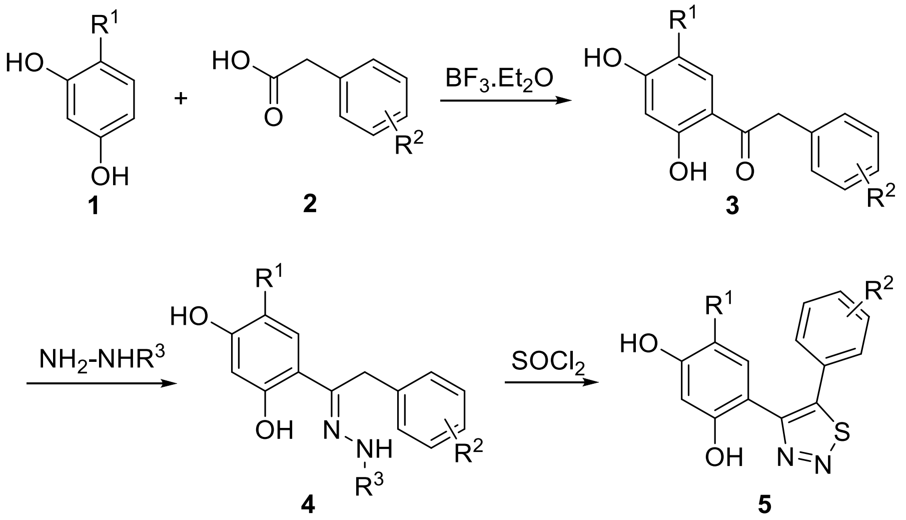

Fig. 1. Synthesis of 4,5-diaryl-1,2,3-thiadiazoles. R^1=Cl, Et; R^2=2-OMe, 3-OMe, 3-Cl; R^3=H, COOEt, Ts

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SYNTHESIS OF 2-SUBSTITUTED 3,5-DIARYLTHIOPHENES *VIA* CYCLIZATION OF 1,3-DIARYLPROPYNONES

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Thiophenes constitute important scaffolds in natural products, pharmaceuticals [1], and most importantly as functional π-electron systems in the science of organic materials [2]. Usually, conjugated thiophenes are substituted in 2 and 5 positions, whereas 2,4-disubstitution pattern due to difficult access are not widely used. Although 2,4-conectivity maintain linear structure it definitely restricts conjugative electronic communication in the ground state [3], 2,3,5-substitution pattern may lead to new possibilities. Therefore we present one step method for synthesis of 2-substituted-3,5-diarylthiophenes *via* cyclization of 1,3-diarylpropynones.

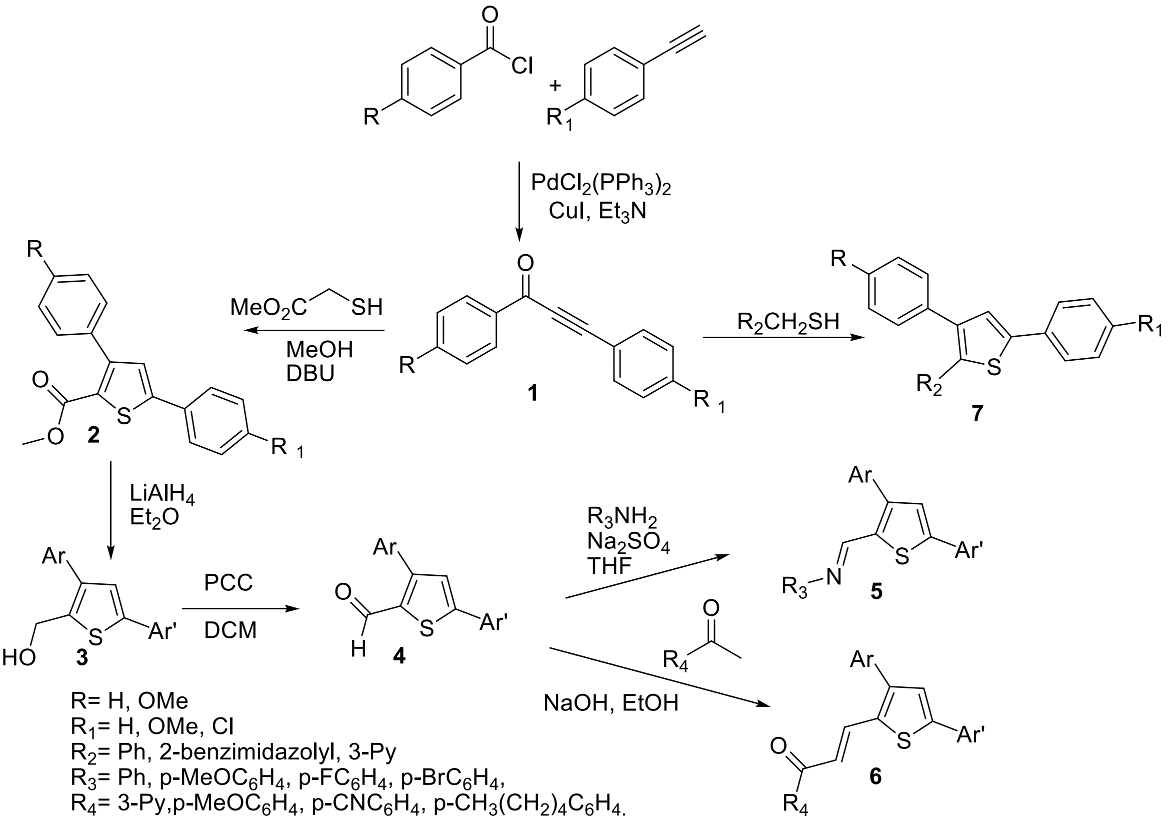

Fig. 1. Synthetic pathway to the 2-substituted 3,5-diarylthiophenes.

Preparation of starting materials **1** was chosen using Sonogashira coupling conditions of commercially available arylacetylenes and aroylchlorides. Next, known conditions [3] using DBU in MeOH were applied for cyclization of methyl 2-mercaptoacetate and 1,3-diarylpropynones **1** to yield thiophenes **2**. Seeking extended conjugated system, compounds **2** were transformed to the corresponding aldehydes **4** and condensed either with anilines or substituted acetophenones obtaining compounds **5** and **6** in good to excellent yields. Cyclization of propynones **1** and Ar-substituted methylene thiols forming thiophenes **7** was not as fluent as expected, due to this scope and limitations of this reaction broadly will be discussed in presentation.

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MANUFACTURING OF BIOLUBRICANTS FROM RENEWABLE RESOURCES

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Every year the global oil market is about 40 million tonnes, including vegetable oil-based lubricants and modifies esters about 10–15% [1, 5]. Half of these lubricants in various ways enter into the atmosphere, water and soil. For these reasons, production of environmentally friendly lubricants is growing rapidly of industrial lubricants branch, which is getting increasingly important over the next century [2, 3]. This affects a number of major international oil and chemical companies aiming to explore and develop environmentally friendly products, such as mineral oil components and conventional additions having a bad biodegradability and high toxicity [4]. The aim of this work is to make comparative analysis of fats, which are inappropriate for food industry. Base and ferment hydrolysis were made in order to exclude free fatty acids from animals and fishes fats. Esterefication of free fatty acids were made by adding higher alcohols and using solid acid catalyst – Amberlyst 15H. Produced esters – animals fats octyl ester (AFOE), fishes fats octyl ester (FFOE), animals fats decyl ester (AFDE), fishes fats decyl ester (FFDE), animals fats (AF) and fishes fats (FF) were investigated by evaluation their physical and chemical properties [Table 1].

Table 1. Properties of produced esters, animals and fishes fats.

Characteristics	Standart	AFOE	FFOE	AFDE	FFDE	AF	FF
Viscosity at 40 °C, $mm^2 \cdot s^{-1}$	ASTM D-445	23,15 ± 0,005774	20,78 ± 0,311769	18,27 ± 0,161658	17,48 ± 0,132791	45,45 ± 0,161658	32,36 ± 0,173205
Viscosity at 100 °C, $mm^2 \cdot s^{-1}$	ASTM D-445	4,81 ± 0,144338	5,17 ± 0,161658	3,83 ± 0,161658	3,55 ± 0,155885	9,43 ± 0,473427	7,62 ± 0,155885
Viscosity index	ASTM D-2270	131,88 ± 12,22	195,39 ± 9,89	94,56 ± 24,42	66,32 ± 25,70	197,27 ± 14,09	216,99 ± 1,56
Density at room temp., $kg \cdot m^{-3}$	ASTM D-1298	854,50 ± 0,02	875,25 ± 0,04	841,50 ± 0,06	850,75 ± 0,2	905,50 ± 0,05	916,25 ± 0,01
Density at 15 °C temp., $kg \cdot m^{-3}$	ASTM D-1298	855,95 ± 0,06	877,20 ± 0,04	843,70 ± 0,07	851,70 ± 0,03	906,25 ± 0,06	918,50 ± 0,02
Pour Point, °C	ASTM D-97	9,00 ± 0,00	-6,00 ± 0,00	9,00 ± 0,00	-3,00 ± 0,00	24,00 ± 0,00	-12,00 ± 0,00
Oxidation Stability, min.	ASTM D-525	21,60 ± 2,97	24,17 ± 1,11	31,20 ± 0,04	44,71 ± 1,81	24,23 ± 0,25	8,57 ± 0,02
Ash content, wt%	ASTM D-482	0,02101 ± 0,00324	0,04184 ± 0,00627	0,03391 ± 0,00184	0,04782 ±0,00793	0,05737 ± 0,00682	0,12010 ± 0,00354

Results were compared to ISO 15380:2011 standard, which describes biolubricants quality parameter’s limits. As a result, octyl esters were produced from animals and fishes fats, which are ascribed to 22, fishes fats to 32, animals fats to 46 class according ISO 15380:2011.

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SYNTHESIS OF NEW HETEROCYCLIC ANALOGUES OF 6-AMINOHEXANOIC ACID

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6-Aminohexanoic acid (ε-aminocaproic acid, EACA) is an antifibrinolytic agent that acts by inhibiting plasminogen activators which have fibrinolytic properties. For this reason it is effective to treat certain hematologic disorders, and is marketed under the brand name *Amicar* among others [1, 2]. Peptides possessing 6-aminohexanoic acid residue, displayed cytotoxic activity against breast cancer MCF-7 and fibroblast cell lines [3]. Recently, heterocyclic analogues of EACA, derivatives of 1-aryl-4-(piperidin-4-yl)pyrazole-4-carboxylic acid, have been patented as active agents to treat or prevent diseases or disorders associated with the cell membrane receptor TGR5 [4], which has emerged as a promising target for intervention in metabolic diseases [5].

In the present work, we developed facile methods for the synthesis of new heterocyclic analogues of EACA, possessing pyrazole, isoxazole and pyrimidine rings. The starting compound **2** was prepared by two step procedure, starting from methyl *N*-Boc-piperidine-4-carboxylate **1** [4]. Heating of compound **2** with phenylhydrazines or their hydrochlorides in ethanol afforded pyrrolidine derivatives **3**, while the reaction with hydroxylamine hydrochloride, afforded isoxazole derivative **4**. The pyrimidine derivative **5** was obtained by the corresponding reaction of **2** with acetamidine hydrochloride. All final amino acids were prepared in the *N*-Boc and *O*-Me protected forms.

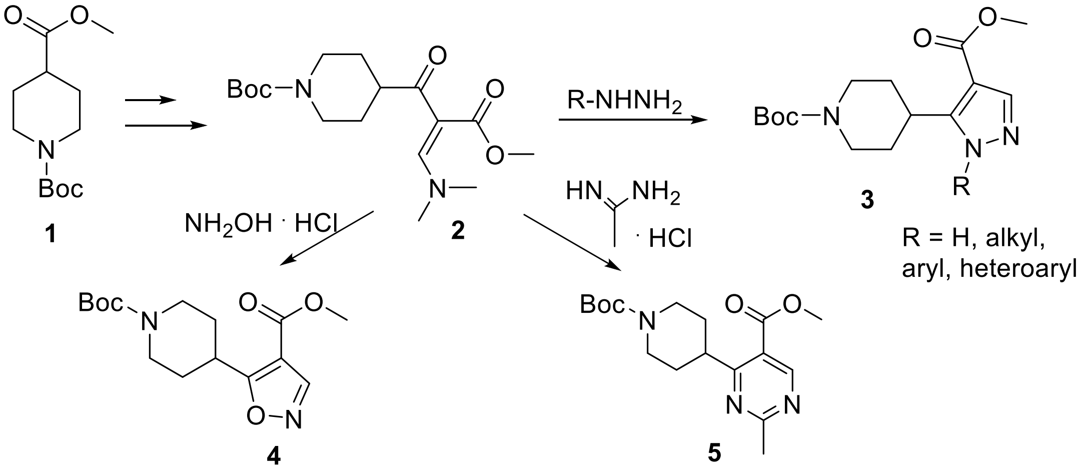

Fig. 1. Synthesis of heterocyclic analogues of EACA.

The structure of synthesized new compounds was confirmed by data of ^{1}H, ^{13}C and ^{15}N NMR spectroscopy and HRMS.

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SYNTHESIS OF NOVEL INDOLIN-2-YL BUTANOIC ACID DERIVATIVES

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Indole carboxylic acid derivatives have a wide variety of applications, considerable number of them being related to the biological activity of said compounds [1].

In the present work, different pathways of 5,7-diaryl and 5,7-dibromo substituted indolin-2-yl butanoic acid and its derivatives synthesis from spiro[indole-2,2'-piperidin]-6'-one (Fig. 1) were examined.

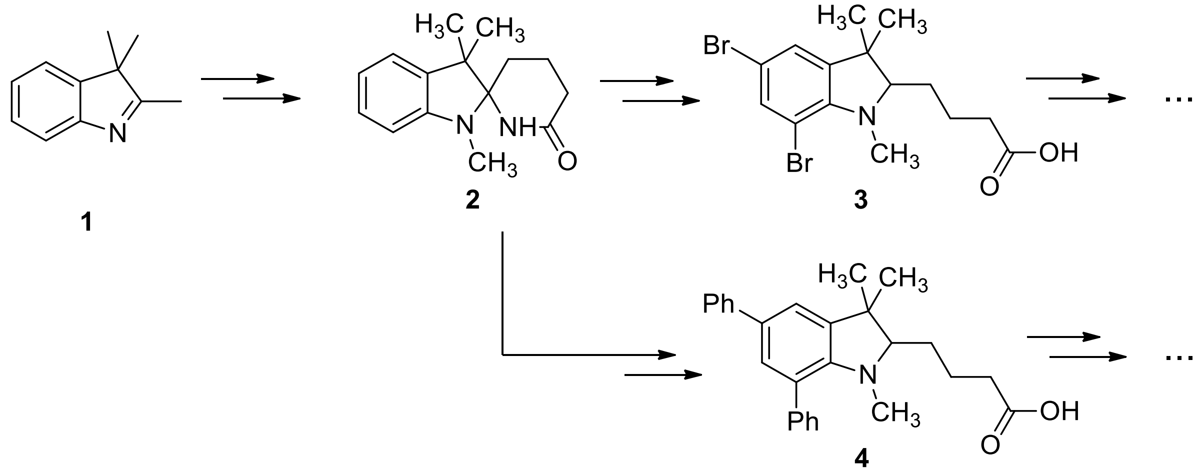

Fig. 1. Scheme of the synthesis

The obtained compounds could be suggested as potential agents in the bacterial quorum sensing research [2].

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SYNTHESIS OF VARIOUS 1,3-DIENES THROUGH ADDITION OF AMINES TO 2-(1-ALKYNYL)-2-CYCLOALKEN-1-ONES

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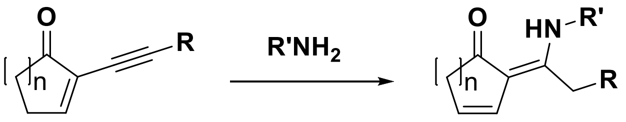
Electron-deficient 1,3-conjugated enynes possessing alkynyl, alkenyl and carbonyl functional groups are able to undergo nucleophilic addition reactions [1]. Typically 2-(1-alkynyl)-2-alken-1-ones participate in transition-metal catalyzed or electrophile-mediated tandem nucleophilic addition-cyclization reactions or cycloaddition-cyclization cascades obtaining polysubstituted furan derivatives [2]. Whereas there are only few publications about the synthesis of polysubstituted pyrroles from 2-(1-alkynyl)-alken-1-one oximes [3] or *in situ* formed imines of 2-(1-alkynyl)-alken-1-ales [4] in the literature. Keeping that in mind we decided to synthesize imines of 2-(1-alkynyl)-alken-1-ones and to investigate their cyclization reactions to polyfunctional pyrrole derivatives, but unexpectedly we found that electron-deficient 1,3-conjugated enynes react with primary aliphatic amines in a unique isomerization-addition manner.

Herein we describe mild and efficient synthesis of functionalized 1,3-dienes, which proceeds *via* regio- and stereoselective nucleophilic addition of primary aliphatic amines to 2-(1-alkynyl)-2-alken-1-ones with double bond migration.



n = 1, 2
R = Ph, 4-MeOC_6H_4, 4-FC_6H_4, 4-ClC_6H_4, *n*-Bu
R' = *c*-Hex, *t*-Bu, *n*-Bu, *i*-Bu, *i*-Pr, *c*-Pr, Bn, $HC{\equiv}CCH_2$, $H_2C{=}CHCH_2$

Fig. 1. Synthesis of functionalized 1,3-dienes.

The scope and limitation of this unprecedented catalyst-free isomerization-addition reaction will be discussed.

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SYNTHESIS AND THERMAL PROPERTIES OF NOVEL TRIPHENYLAMINE DERIVATIVES CONTAINING 1,2,3-TRIAZOLE UNITS

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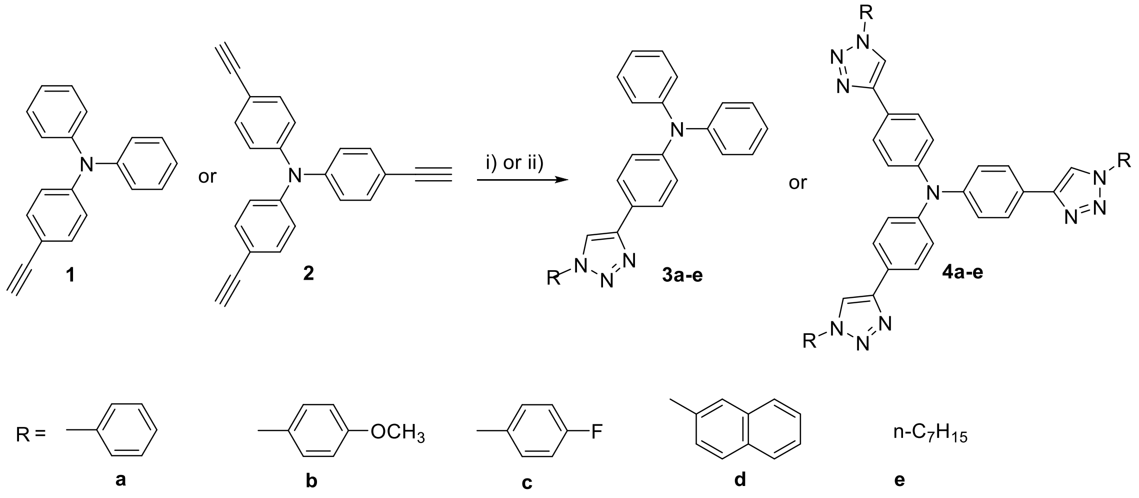
Electron-donating aromatics, such as triarylamines play an important role in optoelectronics as organic charge transporting materials, due to their relatively simple synthetic accessibility, good resistance to oxidation and high charge-carrier mobility [1-2]. For example, the most commonly used hole transporting materials in organic light emitting diodes are triphenylamine derivatives such as *N*,*N*-diphenyl-*N*,*N*-bis(*m*-tolyl)benzidine or *N*,*N*-dinaphthyl-*N*,*N*-diphenylbenzidine with propeller-like structures which prevent them from aggregation and enable to exist in amorphous state that is necessary for thin film formation.



Scheme 1. *Reagents and conditions:* (i) R-N_3 (1.3 eq.), CuI (0.1 eq.), DIPEA (1 eq.), AcOH (1 eq.), CH_2Cl_2, Ar, r.t., 24 h; ii)) R-N_3 (4 eq.), CuI (0.2 eq.), DIPEA (1 eq.), AcOH (1 eq.), CH_2Cl_2, Ar, r.t., 24 h.

In this context, it seemed of interest to synthesize novel triphenylamine derivatives **3-4** containing 1,2,3-triazolyl units which could be easilly constructed by the copper(I)-catalyzed azide-alkyne cycloaddition reaction (CuAAC). To achieve the foreseen aim the palladium(0)- catalysed alkynylination of (tri)bromotriphenylamine and CuAAC reactions were investigated. Novel mono- and tri-substituted triphenylamine derivatives containing 1,2,3-triazole moeties were synthesized using optimized CuAAC conditions (Scheme 1.). Thermal stability of the synthesized compounds was evaluated by thermogravimetric analysis.

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SYNTHESIS OF POLIFUNCTIONALIZED BIS(THIAZOLYL)PHENYL METHANES

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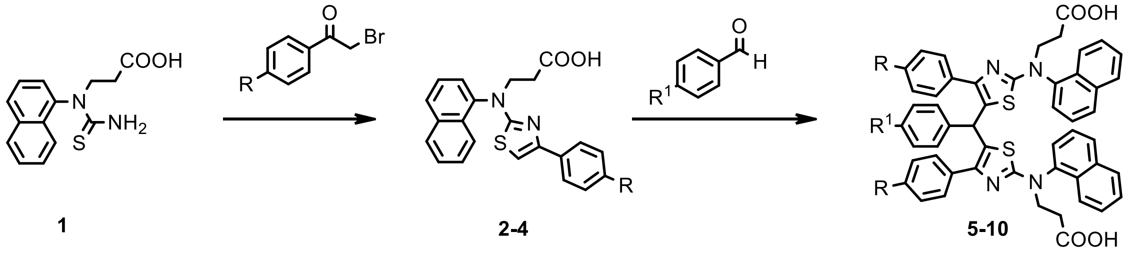
Thiazoles and their derivatives are eligible intermediates in organic synthesis and bear a number of biological properties, such as anti-inflammatory, antibacterial, anti-cancer, antioxidant, antidiabetic and others [1, 2]. The most straightforward procedure is Hantzsch method. Trisubstituted methanes have received considerable attention because of their wide fields of application. They are used as antifungal agents [3], dyes [4], precursors in high performance polymer synthesis [5].

The reactions of thioureido acid **1** with different bromoacetophenones were carried out under reflux in acetone for 2 h (Scheme 1). The formed corresponding hydrobromides of *N*,*N*-disubstituted aminothiazoles then were transferred into the bases **2–4** using sodium acetate. The reactions of compounds **2-4** with aromatic aldehydes in the molar ratio of 2:1 in acetone resulted in a high yield of bis(thiazol-5-yl)phenyl methanes **5-10.**



1

2-4

R=H; F; Cl

5-10

5 R=Cl, R^1= F;
6 R, R^1=Cl;
7 R=Cl, R^1=Br;
8 R=F, R^1=NO_2;
9 R=H, R^1=Cl;
10 R=H, R^1=Br

Scheme 1. Synthesis of functionalized *N*,*N*-disubstituted aminothiazoles **2-10**

The structure of the synthesized compounds was confirmed by ^{1}H, ^{13}C NMR, IR spectral data and mass spectroscopy.

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SYNTHESIS AND BIOLOGICAL ACTIVITY OF HALOGEN-SUBSTITUTED 3-[(4-SULFAMOYLPHENYL)AMINO]PROPANOIC ACID DERIVATIVES

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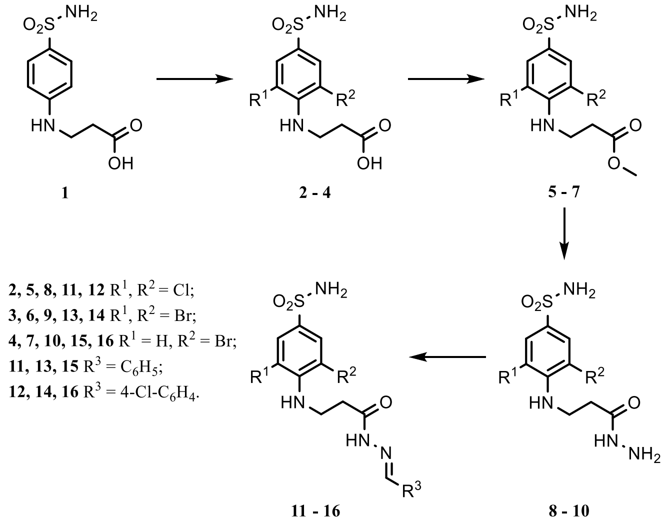
There are known a lot of N-substituted β-alanines and their derivatives that distinguish themselves by biological activity and are used as growth regulators, medicinal preparations, against plant pests and diseases in agriculture and are components of natural compounds [1].

The halogen-substituted 3-[(4-sulfamoylphenyl)amino]propanoic acids **2**, **3** were synthesized from β-alanine **1** and HCl or HBr in the presence of hydrogen peroxide (Scheme 1). 3-((2-Bromo-4-sulfamoylphenyl)amino)propanoic acid (**4**) was obtained when bromination of compound **1** was performed with *N*-bromosuccinimide in DMF. Esters **5-7** were synthesized by esterification of compound **2-4** with an excess (10 times) of methanol under reflux in the presence of a catalytic amount of sulphuric acid. Reaction of esters **5-7** with hydrazine hydrate in 2-propanol under reflux gave hydrazydes **8-10,** which were used for the synthesis of hydrazones **11-16**.



2, 5, 8, 11, 12 R^1, R^2 = Cl;
3, 6, 9, 13, 14 R^1, R^2 = Br;
4, 7, 10, 15, 16 R^1 = H, R^2 = Br;
11, 13, 15 R^3 = C_6H_5;
12, 14, 16 R^3 = 4-Cl-C_6H_4.

Scheme 1. Synthesis of β-alanines and their derivatives **2-16**

The structure of the synthesized compounds was confirmed by ^{1}H, ^{13}C NMR, IR spectral data, and mass spectroscopy.

The synthesized sulfonamides were investigated as inhibitors of twelve catalytically active human carbonic anhydrase isoforms: the cytosolic enzymes CA I, CA II, CA III, CA VII, and CA XIII, secreted protein CA VI, the mitochondrial ones CA VA and CA VB, membrane-associated GPI-anchored enzyme CA IV, and the transmembrane proteins CA IX, CA XII and CA XIV. Low nanomolar dissociation constants were determined for mitochondrial isozyme CA 5B, which is implicated in diseases of the central nervous system and obesity. These compounds can be used for further development of inhibitors with significant binding affinity and selectivity towards CA 5B isozyme.

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N-ACYLATION OF 1- Boc-4-AMINO-4-(2-METHOXY-2-OXOETHYL)PIPERIDINE

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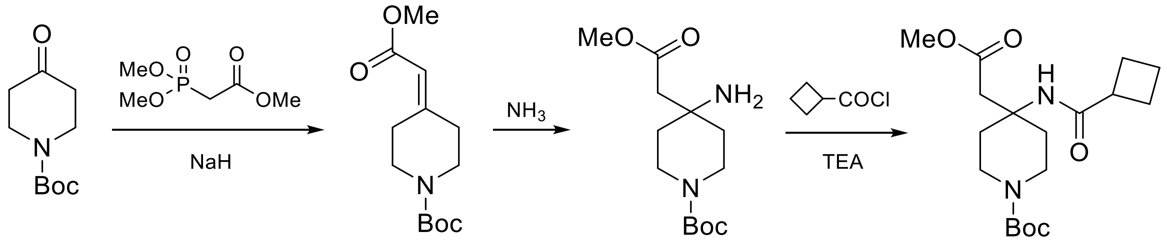
Achiral *β,β*-cyclic-*β*-amino acids containing piperidine core have been used as building blocks for the preparation of such bioactive substances as potent TNH-*α* converting enzyme inhibitors [1] and antibacterial agents against ciprofloxacin resistant *Staphylococcus aureus* [2]. The present work describes the synthesis new 4-alkylcarbonylamino- and 4-cycloalkylcarbonylamino-4-(2-methoxy-2-oxoethyl)piperidine derivatives, possessing Boc-protecting group at the piperidine nitrogen atom.

The preparation of the starting *α, β*-unsaturated ester **2** was accomplished by condensation of *N*-Boc-4-piperidinone **1** with trimethylphosphonoacetate under Horner-Wadsworth-Emmons reaction conditions [3]. Michael addition of ammonia across of the carbon-carbon double bond provided *β,β*-cyclic-*β*-amino acid **3** in a good yield [1].

Acylation of the amine **3** with various aliphatic and cycloaliphatic acid chlorides was carried out in an inert solvent in the presence of tertiary amine as a base. For example, treatment of the substrate **3** with cyclobutanecarbonyl chloride in dichloromethane (DCM) containing triethylamine (TEA) afforded *N*-acylated derivative of *β,β*-cyclic-*β*-amino acid **4**.



1 **2** **3** **4**

The stucture assignments of the synthesized compounds were based on extensive ^{1}H, ^{13}C, DEPT, ^{1}H-^{13}C HMBC and HSQC, ^{1}H-^{15}N HMBC and HSQC NMR spectroscopic data.

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SYNTHESIS AND INVESTIGATION OF V-SHAPED HOLE-TRANSPORTING TPD DIMERS CONTAINING TRÖGER`S BASE CORE

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High-performance charge-transporting materials is a key component for the fabrication of high-efficiency electronic and optoelectronic devices. Molecular structure plays a crucial role in defining the properties of organic materials and their suitability for applications such as solar cells. While these materials are expected to have good hole-drift mobility and high morphological stability as well as to meet certain HOMO and LUMO energy requirements the crystallization of material in the hole conductor layer is undesirable for it would impair the formation of a good contact among the active layer and contact electrodes.

Tröger's base (TB) is V-shaped C$_2$-symmetric chiral molecule consisting of a bicyclic aliphatic methanodiazocine unit fused with two aromatic rings. Its structure allows it to be used as a core which provides orientation to conjoined TPD fragments angle-wise towards each and hampers the crystallization processes making the compound amorphous.

V-shaped hole transporting materials based on TPD-type moieties conjoined by a Tröger`s base core were synthesized and investigated. Hole transporting materials **HTM1**, **HTM2** and **HTM3** were obtained by three step synthetic method employing Buchwald-Hartwig cross-coupling reaction *via* intermediate biphenyl compounds (Scheme 1). These novel materials are fully amorphous, possess high glass transition temperatures, good thermal and morphological stability. Comparatively high charge mobility (up to 0.036 cm^2 V^{-1} s^{-1}) was measured in these hole transporting materials, exceeding that of corresponding methyl and methoxy substituted TPD analogues without TB core by more than two orders of magnitude. Determined ionization potential and charge mobility values permit use of the synthesized compounds as hole transporting materials in fabrication of perovskite solar cells. Fabrication and examination of such cells was performed and power conversion efficiency of 14.6 % under AM. 1.5 G illumination was recorded in the best performing perovskite devices containing **HTM3** as hole transporting material, indicating that investigated TB-linked HTM can function effectively in PSC.

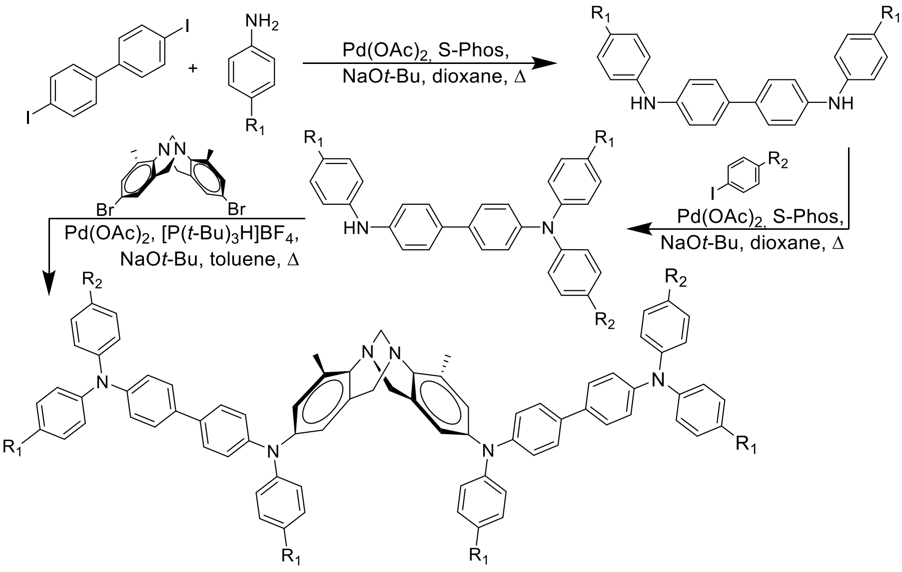

Fig. 1. Synthesis of compounds **HTM1-HTM3.**

SYNTHESIS OF 2-(4-ARYL-1,2,3-TRIAZOL-1-YL)PYRIMIDINES AND PYRROLO[2,3-*d*]PYRIMIDINES

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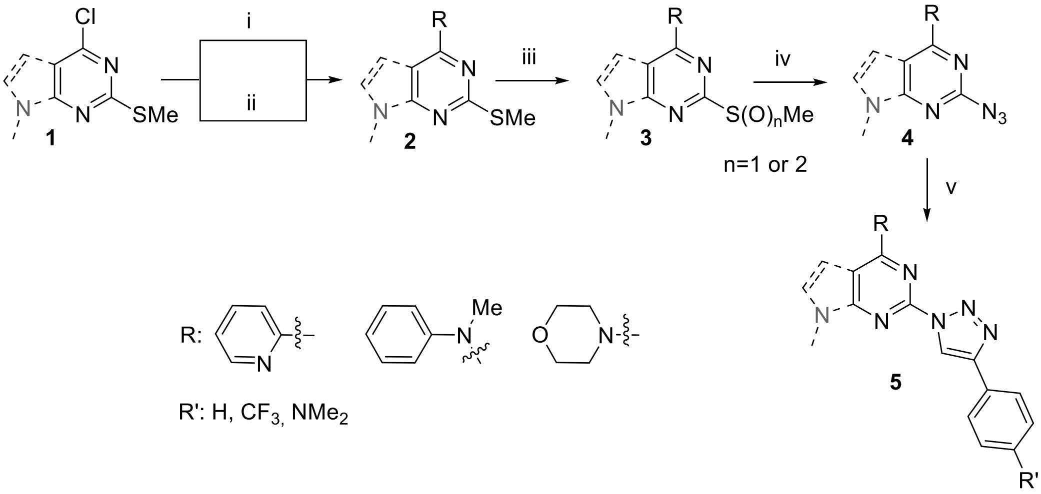
Nitrogen heterocycles − pyrimidine and pyrrolo[2,3-*d*]pyrimidine (7-deazapurine) − are widely spread in nature and occupy an exclusive place, mainly due to their importance for living organisms and wide range of biological activity of their derivatives. On the other hand, pyrimidine ring containing heterocycles owing to their aromaticity, significant π-deficiency, and ability of nitrogen atoms to take part in the chelation processes, are desired structural units to be incorporated in more complex organic structures targeted for numerous applications [1], including bio-materials labelling and metal sensing [2]. Recently, we have shown that triazole–pyrrolo[2,3-*d*]pyrimidine conjugates exhibit strong UV-blue fluorescence and are promising candidates as functional materials [3]. Continuing our work aimed to the search of novel fluorescent materials among pyrimidine ring containing heterocycles we present herein the synthesis of 2-(4-aryl-1,2,3-triazol-1-yl)pyrimidines and pyrrolo[2,3-*d*]pyrimidines **5** as potential hybrid bi- and tridentate ligands for metal ions.



Scheme 1. *Reagents*: i – C_6H_5NHMe or $O(CH_2)_4NH$; ii – (2-pyridyl)Bu_3Sn; iii – m-CPBA or oxone; iv – Me_3SiN_3 or NaN_3; v – 4-R'$C_6H_4C{\equiv}CH$.

The target 2-(1,2,3-triazol-1-yl)pyrimidines and pyrrolopyrimidines **5** were obtained from the corresponding 4-chloro-2-methylthiopyrimidines and pyrrolo[2,3-*d*]pyrimidines **1** *via* nucleophilic aromatic substitution or Stille reactions, oxidation of 2-methylthio group followed by the introduction of azido group and Cu(I)-catalyzed azide−alkyne cycloaddition reaction (Scheme 1).

Acknowledgements
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SYNTHESIS AND SOME TRANSFORMATION OF 9,10-ANTHRACENEDIONE HYDRAZONES

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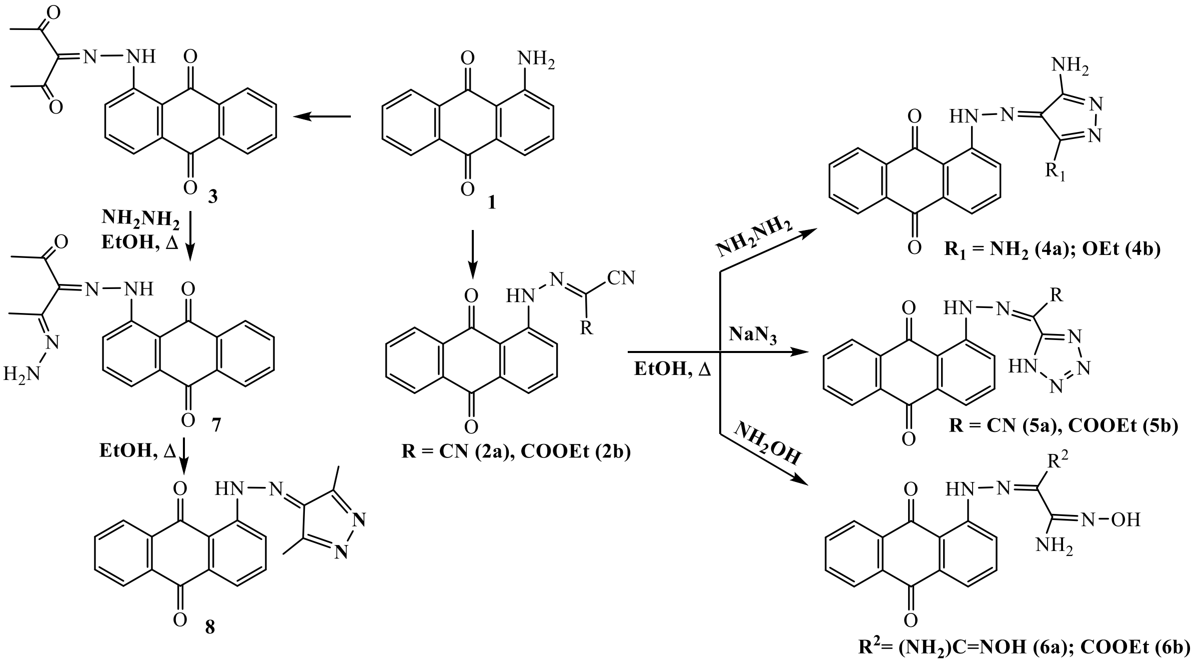
Hydrazones and their derivatives have interesting biological properties, such as anti-inflammatory, analgesic, anticonvulsant, antituberculous, antitumor, anti-HIV and antimicrobial activity [1]. They are important compounds for drug design, espesially for the syntheses of different types of heterocyclic compounds [2].

Therefore, the aim of this work is obtaining of new derivatives 4-8 based on 1-hydrazynyl-9,10-anthracenediones 2a,b and 3. The latter have been obtained by consecutive two-stage refunctionalization of 1-amino-9,10-anthracenedione 1 using the method from work [3]. The interaction of hydrazones 2a,b and 3 with hydrazine gives pyrazoles 4a,b and 8. Hydrazide 7 was isolated as an intermediate of pyrazole synthesis 8. Tetrazoles 5a,b have been synthesized from compounds 2a,b and sodium azide.



It was established that the reaction of hydrazones **2a,b** with hydroxylamine yielded non-cyclic derivatives of hydrazones **6**. Bisamidoxim **6a** has been isolated in case of the interaction of hydrazone **2a** with hydroxylamine.

Structures of the new obtained derivatives were confirmed by the ^{1}H, ^{13}C NMR, IR spectra and elemental analysis data.

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EFFECTIVE CARBAZOLE-BASED HOLE TRANSPORTING MATERIALS WITH EXTENDED CONJUGATION

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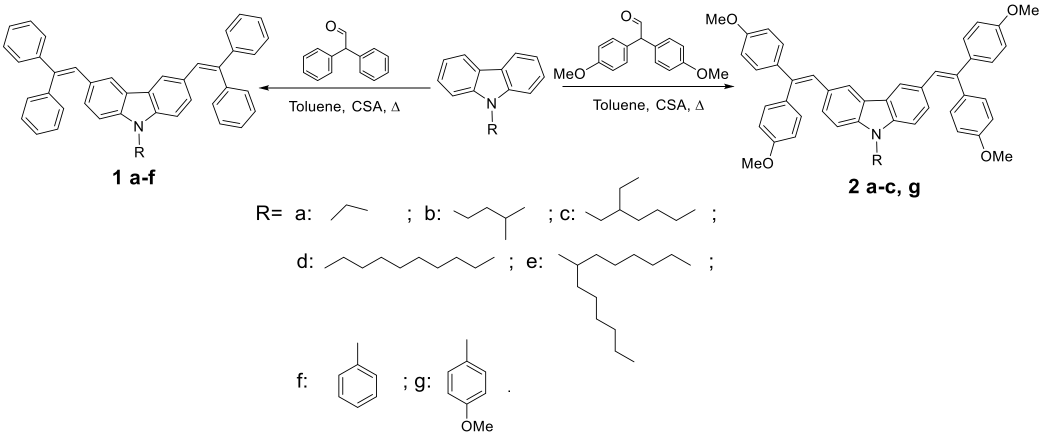
Due to their specific optical and electrochemical properties, carbazole and its derivatives have been widely used as functional building blocks in the fabrication of various optoelectronic devices [1, 2].

Carbazole-based building blocks **1** and **2**, possessing diphenylethenyl or bis(4-methoxy-phenyl)ethenyl fragments, have been synthesized. Condensation of the *N*-substituted carbazole with diphenylacetaldehyde or bis(4-methoxyphenyl)acetaldehyde yields 3,6-substituted products (Scheme 1). The obtained compounds were examined by various techniques including differential scanning calorimetry, NMR, MS, UV, PL spectrometry, and cyclic voltammetry to investigate their thermal, optical, electrochemical, and photo physical properties. The influence of additional *p*-methoxy groups in phenyl fragment on various properties of synthesized derivatives was studied. The carbazole compounds were found to be weakly emissive either in dilute solutions or neat films with fluorescence quantum yields not exceeding a few percent. Low emission efficiency in solution accompanied by fast (<100ps) excited state relaxation was caused by diphenylethenyl moieties facilitating intramolecular torsions and torsion-induced nonradiative deactivation. Remarkably, the neat films of carbazole derivatives exhibited high hole drift mobilities ($>10^{-3}$ cm^2 V^{-1} s^{-1} at high electric fields) due to the proper molecular arrangement promoted by long *N*-aliphatic substituents. The mobility values were lowered with the introduction of additional *p*-methoxy groups due to reduced intermolecular coupling in the neat films.



Scheme 1. Synthesis of compounds **1** and **2**

Commercial availability and relative cheapness of the starting materials, simple synthetic method and synthesis on a multigram scale, as well as solubility in common organic solvents and good charge drift mobility make these materials attractive for optoelectronic applications or promising precursors for further synthesis.

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SYNTHESIS AND INVESTIGATION OF THE ORGANIC HOLE TRANSPORTING SEMICONDUCTORS CONTAINING PYRIDINE GROUPS

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Population growth and ever-increasing energy consumption prompts new search for cleaner and safer alternatives to fossil fuels and nuclear energy. One of the most attractive alternatives is photovoltaic systems. Among them perovskite solar cells received growing interest from research community. They are simple to manufacture and possess good performance. As a result of rapid development in this field, perovskite photovoltaic systems have reached 21,1% efficiency in just a few years [1;2].

The purpose of this research is the synthesis of new hole-transporting materials with pyridine groups. These groups have been selected for their potential ability to improve charge transfer between perovskite and new hole-transporting materials.

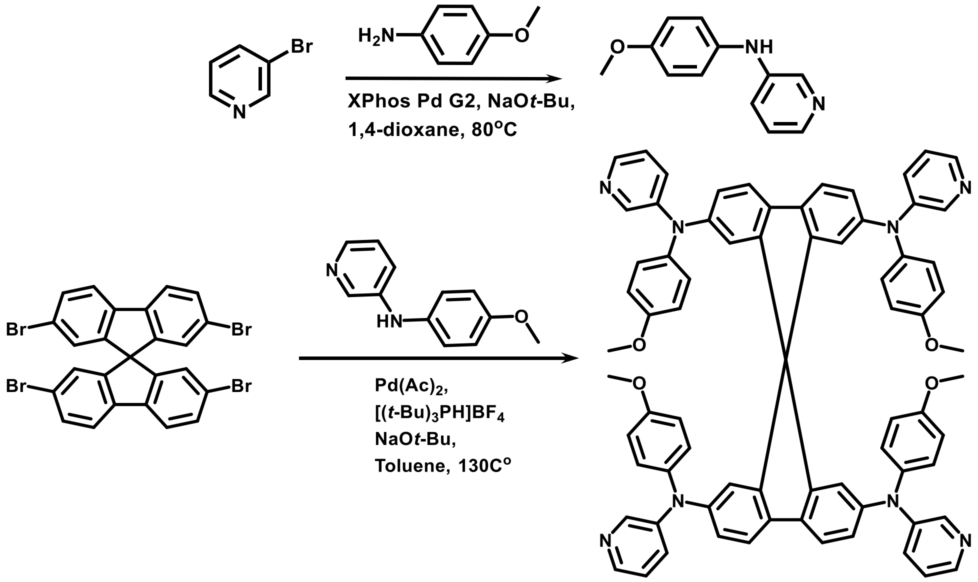

Fig 1. Synthesis of new hole-transporting materials with pyridine groups.

In this work the new hole-transporting materials, containing pyridine fragments, have been synthesized and their thermal, optical, photophysical and photovoltaic properties investigated.

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SYNTHESIS AND TRANSFORMATION OF 1-(5-CHLORO-2-HYDROXYPHENYL)-5-OXOPYRROLIDINE-3-CARBOXYLIC ACID

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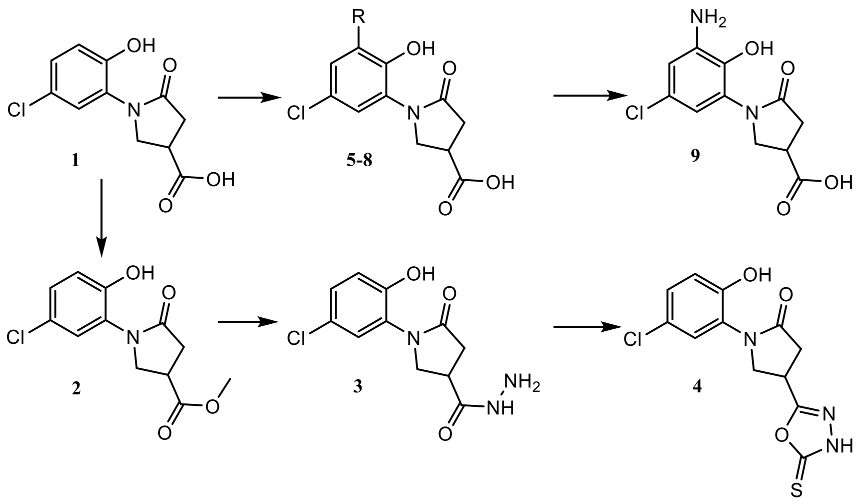
In continuing search of the biologically active compounds containing amino acid moiety, reactions of 1-(5-chloro-2-hydroxyphenyl)-5-oxopyrrolidine-3-carboxylic acid (**1**) were carried out and its novel derivatives were synthesized.

Methyl 1-(5-chloro-2-hydroxyphenyl)-5-oxopyrrolidine-3-carboxylate (**2**) was obtained according to the usual procedure for esterification of carboxylic acids by heating at reflux acid **1** in methanol in the presence of concentrated sulfuric acid as a catalyst. Ester **2** was converted into hydrazide **3** under treatment with hydrazine hydrate. 1,3,4-Oxadiazole **4** was synthesized in the reaction of **3** with carbon disulfide in ethanol in the presence of potassium hydroxide.

The presence of a halogen atom in the structure of organic compounds often enhances their biological activity or evokes new properties. Therefore, additional chlorine or bromine atoms were introduced into the benzene ring of 1-(5-chloro-2-hydroxyphenyl)-5-oxopyrrolidine-3-carboxylic acid. Bromo-derivative **5** was prepared by treating acid **1** with the stoichiometric amount of bromine in acetic acid at room temperature. Compound **6**, containing two chlorine atoms in the aromatic moiety, was obtained by the reaction of acid **1** with 6 M HCl and H_2O_2 at room temperature. Reaction of **1** with 80% H_2SO_4 solution in propan-2-ol resulted in formation of compound **8**. 1-(5-Chloro-2-hydroxyphenyl)-5-oxopyrrolidine-3-carboxylic acid (**1**) underwent facile nitration reaction with nitric acid providing nitro-derivative **7**. Hydrogenation of nitro group over Raney-nickel gave amine **9**, which was isolated by column chromatography.



R = **5**) Br; **6**) Cl; **7**) NO_2; **8**) $(CH_3)_2CH$.

Scheme 1. Synthesis of 1-(5-chloro-2-hydroxyphenyl)-5-oxopyrrolidine-3-carboxylic acid derivatives 2-9

Structures of all synthesized compounds have been confirmed by ^{1}H NMR, ^{13}C NMR, and mass spectrometry data.

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NOVEL INDOLE DERIVATIVES WITH (5-SULFANYL)-1,3,4-OXADIAZOLE FRAGMENT

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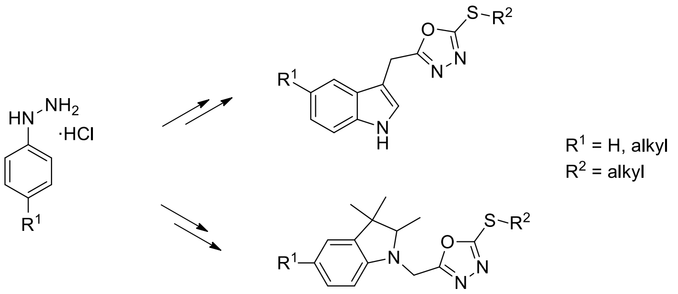
1,3,4-Oxadiazoles are an important class of heterocyclic compounds with a wide range of biological activities such as anti-inflammatory [1], anticancer [2], antiviral [3], antimicrobial [4], antineoplastic [5], fungicidal [6], etc.

Our work is focused on the synthesis of small library of indole derivatives bearing (5-sulfanyl)-1,3,4-oxadiazole fragment (*Scheme 1*). Synthesis of these compounds was accomplished starting from several phenylhydrazine hydrochlorides *via* key-steps of Fischer indole synthesis and formation of (5-sulfanyl)-1,3,4-oxadiazole motif.



Scheme 1

The structures of all new molecules were proven by means of mass spectrometry, IR and NMR spectroscopy.

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SYNTHESIS OF 5-ARYLSUBSTITUTED 1,3,3-TRIMETHYL-3'-PHENYL-1,3-DIHYDRO-4′*H*-SPIRO[INDOLE-2,5'-[1,2]OXAZOLE] DERIVATIVES

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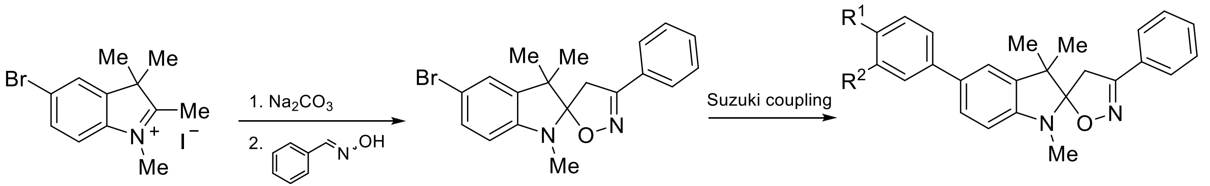
The isoxazole nucleous is an important element of many natural and synthetic molecules with significant biological activities. Functionalized isoxazole derivatives are widely used for antibacterial, antitumor, antiviral drug synthesis and in treatment of diseases caused by hormones [1]. Besides the above mentioned instances, isoxazole derivatives are used in the fungicides, insecticides, herbicides [2]. The aim of this work was synthesis of 5-arylsubstituted 1,3,3-trimethyl-3'-phenyl-4*H*-spiro[indoline-2,5'-isoxazole] derivatives applying palladium catalyzed Suzuki cross-coupling reaction.

Synthesis of starting indolium salt **1** was performed according to the known synthetic procedure [3]. Treatment of indolium iodide **1** with sodium carbonate followed by the 1,3-dipolar cycloaddition reaction with benzaldehyde oxime gave the target 5-bromo-1,3,3-trimethyl-3'-phenyl-1,3-dihydro-4′*H*-spiro[indole-2,5'-[1,2]oxazole] **2**.



1 **2** **3a-d**

3a: R^1=R^2=H; **3b**: R^1=OMe, R^2=H; **3c**: R^1=H, R^2=Cl; **3d**: R^1=R^2=CH=CH-CH=CH

With the key intermediate in hand, Suzuki crosscoupling of 5-bromo-1,3,3-trimethyl-3'-phenyl-4*H*-spiro[indoline-2,5'-isoxazole] **2** with various arylboronic acids was performed and target compounds **3a-d** were obtained. The stucture assignments of the synthesized compounds were based on extensive ^{1}H, ^{13}C, DEPT, ^{1}H-^{13}C HMBC and HSQC, NMR spectroscopic data.

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Polymer Chemistry and Technology

CHANGE OF PHYSICO-MECHANICAL PROPERTIES OF POLYCAPROAMAMIDE FIBERS DURING MODIFICATION BY *BACILLUS* BACTERIA

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Currently the main direction of technical progress in the industry of chemical fibers is not so much the development of new types of polymers, as the modification of the known chemical fibers and the creation of composite materials. When creating new composite materials, the interaction of the components is controlled by various methods, for example, by mechanical, chemical, radiation effects. However, the application of these methods is connected with considerable technological and ecological restrictions. It is especially difficult to reach effect at the modification of modern high-strength fibers. New opportunities are opened by the method of biomodification which is based on impact on chemical fiber by microorganisms and products of their metabolism. Taking into account an almost unlimited spectrum of microorganisms and mild conditions of exposure, the possibility of directional modification of known fibers is opened, with the aim of giving them new, pre-defined properties, improving the quality of finished products and expanding their field of application [1, 2].

In this work the fibers of polycaproamide have been modified by the bacteria *g. Bacillus* when cultured on synthetic media during 7–21 days [3]. The change of the structure of the surface of fibers was investigated by the methods of optical, confocal laser and atomic-force microscopy.

It was noted that bioprocessing of polyamide fibers by the bacteria of the *g. Bacillus* leads to the formation of more developed surfaces with a shallow, fibrillike structure (figure). In the biomodified samples the sizes of the amorphous layer increases to 50 % and the nanosurface to 2,5 times in comparison with a control sample.

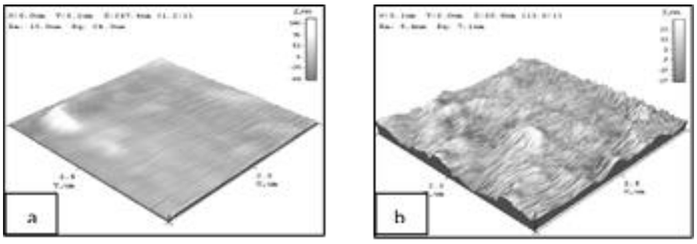

Fig. 1. The surface of the polyamide fiber of the control sample (a) and the sample modified by the bacteria *g. Bacillus* (b)

In the fibers modified by *g. Bacillus* there were also revealed changes in mechanical characteristics. In particular, the strength and the specific elongation at the break of some modified samples increases to 60 %, while of some others they decrease by half as compared to the control sample.

The obtained results broaden the possibilities of using polycaproamide fibers after their biomodification. For example, in the production of thread, it is of interest to increase the strength of monofilament and, in some cases, elongation at break, and in the production of composites, an increase in the nanosurface of the fiber surface contributing to an increase in adhesion and a reduction in the specific elongation at break.

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SYNTHESIS AND PROPERTIES OF AMPHOTERIC HYDROXYETHYL STARCHES

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Amphoteric starches have cationic and anionic groups in the same macromolecule. Generally, cationic derivatives are starch ethers prepared by using tertiary amino or quaternary ammonium reagents, while anionic derivatives are obtained by modifying starch with phosphate, phosphonate, sulphate, sulfonate or carboxyl groups containing compounds. The introduction of positive and negative groups into starch may be realized by using several different approaches: firstly anionization and thereafter cationization or firstly cationization and after that anionization.

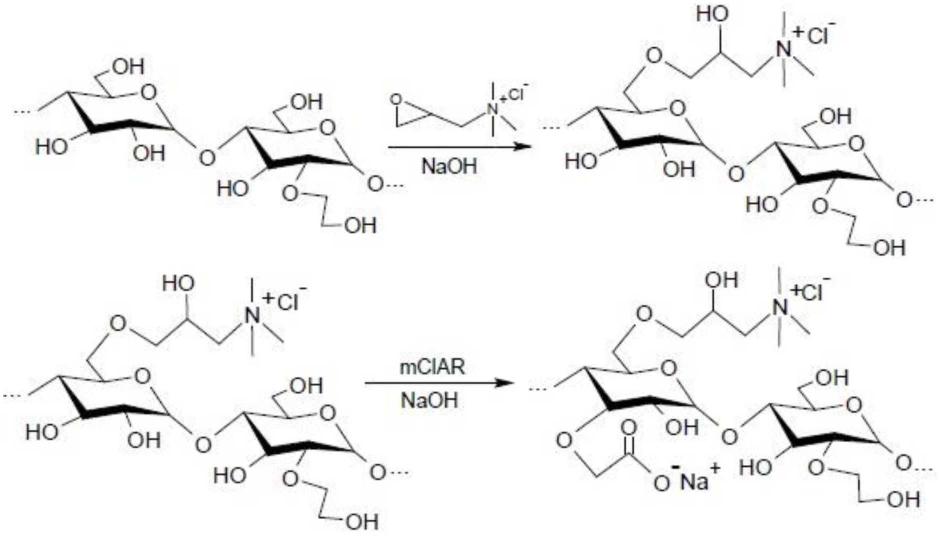

Fig. 1. Two–step synthesis scheme for preparation of amphoteric starches

The aim of this work was to prepare amphoteric hydroxyethyl starches of different degree of substitution of cationic and anionic groups as well as to study their interactions with sodium tripolyphosphate in aqueous medium.

Preparation of amphoteric hydroxyethyl starches (CHES/AHES) has been achieved by two-step synthesis (Fig. 1). Firstly, cationic hydroxyethyl starches (CHES) were prepared by the reaction of hydroxyethyl starch (HES) with (2,3-epoxypropyl)trimethylammonium chloride (EPTMAC) in the presence of sodium hydroxide at 45 °C for 24 h [1]. The molar ratio of HES : EPTMAC : NaOH : H_2O was 1 : 0.35 : 0.04 : 3 and 1 : 1.02 : 0.04 : 8.2 aiming to obtain CHES with a degree of substitution (DS) of cationic groups of 0.29 and 0.58, respectively. Further obtained CHES were reacted with monochloroacetic acid (mClAR) in alkaline solution at 55 °C for 48 h. The molar ratio of CHES : mClAA : NaOH : H_2O was 1 : 1 : 2.4 : 90 and 1 : 1.5 : 3.6 : 90 aiming to obtain amphoteric hydroxyethyl starches with a degree of substitution (DS) of anionic groups of 0.25–0.27 and 0.55–0.57, respectively. Consequently, by changing the molar ratios of cationic and anionic reagents four different amphoteric hydroxyethyl starches were obtained.

Water insoluble polyelectrolyte complexes were prepared by ionotropic gelation between cationic groups of amphoteric hydroxyethyl starches and anionic phosphate groups of sodium tripolyphosphate (NaTPP) in aqueous medium. By changing ratio and concentration of complex forming compounds as well as pH of medium, water insoluble polyelectrolyte complex particles were obtained, which were characterized by using spectroscopic, thermal and microscopy analysis methods.

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INFLUENCE OF ADHESIVE POLYURETHANE FILM TYPE ON BOND STRENGTH

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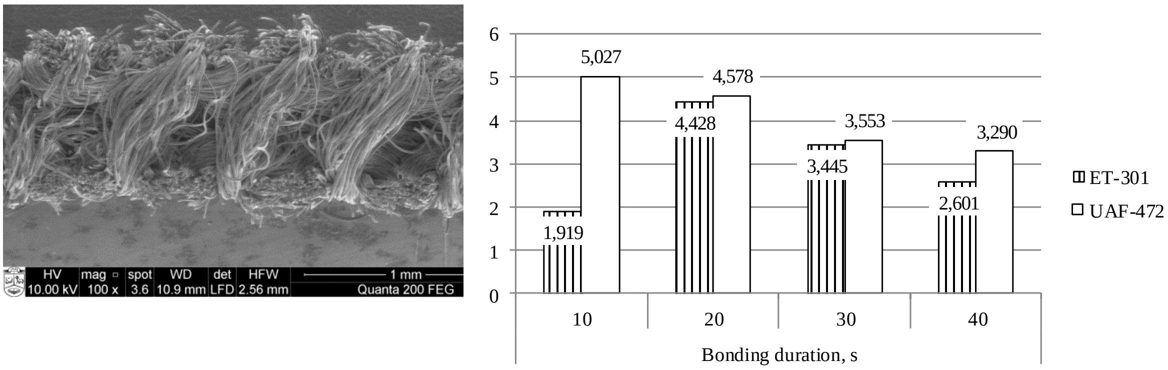
Textile bonding is one of more perspective joining methods for leisure clothing or sportswear manufacture [1]. Bonds are designed joining two layers of textile fabric together by using thermoplastic polyurethane adhesive films with the application of appropriate technological parameters [2, 3]. The properties of the bonds depend on textile properties, bonding technological parameters, seam construction, etc. Thus, the selection of proper technological parameters is dependent on the compatibility of textile and adhesive film. Thus, the aim of this research was to determine the influence of adhesive film thickness on textile bond strength.

Commercially available knitted fabric (thickness – 0.84 mm; surface density – 247 g/m^2; course count – 18 cm^{-1}; wale count – 22 cm^{-1}; fiber content: 96 % polyester and 4 % Spandex) and two polyurethane thermoplastic films of the different thickness: 1.27 mm (UAF472; melt point – 95 °C) and 0.175 mm (ET301; melt point – 90–100 °C) were selected for this study. Bonds were laminated applying the pressing device DEA 25R at constant pressure (5.6 kPa) at 150 °C temperature for 10 s, 20 s, 30 s and 40 s. Before the bond strength testing, the specimens were conditioned at ambient conditions. Bond strength test was carried out using computerized tension machine Tinius Olsen H10 KT under 50 mm/min peeling velocity.

The summary of bond strength testing results is presented in Fig. 1.



a *b*

Fig. 1. SEM image of the tested knitted fabric (a) and bond strength (N/mm)

The higher values of bond strength were determined for the bonds which were laminated using thicker film (UAF472: 1.27 mm) comparing with the ones of thinner film (ET301: 0.175 mm). The analysis of delaminated samples has shown that more regular spreading of adhesive film polymer on both of textile layers appears in the case of thicker film. The highest difference between the values of bond strength was determined when the bonds were pressed for 10 s duration. In this case, the strength of bonds which were laminated with thicker film (UAF472) was in 2.6 times higher comparing with thinner film (ET301). After increasing of pressing duration from 20 s up to 40 s, the differences of bond strength between the analysed adhesive films were insignificant (except the case of 40 s pressing duration, when it was 1.3 times).

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INVESTIGATION OF FLUOROSTYRENE-BASED MONOMERS AND POLYMERS FOR OPTOELECTRONICS

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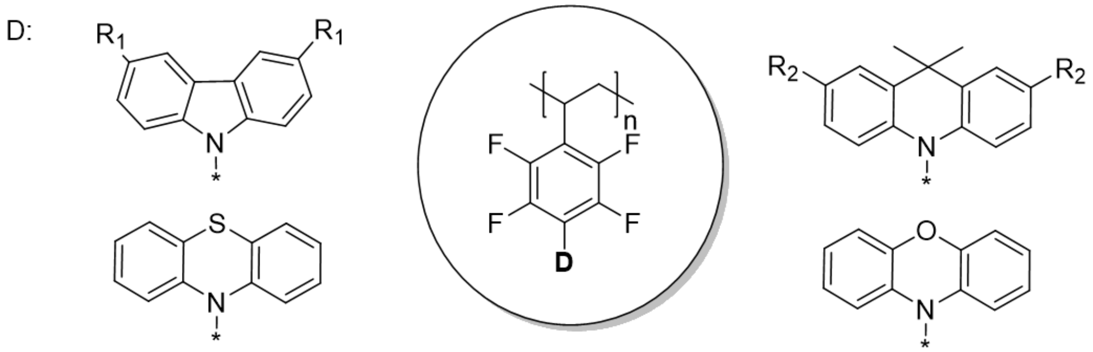
Organic electroactive polymers are known for numerous applications, such as organic thin film transistors, photovoltaic cells, organic light emitting diodes (OLEDs). They are suitable for low-cost manufacturing using solution-processes such as spin coating, screen printing, or ink-jet printing [1]. Solution process is attractive for OLED fabrication because of its potential for simplified processing and possibilities of production of large area devices [2]. Presence of fluorine atom in the molecular structure can significantly change the physical and chemical properties of electroactive compounds in comparison with those non-fluorinated compouns, because of high electronegativity of the halogen atom [3]. A family of the high-molar-mass compounds were synthesized *via* classical radical polymerization of the monomers in THF with AIBN as an initiator and the properties of the polymers were investigated and compared. The monomers comprise tetrafluorostyrene ring as an acceptor moiety and different electron-donating moieties, such as carbazole, dimethyl acridan, phenothiazine, phenoxazine.



The Synthesized monomers and polymers were identified by IR, mass and NMR spectrometries. The average molecular weights and polydispersity indices of the synthesized polymers were estimated by gel permeation chromatography. The number average molecular weights of the polymers range from 6.651 to 144.246. Their polydispersity indices are in the range 1.1-2.7. The molecular weights of the polymers depend on the nature of attached donating unit. Slightly higher molecular weights were achieved for the polymers containing carbazolyl unit in comparison with those containing the dimethyl acridan and other substituents.

The behaviour under heating of the monomers and polymers were estimated by differential scanning calorimetry and thermogravimetric analysis under nitrogen atmosphere. The synthesized fluorostyrene-based monomers and polymers characterized as materials of high thermal stability with the temperatures of the onsets of thermal degradation exceeding 447 °C. The values of initial mass loss depend on chemical structure of the materials. Photophysical properties of monomeric and polymeric materials were compared and investigated. The solid samples of fluorostyrene-based polymers emit light in the range of 458-588 nm which is similar to the emission wavelengths of the respective monomeric compounds.

Acknowledgement
This work was supported by the Horizon 2020 ICT29-2014 project PHEBE (grant No 641725).

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MECHANO-CHEMICAL PRODUCTION OF RUBBER POWDER: THE CURIOUS CASE OF ACETAMIDE ADDITION

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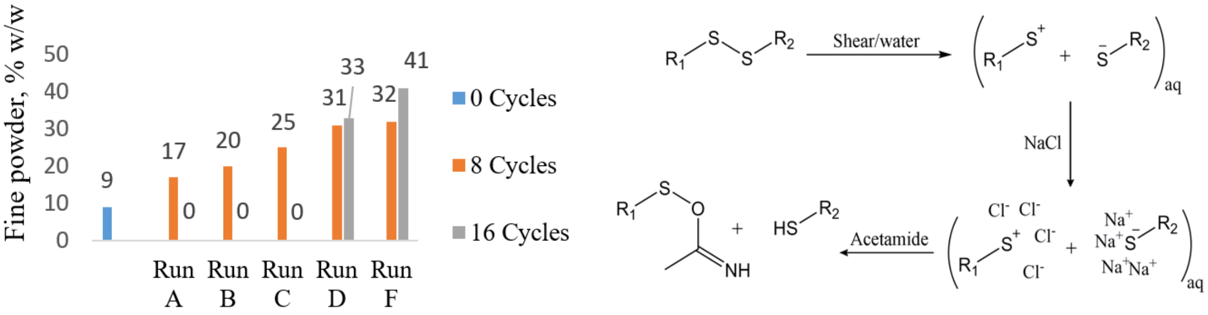
Turning waste rubber into a material, that could be reused has always proven to be a challenge. Reducing the particle size of end-of-life rubber products appears to be a promising path. Rubber that is reduced to crumb could be used as a filler while very fine rubber powder could even be incorporated into new rubber articles [1]. One of the methods of recycled rubber powder production is cryogenic grinding, but the process is not very cost efficient. Another way of rubber powder production is mechano-chemical treatment of rubber [2].

In our experiments we subjected truck tire buffings to mechanical shear in a two-roll mill (XSK-360, *Wuxi Double Elephant Rubber and Plastic Machinery Co. Ltd.*, China) at certain processing conditions: without any additives (Run A); with the addition of 3 % (w/w) of water (Run B); 3 % (w/w) of water and 1 % (w/w) of ascorbic acid (Run C); 3 % (w/w) of water and 1 % (w/w) of acetamide (Run D); 3 % (w/w) of water, 1% (w/w) of acetamide and 0.4 % (w/w) of NaCl (Run E). All tribological parameters were kept constant during the experiments, processing temperature was ambient. After 8 and 16 processing cycles rubber samples were visually inspected and, if possible, the granulometric composition of processed rubber was determined (Fig. 1, *i*).



i) *ii)*

Fig. 1. Granulometric composition of processed rubber (*i*); proposed mechanism of heterolytic cleavage of the weakest bonds in the rubber system with the addition of water, acetamide and NaCl (*ii*)

Experiments showed that neither water, nor radical scavenger (ascorbic acid) helped in efficient production of recycled rubber powder. Rubber powder starts sticking together, forming new macro-structures when processing intensity is increased (evidence of molecular self-healing process). When acetamide was used as a chemical aid in mechano-chemical processing of rubber (run 4) fine powder fraction (particles, smaller than 850 μm) was increased. Moreover - particle agglomeration was diminished when higher processing intensities were employed. These effects were pronounced even more when NaCl together with acetamide were added to the processing mixture. The fact, that traditional radical scavenger (ascorbic acid) is less efficient than acetamide in rubber powder production could mean that when rubber is recycled under mild conditions heterolytic (accountable for ion production), rather than homolytic (radical), cleavage of bonds could be a dominating mechanism (Figure 1, *ii*).

Authors would like to thank Artūras Jukna and Tadas Ikanevičius from JSC “Gumos Technologijos” for providing rubber samples and carrying out mechano-chemical experiments.

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HYDROTHERMAL SYNTHESIS OF HYDROXYAPATITE FROM CUTTLEBONE FOR FILLING BONE DEFECTS

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Biogenic Ca sources, like cuttlebone (CB), with nature-adjusted amounts of trace inorganic elements are ideal starting materials for bone scaffold design. CB is known as biocompatible, osteoconductive and bioactive material [1–2]. However, from the hard-tissue regeneration perspective hydroxyapatite (HAp) is preferred to aragonite presented in CB. In this study a hydrothermal synthesis of HAp from CB microparticles was performed with the aim to develop a cellulose-based composite for bone tissue engineering applications.

The hydrothermal synthesis was performed at 200 °C for 8 h. The amount of materials was calculated to reach Ca:P molar ratio 1.67. Obtained HAp was characterised by the Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and X-ray fluorescence (XRF) techniques. A cellulose-based composite with CB-derived HAp was prepared and characterised by the micro-computed tomography (micro-CT).

CB-derived HAp was obtained *via* the hydrothermal synthesis according to the equation:

$$10CaCO_3 + 6(NH_4)_2HPO_4 + 2H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 6(NH_4)_2CO_3 + 4H_2CO_3$$

Absorption peaks of PO_4^{3-} group at 565 cm^{-1}, 606 cm^{-1}, 960 cm^{-1}, 1029 cm^{-1} and 1090 cm^{-1} were observed in the FTIR spectrum of CB-derived HAp (Fig. 1a); additionally, a X-ray diffraction pattern shows characteristic peaks of HAp (Fig. 1b). XRF data revealed the presence of trace elements in CB-derived HAp, such as Sr, Mg, Si, S, and Fe. The obtained CB-derived HAp was used for the macroporous three-dimensional (3D) cellulose-based composite development.

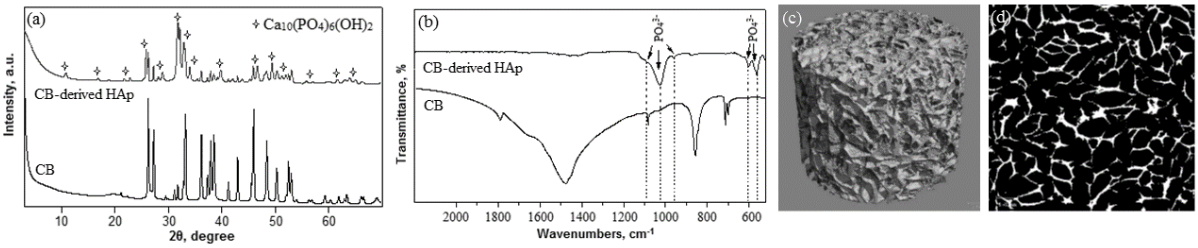

Fig. 1. Illustration of the results for the hydrothermal synthesis of HAp from CB following the development of a cellulose-based composite: XRD patterns and FT-IR spectra of CB and CB-derived HAp (a and b, respectively); 3D reconstruction and 2D image of the composite (c and d, respectively)

The interconnected porous structure of the composite was evaluated by the micro-CT (Fig. 1c, d). Porosity of the composite was 85 %, and the average pore size was 500 µm, showing fulfilment of basic morphological requirements for bone scaffolds.

Hydroxyapatite was synthesised from cuttlebone microparticles *via* hydrothermal reaction in the presence of ammonium phosphate. Present research showed a perspective of a biogenic calcium source, such as cuttlebone, for developing scaffolds for filling bone defects.

Acnowledgement.
The authors thank Prof. Kestutis Baltakys and PhD student Tadas Dambrauskas from Department of Silicate Technology, Kaunas University of Technology, for technical support.

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POLY(2-HYDROXYPROPYLENE IMINE) CONTAINING SEGMENTS OF POLY(ETHYLENE GLYCOL) AS EFFICIENT REAGENT FOR siRNA TRANSFECTION

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Polymeric carriers for transfection of DNA and/or siRNA to cells belong to hot topics in polymer science. The ideal polymeric carrier must have proper molecular weight, structure and protonation ability for achieving long circulation time, low immunogenicity, good biocompatibility, selective targeting and efficient penetration of physiological barrier [1].

Poly(2-hydroxyalkylene imines) possessing both imine and hydroxyl groups in their repeating units have been synthesized recently and shown to be efficient gene transfection reagents [2, 3]. Unfortunately, at higher concentrations these polymers showed substantial cytotoxicity [2]. Cytotoxicity may be reduced by introducing segments of poly(ethylene glycol) (PEG) which is one of the most suitable polymers (oligomers) for modification because of its unique physicochemical and biological properties, including hydrophilicity, solubility in water and organic solvents, lack of toxicity, and absence of antigenicity and immunogenicity [4].

In the present paper, we report synthesis and study of MPEG'ylated derivatives of poly(2-hydroxypropylene imine) (PHPI). Novel branched PHPI derivatives containing terminal segments of MPEG are expected to be non-cytotoxic and efficient reagents for DNA and siRNA transfection.

MPEG'ylated derivatives of PHPI were synthesized by polycondensation of 1,3-diamino-2-propanol and 1,3-dibromo-2-propanol in the presence of MPEG iodide (MPEGI). Trying to find conditions suitable for the synthesis of PHPI derivatives with different content of MPEG chains, MPEGI was added to the initial mixture of the monomers, or it was introduced later, at the end of the reaction. Moreover, MPEGI with different molecular weight (M_n 1000, 2000, and 5000) was used, which expanded possibilities to synthesize PHPI-MPEG derivatives with different structure, i.e. length and density of MPEG chains and molecular weight [5].

Addition of MPEGI to the initial monomer feed resulted in polymers with relatively low molecular weight (M_w 8-53 kDa) and high MPEG content (over 60 mol %, 1 to 1.25 MPEG chains per macromolecule). Introduction of MPEGI during the final stage of the polycondensation gave high-molecular-weight products (M_w 140-160 kDa) with high dispersity and low content of MPEG (less than 9 mol %, 0.09 to 0.22 MPEG chain per macromolecule). Yield of MPEG'ylated PHPI was low, less than 30 %, and these polymers were highly branched.

Compared to PHPI, low MW/high MPEG content PHPI derivatives demonstrated reduced efficiency in DNA transfection. Efficiency of high MW/low MPEG content PHPI derivatives in DNA transfection was similar to that of PHPI. The length of MPEG chains attached to the polymers had no effect over the transfection efficiency. MPEG grafting had a positive effect on siRNA delivery. High MW polymers with low content of MPEG performed significantly better than non-MPEG'ylated PHPI and low-molecular-weight polymers with high content of MPEG. An increase in gene knockdown level using MPEG'ylated derivatives of PHPI in siRNA experiments suggests that MPEG grafting improves siRNA release and fosters its biological activity. Because of lower toxicity and less tendency to aggregation, MPEG'ylated poly(2-hydroxypropylene imine)s provide an advantage for future *in vivo* applications.

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ANTIOXIDANT AND ANTIMICROBIAL FOOD PACKAGING COATINGS

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Active food packaging involves the packaging of foods with materials that provide an enhanced functionality, such as antimicrobial or antioxidant. This can be achieved through the incorporation of active compounds into the matrix of the commonly used packaging materials, or by the application of coatings [1]. Compared to synthetic antioxidants or antimicrobials, natural materials such as herbs and spices are of great interest because of their safety and health characteristics. The serious problem in the food industry consists of protecting shelf-stable food from oxidation reactions and microbial contamination. The most promising strategy to protect the food is delivery of active materials to the food surface through slow release from the packaging material [2-3].

In this study, eugenol (EU), clove (CL) and thyme (TH) essential oils containing coatings based on acrylic component/hydrophobically modified starch (AC/S) or cellulose acetate (CA) were applied on corona treated oriented polypropylene (OPP) film, and investigated for their possible application as active food packaging materials. The antioxidant and antimicrobial properties of the coatings were investigated through the vapor phase by newly developed method. The cellulose acetate or acrylic component/hydrophobically modified starch containing CL or EU showed high inhibition against DPPH free radicals through the vapor phase (Fig 1a). Whereas, acrylic component/hydrophobically modified starch coatings containing TH were active through the vapor phase and could efficiently reduce *E. coli* or *L. monocytogenes* 1000 fold from normal growth (Fig. 1b). In addition, EU was chosen as most effective bioactive compound in the coatings for antioxidant food packaging assay. Lipid oxidation of beef kept in active packaging was approx. 2.5 – 3.0 times lower compared to control sample. Furthermore, beef samples in active packaging showed a good red color stability even after 14 days.

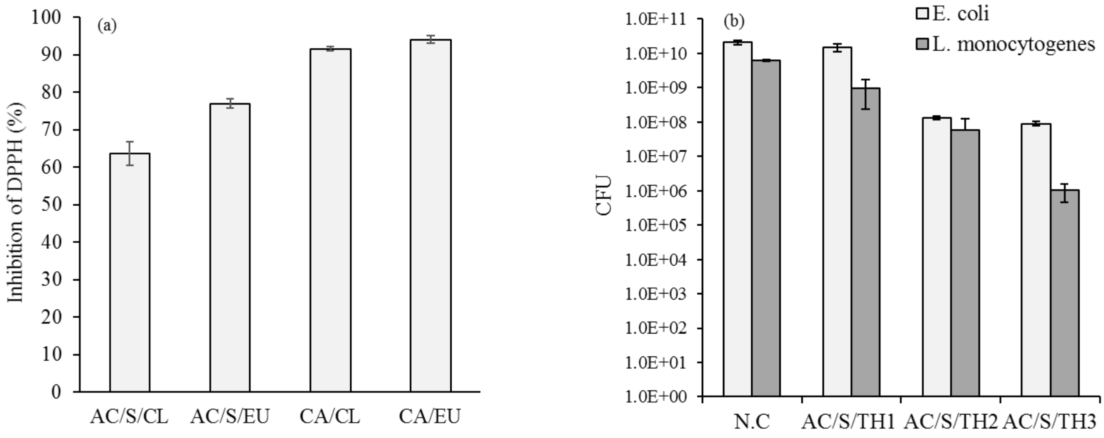

Fig. 1. Antioxidant (a) and antimicrobial (b) activity of coatings through the vapour phase

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IMMOBILIZATION OF ARTICHOKE EXTRACT ON CROSS-LINKED CATIONIC STARCHES

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Polyphenols are abundant secondary metabolites in plants and are known to prevent diseases associated with oxidative stress and its related complications. Chlorogenic acid (CGA) is predominant phenolic compound in artichoke extract (AE). The effectiveness of phenolics depends on preserving their stability, bioactivity and bioavailability. One of the ways to protect the anionic phenolics could be their immobilization on cationic polymers such as cross-linked cationic starch having quaternary ammonium groups (CCS). The purpose of present investigation was to evaluate and compare the equilibrium adsorption of CGA and AE onto CCS at different `temperatures.

The equilibrium adsorption of CGA and AE on CCS with degree of substitution (DS) of 0.42 was investigated at temperatures of 30, 40 and 60 °C. The Langmuir, Freundlich and Dubinin-Radushkevich adsorption models have been used to describe the equilibrium adsorption (see Table 1).

Table 1. Adsorption model parameters for adsorption of CGA and AE on CCS (DS=0.42) at different temperatures

Adsorption temperature (°C)	Langmuir model			Freundlich model		Dubinin-Radushkevich model		ΔG^0 (kJ/mol)	R^2	ΔH^0 (kJ/mol)	ΔS^0 (J/mol·K)	R^2
	Q_L (mmol/g)	*EF* (mol/ekv)	R^2	n_F	R^2	E_{DR} (kJ/mol)	R^2					
Adsorption of chlorogenic acid												
30	1.11	0.61	0.9934	2.96	0.9971	11.60	0.9980	-5.19	0.9936	-8.09	-9.57	0.9999
40	1.10	0.60	0.9921	2.95	0.9963	11.70	0.9940	-5.09	0.9768			
60	1.02	0.56	0.9882	3.06	0.9966	12.00	0.9926	-4.90	0.9750			
Adsorption of artichoke extract												
30	3.25	1.77	0.9821	2.06	0.9978	10.01	0.9962	-5.09	0.9427	19.7	81.61	0.9913
40	3.23	1.77	0.9872	2.30	0.9977	11.06	0.9914	-5.74	0.9531			
60	2.99	1.63	0.9842	2.36	0.9984	11.88	0.9926	-7.51	0.9738			

With the increase of adsorption temperature the values of the Langmuir sorption capacity Q_L and adsorption efficiency *EF* decreased. The values of Freundlich constant n_F showed that conditions for CGA and AE adsorption on CCS are favourable. Moreover, the calculated values of Dubinin-Radushkevich adsorption energy E_{DR} showed that driving forces of adsorption were interactions between cationic groups of CCS and carboxylic groups of CGA. The studies revealed that high amount of AE was adsorbed onto CCS, and alongside the other phenolic compounds from AE were immobilized onto CCS possibly by hydrophobic interactions.

The thermodynamic parameters of the adsorption were calculated. Spontaneous adsorption of both CGA and AE, and great affinity to adsorbent was evidenced by negative values of ΔG^o. In the case of CGA adsorption, the negative values of ΔH^o and ΔS^o showed that adsorption was exothermic process, and the order of the system increased. In contrary, during the AE adsorption onto CCS, the process was endothermic and the order of the system decreased.

The content of phenolics adsorbed on CCS from artichoke extract has been estimated by using UELC-MS/MS method.

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The authors are grateful to the Research Council of Lithuania for the financial support of the project MIP-055/2015.

OLIGOMERS CONTAINING PENDANT 4-ARYL-7-PHENYLFLUORENE UNITS AS HOLE TRANSPORTING MATERIALS FOR OLEDS

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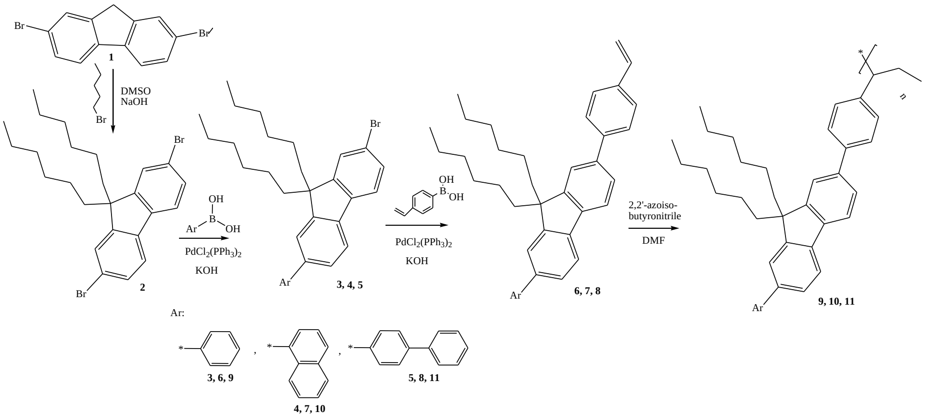
Organic light- emitting diodes (OLEDs) based on organic semiconductors and emitters have attracted much attention because of their potential use in flat panel displays and lighting [1, 2, 3]. Efficient OLEDs can usually be obtained only by building multilayer structures [4, 5]. We will present new oligomers for hole transporting layers the OLED devices. Synthesis of the derivatives **9-11** was carried out according to synthetic route shown in Scheme 1.



Scheme 1

The amorphous materials **9-11** showed very high thermal stability with high glass transition temperatures and are expected to show also high morphological stability of thin films of OLED devices. The electron photoemission spectra of thin layers of the oligomers showed that values of ionization potentials of the derivatives depend on their electro-active moieties and range from 5.7 eV to 6.1 eV. The oligomers were tested as hole transporting layers in bilayer organic light emitting diodes with tris(quinolin-8-olato)aluminium as an emitter. The device with oligomer **11** containing electro-active 2-(4-biphenyl)-7-phenylfluorene units exhibited the best overall performance with turn on voltage of 4.4 V, maximum brightness of 3220 cd/m^2 and current efficiency of 3.6 cd/A. These OLED properties are rather promising among Alq$_3$-based two-layer devices.

Acknowledgements
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PHYSICOCHEMICAL CHARACTERIZATION OF STARCHES FROM VARIOUS LITHUANIAN WINTER WHEAT CULTIVARS

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Wheat is one of the most important crops in Europe and Lithuania is not an exception. Starch is a major component of wheat grains and its functional properties have a significant impact on grain utilisation. *The aim of of the present work was to study the physicochemical properties of starches extracted from eight Lithuanian winter wheat cultivars (2013 yield year), developed at* Lithuanian Institute of Agriculture with a particular focus on aspects of starch granule size distribution, amylose content and corresponding gelatinisation characteristics. The lowest amount of amylose was obtained in waxy wheat starch (6.7 %) and starches isolated from other cultivars, had higher amylose content (24.0 to 28.9 %, Table1). Higher amylose content starch (samples 1-7, Fig.1) give intense blue colour with iodine and amylopectin rich sample gives a reddish-purple colour with iodine (sample 8, Fig.1).

Table 1. Amylose content in various wheat starches

No.	Wheat cultivar	Starch amylose content (%*wt.*)
1	Kovas DS	28.9
2	Alma DS	24.0
3	Ada	25.9
4	Kena DS	28.2
5	Herkus DS	28.5
6	Sedula DS	28.2
7	Gaja DS	26.4
8	Minija DS	6.7

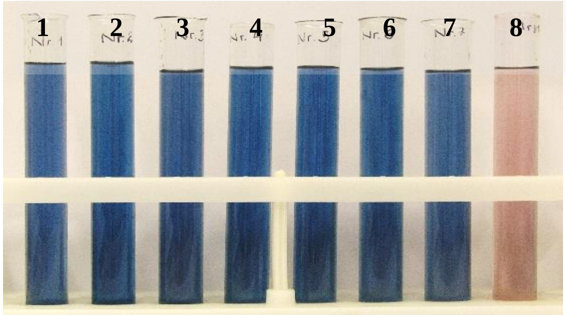

Fig. 1. Photographs of iodine complexes in water with starches from various wheat cultivars

All investigated starches had a bimodal particle size distribution and appeared as spherical shaped granules (see Fig. 2). Volume percentages of A-type granules had ranges of 61–70 %. The lowest amount of A-type granules was observed for waxy wheat starch. Gelatinisation and rheological properties of starch are primary physicochemical properties to determine its applications. The pasting properties were determined using a rapid visco analyzer and the pasting curves showed significant differences in pasting characteristics of the starches. The amylose content in starches affected their pasting properties. The waxy wheat starch showed lowest onset gelatinisation temperature, highest peak viscosity and lowest final viscosity. Furthermore, starches, which had higher amount of amylose, showed higher setback than waxy wheat starch. Ranges of onset gelatinisation temperature were 72.3–83.1 °C for non-waxy starches and 66.7 °C for 'Minija DS' waxy starch.

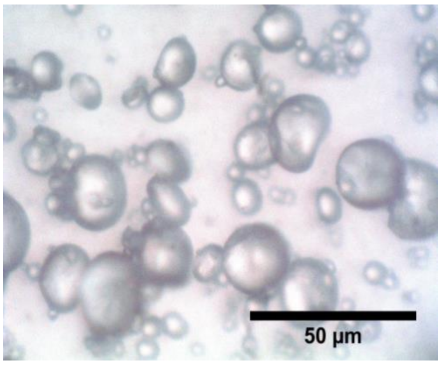

Fig. 2. Optical microscopy image of 'Kena DS' cultivar starch granules

Acknowledgement
This study was partly supported by the long-term research program "Biopotential and Quality of Plants for Multi-functional Use" implemented by Lithuanian Research Centre for Agriculture and Forestry.

SYNTHESIS AND INVESTIGATION OF METHYLMETHACRYLOYL MONOMER CONTAINING TRIPHENYLAMINO AND 1,8-NAPHTHALIMIDE UNITS

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The main difficulty in the preparation of organic light emitting diodes and other optoelectronic devices by solution processing is the solubility of the material which forms the bottom layer onto which the top layer has to be cast, because most organic semiconductors are soluble in the same solvents. One approach that was employed to circumvent this problem is the appliance of electro-active derivatives with reactive functional groups, which could be converted into polymers with lower solubility or even into insoluble networks by cross-linking reactions [1].

High electron-affinity of naphthalimides determines the possibility of their use as electron-transporting media, and the imide nitrogen makes naphthalimides easy to functionalize [2]. They exhibit good photochemical stability and high luminescence quantum yields [3].

In this work we report on the synthesis and investigation of methylmethacryloyl monomer containing naphthalimide moiety which was synthesized by condensation and palladium-catalyzed Suzuki-Miyaura reaction (Fig.1).

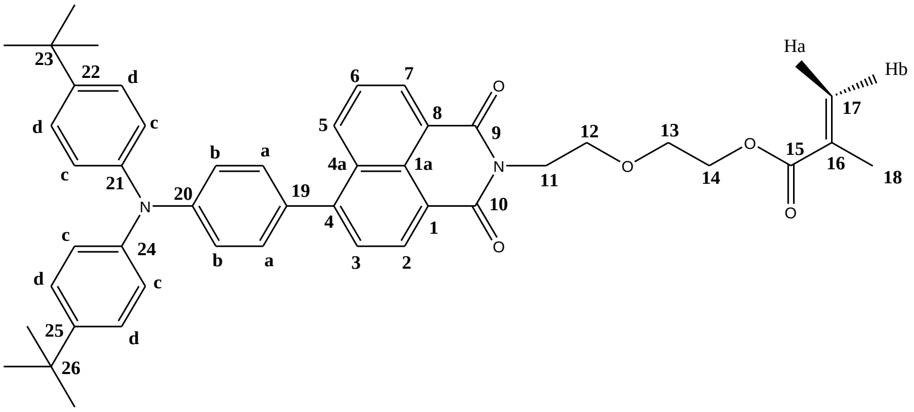

Fig. 1. Structure of naphthalimide-based monomer.

The structure of the synthesized compound was proved by ^{1}H and ^{13}C NMR, IR and mass spectrometries. The thermal, optical, electrochemical and photophysical properties of the synthesized compound were investigated. The synthesized molecule exhibit moderate thermal stability with the thermal degradation onset temperature at 215 °C. Absorption peak which appear at 433 nm apparently corresponds to the intramolecular charge-transfer transition between the triphenylamino donor moiety and the naphthalimide acceptor moiety. The estimated optical band gap of the monomer was 2.49 eV. The dilute THF solutions (10^{-5} M) of the monomer showed orange luminescence peaking at 647 nm. The ionization potential and electron affinity values of the monomer were estimated by cyclic voltammetry and were found to be 5.51 and -3.72 eV, respectively.

Acknowledgment
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THE INVESTIGATION OF DIFFERENT PREPARED HYDROLYSATES FROM PROTEIN RICH LEATHER TANNING INDUSTRY WASTE

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The biggest part of leather industry waste is transported to landfills while 60-65% of solid waste is fleshings and trimmings which are rich in proteins. The world researchers are looking for such waste recycling and recovery methods, to make more efficient waste management by reducing their amount in landfills and their impact to the environment [1]. The seed treatment, e.g. seed coating is simple and effective protective tool which allows to increase plant productivity and to use protein rich leather waste. The aim of this work was to evaluate features and usability of the collagen based leather processing waste (trimmings and fleshings) hydrolysates.

The thermal and enzymatic hydrolysis of the trimmings and fleshings was performed. The kinetics of hydrolysis was determined by determination of the concertation of hydroxyproline. The enzymatic hydrolysis of trimmings and fleshings are faster comparing with thermal hydrolysis. The biggest amount of 0.38 g/kg of hydroxyproline is reached in the enzymatic hydrolysis of trimmings while the biggest amount of 0.32 g/kg for thermal hydrolysis is determined after 4 hours. The biggest amounts of 0.32 g/kg and 0.21 g/kg of hydroxyroline for the enzymatic and thermal hydrolysis were determined, accordingly.

The average molecular weights determined by 12 % SDS-PAGE of the products of the trimmings thermal hydrolysis were in rage of 250 to 45 kDa. The lower average molecular weights of the products (from 22 to 9 kDa) were characteristic for the trimmings enzymatic hydrolysis. The biggest distribution in the average molecular weights of the products of the both hydrolysis of fleshings was determined (from 250kDa to 25 kDa and from 35 to 10 kDa for the thermal and enzymatic hydrolysis, accordingly). Similar distribution of the molecular weight of collagen was made in the case of the hydrolysis of bovine limed split wastes [2].

The film-forming properties of the hydrolysates were investigated. The film was formed only from the hydrolysates of the trimmings obtained by thermal hydrolysis. The film of the products of the enzymatic hydrolysis could not be formed.

It could be concluded that the collagen based hydrolysates obtained by the thermal hydrolysis could be promising in the protective seed coating.

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DEVELOPMENT AND PHYSICOCHEMICAL CHARACTERISATION OF WITEPSOL/CUTTLEBONE SUPPOSITORIES WITH LIDOCAINE

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Development of multifunctional suppository formulations is one of the cutting edge issues in pharmaceutical engineering. Natural-based alternatives to conventional solutions in treatment of topical or mucous pathological conditions are thoroughly investigated. Cuttlebone (CB) is a natural material with promising applications in soft tissue engineering, possessing antioxidative, haemostatic, bioactive and non-cytotoxic features [1–2]. It consists of polysaccharide chitin and aragonite in an approximate ratio 1 : 9. Combination of hydrophobic local anaesthetic lidocaine (LID) with CB-derived aragonite/chitosan complex could guarantee several pharmacological actions in one medicament, such as numbness of painful area, haemostatic effect and regeneration of injured mucosa. Witepsol is a well-established commercial type of suppository bases, consisting of mono-, di- and triglycerides from natural origin. In this study powdered CB was used for haemostatic effect, and loading of LID in Witepsol/CB formulation was tested *via* drug release study.

Powdered CB was subjected to deacetylation of composing chitin using 40 % NaOH solution. Witepsol melting point was determined using open capillary tube technique. Haemostatic effect of modified CB was performed *via* evaluation of blood coagulation rate [3]. Further, semi-solid samples were prepared by pour moulding technology from 10 % modified CB and 2 % LID using Witepsol H35 as a base. *In vitro* drug release study was performed using basket method according to the European Pharmacopeia recommendations, and the recording of LID concentration in dissolution medium was measured spectrophotometrically at 260 nm.

Aragonite-chitosan complex was obtained by deacetylation of CB microparticles and the 20.5 % decrease in clotting time was further observed. Witepsol/CB formulation was prepared by pour moulding technology using LID and modified CB as active substances (Fig. 1a, b).

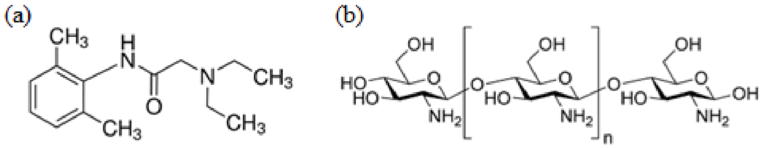

Fig. 1. Active substances of Witepsol/CB formulation: (a) lidocaine; (b) chitosan

Melting point of Witepsol H35 was at about 33.5 °C. Addition of solid paraffin as a hardener raised the melting point of this base up to 37 °C, and therefore ensured proper melting process at the average internal human body temperature. Drug release study revealed the first data point of LID in dissolution medium after 15 min and further gradual release within 40 min, while showing *in vitro* early onset of LID activity and appropriate drug-release profile.

In this study anaesthetic lidocaine and aragonite-chitosan complex from cuttlebone were successfully combined using Witepsol H35 as a base. Prepared Witepsol/cuttlebone formulation with lidocaine could be a promising basis for a development semi-solid medicaments with multifunctional pharmacological action.

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BIODEGRADABLE THERMOPLASTICS BASED ON CELLULOSE ACETATE

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The use of plastic materials is widespread in everyday life for diverse applications. Most of the plastics for common use are currently produced from fossil fuels and consumed and discarded into the environment, taking a very long time to degrade and causing the related problems of collection and disposal, often ending up in landfills or in waste incinerators for energy recovery. The increasing pressure on manufacturers by new environmental and waste management policies and consumer demand, in addition to the escalation of oil prices, are steering the trends of polymer technology away from traditional materials towards materials produced by renewable resources. For these reasons, the new field of biodegradable and biobased polymers, which have some environmentally-friendly properties (materials in which the production is based on renewable resources, characterized by low energy consumption, low CO_2 emissions, with possibility for composting, biomethanation or recycling), has received growing consideration [1].

Cellulose derivatives like cellulose diacetate can be used to make biodegradable plastics. The main drawback of cellulose acetate is that the melt processing temperature exceeds its thermal decomposition temperature. This dictates that cellulose acetate needs to be plasticized. Plasticizers have long been known for their effectiveness in producing flexible plastics for applications ranging from the automotive industry to medical and consumer products. Plasticizers are used for biodegradable plastics as well. There are more stringent requirements on these plasticizers, though, since by definition they will be released into the environment during product use. Health and safety issues dominate the research in this field, with benign, often natural substances having nearly as great importance as the ability to lower the Tg of the polymer. The objective of the present research was to investigate the influence of eco-friendly and food-grade plasticizers on rheological, thermal, mechanical and biodegradability properties of cellulose acetate.

The addition of plasticizers allowed melt processing of cellulose acetate. The effect of plasticizing was clearly observed with an increase of the ductility of the cellulose acetate films containing plasticizers. Moreover, biodegradability of plasticized cellulose acetate much exceeded that of pure cellulose acetate. Thermal analysis showed, that thermal events of plasticized cellulose acetate proceeds in two stages. The first thermal event (115–320 °C) is related to the elimination of physically retained plasticizer. After evaporation of plasticizer molecules, the chemical degradation of cellulose acetate occurs at 335 °C. Plasticizers do not influence thermal degradation of cellulose acetate, since they evaporate from plastic at lower temperatures, than the thermal decomposition temperature of cellulose acetate.

Acknowledgement
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BIODEGRADABLE POLYMERIC COMPOSITES FILLED WITH INDUSTRIAL WASTE MATERIALS FOR MULCHING COATINGS

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Plastic mulch films protect moisture, are transparent with respect of the sunbeams and thus contribute to the increase of the temperature of soil, they also effectively protect from the germination of weeds and can be used for mulching of big areas. The aim of this work was the preparation of biodegradable polymeric composites from renewable recourses filled with industrial waste materials which could be applied as mulching films in agriculture and forestry.

Linseed oil-based polymer with bisphosphonate crosslinks was used as polymeric binder in prepared composites. The following industrial waste materials were used as fillers: horn meal, phosphogypsum, rapeseed cake, pine needles, pine bark, grain mill waste, and mix of grain waste and weeds. After decomposition of such polymeric composite mulches, the released fillers of natural origin could improve the physical, chemical and biological properties of soil, increase the amount of nutrients and humus in it and thus stimulate the growth of plants.

Polymeric composite films were formed by casting from solution of the mixture consisting of epoxidized linseed oil, **1-hydroxyethane-1,1-diphosphonic acid, and different amounts of industrial waste materials.** Dependency of composite film curing time on temperature, dilution, filler type and amount was investigated. Mechanical and thermal properties, combustibility, moisture permeability, surface wetting, swelling in water, and biodegradability of the formed polymeric composite films were investigated. The results of the soil burial test of the selected polymeric composites with two different fillers are shown in Figure 1.

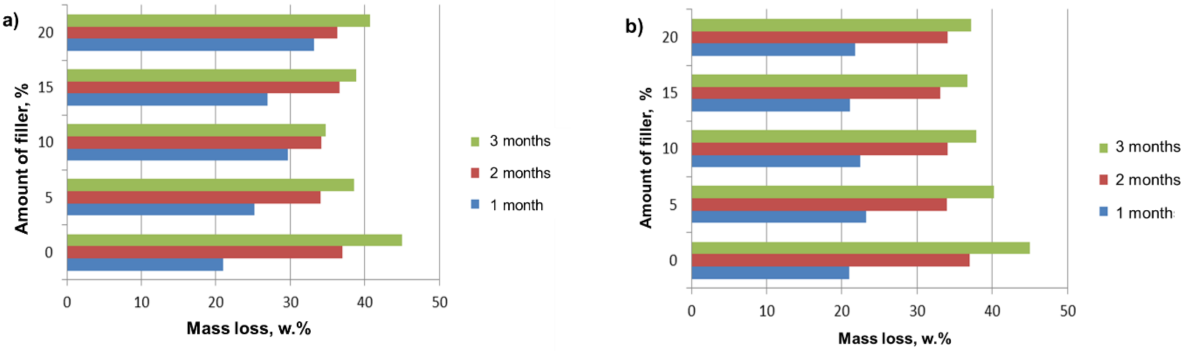

Fig. 1. Mass loss of the specimens of the polymeric composites filled with the rapeseed cake (a) and with the grain mill waste (b) after 1–3 months exposition in soil

The investigated properties show that prepared polymeric composites filled with industrial waste materials are thermally stable up to 200 °C, are less flammable than conventional synthetic polymer films, their mechanical characteristics deteriorate with increase of amount of filler, their values of wetting angle are similar to that of polypropylene film, swelling values in water of composite films are lower than that of the film without filler. Prepared composite films protect moisture is soil, are biodegradable and can be applied as mulching films in agriculture and forestry.

Acknowledgement
Financial support of this research by the Research Council of Lithuania (project No. MIP-066/2015) is gratefully acknowledged.

PHOTORHEOMETRICAL STUDY OF CROSS-LINKING KINETICS OF ACRYLATED SOYBEAN OIL AND AROMATIC DITHIOLS

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Vegetable oils are potential starting materials for the preparation of polymers due to their ready availability, inherent biodegradability, limited toxicity, and existence of modifiable functional groups [1]. Thiol-ene addition reaction was selected for the synthesis of vegetable oil-based polymers due to its high conversion, fast reaction rates, low oxygen inhibition, and good tunability of the resulting polymer networks [2]. Photorheometry allows to monitor typical rheological properties such as viscosity and shear modulus while a material is irradiated with UV or visible light. Rheometric evaluation of photocuring kinetics provides a more physical complement to traditional chemical kinetics measurement techniques such as photo-DSC or real-time IR spectroscopy [3].

Photocross-linking kinetics of acrylated soybean oil (ASO) and 1,3-benzenedithiol (1,3BDT) or 1,4-benzenedithiol (1,4BDT), using photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) or 2-hydroxy-2-methylpropiophenone in different quantities was monitored by a MCR302 rheometer from Anton Paar equipped with UV/Visible spot curing system OmniCure S2000 and the plate/plate measuring system.

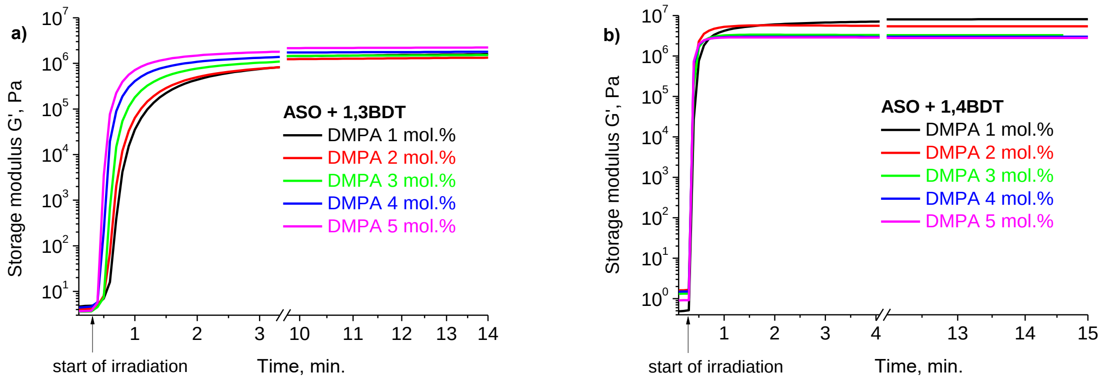

Fig. 1. Storage modulus G‘ dependence on the irradiation time for ASO/1,3BDT (a) and ASO/1,4BDT (b) when 1-5 mol.% of DMPA were used

It was determined that photocross-linking of all studied systems was faster when the amount of photoinitiator was higher. The values of storage modulus G‘ and loss modulus G“ depended on the ratio of starting compounds. The lower ratio caused the higher values of modules G‘ and G“ and thus the higher hardness of the obtained polymer films. Photocross-linking was faster and the better mechanical properties of polymers were obtained when ASO/1,4BDT (ratio of functional groups 1:1) and DMPA were used (Fig. 1).

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ANALYSIS OF POLYMER FIBER FORMATION BY MELT ELECTROSPINNING

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Over the last decade, melt electrospinning has emerged as an alternative polymer processing technology to alleviate concerns associated with solvents in traditional electrospinning. This has resulted in the fabrication of ultrafine fibers from an increasing range of synthetic polymers and composite systems, to materials including ceramics, driving new applications in technical areas such as textiles, filtration, environment and energy as well as biomedicine [1]. Many authors working in this field choses to work with specific polymers, such as polylactic acid (PLA), polycaprolactone (PCL) or other polymers which are usually synthesized specially for this purpose. Because of biodegradability of first two polymers and lack of accessibility of others, we decided to look in to commercially available polymers. So in this study we are analysing fiber formation of different commercially available polymers by melt electrospinning.

For the experiments 15 different polymers, from 6 different suppliers was chosen. Main polymer characteristics needed for fiber formation by melt electrospinning was melting point (60–180 °C) and melt flow rate (2,01–81 cm^3/10 min). Chosen polymers was PCL from two suppliers, four types of nylon 12 (PA 12), 3 – low density polyethylene (LDPE), 2 – thermoplastic polyaniline (TPA), 3 – thermoplastic coployester (TcPE) and one nylon 10 (PA 10).

The best results with fiber diameters of 1,2–3 µm was shown by PA 12 (Code: L 160o) (Fig. 1). In most other cases fibers were either much thicker or had inconsistent diameters (Fig. 2). For more precise results mote testing with different conditions (melting and environment temperatures, voltage, needle-collector distance) is needed.

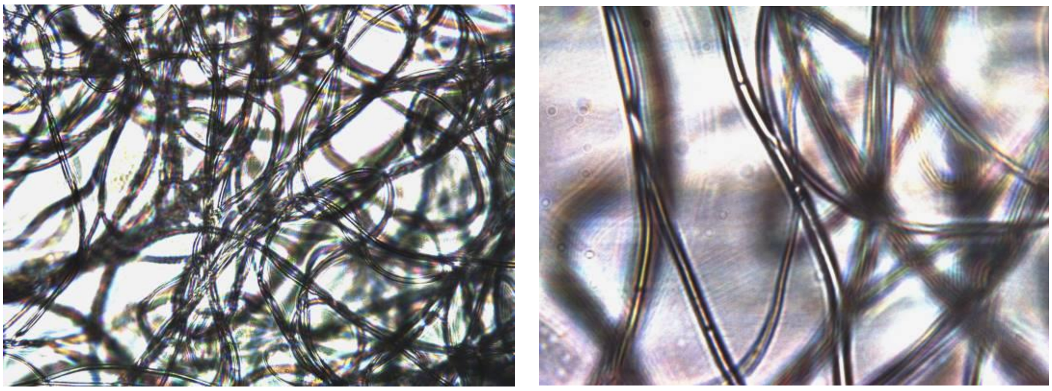

Fig. 1. Microscopic picture of PA 12 fibers (enhancement ×40; ×100)

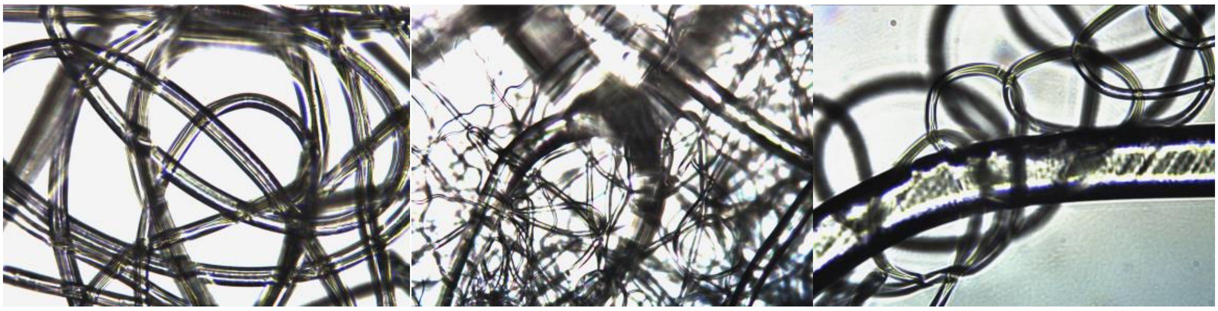

Fig. 2. Microscopic picture of other polymer fibers (enhancement ×40)

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Chemistry and Technology of Inorganic Materials

FORMATION OF COBALT SULFIDE LAYERS ON POLYAMIDE 6 USING SOLUTIONS OF DODECATHIONIC ACID, $H_2S_{12}O_6$

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Cobalt with sulfur forms various crystalline phases: CoS, Co_3S_4, CoS_2, $Co_{1-x}S$, Co_4S_3, Co_2S_3 and Co_9S_8 [1]. They have potential applications in solar energy conversions, optical filters, sensors, IR detectors, magnetic recording devices, anodes for batteries, catalysts [2–5].

Cobalt sulfide thin films were prepared by the electrodeposition technique, the chemical bath deposition or modified chemical deposition method. In our studies the layers of cobalt sulfide on polyamide 6 (PA) were formed by a sorption-diffusion method. The method consists of two stages. In the first stage - sulfurization of the polymer PA films were treated with the solution of dodecathionic acid, $H_2S_{12}O_6$, the molecules of which contain chains of divalent sulfur atoms of low oxidation state, $^{-}O_3S–S_{10}–SO_3^{-}$. In the second stage, the sulfurized polymer was treated with a solution of Co(II) salt and layers of cobalt sulfides were formed on the surface of a polymer.

The aim of present work was to study the composition of Co_xS_y layers on PA, using X-ray photoelectron spectroscopy (XPS).

In the surface of PA samples, modified by cobalt sulfides, the presence of various cobalt, sulfur and oxygen compounds (CoS, Co_9S_8, CoS_2, $Co(OH)_2$) was determined.

In the XPS study of the cobalt sulfide coating, we paid attention to the distribution of Co, O, and S elements over the surface and throughout the depth of the coating. The processes of PA film sulfurization and cobalt sulfide containing layer formation take place in a natural environment; therefore, it is impossible to prevent its influence. Semi hydrophilic polymer PA, under the action of environment, absorbs on its surface oxygen, moisture and other compounds. Our results show that the surface of the coatings contains up to ~35 at.% oxygen and ~ 26 at.% oxygen was found in deeper layers of the coating.

The $Co2p_{3/2}$ spectrum contains a main peak located at a binding energy value of 779.9 eV and a shake-up feature at higher binding energy. These peaks can be assigned to Co^{2+} of CoS phase as supported by the literature. Further, the $Co2p_{3/2}$ spectrum can be de-convoluted into couple of more constituent components corresponding to the following chemical states as $Co(OH)_2$.

The binding energy value of $S2p$ is around 162.5 eV, indicating that most of the S species exist as S^{2-} (CoS phase). This compound was detected after the 4 nm thick was etched with Ar^+ ions. The most intense peak at a binding energy 169.75 eV, which can be assigned to sulfur S^{6+} bond to oxygen ($CoSO_4$). This compund was detected only on the surface of the coatings.

The measured binding energines E_b of $O1s$ (532.5 eV) electrons suggest that oxygen occurs in the form of $Co(OH)_2$. These compounds were detected not only on the surface, but also in deeper layers of the coating. $Co(OH)_2$ may be formed while washing coatings with water. In the same $O1s$ region (at 531.35 eV) is peak of PA 6 binding energy.

Thus the results of XPS study confirmed the formation of cobalt sulfide containing layers on the surface of PA: on the layer's surface and in the etched surface various cobalt sulfide and cobalt hydroxide ($Co(OH)_2$) are present. From the data of analysis it follows that the composition of the layers formed in different conditions is rather similar.

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SPECTROSCOPIC STUDY OF COMPOSITE MATERIAL FILMS BASED ON POLYAMIDE

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Organic-inorganic hybrid materials are composites containing both inorganic and organic building blocks linked via stable covalent bonds and can be broadly described as multicomponent systems combined with the goal of forming new nanomaterials exhibiting unique properties [1]. Inorganic materials typically used to form composites are I-VI/II-VI semiconductors. Polyamide 6 as a semi-hydrophilic polymer is capable of adsorbing ions from aqueous solutions of various electrolytes [2]. In this work, $SeS_2O_6^{2-}$ anions were incorporated from aqueous solutions of $K_2SeS_2O_6$. Subsequent modification of the obtained PA6/$SeS_2O_6^{2-}$ composite with the aqueous solution of Cd and Ag salts resulted in formation of metal chalcogenide thin films.

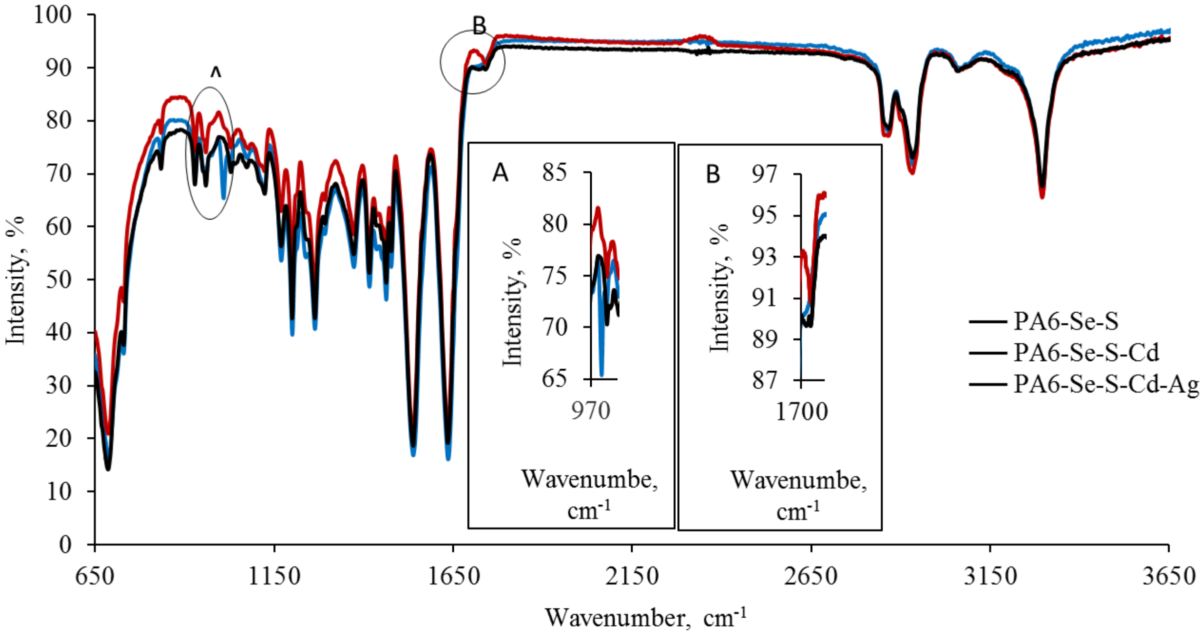

Fig. 1. FTIR spectra of PA-Se-S, PA-Se-S-Cd, and PA-Se-S-Cd-Ag composites

As seen from the data obtained (Fig.), N–H peak shifts towards lower wavenumbers at 3291 cm^{-1} than the one for non modified PA6. C–N peak shifts towards higher wavenumbers (1548 cm^{-1}). This suggests that chemical interaction between PA6 and $SeS_2O_6^{2-}$ ions takes place. This binding interaction is further substantiated by the appearance of three new peaks in the spectra. The deformation and valence vibrations of the S–O bond appear in 1250–500 cm^{-1} regions. The vibrations of ν(Se–S), δ(S–Se–S), $\gamma_r(SO_3)$ bonds are observed in 500–200 cm^{-1} region (not shown here). The lower frequency vibration peak at 688 cm^{-1} could be assigned to the symmetric deformation O−S−O vibrations, the bands in the interval of 790–1302 cm^{-1} correspond to the symmetric and asymmetric valence S−O vibrations in the terminal SO_3 groups of the selenotrithionate [3]. After exposure of the chalcogenized PA6 to the Cd salt solution, the peak at 1009 cm^{-1} has disappeared, instead a new peak at 1747 cm^{-1} has appeared. After exposure of the samples to Ag salt solution, this peak has shifted to 1736 cm^{-1}. The data prove the formation of metal chalcogenide thin films.

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MODIFICATION OF POLYAMIDE SURFACE WITH Cu_xS LAYERS

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Various polymers, modified by copper sulphides, represent a new class of materials – composites with novel properties. Copper sulphide is an interesting material for its metal–like electrical conductivity, chemical–sensing capability and ideal characteristics for solar energy absorption. Consequently, copper sulphides modified polymers are used: i) as the conductive substrates for deposition of metal and semiconductors; ii) as gas sensors functioning at temperatures tending to room temperature; iii) as polarizer of infrared radiation; and iv) as active absorbents of radio waves.

Electrically conductive Cu_xS layers can be prepared by the sorption-diffusion method, described earlier [1–3]. By this method, the surface of a polymer is initially treated by the solution containing sulfurization agent, and then by the aqueous solution of metal salt. Sodium polysulphides, polythionic acids and polythionates, thiourea, and sulphur in carbon disulphide solution have already been used for sulfurization of polymer foils by different methods. The sulfurization process using these agents is prolonged, many of them are quite harmful, and sometimes their preparation is complicated.

We have chosen polyamide as a cheap, chemically stable and flexible substrate. Polyamide (PA) as semi-hydrophilic polymer is capable to absorb ions or molecules of various electrolytes from aqueous and no aqueous solutions.

In this work we report the preparation of electrically conductive Cu_xS layers on polyamide by the sorption-diffusion method with the use of molten sulphur as the sulfurization agent.

The phase composition of the Cu_xS layers, their electrical conductance were studied by the methods of X–ray diffraction (XRD) and by the measurements of electrical sheet resistance.

XRD investigation showed Cu_2S [JCPDS 12-227] existence in layers on PA, and sheet resistance of formed layers was till 100 kΩ $/cm^{-1}$.

Cu_xS layers conductivity measurements were performed by Scanning electrochemical microscopy (SECM) feedback mode. SECM does not require connection of surfaces to potentiostat for conductivity measurements, therefore, it is simple way to investigate conductivity of surfaces.

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XRD STUDIES OF COPPER AND INDIUM SELENIDE LAYERS ON GLASS

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The main benefits of solar cells are that that they are sustainable, renewable, clean, completely noise free, scalable, minimal amount of maintenance is required and they produce no emissions. One the most prominent semiconductor for solar cell application $CuInSe_2$ exhibits great optical properties, like absorption coefficient ($>10^5$ cm^{-1}) [1], low direct band gap (1.04 eV) [1] and high thermal resilience [2]. Today, $CuInSe_2$ layers can reach 20.5% efficiency, while in solar cell 18.7% [3]. $CuInSe_2$ layers can be obtained using chemical or physical deposition. Chemical deposition offers low cost is easy to scale for large surface area coatings, but often requires annealing. Physical deposition, on the other hand, offers better quality layers, while often requiring high cost equipment, also it does not offer good scalability for large area coating and often requires annealing in toxic H_2Se atmosphere. $CuInSe_2$ layers were deposited using SILAR method and annealed in nitrogen atmosphere. Phasal composition and effect of annealing in inert atmosphere were studied in this work.

In this work Cu-In-Se thin films were deposited using three step successive ionic layer adsorption and reaction (SILAR). Firstly, glass substrate was cleaned ultrasonically, then, selenium layer was deposited from 0.2 M diselenotetrathionic ($H_2Se_2S_2O_6$) acid solution. Next, selenized samples were treated with 0.4 M copper(II/I) sulfate solution. In the third step, they were treated with 0.1 M indium chloride solution and finally annealed in nitrogen atmosphere at 100 °C.

After selenization, deposited film color was dark cherry red indicating formation of elemental selenium layer. After copper(II/I) salt solution treatment it became dark gray, which is indicative of copper selenide formation. Indium salt solution treatment and annealing did not affect film color. Samples were studied using X-ray diffraction analysis method. It shows multiple phases formed, including two phases of In_2Se_3, $Cu_{0.87}Se$ phase and $CuInSe_2$.

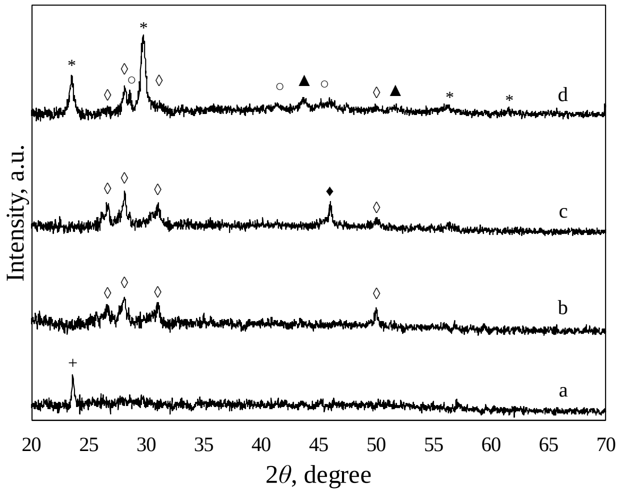

Fig. 1. XRD patterns of copper and indium selenide layers on the glass substrate obtained on different steps of their formation process: (a) the deposition layer of selenium; (b) the formation layer of copper selenide; (c) the formation layer of copper and indium selenide layers; (d) after annealing the formed layers. Peaks were identified and assigned as follows:(+) – Se (24-714) monoclinic selenium; (*) – Se (73-465) hexagonal selenium; (◊) – $Cu_{0.87}Se$ (83-1814) hexagonal klockmanite; (♦) – In_2Se_3 (20-492) cubic indium selenide; (○) – In_2Se_3 (17-356) indium selenide; (▲) – $CuInSe_2$ (23-207) cubic copper indium selenide.

The method of SILAR is simple and suitable for formation of multiphase Cu-In-Se thin film on glass substrate.

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SYNTHESIS OF BELITE CALCIUM SULFOALUMINATE CEMENT USING HARD COAL FLY ASH

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Ordinary Portland cement (OPC) is the most used construction material worldwide. Unfortunately, its manufacture produces a huge amount of CO_2 gas – around 5 % of all anthropogenic CO_2 emissions come from the production of clinker [1] which is one of the most energy-consuming processes – it consumes around 3 % of total world energy production [2]. One solution to solve these problems is alternative binder materials, one of which is belite calcium sulfoaluminate cement (BCSA cement) [3]. BCSA cement can be produced at lower burning temperatures and with less limestone content than OPC. It is mainly composed of the phases belite (40–50 wt.%) and ye'elimite (20–30 wt.%) and the paste is known for its high early strength [4].

In the present investigations, the raw meal for BCSA clinker consisted of 29 wt.% hard coal fly ash, 63 wt.% limestone and 8 wt.% anhydrite. The materials were homogenized for 5 h in a tumble mixer and ground in a disc mill for 1 min to a specific surface area of 566 m^2/kg. Afterwards, the raw meal was mixed with 6 wt.% distilled water and compressed (19.63 kN) into 50×50 mm cylinders which were dried (40 °C, 24 h) and then placed on a Mg-Spinel plate in a furnace and burned at 1225, 1250 or 1275 °C for 1, 3 or 6 hours at each temperature (heating rate – 10 °C/min). Afterwards the clinker cylinders were immediately removed from the furnace and broken to promote rapid cooling. After cooling to the room temperature, the cylinders were ground to a specific surface area of 420 m^2/kg. The sample compositions were analysed by quantitative XRD and their hydration processes by heat-flow calorimetry. In order to find the optimal addition of gypsum to the clinker, three different SO_3:ye'elimite molar ratios were chosen: 1, 1.5 and 2 (3.57, 6.64 and 9.52 wt.% of gypsum, respectively). The gypsum was mixed with the clinker for 5 h in a tumble mixer and calorimetric analysis performed.

After thermal treatment, all the samples contained the phases β-C_2S, α'_H-C_2S, ye'elimite, bredigite, periclase, quartz, aphthitalite, maghemite, gehlenite and calciolangbeinite. The content of the main phases β-C_2S and ye'elimite varied only slightly: β-C_2S – from 61.4 % (in the sample treated at 1225 °C for 1 h) to 66.3 % (1275 °C for 6 h), ye'elimite – from 21.6 % (1225 °C for 1 h) to 25.1 % (1275 °C for 6 h). A small quantity of another modification of dicalcium silicate α'_H-C_2S occurred in all samples (0.8 to 1.8 wt.%). Since the temperature and/or burning duration does not have a significant impact on phase content, samples burned at 1225, 1250 and 1275 °C for 1 h were chosen for calorimetric analysis. After 5 min, the maximum heat-flow (0.0269 mW/g) due to the first hydration reaction was reached for the sample burned at 1225 °C for 1 h. No further changes in heat-flow occurred after 35 min. However, the highest total heat release after 72 h (133.08 J/g) was achieved by the sample burned at 1275 °C for 1 h. This sample was chosen for investigating the effect -of SO_3 (gypsum) addition on the cement hydration. The highest total heat (133.55 J/g) was obtained with 6.64 wt.% (SO_3:ye'elimite molar ratio of 1.5) gypsum addition.

It is concluded that raw meal containing hard coal fly ash, limestone and anhydrite should be burned at 1275 °C for 1 h and the finely ground clinker mixed with gypsum at a SO_3:ye'elimite molar ratio of 1.5 to produce the most reactive BCSA cement.

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COATING OF FERTILIZER STICKS

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Many traditional mineral fertilizers, especially the ones containing nitrogen, are well soluble in water so the plants can absorb nutrients in a short period of time. However, such fertilizers have some drawbacks: due to high solubility some nutrient losses may occur so plants would receive only 30–50 % of nutrient input [1]. In order to avoid these drawbacks and completely or partially reduce the losses in fertilizer industry, special fertilizers and their modifications are developed – slow-release/controlled-release fertilizers and fertilizers stabilized with nitrification and urease inhibitors [2–4]. According to statistics provided by International Fertilizer Organisation (IFA), the annual consumption of synthetic slow-release fertilizers (SRF) in the world comprises 562 000 tonnes, which represents about 0.15 % of the total world fertilizer consumption [3–5]. SRF is considerably more expensive than traditional fertilizers and this severely limits their usage. Intensive scientific research and development of slow-release fertilizers is conducted in the US, Germany, Japan and elsewhere [1, 3, 4] in order to reduce the cost of such fertilizers and expand their assortment.

The object of this study is experimental analysis of compound fertilizers produced by extrusion, and investigation of coating materials influence on their reduced solubility. The possibility of production of compacted and coated complex fertilizers with reduced nutrient solubility was analyzed and their characteristics were investigated to expand the assortment of special fertilizers.

Coating films for slow release fertilizers of various composition were prepared and optimal ratios of raw materials were determined as well as conditions of their preparation. Chemical and instrumental analysis was used to evaluate raw materials and finished products.

Extruded fertilizer sticks were prepared and their properties were assessed: pH, moisture content. The results suggest that the moisture content of the product does not depend on the initial moisture content of raw materials, and pH of all samples appeared to be neutral.

Water sorption studies at different relative humidity (90 and 66 %) were carried out. Raw materials with higher moisture content resulted in forming of the lowest moisture absorbing fertilizer. They have longer drying time, but the mass is more plastic and fertilizer stick comes out better compressed. Fertilizers produced from raw materials with the lowest moisture content had the highest sorption capacity for moisture. It was determined that sorbed moisture content depends on the sample compression.

Ammonium phosphate fertilizer sticks were prepared with different Kollotex starch coatings (5, 10 and 20 % of PVA was added during production). Coated sticks absorbs less moisture as compared to non-coated samples at 90 % relative humidity.

The influence of the coating on fertilizer sticks solubility was examined. It is noted that with the higher coat weight the nutrients (nitrogen, phosphorus) are released more slowly. Also at longer dwell time more nutrients is released.

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FORMATION OF INTERMEDIATE PHASES DURING 1.13 nm TOBERMORITE SYNTHESIS

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Tobermorite $Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$ and xonotlite $Ca_6Si_6O_{17}(OH)_2$ are rarely encountered in nature but often found in autoclaved concrete products [1]. New publications show possibilities to synthesize these calcium silicate hydrates from fly ash [2], diatomite [3] silica fume, quartz sand and other unconventional raw materials [4]. Unfortunately, the data about 1.13 nm tobermorite formations kinetic are often contradictory and not allow for precise determination of this compound synthesis conditions. Occurring chemical reaction mechanism and kinetic can be precisely set only using reagent grade raw materials.

The materials for initial mixtures were prepared as follows. $SiO_2 \cdot H_2O$ ("Reachim", Russia, a. g.) was milled in ball mill until $S_a = 1814\ m^2 \cdot kg^{-1}$; ignition losses – 18.32 %. CaO was prepared by heating $CaCO_3$ ("Reachim", Russia, a. g.) at 950 °C for 1 h and milled in ball mill until $S_a = 616\ m^2 \cdot kg^{-1}$; the amount of $CaO_{free} = 98$ %. Al_2O_3 was obtained by burning $Al(OH)_3$ ("Sigma – Aldrich", Germany, a. g.) at 475 °C for 5 h. Dry raw meals with molar ratios $C/(S+A) = 0.83$; $A/(S+A) = 0$ or 0.025 were mixed in a homogenizer Turbula Type T2F for 1 h at 49 rpm and poured with water to get suspension with $W/S = 10.0$. The hydrothermal synthesis was carried out at 180 and 200 °C for 2, 4, 8, 12, 24 and 72 h in unstirred suspension. The samples were analysed by XRD, DSC/TG and IR-spectroscopy.

The formation of crystalline 1.13 nm tobermorite at 180 °C in CaO mixture with amorphous SiO_2 goes very slowly. In the beginning of the synthesis (4–8 h), the compound α-C_2SH with a higher C/S is formed, due to the fact that the initial solution contains excess of CaO. When the synthesis is continued (24–72 h), the basicity of compounds to be formed reduces, C/S approaches the calculated composition ($C/S = 0.83$); therefore, 1.13 nm tobermorite starts to prevail in the products. Surprisingly, together with this compound after 24 h of synthesis exist and low base calcium silicate hydrate – z-phase, which transform to gyrolite after 72 h of curing. Elevating the temperature of the synthesis to 200 °C led to a significant acceleration of the hydrothermal reactions and 1.13 nm tobermorite together with z-phase start form after 8 h of isothermal curing. The last compound after 24 h finally transform to gyrolite, whose peaks intensity in XRD pattern significantly increased and after 72 h of synthesis. In the beginning of the synthesis formed α-C_2SH finally decomposed after 24 h of curing. It should be underlined that 1.13 nm tobermorite start to recrystallize to xonotlite by prolonging the synthesis to 24 h.

The obtained experimental data confirmed that Al_2O_3 additive accelerates the formation of 1.13 nm tobermorite: it is the main compound in 4–72 h synthesis products. α-C_2SH and z-phase do not form in this mixture. Negligible amounts of xonotlite and gyrolite forms only at the end of isothermal curing (after 72 h at 180 °C and after 24–72 h at 200 °C). The main peak of 1.13 nm tobermorite in XRD patterns coherently increases by prolonging the hydrothermal synthesis to 24 h and then due to recrystallization to other calcium silicate hydrates slightly decreases.

Hence, even in the reagent grade CaO–SiO_2–$n \cdot H_2O$ system is difficult to obtain pure 1.13 nm tobermorite – it coexist with other calcium silicate hydrates.

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CONVERSION BETWEEN KCl AND $NH_4H_2PO_4$ AND THEIR PRODUCTS

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In the context of the systematic growth of the worldwide population without the increase of the total area of arable land, the sufficient amount and quality of food products may only be ensured by employing all the available strategies contributing to the efficiency of agriculture [1]. In order to achieve the maximum potential of fertility of various crops, the fertilizers are used and well as their manufacturing technologies are being systematically improved, novel fertilizers are being devised, and new methods of obtaining fertilizers in more efficient ways are being sought after. The focus of scholarly research has been directed towards the use of renewable resources, i.e. various biomass in agriculture; however, biomass by itself fails to ensure full range of at the nutrients to the crops as specific elements which are vital to plants may be absent [2].

One of the ways of boosting the impact of fertilizers is the production of concentrated fertilizers, featuring the use of the cheapest available raw materials and the simplest method of manufacturing. A highly concentrated fertilizer is potassium phosphates (*potassium hydrogen phosphate* and *potassium dihydrogen phosphate*) which, unfortunately, is usually prohibitively expensive due to excessive manufacturing costs. As a result of high prices, the common use potassium dihydrogen phosphate is usually restricted to highly chlorine-sensitive plants, i.e. flowers and vegetables grown in greenhouses [3].

There is no data concerning the production of potassium dihydrogen phosphate from potassium chloride and ammonium dihydrogen phosphate via conversion.

Aim of the work is to determine the conditions of the aqueous solutions of potassium chloride and ammonium dihydrogen phosphate to optimize the yield of potassium dihydrogen phosphate via conversion.

The equilibrium of the solid-liquid phases in aqueous solutions of potassium chloride and ammonium dihydrogen phosphate was investigated. It has been established that the optimal conditions of obtaining potassium dihydrogen phosphate are as follows: the reaction temperature of 40–60 ^{0}C and the molar ratio of the source materials KCl : $NH_4H_2PO_4$ = 0.8:0.2.

It has been discovered that the optimal conditions to obtain crystal potassium dihydrogen phosphate obtained via conversion are drum granulator with the tilt angle of 5 ^{0}, the temperature in the range of 55–65 ^{0}C, the rotation speed of 27 rpm, 21% humidity and the cellulose content 5 %. The parameters of the obtained granulated product were as follows: chemical composition: 1.89 % nitrogen; 21.66 % (49.67 %) phosphorus (recalculated as P_2O_5); 32.27 % (41.28 %) potassium (recalculated as K_2O); 1.87 % chlorine. The yield of premium retail fraction (defined as 1–3.15 mm granule size) was 65 %; the solidity of the pellet: 8.73 N/gran.; the moisture of the pellet: 1.67 %; the bulk density of bulk-heaped pellets: 790 kg/m^3; pH of the 10 % solution: 3.9. The interaction of the liquid phase produced via conversion with carbamide and ammonium nitrate has been explored. Having performed agrochemical evaluation of a liquid potassium fertilizer featuring carbamide or ammonium nitrate, it has been discovered that the fertilizer sample featuring ammonium nitrate is more efficient. It increased the test plat dry weight by 68 %, the ash content by 62 % and the height of the plants by 43 %.

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SEM-EDS ANALYSIS OF MOLYBDENUM AND COPPER SULFIDES LAYERS ON GLASS

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In the recent years, there has been a great deal of interest in the study of metal dichalcogenides because of their possible applications in lubricants, in photoelectrochemical solar energy converters [1]. Transition metal dichalcogenides have unusual crystal structure and unique physical and chemical properties. Atomically thin structures of layered materials, such as transition metal dichalcogenides, are of great interest in condensed matter physics due to their remarkable electronic properties and applicability in nanoscale devises [2-5].

In this study molybdenum and copper sulfides layers were formed on glass slides of dimension 10 mm×10 mm. Slides were thoroughly cleaned with cleaning liquid soap and ultra-sonic cleaning was carried out by dipping the glass slide into acetone at 40 °C for 10 min, then rinsed with distilled water and dried. Sulfur layers on glass have been formed by the use of elemental sulfur powders mixed with acetone. Then the mixture was placed on glass and annealed at 160 °C for 10 min. For the formation of copper sulfide layers the sulfurized sample was treated with 0.4 M Cu(II/I) salt solution at 40 (samples No 2 and 3) or 60 °C (samples No 5 and 6) for 10 (samples No 2 and 5) or 20 (samples No 3 and 6) min. For the formation of molybdenum sulfide layers the sample was treated with Mo(IV) salt solution at 40 °C for 10 min. 0.05 M Mo(IV) salt solution was made from crystalline $(NH_4)_6Mo_7O_{24}\times4H_2O$ using a reducing agent–hydroxylamine hydrochloride [6].

Obtained sulfide layers composition and the surface morphology were investigated by SEM-EDS analysis. From scanning electron microscope analysis, it is found the surface appears to be comparatively granular with irregularly shaped grains. In the micrographs of samples obtained by the use of Cu(II/I) salt solution at lower (40 °C) temperature could be seen inhomogeneous surface with grains of different size and shape. When the temperature of Cu(II/I) salt solution is higher (60 °C) the obtained layer has more denser microstructure, but the surface is rough, having dimples and elevations. Grains are bigger and closer each other, not equally located on the surface. When the treatment in Cu(II/I) salt solution prolonged (20 min) the surface is more equal, looks like made from agglomerated sulfide particles.

Energy dispersive spectroscopy was used to determine the chemical composition of the obtained layers. EDS shows the presence of Mo, Cu, S and O peaks.

Table 1. Elemental composition of obtained layers

Sample No	S (at. %)	Cu (at. %)	Mo (at. %)	O (at. %)
2	42.6	14.8	11.5	31.1
3	27.4	35.9	13.9	23.1
5	19.1	38.5	11.9	30.5
6	20.4	38.3	12.4	28.9

The results indicate that layers are rich in copper (14.8–38.5 at.%). The lowest amount of copper was in the sample, which was 10 min treated with Cu(II/I) salt solution at 40 °C. The amount of molybdenum in all samples was similar.

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THE EFFECT OF LIMESTONE ON NEUTRALIZATION OF SEMI-HYDRATE PHOSPHOGYPSUM IMPURITIES

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Phosphorus fertilizer manufacturing generates a large amount of waste material - phosphogypsum. This by-product could be usable as gypsum binding materials. The chemical composition of semi-hydrate phosphogypsum indicated that it consists of relatively pure semi-hydrate calcium sulfate. Impurities are only 2.21 %. The water soluble phosphates ($P_2O_{5w.s.}$) is 0.35 %. The pH of this phosphogypsum is 4.3. The liquid phase of construction materials is usually neutral or alkaline, i.e. the pH value of gypsum binding material should be not less than 6–7. Thus, semi-hydrate phosphogypsum should be neutralized then gypsum binding materials are produced. The acid impurities could be washed out or combined to form insoluble or slightly soluble compounds [1-3]. The aim of the paper is to determine the properties of semi-hydrate phosphogypsum obtained from Kovdor apatite and establish the possibility to produce gypsum binding materials from this material, when acid impurities are neutralized using the calcium carbonate rock - limestone.

The formation mixture of semi-hydrate phosphogypsum and limestone was prepared in two ways: the first – mixing them dry (Table 1, lines 1-2) and the second – mixing them and using a ball mill (specific surface area 350 m^2/kg) (Table 1, lines 3-5).

Table 1. Physical-mechanical properties of semi-hydrate phosphogypsum

No	Limestone, %	pH	W/G	Setting time, min		Ignition loss, % Compressive strength, MPa		
				Initial	Final	2 hour	1 day	Dry samples
1	0	4.3	0.80	6	9	19.4 3.7	19.8 3.8	19.8 11.0
2	10	5.6	0.80	57	117	9.8 -	18.4 1.9	18.7 6.6
3	0	4.2	0.42	2	3	18.7 7.7	19.2 11.3	19.4 20.9
4	5	6.0	0.40	21	26	17.9 5.6	19.1 9.1	19.3 18.9
5	10	6.4	0.39	16	28	17.1 5.1	18.6 9.0	18.9 18.5

The results indicated that grinding semi-hydrate phosphogypsum with 5 % of limestone neutralizes semi-hydrate phosphogypsum. pH is 6.0. Increasing the amount of limestone till 10 % pH value hardly changes, pH is 6.4. The compressive strength of phosphogypsum plaster after 2 hours of hydration is 5.6 MPa and 5.1 MPa, respectively. The compressive strength of dry samples is 18.9 MPa and 18.5 MPa, respectively.

The best way is to neutralize semi-hydrate phosphogypsum by grinding it with 5 % of limestone.

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SYNTHESIS OF COBALT FERRITE NANOPARTICLES AND ITS APPLICATION AS ANTIBACTERIAL AGENT

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Superparamagnetic cobalt ferrite nanoparticles are attractive candidates for magnetic resonance imaging of the body, magnetic field-assisted drug delivery and magnetothermal therapy. Thus it is important to obtain monodispersed particles with good magnetic characteristics. The size and stabilization shell of nanoparticles have high impact on these parameters [1, 2].

Cobalt ferrite ($CoFe_2O_4$) nanoparticles size and shape mostly depend on the solvent used for synthesis, reaction temperature and time. The shape of nanoparticles could also be controlled by choosing different surfactants and their concentrations [3].

In this study $CoFe_2O_4$ nanoparticles were synthesized by thermal decomposition method in order to better control their size and shape. Syntheses were performed using benzyl ether as solvent, Co(II) acetylacetonate and Fe(III) acetylacetonate as components of the reaction solution. Trimethylamine-N-oxide was used as oxidator. Different additives, such as dodecylamine, oleylamine and oleic acid, were tested in order to obtain pure phase and monodisperse nanoparticles. Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and X-ray diffraction (XRD) were employed in this study.

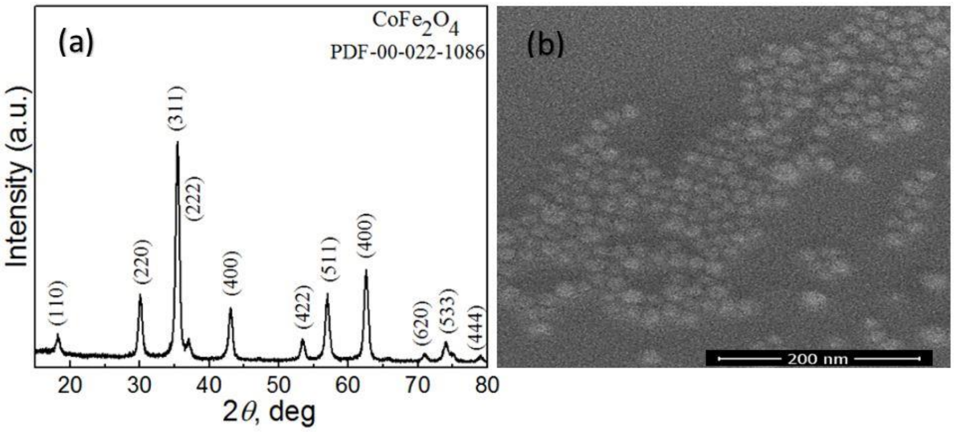

Fig. 1. XRD pattern (a) and TEM image (b) of cobalt ferrite nanoparticles synthesized by thermal decomposition method

It was determined that thermal decomposition method is good technique to obtain non-aggregated magnetic particles with low size distribution. It is possible to form 12,5 nm size in average cubic structure particles by adding oleic acid in synthesis solution (Fig. 1). Cobalt ferrite nanoparticles of 12,5 nm size in average and cubic shape could be synthesized after addition of oleic acid to synthesis solution.

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KINETICS OF CATALYTIC OXIDATION OF BENZENE, TOLUENE AND o-XYLENE ON THE SURFACE OF CuO-CeO$_2$/NaX CATALYST

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Benzene, toluene and xylenes (BTX) are very important petrochemical materials, which can cause negative effects on the environment if emitted. Because of their aromaticity related stability and low concentration in the gaseous emissions, heterogeneous catalytic oxidation by air oxygen is one of the best available and most widely studied decontamination techniques for benzene, toluene and xylene. CuO is one of the most active and least expensive components for oxidation of volatile organic compounds (VOCs); however, its activity is comparably lower in the oxidation technologies of BTX. Catalysts' performance might be improved with the addition of other strong oxidizing agents, for example ceria CeO$_2$, which can store larger amounts of highly mobile oxygen.

At low concentrations of contaminants, conventional heterogenic catalytic oxidation becomes too expensive and not sufficiently effective. Reaction rate of the catalytic oxidation might be increased by pre-adsorption of VOCs on the surface of the adsorbent-catalyst and subsequent catalytic oxidation to CO$_2$ and water vapor during thermal regeneration. In this study, kinetics of catalytic oxidation of toluene and o-xylene was investigated at different saturation of CuO-CeO$_2$/NaX adsorbent-catalyst and at constant flow of regenerative air (3000 cm^3/min). After pre-adsorption stage at 20 ºC when concentration of VOCs on the surface of catalyst reaches 2–10 mg/g, catalytic oxidation of adsorbates is initiated by increasing temperature up to 400 °C. Catalytic oxidation requires more energy as compared to desorption of adsorbates so in this case some of VOCs desorb unreacted until light-off temperature is reached. Average reaction rates were calculated as reacted (but not desorbed) amount of adsorbate in the course of oxidation time, which independently on the amount of VOC was 780 s for toluene and 840 s for o-xylene. As results of linear regression analysis show, the calculated slopes of obtained straight lines in the coordinates are close to unity and are equal to 0.996 for toluene and 0.987 for o-xylene. Slopes indicate that catalytic oxidation reactions are indeed first-order reactions which rates are directly proportional to the adsorbed amount of VOCs. It could also be assumed that reaction rate is independent on the amount of oxygen in the regenerative air since it is in a large excess. The calculated average reaction rate constants of toluene and o-xylene oxidation are also very similar – $1.243 \cdot 10^{-3}$ and $1.136 \cdot 10^{-3}$ s^{-1} respectively.

Adsorptive-catalytic decontamination of benzene appeared to be not effective enough since only 77.5 % conversion was achieved. In this case, it is recommended to employ conventional catalytic oxidation in which benzene-containing air passes through the pre-heated catalyst load. Kinetic parameters of benzene oxidation was determined at constant benzene concentration and different flow rates of contaminated air resulting in different contact times τ. Contact time represents the duration of interaction between reactant and catalyst and in this instance, it depends on porosity and volume of catalyst as well as benzene-containing air flow. Calculated values of contact time for benzene oxidation ranged from 0.293 to 0.732 seconds. After experimental runs achieved conversions of benzene α were inversely proportional to contact time and were used to calculate reaction rate constant assuming it is first-order reaction, which is independent on the oxygen in the air. As results show, rate constants of benzene oxidation reaction increases from 1.72 to 7.09 s^{-1} when temperature increases from 260 to 340 ºC. Applied Arrhenius equation yielded activation energy of benzene oxidation that appeared to be 49.3 kJ/mol and is reasonably comparable to the results obtained by other authors [1-3].

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STRUCTURE AND MORPHOLOGY OF Co-Mo-S FILMS ELECTRODEPOSITED ON FTO SUBSTRATE

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Nanostructured metal chalcogenides are regarded as the most prominent candidates for various energy-related applications, such as water electrolysis, supercapacitors and dye-sensitized solar cells (DSSC). Among others, cobalt-based chalcogenides and their composite materials were found to have a considerable potential to replace platinum (Pt) as the most effective but unacceptably costly HER electrocatalyst. Recently, cobalt sulfide (Co–S) was identified as a promising counter electrode material in DSSC and photocathode for photoelectrochemical water splitting. However, various promotional effects were studied in order to improve the stability and catalytic activity of Co–S electrodes. For this purpose, Co–S combination with molybdenum sulfide, known as more stable transition metal electrocatalyst, could lead to the desired electrocatalytic material with high activity and long-term stability [1–3].

The aim of this work was to prepare Co–Mo-S thin films on conductive glass substrates using electrochemical deposition technique and to study their structure, morphology and electrochemical behavior in aqueous solutions.

Potentiodynamic electrochemical deposition was employed to prepare cobalt–molybdenum-sulfur composite catalyst (denoted as Co-Mo–S) films on FTO glass substrate. In a typical deposition procedure, aqueous solutions of cobalt chloride, ammonium molybdate and thiourea were used as cobalt, molybdenum and sulfur precursors, respectively. The synthesis was performed by varying the number of cyclic voltammetry (CV) deposition sweep cycles, the potential range and the ratio of the precursors. 0.1 M potassium phosphate buffer solution (pH 7) was used as a supporting electrolyte for the electrochemical measurements. Structural and chemical characterization of the prepared films was carried out by means of scanning electron microscopy and energy dispersive spectroscopy, X-ray powder diffraction, X-ray photoelectron, Fourier transform infrared, Raman and UV-Vis diffuse reflectance spectroscopic techniques.

The experimental results revealed that the synthesis conditions and the heat-treatment of electrocatalysts significantly influence the structure and morphology of prepared films. Different types of deposition mechanisms were determined by varying the ratio of the precursors in deposition bath, conductivity and pH of the deposition solutions. The electrocatalytic performance of prepared Co-Mo–S films in hydrogen evolution reaction (HER) was evaluated in phosphate buffer solutions. The electrodeposition was proved to be versatile one-step synthesis method to prepare stable and catalytically active Co–Mo-S films.

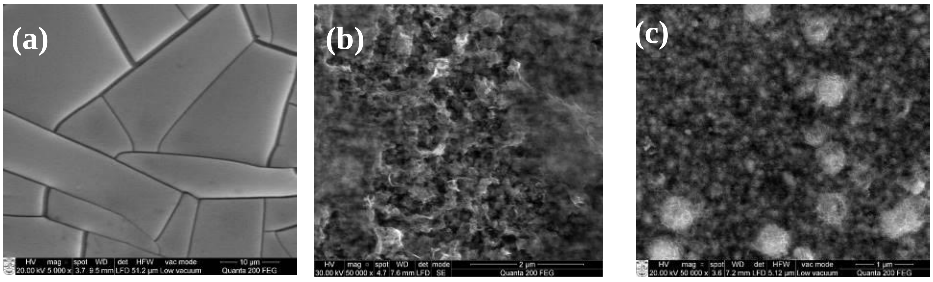

Fig. 1. SEM images of the films on FTO substrate prepared by varying Co:Mo ratio in the deposition bath: (a) 0:1, (b) 1:0, (c) 1:1

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AN ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY STUDY OF SnO_2/H_2SeO_3 SOLUTION INTERFACE

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In aqueous acidic solution, the reduction of Se(IV) has been proposed to follow different pathways depending on the conductivity of the SnO_2 electrode and the composition of the solution. So far, the majority of studies have been focused on the kinetics [1–2] and the nucleation mechanisms of the film growth [3]. A literature review reveals that authors very often neglect the change in energetic state of the semiconducting properties of the SnO_2 electrode during electrodeposition, even though that change could be very important and should be considered. The electronic properties of the semiconductor substrate (concentration of surface donors and band bending at different potentials) modify the kinetics and mechanism of the electrodeposition process. Thus, the space charge in the electrode must be taken into account.

In the present paper, electrochemical impedance spectroscopy experiments were performed to gain further insight into some of the electronic properties of the SnO_2 electrode in sodium citrate solution containing SeO_2.

Electrochemical impedance spectroscopy measurements were performed, employing a potentiostat/galvanostat model SP-150 (BioLogic Science Instruments SAS, France) interfaced with ECLab v10.39 software. The measurements were performed at the steady-state open-circuit potential E_{OCP} (to eliminate current related effects) in the frequency range 1×10^{-1} to 1×10^{5} Hz. The amplitude of voltage sinusoidal oscillations was set 0.01 V.

The Nyquist plots, shown in Fig. 1, were obtained and described based on equivalent electrical circuits models (Fig. 2) proposed to fully characterize these plots. The physical meaning of discrete elements is discussed.

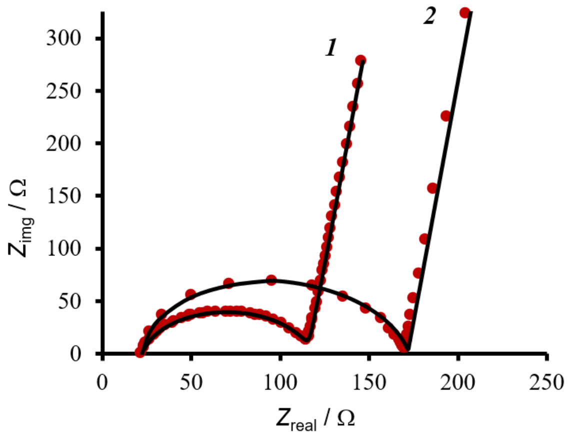

Fig. 1. The Nyquist plots obtained from the SnO_2 electrode in 0.2 M sodium citrate solution (1) and sodium citrate solution containing 1 mM SeO_2 (2) at E_{OCP}. *Dots* are experimental data; *the line* is the fit according to the equivalent circuit shown in Fig. 2

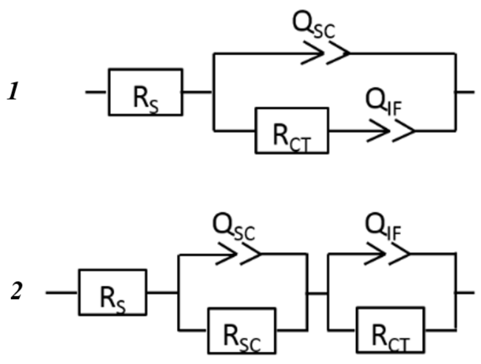

Fig. 2. Equivalent electrical circuit used to fit the electrochemical impedance spectroscopy data for SnO_2 electrode in 0.2 M sodium citrate solution (1) and sodium citrate solution containing 1 mM SeO_2 (2) at E_{OCP}

Also, Mott-Schottky analysis has been performed in order to evaluate semiconductor properties of the SnO_2 electrode in the absence and the presence of the SeO_2 in 0.2 M sodium citrate solution.

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A STUDY ON THE THERMAL STABILITY OF CALCIUM ALUMINIUM HYDRATE SYNTHESIZED UNDER HYDROTHERMAL CONDITIONS

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Geopolymers are defined as amorphous to semi-crystalline three dimensional aluminosilicate structures [1]. The hydrogrossular series [$Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$ ($0 \leq x \leq 3$)] can be located in the CaO–Al_2O_3–SiO_2–H_2O system and consists of a solid solution from grossular (x=0, $Ca_3Al_2Si_3O_{12}$) to katoite (x=3, $Ca_3Al_2(OH)_{12}$). This group of compounds have been synthesized by various preparative methods [2]. During hydrothermal synthesis the interaction between silica, alumina and calcium oxide/hydroxide results the formation of compounds such as calcium silicate hydrates (CSH), calcium aluminium hydrates (CAH) and calcium aluminium silicate hydrates (CASH). The formation of mentioned structures with certain structural and physical properties is mainly affected by the synthesis conditions (the properties of raw materials, the duration and temperature of synthesis, C/S ratio of primary mixtures and etc.) [3-4]. Li et al. [5] determined that the formation of $Ca_3Al_2(OH)_{12}$ phase during hydrothermal treatment favors, or accelerates the formation of mayenite phase at a rapid rate even at a low calcination temperature of above 400 °C.

For this reason, the aim of this work is to investigate the thermal stability of calcium aluminium hydrates synthesized under hydrothermal conditions.

Dry primary mixtures with $CaO/(SiO_2+Al_2O_3) = 0.55$ and $Al_2O_3/(SiO_2+Al_2O_3) = 0.1$ or 0.15 were mixed with water to reach the water/solid ratio of the suspension equal to 10.0. The hydrothermal synthesis has been carried out in unstirred suspensions under saturated steam pressure at 200 °C temperature for 4 hours. It was determined that after 4 h of hydrothermal synthesis, calcium aluminium hydrate was formed. On DSC curve the decomposition of CAH was observed in a 245-350 °C temperature range. The quantity of Al_2O_3 additive ($Al_2O_3/(SiO_2+Al_2O_3) = 0.1; 0.15$) in the primary mixtures affected the amount of formed CAH: the heat values of the CAH dehydration at ~300 °C temperature as well as the diffraction maximums were ~1.5 times.

In order to determine the obtained compounds and to investigate their thermal stability calcination was carried out at 350 °C. The results demonstrate that the crystal structure of CAH was already destroyed and fully recrystallized after 1 h of calcination at 350 °C temperature, because diffraction peaks characteristic to mayenite was observed in XRD patterns. The products of synthesis and calcination were characterized by XRD, STA and DSC analysis.

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THE ADSORBTION CAPACITY OF α-C_2SH FOR Cu^{2+}, Cr^{3+}, Co^{2+} IONS

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In the last few decades by seeking to resolve various environmental problems, adsorption has become a well-established technique to remove pollutants from wastewater. There are many types of inorganic, organic and synthetic adsorbents. The most important properties of an adsorbent are capacity, selectivity and and cation-exchange properties [1]. It is known that calcium silicate hydrates acts as adsorbent for the purification of water with heavy metals ions [2]. α-C_2SH ($2CaO{\cdot}SiO_2{\cdot}H_2O$) is one of members of the nesosilicates and is characterized by isolated tetrahedrons possess the lowest degree of polymerization. This dibasic calcium silicate hydrate does not exist in natural environment and forms during hydrothermal synthesis [3–4]. There are no literature data concerning α-C_2SH adsorption properties, for this reason the aim of this work was to determine synthetic α-C_2SH ion exchange capacities and selectivity sequences for Cu^{+2} , Co^{+2}, Cr^{+3} ions.

α-C_2SH was synthesized under hydrothermal conditions at 175 °C temperature, when the duration of isothermal curing was 24 hours and the molar ratio of primary mixture was $CaO/SiO_2=1.5$. Adsorption experiments were carried out at 25 °C temperature in the thermostatic absorber Grant SUB14 by stirring 5 g of synthetic α-C_2SH in 500 ml of $Co(NO_3)_2{\cdot}6H_2O$, or $Cr(NO_3)_3{\cdot}9H_2O$ or $Cu(NO_3)_2{\cdot}3H_2O$ solutions containing 1 and 10g of Co^{2+},Cr^{3+}, Cu^{2+}/dm^3 for 0.5 – 30 min. The concentrations of heavy metal ions were determined using a Perkin-Elmer Analyst 4000 spectrometer.

The obtained results showed that penetration of heavy metals ions into structure of α-C_2SH depends on the the chemical nature of adsorbate. It was determined that, at the beginning of the process (30 s), when the initial concentration of Me^{x+} was equal to 100 mg/dm^3 liquid medium, 90.01 % of Co^{2+} (90.01 mg Co^{2+}/g), 86.14 % of Cr^{3+} (86.14 mg Cr^{3+}/g) and only 72.91 % of Cu^{2+} (72.91 mg Cu^{2+}/g) ions were intercalated into the structure of α-C_2SH. It was examined that after 3 min for Cr^{3+}, 15 min for Co^{2+} and 30 min for Cu^{2+}, the equilibrium (100 mg Me^{x+}/dm^3) is attained and the removal of mentioned ions is complete. It should be noted that in higher concentration solution (10 mg Me^{x+}/dm^3) adsorption reaction proceeded differ, due to α-C_2SH stability. The selectivity sequence of studied metal ions by α-C_2SH can be written as follows: $Cr^{3+} > Co^{2+} > Cu^{2+}$. Synthesis and adsorption products were characterized by XRD, XRF and STA.

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THE ROLE OF IMPURITIES OF UNREFINED SILICA GEL IN HYDROTHERMAL CHS SYNTHESIS

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The manufacturing process of aluminum fluoride AlF_3 yields a lot of fluorine-rich silica gel waste [1, 2]. As the pollution limits usage of the waste in a great way, the silica is usually stored in landfills. While being dumped, fluoride is openly exposed to the environment: it can evaporate or leak with rain causing groundwater contamination [3]. One of the ways to reduce the amount of the silica waste is to use it as source of silicon in hydrothermal calcium silicate hydrates (CSH) synthesis [4]. The main goal of this work was to investigate the sequence of compounds formation in CaO-silica gel waste-H_2O mixture under hydrothermal synthesis condition.

In this work silica gel waste was used (JSC Lifosa (Kėdainiai, Lithuania)). The instrumental and chemical analysis of silica gel waste showed that, it consists of 85.0 % silicon dioxide, 8.8 % fluoride and 5.4 % aluminum ions. X-ray diffraction analysis data showed that the main compound containing fluoride ions in silica gel waste is $AlF_3 \cdot 3\ H_2O$. Furthermore, the silicon dioxide is amorphous because a broad peak in the angle of diffraction that varied from 18 to 26° was observed.

The hydrothermal synthesis of calcium silicate hydrates has been carried out in unstirred suspensions in autoclave under the saturated steam pressure at 200 °C, when the duration of synthesis were 4, 16, 24 and 72 h and the molar ratio of primary mixture was $CaO/SiO_2 = 1 : 1$.

It was determined that, in CaO-silica gel waste-H_2O mixture after 4 h of isothermal treatment, dibasic calcium fluoride silicate hydrate – cuspidine $Ca_4(Si_2O_7)(F,OH)_2$, katoite $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$ $(1.5 < x < 3.0)$ and 1.13 nm tobermorite $Ca_5Si_6O_{16}(OH)_2 \cdot 4\ H_2O$ were formed. Further, by prolonging the duration of the hydrothermal synthesis to 16 and 24 h, the quantity of 1.13 nm tobermorite increased. It should be noted, that after 72 hours of hydrothermal synthesis together with mentioned compounds, the traces of kilchoanite $Ca_6(SiO_4)(Si_3O_{10})$ was observed. Additionally, the chemical analysis data of liquid medium showed that all fluoride ions were not released to the liquid medium after the hydrothermal synthesis.

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SYNTHESIS AND X-RAY DIFFRACTION ANALYSIS OF CALCIUM AND STRONTIUM DOPED LANTHANUM MOLYBDATE

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For the past 10 years, lanthanum molybdate with crystal structure $La_2Mo_2O_9$ has attracted close attention because of their physical and chemical properties such as ionic conductivity and phase transition. Moreover, this LAMOX family group showed unique electrochemical properties as a solid electrolyte solution. These properties make it a viable material for technological applications in solid oxide fuel cells (SOFCs) as oxide-ion electrolyte in the intermediate temperature range (600-800 °C). Lanthanum molybdate can exist in two crystalline forms. Monoclinic α phase ($P2_1$) exists at room temperature. Phase transition to cubic β phase ($P2_13$) occur at 580 °C [1]. The high-temperature β phase was reported to exhibit ionic conductivity of about 0.06 S/cm at 800°C [2]. To stabilize lanthanum molybdate β phase in low temperatures, K^+, Sr^2+, Ba^{2+}, Bi^{3+}, V^{5+}, S^{6+}, Cr^{6+}, W^{6+} and other ions can be used to suppress the phase transition to the α phase [3].

Substitution of La^{3+} for lower valence cations could stabilize the structure of β phase and increase oxygen-vacancy concentration. Moreover, it is known that transport properties strongly depend on the preparation method of polycrystalline powders. Negative effect of these properties can be caused by porosity, impurities and low connectivity between the grains [4, 5]. The variation of the lattice parameter with x content strongly depends on the synthesis method. Using solid-state method, solubility limit is $x = 0.08$, wet chemical procedure – $x = 0.04$, but using co-precipitation synthesis solubility limit was increased to $x = 0.1$ and no secondary phase was detected [4].

In this paper, we report on the aqueous sol-gel synthesis method used for the preparation of the La-Ca-Mo-O and La-Sr-Mo-O nitrate-tartrate gel precursors with the initial composition for $La_{2-x}M_xMo_2O_{9-\delta}$ (M=Ca, Sr; x=0.001, 0.01, 0.05, 0.1, 0.2) ceramics, which were additionally annealed at 1000°C temperature. For crystal structure determination X-ray diffraction analysis was performed.

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THE KINETIC PARAMETERS OF SIMULTANEOUS ADSORPTION OF HYDROTALCITE FOR Co^{2+}, Cu^{2+} AND Cr^{3+} IONS

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Adsorption kinetic models are the most often used to analyze the kinetics of the adsorption process [1]. These models not only allows estimation of adsorption rate but also provides insights into rate expression characteristic of possible reaction mechanism. It was pointed out that pseudo-second-order adsorption model was based on the assumption that the rate-controlling step of chemisorption involved valence forces through sharing or exchange of electrons between adsorbent and adsorbate, was able to better describe the adsorption kinetic [2–3]. For this reason, the aim of this work was to determine the kinetic parameters of simultaneous adsorption of hydrotalcite for Co^{2+}, Cu^{2+} and Cr^{3+} ions at different temperature.

Simultaneous adsorption experiments were carried out in the thermostatic adsorber Grant SUB14 by stirring 1 g of synthetic hydrotalcite (Mg/Al = 2, 3h, 200 °C) in 100 ml of heavy metals ions aqueous solution containing 0.75 g/dm^3 of Me (where Me is Co^{2+}, Cu^{2+}, Cr^{3+} ions, respectively). Duration of adsorption at 25, 35 and 45 °C temperature was 0.5, 1, 3, 5, 10, 15 and 30 min. Two kinetic models, the pseudo-first order [4] and the pseudo-second order [5], have been used to analyze the rate constant of simultaneous adsorption.

It was determined that the pseudo-first order equation did not fit well for description mechanism of heavy metal ions simultaneous adsorption because the values of correlation coefficient (R_2) are low (R_2 = 0.61 – 0.91) as well as the calculated $q_{e(cal)}$ values disagreed with the experimental $q_{e(exp)}$ values (Table 1). It was observed that the experimental data are in well agreement with the pseudo-second order model. It should be noted that the largest rate constant (k_2) is typical for chrome ions ($k_2 = 0.33$ $g·min^{-1}·mg^{-1}$) at 25 °C temperature, while the minimum k_2 value – for cobalt ions ($k_2 = 0.02$ $g·min^{-1}·mg^{-1}$) at 35 °C temperature. It was found that the rate constants of Cr^{3+} ions was depended on the temperature: k_2 were decreased (k_2 = 0.33 – 0.05) when the temperature of adsorption increased from 25 to 45 °C. Also, an agreement between $q_{e(exp)}$ experimental and $q_{e(cal)}$ calculated values of the pseudo second order model was observed (Table 1).

Table 1. Kinetic parameters obtained using pseudo-first order and pseudo-second order models

Metal ions	Adsorption temperature, °C	Experimental q_e, mg g^{-1}	Pseudo-first order			Pseudo-second order		
			R^2	$q_{e(cal.)}$, mg g^{-1}	k_1, min^{-1}	R^2	$q_{e(cal.)}$, mg g^{-1}	k_2, g min^{-1} mg^1
Cu^{2+}	25	19.48	0.83	7.68	0.24	0.99	19.72	0.16
	35	17.96	0.91	11.68	0.25	0.99	18.86	0.05
	45	14.63	0.73	5.11	0.17	0.99	14.29	0.24
Co^{2+}	25	12.16	0.91	9.55	0.15	0.99	12.22	0.04
	35	16.98	0.81	8.83	0.34	0.98	16.27	0.02
	45	12.69	0.69	6.10	0.10	0.99	11.29	0.19
Cr^{3+}	25	24.36	0.73	21.35	0.12	0.99	21.48	0.33
	35	21.42	0.91	11.56	0.29	0.99	22.37	0.06
	45	18.54	0.90	12.26	0.19	0.99	18.69	0.05

R^2: correlation coefficient; $q_{e(exp)}$: the equilibrium adsorption capacity, $mg·g^{-1}$, calculated from experimental data; $q_{e(cal)}$: the equilibrium adsorption capacity, $mg·g^{-1}$, calculated from equations of kinetic models, k_1: the rate constant of pseudo-first order model, min^{-1}, k_2: the rate constant of pseudo-second order model, g min^{-1} mg^1

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SYNTHESIS AND CHARACTERIZATION OF Tb^{3+}, Eu^{3+} AND Tb^{3+}/Eu^{3+} METAL-ORGANIC FRAMEWORKS WITH BTC LINKERS

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In this study, terbium Tb^{3+}, europium Eu^{3+} and mixed metal Tb^{3+}/Eu^{3+} metal-organic frameworks (MOFs) based on 1,3,5-benzenetricarboxylate (BTC) were synthesized by solvothermal method [1]. The powders insoluble in aqueous media [2] and polar solvents [2, 3] were obtained.

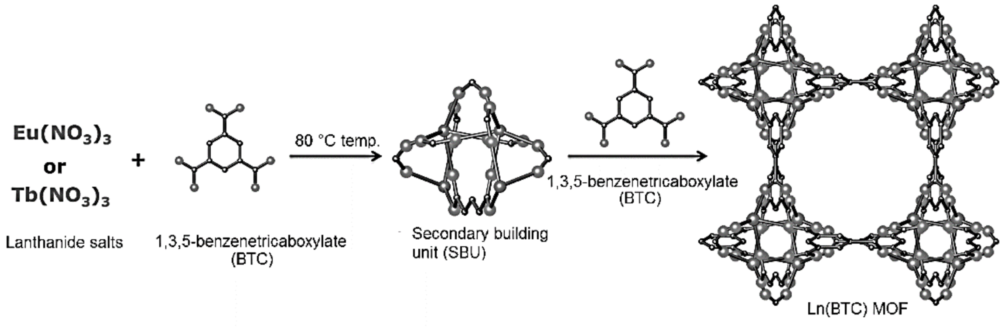

Fig. 1. Synthesis scheme of Ln (BTC) MOFs

The phase and chemical composition, microstructure and properties of Tb^{3+}, Eu^{3+} and Tb^{3+}/Eu^{3+} MOFs were evaluated and discussed. The synthesized terbium and europium metal-organic frameworks were characterized by thermal (TG/DSC) analysis, X-ray diffraction (XRD) analysis, infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and fluorescence spectroscopy (FLS).

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INVESTIGATION OF RANKINITE ACTIVATION AND HARDENING IN CO_2 ATMOSPHERE

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Rankinite ($3CaO{\cdot}2SiO_2$ or C_3S_2) is a low-lime cementitious material, therefore, amount of limestone required to synthesize this calcium silicate is lower than that of OPC and hence contribute to the reduction of CO_2 emission from the calcination process involved in cement production [1]. Moreover, due to low synthesis temperature, the energy consumption during manufacturing of this material is lower as well. However, unlike conventional hydraulic calcium silicates, C_3S_2 is a non-hydraulic material and one of the ways to activate it is curing in the CO_2 atmosphere [2]. In this work, C_3S_2 carbonation process was investigated, considering pressure, exposure time, temperature and moisture content.

The following materials were used: C_3S_2, synthesized by exposing pellets made of stoichiometric mixture of opoka and lime (C/S = 1.5) to 1250 °C for 45 min; Portland cement CEM I 32.5 R; CEN standard sand EN-196-1. Samples were prepared by mixing C_3S_2 or OPC with sand (15:85 wt%) and adding distilled water (w/c = 0.35) and pressed in hydraulic press (pressure – 20 MPa, speed – 2 MPa/s, exposure at maximum pressure – 10 s) to form 50×50±0.1 mm cylinders; 205±0.01 g of mixture was used to make one sample. Samples were treated in a reactor using gaseous CO_2 (5 and 50 bar at 20 and 50 °C) and super critical CO_2 (SCC) (150 bar at 50 °C; pressure increased by 2.5 bar/min) for 4 and 24 h. After carbonation, the mechanical properties of the samples were determined. Dried samples were analysed by XRD using Rietveld refinement, thermal analysis, and mercury intrusion porosimetry.

It was determined that with increasing CO_2 pressure, exposure time and/or temperature the carbonation process is intensified, both C_3S_2 and OPC sample compressive strength is highly increased (Fig. 1, a). Thought it can be concluded that sample carbonation at low pressure or exposure time, e.g. 5 bar and 4 h, is not sufficient, since according to the obtained results both C_3S_2 and OPC samples were not fully carbonated. Carbonating samples at SCC conditions (150 bar, 4 h) led to full carbonation and the highest strength. Compressive strength is directly dependant on sample porosity (Fig. 1, b), which is reduced by formation and precipitation of $CaCO_3$ in the pores. Since C_3S_2 samples were almost equally reactive to carbonation and showed similar or even greater results than Portland cement, therefore carbonation reaction using compressed CO_2 could be used for the production of a broad range low lime based materials. The importance of moisture should also be emphasized – water is necessary to promote the reaction with CO_2, however too much water limits the reaction due to blockage of the pores in the solid material [3].

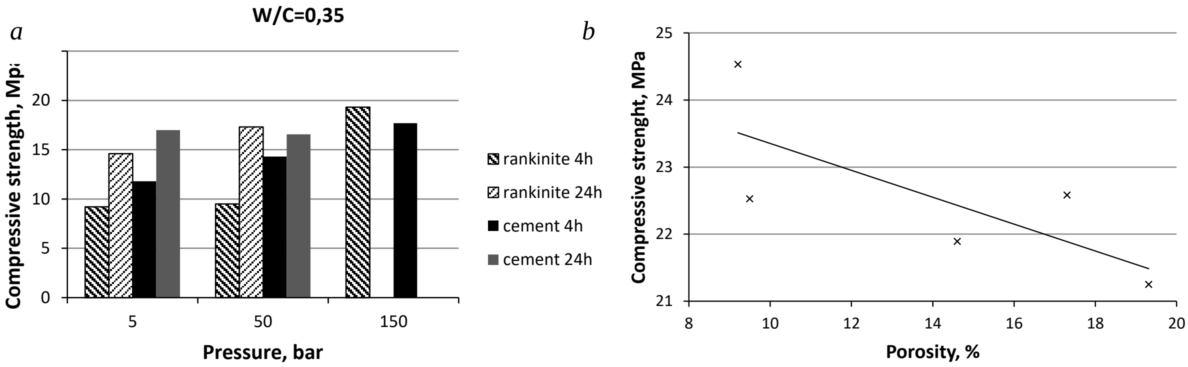

Fig. 1 Compressive strength of C_3S_2 and OPC samples carbonated at different pressure and duration conditions (a) and C_3S_2 sample strength dependence on porosity (b)

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THERMAL DECOMPOSITION OF HYDRAZINE URANYL FLUORIDE PREPARED BY STRIPPING

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The previous study showed that the use of a hydrofluoric acid solution with the addition of hydrazine hydrate for stripping from loaded organic phases (tri-*n*-butyl phosphate) results in the precipitation of uranium in the form of a hydrazine uranyl fluoride complex – $UO_2F_2N_2H_42HF{\cdot}1.25H_2O$ [1]. It is known that thermal destruction of hydrazine uranyl fluoride complex in a vacuum leads to the formation of UF_4 [2]. The number of uranium processing operations could be significantly reduced by obtaining uranium tetrafluoride directly after the stripping stage. Therefore, the thermal decomposition of hydrazine uranyl fluoride complex obtained by stripping was investigated.

The thermal decomposition procedures were performed in a pipe furnace at a temperature of 100–600 °C in vacuum and in a hydrogen stream. All uranium compounds were analyzed using various physicochemical methods.

According to the study, the uranium tetrafluoride with a low content of UO_2 (< 4 %) could be prepared by calcination of hydrazine uranyl fluoride complex at a temperature of 450–500 °C in a hydrogen stream. Calcination time is not more than 3 hours. The thermal decomposition of hydrazine uranyl fluoride complex involves several steps. Uranium fluoride oxide and uranium dioxide are intermediate products of this process. Uranium tetrafluoride is formed at a temperature above 400 °C. The overall reaction is written as:

$$UO_2F_2N_2H_42HF{\cdot}1.25H_2O \rightarrow UF_4 + H_2 + N_2 + 3.25\ H_2O \qquad (1)$$

The results indicate that degree of uranium reduction increases and nitrogen content in the final product decreases as the temperature and process time increases. But in this case, the uranium tetrafluoride decomposition by water vapor increases:

$$UF_4 + 2\ H_2O \rightarrow UO_2 + 4\ HF \qquad (2)$$

The final product of calcination at a temperature of 450–500 °C in a vacuum is a mixture of UF_4 and UO_2, at 55–60 % and 40–45 %, respectively. The reaction (2) results in a high uranium dioxide content in the product. Forced gas flow during calcination in vacuum is absent. Therefore, the efficiency of the uranium tetrafluoride formation is limited by the diffusion rate of water vapor in the furnace. The diffusion rate of water vapor is increased due to the continuous hydrogen flow in the furnace, and pyrohydrolysis of UF_4 is suppressed.

According to the results of the analyses, the uranium tetrafluoride prepared by calcination of hydrazine uranyl fluoride complex at a temperature above 450 °C in a hydrogen stream meets the requirements imposed on UF_4 at conversion plants.

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KINETIC MODELING OF Tl (I) SORPTION ON SELENIZED PA 6

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TlX and $TlMX_2$ (M = Ga, In; X = Se, S, Te) binary and ternary chalcogenides were shown to be prospective for applications in laser technique and in non-linear optics, in electro-luminescence and switching devices, as modulators and frequency converters in infra-red and visible regions, as strain (gage) sensors, etc. [1]

In this work, using two stages sorption-diffusion method, thallium selenide Tl_xSe_y layers were formed on semi hydrophilic polyamide PA 6 surface (70 μm and 500 μm thickness). In the first stage, PA 6 samples were selenized for 90 min in 0.05 mol·dm^{-3} $K_2SeS_2O_6$ at pH 2.15, adjusted using 0.1 mol·dm^{-3} HCl at 60 °C. In the second stage, selenized samples were treated in 0.1 mol·dm^{-3} thallium sulfate salt bath at pH 11.5 and 60 °C. Deposited thallium concentration in the layers of thallium selenide on PA 6 surface was studied depending on process duration (1–75 min) using atomic adsorption spectroscopy.

Several mathematical models can be used to describe experimental data of adsorption kinetic. In order to quantify the extent of uptake in adsorption kinetics six simple adsorption reaction and adsorption diffusion models were tested: Lagergren's pseudo first-order rate equation [1], Ho's pseudo second-order rate equation [3], the simple Elovich's equation [4], Boyd‘s film diffusion mass transfer rate equation [5], Weber-Morris [6] and Dumwald-Wagner [7] intraparticle diffusion models. This work aims to find the models that can describe with precision the experimental results, specify the parameters that can be determined and determine the theoretical adsorption equations. Physicochemical parameters that provide information about adsorption process mechanics, rate and adsorbent's surface properties were calculated. The experimental values of adsorption capacity are initially treated with the linearized equations in order to determine the models parameters and the kinetic equations are reconstituted using the determined values if correlation coefficient $r^2 > 0.95$. Linear correlation coefficients (r^2) showed the fit between experimental data and linearized forms of kinetic equations. The average percentage errors (APE) indicated the fit between the experimental and predicted values of adsorption capacity used for plotting kinetic curves [8].

The Weber-Morris kinetic model and Elovich‘s equation have been applied to describe the feasibility of Tl(I) sorption onto PA 6 which fitted best the experimental results and indicated minimal average percentage errors. The maximum adsorption capacity increased as the duration of process increases and reached 1,305 μmol·cm^{-2} for 70 μm and 1,541 μmol·cm^{-2} for 500 μm PA 6, respectively. The molar ratio of Tl/Se after 75 min of treatment in thallium sulfate bath is 1.243 for 70 μm PA 6 and, respectively, 1.253 for 500 μm PA 6. The adsorption rate constants, the initial adsorption rate, liquid film diffusion constant and intraparticle diffusion rate constant were found to be higher in the case of 70 μm PA 6.

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THE ELECTRODEPOSITION OF Pb AND PbO_2 ON GRAPHITE FELT

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In this study we investigated the possibility to replace heavy lead grids which constitute about 40 % of the total weight of the electrodes in lead-acid batteries [1] with a much lighter material – graphite felt (GF). This material has large a surface area ($0.8–2.8 \cdot 10^6$ $m^2 \cdot m^{-3}$), low specific electrical resistance (in different directions, from $2.4 \cdot 10^{-1}$ to $2.7 \cdot 10^{-3}$ $\Omega \cdot m$) and high tensile strength (2.21–3.58 GPa) [2].

Two GF electrodes simultaneously were electrochemically modified in a potentiostatic mode with Pb and PbO_2 – the electrochemically active materials for a lead-acid battery. The electrodeposition was carried out at room temperature (20 ± 1 °C) in a stirred aqueous solution which contains 0.5 M $Pb(NO_3)_2$ and 0.1 M HNO_3. DC voltage between GF cathode and anode was maintained at 2.5 V. Duration of electrodeposition for each side of both GF electrodes was 45 minutes.

The structure and morphology of deposits on the filaments of both modified GF electrodes were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. It was determined that on the filaments of positively polarized GF electrode (anode) the mixture of α and β-PbO_2 phases was deposited (Fig. 1.). Meanwhile, metallic lead, partially oxidized to α and β-PbO, were identified on the filaments of negatively polarized GF electrode (cathode) (Fig. 2.). SEM images show that PbO_2 was deposited in almost uniform layer (Fig. 3. A), while Pb formed big clumps and dendrites on the surface of GF filaments (Fig. 3. B).

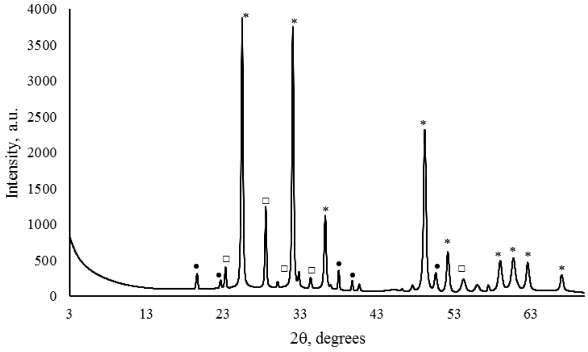

Fig. 1. XRD pattern of positively polarized GF. Where: ∗ – β-PbO_2, □ – α- PbO_2, • – $Pb(NO_3)_2$

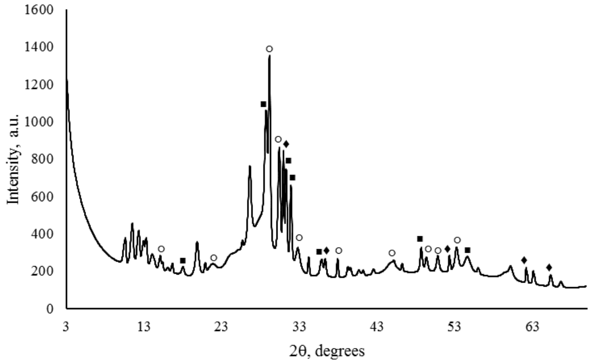

Fig. 2. XRD pattern of negatively polarized GF. Where: ♦ – Pb, ○ – β-PbO, ■ – α-PbO

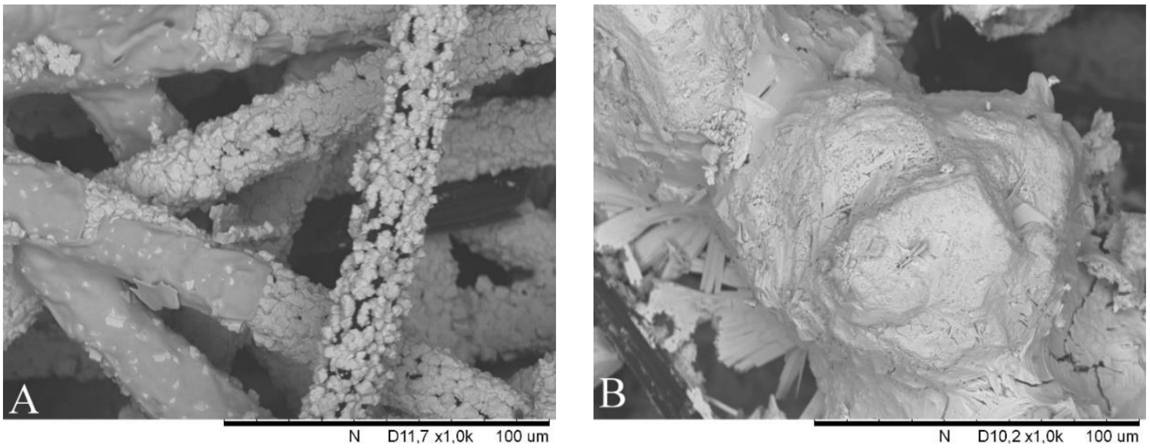

Fig. 3. SEM images of GF filaments coated with PbO_2 (A) and Pb (B)

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Cr^{3+} AND Tb^{3+} CO-DOPED YAG: PROMISING PHOSPHORS FOR SOLID-STATE LIGHTENING

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Luminescent materials, also known as phosphors, are widely used today. Major application are used in optical technologies, emissive displays, fiber-optic telecommunication system, lasers and so on and so forth. In last two decades a lot of phosphors were invented. Inorganic phosphors are composed of an inert host lattice and optically excited activator, for example 3d or/and 4f electron metal, such as Ce^{3+}, Cr^{3+}, Eu^{3+}, Tb^{3+}[1-3].

For a successful growth of plant need to satisfy photo-physiological processes, which require light in far-red (700–760nm), red (620–680nm), and blue (400–500nm) spectral ranges [4]. It is well known that yttrium aluminum garnet (YAG) doped Cr^{3+} possess a broad absorption peak around 450 nm and 650nm. These peaks corresponds to $^4A_2 \rightarrow {}^4T_1$ and $^4A_2 \rightarrow {}^4T_2$ transitions, respectively. Emission originates in far-red spectral region with $^2E \rightarrow {}^4A_2$ transition at around 610–800 nm [5]. It is noticed that co-doping YAG : Cr^{3+} with Tb^{3+} ions occurs energy transfer from Tb^{3+} to Cr^{3+} ions. In garnets Tb^{3+} $[Xe]4f^8 \rightarrow [Xe]4f^75d^1$ low and high spin transitions is observed at around 250 nm and 320 nm, respectively. Emission originates in red (610–635 nm ($^5D_4 \rightarrow {}^7F_3$)), orange (580–610 nm ($^5D_4 \rightarrow {}^7F_4$)), green (535–565 nm ($^5D_4 \rightarrow {}^7F_5$)) and blue (480–510 nm ($^5D_4 \rightarrow {}^7F_6$)) spectral regions [2, 5-9].

The quantum efficiency of YAG depends on the purity of its composition. Before getting single phase garnet there is two intermediate phases: yttrium aluminum monoclinic (YAM) and yttrium aluminum perovskite (YAP). If any of these phases coexists, the quantum efficiency decreases [10]. Single phase formation is finished at ~870 ºC [11], but samples were prepared at 1500 ºC to avoid crystal lattice defects.

Doped and co-doped YAG was made in sol-gel route. Quantum efficiency were measured in all samples. There were compared YAG : Tb^{3+} and YAG : Cr^{3+}, Tb^{3+} series of samples, and noticed that co-doping with Cr^{3+} ions improves quantum efficiency.

The energy transfer $Tb^{3+} \rightarrow Cr^{3+}$ in garnets was first mentioned in our work group paper [11, 12]. The aim of this study is to continue the started investigation in more detailed way. The synthesis were made by sol-gel route, which is advantageous and useful to get single phase garnets [13].

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A NOVEL APPROACH FOR THE SYNTHESIS OF LAYERED DOUBLE HYDROXIDES $Mg_3/Al_{1-X}Eu_X$

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Layered double hydroxides (LDHs) are compounds composed of positively charged brucite-like layers with an interlayer gallery containing charge compensating anions and water molecules. The metal cations occupy the centres of shared octahedral whose vertices contain hydroxide ions that connect to form infinite two-dimensional sheets [1–4]. With this structure the most know mineral is hydrotalcite, $[Mg_{0.75}Al_{0.25}(OH)_2]\ (CO_3)_{0.125}\cdot 0.5H_2O$. LDHs have unique intrinsic advantages: their layer sizes are highly tunable; their constituents can be conveniently controlled and varied. LDHs, unlike common clay minerals such as montmorillonite, cannot swell automatically in water, and their delamination is much more difficult due to their high surface charge density as well as the strong attractions between adjacent nanosheets [5].

Recently, considerable attention has been focused on incorporating rare earth ions into LDHs hosts to develop new functional materials, which resemble designed optical properties [6]. Lanthanide-doped luminescent materials have drawn increasing attention as potential phosphor materials for use in optical devices [7]. Europium compounds are the most widely used due to their visible luminescence [8].

Sol-gel synthesis route for mixed metal oxides and related compounds have some benefits over other methods such as simplicity, synthesis at low temperatures, effectiveness, suitability for different systems and cost efficiency [9–12]. In this study the lanthanide-doped LDHs were synthesized by novel sol-gel synthesis processing. In the LDHs $Mg_3/Al_{1-x}Eu_x$ system, the Eu^{3+} concentration in the crystal lattice was changed from 0.05 to 10 mol%. The samples were characterized by X-ray diffraction (XRD) analysis, Fourier Transform Infrared spectroscopy (FT-IR), thermogravimetric (TG) analysis, fluorescence spectroscopy (FLS) and scanning electron microscopy (SEM). The results revealed that europium enters into a hydrotalcite structure containing Mg^{2+} and Al^{3+} cations in the brucite-like layers and carbonate in the interlayer. This feature makes it possible to combine the optical properties of molecular compounds with the chemical stability of a solid matrix.

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THE INFLUENCE OF GRANITE DUST ON CALCIUM ALUMINATE CEMENT PROPERTIES

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Calcium aluminate cement is specific hydraulic binder, which primarily contains of monocalcium aluminate and has properties such as rapid hardening, high early strength and resistance to fire, abrasion, sulphate attack and alkali-silica reaction. Calcium aluminate cement usually is produced by fusing together a mixture of calcium bearing material (limestone) and aluminum bearing material (bauxite or refined alumina) [1]. In order to cheapen production, various types of additives or waste are applied. However, there is a lack of information about Alumina Cement Hydration using granite dust [2]. Therefore, the aim of this work is to determine the influence of different additives in early hydration stage of calcium aluminate cement in different environment.

Calcium aluminate cement Gorkal 70 (Gorka Cement, Poland), having a specific surface area by Blaine S_a = 466.5 m^2/kg, density ρ = 3.15 g/cm^3 was used. The main elements are aluminium and calcium. The dominant minerals are calcium aluminum oxide – $CaO{\cdot}Al_2O_3$ and grossite – $CaO{\cdot}2Al_2O_3$. Granite cutting waste (S_a = 913 m^2/kg, ρ = 2.9272 g/cm^3) consist of silicon, aluminium, iron, potassium elements. The dominant minerals are quartz (SiO_2) microcline ($KAlSi_3O_8$,) annite ($KFe_3AlSiO_{10}(OH)_2$), albite ($(Na,Ca)Al(Si,Al)_3O_8$), cordierite ($(Mg,Fe)_2Al_2Si_5O_{18}$).

Several types of mixtures which contains of main material G70 cement were prepared. Different amount (4 or 12 %) of additive – granite cutting waste – was added. Materials and mixtures were characterized by X-ray fluorescence spectroscopy, X-ray diffraction analysis. Heat evaluation rate and heat flow of hydration process was measured by using TAM Air III isothermal calorimeter.

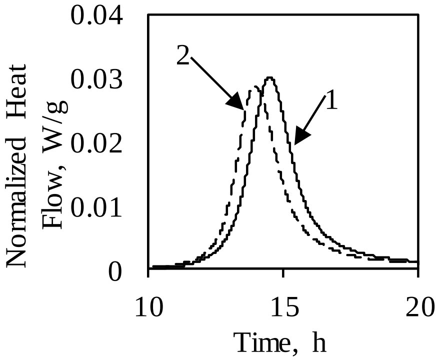

Fig. 1. Heat evaluation rate of calcium aluminate cement samples: 1 – pure, 2 – with 12 % of granite dust additives.

It was determined that 12% of granite dust has positive influence on calcium aluminate cement hydration. Firstly, the additive accelerates hydration reaction and reduces the evaluation of heat flow. It was noticed that the duration of second exothermic reaction decreased from 6.7 h to 6.1 h in samples with granite dust. Furthermore, the peak of second exothermic reaction acceleratory moment in pure cement was marked after 14.5 h and the heat release rate at that moment was 0.032 W/g. Meanwhile in samples with granite dust, the peak was reached 0.5 h earlier and the heat release rate was 0.029 W/g (Fig.1.) Moreover, the additive reduces the amount of released heat, because after 25 h of hydration reaction total heat flow in pure cement was 293 J/g, whereas 273 J/g of heat was released in samples with granite dust.

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TRIBOLOGICAL BEHAVIOR OF Cr COATINGS OBTAINED FROM Cr(III) BATH

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In view of very high toxicity of Cr(VI) compounds, the development of alternative process hexavalent chromium plating is urgently needed. According to EU Regulation (EC) No 1907/2006 ("REACH") the use of chromium trioxide baths for functional and decorative chromium plating will be forbidden or severely limited after 1 September, 2017.

In this study, tribological properties of Cr coatings obtained from Cr(III) sulphate baths with complexing agents (formate-urea, glycine and oxalate) prepared on 316Ti stainless steel (Fe-17.5Cr-10.4Ni-0.48Mo-0.59Si-0.69Ti-0.12Cu, in wt.%) have been investigated. For the sake of comparison of tribology properties, Cr(VI) coating was also prepared in 120 g/l CrO_3 and 2.5 g/l Limeda Ch-3, i_k=40 A/dm^2, t=50 ^oC, τ=10 min. The additive Limeda Ch-3, which represents a mixture of sodium fluorosilicate $Na_2[SiF_6]$ and sulphate $KAl(SO_4)_2$ $12H_2O$ (potasium aluminium sulphate dodecahydrate) compounds was created in the Institute of Chemistry, Vilnius, Lithuania.

To assess the tribological behavior of the coatings, dry sliding wear test against a 100Cr6 steel ball was assessed by using a ball on flat configuration. The test results suggest that Cr coatings deposited in Cr(III) baths have better tribological properties as compared to those of Cr coatings deposited in Cr(VI) baths.

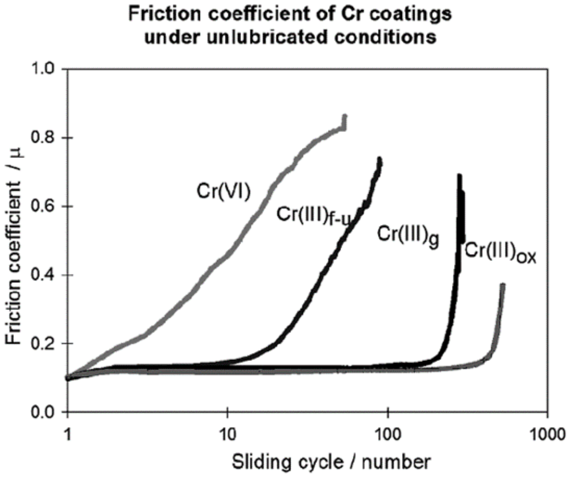

Fig. 1. Friction coefficient (µ) of Cr coatings as a function of the number of friction cycles of Cr(VI), Cr(III)$_{f\text{-}u}$, Cr(III)$_g$ and Cr(III)$_{ox}$ of coatings as deposited

The coefficients of friction for four different Cr coatings are shown in Fig. 1. As one can see the friction coefficient of the Cr coating deposited in the Cr(VI) bath apparently quickly increases from the first friction cycles the Cr coatings deposited in the Cr (III) baths maintain a low friction coefficient (~ 0.12) with the first friction cycles. With increasing number of friction cycles (> 10) the low friction coefficient is lost by Cr(III)$_{f\text{-}u}$, after > 100 cycles - by Cr(III)$_g$ and finally, after reaching >200 friction cycles, Cr(III)$_{ox}$ fails too.

Thus, it has been determined that the Cr coatings deposited in the Cr(III)$_{ox}$ baths possess better tribological properties as compared to those obtained in the Cr (VI) baths.

GOLD COATED COBALT FERRITE NANOPARTICLES VIA METHIONINE-INDUCED REDUCTION

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Biocompatible superparamagnetic iron oxide nanoparticles (NPs) through smart chemical functionalization of their surface with fluorescent species, therapeutic proteins, antibiotics, and antibodies offer remarkable potential for diagnosis and therapy of disease sites at their initial stage of growth. This problem can be solved by creation of the proper linkers between magnetic NP and fluorescent or drug probes, such as gold since gold is chemically stable, nontoxic and capable to link various molecules through sulfur. However, the electroless plating of iron oxide-based NPs with gold is still problematic since in the most cases Au species are formed in the solution bulk. In this study, we present the way for a simple and reliable attachment of gold quantum dots (QDs) to the surface of magnetic NPs. Emphasis is put on the synthesis of magnetic NPs by co-precipitation way using methionine amino acid as NP growth stabilizing agent capable later reduce and attached gold species. The surface of these NPs can be further conjugated with targeting agents, such as anticancer drug doxorubicin, for specific applications.

In order to verify our findings, high-resolution transmission electron microscopy (HRTEM), EDX mapping, FTIR spectroscopy, inductively-coupled plasma mass spectroscopy (IC-PMS), selected area electron diffraction (SAED), and cyclic voltammetry of as-formed $CoFe_2O_4$@Meth NPs before and after decoration with gold QDs have been employed.

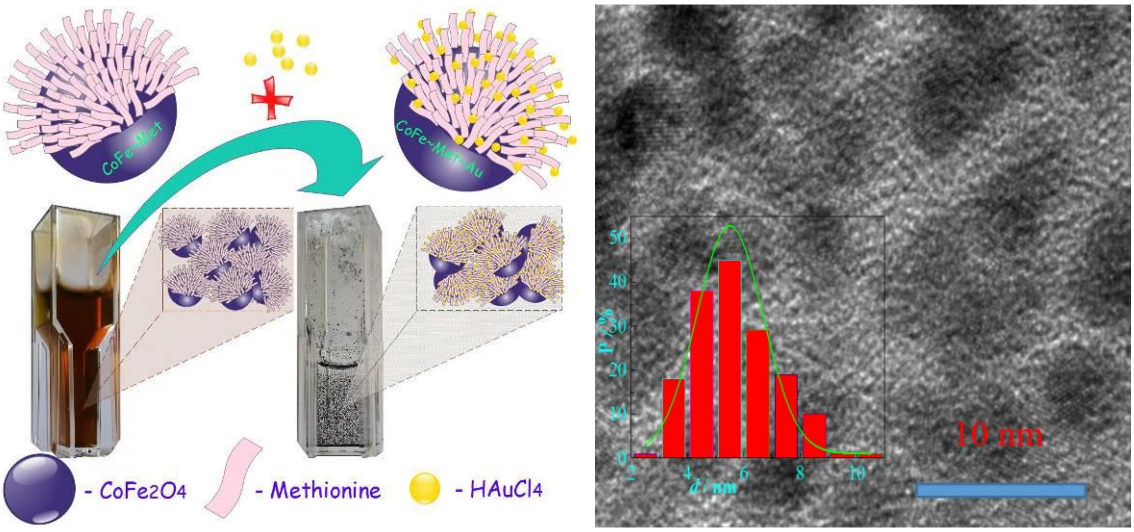

Fig. 1. Scheme of Gold Coated Cobalt Ferrite Nanoparticles via Methionine-Induced Reduction synthesis.

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STATIC AND DYNAMIC FRICTION EVALUATION OF ANODIZED ALUMINUM SURFACES

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Static friction relates to the lateral force between two surfaces at the onset of the movement and represents an important parameter when designing moving units with occasional stagnation. To the contrary, dynamic friction refers to the frictional force of a moving object [1]. With rapid spread of lubricant-free systems, anodized surfaces are often used due to their hardness. In this study static and dynamic Coefficients of Friction (COF) were evaluated on Al surfaces, anodized using different electrolytes and process conditions for better understanding of main factors affecting their dry friction.

Anodization was performed in aqueous phosphoric or sulfuric/oxalic electrolytes to produce Al_2O_3 coatings over 10 μm thickness. Beforehand 1050 and 6082 Al discs of 99.67 % and 96.72 % purities respectively were etched, cleaned and rinsed as described previously [2] then placed into electrolyte and anodized at 15 °C. Phosphoric (4% H_3PO_4 for 150 min at 50V, 100V or 150V) and sulfuric/oxalic (175 g/L H_2SO_4+30 g/L $(COOH)_2{\cdot}2H_2O$+55.5 g/L $Al_2(SO_4)_3{\cdot}18H_2O$ at 20V for 30 min) electrolytes were screened. After anodizing discs were dried at 50°C for 30 min before tribotesting.

CSM tribometer was used for friction tests in ball-on-plate linearly reciprocal configuration with 6 mm OD corundum (Al_2O_3) balls at 2 cm/s velocity and 8 mm cycle length [2]. Static COF was measured under 1 N load using 100 Hz data collection rate. Consistency of friction was verified for 10 cycles and static COF was established at the maximum of the first friction cycle. Fluctuations were leveled by averaging 15 data points.

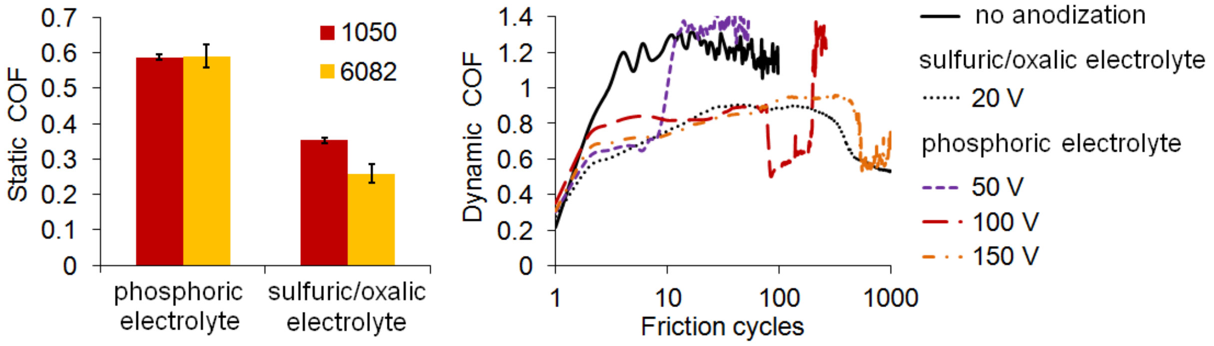

Fig. 1. Influence of anodization in phosphoric (150 min at 120 V) and sulfuric/oxalic (30 min at 20 V) electrolytes on static friction (left). Effect of anodization conditions on dynamic friction of 1050 alloy (right).

Surfaces anodized in phosphoric electrolyte showed average static COF of 0.59, see Fig. 1. Sulfuric/oxalic anodization at 20 V for 30 min led to significant difference between 1050 and 6082 and much lower static COF of 0.35 and 0.26 respectively. Static friction could go down due to changes in roughness or porosity and microscopy data might provide some explanations. Dynamic friction was tested on 1050 alloy using 10 N load. Much higher voltages and durations of 150 min were necessary for anodization in H_3PO_4 electrolyte to produce coatings over 10 μm in thickness, while 30 min was sufficient to produce similar thickness in sulfuric/oxalic electrolyte. No friction reduction could be observed in H_3PO_4 anodization specimens, despite expected phosphate role as Anti Wear compounds. Clearly, roughness and porosity strongly influence COF and this is very evident in static friction.

Acknowledgments

Experimental assistance and technical advice of Dr. Gedvidas Bikulčius, Dr. Ignas Valsiūnas, Dr. Sigitas Jankauskas, Dr. Alma Ručinskienė, Dr. Svetlana Lichušina is cordially appreciated.

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FABRICATION OF CALCIUM HYDROXYAPATITE NANOPARTICLES FOR DENTAL APPLICATIONS BY SIMPLE SOLID-STATE REACTION METHOD

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Every day, millions of patients from all parts of the world are suffering from bone defects arising from trauma, surgery or different diseases. Thus, the requirement for new bone to replace or restore the function of diseased or damaged is a major clinical and socioeconomic need. Calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, commonly referred as CHAp, is one of the calcium phosphate based bioceramic material which makes up the majority of the inorganic components of human bones and teeth. Synthetic CHAp is known to be one of most important implantable materials or component of implants due to its biocompatibility, bioactivity and osteoconductivity coming from the analogy and crystallographic similarity to the mineral components of natural bones.

In this study, a simple solid-state reaction synthesis route based on ammonium–hydrogen phosphate as the phosphorus precursor and calcium acetate monohydrate as source of calcium ions have been used to prepare calcium hydroxyapatite. These mixtures were heated for 5 h at different temperatures (1000 °C, 1100 °C and 1200 °C). The phase purity and microstructural changes in the polycrystalline samples were studied by infrared spectroscopy (FTIR), X-ray powder diffraction analysis (XRD) and scanning electron microscopy (SEM). Morphology and physical properties of the samples before and after milling were also investigated. The samples with milling treatment presented smaller particle size and better particle dispersion. The obtained nano-sized calcium hydroxyapatite powders (see Fig. 1) were used in the surgery and dental applications, including the products for 3D open cell scaffolds and tooth remineralization pastes.

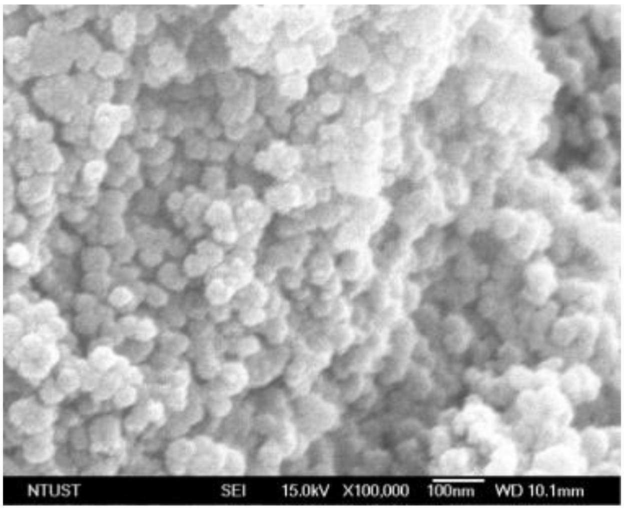

Fig. 1. SEM micrograph of nano-sized CHAP

Besides, the in-vitro study demonstrated that the use of 5 % nano-CHAp on the testing teeth could promote in vitro remineralization of dental enamel to 31.3 % ± 13.9 %.

Acknowledgments

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Biotechnology, Environmental Chemistry and Technology

OCCURRENCE OF TRIHALOMETHANES IN ISPARTA CITY, TURKEY

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In recent years, one of the biggest problems in the drinking water treatment sector is the formation of carcinogenic and mutagenic disinfection by-products (DBPs) (Kitis et al., 2010). Since trihalomethanes (THMs) were first discovered in drinking water in the early 1970s (Rook, 1974), much research has been directed toward improving our understanding of DBPs. DBPs form from reactions between organic (i.e., a heterogeneous mixture of various organic molecules in natural waters) and inorganic (e.g., Br^-, I^-, NO_2^-) precursors in natural waters and oxidants/disinfectants (chlorine, chlorine dioxide, chloramine, ozone) used during drinking water treatment operations (Gan et al., 2013). TTHMs should not exceed 100 µg/L for drinking water in the distribution system according to regulations in Turkey. The main objective of this study is to investigate seasonal variations of formation and specification of THMs in Isparta drinking water distribution system. THM formations were monitored at 5 different sampling points monthly for one year period in Isparta distribution system. Besides THMs, dissolved organic carbon (DOC), UV_{254}, specific ultraviolet absorbance ($SUVA=UV_{254}/DOC$), Br^-, total nitrogen (TN), NO_3^-, NO_2^-, NH_3, dissolved organic nitrogen (DON) were monitored. TOC, UV absorbance and free residual chlorine levels of the 5 sampling points during sampling period were ranged between 1,07–3,60 mg/L, 0,06–0,049 cm^{-1}, 1,24–0,10 mg/L, respectively. $SUVA_{254nm}$ values of the water distribution system was generally lower than 2.0 L/mg-m indicating that natural organic (NOM) in the water distribution system dominantly non-humic and hydrophilic character (Kitis et al., 2010). Maximum THMs formation was observed as 59 µg/L in Isparta distribution system and chloroform was the dominant species. An increase in THMs formation was observed in the spring and summer for Isparta distribution system.

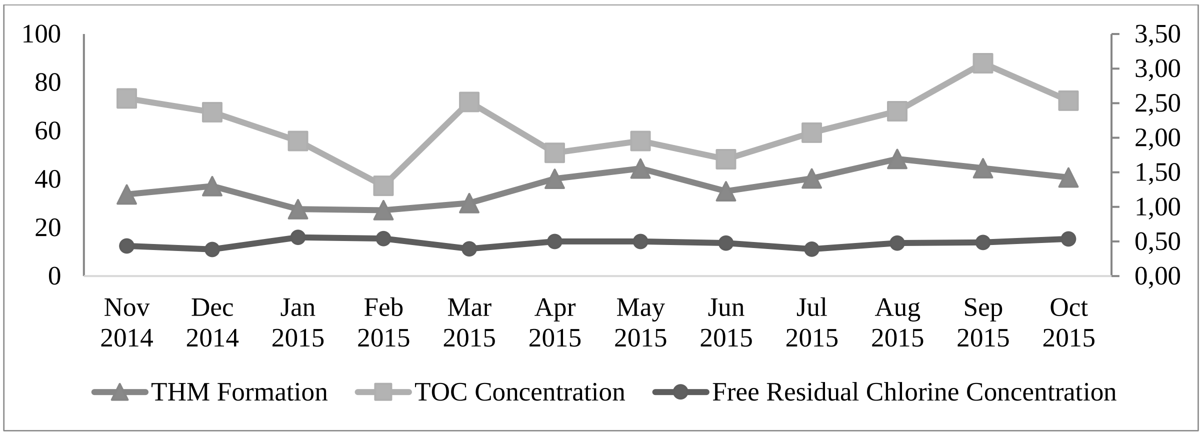

Fig. 1. THM formation against TOC and Free Residual Chlorine

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LACTIC ACID PRODUCTION FROM AGRO-INDUSTRIAL BY-PRODUCTS APPLYING BY ENZYMATIC HYDROLYSIS AND LACTIC ACID BACTERIA FERMENTATION

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Recently, considerable interest has been arisen in the bio-recycling of agro-industrial by-products into the valuable chemicals such as lactic acid due to the prospects of environmental friendliness and of using renewable resources instead of petrochemicals. The chemical route produces a racemic mixture of DL-lactic acid, while optically pure L(+)- or D(–)-lactic acid can be obtained by microbial fermentation [1]. Moreover, biotechnological recycling of agro-industrial by-products could effectively reduce the costs of lactic acid production which is widely used in the food and beverage sector, pharmaceutical, cosmetic and chemical industries. Higher economical effect has been found by using biological conversion of wheat biomass to lactic acid vs chemical synthesis by increasing the energy efficiency by 47% and decreasing the total costs by 17 % [2].

The aim of research was to investigate the usability of agro-industrial by-products, such as wheat bran and wheat straw in the production of L-lactic acid via fermentation applying by newly isolated lactic acid bacteria strains (LAB) belonging to *Lactobacillus* genera.

Agro-industrial by-products were fermented with thermophilic and mesophilic LAB belonging to *Lactobacillus sanfranciscensis*, *Lactobacillus delbrueckii*, *Lactobacillus rossiae*, *Lactobacillus casei*, *Lactobacillus rhamnosus*, *Lactobacillus acidophillus* and other species. Before fermentation enzymatic treatment of by-products was carried out using carbohydrases (enzymatic preparations Celustar XL). An enzymatic test K-DLATE 08/11 (Megazyme Int. Ireland, Wicklow, Ireland) was used for lactic acid and D/L-lactates determination. The influence of magnesium, calcium and sodium salts on enzymatic hydrolysis efficiency was evaluated.

The addition of 50 mg/ml of $CaCl_2$, 100 mg/L of $MgSO_4 \cdot 7H_2O$ in straw medium increased enzymatic hydrolysis efficiency, whereas the addition of NaCl in range 50–175 mg/L decreased cellulase activity. *Lactobacillus delbrueckii* subsp. *bulgaricus* and *Lactobacillus sanfranciscensis* MW15 produced the highest amount of lactic acid in the wheat straw (respectively up to 6.3 and 5.1 g/L), whereas other LAB strains produces less content of lactic acid in straw medium. *Lactobacillus sanfranciscensis* MR29 and *Lactobacillus sanfranciscensis* W19 previously isolated from sourdough have produced pure L-lactic acid isomer (~3 g/L in wheat straw media). Higher content of lactic acid was produced in wheat bran medium in comparison with wheat straw medium. *Lactobacillus delbrueckii* subsp. *bulgaricus* MI strain produce pure L-lactic acid in wheat bran medium (5.7 g/L).

The results confirm that tested agro-industrial by-products could be used for L-lactic acid production using selected enzymes and lactic acid bacteria strains.

Keywords: lactic acid; lignocellulose, *Lactobacillus*, hydrolysis

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STRATEGIES FOR THE IMPROVEMENT OF FUNCTIONAL AND TECHNOLOGICAL PROPERTIES OF CORN WASTE PROTEINS WITH A POTENTIAL APPLICATION IN FOOD PRODUCTION

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Corn by-products have valuable proteins, fats and dietary fiber, furthermore its application in food industry enables decrease the cost of products. For centuries, fermentation with lactic acid microorganisms has been a simple and inexpensive method to improve the functional and nutritional value of foods, and ensure food preservation.

The aim of this study was to develop the technologies for corn processing waste utilization into biologically valuable ingredients, and to evaluate their possible use for functional food production. The rational use of natural by-products and wastes generated during the production of grain is very important and promising area. The use both of alternative heat treatment methods for microbial stabilization of such materials, and the innovative biotechnological instruments - enzymatic hydrolysis and microbial fermentation - for the natural plant components production, which could be used for safe food production. Protein content, water absorption capacity, water solubility index, foaming capacity and foam stability, and emulsifying properties of albumins and globulins obtained from natural, extruded and treated by infrared irradiation corn by-products were determined. Lacto-fermentation with pediococci improved the functional properties of corn albumin and globulin fractions, also the digestibility and solubility of zein. The use of new cellulase-xylanase complex allowed increase the yield of zein fraction. Therefore, peptides produced by *P. acidilactici* and *P. pentosaceus* during fermentation of corn medium showed strong inhibition of the sporulation and growth of *Fusarium graminearum*. Furthermore, longer peptides displayed potent fungicidal activities against a variety of important filamentous fungi, including *F. culmorum*.

Keywords: corn by-products, lacto-fermentation, acidity, protein fractions, L(+) and D(-)- lactic acid

OZONE BASED ADVANCED OXIDATION FOR WATER TREATMENT

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Application of advanced oxidation (AO) methods for water treatment including ozonation, photocatalysis, peroxide based and others [1], are under intensive exploration during the recent years. The AO technology is able to decompose toxic and persistent organic compounds in water, which are hardly degradable using conventional technologies. The AO processes utilize the in-situ formation of reactive hydroxyl and oxygen radicals, which serve as oxidative agents for degradation of organic pollutants. Ozone based AO systems reported [2] as some of the most technologically efficient, and at the same time being versatile and flexible to operate in order to maintain robustness under changing composition and matrix of wastewater, pH value, etc.

At our experiment, the experimental bench scale reactor was used for testing of various ozone based AO methods – ozonation, catalytic ozonation, photolytic ozonation and photocatalytic ozonation. The photocatalysis and photolysis experiments were performed for comparison. The TiO_2 coated glass rods was used as a catalysts at this investigation, the UVC lamp (254 nm, 40W) used as a UV source, the ozone generator working on dielectrical barrier discharge principle served as ozone source. The degradation of various chemical substances – 2-naphthol, phenol, phthalate and oxalic acid was tested. The degradation results (as a residual total organic carbon concentration) are presented in Fig.1.

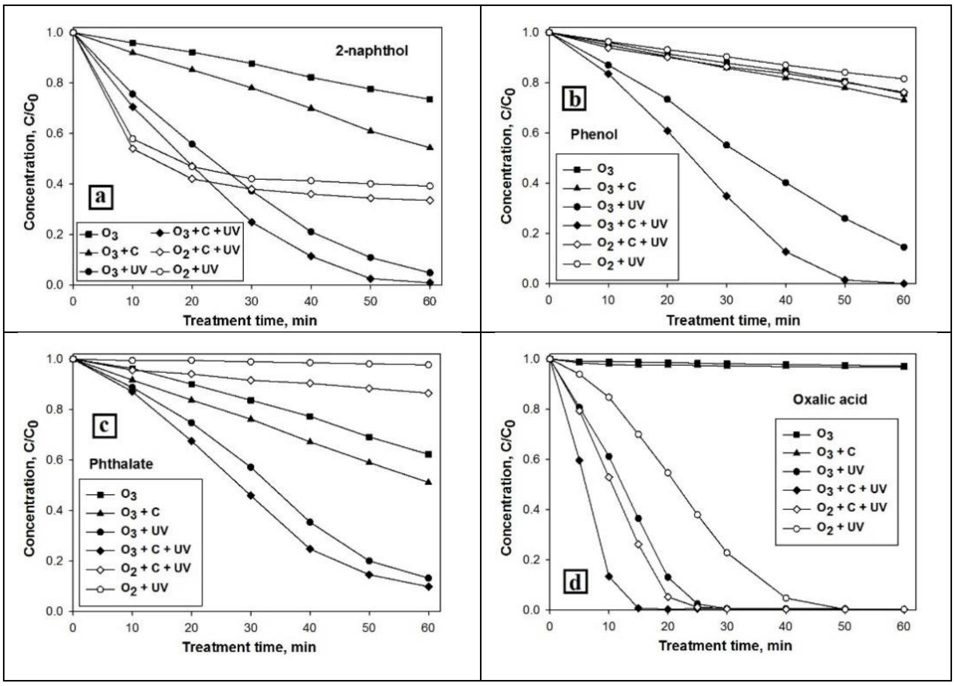

Fig. 1. Degradation kinetics at different experimental conditions using 2-naphthol (a), phenol (b), phthalate (c) and oxalic (d) acid as model pollutants

The photocatalytic ozonation confirmed as the most effective experimental conditions at tested model pollutants. The second most effective was photolytic ozonation, while single ozonation was founded to be comparatively inefficient at our experiment.

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MODIFICATION OF TiO_2 NANOFIBERS FOR ENVIRONMENTAL PHOTOCATALYTIC APPLICATIONS

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Photocatalysis is considered as an environment friendly process able to decompose organic pollutants and can be used for many applications including water and air purification. Titanium dioxide has been established as the most popular due to its chemical stability, availability, and competitive cost [1]. Fibrous photocatalysts are attractive candidates for practical applications in clean-tech sector due to their structural dimensionality and potentially improved photocatalytic performance. TiO_2 shows relatively high reactivity under ultraviolet light due to its large band gap. The development of photocatalysts exhibiting high reactivity under visible light ($\lambda > 400$ nm) should allow the main part of the solar spectrum to be used [2], including other light source than mercury lamps, which are toxic and controlled substances.There were several approaches for TiO_2 modification such as non-metal doped-TiO_2, composites of TiO_2, metal-ion implanted TiO_2 using transition metals. Amongst a variety of transitional metals, iron has been considered to be an eligible candidate due to the fact that the radium of Fe^{3+} is similar to that of Ti^{4+}, so iron can be incorporated into the crystal lattice of TiO_2, furthermore, iron can provide a trap for photo-generated electron because the energy level of iron ions lies close to that of titanium, consequently resulting in the improvement of quantum yield [3].

Experimental. PVP (M_w=1x10^6 g/mol), titanium butoxide ($Ti(OBu)_4$), acetic acid, ethanol, iron (III) nitrate nonahydrate were used as received. PVP was dissolved in ethanol to form solution of 10 wt%. In a separate vial certain amount of ethanol, acid, $Ti(OBu)_4$ and iron salt were mixed. Then the latest solution was slowly dropped into the first one. The final concentration of iron ions was 1 at. %. The electrospinning technique was used to prepare the iron-doped TiO_2 nanofibers. The prepared solution was loaded into syringe equipped with 23G needle. The voltage source of 27 kV was used. The rotating collector was covered with stainless steel plate. The distance between the tip of needle and collector was fixed at 16 cm. The feed rate of the solution was kept at 1.3 ml/h. As spun fibers were calcined at 500 °C for 2 h in air, in order to eliminate the organic components and to activate the crystallization of titania. The characterization of the fibers was made SEM-EDX, XRD and FTIR.

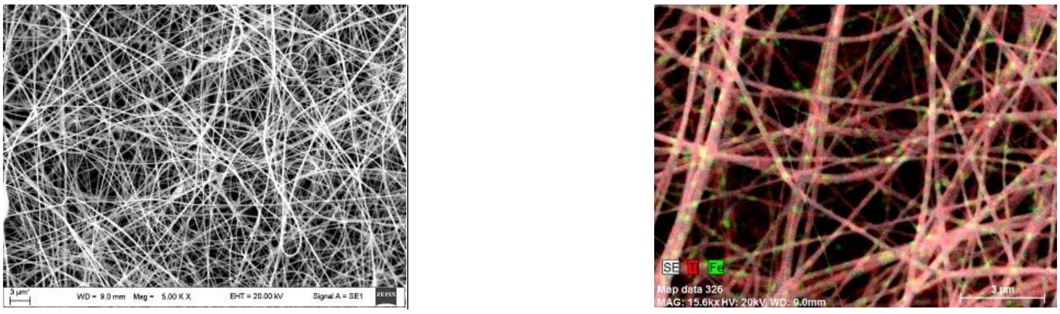

Fig. 1. SEM (left) and EDX (right) results of iron-modificated TiO_2 nanofibers

Results. The final fiber layer was characterized as smooth and uniformly deposited. The diameters of fibers were ~200 nm (Fig. 1 left). The XRD analysis showed that at the presented temperatures only anatase phase is activated. The formed fibres were mainly composited of TiO_2, with additions of iron, which was releveled being evenly distributed over fibers length (Fig. 1 right), as well as with additions of carbon as a product of the calcination of PVP. The presence of Fe-O bending was confirmed by the results of FT-IR analysis. Electrospun iron-doped TiO_2 have a great potential for applications as photocatalysts, which will further be determined in a complex system for air purification.

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ANALYSIS OF ELEMENTAL AND MINERAL COMPOSITION OF THE CAR BRAKE PADS

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After the ban of asbestos fibers for brakes manufacturing in mid-90s, composition of brake linings has rapidly changed but there is still a number of possible toxics used (heavy metals, their sulphides, PAHs etc.) [1]. Detailed information on materials used for creating brake pads is not provided by manufacturers. According to the literature [2, 3], brake pads include materials that cause metallic friction (Fe and Fe-Cu oxides), lubricants (graphite and Fe-Sb-Ba-Sn-Mn sulphides) and mineral fibers (Ba, Ca, and Al-silicates) used as fillers.

This study aims to investigate elemental and mineral composition of different brake pads including most popular in the country. The information acquired through research is important for emission inventories and toxicological studies.

The elemental composition of brake pads was studied using X-ray Fluorescence spectrometry, Scanning Electron Microscope (SEM) and EDS. While X-Ray Diffraction spectrometry (XRD) was used for the identification of mineral composition. After analyzing the results popular element composition is Ca, Fe, S, Al, Ba, Si, Cu and mineral composition ($BaSO_4$, CuO, Fe_2O_3, ZnO, TiO_2). The brake pads have different microstructure, which showed different elements distribution in surface by SEM.

Table 1. Elemental analysis of two different brake pads with XRF and SEM

Component, % (wt)	Ca	Fe	Si	Al	Zn	S	Mn	Ti	Cl	Ba	Cu	Cr
S1 (XRF)	1,68	16,00	3,57	3,36	2,43	1,15	0,13	0,18	0,15	4,53	3,97	-
S1 (SEM)	2,05	18,17	2,67	3,37	1,06	1,39	0,41	0,71	0,19	9,55	0,83	0,22
S2 (XRF)	3,35	19,00	2,81	1,07	1,81	0,43	0,13	0,16	1,69	1,14	1,31	0,14
S2 (SEM)	4,46	33,05	2,03	1,45	2,17	0,50	0,22	0,29	3,07	2,02	1,88	0,22

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OPTIMIZATION OF XANTHAN PRODUCTION FROM *XANTHOMONAS CAMPESTRIS*

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Xanthan is a important industrial biopolymer for commercial purpose and it is produced by *Xanthomonas campestris* using microbial fermentation. Xanthan has been used in a wide variety of food industry for a number of important reasons, including emulsion stabilization, temperature stability, compatibility with food ingredients, and its pseudoplastic rheological properties. Because of its properties in thickening aqueous solutions, as adispersing agent, and stabilizer of emulsions and suspensions, xanthan is used in pharmaceutical formulations, cosmetics, and agricultural products. The toxicological and safety properties of xanthan for food and pharmaceutical applications have been extensively researched. Xanthan has been approved by the United States Food and Drug Administration (FDA) for use a food additive without any specific quantity limitations [1].

Xanthomonas is a genus of the *Pseudomonaceae* family. *Xanthomonas* cells occur as single straight rods, 0.4 ± 0.7 µm wide and 0.7 ± 1.8 µm long. *Xanthomonas campestris* is identified as a production strain. In the industrial production is used 2–4 % of carbon source as sucrose or glucose, and 0.05–0.1 % of nitrogen source as yeast extract, peptone, ammonium nitrate or urea [2]. Rheological properties and yield of xanthan depends on the culture medium used in the fermentation process [3].

The main objective of the present study was to investigate of different media composition for *Xanthomonas campestris* growth and to select optimal conditions for purification of xanthan.

Xanthan production is influenced by several factors that include medium composition, cultivation conditions (temperature, pH, stirrer speed), fermentation time, and post-fermentation conditions (heat treatment, recovery, purification).

Xanthomonas campestris bacteria was cultivated in different formulated media and the correspondent biomass produced was analysed to determine optimal conditions for xanthan production. The influence of different carbon and nitrogen sources for bacteria *Xanthomonas campestris* growth during fermentation was examined. Sucrose, glucose, maltose, lactose as carbon and soya-peptone, yeast extract, peptone bacteriological, peptone from casein as nitrogen sources were examined on xanthan production. Different purification methods using different solvents (i.e. isopropanol, acetone, ethanol, methanol) were analyzed.

The present work revealed, that the growth medium used for production of inoculum is a factor impacting the xanthan production. It was found, that the most effective *Xanthomonas campestris* growth was in the media enriched with sucrose and yeast extract. It was found, that among the purification techniques, acetone gave the highest purification yield of xanthan.

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DISTRIBUTION OF ALUMINIUM IN SYSTEM „SOIL – WATER“

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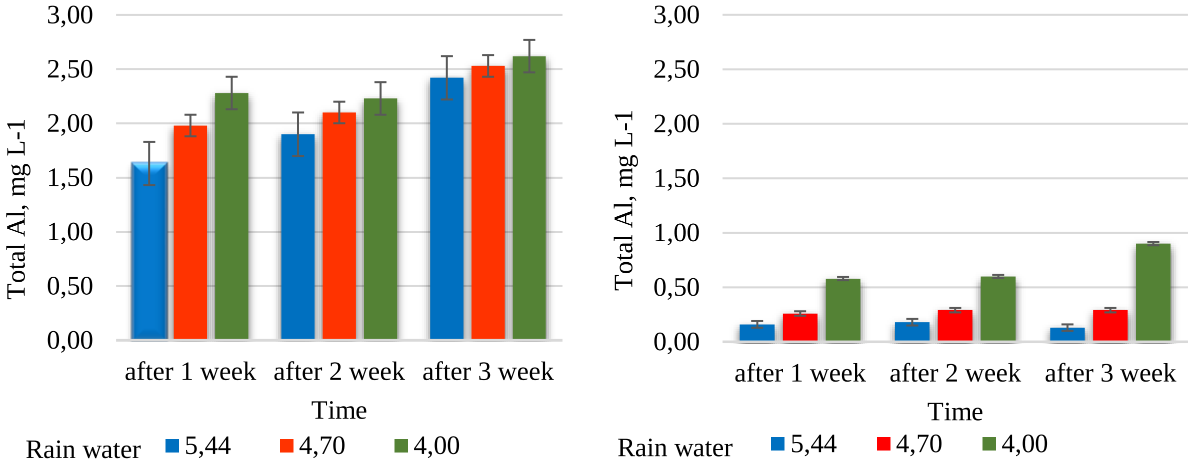
Acidification of waters and soils is a problem in many countries. Areas that are affected by acidification – Scandinavia, Central Europe, Scotland, United Kingdom, Canada, United States. Several natural and anthropogenic factors affect acidity – acid rain, deposition of air pollutants, use of nitrogen fertiliser [1].

The acidity of soils release of aluminium ions from soils and their migration to surface and undergound water, and here sediments accumulating on the bottom various forms of aluminium [2]. The elevated Al levels in acidic waters may be toxic to fish, algae, shelfish, plankton. Aluminium specation, solubility and toxicity are affected by wide variety of environmental parameters including soil pH, rain pH, temperature, organic carbon and numerous ligand (e.g. F^-, Ca^{2+}) [3, 4]. The aim of research was to determine aluminium species and concentration in acid and limed soil and of simulated acid rain to aluminium concentration in soil filtrate.

This study investigated the dynamics of aluminium from Albeluvisol soil under the influences of simulated acid rain. Laboratory experiments were performed by leaching the soil columns (9 – from acid Albeluvisol (pH = 4.12); 9 – from limed Albeluvisol (pH = 6.65) with simulated acid rain at pH levels ranging from 4.00 to 5.44 over a 3 week experimental period.



a *b*

Fig. 1. Al concentration in leaching water: *a* – acid soil, *b* – limed soil

The results of research showed that when rain water was 5,44, 4,7 and 4,0, Al concentration have been estimated 1,63 mg L^{-1}, 1,98 mg L^{-1} and 2,28 mg L^{-1}in acid soil, while in limed soil – 0,16 mg L^{-1}, 0,26 mg L^{-1}, 0,34 mg L^{-1} respectively [Figure 1].

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MICROWAVE-ASSISTED SYNTHESIS AND ANALYSIS OF BIOLOGICAL ACTIVITY OF QUINAZOLIN-4(3*H*)-ONE ANALOGUES

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Quinazolin-4(3*H*)-one derivatives exhibit a wide range of biological activities such as antibacterial, antifungal, antiviral and antioxidant. They can be used as herbicides or plant growth regulators [1, 2].

2-(Het)arylquinazolin-4(3*H*)-ones **3a-f** can be directly obtained from 2-thioxo-2,3dihydroquinazolin-4(1*H*)ones in good to excellent yields by Pd-catalysed Stille-type CuBr·Me_2S promoted Liebeskind-Srogl reactions with (het)arylstannanes or by a two-step procedure via their S-benzylated derivatives 4a,b applying CuMeSal promoted Suzuki-type Liebeskind-Srogl reactions with arylboronic acids [3].

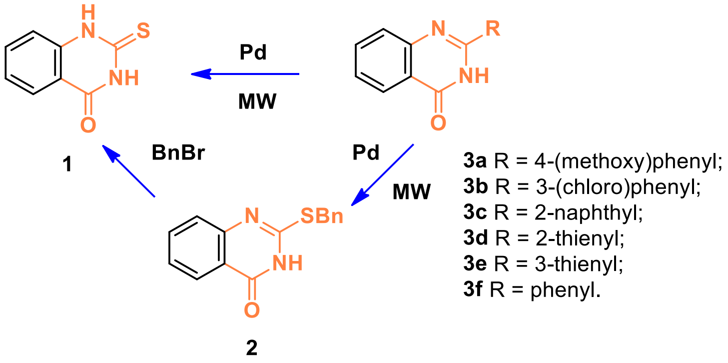

Fig. 1. Retrosynthesis of *N*(3)unsubstituted 2-(het)arylquinazolin-4(3*H*)-ones

Selective S-benzylation of 2-thioxo-2,3-dihydroquinazolin-4(1*H*)-one **2** can be performed with excellent yields by their reaction with benzyl bromide in dioxane.

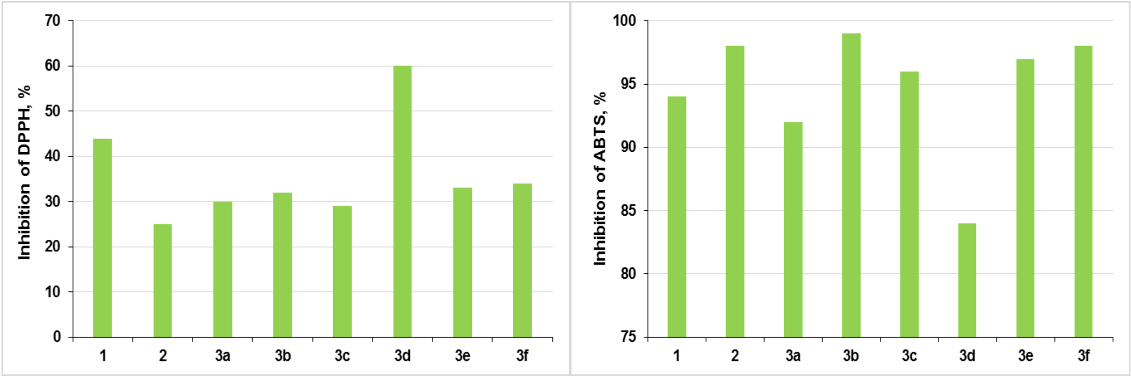

Fig. 2. Inhibition of DPPH and ABTS free radicals using derivatives of quinazolin-4(3*H*)-one

DPPH and ABTS free radical scavenging methods are usually applied to estimate antioxidant properties of examined compounds [4]. FRAP method, analysis of antimicrobial and reducing properties were done to assure biological activity of **3a-f** compounds. Moreover, **3a-f** compounds were tested as growth regulators on rapeseeds.

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INTENSIFICATION OF OIL PRODUCTS BIODEGRADATION PROCESS

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Oil spill accidents are a widespread problem due to the vast production, refining, storage, and distribution of petroleum derived products [1, 2]. Bioremediation is an attractive approach for cleaning up petroleum hydrocarbons because it is simple to maintain, applicable over large areas, cost effective and leads to the complete destruction of the contaminants. These treatments have emerged as a "green" alternative for treating these environmental contaminants [3, 4]. Many modern treatment technologies of oil contaminated soil evolve by developing new and effective bio - agents that help to degrade of oil products. The production of biopreparatus requires both material and energy resources. Waste - sewage sludge biological treatment technology is new and complex approach to the problem, which not only solves the sludge disposal problem, but additionally saves materials and energy resources that are necessary for the production of biopreparats. Therefore, the aim of this work was to determine how sewage sludge can influence the biodegradation activity of soil contaminated with oil products, as well as to determine what groups of microorganisms influence these processes most.

The experiment was carried out in the *in vitro* conditions in the laboratory in pots filled with 5 kg of air-dried soil. In one treatment the soil was artificially contaminated with black oil (30 g kg^{-1} and 15 g kg^{-1}) and in the other treatment with diesel fuel (30 g kg^{-1} and 15 g kg^{-1}). Additionally, the soil was supplemented with additives by creating 9 treatments: I - without additives, II - 5% chemical industry plants sludge, III – 10 % chemical industry plants sludge, IV - 5 % SC "Klaipedos vanduo" wastewater treatment plant sludge, V – 10 % SC "Klaipedos vanduo" wastewater treatment plant sludge, VI - 5 % small water treatment plant sludge, VII – 10 % small water treatment plant sludge, VIII – 5 % paper industry sludge, IX - 10% paper industry sludge. Treatment I was used as a control. The concentrations of oil products in soil were tested during 120 days' period with a gas SHIMADZU GC-2010 (Japan), with a non – polar column and a flame ionization detector (FID) according to ISO 16703:2004 standard.

The current study confirmed that during the treatment of soil polluted with black fuel oil (15 and 30 g kg^{-1}) the best tendency to treatment efficiency was achieved by adding 10 % of the small water treatment plant activated sludge into the soil. Diesel fuel was most effectively decomposed in the pots with sludge from chemistry industry sewage treatment plant. The experiment demonstrated the sewage sludge can employed as source of microbes for oil products biodegradation. The usage of sewage sludge for oil products biological technology reduces the time as well as cost of treatment. In conclusion, there is a possibility to create combined and integrated systems, where waste from waste water treatment plants would be used as bioagents for improving decomposing of oil products.

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ANTIOXIDANT ACTIVITY OF THE EXTRACTS FROM ROSEHIP WILD-GROWING IN WESTERN GEORGIA

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We have investigated antioxidant activity of the extracts from Rosehip wild-growing in western Georgia. Antioxidant activity in the researched object has been determined by DPPH method (free radical colorimetry, with 50 %-inhibition of radical). To identify some bioactive compounds, there have been used the ultra-high pressure liquid chromatography by using a mass-detector (Waters, UPLC Acquity, QDa Detectore), mass scanning m/z 100–1200. For separation of compounds, there has been used a chromatographic column Acquity UPLC BEN C18, 1.7m, solvent system in a 50 % acetic methanol (solvent A), and in a 0,5 % acetic water (solvent B). The gradient solvent is 5 % (0–3 min), with an increase in concentration up to 75 % (7 min), and further decrease up to 5% (10th min). There have been identified: galangin, ellagic acid, catechin, and quercetin.

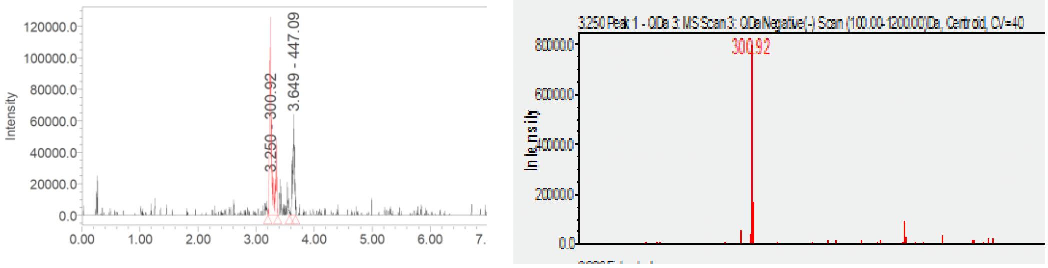

Fig. 1. Rosehip fruit mass-chromatogram (catechin)

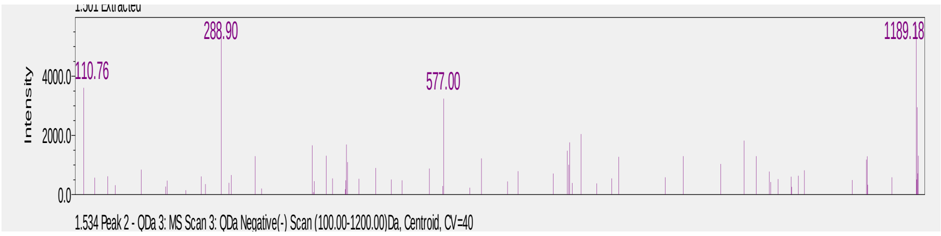

Fig.2. Rosehip fruit mass-chromatogram (ellagic acid)

Table 1. Antioxidant activity of Rosehip fruit (AA)

Rosehip pulp	Extract characteristics			
	m, g	V, ml	F solution	AA %
Water	10	100	25	42,3
40 %- ethyl alcohol	10	100	25	36,45
80 %- ethyl alcohol	10	100	25	40,7
Aqueous concentrate, recovered	10	100	25	39,8
Concentrate 40 %- ethyl alcohol, recovered	10	100	25	35,5
Concentrate 80 %- ethyl alcohol, recovered	10	100	25	40,0

The aqueous extracts showed higher antioxidant activity than 40 % and 80 % ethyl alcohol extracts. regarding the appropriate concentrates, it has been possible to preserve antioxidant activity in them. Naturally, from an economic standpoint, it would be preferable to produce aqueous concentrates of Rosehip fruits.

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THE IMPACT OF THE FERMENTATION PROCESS ON ANTIOXIDANT ACTIVITY OF GEORGIAN RED-FRUITED GRAPE SEED

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The impact of the fermentation process on antioxidant activity of Georgian red-fruited grape seed has been studied. Antioxidant activity in the researched object has been determined by DPPH method (free radical colorimetry, with 50 %-inhibition of radical). To identify some bioactive compounds, there have been used the ultra-high pressure liquid chromatography by using a mass-detector (Waters, UPLC Acquity, QDa Detectore). Mass scanning m/z 100-1200.

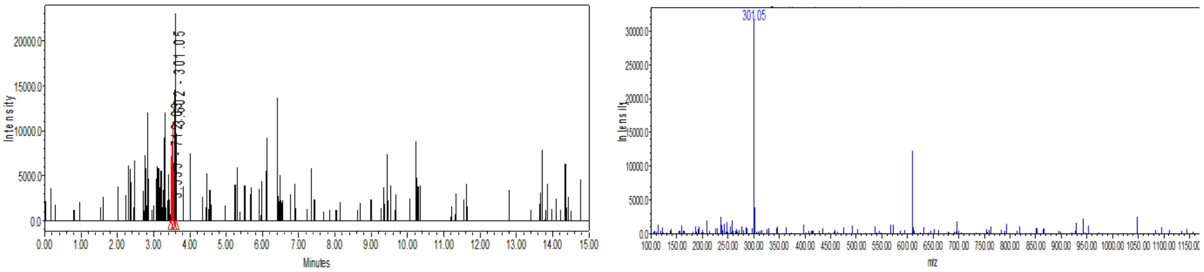

Fig. 1. Grape seed quercetin mass-chromatogram

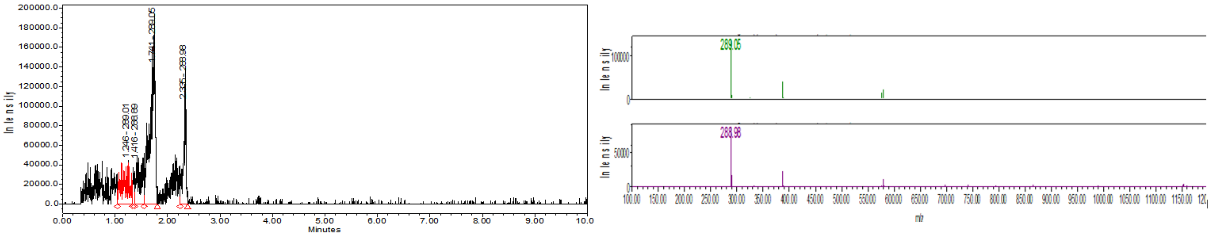

Fig.2. Grape seed catechin and epicatechin mass-chromatogram

Table 1. Antioxidant activity of different grape seed varieties (AA)

Grape seed extract		Extract characteristics			
		m, g	V, ml	F solution	AA %
Ojaleshi variety (Samegrelo)	Raw	1	50	100	60,5
	Fermented	1	50	25	41,86
Otskhanuri Sapere variety	Raw	1	50	100	76,6
	Fermented	1	50	25	60,89
Mujuretuli variety	Raw	1	50	100	71,4
	Fermented	1	50	25	79,07
Aleksandrouli variety	Raw	1	50	100	70,2
	Fermented	1	50	25	58,04

As a conclusion, it can be noted that the use of the red-fruited grape seed for obtaining the bioactive preparations is preferable prior to the fermentation.

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RECYCLING OF FULL-SIZE WASTE PRINTED CIRCUIT BOARDS USING AN ORGANIC SOLVENT

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According to the Solving the E-Waste Problem (StEP) Initiative, about 65.4 million tons of E-waste are generated in 2017 around the world. Waste Printed Circuit Boards (WPCBs) represent about 10 % of total mass of E-Waste. Recycling of WPCBs receives significant attention since they are composed of approximately 30% metals (including precious), 70 % fiberglass and epoxy resin. This work aims to separate all elements of WPCBs (PC Video card) by using organic solvent di-methyl formamide (DMF) and ultrasonic treatment applied to raw material placed inside reaction chamber at lower temperatures (50 °C). At the beginning experiments were conducted on powder and small pieces (100 mm^2) of WPCBs in order to determine the optimum conditions, then obtained data were used in separation of video card by cleaving the macromolecular reticulate structure of brominated epoxy resin (BER). Thus, dissolution of BER was performed, copper foils and woven glass fiber layers were separated. Also, rotary decompression evaporator was used to regenerate used DMF and extract BER. Ultraviolet-visible spectroscopy, metallographic microscope, and EDX were used to examine the recovered BER and fiberglass structure and main metal composition of each sample. The results showed that the developed approach is more efficient for the countries having a hot climate, because the developed technique doesn’t need a high heating rate since used temperature was 50 °C. Also, it was determined that video card PCB consists of 10 woven glass fiber layers (6 substrate layers and 4 isolating layers), copper, aluminium, lead, tin and BER.

APPLICATION OF SURFACE COMPLEXATION AND ION EXCHANGE MODELING FOR THE ESTIMATION OF BENTONITE SORPTION CAPACITY ON SELECTED RADIONUCLIDES UNDER POSSIBLE DISPOSAL CONDITIONS IN LITHUANIA

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Designing of the repository for radioactive waste as a multi-barrier system with predefined multiple safety functions provides protection of people and environment from harmful effect of ionising radiation of radionuclides once released from high-level radioactive waste. The multi-barrier system is comprised of the engineered barrier system (EBS) and it surrounding natural environment. Because of high retention capacity for the radionuclides the various forms of bentonite is usually considered as a part of EBS in the design of radioactive waste repositories. Laboratory batch experiments with natural sediments illustrate that the sorption (and Kd values) is sensitive to aqueous chemical conditions, including pH and the dissolved carbonate concentration as well as mineralogy and surface area of bentonite buffer [1-2]. In this study a potential retardation of sorbing radionuclides (Cs, Ni, Eu) as a function of aqueous chemical conditions in the groundwater of Lithuanian crystalline basement contacting the bentonite material was estimated. Ion exchange and surface complexation models (CE-SPNE) and computer program PHREEQC (USA) were applied for the modelling of the interaction within the radionuclide/water/bentonite system. Modelling of *Kd* values under different pH conditions and a given partial pressure of carbon dioxide in the gas phase was performed.

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CURRENT CHALLENGES OF HEALTH-CARE WASTE MANAGEMENT IN GEORGIA

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According to the WHO guidance documents the total amount of waste generated by health-care activities, about 75-90 % is general, non-hazardous waste; The remaining 10–25 % is considered hazardous material that may be infectious, toxic or radioactive. The rapid increase of health-care waste generation and environmental pollution represent one of the most urgent problems for Georgia.

In 2016 the Ministry of Environment and Natural Resources Protection of Georgia (MENRP) elaborated National Waste Management Strategy (2016–2030) and a National Waste Management action plan (2016–2020) and update them according to the Waste Management Code within the framework of Association Agreement with the EU. The Strategy will have a special positive effect for the Occupational Health and Safety.

No data on the amounts generated annually is available neither on health-care nor any other specific waste types. The health-care waste segregated fractions and the appropriate treatment options is shown on Fig. 1. Not all medical institutions have contractual agreement with a healthcare waste operator; therefore some portion of health-care waste is still disposed at landfills without any pre-treatment. Only a limited amount of health-care waste is disinfected or goes through thermal pre-treatment. The capacity of thermal pretreatment installations is not sufficient. Separation at the source of healthcare waste is important for safely handling the waste. Pre-treatment of healthcare waste is energy consuming while incineration entails energy recovery.

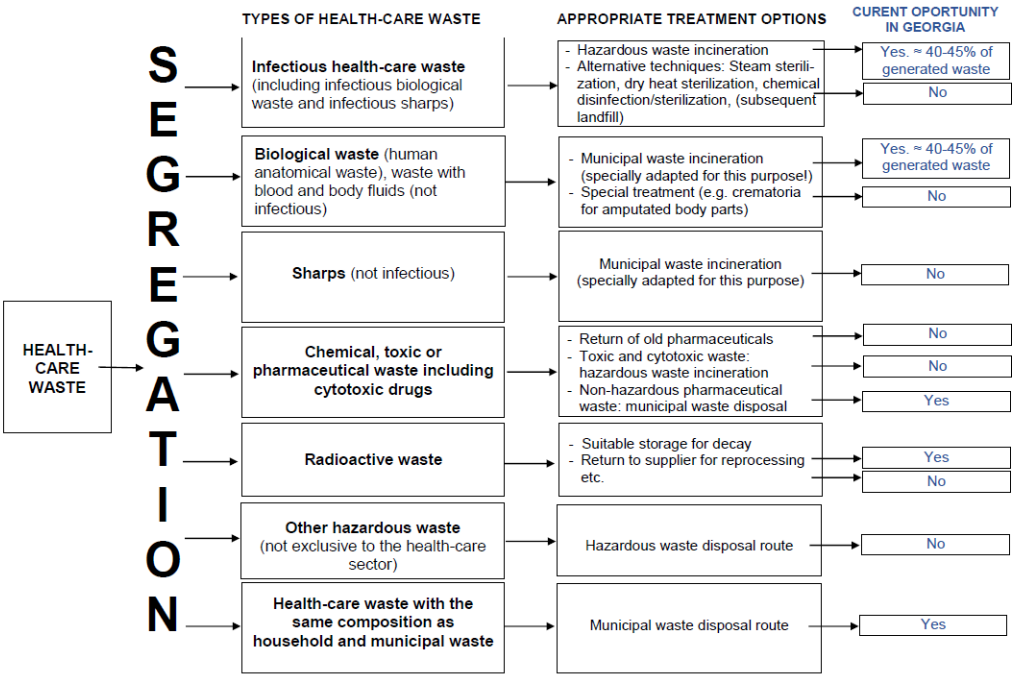

Fig. 1. The health-care waste segregated fractions and the appropriate treatment options

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SORPTION OF HEAVY METALS BY UNDERGROUND WATER DEIRONING RESIDUALS

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A non-hazardous waste material produced by aeration of underground water was examined as a low cost sorbent for heavy metal ions. The quality of water treatment residuals depends on the quality of raw water [1]. Deironing of underground water without the addition of chemicals leads to the formation of eco-friendly waste, suggesting that it may be utilized as natural sorbent [2]. The obtained samples of water deironing residuals were characterized by using XRF, SEM, and XRD methods. Chemical composition of amorphous solid waste expressed in the form of main oxides was as follows: 78% Fe_2O_3, 7.4 % P_2O_5, 7.4 % CaO, and 5.2 % SiO_2. The stability of sorbent in acidic solutions was evaluated by varying initial solution pH from 2 to 6. The leached concentration of Fe(III) ions was negligible when the solution pH was ≥ 3. The removal efficiency (RE) of heavy metals from single-metal solutions was determined to decrease in the following order: Pb > Cu > Zn > Cd > Ni. The effect of various factors for the sorption capacity of natural sorbent towards heavy metal ions was investigated using single-metal and binary Pb(II) – Cu(II) solutions. Different initial heavy metal concentrations varying from 0.5 to 20 mM were used to obtain equilibrium sorption isotherms. It was determined that the sorption capacity depends on initial solution pH, heavy metal concentration and temperature. Fig. 1 shows that a higher temperature (40 or 60 °C) is more favorable for Pb(II) and Cu(II) uptake from the solutions of higher concentration.

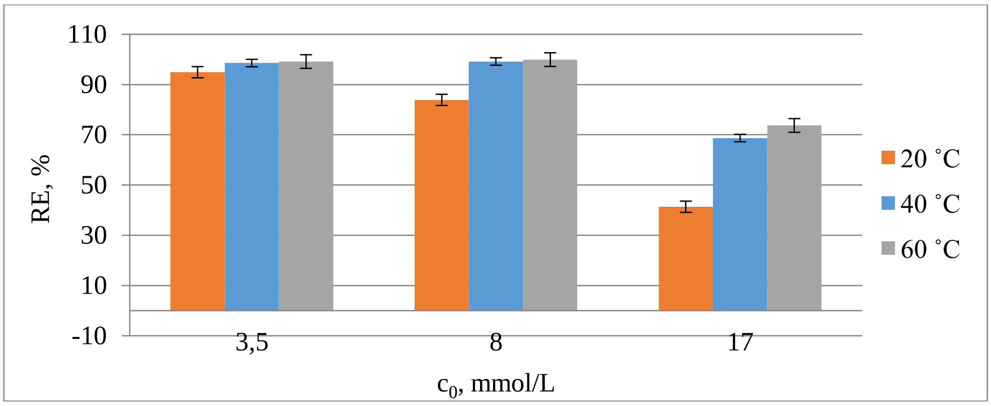

Fig. 1. Dependence of Pb(II) removal efficiency on initial solution concentration and temperature.

Under the conditions of concurrent Pb(II) and Cu(II) sorption the removal efficiency of individual ions decreases but the total sorption capacity increases. The kinetics of Pb(II) and Cu(II) sorption was also studied in single-metal and binary solutions. The study revealed that sorption of Pb(II) and Cu(II) was very rapid in the initial stage of the process, and more than 90 % ions was removed during the first 20 min when the initial Pb(II) and Cu(II) concentration was 2.5 mM. Experimental kinetic data were in accordance with pseudo-second order kinetic model. In the extensive literature review presented in [3] it was also found that in most cases the sorption of metal ions on inorganic solids follows the second order kinetics. Applicability of water deironing residuals for the removal of heavy metals in the batch systems has been confirmed by X-ray fluorescence analysis of solid sorbent after the heavy metal removal procedure. According to the experimental results the amorphous waste could be utilized for the treatment of polluted water without any pretreatment procedure.

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SYNTHESIS AND EFFICIENCY EVALUATION OF PHENOTHIAZINE AND CARBAZOLE-BASED DERIVATIVES IN *SALMONELLA ENTERICA*

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Antimicrobial resistance is a worldwide problem in human and veterinary medicine. Commonly, an extensive use of antimicrobials that leads to the dissemination of resistant bacteria and resistance genes in animals and humans [1]. The appearance of multiple resistant bacteria of human and veterinary origin is probably accompanied by co-contamination of the environment apparently leading to a great health concern [2]. As in the hospital environment, the agricultural use of antimicrobials agents selects for antibiotic resistance. These antimicrobial drugs from both hospital and agricultural sources can persist in soil or aquatic environments, and these compounds may affect the treatment of human diseases [3]. In fact, most antimicrobial agents are produced by strains of fungi and bacteria that occur naturally in all environments [4].

Nowadays antibiotic resistance seems inevitable. Over the years, many different solutions have been proposed to solve this problem.

As the ability to pump antibiotics out of cells is a common feature of most environmental microbes and their pathogenic relatives and is the most widespread form of resistance to most classes of antibiotics that is why it is very important to discover molecules inhibiting efflux pumps as well as to reveal the inhibition mechanisms. There is another possibility to investigate similar substances as competitors of antibiotics.

Derivatives of carbazole and phenothiazine could be considered as potential efflux pump inhibitors or substrates. For many years phenoathiazine has been used in veterinary medicine as an antihelminic drug. These compounds having amino alkyl side chain connected to the nitrogen atom are playing crucial role in medicinal chemistry. The investigation of substituted 10*H*-phenothiazines has strong growth during the last years because of a wide range of applications. Such derivatives are widely employed as antibacterial, antiviral, anti-inflammatory, anticancer, sedatives or tranquilizers agents. The slight change in the structure of these compounds causes distinguishable difference in their biological activities. Carbazole is also heterocyclic compound with two benzene rings linked in a tricyclic system through nitrogen atom and also could be employed as biological active compound.

In this work we have synthesized phenothiazine and carbazole-based molecules and studied their interaction with efflux pumps in *Salmonella enterica* bacteria. Synthesis paths, studies of the synthesized compounds using ethidium bromide agar cartwheel method, data on the minimal inhibitory concentrations of those compounds, and effects of the compounds on accumulation of the efflux indicator tetraphenylphosphonium will be presented.

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NEW VEGETABLE TANNINS FOR LEATHER PROCESSING

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Most of the biological activities of plant extracts can be explained by their high content of polyphenols [1], these species may also become important sources for medicinal remedies as an alternative to chemical drugs, e.g. in antimicrobial therapy. *Potentilla erecta (L.) Raeusch* traditionally is used for inflammations, treatment of wounds, bleeding, dysentery, diarrhoea, inflammatory bowel disease, bacterial, fungal and viral infections, certain forms of cancer, antiseptic for the mouth and throat [2]. *Potentilla* is widespread in Baltic States [3].

The leather tanning technology, known as vegetable tanning, was during centuries the dominant leather making process in Europe until it has gradually been replaced by chromium mineral tanning by the end of the 19th century [4]. Still, until nowadays the vegetable tannins have been considered as a suitable eco-friendly option to replace or diminish chromium compounds use in tanning process.

Unfortunately, the vegetable sources with importance for leather tanning is limited in number of plant materials [5]. *Potentilla* is considered as tannin-rich plant [6]. It is estimated that tannins content in *Potentilla erecta (L.) Raeusch* is approx. 15-22% [7]. So, its use for leather tanning could be very promising.

The results of present study have shown that *Potentilla erecta (L.) Raeusch* could be the characterized as potential tannin rich plant source for leather tanning industry. The results have shown that extracts of *Potentilla* mainly contains condensed tannins, but also some amounts of hydrolysable tannins are present.

The analysis of prepared *Potentilla* extract have shown that the radices of *Potentilla* consist from 24.5 % of tannins and 45.2 % of substances is soluble in water. The *Potentilla* extract has comparable tannin content with the commercial tannins as *Ouebracho* and *Chestnut* which are widely used in leather industry. Only amount of non-tannin substances is considerably higher (21.0 %).

Leather tanned with *Potentilla* tannin had low tensile strength (14.6 N/mm^2) and high percentage extension (79.3 %), but tannin content in leather was similar as after tanning with commercial products (*Quebracho* and *Chestnut*). The investigation results lead to assumption that leather tanning process need to be adjusted in further, because *Potentilla* tannin uptake was low: 26.8 %.

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THE DETERMINATION OF BIOLOGICALLY ACTIVE LIPIDS FROM COW COLOSTRUM

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Colostrum is a mammary secretion which has unique benefits for health [1]. The cow colostrum contains a wide range of growth factors, fatty acids, immunoglobulins and antimicrobial peptides [2]. First milking colostrum is especially valuable source of fats, making up about 20-25 % of total solids. Fat plays an important role in energy supply, improve metabolism, protects against microbial infections. The important fat soluble vitamins, as well as some of the immunoglobulins/antibodies stick to the surface of fat particles [3]. Recently, scientists have been interested in appliance of colostrum fat for cosmetic purpose and cell regeneration. So, the aim of research work was to compare the fatty acid content of cow colostrum and milk fats. Fatty acids were determined by gas chromatography with flame ionisation detector. According to obtained chromatograms, 24 out of a possible 37 fatty acids were identified in colostrum fat. The amount of saturated fatty acids (C4:0, C6:0, C8:0, C10:0, C11:0, C12:0, C13:0, C15:0, C18:0, C21:0, C23:0) were observed less in colostrum in comparison with milk. Meanwhile the content of palmitic acid (42.94 %) was observed significant higher in colostrum in comparison with milk (29.83 %). Among monounsaturated fatty acids the oleic acid was dominant in both fats: milk and colostrum (approx. 20.83 %). In colostrum was found polyunsaturated eicosapentaenoic acid and docosahexaenoic acid, whereas in milk these acids were not detected. Due to high content of biologically active compounds such as palmitic acid, and polyunsaturated fatty acids the colostrum fat could be applied in cosmetic production for rebuilding and repairing cellular tissues as well as skin elasticity increasing.

Keywords: cow colostrum fat, milk, fatty acids

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