OPTIMIZATION OF METHODS FOR REMOVING VARIOUS TYPES OF POLLUTIONS FROM MODEL SOLUTIONS AND WASTEWATERS

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The increasing amount of contaminants discharged into the environment as a result of active human activity and intensive development of industry results in development of new efficient physicochemical methods which could be applied for their removal. Particular attention should be paid to textile, metallurgical, agrochemical industry, nuclear power plants – the branches of industries that consume significant amounts of water or/and generate significant quantities of wastewaters containing harmful and toxic substances [1, 2]. Heavy metal ions, dyes, lanthanide ions as well as auxiliary substances (surfactants, salts, bases, acids, reducers, oxidants) are present in such types of wastewaters [3]. Among the physicochemical methods applied for heavy metal ions and dyes removal chemical precipitation (hydroxide, sulfide precipitation, heavy metal chelating precipitation), ion-exchange, adsorption (e.g. activated carbon adsorbents, carbon nanotubes adsorbents, low-cost adsorbents, bioadsorbents), membrane filtration (ultra- or nanofiltration, reverse osmosis, electrodialysis), coagulation–flocculation, flotation, electrochemical methods or combined methods are known and commonly applied [2]. Due to the inherent advantages and limitations of the above-mentioned methods, their optimization is extremely important. In addition, the choice of the removal method depends on the composition and concentration of a pollutant present in the wastewaters.

The aim of this study was to apply the adsorption method and its optimization for removal of toxic heavy metal ions e.g. Cr(VI), Ni(II), Co(II), Zn(II), Cu(II), U(VI), Cd(II), Fe(III), lanthanide ions(III) e.g. La(III), Ce(III) and Nd(III), dyes e.g. C.I. Acid Red 183, C.I. Reactive Blue 21, nickel(II) phthalocyanine-tetrasulfonic acid tetrasodium salt, C.I. Acid Orange 7 (AO7), C.I. Reactive Black 5 (RB5) and C.I. Direct Blue 71 (DB71) from the aqueous solutions and wastewaters using different types of sorbents e.g. Lewatit Mono Plus SR-7, Lewatite MonoPlus TP 220, Lewatite VPOC 1065, Dowex PSR2, Adsorbsia^{TM}As500, biochar, alginates, magnetic sorbents, chitosan/magnetite nanocomposites etc. The kinetic, equilibrium, thermodynamic studies were carried out and the kinetic and isotherm models such as the pseudo-first (PFO) and pseudo-second (PSO) kinetic ones, the intraparticle diffussion model as well as the Langmuir, Freundlich, Tempkin isotherm models etc. were applied. The effects of various parameters (optimization processes), which could influence the adsorption efficiency, were taken into account e.g. mass of sorbent, pH, phase contact time etc. The point of zero charge, pH_{PZC} of the selected sorbents, influence of the initial concentration on the sorption process, maximum sorption capacity, effects of hydrochloric acid concentration, auxiliaries such as sodium sulfate(VI), acetic acid, surfactants, phosphates were determined and/or analyzed. The static and column methods were applied. The obtained results show the efficient sorption of Cr(VI) ions using Dowex PSR-2 and the fast kinetics of Cr(VI) ion sorption. The reduction of Cr(VI) to Cr(III) was confirmed, Cr(III) was present in the solid phase of Dowex PSR-2 in the pH range 1.5-10 [4]. Removal of the dyes AO7, RB5, DB71 by means of Lewatit MonoPlus SR-7 follows the PSO kinetic model, the sorption capacities were the highest for the RB5 dye - 957.2 mg/g (AO7 - 713.4 mg/g, DB71 - 850.2 mg/g) and the Langmuir isotherm model shows the best fitting. In the case of DB71 the effects of salts and surfactants on dyes removal were observed. The selectivity series obtained by the static method RB5>DB71>AO7 was different from that determined by the dynamic method AO7>RB5>DB71 toward Lewatit MonoPlus SR-7 and can be presented as follows: AO7 (68 mg/ml)>RB5 (39 mg/ml)>DB71 (0.5 mg/ml). The effect of initial pH of dyes solution on removal efficiency using Lewatit MonoPlus SR-7 was not observed [5]. The sorption of AR183, RB21, NiPc-TSATSS and Cr(VI), Ni(II), Cu(II) on Adsorbsia^{TM}As500 and Lewatit VPOC 1065 shows the highest sorption capacity 816.1 mg/g for AR183 (pH_{PZC}=5.63-TiO_2, pH_{PZC}=2.45-Lewatit VPOC 1065) and the Lewatit VPOC 1065 gives much higher or slightly higher % removal of toxic substances than TiO_2, the Cu(II) sorption was not observed. The reduction of Cr(VI) to Cr(III) was also found. The % removal of heavy metal ions depended on the solution acidity and the sorption capacity for AR183 dropped insignificantly with the NaCl and SDS addition and increased with the increasing CH_3COOH concentration [3]. Sorption of U(VI) in the presence of phosphate was efficient using inulin, the sorption capacity 78 mg/g and applying the Langmuir–Freundlich model. Two $(UO_2)_3(OH)_5H_2PO_4$ and $(UO_2)_3(PO_4)_2$ complexes were responsible for uranium sorption [6]. Lanthanides and heavy metal ions removal on alginates was the largest at pH=5 and the sorbent mass=0.05 g (the maximum amounts of adsorbed metals 37.59 mg/g-La(III), 20.08 mg/g-Cd(II) and 15.09 mg/g-Cu(II). The thermodynamic studies indicate the spontaneous and exothermic process [7].

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STUDIES OF ELECTRODE PROCESSES AND PRECONCENTRATION OF TRACE ELEMENTS AND BIOLOGICALLY ACTIVE COMPOUNDS AND ITS EXPLOITATION FOR ANALYTICAL PURPOSES

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The aim of the study was to show a new application of boron doped diamond electrode (BDDE) for voltammetric determinations. The BDDE was applied for dopamine (DA) and paracetamol (PA) determination with the use of differential pulse voltammetry.

Dopamine (DA) is a neurotransmitter from the catecholamine group playing an important role in the proper functioning of the central nervous system and the renal, hormonal and cardiovascular systems [1]. It plays crucial role in the regulation of cognitive functions (stress, behavior, attention) [2]. Paracetamol (acetaminophen, PA) is one of the most commonly used over-the-counter analgesic and antipyretic drugs. PA taken in therapeutic doses is a very effective and safe drug. However, exceeding the therapeutic doses leads to the accumulation of its toxic metabolites and this can cause hepatotoxicity and nephrotoxicity [3].

The wide linear range of calibration graphs: from 1×10^{-7} to 5×10^{-4} mol L^{-1} for DA and from 1×10^{-7} to 2×10^{-4} mol L^{-1} for PA, and very low detection limits were achieved at the BDDE, equaling 2.30×10^{-8} mol L^{-1} for DA and 1.35×10^{-8} mol L^{-1} for PA. The proposed sensor was successfully applied for determination of dopamine in urine samples, paracetamol in syrups for children, and for simultaneous determination of paracetamol and dopamine in blood and serum samples. Proposed method is characterized by its simplicity, short time of execution in the result of lack of electrode surface modification, no accumulation stage and simplistic process of sample preparation.

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Nitrates are environmentally ubiquitous due to their widespread application for many industrial, agricultural and domestic purposes. They are widely used in inorganic fertilizers, in production of explosives and for glass making. Nitrates also occur naturally in plants. They are present both in surface waters and groundwater as a consequence of agricultural activity, from waste water treatment and from oxidation of nitrogenous waste products in human and animal excreta. The main source of nitrate exposure for humans other than drinking water is food, in particular vegetables, cured meat, fish and dairy products. The nitrate concentration in vegetables depends on the use of fertilizers and growing conditions. Nitrates are also popular food additives having antimicrobial action. Their addition is officially allowed in such foodstuffs as meat products, cheese and fish. The toxicity of nitrate to humans is attributable to its reduction to nitrite. Nitrites can cause the oxidation of normal haemoglobin (Hb) to metHb which is unable to transport oxygen to tissues. Moreover, the interaction between nitrite and secondary amines led to the formation of N-nitroso compounds associated with gastric cancer. Taking into account the above information analytical control of nitrate concentration in food especially in vegetables and in drinking water is important.

Potentiometry with ion-selective electrodes (ISEs) allows one to determine directly free ion concentration in various water samples [1-3]. The most attractive features of this technique are low cost and minimum analysis time together with portability of the device, non-destruction of the sample and minimum sample pretreatment. Among various ISEs constructions the solid contact solvent polymeric membrane ISEs (SCISEs) turned out to be reliable potentiometric-sensing devices with unique advantages including small size, simple construction, low cost of production.

The aim of this work was application of multiwalled carbon nanotubes (MWCNTs) to the construction of solid contact ion-selective electrode sensitive to nitrate ions. MWCNTs are suitable to acts as an ion-to-electron transducer due to their high electronic conductivity and large redox capacitance. Moreover their hydrofobicity prevents the formation of interfacial water layer between an ion-selective membrane and electric contact. Solid contact ISEs based on carbon nanomaterials possess high potential stability and reproducibility and exhibited resistance to light, redox interferences and presence of gases such as CO_2 or O_2 [4].

In the present research nitrate selective electrodes based on glassy carbon electrode and gold electrode as internal electrode were constructed and studied. The MWCNTs were directly dispersed in the polymeric membrane thanks to this membrane preparation was one step. Such method is simpler and faster and allows to avoid the formation of water layer between internal electrode and ion sensitive membrane. The optimal composition of the nitrate ion-selective membrane was as follows (% wt.): 33% PVC, 61 % NPOE (2-nitrophenyl octyl ether), 5% trihexyltetradecylphosphonim chloride (THTDPCl) and 1% MWCNTs.

Before the electrode preparation the internal electrodes were polished with 0.3 µm Al_2O_3 powder in the case of glassy carbon electrode and with fine-grained sandpaperand in the case of gold electrode and well rinsed with water and THF. The membrane components were weighed and thoroughly mixed and dissolved in PHF. Then the mixture was applied on an internal electrode by drop-casting 3 x 25 µl of the membrane cocktail and left to dry. For comparison purpose another solid contact electrode so called coated disc electrode having the same construction and containing no MWCNTs in the membrane were constructed and studied.

The potentiometric response of studied nitrate electrodes was determined in the sodium nitrate solutions of the concentration $1x10^{-1}$-$1x10^{-7}$ mol L^{-1}. From the results of these measurements the analytical parameters of individual sensors were determined and summarized in Table.

Table 1. Comparison of analytical parameters of nitrate solid contact electrodes

Parameter	GC/(CNTs) NO_3^--ISM	GC/NO_3^--ISM	Au/(CNTs) NO_3^--ISM	Au/NO_3^--ISM
Characteristic slope mV/pa	58.3	56,7	56.9	52.4
Detection limit, mol L^{-1}	$3,8\times10^{-7}$	$5,1\times10^{-6}$	$1,8\times10^{-6}$	$2,4\times10^{-5}$
Measuring range, mol L^{-1}	1.0×10^{-6}-1.0×10^{-1}	1.0×10^{-5}-1.0×10^{-1}	5.0×10^{-6}-1.0×10^{-1}	5.0×10^{-5}-$1,0\times10^{-2}$
Response time, s	3-8	10-20	3-8	10-20
Potential drift, mV/dzień	0.54	7.5	0.11	6.1

As it can be seen in Table 1 electrodes containing MWCNTs as additional membrane component exhibited better analytical parameters than electrodes having conventional membrane composition. Presence of carbon nanotubes in the ion-selective membrane cause facilitates the ion to electron transduction processes at the interface between inner electrode and ion-sensitive membrane. In consequence electrodes with modified membrane exhibited lower detection limit, wider measuring range, shorter response time and higher potential stability than electrodes without carbon nanotubes in the membrane. ..

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The purine nucleoside adenosine plays a neuromodulatory role in the brain and is directly involved in a number of functions including metabolism and DNA methylation. Adenosine molecule contains $–NH_2$ group which indicate its comlexing power. Aromatic character of adenosine allows predicting on mechanism of its adsorption on electrode surface. Adsorption properties of adenosine in acetic buffer solutions pH =4 and pH=6 were determined based on experimental data derived from differential capacity of double layer, zero charge potential and surface tension at zero charge potential. Curves of diffential capacity of double layer in the absence of adenosine have other course in buffer solution of pH = 4 in comparison to buffer solution of pH= 6. It is due to different composition of studied solutions. Adsorption in the solution of pH =4 concern mainly CH_3COOH molecules, whereas in buffer of pH=6 concern CH_3COO^- ions.

Analysis of dependencies C=f(E) in solutions with addition of adenosine indicate apparent decrease of differential capacity in relations to base electrolytes related to significant adsorption of adenosine on the electrode surface. In the lower electrode potentials adenosine molecules undergo desorption, therefore in this potential region specific „hump" is formed, its height arises with increase of adenosine concentration.

Shift of zero charge values in both base electrolytes into more negative potentials with addition of adenosine (Tab. 1) indicates adenosine molecules orientation with its aromatic ring directed to mercury electrode surface. Based on collected data adsorption parameters as: maximum adsorption potential, E_{max} and maximum adsorption charge, σ_{max} were determined. Possibility of precise determination of E_{max} and σ_{max} parameters indicates physical character of adenosine adsorption.

Table 1. The values of the zero charge potentials $-E_z$/mV vs Ag/AgCl electrode, the values of surface tension γ_z/mN·m^{-1} at E_z and standard rate constant k_s/cm·s^{-1} for the studied systems.

c [mol/L]	$-E_z$		γ_z		k_s	
	pH=4	pH=6	pH=4	pH=6	pH=4	pH=6
0	0.38	0.42	460	472	$3.59 \cdot 10^{-3}$	$4.11 \cdot 10^{-3}$
$1.0 \cdot 10^{-4}$	0.39	0.42	462	465	-	$6.02 \cdot 10^{-3}$
$3.0 \cdot 10^{-4}$	0.39	0.42	457	464	-	-
$5.0 \cdot 10^{-4}$	0.40	0.42	452	460	$2.65 \cdot 10^{-3}$	$6.11 \cdot 10^{-3}$
$8.0 \cdot 10^{-4}$	0.41	0.43	451	456	-	-
$9.0 \cdot 10^{-4}$	0.41	0.43	450	456	-	-
$1.0 \cdot 10^{-3}$	0.41	0.43	445	455	$3.69 \cdot 10^{-3}$	$6.06 \cdot 10^{-3}$
$2.0 \cdot 10^{-3}$	0.43	0.45	441	455	-	-
$3.0 \cdot 10^{-3}$	0.44	0.47	440	454	$6.61 \cdot 10^{-3}$	-
$5.0 \cdot 10^{-3}$	-	-	-	-	$8.98 \cdot 10^{-3}$	$6.09 \cdot 10^{-3}$

To appoint the influence of adenosine adsorption on reduction kinetics of Zn^{2+} ions on mercury electrode voltamperometric curves CV and polarograms DC in solutions with Zn^{2+} in both studied buffers in absence and in presence of selected adenosine concentrations were recorded.

Values of standard rate constants for Zn^{2+} electroreduction in tested experimental systems were calculated based on recorded data. It was fund that in acetic buffer of pH = 4, adenosine at $5\cdot10^{-4}$ mol/L concentration, inhibited electroreduction of Zn^{2+} ions on mercury electrode. The increase of adenosine concentrations resulted in progressive increase of k_s, values which indicated rise of catalytic properties of adenosine. In acetic buffer of pH = 6 adenosine accelerated electrons exchange between Zn^{2+} and electrode in all tested concentrations. Comparison of respective values of k_s for both buffer solutions confirms stronger catalytic effect of adenosine in lower pH. Effect of inhibition at low adenosine concentration in acetic buffer pH=4 can be explained by blocking mercury electrode by flat adsorbed adenosine molecules. Such flat placed molecules on electrode surface hinder the ions of depolarizer access to electrode and slow down the rate of electron transfer. Increased concentration of adenosine in acetic buffer of pH=4 causes change in adenosine orientation to diagonal or perpendicular and promote electron transfer. Catalytic properties of adenosine can be explained by both the labile binding of adenosine by the mercury electrode surface and formation of an active complex between Zn^{2+} ions and adenosine molecule. Such complex can act as a bridge which facilitates the electron exchange between electrode and ions of depolarizer. [1].

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The knowledge of the organic substances effect on the electrode reaction rate is of significant importance in the analytics as well as elaboration of technological and pharmacological characteristics. It was found that an essential role in the electrode process acceleration is played by the ability of organic substance, undergoing adsorption on the electrode, to form complexes with the depolarizer in the circum electrode layer and location of the depolarizer reduction potential in the area of labile adsorption equilibrium of the organic substance [1 – 2]. The previous studies proved a significant effect of water activity, some amino acids as well as change of the protonation of the amino acids on mechanism and kinetics of Bi(III) ions electroreduction, which developed the interpretation of the „cap – pair" effect mechanism [3 – 4].

Ethionine plays an important role in maintaining of homeostasis in living organism. Ethionine has a very destructive influence on the livers of living organisms and disrupts the activity of many enzymes. It is a strongly carcinogenic metabolite contributing to the development of most types of human cancer [5].

The effects of ethionine protonation on the kinetics and the mechanism of multi-step process of Bi(III) electroreduction in chlorates(VII) with varying water activity has been studied. The methodology of the study is based on electrochemical methods: DC polarography, square wave voltammetry SWV, cyclic voltammetry CV and electrochemical impedance spectroscopy EIS.

The multistep Bi(III) electroreduction process is controlled by the kinetics of the formation of active complexes Bi – ethionine on the electrode surface. The largest catalytic activity is observed for the chlorates(VII) solutions of great water activity [6]. According to the Marcus theory [3] the composition of active complexes after subsequent electron transfers is changed, which results from change in the solvatation shell of the ion after a partial loss of charge.

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Ruthenium due to its unique physical and chemical properties is widely used in the electrochemical, electrical, chemical, metallurgical industry as well as in medicine. The addition of metal to the alloys causes a significant increase of the hardness and resistance of jewelry and dental products. Due to its catalytic properties, ruthenium is also used during organic syntheses. Some ruthenium compounds have anti-cancer effects and can be successfully used as an alternative to the platinum anticancer drugs. Therefore, the demand for this metal is increasing. Ruthenium is mainly obtained from by-products of metal processing and from precious metal ores. Another source of ruthenium are e-waste.

The common use of ruthenium incline to develop of new selective and sensitive methods of its determination. Due to the low concentration of ruthenium in environmental samples the preconcentration of analyte before determination is often necessary. It can be realized by the application of solid phase extraction (SPE). SPE can be also applied as a tool for ruthenium recycling from waste.

Among the wide range of sorbents silica based ordered mesoporous materials characterized by mechanical and chemical stability, as well as simplicity of surface modification, seem to be especially attractive. Large surface area, thick pore walls and high pore volume of SBA-15 cause the material ideal inorganic support for modification with organic functional groups. The wide possibilities of modification allow to create material exhibiting adsorption affinity towards particular ions. However, organic groups present onto the silica surface are usually not enough selective and, besides Ru(III) ions, bind various ions of similar properties. In order to improve the selectivity and adsorption capacity of material the introduction of ion-imprinting adsorption centres is necessary. In order to synthesize ion-imprinted organosilica mesoporous material imprinted ions are added to the reaction mixture and form complex with organic groups. As the result organosilica hybrid material containing inorganic ions is obtained. The specific bonding sites are generated after the extraction of imprinted ions.

In the present work, Ru(III)-imprinted thio-functionalized SBA-15 and analogous material without imprinting were synthesized and compared as sorbents of Ru(III) ions. The basic parameters affecting the adsorption of ruthenium ions onto Ru(III)-imprinted modified SBA-15 such as contact time and pH of the solution were studied and optimized.

The Ru(III) ion imprinted thio-functionalized SBA-15 was obtained by using of sol-gel one-pot route synthesis procedure. Firstly, 2 g of P123 was dissolved in 72 ml of 1.6 mol/L HCl under vigorous stirring at 40°C. After 8 h 15 mg of ruthenium(III) chloride, 18 mmol of tetraethoxysilane (TEOS) and 2 mmol of (3-mercaptopropyl)trimethoxysilane (MPTMS) were added to this solution. The resulting mixture was stirred at 40°C for 24 h and aged at 100°C for next 48 h. The obtained solids were thoroughly washed with deionized water, filtered and dried at 100°C. Pluronic123 was removed by three-time extraction with acidified ethanol

(99.8%) at 78°C. Finally the template Ru(III) ions were removed from the material using 0.5 mol/L thiourea in 5% HCl. For comparison, the non-imprinted material was also prepared and treated under identical conditions without adding Ru(III) ions. The ion imprinted and non-ion imprinted sorbents were named as Ru(III)MPTMS and MPTMS, respectively. In the case of Ru(III)MPTMS the removal of imprinted ions was not total. Before the extraction of Ru(III) by thiourea solution the content of ruthenium was 2.57 μg/g, whereas after the thiourea treatment it decreased to 2.07 μg/g. The remnants of ruthenium could not be removed by extraction.

Adsorption studies were carried out using adsorption systems containing 5 mg of solid and 5 mL of Ru(III) solution. The initial pH value of Ru(III) solutions was 1.0. For pH higher than 1.5 the concentration of Ru(III) in the bulk decreased during storage. In Fig.1. adsorption isotherms of Ru(III) onto synthesized materials are shown. The maximum adsorption capacity of Ru(III) was 28 and 19 mg/g for Ru(III)MPTMS and MPTMS, respectively. The initial runs of these isotherms were different. In the case of Ru(III)MPTMS material for initial concentrations of Ru(III) lower than 5 mg/L the quantitative adsorption was observed, which does not take place in adsorption systems containing MPTMS sorbent.

The relation describing the influence of shaking time on the adsorption of Ru(III) is presented in Fig.2. For both studied sorbents adsorption is slow, the equilibrium state is achieved after 24 hours. However for sorbent Ru(III)MPTMS in the first 6 hours 82% of the equilibrium adsorption value is achieved, whereas for MPTMS only 56%. The presence of ion imprinted sites in Ru(III)MPTMS leads to the increase of the adsorption capacity and adsorption rate.

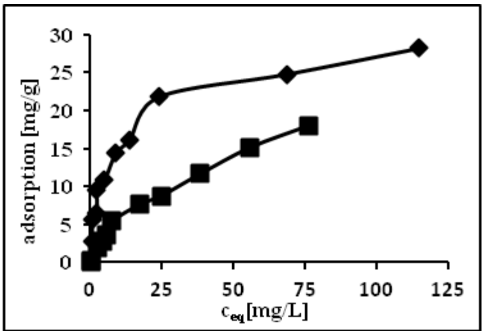

Fig.1. Adsorption isotherms of Ru(III) onto ♦ Ru(III)MPTMS and ■ MPTMS; t= 24h, T = 25°C.

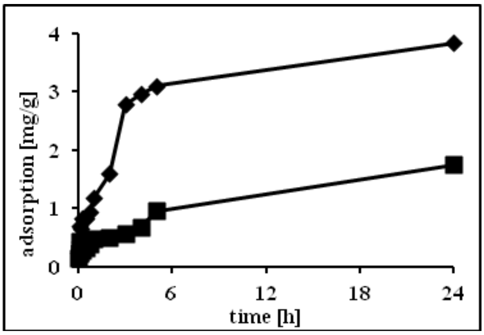

Fig.2. Adsorption kinetics of Ru(III) onto ♦ Ru(III)MPTMS and ■ MPTMS; c_{Ru}= 4 mg/L, pH =1

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Cd(II) and Pb(II) occur in close association in nature and are known to be hazardous environmental pollutants with toxic effects on living organisms. These metal ions are added to air, water and soil as a consequence of human activity. There has been growing concern about heavy metal contamination which led to increasing need to monitor trace metals in a variety of samples of environmental, clinical and industrial origin. Anodic stripping voltammetry (ASV) has been proved to be a useful and versatile technique for the determination of metal ions on trace levels thanks to the 'built-in' preconcentration step during which the target metals are deposited on the surface of working electrode. The electrodes made from various materials such as mercury, bismuth, antimony or tin were used for determination of Cd(II) and Pb(II). Among them mercury and bismuth were most frequently used [1-4]. Taking into account lower toxicity of bismuth and the fact that there is no necessity of removing oxygen from the solution in the case of application of bismuth electrodes new procedures for determination of Cd(II) and Pb(II) ions with the use of these electrodes by ASV were most often reported. Among many different voltammetric sensors, microelectrodes offers a lot of advantages. Firstly, microelectrodes give the opportunity to analyze samples with very small volumes, from diluted solutions and solutions with organic solvent. Next, microelectrodes utilization gives a possibility of miniaturization of measurements arrangement.

In these investigations a novel procedure which combines the advantages of anodic stripping voltammetry with those of the use a bismuth microelectrode activated with an application of a negatine step potential is demonstrated. Such an electrode activation led to a decrease of background current. The fact that there is no need to added bismuth ions to the supporting electrolyte in order to plate bismuth film on the surface of working electrode makes proposed sensor environmentally friendly.

Standard procedure of measurements

A given volume of the sample was transferred into the voltammetric cell and then 1000 μL of 1 mol L^{-1} acetate buffer was added and adjusted to the volume of 10 mL with purified water. To begin with the activation step was performed at potential of -2.5 V within 1 s. Then deposition step was performed using a bismuth microelectrode at a potential of -0.85 V for 120 s from stirred solution. After equilibration time of 5 s a square wave voltammogram (frequency of 100 Hz) was recorded while the potential was changed in the range from -1.0 to -0.2 V. The measurements were performed without solution deoxygenation.

Results and discussion

The calibration graph for Cd(II) for an accumulation time of 120 s was linear in the range from 5×10^{-8} to 2×10^{-6} mol L^{-1} and obeyed the equation $y = 0.0047x - 0.0321$, where y and x are the peak current (nA) and Cd(II) concentration (nmol L^{-1}), respectively. The linear correlation coefficient r was 0.9985. The relative standard deviation (RSD) from five determinations of cadmium at a concentration of 5×10^{-8} mol L^{-1} was 4.5 %.

The calibration graph for Pb(II) for an accumulation time of 120 s was linear in the range from 1×10^{-8} to 2×10^{-6} mol L^{-1} and obeyed the equation $y = 0.0207x – 1.0421$. The linear correlation coefficient r was 0.9927. The relative standard deviation (RSD) from five determinations of lead at a concentration of 1×10^{-8} mol L^{-1} was 4.8 %.

The interference of foreign ions was studied for a solution containing Cd(II) and Pb(II) ions at a concentration of 2×10^{-7} mol L^{-1} and the deposition time of 120 s. It was observed that 100-fold excess of V(V), Mn(II), Fe(III), Cu(II) and Ni(II) does not influence Cd and Pb peak currents. Interferences occurring only in the presence of 100-fold excess of Mo(VI).

The usefulness of the present method was evaluated by determining Cd(II) and Pb(II) in certified reference material SPS-WW1, a synthetic waste water sample. Cadmium content in this material was below the detection limit of the developed procedure and so the correctness of this procedure was checked by determination of lead ions. The determination was carried out using the method of standard additions. The obtained results of 114 µg/L with the standard deviation of 5.1% are in accordance with the certified value of 100,0±0.5 µg/L. The obtained results confirm the possibility of Pb(II) determination in real water samples with the use of the proposed procedure.

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STUDIES OF INTERIOR PHENOMENA AT DIFFERENT INTERFACES INCLUDING SURFACTANTS AND BIOSURFACTANTS SYSTEMS

SURFACE AND AGGREGATION PROPERTIES OF CHOSEN BIOSURFACTANT

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DEPARTMENT OF INTERFACIAL PHENOMENA

Surfactants because of their amphiphilic molecules show specific properties [1]. They decrease the water-air and water-oil interface tension and change the solid-water one by the adsorption on these interfaces as well as form aggregates at proper concentration called critical micelle concentration (CMC). These two properties decide that surfactants are widely used for industrial applications and every day live [2,3]. Despite of many advantageous properties, production of surfactants in the amount of several dozen million tons yearly causes a rapid increase of their concentration in sewages, surface waters and soil which makes a serious ecological problem. The proecological tendencies in the surfactants area aim at reduction of poorly biodegradable compounds production and their gradual replacement by the surfactants prepared by chemical syntheses but based on natural substrates (semisynthetic surfactants) or natural compound (biosurfactants) [2,3]. Therefore, the biosurfactants are more frequently applied as supplements of the synthetic surfactants [1-3]. They have advantages over their synthetic counterparts because are biodegradable, have low toxicity, are effective at extreme temperatures or pH values and show better environmental compatibility [2,3]. Unfortunately such properties as adsorption activity and volumetric properties of biosurfactants in aqueous media are not complete known and the practical applications of biosurfactants repeatedly overtake the systematic studies on their properties.

Due to the above mentioned facts, a lack or unsystematic literature data according to micellization and adsorption process of biosurfactants as well as many discrepancies between the presented physicochemical parameters values the purpose of our studies was to determine the thermodynamic parameters of the chosen anionic biosurfactant (sodium cholate (NaC)) adsorption the water-air interface and aggregation process. For this purpose the measurements of equilibrium surface tension, specific conductivity, density, dynamic viscosity and pyrene fluorescence intensity of the aqueous solutions of sodium cholate at 298 K were made.

The above mentioned methods allows us to describe the CMC for the NaC. The values of CMC determined from the surface tension, specific conductivity, density, dynamic viscosity and pyrene fluorescence intensity measurements were equal to 9, 16.5, 10, 5 and 7.5 mM, respectively. The obtained CMC values of studied surfactant are in the range of those reported in the literature [1].

In order to calculate the amount of studied surfactants adsorbed per unit area at the air-water interface (the Gibbs surface excess concentration of surfactant at the water-air interface (Γ_S)), the measured equilibrium surface tension data were treated in terms of the Gibbs adsorption equation [1].

This equation for the dilute solutions of surfactants (10^{-2} M/dm^3 or less) is as follows [1]:

$$\Gamma_S = -\frac{C_S}{nRT}\left(\frac{\partial \gamma_{LV}}{\partial C_S}\right)_T = -\frac{1}{nRT}\left(\frac{\partial \gamma_{LV}}{\partial \ln C_S}\right)_T = -\frac{1}{2.303nRT}\left(\frac{\partial \gamma_{LV}}{\partial \log C_S}\right)_T \qquad (1)$$

where: R is the gas constant, T is the absolute temperature, γ_{LV} is the surfactant solution surface tension, C_S is the concentration of surfactant and n is the constant which depends on the kind of surfactant (for nonionic surfactants it is equal to 1).

Γ_S of the studied surfactant corresponding to the unsaturated adsorption monolayer at the water-air interface was determined from Eq. (1) and using the second order polynomial equation describing the relationship between γ_{LV} and C_S of a given surfactant at a given temperature. The maximal Γ_S value ($\Gamma_S^{\max}$) corresponding to the saturated adsorption monolayer of NaC at the water-air interface was determined from the linear dependence of γ_{LV} vs. $\log C_S$. Based on the dependence between Γ_S and C_S for the NaC the standard Gibbs free energy (ΔG^0_{ads}) of its adsorption at the water-air interface at 298 K was determined applying the Langmuir equation. It occurs that the calculated ΔG^0_{ads} values are constant only in the range of NaC concentration corresponding to the unsaturated monolayer at the water-air interface.

An aggregation process is strongly connected with the changes of the volumetric properties such as, for example the density and partial molar volumes ($\bar{V}_M$) of surfactants in solution [1]. The observed increase of the partial molar volume at the NaC concentration lower than its CMC is probably connected with the formation of small aggregates of surfactant molecules before the CMC is reached. Further increase of the partial molar volumes can suggest that probably the size and shape of surfactant micelles change continuously with the increase of the surfactant concentration in solution, or because of the water structure modification around the surfactant molecule.

Summarizing, we can state that the changes in the behaviour of the surfactant molecules in the bulk phase resulting from the changes in the molecules structure strongly influence also their adsorption properties at air–water interface.

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STUDIES OF INTERIOR PHENOMENA AT DIFFERENT INTERFACES INCLUDING SURFACTANTS AND BIOSURFACTANTS SYSTEMS

SURFACE PROPERTIES OF GELATIN LAYERS DEPOSITION ON PLASMA MODIFIED GLASS

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DEPARTMENT OF INTERFACIAL PHENOMENA

Plasma surface modification is an effective and economical surface treatment technique for many materials and of growing interest in biomedical engineering and food technology [1]. It is environmentally friendly, which is a very important aspect nowadays [2]. Plasma meets the requirements for non-thermal methods therefore it is used for food preservation and decontamination of food packages.

The aim of the study was to use the plasma for glass disinfection thereby the effect of modification of the package surface on the properties of stored food, in this case gelatin. Gelatin is one of the most popular gelling agents widely used in food industry as a thickening agent in gravy and desserts, a stabilizer in ice cream and a texturizer in confectionaries, salad dressing as well as a gelling agent. In addition, it is employed as food foams [3]. Moreover, gelatin has wide applications in many fields, such as pharmaceutical, cosmetic, biomedical materials and other industries, owing to its unique chemical and physical properties.

Gel layers of food gelatin, which were obtained from the solutions of gelatin sol at the concentrations of 3, 4 and 5% after the gelation process on the glass plates previously treated for 60 s by cold plasma using argon and air, were used for the investigation. Wetting and energetic properties of gelatin films on both sides were determined, i.e. on the outer side (S1) and on the inner side previously attached to the glass support (S2) (Fig. 1). Optical profilometry was used for the characterization of the gels surface topography.

Fig. 1. Diagram of the contact angle measurements on the surface of the gelatin layer on the glass and on the surface of the gelatin film detached from the glass.

Measurements of advancing and receding contact angles of the two liquids: polar water and non-polar diiodomethane on the gels layers on both sides were made which allowed describing their hydrophilic-hydrophobic character before and after treatment of the substrate with two types of plasma. The surface free energy was determined applying the contact angle hysteresis of probe liquids (CAH approach) [4]. It was found that the surface properties of gel layers depend upon the concentration of gelatin and type of plasma used for modification of glass support. It is manifested in the changes of contact angles of probing liquids, surface free energy and topography of both sides of gel layers. As an example, Fig. 2 shows the contact angles of water measured on the gel layers deposited on the glass and that modified by argon and air plasma (S1) as well as on the gels detached from the glass support (S2).

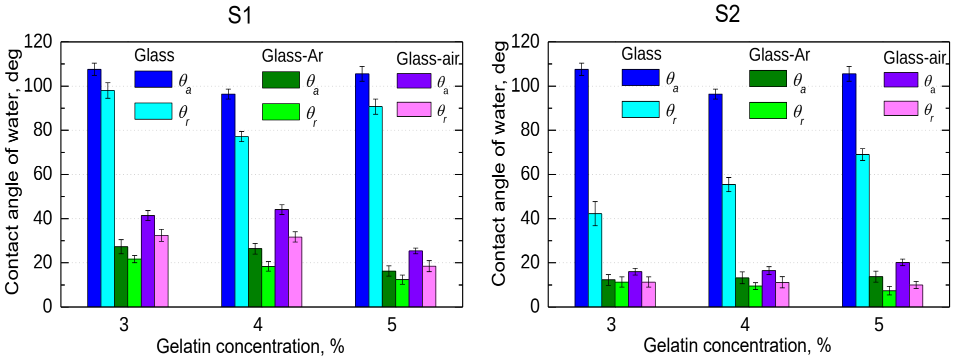

Fig. 2. Advancing and receding contact angles of water on the gel layers deposited on the glass and that treated by argon and air plasma (S1) as well as on the gel layers detached from the glass support (S2).

As can be seen reproducibility of the contact angles is very good (vertical bars show standard deviations). Analysing the results in Fig. 2 it can be seen that treatment of the glass surface with Ar and air plasma significantly increases the hydrophilic properties of the both sides (S1 and S2) of gel films. Greater changes in wettability were observed for the gel surfaces detached from the modified glass support (S2). The use of argon plasma for activation of the substrate affects significantly the increase in gel films polarity which is evidenced in the increase in their surface free energy.

For all studied systems the surface roughness parameters characterizing topography have been determined. It was found that the gel surfaces become rougher with the plasma treated glass support, regardless which gas was used. Increased roughness of the gels caused a decrease in the contact angles and an increase of surface free energy.

Taking into account the practical aspect, it can be concluded that the increase in the polar nature of gel films will affect their adhesion to the substrate, which is important for storing food products containing gelatin in glass packages whose surface was disinfected with plasma.

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CHROMATOGRAPHIC AND SPECTROSCOPIC PROCEDURES IN ANALYSIS OF ORGANIC, BIOACTIVE COMPOUNDS

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DEPARTAMENT OF CHROMATOGRAPHIC METHODS

Formation of aqueous and alcoholic adducts of curcumin during its extraction. Curcumin is one of the most popular natural polyphenols derived from Curcuma longa L. Its concentration in the dried rhizomes of the plant is estimated to be between 1 and 6% [1]. This compound demonstrates a wide spectrum of properties, especially appreciated in the pharmaceutical and food industries [2]. Due to its antioxidant, anti-inflammatory and antiproliferative properties it has been used as a component of medicaments and dietary supplements [3]. Nowadays curcumin is applied as a coloring, flavoring and preservative agent in foods – e.g. in curry, confectionery, fish sticks breadcrumbs, margarine, processed cheese and spicy rice. In common domestic food preparation, curcumin is used in the form of turmeric and/or spices containing turmeric, the quality of which depends on curcumin concentration.

Most approaches to plant material analysis involve the application of liquid extraction methods for the isolation of substances. Alcohols (methanol or ethanol) and their aqueous solutions are most commonly used for phenolic compounds isolation from plants, also in the analytical aspect. As results from [4,5], high-temperature extraction of some phenolics by alcoholic mixtures with water leads to the formation of many derivatives among which adducts with water and/or alcohol have been identified only recently. Quinine, rutin and chlorogenic acid are good examples of such compounds.

Curcumin is a highly labile compound which, according to the literature [6] may degrade to trans-6-(4′-hydroxy-3′-methoxyphenyl)-2,4-dioxo-5-hexenal, vanillin, ferulic acid and feruloylmethane. The question appears about the possible formation of curcumin adducts with water and alcohol, the more so that such process seems very probable due to the presence of two double bonds in the aliphatic part of curcumin structure.

The performed experiments have proved that curcumin easily transforms also to ketonic/enolic structural isomers and forms adducts with water and alcohols. The formation of the curcumin derivatives is facilitated by an alkaline environment. The identified curcumin derivatives can be mistakenly treated as new components, not naturally present in the plant. This is why the presented results are important for scientists studying the metabolism and/or transformation pathway of biologically active compounds, such as curcumin in Curcuma longa, and they suggest the application of the SSDM method in such research.

Curcumin instability and the formation of its hydroxyl and alcohol derivatives should draw the attention of average consumers and food manufacturers using this compound as the bioactivity of the curcumin derivatives, forming during food production and preparation process, is still unknown. Although a number of scientific papers present perspectives of the curcumin derivatives use as active substances of pharmaceuticals applied in anticancer therapy it is worth noting, however, that the impact of some its derivatives on the human body may also be negative.

The hydroxy and alkoxy curcumin derivatives are new discovered compounds and for this reason their biological activity should be recognized, the more that significant amount of curcumin is transformed to these derivatives.

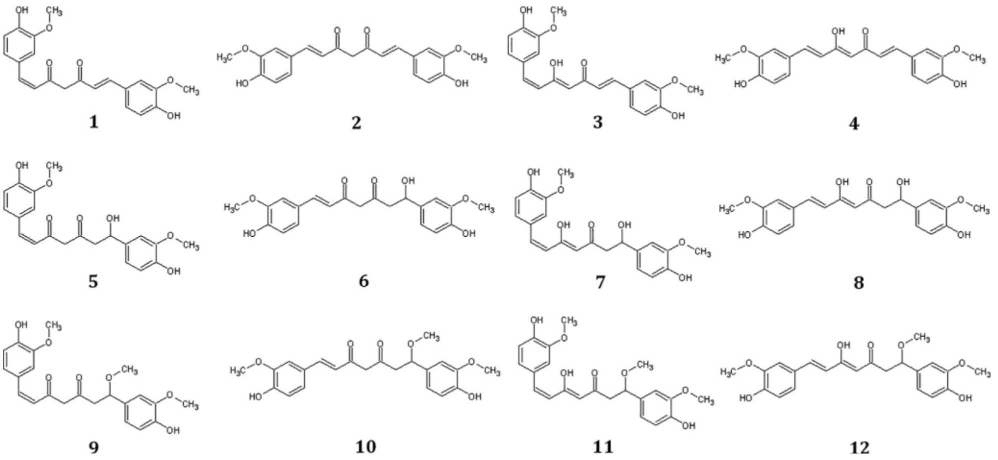

Fig. 1 Molecular structures of the identified curcumin transformation products:
(1Z,6E)-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,6-diene-3,5-dione;
(1E,6E)-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,6-diene-3,5-dione;
(1E,4Z,6Z)-5-hydroxy-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,4,6-trien-3-one;
(1E,4Z,6E)-5-hydroxy-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,4,6-trien-3-one;
(1Z)-7-hydroxy-1,7-bis(4-hydroxy-3-methoxyphenyl)hept-1-ene-3,5-dione;
(1E)-7-hydroxy-1,7-bis(4-hydroxy-3-methoxyphenyl)hept-1-ene-3,5-dione;
(4Z,6Z)-1,5-dihydroxy-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-4,6-dien-3-one
(4Z,6E)-1,5-dihydroxy-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-4,6-dien-3-one
(1Z)-7-methoxy-1,7-bis(4-hydroxy-3-methoxyphenyl)hept-1-ene-3,5-dione;
(1E)-7-methoxy-1,7-bis(4-hydroxy-3-methoxyphenyl)hept-1-ene-3,5-dione;
(4Z,6Z)-5-hydroxy-1-methoxy-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-4,6-dien-3-one;
(4Z,6E)-5-hydroxy-1-methoxy-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-4,6-dien-3-one.

Effect of extraction conditions on chemical differentiation of antifungal properties of walnut's green husk extracts. A growing concern for the environment, a desire to secure health food without synthetic chemical preservatives, as well as the increasing resistance of plant pathogens to fungicides, these are the main reasons searching for a new effective, and more environmentally friendly plant protectants. Recently, much attention has been paid to plant waste materials from agriculture industry as an easily accessible source of many chemical compounds which can be utilized for non-food purposes including the production of cheap natural plant protectants.

Walnut (*Juglans regia* L.) is a tree widely cultivated for its valuable nuts and wood. Every year, the walnut production in the European Union is estimated at approximately 100 thousand of metric tonnes. Walnut's green husk is one of the major wastes produced in walnut cultivations having little use, as yet. Literature data suggests, however, that walnut's green husk can be a valuable source of natural compounds exhibiting many biological activities, including antifungal properties.

The report presents the results of research work on the influence of extraction conditions on chemical compositions and antifungal properties of walnut's green husk extracts. To estimate the antifungal properties of the extracts, the *in vitro* growth inhibitions of the fungus pathogenic to plants (*Rhizoctonia solani*, *Alternaria alternata*, *Phytophthora cactorum*, *Fusarium culmorum*, *Botrytis cinerea*) and to bees (*Ascosphaera apis*) were tested. The inhibition activity of the extracts was compared with the activity of juglone solution applied at the same concentration as that of juglone in the corresponding green husk extracts. To assess the chemical composition of the obtained extracts GC-MS and LC-MS analysis were applied.

The data presented in Fig. 1 prove that the walnut's green husk extracts are very effective natural protectants of plants, and particularly bees. The extraction conditions chemically differentiate the antifungal activity of the extracts. The increase in the extraction temperature leads to a significant reduction in the antifungal activity of the extracts. The change of the extractant type causes a qualitative differentiation of the extracts composition and, as a result, modifies the overall activity of the extracts. The observed changes in the fungicidal properties of the extracts are consistent with the change of juglone content in these extracts. Yet, considering the juglone concentration providing 50 % inhibition in the growth of individual mycelia (see Tab. 1), the observed differentiation of the extracts properties cannot be combined only with the juglone content in these extracts.

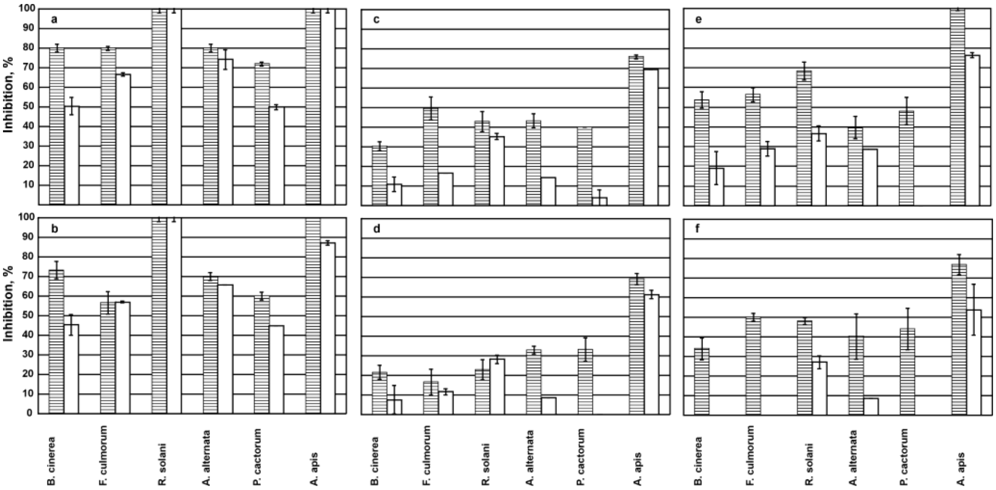

Fig. 1 Inhibition activity of mycelium growth by walnuts' green husk extracts (striped bars) and by juglone (white bars): a) the activity of low-temperature chloroform extracts at concentration 20,000 mg/L and of juglone at concentration 7,980 mg/L; b) the activity of chloroform extracts at concentration 10,000 mg/L and of juglone at concentration 3,990 mg/L; c) the activity of low-temperature ethyl acetate extracts at concentration 20,000 mg/L and of juglone at concentration 420 mg/L; d) the activity of the ethyl acetate extracts at concentration 10,000 mg/L and of juglone at concentration 210 mg/L; e) the activity of high-temperature chloroform extracts (20,000 mg/L) and of juglone (240 mg/L); and f) the activity of high-temperature ethyl acetate extracts (20,000 mg/L) and of juglone solution at concentration 98 mg/L

In the light of the above, we postulate that 1) other components of walnut's green husk extracts, besides juglone, exhibit the inhibition activity of mycelial growth or, 2) the other components of extracts enhance the antifungal properties of juglone, although they do not show this effect themselves. Other words, there is a synergistic antifungal action of the other components of walnut's green husk extracts.

Table 1. Juglone concentration (in [mg/L] ± SD) providing 50 % inhibition (IC_{50}) in the mycelia growth

	Mycelium type					
	B.	***F.***	***R.***	***A.***	***P.***	***A. apis***
IC_{50}	7350 ± 4	2380 ± 0	448 ± 4	1696 ± 1	10360 ± 0	46 ± 13

The results can be used to develop new and safe plant protectants. The fact that this can be done from plant waste materials is an additional value of this work.

Composition and antibacterial activity of Chelidonium majus and its derivative Ukrain^{TM} drug The therapeutic properties of Chelidonium majus L. (the greater celandine) are mostly related to the high content of biologically active isoquinoline alkaloids as: chelidonine, sanguinarine, chelerythrine, berberine, protopine and coptisine and about twenty other alkaloids [7]. C. majus extracts and related drugs have calming, anti-inflammatory, cytotoxic, antispasmodic, cholagogic, analgesic, anticonvulsant, and hypnotic effects. They are used in digestive problems, liver and gallbladder diseases, as well as in therapy of warts and skin cancers.

One of drugs based on C. majus root extract is Ukrain™, known as a semi-synthetic C. majus alkaloid derivative, with strong cytostatic and cytolytic properties [8,9]. It exhibits antymitotic action against tumors, inhibits angiogenesis and stimulates immune system. Ukrain™ is reported to be a selectively toxic against cancer cells, leaving normal cells undamaged. The drug is used for the treatment of pancreatic, colorectal, breast, rectum, bladder, prostate, ovarian and endometrial cancer as well as of leukemia.

In contrast to its well documented antitumor properties there is still much controversy over the drug composition. At first, the Ukrain™ molecule has been reported as C. majus alkaloid – chelidonine – alkylated by thiophosphoric acid with [C66H72N6O15PS]3+ formula and 1522.16 Da molecular mass [8,9]. In mass spectrometric analysis the presence of this semisynthetic thiotepa derivative should be confirmed as m/z 417.2 ion. Various analytical methods like TLC, HPLC, UV-spectroscopy and LC-MS/MS analysis were used to determine Ukrain^{TM} composition. However, the proposed in [8,9] Ukrain™ molecule structure as well as related to it isotopic pattern was not found and confirmed. Recently, it has been reported that Ukrain™ is a mixture of C. majus alkaloids present as underivatized compounds. Eight alkaloids were found; five of them were identified by LC-MS/MS technique (chelidonine, sanguinarine, chelerythrine, protopine, allocryptopine) [10] and three others on the basis of their UV spectrum (homochelidonie, berberine, coptisine) [11].

The aim of this study was to establish composition of Ukrain™ using analytical TLC, semi-preparative TLC and LC-MS/MS techniques bio-guided by TLC-direct bioautography [12]. The results were compared with those obtained for the alkaloid extract of C. majus roots [13,14]. Multi-component composition of Ukrain□ drug was confirmed. TLC-DB indicated activity of sanguinarine, chelidonine, α-homochelidonie and chelerythrine against Gram-positive bacteria Bacillus subtilis. LC-ESI-CID-Q/TOF spectra of compounds present in the fractions isolated from Ukrain^{TM} by means of semi-preparative TLC allowed for the tentative identification of the drug components. The main components are chelerythrine, allocryptopine, sanguinarine and chelidonine while berberine and coptisine are in trace amounts [14]. In contrast, according to the literature [7], chelidonine was found as a main component of C. majus alkaloid root extract together with sanguinarine, coptisine, chelerythrine and berberine which were present almost at the same, as chelidonine, concentration level. The experiments on Ch. majus and Ukrain^{TM} are continued; they concern stability of the drug and other then antibacterial biological activities of both great celandine and Ukrain^{TM}

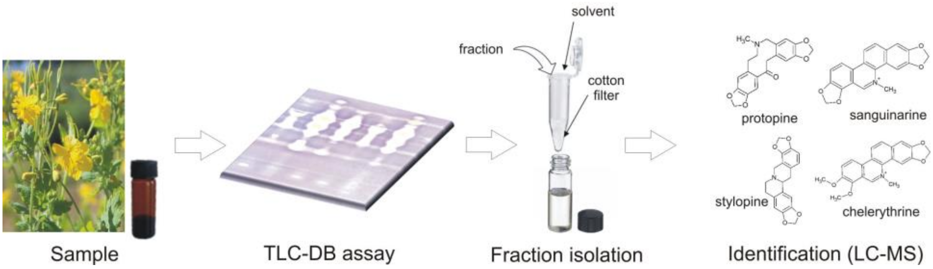

Fig.1 The scheme of TLC-DB and LC-MS of Ukrain™ and *Ch. majus* root extract.

Structural, thermal and energetic characteristics of synthetic active carbons prepared on the basis of ion-exchange resin Amberlite IRC 84 Heavy metals are often used in many industrial, technological and scientific areas. They are present also as a result of deionization of boiler water, usage of water in nuclear power plants and sewage treatment, etc. They are harmful for the natural environment so, removal of them from the environment is an essential problem. The use of ion-exchange resins is an effective way to remove the contaminants. Such spent resins undergo very slow degradation. One of the alternative ways of utilization of such organic wastes is their carbonization and activation in order to prepare active carbons. Some surface impurities can affect yield of carbon material pyrolysis as well as their mechanical and adsorption properties. They ensure stabilization and reinforcement of spatial structure of the initial polymer, to become finally an active site, attractive for different adsorption processes. Whereas synthetic carbons have many advantages due to a set of unique properties: regular spherical shape of the granules, high mechanical strength and sorption capacity as well as high purity.

Properties of active carbons depend on pyrolysis conditions, such as range of temperature, heating rate, atmosphere of carbonization and activation, etc. The porous structure of synthetic active carbons consists of micro- and mesopores of different dimensions and low macropores volume. Traditional characterization (N2 adsorption) has been mainly focused on the determination of specific surface area and the pore size distribution. But synthetic active carbons have also energetic heterogeneity caused by non-uniformity of porous structure and non-homogeneity of chemical composition. Complementary characterization can be made using thermogravimetric analysis (TG), especially carried out under the quasi-isothermal conditions (Q-TG). The aim of the paper was the discussion of possibilities of the N2 adsorption and TG/Q-TG methods to determine the characteristics of synthetic active carbons of different Ca2+ content. Special attention was paid to differentiated porosity and characterization of the interfacial water layers of porous adsorbents. In particular, it studies the effect of Ca2+ ions content and pyrolysis conditions on the structure and properties of hydration layers formed on the complex surfaces of polymer-derived active carbon.

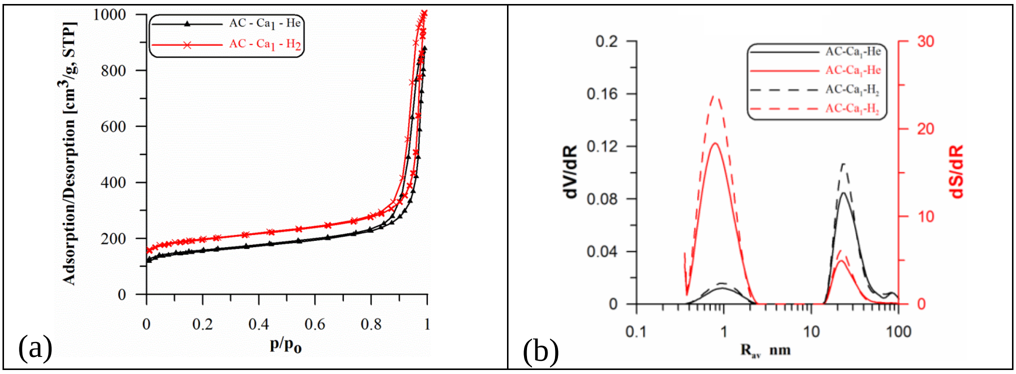

Fig. 1. The isotherms of N2 adsorption/desorption (a) and the curves of distribution of volume (PSDv) and surface (PSDS) of pores (b) for active carbons AC-Ca1–800He and AC-Ca1–800H2

Carbon sorbents were prepared from the ion-exchange acryl resin Amberlite IRC-84 in the calcium form (i.e., 0.5, 1.9 and 5.6% by mass after impregnation in calcium acetate of the concentrations: 0.04 M 0.1 M and 1 M, respectively). Carbonization was performed at 430 °C. After washing, thermal activation (800 °C) was carried out in the helium atmosphere (0.5 dm3 min-1) or using the reaction mixture H2/He of the total gas flow intensity 0.5 dm3 min-1.

It was shown that the surfaces of activated carbons prepared from ion exchange resins in the cationic form are complex with respect to both their texture (characterized by developed micro- and mesoporosity) and chemistry. The Ca2+ ions content influences positively on the structural parameters of carbons (Fig. 1). The best parameters were observed for the carbons of maximal Ca2+ content. It was shown that the atmosphere of pyrolysis has also impact on the obtained carbon characteristics. In the case of carbon of maximal Ca2+ ions content, the addition of H2 (He/H2) to pyrolysis atmosphere is favorable (Fig. 1).

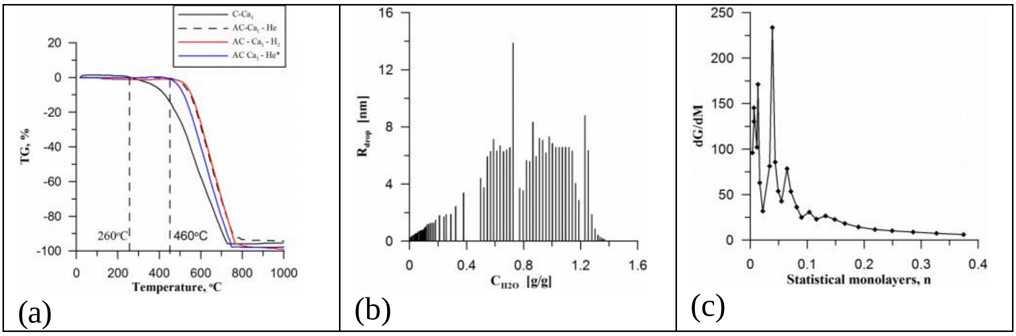

Fig. 2. The course of the TG% curves (a) for the carbons containing 5.6% of Ca2+ ions, the dependences of the effective radius of the evaporating drop on the concentration of the adsorbed water (b) and dG/dM with small filling of the surface with the adsorbed water on the statistical monolayers number (c) for the carbon AC–Ca01–H2

The surfaces of carbon adsorbents possess a complex character. The evidence of this is the increasing of thermal stability (Fig. 2a) and number of adsorption sites (responsible for water adsorption) with the Ca2+ content increasing. These adsorbents show complex porous structures over micro- and mesopore ranges, which causes changes in evaporation of water drop profiles (Fig. 2b), number and structure of water monolayers and energetic characteristics of adsorbed water (Fig. 2c) [15].

Theoretical investigation of water and formaldehyde adsorption on the functionalized carbon surfaces Formaldehyde is one of the most common indoor pollutants, classified as a known human carcinogen. It is frequently released from various paintings, varnishes, and different types of coatings. The problem of formaldehyde removal from the environment becomes a crucial issue to a number of research groups. It seems that the advanced adsorption techniques may be of significant help in this field. In particular, adsorption by activated and functionalized carbons, as described in the literature, may be very promising in this respect [16-18].

As commonly known the effectiveness of the adsorption process is strongly related to the adsorbent porosity and surface chemistry. Introduction of various types of functionalities, especially those nitrogen-based, may significantly improve/magnify the adsorption capacity of different pollutants [19,20]. The electron-rich carbon (graphite) surface is capable of forming only weak intermolecular complexes, e.g., of CH···□ type, with an adsorbate. The binding energy of such a complex is of the order of merely a few kcal/mole, which indicates that it can easily disintegrate at room temperature. However, introduction of various functionalities covalently bonded to the surface, which exhibit specific interactions with adsorbate molecule may lead to significant increase in the binding energies. Such energies are typically not available from the experiment; thus theoretical approach appears to be the method of choice. Methods such as, e.g., DFT are capable of predicting binding energies (as well as many other properties) with remarkable accuracy. Proper prediction of those energies, and therefore the effectiveness of the potential adsorption capabilities of the active spots on the sorbent surface may help to understand the adsorption mechanism and to design the possible routes of the experimental surface modification. The present work focuses on DFT calculations of the adsorption process of water and formaldehyde molecules on the functionalized carbon surfaces.

Significant formaldehyde adsorption is due to the nitrogen-containing groups on the activated carbon surface. In addition, the surface is also abundant in the oxygen-containing groups. Two adsorption mechanisms were investigated using QC calculations: physical sorption (hydrogen bond formation) and chemisorption (here, Mannich reaction). Interaction energies of water and/or formaldehyde molecules with a number of nitrogen-containing groups in the presence of oxygen-containing groups were analyzed. Amine, pyrrole, pyridine, amide and nitro groups (and many others) in the presence of hydroxyl and carboxylic groups were considered. In the following only one selected system, namely adsorbent with one amine and one hydroxyl group will be presented.

In the case of water adsorbate a number of structures were found. The binding energies were calculated to cover the range -2.0 – -6.2 kcal/mole. The negative sign indicates that the complex is more stable than the initial individuals. In the case of formaldehyde the binding energies were slightly less negative. The representative fragments are given in Fig. 1.

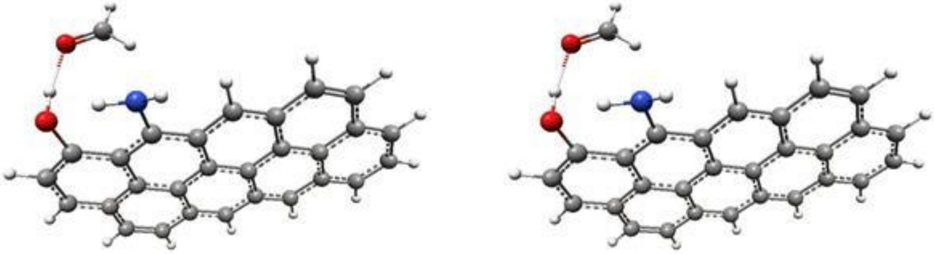

Fig. 1. Representative fragments of functionalized carbon surface with the adsorbed water and formaldehyde molecules

Chemisorption of formaldehyde is accomplished by the formation of the covalent CN bond (Mannich reaction). Carbonyl oxygen atom must be protonated first. This enables carbon atom to approach nitrogen with the simultaneous transfer of amine proton to oxygen. The Mannich reaction mechanism and the energetics (in kcal/mol) is given in Fig. 2.

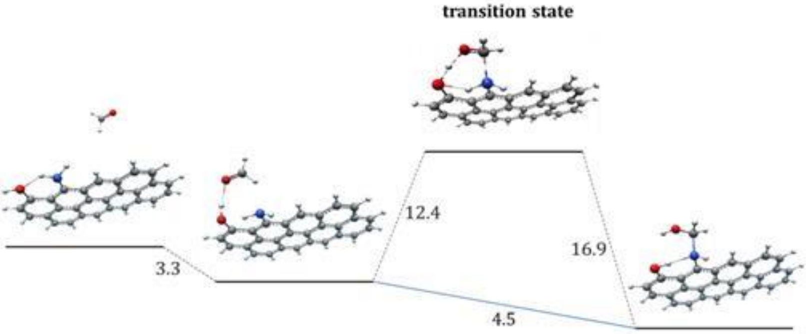

Fig. 2. Mannich reaction mechanism

The following conclusions can be drawn:

1. physical adsorption slightly favors binding of water molecules;
2. chemisorption on account of Mannich reaction provides somewhat better stabilization with the stabilization energy being c.a., -8 kcal/mole (3.3+4.5; cf. Fig. 2);
3. the energy barrier of 12.4 kcal/mole towards the C-N bond formation can be easily overcome at room temperature. The opposite direction is less favorable. Therefore the rate of formaldehyde release should be lower compared to water.

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MONTE CARLO COMPUTER SIMULATIONS OF 2D METAL-ORGANIC STRUCTURES ON A SOLID SURFACES

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2D metal-organic frameworks are the class of coordinative polymers, fabricated mainly with the use of self-assembly of simple organic molecules and metal atoms on solid surfaces [1-4]. Due to their tunable properties and periodic distribution of organic ligands and metal atoms, such molecular structures are fascinating nanomaterials with potential applications in many fields of science like medicine, chemistry and pharmacy [5-6]. However, experimental fabrication of supramolecular structures with pre-defined properties is not an easy task. Nowadays the designing of new metal-organic connections stabilized by coordinate bonds is mainly based on the trial and error method. This is related to the variety of available organic ligands/metal atoms that can be potentially used for this purpose. Moreover, even small changes in the structure of organic ligands can have a profound effect on the morphology of emerging metal-organic connections [7]. Therefore, it is difficult to imagine the future development of supramolecular chemistry without the support of advanced computer modelling. However when large molecular systems are investigated a detailed description of investigated assemblies can be time-consuming or not possible at all. One of the possible solutions is the use of simplified models, in which investigated molecules are mapped on a regular lattice (triangular, square or hexagonal) as a collection of rigid and interconnected segments with properly assigned directional interactions (Fig. 1). This approach can be an especially effective in combination with Monte Carlo (MC) computer simulations [8-12].

In our investigations we use lattice MC simulations as a complementary tool for experimental studies of complex, self-assembled molecular architectures [13-14]. Coarse-grained representation of the real molecules/metal atoms adsorbed on solid substrates give us an opportunity to study molecular assemblies comprising up to few thousands of components, in a relatively short period of time [15]. Above-mentioned approach can reduce significantly the number of test laboratory experiments which are necessary to prepare metal-organic frameworks with precisely defined morphology. Moreover, the findings of our theoretical investigations can be helpful in designing of new functional molecules and programming their interactions to create 2D metal-organic connections with interesting structure and properties.

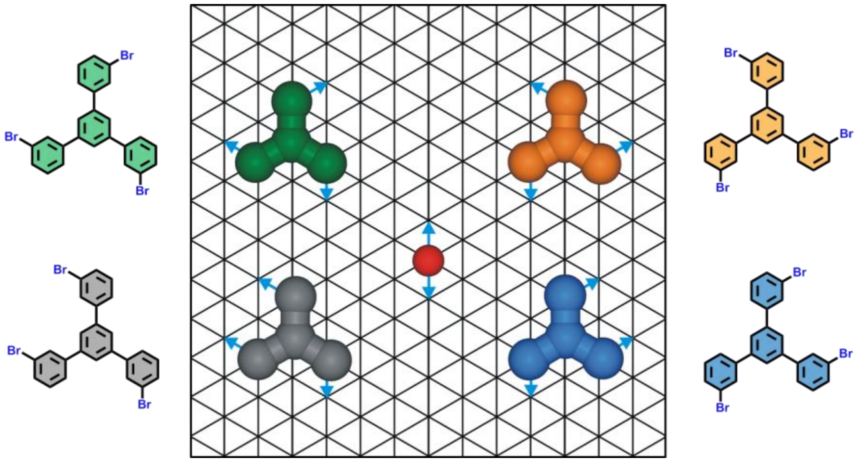

Fig. 1. Schematic representation of surface conformers of conformationally flexible 1,3,5-tris(3-bromophenyl)benzene molecule on a triangular lattice, which in our model represents a crystal surface with (111) geometry like, for example Au(111), Ag(111) or Cu(111). Individual conformers of 1,3,5-tris(3-bromophenyl)benzene are modelled on a triangular grid as a collection of rigid segments (each segment represents an aromatic ring of a real molecule), while connections between them correspond to C-C sigma bonds. The blue arrows indicate positions of halogen atoms, which after thermal activation (as free radicals) can form directional, reversible coordinate bonds with co-adsorbed metal atoms. Functional groups (-Br) are attached to the terminal segments of investigated molecules in *meta* positions only. The two-fold coordinated metal atom is modelled as single, isolated segments (marked in red) on a triangular lattice.

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PREPARATION AND INVESTIGATION OF CATALYTIC SYSTEMS IN THE REACTIONS INVOLVING CARBON OXIDES, HYDROCARBONS AND THEIR OXYGEN CONNECTIONS

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Catalytic materials for the process of removal (oxidation) of soot from Diesel exhaust gases

Investigations associated with the search of a highly active and selective catalytic material for the process of soot oxidation from diesel exhaust gases were continued. It is very important issue because the emission of soot into the atmosphere is highly undesirable. Diesel soot is strongly toxic for living organisms and contributes to the greenhouse effect.

Cobalt, cobalt-manganese and manganese catalysts prepared by a co-precipitation method and calcined at 400^{o}C were tested. Their catalytic properties (activity and selectivity) were measured in the "tight contact" using model soot (Printex U) and the reaction mixture containing 10 vol.% of O_2 and inert gases (argon and helium). The studies were conducted in a quartz reactor filled with 50 mg of the catalyst-soot mixture (45 mg of catalyst and 5 mg of soot) and 450 mg of finely ground quartz. The effects of soot oxidation during the temperature-programmed experiment (ramp rate was 5^{o}C/min) were analyzed by a mass spectrometer. Moreover, their physicochemical properties were analyzed by nitrogen adsorption, fluorescence spectroscopy and X-ray diffraction.

The manganese catalyst demonstrates the lower activity and selectivity in the process of soot oxidation than the cobalt catalyst, but it properties are better than cobalt-manganese catalysts. Thus, the addition of cobalt to manganese catalysts does not improve their activity and selectivity, but gives the opposite effect. Moreover, the cobalt-manganese catalyst prepared at 60^{o}C demonstrates higher activity and selectivity in the process of soot oxidation than the cobalt-manganese prepared at 40^{o}C. These properties are probably connected with the higher BET surface area and the lower average size of crystallites.

Ethanol steam reforming

Steam reforming of ethanol (ESR) is one of the most attractive ways of hydrogen production from biomass ($C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2$). The reaction can be performed at moderate temperatures (350 – 500 ^{o}C) under ambient pressure over noble and non-noble metal catalysts. Numerous metal oxides have been proposed as supports for the development and stabilization of active metal nanoparticles.

Our studies were focused on the development of new methods of catalysts synthesis and determination of their activity, durability and resistance for carbon deposit formation. The first method of catalysts synthesis was based on the controlled decomposition of cryptomelane-based one-dimensional cobalt modified manganese oxides. The second method was connected with the impregnation of as prepared dealuminated BEA zeolites. The details of synthesis procedures and main results were presented in the references [1,2].

It was found that synthesis of cobalt manganese oxides by the redox precipitation method led to the strong initial dispersion of cobalt ions within one-dimensional network of manganese oxide structure. However manganese oxide structure during activation was disrupted, which facilitated formation of relatively large metallic nanoparticles. In turn, an impregnation of dealuminated zeolites led to the preferential location of Ni^{2+} ions on the specific active sites in the zeolite structure. Ni modified dealuminated BEA zeolites showed high nickel dispersion after activation. The catalysts displaced high initial activity in the ESR reaction, however the deactivation of catalysts was observed with the time on stream. Detailed X-ray diffraction, electron microscopy studies, temperature-programmed methods, FT-IR (Fourier transform infrared), RAMAN and NMR (nuclear magnetic resonance) analysis indicated that deactivation of catalysts was connected with formation of carbon deposits. The nature of deposits was strongly related to the active phases of catalysts, surface properties and porous structure of supports.

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OPTIMIZATION OF MUNICIPAL WASTE MANAGEMENT SYSTEMS INCLUDING METHODS FOR MECHANICAL BIOLOGICAL TREATMENT OF THE WASTE

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In 2017, about 12 million tones of municipal waste were generated in Poland and production has increased by 2.7% compared to the previous year. This means an increase in the amount of municipal waste generated per one inhabitant of Poland from 303 kg in 2016 to 311 kg in 2017. The average amount of municipal waste generated per one inhabitant of the European Union in 2016 amounted to 483 kg [1]. These waste includes a lot of recyclable materials such as paper, plastics, glass and metals. Selective waste collection is the basis of a modern waste collection system [2].

The studies on the effectiveness of the municipal waste selective collection and treatment system were carried out in two cities: Lublin and Radzyń Podlaski. In addition to waste collected selectively, a large mass of waste is collected as mixed waste. The waste also includes secondary raw materials and organic waste, which must be processed in an oxygen composting plant (oxygen stabilization) [2, 3].

Samples of waste mixed after oxygen stabilization in summer and winter were collected for the tests (on average of 2 samples). The results of the tests are presented in Table 1.

Table 1. Waste composition (%) after aerobic stabilization in Lublin and Radzyń Podlaski.

	Summer		**Winter**	
component	**Radzyń P.**	**Lublin**	**Radzyń P.**	**Lublin**
paper	5,2	10,3	5,4	11,8
plastics	11,9	17,5	6,3	10,6
glass	26,5	27,7	13,8	17,5
metals	4,3	3,7	1	3,9
other waste	52,1	40,8	73,5	56,2

These studies show that the composition of waste transported for storage varies and depends on the place of waste generation at the seasons. The weight of recyclable materials in waste varies between 26.5% and almost 60%. The largest amount of raw materials in waste is in the summer, with the least amount of metals and a lot of broken glass. In the winter period, large differences in the composition of waste between cities were observed. In Radzyń Podlaski the weight of raw materials decreases to 26.5%, and the mass of other waste increases. In Lublin this decrease in the content of secondary raw materials is lower. It is connected with a large share of the remaining ash in the waste from single-family houses in Radzyń Podlaski. Figure 1 compares the average composition of waste to be stored from two research places.

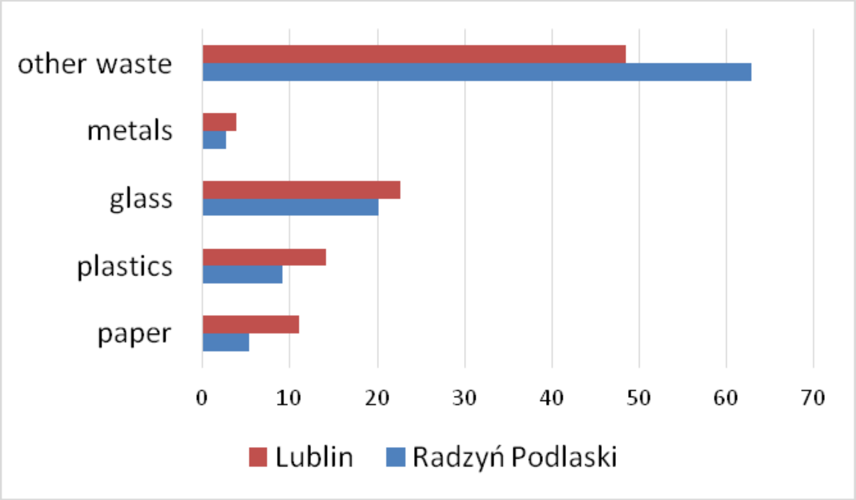

Fig.1. Composition of waste for storage in Lublin and Radzyń Podlaski.

These studies show that there are much more secondary raw materials in waste destined for storage in Lublin than in Radzyń Podlaski. The large mass of glass in this storage waste shows that the selective collection of this material group should be improved.

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STABILITY AND ADSORPTION OF THE CHITOSAN/SILICA SYSTEM

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Małgorzata PASZKIEWICZ, Jacek PATKOWSKI, Marek RESZKA,
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Stability of colloidal suspensions is a very important issue in many branches of industry. As the complexity of this matter is so tremendous, different aspects and mechanisms that influence this process can be distinguished. Besides the common factors such as temperature, presence of ions and pH, there is still another one. This is the addition of macromolecules such as polymers which can influence the stability of the studied system. Referring to the current trends in science and industry, the use of biodegradable and biocompatible polymers is getting even more attention [1-2]. Because of that, the use of natural and modified polysaccharides is the top-notch solution for the problems of the outdated and non-degradable chemistry [3].

The aim of this study was to analyze stability and adsorption of suspensions containing chitosan (Ch) and silica (SiO_2). Chitosan, the second most abundant natural polysaccharide, biodegradable and relatively cheap can be very good alternative for artificial polymers used in the stabilization of metal oxide suspensions. The results obtained from spectrophotometric and turbidimetric stability measurements results show that chitosan can adsorb on the silica surface and the mechanism of its adsorption is electrostatic. The molecular weight (MW) of the polymer (ChM1- the lowest MW, ChM2 – medium MW and ChM3 – the highest MW) also influences the adsorption process due to the fact that with the increasing length of the polymer chain, the number of reactive groups also increases. Moreover, the influence of pH on the adsorption capacity of chitosan on SiO_2 was investigated. Because of the cationic nature of this polymer, the adsorption increases with pH. The reason for that is the effective protonation of the amino groups present in the polymer macromolecule as well as the increasing negative charge of silica surface accompanying the increase of pH. The addition of chitosan has a significant influence on stability of the silica suspensions. The highest stability was observed for the largest concentration of the used polymer. The mechanism of the stabilization is the electrosteric one because the studied polymer not only adsorb on the silica surface but also possesses amino groups creating additional charge barrier preventing from flocculation. Moreover, there is no significant influence of chitosan molecular weight on stability of studied suspensions when concentration of the polymer is relatively low (60 ppm - 120 ppm). However, for higher concentrations of chitosan (200 ppm - 800 ppm) stability increases with the increase of its molecular weight as well as the adsorption of this polymer on the silica surface. All the conducted measurements that characterize the chitosan/silica systems give a foundation to even more specialized measurements such as QCM-D that would allow description of the adsorption layers as well as structural conformations of the polymer chains in the solution and on the solid surface.

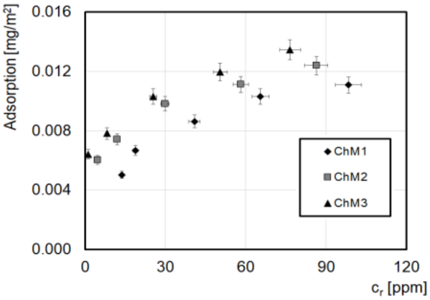

Fig.1. Adsorption of chitosan on SiO_2, 0.01 mol dm^{-3} NaCl, pH=5.

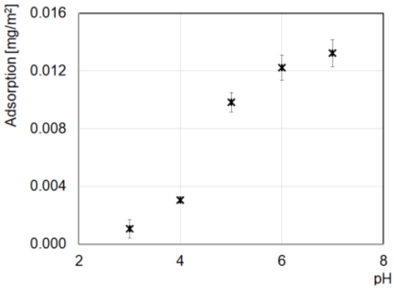

Fig.2. Influence of pH on the adsorption of ChM2 on SiO_2, 0.01 mol dm^{-3} NaCl.

Table 1. Values of the TSI parameter over time for the chitosan/silica systems for low (ChM1), medium (ChM2) and high (ChM3) molecular weight of chitosan and its concentrations (60, 120, 200 and 800 ppm); pH=5.

Concentration [ppm]	Time [h]	TSI ChM1	TSI ChM2	TSI ChM3
0	1	46.49	46.49	46.49
60	1	28.71	27.26	28.47
120	1	27.74	25.70	27.0
200	1	26.19	25.79	26.05
800	1	21.68	21.31	19.15
60	2	36.84	36.02	37.12
120	2	36.62	43.78	45.74
200	2	44.52	43.88	44.26
800	2	37.79	37.18	33.89
60	10	65.16	66.30	67.16
120	10	67.32	68.9	69.58
200	10	69.32	68.65	68.65
800	10	66.53	65.66	63.65
60	15	70.71	72.83	73.37
120	15	73.93	73.07	73.26
200	15	73.34	72.70	72.56
800	15	72.41	71.51	70.51

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SYNTHESIS AND CHARACTERIZATION OF d- AND f-ELECTRON METAL COMPLEXES AND NOVEL N/O/S DONOR LIGANDS

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The strategies of construction and characterization of novel multifunctional ligands as well as metal complexes are of great attention due to their intriguing structural features and potential applications in: catalysis, medicine, magnetic and luminescent materials, sensors, molecular separation, and so on. We have synthesized novel molecular and polymeric complexes of d- and f-block elements with different ligands. The obtained complexes were characterized by methods: X-ray single crystal and powder diffraction techniques, photoluminescence, CHN, TG-DSC, TG-FTIR, FT-IR, Raman, UV-VIS, XANES, XPS, biological, magnetic studies as well as quantum chemical calculations.

The new N_3O_2–donor Schiff base (H_2L) in the reaction of diethylenetriamine with *o*-hydroxybenzophenone amine and its complex with Cu^{II} ions have been synthesized and characterized. The computational studies show that the phenol-imine and zwitterionic forms are most stable in vacuum. This is in agreement with the crystal structure of the Schiff base *i.e.* the compound occurs as a mixture of mentioned above forms. The complexation process of Cu^{II} ion via the studied Schiff base results in formation of the unusual cyclic, tetranuclear complex ($[Cu_4L_2ac_4]\cdot 4CH_3OH$, where ac – acetate ion**)**. The coordination geometry around each metal centers is distorted square pyramid. The solvent molecules stabilize the crystals of complex in solution. Outside their mother liquor they are transformed into the polycrystalline complex $[Cu_4L_2ac_4]\cdot H_2O\cdot CH_3OH$.

A new series of heteronuclear complexes Zn^{II}–Ln^{III}–Zn^{II} (Ln = Nd(**1**), Sm(**2**), Eu (**3**), Tb (**4**), Dy (**5**)) with *N,N'*-bis(5-bromo-3-methoxysalicylidene)-1,3-diamino-2-propanol were synthesized and characterized. The compounds **1**, **3**–**5** show a blue emission attributed to the emission of the ligand. For complex **2** the characteristic emission bands of f-f* transitions were observed. The magnetic properties for compounds **1**, **4** and **5** are characteristic for the paramagnetism of the corresponding lanthanide(III) ions. New Pd^{II}–Ln^{III}–Pd^{II} complexes of hexadentate N_2O_4 Schiff base ligand (*N,N'*-bis(2,3-dihydroxybenzylidene) -1,3-diamino-2,2-dimethylpropane) with Eu (**1**), Tb (**2**), Er (**3**) and Yb (**4**) were also synthesized and characterized structurally and physicochemically. The compounds **1**–**4** are built of cationic heterometallic Pd^{II}–Ln^{III}–Pd^{II} trinuclear units. The palladium(II) centers adopt a planar square geometry occupying the smaller N2O2 cavity of the Schiff base ligand. The lanthanide(III) is surrounded by two Schiff base ligands (eight oxygen atoms) and its coordination sphere is supplemented by a chelating bidentate nitrate ion in **1** or by a water molecule in **2**–**4**. The decomposition process of the complexes results in mixtures of: PdO, Pd and respective lanthanide oxides Eu_2O_3, Tb_2O_3, Tb_4O_7, Er_2O_3, Yb_2O_3. The luminescent measurements show low efficiency intramolecular energy transfer only in the complex of terbium(III) (**2**).

The 4-chloro-2-methylphenoxyacetates of selected transition metal ions form compounds of general formula $ML_2 \cdot nH_2O$ where: L = $C_9H_8ClO_3$, M(II) = Mn, Co, Ni or CuL_2, n = 2 for Mn (II), n = 5 for Co (II) and Ni (II) compounds. The Mn(II), Co(II) and Ni(II) complexes crystallize in a monoclinic system while the Cu(II) complex in triclinic system. The carboxylate group is bidentate. During heating in air (293-1173 K) complexes decompose in two or three stages. The enthalpy of the dehydration process varies from 21.75 kJ/mol to 38.38 kJ /mol. Magnetic moments confirm that investigated complexes are paramagnetic and obey the Curie-Weiss law.

The DFT analysis of 1,2,4-triazole-3-thioacetic acid as O, N, S-donor organic linker for construction of coordination polymers was made. The synthesized compound was subjected to IR and Raman spectroscopic profiling. The experimental data were correlated with the results obtained on the basis of theoretical calculations made by DFT. The optimized geometry and vibration data were compared with experimental results, achieving good correlation between data sets. The calculated Mulliken charges indicate with a good accuracy the location of hydrogen bonds. The generated MEP map shows that the highest positive potential is accumulated around the carboxyl and triazole hydrogen atoms, and the negative one is found on electronegative atoms. These sites confirm the formation of the same hydrogen bonds that exist in the crystal structure of the acid.

The new Eu(III) and Tb(III) complexes with 4,4'-biphenyldicarboxylic acid (H_2L) and 1,10-phenanthroline (phen) complexes were obtained under solvothermal conditions. The complexes of the general formula $Eu(Tb)_2L_3(phen)_5$ are crystalline powders hardly soluble in common organic solvents. They do not contain in their structure solvent molecules while their coordination environments consist of nitrogen atom from 1,10-phenathroline and carboxylate oxygen atoms. Thermal analysis of complexes indicates their thermal stability up to about 250°C. Heating of the complexes leads to the two-stage decomposition. They exhibit good luminescent properties due to energy transfer from organic ligands to metal centers.

Five new copper(II) complexes with trisubstituted N^1-acylamidrazones were obtained in equimolar reaction of the appropriate ligand with $Cu(OAc)_2$ or $CuCl_2$ using water, methanol, ethanol or ethanol/water (1:1) mixture as a solvent. Single-crystal X-ray analysis revealed that all complexes crystallize in centrosymmetric space groups: $P\text{-}1$, $P2_1/c$, $P2_1/n$, or $Pbca$. The reaction with copper(II) acetate results in double deprotonation of the ligands and leads to creation of centrosymmetric binuclear species with CN = 4. Deprotonation of the carboxylic and amide groups induces considerable π-electron delocalization along the whole acylamidrazone system. Furthermore, the ligands configuration is transferred from *Z* to *E* upon metal complexation. Isomerization around the C=N bond allows the L^{2-} ions to chelate the Cu^{2+} ion through its pyridine N, amide O and imine N atoms. The carboxylate O atoms from the adjacent, inversion-related molecule complete the square-planar donor arrangement around the metal center.

SYNTHESIS AND PROPERTIES OF POLYMERS

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TOMASIK, Beata PODKOŚCIELNA, Maciej PODGÓRSKI, Andrzej
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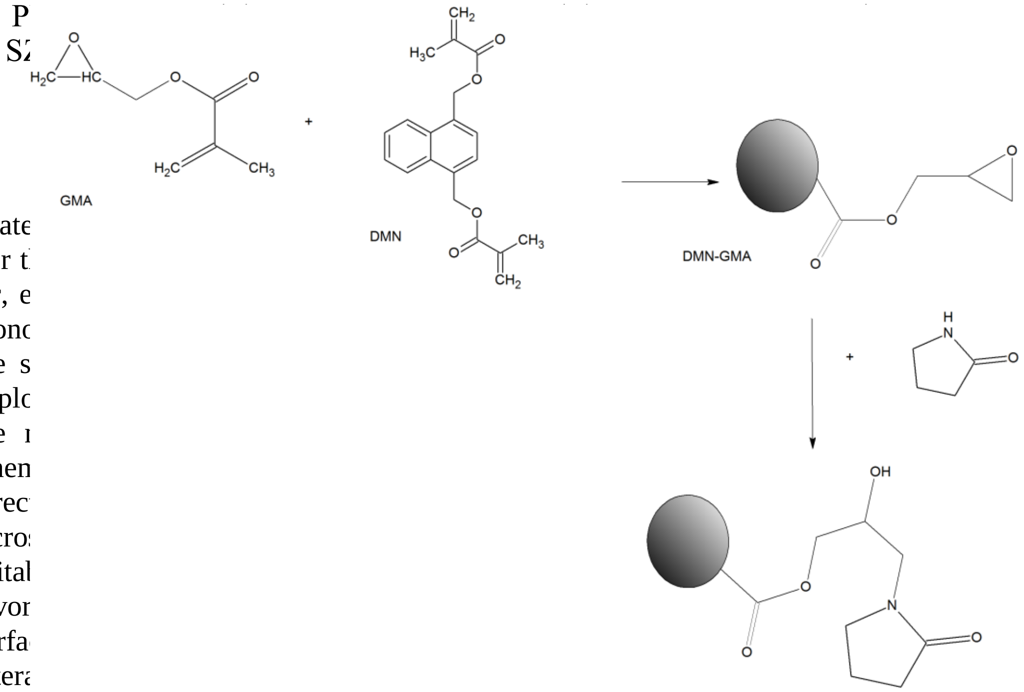

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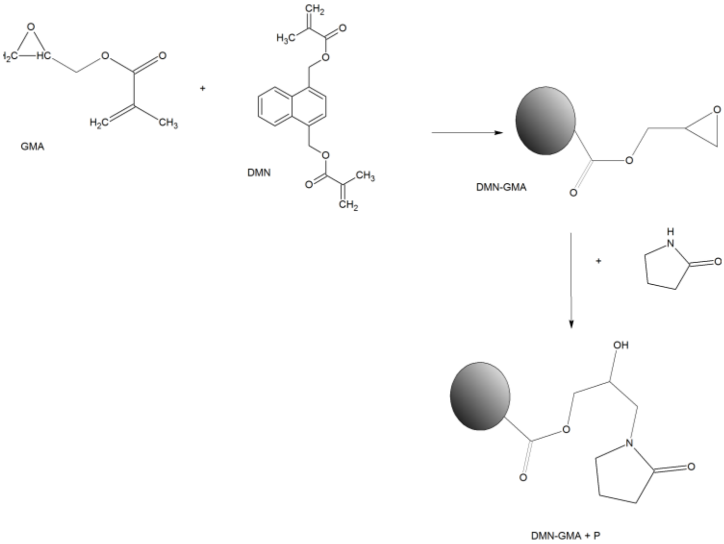

Fig. 1 The scheme of synthesis and modification of poly(glycidyl methacrylate-*co*-di (methacryloyloxy methyl) naphthalene) with pyrrolidone

As polar monomers e.g acrylonitrile methacrylonitrile, cyanomethyl styrene, N-vinylimidazol, 4-vinylimidazole, 1-vinyl-2-pyrrolidone, 2-hydroxyethyl methacrylate, 4-vinylpiridine have been used. Among crosslinking agents divinylbenzene and the more polar crosslinkers like ethylene glycol dimethacrylate, trimethylolpropane trimethacrylate are commonly applied.

The aim of the presented study was to obtain polar copolymers with good thermal characteristic. For this purpose aromatic 1,4-di(methacryloyloxy methyl)naphthalene (DMN) was applied as crosslinker whereas glycidyl methacrylate (GMA) served as functional monomer. DMN is responsible for the mechanical and thermal properties of the resulting polymeric matrix. GMA provides epoxy groups which are effective for introducing the target groups. The molar ratio of the functional monomer to the cross-linker was increased from 1:1 to 1:5. The value of specific surface area varied from 106 to 42 m^2/g depending of the molar ratio of functional monomer to crosslinker. The resulting poly(DMN-*co*-GMA) microspheres were functionalized by ring-opening reaction of oxirane with the pyrrolidone to produce DMN-GMA+P adsorbent as shown in Fig.1. Pyrrolidone was chosen for modification process, because it contains a highly polar amide group conferring hydrophilic and polar–attracting properties and also apolar methylene groups in the backbone and the ring, conferring hydrophobic properties. The newly obtained modified copolymers considerably differ from the parent ones in terms of porous structure parameters First of all, the modification process leads to noticeable decrease of the basic parameters of the internal structure. The value of specific surface area decreases from 106 m^2g^{-1} for DMN-GMA1 to 73 m^2g^{-1} for DMN-GMA1+P copolymer. At the same time pore volume declines from 0.380 cm^3g^{-1} to 0.254 cm^3g^{-1} . Pore size distribution maintains its bimodal character, but the maxima are shifted towards smaller values (19 and 22 nm).

The thermal behavior of the parent and modified materials was studied using TG/DSC/FTIR methods It was foud out that the process of modification of the DMN-*co*-GMA copolymers with pyrrolidone improves the thermal properties of the newly obtained materials. The initial temperature of decomposition increases from 269 ^oC for parent DMN-GMA1 copolymer to 274 ^oC for modified DMN-GMA+P. At the same time the final decomposition temperature increases from 521 ^oC to 621 ^oC. The differences in thermal behavior between parent and functionalized copolymers were also noticed during DSC measurements. For the DMN-GMA copolymers an exothermic peak at about 260 °C was observed due to presence of unreacted double bonds. After the process of modification it not appear.

It can be concluded, that thanks to the modification reaction a new polar copolymers with very good thermal resistance can be obtained.

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EPITAXIAL ULTRA THIN FILM OF BI_2O_3 ON SAPHIRE (0001) SURFACE

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Bismuth oxide (BO) is a wide-band-gap semiconductor, with a bandgap spanning between 2.4 to 4 eV, exhibiting strong polymorphism. The known polymorhps are two stable (α-monclinic, δ-fcc) and four metastable (β-tetragonal, γ-bcc, ε-orthorhombic, and ω-triclinic) phases. The most investigated is the high temperature γ-phase which is considered as one of the most efficient oxygen ion conductor suitable for application in solid oxide fuel cells (SOFC) [1]. The α-phase which has a high optical refractive index has application in nonliniear optical devices. Recently, it has been reported [2] that α- and γ-phases can be successfully applied in a construction of new aqueous rechargeable batteries exhibiting outstanding rate performance and life time. Although, it is established that BO exhibits a range of interesting properties (high refractive index, dielectric permittivity, photoluminescence, optical nonlinearity) with a broad applications (heterogeneous catalyst, solid oxide fuel cells, nonlinear optics, batteries, solar cells, sensors) there is no consistent picture in literature describing growth kinetics of thin BO films and their phase transitions [3]. Based on our study of the growth of ultra-smooth Bi films on an insulating substrate [4,5], we performed an in-situ and real-time GSAXS and SXRD investigation of the growth kinetics and phase transition of ultra-thin BO films on the α-Al_20_3(0001) surface. The aim of the experiment was to establish a uniform picture of BO growth kinetics as a function of substrate temperature, film thickness, and oxidizing conditions. The secondary goal of this experiment was a search for new metastable oxide phases, which thanks to the unique experimental conditions (use of the atomic oxygen source, very broad range of substrate temperatures) offers a variety of growth scenarios, hardly achievable by other methods (ALD, CVD, magnetron sputtering).

In our previous works [4, 5], we managed to master the controlled growth of Bi on the α-Al_20_3(0001) surface, revealing different nucleation scenarios as a function of substrate temperature. In short, Bi deposited at very low temperatures (40 K) grows, using rombohedral notation of the unit cell, in (110) orientation parallel to the substrate. The mild annealing up to 300 K smoothens Bi(110) films which are composed of azimuthally randomly oriented domains on the substrate. At around 400 K Bi(110) transforms to Bi(111) structure, forming ultrasmooth films (Fig 1a) which are stable up to Bi melting point at 540 K. Real-time SXRD observations of film melting revealed rapid Bi dewetting [5] just few degrees before film liquification indicated by a sharp increase of the Bi(111) Bragg peak intensity, followed by the film melting seen as a sudden disappearance of the Bragg peak and an increase of a diffuse background. Subsequent sample cooling results in the formation of Bi sub-microcrystals, nucleating 100 K bellow the melting point of Bi (supercooling). A new experimental data should provide information about the phase diagram of BO thin film oxide phases as a function of temperature, film thickness and orientation. This will allow us to gain insight into the controlled growth of BO thin film phases and their transitions.

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ENVIRONMENTAL EFFECT OF ANTHROPOGENIC NANOMATERIALS

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Given its natural state and cost-effectiveness, cotton can be an ideal material for the fabrication of high performance catalysis and adsorbents for pollutant removal from the various compartments of the environment. In the present study, the cotton-derived carbon microtubes (CMT) were prepared by thermal treatment of cotton in an argon atmosphere. CMTs were used as a tannic acid (TA) adsorbent. TA is widely distributed in the environment and has a simpler chemical structure than humic acid. TA was selected as a model DOM [1]. Since DOM can influence the stability of CMT water solutions, the tests with tannic acid (20 mg L^{-1}) were performed and the results are presented in Fig. 1. Results showed that in water solution without TA almost all CMT deposited rapidly. The most significant changes in CMT stability were observed during the first 24-48 hours (Fig. 1a). The highest stability was found for CMT9 and CMT13, which is determined by their surface charge and composition due to the highest oxygen content. The CMT11 and CMT15 had the lowest stability. Faster deposition observed for CMT11 and CMT15 may result from the presence of large amount of surface –COOH groups [2].

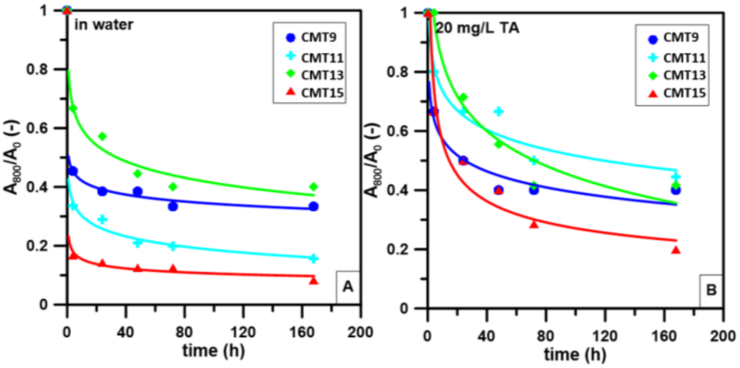

Fig. 1. CMT stability (2 mg·L^{-1}) in water and tannic acid solution (20 mg·L^{-1}).

The stabilization of carbon based agents through natural organic matter (NOM) in water solutions can be attributed to the van der Waals forces and Brownian motion (the electrical double layer repulsive forces) [3]. The addition of TA increased the stability of carbon microtubes (Fig. 1b). TA changed both the stability of CMT and the time, when the stability was established. Generally, the greatest changes were observed during the first 72 hours what may indicate that TA prolonged the time necessary to establish the equilibrium. In general, in the presence of TA, CMTs did not settle down and formed stable solution (Fig. 1b). The greatest stability was observed for CMT11 and CMT13. However, the greatest impact of TA was observed on CMT11.

The presence of TA was attributed to the monolayer absorption of TA onto the surface of CMTs [1]. The π-π interactions (aromatic rings of TA and microtubes) or other polar interactions (e.g., hydrogen bonds with the dissolved TA) increased the steric repulsion between individual tubes and hence increased their stability. Semi-dispersed or dispersed CNT showed higher bioavailability than deposited or soluble forms [4].

The process of TA adsorption was limited by chemical reaction of TA with CMT surface (a pseudo-second order kinetics). Fitting of the experimental data to the Langmuir model with simultaneously good fitting to other tested models (Freundlich, Dubinin-Radushkevich or Temkin) indicated that monolayer sorption was the first step of TA adsorption onto CMT. The mechanism involved was found to be π-π interactions and hydrogen bonds between TA and CMT surface [5].

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ENGINEERED BIOCHAR MODIFIED WITH IRON AS A NEW ADSORBENT FOR TREATMENT OF WATER CONTAMINATED BY SELENIUM

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Selenium (Se) exhibits toxic activity towards living organisms at doses exceeding the recommended intake. Therefore, it is essential to remove it from the environment. Among methods used for ions removal from water, different adsorbents are most common way of treating of contaminated water [1,2]. An activated carbon is one of the most popular and most frequently used adsorbents for this purpose. However, the activated carbon based on coal is getting expensive and brings environmental drawback such as the exploitation of a non-renewable resource. One of the cheap sorbent materials recently gaining popularity is biochar, a product of biomass pyrolysis produced in order to apply as a soil amendment [3,4]. Biochar contains functional groups on its surface, such as carboxyl, hydroxyl and phenolic, and is characterized by its high specific surface area. Because of that biochar is able to adsorb inorganic contaminants from soil and water (Ahmad et al., 2014), although in many cases the adsorption abilities of pristine biochar are not enough. In order to obtain a material that is more selective towards chosen contaminants, improving its effectiveness, biochars can be modified or activated [5]. Modification methods used to change selectivity of biochars are chemical, physical, magnetic and by impregnation with mineral sorbents. Impregnation with iron(III) nitrate(V) and its further thermal decomposition can be an interesting way of improving adsorption abilities of biochar towards Se(VI) ions, since that kind of modification enhanced sorption abilities of other oxyanions, such as nitrate and phosphate [5].

The aim of this study was to propose an efficient method of biochar modification for effective removal of Se(VI) ions from water. Biochar produced from wheat straw at 650°C was modified by impregnation in three concentrations (0.8, 4 and 10% w/v) with iron(III) nitrate(V). Optimum pH, adsorption kinetics, and Se(VI) adsorption isotherms were determined for the biochars studied. The Langmuir and Freundlich models were applied to characterize adsorption isotherms. Changes in the chemistry of the adsorbent surface after modification were evaluated using FTIR-PAS and XPS techniques. The modification significantly increased biochar's ability to adsorb Se(VI). The biochar modified with a 10% iron(III) nitrate(V) solution showed the highest adsorption effectiveness. The experimentally determined maximum adsorption capacity, which was 14.3 mg g-1, was similar to the theoretical values derived from the Langmuir model, which best reflected the experimental data.

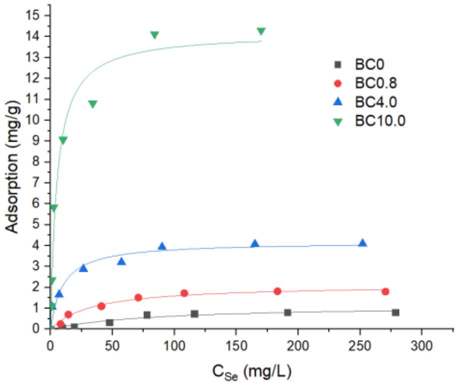

Fig. 1. Adsorption isotherms of Se onto biochars; m= 0.08 g, V= 10 mL, pH 5, t= 30 min, T= 22.2± 2 °C. BC0 – pristine biochar, BC0.8 – biochar modified with 0.8% $Fe(NO_3)_3$, BC4.0 – biochar modified with 4% $Fe(NO_3)_3$, BC10.0 – biochar modified with 10% $Fe(NO_3)_3$, solid lines present Langmuir fitting.

An analysis of the adsorption kinetics showed that an equilibrium was reached after 5h in the case of the biochar modified with the 10% solution. The optimum pH value for adsorption was 5. XPS and FTIR-PAS investigation confirmed the presence of iron oxides/hydroxides on the surface of the modified biochar and the modification also caused the formation of oxygen functional groups. The study demonstrated that the proposed modification can be efficient in increasing the effectiveness of biochar in removing Se(VI) from water. Given the low biochar production cost (due to the possibility of using waste for its production) and also the high adsorption capacity, comparable to that of mineral adsorbents, this can be an interesting direction for simultaneous waste management and production of efficient adsorbents.

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NEW METHODOLOGIES IN THE SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS

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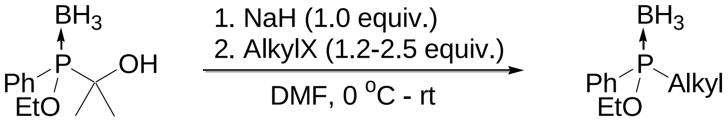
The major research topic in the Department of Organic Chemistry is associated with the development of new synthetic methodologies in organophosphorus chemistry. The first topic was devoted towards the application of □-hydroxyalkylphosphorous acid-borane derivatives as equivalents of >P(BH_3)H-type compounds in alkylation reaction. A treatment of phenyl(1-hydroxy-1-methyl)ethylphosphinous acid-borane ethyl ester with an equimolar amount of sodium hydride followed by an addition of an alkyl halide has been monitored (scheme 1).

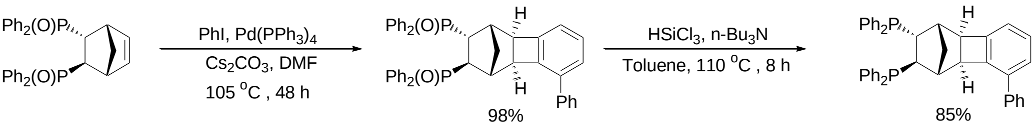


Alkyl = $PhCH_2$ (76%)
Alkyl = Me (87%)
Alkyl = *i*-Pr (62%)
Alkyl = Allyl (79%)
Alkyl = $MeOCH_2$ (65%)

Scheme 1

Under the reaction conditions, substrate undergoes deprotonation of OH group in alkyl substituent. The formed anion liberates acetone moiety which in turn leads to the formation of >P(BH_3) anion. A treatment of this intermediate with an alkyl halide led to the formation of the appropriate phosphinous acid-borane ethyl ester with good yields. This method offer a simple approach to a very specific phosphorus anions which are hardly affordable by other methods.

The second topic is associated with the synthesis of structurally more complex NORPHOS derivatives via modification of norbornene skeleton (Scheme 2).



Scheme 2

Starting diphosphine dioxide possessing norbornene skeleton, when treated with phenyl iodide in the presence of palladium(0) complex and a base afforded an unusual product possessing benzocyclobutane framework coupled with norbornane. Reduction of P=O bond using trichlorosilane in the presence of trialkylamine afforded the target diphosphine possessing modified norbornane core.

The ligand has been used in palladium-catalyzed asymmetric alkylation of racemic (*E*)-1,3-diphenylallyl acetate with dimethyl malonate. In all cases, product was obtained with good yields and enantiomeric excess up to 90% ee. The developed method offers the synthesis of diphosphine ligands with unusual frameworks via simple methodology starting from readily available precursors. The scope of the reaction and catalytic tests are currently underway in the laboratory.

Project: Statutory research project BS-P-03-002-18-N-01.

STUDY OF THE THERMODYNAMIC PROPERTIES AND STRUCTURE OF THE SELECTED SURFACE SYSTEMS

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THE WETTING OF HIGHLY NON-ADDITIVE SYMMETRIC MIXTURES AT NON-SELECTIVE WALLS

From the earlier study of bulk symmetric mixtures [1,2], it follows that the both the non-additivity of interactions determines their phase behavior. In perticular, the mixtures with negative geoemetric and energetic non-additivities, have been found to show the closed loop immiscibility gap. We have studied the wetting behavior of such mixtures at nonselective walls [3]

We have considered the mixtures, with the components A and B interacting via the truncated (12,6) Lennard-Jones potential

$$u_{ij}(r) = \begin{cases} 4\varepsilon_{ij}\left[\left(\sigma_{ij}/r\right)^{12} - \left(\sigma_{ij}/r\right)^{6}\right] & r \le r_{max} \\ 0 & r > r_{max} \end{cases}$$

where r is the distance between a pair of the particles i and j. We have assumed that $\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon$ is the unit of energy, and $\sigma_{AA} = \sigma_{BB} = \sigma$ is the unit of length. We have used the reduced temperature, $T^* = kT/\varepsilon$. The fluid-wall interaction potential has been represented by the following equation:

$$v(z) = \varepsilon_{gs}\left[\left(\frac{\sigma}{z}\right)^{9} - \left(\frac{\sigma}{z}\right)^{3}\right]$$

In the above,ε_{gs} is a measure of the fluid-wall interaction strength.

The model has been studied using the Monte Carlo simulation method in the grand canonical ensemble [3]. The quantities recorded included the average numbers of particles $A(N_A)$ and $B(N_B)$, and the density profiles for each component, $n_k(z)$. With the density profiles, one can calculate the surface excess densities of the components, $\rho_{k,ex}$and the total excess density $\rho_{ex} = \rho_{1,ex} + \rho_{2,ex}$.

The mixtures with large negative geometric non-additivity, do not undergo demixing transition in the liquid state, and hence their wetting behavior is bound to be similar to the wetting of simple, one-component, fluids. We have found that upon the increase of the fluid-solid interaction, the wetting temperature decreases down to the triple point. Then for still higher fluid-solid interactions, the triple wetting has been found to occur.

In the case of mixtures exhibiting the closed immiscibility loops, The wetting behavior has been found to be different, In particular, we have found that two (lower and upper) wetting temperatures may appear. This is a consequence of the fact that in the mixtures with a negative energetic non-additivity the demixed fluid exibits relatively weaker interaction with the solid than the mixed liquid. A complete wetting requires the formation of a macroscopic liquid film at the surface.

In the systems with closed immiscibility loops, the demixed liquid is stable only over a certain range of temperatures. Such mixtures may exhibit a complete wetting at the temperatures below the bulk demixing point, and an incomplete wetting at higher temperatures. Such situation occurs when the adsorbed film remains mixed up to the bulk coexistence. However, close to the bulk tricritical point, being the onset of the continuous demixing transition, a second wetting transition takes place, as predicted by Cahn [4]. On the other hand, in the systems in which the adsorbed films undergo the demixing transition, a complete wetting may occur below as well as at and above the bulk demixing transition temperature.

It has also been demonstrated that the wetting behavior depends strongly on the strength of the surface-fluid interaction.

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THE MODELING OF SELF - ORGANISATION AND INTERFACIAL PROPERTIES IN COMPLEX SYSTEMS

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STRUCTURE AND PHASE BEHAVIOUR OF DIBLOCK COPOLYMER MONOLAYERS INVESTIGATED USING DENSITY FUNCTIONAL THEORY

Thin molecular films formed on the solid surface have attracted a considerable attention due to their practical applications. Of particular interest is the behaviour of monolayers of diblock copolymers. These molecules are built of two different, fully flexible or partially rigid, homopolymer chains connected by covalent bond. The presence of chemical joining between both subunits makes total macrophase separation impossible. Nevertheless, it does not prevent from microphase separation. In consequence, it gives rise to the formation of complex, ordered structures, and copolymer systems have an ever growing number of technological applications including nanotemplating and nanolithography [1,2].

We have proposed a density functional theory (DFT) for diblock copolymers in two dimensions. Our theoretical framework is based on Wertheim's first order thermodynamic perturbation theory and closely follows its 3D counterpart put forward by Yu and Wu [3]. The used theoretical approach is an extention of theory which was recently developed for polymeric monolayers [4]. It is based on the accurate FMT-based density functional theory for hard disks [5] and the attractive part is treated in the mean-field fashion. We use the DFT to investigate the structure and phase behaviour of monolayers of symmetric diblock copolymers.

We point out that the phase behaviour of symmetric diblock copolymer monolayers is similar to that in 3D. This includes the scaling of the equilibrium lamellar width with chain length. The topology of the resulting phase diagrams depends on the unlike segment interaction incompatibility and the chain length (cf. Fig 1.). For longer chain, the global phase diagram features one triple point. At this point three distinct phases - the gas phase, the disordered liquid phase, and the lamellar phase are in mutual equilibrium. The phase behaviour changes for shorter chains. The lamellar phase, similar to that observed for longer copolymer molecules, still can be detected. However, in addition we find another ordered phase of lamellar symmetry, in which the polymer chains are much more elongated. This kind of ordered structure was reported in computer simulations of monolayers of diblock copolymers [6]. The phase diagram contains three triple points (one of them being the peritectic point).

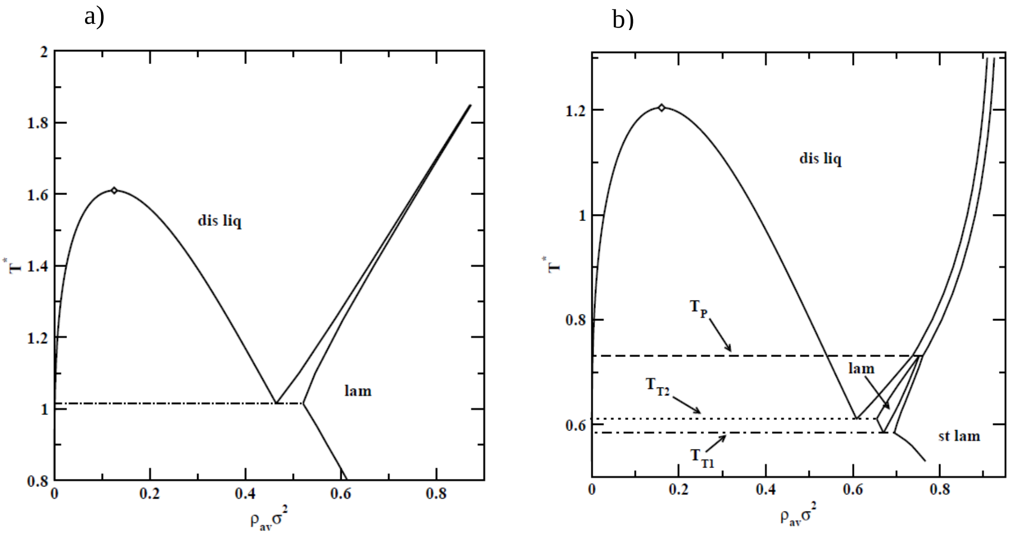

Fig.1. The phase diagram in the temperature-average density plane of monolayer of symmetric diblock copolymer consisting of M segments (M=16 (a) and M=8 (b)). The solid lines represent the binodals, the dashed line marks the locations of the triple point temperatures and the diamond denotes the critical point of the gas - disorder liquid phase transition. The locations of the disordered liquid (”dis liq”), lamellar (”lam”) and stretched lamellar (”st lam”) phases are marked in the figure [7].

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RESEARCH ON THE PROCESS OF COMBINING POLYMER PHASE WITH INROGANIC OXIDE PHASE

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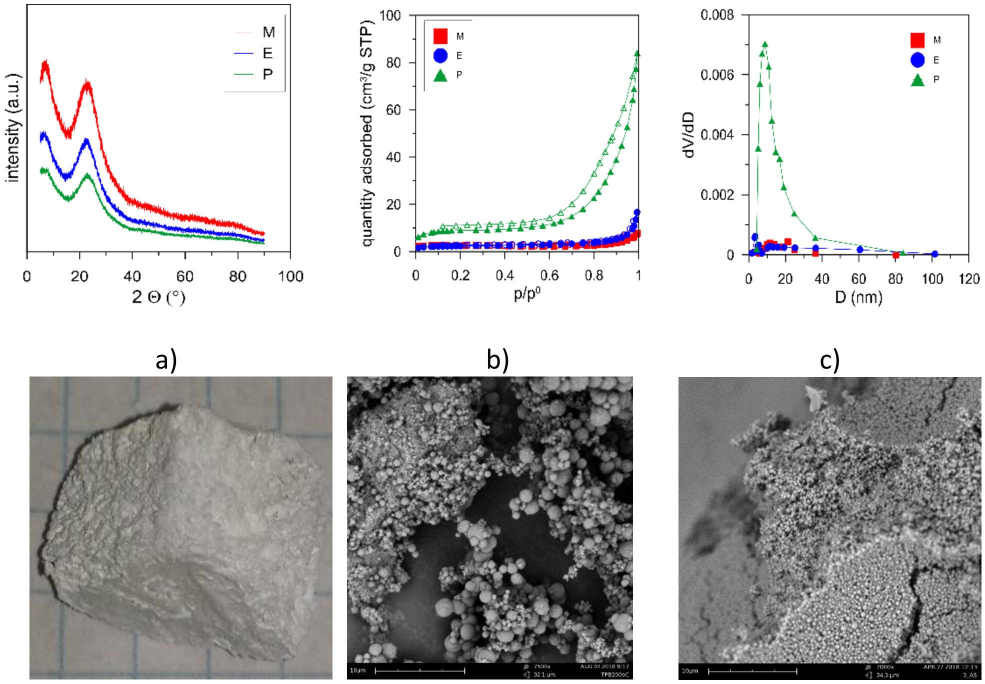
The hard templating of inorganic oxide by using polymer matrix is a very interesting subject of research. Recently it has been reported that Amberlite resin XAD7 HP is able to swell in various silica precursors such as tetramethyl orthosilicate and (3-(2-Aminoethylamino)propyl]trimethoxysilane) and can be used to obtain porous amorphous SiO_2 as well as polymer-silica composites [1, 2]. Hydrolysis followed by condensation of the silica precursor within polymer matrix can be performed in vapours of hydrochloric acid or ammonia [3]. Occurrence of this transformation within polymer matrix restrains ‘free’ SiO_2 formation leading to a ‘templating’ phenomenon. Since described process can be considered as a green approach towards synthesis of potentially useful composites it is key issue to replace artificial and quite expensive Amberlite resin with natural biopolymer such as agar [4]. Agar has been reported as a co-templating agent with surfactant (F-127) in preparation of modified MCM-41 material [5]. However best to our knowledge no further works considering agar as a templating agent were reported up to this date.

The present paper describes the synthesis of silica materials by the use of biopolymer as a hard template and different alkoxysilanes i.e. tetramethoxy (TMOS), tetraethoxy (TEOS) and tetrapropoxysilanes (TPOS) as SiO_2 precursors. Prior to the introduction of precursors into the hard template, the agar gel was lyophilized. Lyophilization leads to formation of quite thick and sponge-like structure composed of clearly visible white polysaccharide chains, which preserves shape of gel and creates possibility to introduce into agar matrix liquid silica precursor. Lyophilized agar gels were wetted with silica precursors up to the point of ‘agar sponge’ saturation. Next, all samples were placed for 72 h at room temperature in a vessel in which atmosphere was rich in ammonia and water vapours. During this time all liquid silica precursors transformed into amorphous silica gel (Fig. 1a). All samples under study were subsequently calcined in air at 550 °C for 6 h. This process resulted in creation of pure silica network in a shape of lyophilized agar discs (Fig 1d) which were named accordingly to precursors used i.e. TMOS – M, TEOS – E, TPOS – P. TMOS upon hydrolysis and condensation creates nonporous amorphous silica with rather smooth surfaces (micrographs not shown). Presence of agar template does not affect in a significant way that process, however low temperature nitrogen adsorption desorption measurements reveal small specific surface area equal 10 m^2/g. In case of TEOS and TPOS both silica precursors when hydrolyze and condense without polymer matrix they from materials that are predominantly composed of small silica spheres (Fig. 1e). They both can be considered as porous materials, especially the P silica (S_{BET_E} = 24

m^2/g; S_{BET_P} = 114 m^2/g). When it comes to the templating effect the E sample forms continuous surface with wrinkles (micrographs not shown). On the other hand the P sample is in form of monodispersed nanospheres.



a) b) c)

d) e) f)

Fig. 1. The XRD patterns (a), low temperature nitrogen adsorption-desorption isotherms (b) and corresponding pore size distributions for samples under study. The photograph of E sample (d). The SEM micrographs of silica obtained in ammonia vapours at same magnification from TPOS, without agar (e) and P sample (f).

To sum up it is possible to use lyophilized agar gel as a templating agent for preparation of amorphous porous silica from liquid precursors.

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SYNTHESIS, MODYFICATIONS AND STUDIES OF MATERIALS WITH DIFFERENTIATED STRUCTURAL AND SURFACE CHARACTERISTICS WITH REGARD TO APPLICATIONS IN SORPTION PROCESSES

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Efficiency of the phenoxyacid pesticides removal from aqueous solutions by using activated carbon was studied. The effect of properties of halogenated phenoxyacid adsorbates (2-chlorophenoxyacetic acid (2-CPA), 4-chlorophenoxyacetic acid (4-CPA), 2,4-dichlorophenoxyacetic acid (2,4-D), 3-bromophenoxypropionic acid (3-BrPP) 4-bromophenoxypropionic acid (4-BrPP), 4-chlorophenoxypropionic acid (4-CPP) and 4-fluorophenoxypropionic acid (4-FPP)) on effectiveness of the process of their adsorption on activated carbon F300 from aqueous solutions was estimated. The equilibrium adsorption isotherms and kinetic curves were measured. The experimental data of adsorption processes were described using generalized Langmuir (GL) isotherm equation. The measured concentration vs. time profiles for all adsorption systems were analyzed using mixed 1,2-order (MOE) and fractal-like MOE (f-MOE) with corresponding simpler (1st and 2nd order non-fractal and fractal-like) equations, diffusion models: intraparticle diffusion (IDM) and pore diffusion model (PDM) as well as multi-exponential equation (m-exp). The relations between the adsorbate structure and properties, and adsorption uptake and rate were discussed in details. The usability of the kinetic models and equations was analyzed with regard to fitting quality and consistency with adsorption process mechanism.

Strong influence of structure and physicochemical properties of adsorbates on adsorption equilibrium and smaller effects on adsorption kinetics were found. In the case of phenoxyacetic herbicides (2,4-D, 4-CPA, 2-CPA) differentiated in position and number of substituents in the aromatic ring, relatively small differences in adsorption values were found. It was stated that the solubility/hydrophobicity was not the only factor determining the adsorption process. The effects of oxygen surface groups of adsorbent, and type and position of chlorines attached to the benzene ring of the adsorbate molecules were discussed: the steric effect, formation of local positively charged sites, the dispersion, donor-acceptor and repulsive electrostatic interactions, formation of hydrogen bonds with neighboring solute molecules or surface oxygen groups of adsorbent, facile access of the symmetrical solute molecules into carbon micropores. In the case of phenoxypropionic herbicides differentiated in type of halogen substituent at the para - position in aromatic ring stronger adsorption of bromo derivative in comparison to chloro and fluoro ones (4-BrPP> 4-CPP> 4-FPP) was found. This differentiation in adsorption affinity correlates well with the Hammett constants and indicate the mechanism of creating the electron donor-acceptor complex as important in adsorption process. The experimental isotherms were successfully analyzed by the Generalized Langmuir equation and in the case of all systems, except one, the heterogeneity parameters were lower than unity, reflecting the significant impact of energetic heterogeneity. For one system the Langmuir isotherm was found to be the best; it was explained by compensation of the effect of energetic heterogeneity and lateral interactions in adsorption space.

The influence of differentiation of adsorbate properties on adsorption rate was also investigated. The measured concentration vs. time profiles for all adsorption systems were analyzed using the diffusion models (IDM and PDM), mixed 1,2-order (MOE with FOE/SOE), fractal-like MOE (f-MOE and f-FOE/f-SOE) and multi-exponential equation. In the case of both diffusion models no satisfying results were obtained, the deviations were found to be of systematic character and some parameters attained unrealistic values, which means that the models are inconsistent with the mechanism of the observed process. Our conclusion was that concentration change during adsorption exerted much smaller influence on adsorption process than it was assumed in the model; other factors than diffusion should be taken into account. In the case of McKay pore diffusion model (PDM) a limitation of its applicability in the ranges closer to equilibrium was obtained. In both models, treatment of the ueq parameter as free and optimized one, independently on equilibrium concentration gives better fitting results; moreover, the other parameters attain the realistic values. For both models, the driving force of diffusion process changes slower than it results from concentration change during adsorption. However, IDM requires that the initial kinetics follows $c/c_o \sim t_{1/2}$ dependence, whereas the initial PDM kinetics may be time-linear ($c/c_o \sim t$), i.e. more akin to the behavior of our experimental systems.

Unlike for the FOE/SOE/MOE, relatively consistent and good fits were found for f-MOE. For all systems optimized f_2 was close to 0, hence simpler f-FOE was used (with slightly higher deviations), with relatively narrow range of fractal parameters p. f-FOE may treated as first order kinetics with a certain monomodal distribution of rate coefficients (range of log k_1 is unlimited); while it is less flexible, it has properties similar to the m-exp equation (finite range of logk_1).

The multi-exponential equation occurred to be by far the best one for analysis of the studied adsorption systems; very good fitting quality was obtained over the whole adsorption range (f-MOE - the next best equation - had deviations 2 times higher). High similarity of kinetic curves, and corresponding distributions of rate coefficients, was found for all adsorbates, which suggests a similar mechanism of adsorption process. Minor differentiation in kinetic profiles is a result of differences of number and type of functional groups and their positions on aromatic ring of adsorbates.

THIN LAYER CHROMATOGRAPHY OF SOME DERIVATIVES 2-(2,4-HYDROXYPHENYL)-1,3,4-THAIDIAZOLES IN MAGNETIC FIELD

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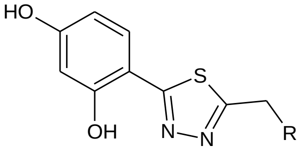
Thin Layer Chromatography is one of the most popular methods of the separation of mixture components and investigation of interaction of compounds with different surfaces. The last topic is very important in physicochemical, biological and medicinal applications. There are some factors influence chromatographic retention, system efficiency and solute separations. One of them is magnetic field. Influence of the field of interphase interactions is very interesting, especially in medicine and pharmacy because a lot of therapies are carried out in strong magnetic fields. The effect of magnetic field on chromatographic separation was firstly investigated by Barrado et al. [1,2] in chromatographic system with magnetic stationary phases, and Malinowska et al. for typical chromatographic systems[3]. Presence of permanent magnetic field even relatively small inductivity (about 0.4 T) can cause changes in chromatographic systems separation values. This paper, continues our earlier investigations.

The investigation on effect of magnetic field on interphase phenomena influencing chromatographic separation using TLC method was performed. The presence of perpendicular to plane of plate and direction of chromatogram development magnetic field influences interaction among all components of chromatographic system. In consequence, the retention and efficiency of investigated compounds in the given system should be altered. In this paper, the effect of the field presence regarding retention mechanism, distance of development, and particle size of stationary phase for chosen derivatives of 2-(2,4-hydroxyphenyl)-1,3,4-thaidiazoles is being investigated. (Fig. 1)



R1: NH_2
R2: NH-methyl
R3: NH-cyclohexyl
R4: NH-tertbuthyl
R5: NH- prop-2-en-1-yl
R6: NH-phenyl
R7: CH_2-phenyl

Fig 1 Formulas of investigated compounds

For better presentation, and in consequence better understanding of results, ΔR_F value was lead. The way of calculating it is explained as follows:

$$\Delta R_F = R_{Fmag} - R_{Fnmag}$$

R_{Fmag} – value of R_F obtained in experiment carried out in magnetic field
R_{Fnmag} – value of R_F obtained in experiment carried out outside the generated field
Example results are depicted on Fig. 2.

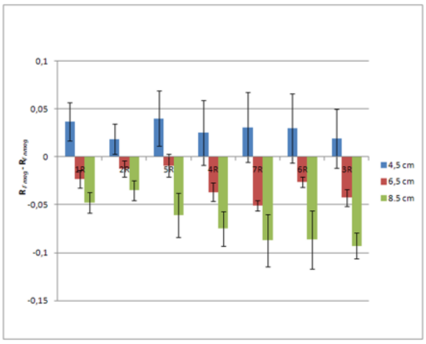


Fig 2 Differences between R_F values (□R_F) obtained in perpendicular magnetic field and outside it for different distances of development. Stationary phase: TLC SiO_2 60 F_{254}. Mobile phase: acetone/toluene/n-hexane 1/1/1 (v/v/v) Distances of development: 4.5 cm, 6.5 cm and 8.5 cm with error bars. Substances are ordered according to ascending molar masses.

The effect of magnetic field on plate height is depicted on Fig. 3.

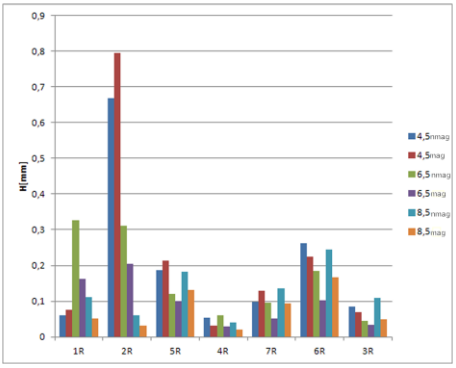


Fig 3 Mean HETP in millimetres calculated for development distances 4.5 cm, 6.5 cm and 8.5 cm in magnetic field (m - signed) and outside it. Stationary phase: TLC SiO_2 60 F_{254}. Mobile phase: Acetone/toluene/n-hexane 1/1/1 (v/v/v) Distances of development: 4.5 cm, 6.5 cm and 8.5 cm. Substances are ordered according to ascending molar masses.

The change of every mentioned above parameter affects the retention change caused by the field. It was also observed that the retention changes depend also on structure of investigated compound, what may be useful information for investigations on properties of newly synthesized compounds.

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SPECIAL PURPOSE SUBSIDY TO CONDUCT RESEARCH AIMED AT DEVELOPING YOUNG SCIENTISTS AND DOCTORAL STUDENTS

SORPTION OF PHENOL AND URANYL IONS ON PLANT MATERIALS

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The issues related to the environmental protection are a very important and still topical subject, due to the constantly developing industry and technologies that introduce various toxic substances into the natural environment. The problem is not only to reduce their emissions, but also to remove them from sewages or drinking water, or natural surface waters. Among the many methods and techniques used in the elimination of pollutants from the aquatic environment there should be mentioned: adsorption, ion exchange, membrane filtration, extraction and biological reduction. One of the most common methods is adsorption on natural materials, which makes this method quite attractive due to relatively low costs. The natural sorbents of great interest for researchers include silicates, zeolites, waste materials (orange peels, straw, leaves and others) and biosorbents (algae, fungi or sorbents containing appropriate bacterial strains). The removal of uranium and phenol ions is an interesting and very important issue due to high toxicity of both ions [1-3]. Phenol is used for the production of resins, dyes, plant protection agents and detergents. It is a toxic compound as it has destructive effects on mucous membranes and airways. On the other hand, uranium is known as an element with mutagenic and carcinogenic activities, the toxicity of which is comparable to that of such heavy metals as mercury, cadmium, lead or arsenic. The hazard of uranium compounds is constantly current, because it is used as fuel in nuclear power plants as well as it occurs in nature in the form of such minerals as, for example, tar pitch and uraninite. Due to the increase in the concentration of phenol and uranium (VI) ions in nature, particularly in water, an important aspect seems to be the development of more and more effective and low-cost methods of their removal from the environment.

The aim of the research was to obtain natural sorbents based on aluminosilicates (bentonite, red clay) with the addition of inulin and starch. Inulin was obtained from dahlia tuber, which after washing and drying was lyophilized at -40 ºC. Finally, they were ground in a mill to give a powder. The source of starch, however, were acorn oak. The treatment of the acorn included initial removal of the shell and the outer casing. Seeds prepared in this way after drying are ground in a mortar. Thus prepared sorbents were then used to remove uranyl ions and phenol from aqueous solutions in the systems with variable pH or various concentrations of the studied ions. Sorption of each individual ion and their common sorption found in the solution was investigated. This is a very important issue, due to the fact that usually in the systems in the human environment, we deal with the occurrence of more than one ion next to each other. This applies to both aqueous solutions found in nature as well as industrial sewages. The final comparison of the four sorbents showed that they are effective in removal of uranyl ions and phenol from aqueous solutions. The highest percentage of sorption for both phenol (66%) and U(VI) ions (94%) was obtained for the sorbent based on bentonite and inulin, and the lowest for clays and acorns, in which sorption of phenol was 44% and uranyl ions 89%. The most favourable pH area of the solutions was in the range from 4 to 10. The adsorption energy calculated on the basis of the Dubinin-Raduszkiewicz isotherm model indicates the physical nature of the reaction in the case of phenol and the physicochemical sorption process for the uranyl ions. Adsorption of uranyl ions on the tested composite was spontaneous and endothermic whereas in the case of phenol no effect of temperature on the whole process was observed. A full characterization of this process was developed based on the UV-Vis, XPS and FTIR spectroscopic analyses showing that the adsorption mechanism is complex, consisting in surface complexing, precipitation and diffusion in the pores. This is probably also the effect of adsorbate interactions with both the surface of the modified mineral and its interior as well as various forms of uranyl ions and phenol with each other.

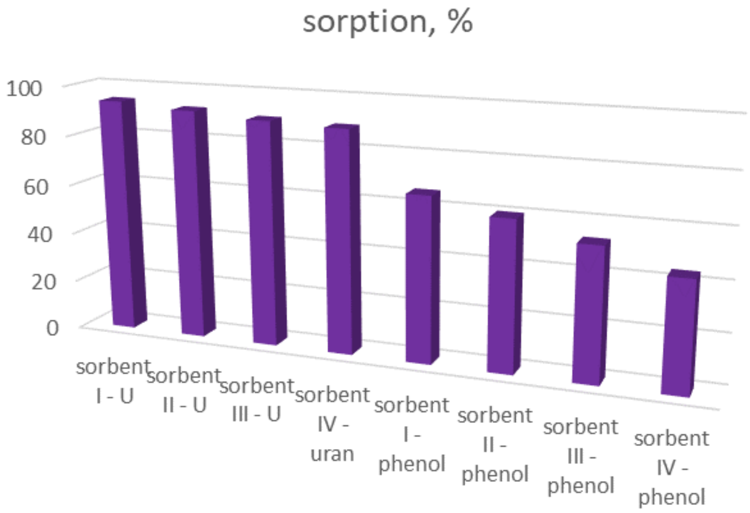

Fig.1. Sorption of phenol and U(VI) on natural sorbents: sorbent I (bentonite+inulin), sorbent II (bentonite+starch), sorbent III (red clay+inulin), sorbent IV (red clay+starch).

The research was carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the Operational Program Development of Eastern Poland 2007–2013 (Contract No. POPW.01.03.00-06-017/09).

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USE OF BIOCHAR IN THE PROCESS OF OBTAINING VALUABLE METALS OF STRATEGIC IMPORTANCE

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Biochar is a carbon material obtained by heating biomass in the following processes: pyrolysis, gasification, carbonization and others. Gasification is a process of partial combustion of biomass in the temperature range 873-1473 K, in oxygen-starved and with the residence time of biomass 10-20 seconds. Conducting the process in the atmosphere lacking oxygen allows to control the amount of formed NO_x. In gasification process biochar is a main product . However, liquid products as well as gas mixture are formed. Proper selection of the process conditions for instance: temperature and retention time permits to control the properties of the resulting sorbent. Additionally, biochar is prepared from such wastes as: wood, manure, empty fruit brunch, rice husks and many others. Biochar obtained in the gasification process is characterized by suitable porosity, specific surface area and cation exchange capacity [1-3]. These features cause that the biochar is used as a sorbent for the removal of heavy metal ions and organic compounds from aqueous solutions.

In order to modify the biochar surface chitosan was applied. Chitosan is a polysaccharide produced by the deacetylation of chitin which is a component of crustacean shells. It belongs to the most widespread biopolymers in nature [4]. The ordered structure of chitosan is due to the presence of intra- and intermolecular hydrogen bonds in the network. Chitosan is characterized by biodegradability, non-toxicity, availability and low price. Chitosan is often used as a source of surface amino groups in various modifications with a strong ability to bind metal ions. This modification is effective because it combines both biochar and chitosan advantages maintaining low-cost and green materials of great availability. Additionally, it can be used to intensify its affinity for heavy metal ions. Various types of biochar composites were prepared by the different mass ratios of biochar to chitosan BC:CS such as 1:1, 2:1, 4:1 and 8:1.

The equilibrium capacities for the simultaneous sorption of heavy metal ions for different mass ratios of BC to CS are listed in Table 1. The effect of phase contact time on the simultaneous sorption of heavy metal ions at the mass ratio of BC:CS 4:1 is presented in Fig.1.

Table 1. Equilibrium capacities for the simultaneous sorption of heavy metal ions for different mass ratios of BC to CS.

Ions	BC:CS			
	1:1	2:1	4:1	8:1
Cu(II)	17.46	16.22	18.05	17.66
Cd(II)	2.91	2.59	3.92	2.88
Co(II)	1.77	1.52	1.95	1.83
Zn(II)	2.16	1.89	2.67	2.61
Pb(II)	20.37	17.78	20.78	19.85

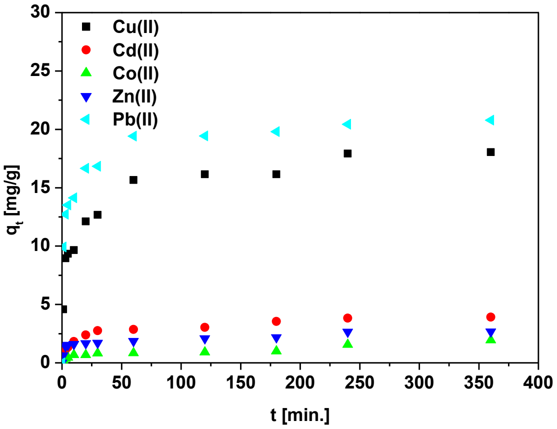

Fig.1.Effect of phase contact time on the simultaneous sorption of heavy metal ions at the mass ratio of BC:CS 4:1 (t 1-360 min, C_0 100 mg/dm^3, pH 5, 180 rpm, 295 K).

As follows from these data it can be stated that:

- the range of heavy metal ions affinity is as follows: Pb(II) > Cu(II) > Cd(II) > Zn(II) > Co(II),
- the highest amounts of adsorbed ions were found for the mass ratio of BC:CS 4:1. Chitosan modified biochars are effective sorbents for removal of heavy metal ions from aqueous solutions.

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SCREEN-PRINTED CARBON ELECTRODES MODIFIED WITH METAL: PREPARATION, CHARACTERIZATION AND NEW APPLICATIONS

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For the first time for the determination of Tl(I) integrated three-electrode screen-printed sensor with carbon electrode electrochemically covered with bismuth film was applied. The chosen electrode characterizes commercial availability, small size, low cost and sufficient for quantitative analysis repeatability, reproducibility and simple modification process. Bismuth was in situ plated on the working electrode surface as a result of electrochemical reduction of bismuth(III) ions during thallium deposition. Furthermore, the proposed sensor is environmentally friendly. The surface of bare and modified working electrode was compared through imaging by optical and scanning electron microscopes. Performed experiments allowed to obtain a new, sensitive, fast and cheap voltammetric method of Tl(I) quantification in natural water samples without long and complicated pretreatment step.

Optimized method characterizes low detection limit 8.47×10^{-10} and 6.71×10^{-12} mol L^{-1} and wide linear range of calibration graphs 5×10^{-9} to 1×10^{-6} mol L^{-1} and from 5×10^{-11} to 1×10^{-9} mol L^{-1} for deposition time of 60 and 300 s, respectively. In order to apply the method for Tl(I) determination in natural water samples, the influence of organic substances (surfactants) and metal ions was tested. Both metal ions and surfactants have negative influence on analytical signal of Tl(I) (reducing of the signal high or overlapping of the thallium and other metal signals). To minimize/eliminate this impact and mask the presence of metal ions, EDTA (disodium salt of ethylenediaminetetraacetic acid) in experimentally appropriately selected concentration (1×10^{-5} mol L^{-1}) was added to the sample solution. The use of EDTA resulted in complexing disturbing ions, mainly Cd(II) and Pb(II). Occurred in natural water samples surface active substances was removed through mixing the sample with 0.5 g of resin Amberlite XAD-7 for 30 s. The resin was added to the electrochemical cell and was not remove before voltammetric analysis.

Proposed method was applied for Tl(I) quantification in certified reference materials: SPS SW-2 (surface water), SRM 1640a (natural water) and TMRAIN-04 (rain water). Obtained results, similar to certified values prove that the method is appropriate for Tl(I) determination. Besides, proposed procedures for interferences minimizing derived from foreign metal ions and organic substances through EDTA addition and resin Amberlite XAD-7 using proved effective. Measured and certified values of Tl(I) concentration and the relative mark error obtained during quantification of Tl(I) in certified reference materials are presented in Table. 1.

Table. 1. Results obtained during quantification of Tl(I) in certified reference materials.

Certified reference material	Measured value ± SD (n = 3) [nmol L^{-1}]	Certified value ± SD (n = 3) [nmol L^{-1}]	Relative error [%]
SRM 1640a	7.86 ± 0.27	7.86 ± 0.073	0
SPS SW-2	0.128 ± 0.013	0.122 ± 0.00098	4.92
TMRAIN-04	1.91 ± 0.095	1.84 ± 0.29	3.66

Received results prove that the developed method with the use of integrated three-electrode screen-printed sensor with carbon working electrode modified with bismuth characterizes good accuracy and precision of determinations [1].

Reference:

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Grant No. BS-M-03-002-17-B-04

HIGH RESOLUTION ATOMIC ABSORPTION SPECTROMETRY IN STUDIES OF CONCENTRATION AND DISTRIBUTION HETEROGENEITY OF TRACE AND ULTRATRACE ELEMENTS IN SOLID SAMPLES

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High-Resolution Continuum Source Atomic Absorption Spectrometry (HR-CS AAS) is selective and sensitive analytical technique applied for determination of trace elements. Besides usually analysed solutions also slurries and solid materials are analysed by using HR-CS AAS. Thanks to the advanced software used for the processing of results the effective correction of significant background values is provided. Despite this in some cases, when the chemical interferents strongly affects the atomisation process, the direct determination of trace elements present in composed, strongly interfering matrix is impossible. The solution of this problem is the selective and quantitative extraction of analyte to the solution or solid, which would not be the reason of interferences.

In this work the results concerning the determination of platinum by AAS in alumina-nickel-iron based catalysts are shown. It was stated that in the case of direct analysis of solid catalysts by HR CS AAS the matrix elements strongly suppress the analytical signal of Pt. To overcome this limitations the samples were digested in *aqua regia* and analysed by HR CS AAS.

However, the digestion of samples does not cause the satisfactory improvement of the efficiency of atomization. In order to identify the main source of interferences the impact of iron, aluminium and nickel on platinum signal was investigated and presented in Fig.1. As can be seen the presence of iron and aluminium strongly supress the signal of platinum. The presence of aluminium at 500 mg/L leads to the decrease of signal at about 75%, whereas the same concentration of iron causes 30% decrease. In the solution obtained after the acidic digestion of catalysts the concentration of iron was found to be about 4.5 g/L. Due to the only partial dissolution of aluminium oxide in *aqua regia*, iron was found to be the main source of chemical interferences.

In order to determine platinum in solution containing high excess of iron the adsorption of analyte onto carbon materials was proposed. In order to ensure the quantitative and fast adsorption of platinum from the acidic solutions three carbon materials were tested. The first was microporous medical carbon, the other two materials are ordered mesoporous CMK-3 carbon and CMK-3 oxidized by H_2O_2.

The experiments concerning the adsorption of Pt(IV) ions onto above-mentioned carbons were performed using static arrangement consisted of 10 mg of sorbent and 10 mL of solution. In Fig. 2. the impact of pH on the adsorption of

Pt(IV) is presented. In the case of CMK-3 and oxidized CMK-3 the highest adsorption is obtained in acidic environment, the increase of pH leads to the decrease of the adsorption in studied pH range. For medical carbon the adsorption is constant regardless of pH value.

Based on the adsorption isotherms of Pt(IV) onto studied carbon materials the maximum static adsorption capacities were found to be 26.4 mg/g for oxidized CMK-3, 100 mg/g for pristine CMK-3 and 110 mg/g for medical carbon. Taking into account the runs of adsorption isotherms medical carbon was chosen for preconcentration of platinum from solutions obtained after digestion of catalysts. For this material the quantitative removal of Pt(IV) from the solution was observed up to concentration of 50 mg/L, whereas other two materials do not adsorb Pt(IV) quantitatively even from 1 mg/L solution.

It was stated that adsorption of Pt(IV) is rather fast process and only few hours of suspension shaking are required to reach adsorption equilibrium state. The studies concerning the impact of nitrates and chlorides (present in *aqua regia*) on Pt(IV) adsorption proved that both anions strongly suppress adsorption, wherein 1 mol/L solution of chlorides decreases it at about 70%, whereas the same concentration of nitrates completely prevent adsorption. Thus nitrates were removed from digested catalysts by evaporation. The preconcentration of platinum was carried out for 24 h in adsorption systems containing about 10 mg of carbon and 20 mL of solution. The slurries were centrifuged and the solution containing matrix elements were separated. The solid sorbents were mixed with 1 mL of 5% HCl and such slurries were analyzed by GF AAS technique. The correctness of obtained results was monitored based on the recovery of platinum added to the catalysts before digestion. The results of Pt determination by the proposed procedure are presented in Table 1.

Table 1. The results of Pt determination in aluminum-nickel-iron catalysts.

Sample	Content [μg/g]	Pt addition [μg/g]	Content with addition [μg/g]	Recovery [%]
A	41.8 ± 0.7	20	60.4	95
B	29.2 ±1.3	20	48.6	99
C	41.1 ±2.1	20	60.1	97

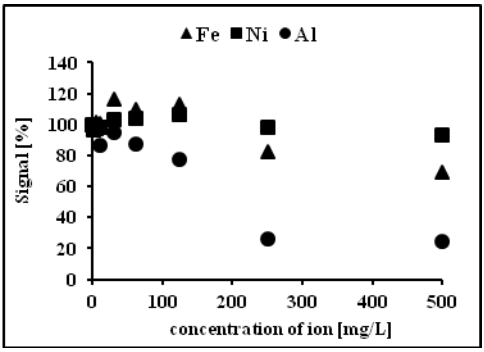

Fig.1. The influence of iron, nickel and aluminum on the signal of platinum contained in water solution (400 μg/L).

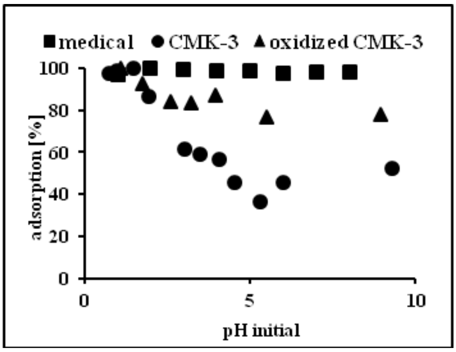

Fig.2. The influence of initial pH on the adsorption of Pt(IV) onto carbon materials; , $C_{o(Pt)\ \mathrm{CMK\text{-}3,\ oxidized\ CMK\text{-}3}}$ = 20 mg/L, , $C_{o(Pt)\ \mathrm{medical}}$ = 100 mg/L, t_{eq} = 24 h.

THE USE OF MICRO- AND NANOMATERIALS FOR THE CONSTRUCTION OF NEW ELECTRODES AND THEIR APPLICATION TO THE DEVELOPMENT OF HIGHLY SELECTIVE PROCEDURES FOR THE DETERMINATION OF TOXIC ELEMENTS BY THE STRIPPING VOLTAMMETRY METHOD

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Arsenic and thallium are the heavy metals and their contents in the earth's crust are 2.5 and 0.6 ppm, respectively. In nature, arsenic occurs both in the form of inorganic compounds as well as organic compounds. The most frequent forms of arsenic that occur in the water samples are inorganic forms As(III) and As(V). The toxicity of these form of arsenic is different – As(III) is much more toxic than As(V)[1]. Thallium is well-known toxic contaminant in environmental and even its low-levels have carcinogenic and teratogenic toxicity to human being. Moreover, toxicity of Tl^+ is even higher than the toxicity of Hg^{2+} and Pb^{2+} [2]. Therefore, trace and speciation analysis of arsenic and thallium is needed for the determination of trace levels of these elements as well as the distinction of their individual forms.

Stripping analysis allows for the direct determination of different forms of elements and it is characterized by a low detection limit. In addition, the apparatus required for the analysis is cheaper than in other analytical methods. Very important issue in the voltammetric method is the selection of the working electrode, wherein the material has an effect on the available range of potential and also to the limit of quantification. The aim of the project was to develop and practical application of the composite electrode made of carbon materials, and gold nanoparticles to determine arsenic speciation and a silver microelectrode made of silver wire with a diameter of 25 um was used for thallium determination. For composite electrode material, various carbonaceous materials containing gold were tested. Carbon black acetylene 100% compressed with the addition of 0.5 – 0.8 μm gold particles was used as the optimal electrode material. The obtained electrode is characterized by a low background value and a well-shaped current peak. These electrodes are environmentally friendly and mercury-free.

The standard procedure of measurement of As(III) was performed in a following way. The 10 mL of the solution containing the analyzed sample, 0.1 mol L^{-1} acetate buffer and 3×10^{-5} mol L^{-1} EDTA was prepared. The deposition of As(III) at the Au/CB electrode was carried out at -0.8 V for 30 s from the stirred solution. Stirring was preformed using a magnetic stirring bar. After a rest period of 10 s a square wave voltammogram recorded at a frequency of 200 Hz, while the potential was changed from -0.75 to 0.3 V. The amplitude and the potential step were 25 and 5 mV, respectively. All measurements were carried out from undeaerated solutions.

Under the optimized conditions the calibration graph for As(III) with application of developed electrode was linear from 5 × 10^{-9} to 2 × 10^{-7} mol L^{-1} following deposition times of 30 s. Voltammograms obtained for solutions containing increasing concentrations of As(III) are presented in Fig. 1. The detection limit for As(III) following the deposition times of 30 s, calculated as a 3-σ for a low concentration of As(III) was equal to 2.1 × 10^{-9} mol L^{-1}.

The standard procedure of measurement Tl(I) was performed in a following way. The 10 mL of the solution containing the analyzed sample, 0.05 mol L^{-1} acetate buffer and 2 × 10^{-4} mol L^{-1} DTPA was prepared. The deposition of Tl(I) at a silver microelectrode was carried out at -1.1 V for 120 s from the stirred solution. After a rest period of 10 s a square wave voltammogram recorded at a frequency of 50 Hz, while the potential was changed from –1.1 to 0.0 V. Under the optimized conditions the calibration graph for As(III) with application of developed electrode was linear from 5 × 10^{-9} to 1 × 10^{-7} mol L^{-1} following deposition times of 120 s. Fig. 3. Influence of the pH on the Tl(I) current is presented in Fig. 2.

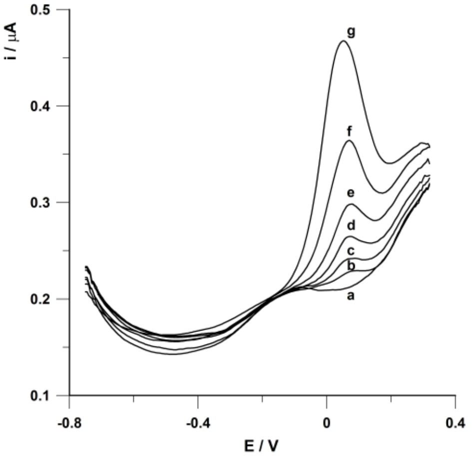

Fig. 1. Square wave voltammograms obtained for solutions containing low concentration of As(III): (a) 0; (b) 5; (c) 10; (d) 20; (e) 50;(f) 100; (d) 200 nmol L^{-1} As(III). Deposition at -0,8 V within 30 s.

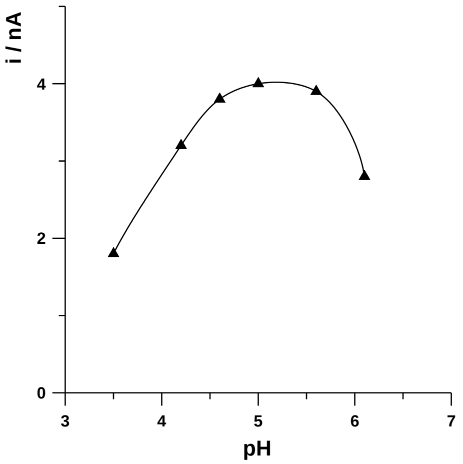

Fig. 2. Influence of the pH on the Tl(I) peak current. Concentration of Tl(I) 5×10^{-8} mol L^{-1}. Deposition time 120 s.

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NEW PROCEDURES FOR THE DETERMINATION OF SELECTED METAL IONS AND BIOLOGICALLY ACTIVE COMPOUNDS BY STRIPPING ANALYSIS WITH THE USE OF A NEW TYPE OF ELECTRODES

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Because of a wide use of bismuth in such areas of human activity as: medicine, chemical industry, metallurgy, catalysis or cosmetology, living organisms are exposed to contact with this element. Due to this fact monitoring of bismuth content in environmental samples is required. For the determination of bismuth(III) in environmental samples, there are several frequently adopted analytical methods. Among them voltammetric methods are recognized as a powerful tool because of its sensitivity in connection with relatively inexpensive instrumentation.

The main aim of this work was to determine trace amounts of bismuth by anodic stripping voltammetry using a new type of electrodes to previously proposed double deposition and stripping step [1-3] and elimination of interfering ions effect. There were two working electrodes that differed significantly in their surface areas and built-in the voltammetric cell used in research: a gold film electrode plated ex situ on glassy carbon substrate as an electrode with large surface area and a gold film microelectrode plated ex situ on an ensemble of carbon fibers microelectrode as the second one. This kind of electrodes is environmentally friendly in comparison to the commonly used hanging mercury drop electrode. Bismuth was at first deposited at the electrode with a large surface area. As the deposition step at the first electrode was finished, the electrode was shifted at a short distance to the small one and the first stripping step was performed. Then the second deposition step was carried out using microelectrode ensemble. Taking into account the very small volume of space between the working electrodes, the concentration of Bi(III) between the electrodes was much higher as compared to that in the bulk solution. Due to the fact that the second deposition step was performed from solution with a much higher concentration of Bi(III), the detection limit was lowered.

This procedure was optimized by selection of various conditions, such as the supporting electrolyte, pH, accumulation potential and time. The additional purpose was a precise study of the influence of Cu(II) ions on the bismuth voltammetric peak current, because the presence of these ions causes the main interference effect in the case of bismuth determination due to the fact that anodic stripping signals of bismuth and copper are highly overlapped. The correctness of this procedure was tested by determination of Bi(III) in river water samples. The obtained results show that the proposed procedure can be applied to real water samples analysis and environmental monitoring for Bi(III) without the additional pre-concentration step.

Standard procedure of measurements

Working electrodes were prepared as follows. The gold film was plated ex situ on glassy carbon substrate (Ø 12 mm) and on an ensemble of carbon fibers microelectrode by electrolytic deposition of gold from solution containing 2.5×10^{-4} mol L^{-1} Au(III), 0.025 mol L^{-1} HCl and 4 g L^{-1} urea. Gold deposition was carried out at the potential of -0.6 V for 180 s. V. Then the gold film was polarized at the potential of 0.2 V within 15 s for stripping impurities from the gold film. Working electrodes were polished and the gold films were plated daily before starting the measurements.

Determination of Bi(III) was performed in a following way. The sample was pippeted to the voltammetric cell and 7.5 mL of 1 mol L^{-1} acetate buffer (pH 4) was added. The sample was adjusted to the volume of 30 mL with water. Recommended procedure consists of the following steps: to obtain a low detection limit of Bi(III) determination before voltammetric stripping on microelectrode ensemble the Bi(III) ions was initially deposited on a gold film electrode (-0.35 V for 240 s). After that the large electrode was placed very near an microelectrode ensemble and the polarization of this electrode was stopped. During this step Bi(III) was stripped from the large electrode using air dissolved in the solution. Thus Bi(III) deposited on the large electrode went directly to the solution between the surface of a large electrode and microelectrode ensemble. Next deposition of Bi(III) on microelectrode ensemble was performed (-0.3 V for 120 s) from the non-stirred solution containing Bi(III) at a much higher concentration than that of the bulk solution. At the end the square wave voltammogram was recorded with the bismuth signal proportional to its concentration. After each measurement both working electrodes were cleaned electrochemically at the potential of +0.3 V for 15 s. All measurements were carried out without solution deoxygenation.

Result and discussion

For Bi(III) determination by ASV using gold film electrodes acetate buffer CH_3COOH + CH_3COONa (pH = 4.0) was used for these studies as a supporting electrolyte.

The accumulation potential at the first electrode was changed from -0.6 to +0.2 V while accumulation potential at the second electrode was -0.6 V. It was observed that the Bi(III) peak current attains the maximal value of deposition potential in the range from -0.4 to -0.1 V. Further measurements were carried out at deposition potential of -0.35 V.

The accumulation potential at the second electrode was changed from -0.6 to +0.2 V while accumulation potential at the first electrode was -0.35 V. It was observed that the Bi(III) signal attains the maximal value at deposition potential in the range from -0.3 to -0.1 V. For further studies deposition time of -0.3 V was chosen.

It was found that the calibration plot for Bi(III) with application of double deposition and stripping steps was linear from 2.5×10^{-9} to 2×10^{-8} mol L^{-1} following deposition times of 300 s at the first and second electrode, and obeyed the equation $y = 0.12x + 0.018$, where y and x are the peak current (nA) and Bi(III) concentration, respectively. The linear correlation coefficient r was 0.999. The estimated detection limit for Bi(III) following the deposition times of 300 s at the both working electrodes calculated as a 3 σ for a low concentration of Bi(III) was equal to 1.2×10^{-9} mol L^{-1}.

The main attention was paid on the Bi(III) determination in the presence of excess of Cu(II) as anodic stripping signals of these metals overlap and this fact makes the Bi(III) analytical signal difficult to interpret. The interference of Cu(II) ions on bismuth peak current was studied for a solution containing Bi(III) at concentration of 4×10^{-8} mol L^{-1}. The obtained results show that in the presence of 3-fold excess of Cu(II) interference effect on Bi(III) signal was observed in the course of determination using one electrode, however, application of double deposition and stripping step leads to elimination of this interferences.

Taking into account that in acetate buffer interference of Cu(II) on Bi(III) signal was eliminated only in the presence of small excess of Cu(II) further measurements were performed in the acidic solutions using H_2SO_4 at concentrations of 0.02, 0.005 and 0.001 mol L^{-1}. In this case stripping of Bi(0) from the first electrode was carried out using air dissolved in a solution. It was observed that in 0.02 mol L^{-1} H_2SO_4 Bi(0) is dissolved from the electrode during 60 s. In solutions containing lower concentrations of H_2SO_4 Bi(0) is not dissolved completely within 60 s from the electrode using dissolved air. Analogous measurements studying dissolution of Cu(0) from the first electrode in air dissolved in solution were performed. In solution containing 0.02 mol L^{-1} H_2SO_4 Cu(0) is partially oxidized with air. 35 to 45 % of Cu(0) is dissolved from the first electrode and causes interference in subsequent step of measurements. At lower concentrations of H_2SO_4 dissolution rate of Cu(0) with air dissolved in solution decreases, however at such concentrations of H_2SO_4 Bi(0) dissolution is incomplete. The performed research show that for elimination of high excess of Cu(II) interference on Bi(III) determination further study are required.

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VOLTAMMETRIC METHODS OF DETERMINATION OF TRACE CONCENTRATIONS OF SELECTED ELEMENTS USING VARIOUS WORKING ELECTRODES

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Electrochemical techniques seem to be suitable for direct metal ion determination because they offer highly sensitive detection limit with low-cost portable instrumentation and are simple, reliable and easy to use. In trace analysis of gallium, anodic stripping voltammetry (ASV) and adsorptive stripping voltammetry (AdSV) are mainly use. The unusually high sensitivities AdSV method are based on the fact that the analyte is pre-concentrated on the working electrode before the potential scan is performed. The selection of a working electrode material is critical to experimental success. Ideally the electrode should provide a high signal-to-noise ratio over a wide potential range as well as a reproducible response and renewable surface [1]. In this study a lowering of the detection limit of Ga(III) ions determination by stripping voltammetry with the use of a new type of mercury electrode has been proposed. Gallium is a chemical element that is relatively rare and it occurs in nature as gallium(III) compounds. The interest in the determination of gallium traces in the environment is connected with increasing applications of this element in the fields of electronics and medicine [2]. Mercury electrodes are almost ideal for this purpose because they have good adsorptive properties, they are ideally polarizable, have the ideally smooth surface and have a broad negative potential window. That is why, in the above-mentioned voltammetric procedures of gallium determination, in the majority of cases mercury electrodes were used. However, because of the toxicity of mercury a renewable mercury film silver based electrode (Hg(Ag)FE) as a human-friendly construction was used in the proposed work. The possibility of its application for direct determinations in environmental water samples containing organic substances are additional advantages of the proposed idea.

The Ga(III) determination procedure consists of the following steps:
The sample was pippeted to the voltammetric cell and the following reagents were added: 1 mL 1 mol L^{-1} acetic acid + 100 μL 1×10^{-2} mol L^{-1} cupferron. The sample was adjusted to 10 mL with water. The accumulation of the Ga(III)-cupferron complexes was carried out at -0.2 V for 30 s from the stirred solution. This process is the result of adsorption of the Ga(III)-cupferron complexes on the surface of Hg(Ag)FE electrode and it is a non-faradaic process. After the equilibration time of 5 s, the differential pulse voltammogram was recorded, while the potential was scanned from -0.4 to -0.9 V, with the intensity of the obtained peak directly proportional to the concentration of Ga(III) in the sample. During this step, Ga(III)

was reduced to the metallic state. The measurements were carried out from undeaerated solutions. After each measurement a conditioning step was used to remove the target metals from working electrode before the next measurement [3,4].

Results:

Introductory studies with Hg(Ag)FE in acetic-acetate solution containing Ga(III) and cupferron produced a reduction peak at the differential pulse voltammogram, so the optimization of experimental parameters in the determinations of gallium, such as pH and concentration, potential and time of accumulation was performed.

The optimum deposition potentials were found to be -0.2 V. In the case of higher potential a decrease of the gallium peak height was observed. The influence of deposition time on Ga(III) peak current was studied and it was observed that analytical signal of gallium increased almost linearly with accumulation time prolonged to 60 s, in the case of longer accumulation times the peak current of gallium increased insignificantly. In order to shorten time of measurements further studies were performed at deposition time of 30 s.

The optimization measurement were performed for solutions containing following supporting electrolyte: 0.1 mol L^{-1} CH_3COOH (pH=2.88) and CH_3COOH/CH_3COONa in the range from 3.0 to 6.0 (CH_3COOH or NaOH was used to obtain the required medium). It was observed that the extreme signal was obtained in acetic acid and with the increase of pH the signal of gallium decrease.

Cupferron concentration had a considerable influence on the sensitivity of the methods. The results show that the highest peak of Ga(III) appeared at the concentration of cupferron equal 1×10^{-4} mol L^{-1}, so this concentration was adopted as the optimum for further experiment.

The linear range for Ga(III) determination was evaluated under optimum experimental conditions. The peak currents were found to increase linearly with Ga(III) concentration over the range of 5×10^{-10} mol L^{-1} to 3×10^{-7} mol L^{-1} with accumulation time of 30 s. The detection limit estimated from three times the standard deviation for the lowest studied Ga(III) concentration and accumulation time of 30 s was about 2.1×10^{-10} mol L^{-1}. The RSD from solution at a concentration of 1×10^{-7} mol L^{-1} Ga(III) was 3.9 %. The calibration plot was determined by use optimized analytical parameters (the potential accumulation -0.2 V, the detection limit 30 s) from solution containing 0,1 mol L^{-1} CH_3COOH, 1×10^{-4} mol L^{-1} cupferron and appropriate concentration of gallium [3,4].

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NEW, MINIATURIZED VOLTAMMETRIC SENSORS FOR HEAVY METAL IONS MONITORING IN WATER SAMPLES

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Based on performed experiments, a new, simple and fast voltammetric method for Mo(VI) determination in natural water samples was developed. The application of miniaturized, integrated three-electrode screen-printed sensor allows to perform quantitative analysis of Mo(VI) in portable apparatus in field (outside the laboratory), rapid analysis. This approach eliminates problem of samples transport and their storing.

For the determination of Mo(VI), commercially available integrated screen-printed electrode with carbon working electrode was used. The surface of the working electrode was additionally modified with lead on the way of electrochemical reduction of lead(II) ions added to the supporting electrolyte during measurement. This simple step of electrode modification caused significant enhance of analytical signal of Mo(VI) and in consequence leads to lowering the detection and quantification limit. The effect of working electrode covering with lead for the increasing concentration of Pb(II) added to the solution, was imaged for a bare and modified electrodes obtained through transmission electron microscope (TEM) and the presence of Pb on modified working electrode surface was confirmed by energy dispersive X-ray spectroscopy (EDS).

The application of proposed electrode allowed to gain low detection and quantification limits equal 2.12×10^{-11} and 7.06×10^{-11} mol L^{-1}, respectively for deposition time of 60 s. Therefore, calibration curve characterizes wide linear range from 1×10^{-10} to 5×10^{-8} mol L^{-1}.

In order to use the developed method for Mo(VI) quantification in natural water samples, the influence of foreign metal ions: Zn(II), Co(II), Cu(II), Ni(II), Fe(III), Mn(II), Cd(II), V(V), Al(III), Cr(VI), Sn(IV), W(VI), Mg(II) and surfactants: Triton X-100, sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB) was checked. In case of metal ions no influence was observed when the natural excess relative to Mo(VI) concentration occurred, but even small concentration, about 0.5 mg L^{-1} of CTAB or 1 mg L^{-1} of Triton X-100 caused decrease (> 5 %) of Mo(VI) signal. The peak changes of Mo(VI) high relative to output value in the presence of surfactants are shown in Table 1.

Table. 1. The influence of the presence of surfactants in water samples on 5 × 10^{-10} mol L^{-1} of Mo(VI).

$C_{surfactant}$ (mg L^{-1})	**I/I_0 in presence of CTAB ± RSD (n = 3) (%)**	**I/I_0 in presence of Triton X-100 ± RSD (n = 3) (%)**	**I/I_0 in presence of SDS ± RSD (n = 3) (%)**
0.2	102.0 ± 0.4	101.4 ± 0.5	102.3 ± 1.1
0.5	80.3 ± 1.3	101.4 ± 2.0	102.7 ± 0.9
1	57.9 ± 6.9	75.7 ± 1.3	102.0 ± 2.4
2	38.9 ± 1.6	58.6 ± 4.2	101.8 ± 1.9
5	20.8 ± 1.0	41.3 ± 5.8	98.7 ± 2.0
10	11.6 ± 5.7	26.1 ± 6.9	89.6 ± 3.7
20	0	0	54.9 ± 4.8
50	0	0	0

For minimizing the negative influence of surfactants, the resin Amberlite XAD-16 was used. Mass of the resin and time of their shaking with 10 mL of the sample was optimized and it was found that 30 s of the sample mixing with 25 mg of Amberlite XAD-16 is enough for removing disturbing surfactants from natural sample.

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APPLICATION OF MINIATURE SCREEN-PRINTED SENSORS IN VOLTAMMETRIC DETERMINATIONS OF SELECTED BIOLOGICALLY ACTIVE COMPOUNDS

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During the research project, a new voltammetric method was developed for the determination of sildenafil citrate at the integrated three-electrode screen-printed sensor. The commercially available unmodified or modified sensors were checked during the tests (Fig. 1) and the highest signals and the most-defined peaks derived from sildenafil citrate were found on an unmodified sensor in which the working electrode and an auxiliary electrode are screen-printed carbon electrodes, while the reference electrode is silver (a). The results were compared with other sensors in which the working electrode was a carbon electrode (an auxiliary platinum electrode) (b), a carbon electrode modified with carbon nanofibers (c) and a carbon electrode modified with carbon nanotubes (d). The surface of the selected three-electrode sensor was analysed using an optical microscope.

During the tests, the composition of the basic solution was optimized: 0.15 mol L^{-1} acetate buffer pH 5.0 ± 0.1 and electrochemical parameters: differential-pulse voltammetry, amplitude of 100 mV and scan rate of 175 mV s^{-1}. Before each measurement, the solution was mixed using a magnetic stirrer for 180 seconds, during which no potential was applied to the sensor. The calibration curve of sildenafil citrate is linear in the concentration range from 2×10^{-9} to 2×10^{-7} mol L^{-1} and the limit of detection is equal to: 5.94×10^{-10} mol L^{-1}. Using cyclic voltammetry, the nature of the processes occurring on the surface of the electrode was checked, it was found that the analyte approaches the surface of the electrode by diffusion. The influence of many interferents that may be present in pharmaceutical preparations was checked and there was no significant influence of any of them on the height of the analytical signal. The developed method was used to determine the content of sildenafil citrate in two commercially available pharmaceutical preparations Viagra, obtaining satisfactory results.

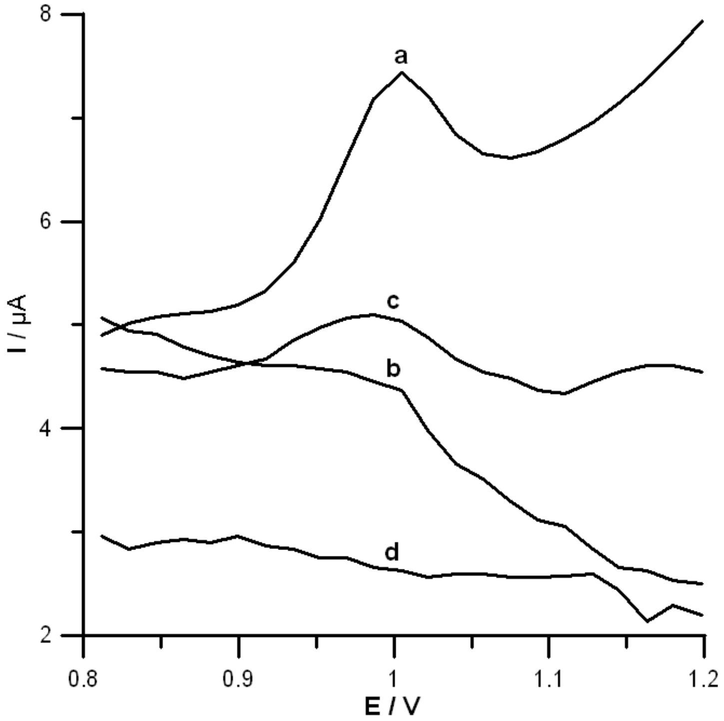

Fig. 1. Differential pulse voltammograms obtained at integrated three-electrode screen-printed sensor (a) carbon working electrode (carbon auxiliary electrode); (b) carbon working electrode (platinum auxiliary electrode); (c) carbon working electrode modified with carbon nanofibers; (d) carbon working electrode modified with carbon nanotubes. Solution containing 1 × 10^{-7} mol L^{-1} sildenafil citrate.

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THE USE OF A NEW DESIGN OF WORKING ELECTRODES FOR MINIMIZATION OF INTERFERENCES IN STRIPPING ANALYSIS

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Stripping voltammetry (SV) is one of the most sensitive electroanalytical method and can be used for determinations of various forms of elements including uranium. The choice of the working electrode is often a very important issue. The electrode material affects the available range of potentials as well as the limit of quantification. Uranium can be determined on mercury or metal film electrodes [1-2]. The disadvantage of mercury electrodes is the high toxicity of mercury. In case of film electrodes the stage of deposition of the metal film is necessary. The aim of the project was to use a new type of electrodes made of metallic lead. The advantage of the proposed electrode is the absence of metal salt needed for the deposition of film in supporting electrolyte. Furthermore, elimination of the metal film forming step reduces the measurement time. A constructed electrode was applied for U(VI) determination by adsorptive stripping voltammetry.

A solid lead electrode has been applied for adsorptive stripping voltammetric determination of trace concentrations of uranium in the presence of cupferron as a complexing agent. For determination of U(VI) acetate buffer was used as a main component of the supporting electrolyte. The standard procedure of measurement was performed in a following way. The volume of 10 mL of the solution containing the analyzed sample, 0.1 mol L^{-1} acetate buffer (pH 5,0) and 2×10^{-4} mol L^{-1} cupferron was prepared. The accumulation of U(VI) at the solid lead electrode PbE was carried out at -0.85 V for 120 s from the stirred solution. Stirring was preformed using a magnetic stirring bar. After a rest period of 10 s a square wave voltammogram was recorded at a frequency of 200 Hz, while the potential was changed from -0.7 to -1,3 V. All measurements were carried out from undeaerated solutions.

Under optimized conditions the calibration graph for U(VI) with application of proposed electrode was linear from 1×10^{-9} to 5×10^{-8} mol L^{-1} following accumulation time of 120 s. Voltammograms obtained for solution containing increasing concentrations of U(VI) are presented in Fig. 1. The detection limit for U(VI) following the accumulation times of 120 s, calculated as a 3-σ for a low concentration of U(VI) was equal to 4.8×10^{-10} mol L^{-1}. Interferences of foreign ions were studied for a solution containing U(VI) at a concentration of 1×10^{-7} mol L^{-1}. The potential and accumulation time were -0.85V and 60 s respectively. The obtained results are presented in Table 3. The results show that each examined foreign ion at 100-fold excess does not disturb seriously the U(VI) peak current. Cd(II) present in 100-fold excess and Mo(VI) present in 10-fold excess showed a more noticeable interference, partially decreasing uranium signal however, such concentrations of these ions are sparsely present in natural water samples.

The proposed procedure was used for uranium determination in a Czechowka river water samples using the method of standard additions. Because the U(VI) concentrations in analyzed water samples were below the detection limit, recoveries of uranium from the sample spiked with increasing U(VI) concentrations were studied. The obtained recoveries of U(VI) were in the range from 97,5 to 107%. The above results show that the proposed procedure with the use of a solid lead electrode can be applied for the U(VI) determination in natural water samples.

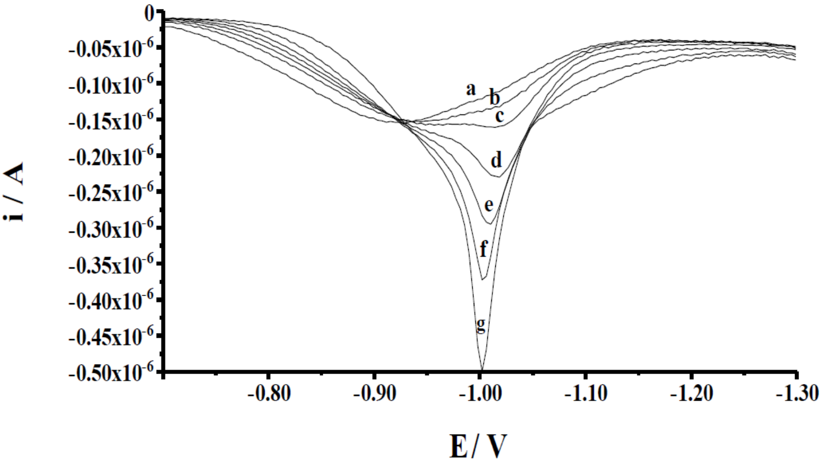

Fig. 1. Square wave voltammograms obtained for solution containing increasing concentration of U(VI): (a) 0; (b) 1; (c) 2; (d) 5; (e) 10;(f) 20; (d) 50 nmol L^{-1} U(VI). Deposition at -0,85 V within 120 s.

Table 1. Relative U(VI) signals in the presence and absence of foreign ions. Concentration of U(VI) was 1×10^{-7} mol L^{-1}.

Foreign ion	Molar excess of foreign ion	Relative signal of U(VI)
Cu(II)	100	118
Zn(II)	100	119
Ni(II)	100	116
Mn(II)	100	106
V(V)	100	101
Pb(II)	100	99
Bi(III)	100	94
Cd(II)	100	55
Mo(VI)	10	88

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THE CATALYTIC IMPACT OF ETHIONINE ON THE ELECTROREDUCTION OF BI(III) IONS IN THE ASPECT OF THE “CAP – PAIR” EFFECT

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Ethionine is an ethyl analogue of methionine and has a very destructive influence on the livers of living organisms and disrupts the activity of many enzymes. Ethionine interferes with the methionine metabolism, leading to depletion of the primary methyl donor, S-adenosylmethionine. It is a strongly carcinogenic metabolite contributing to the development of most types of human cancer [1].

Therefore, it is necessary to monitor the level of ethionine and to demonstrate new methods for determination of this amino acid in various environments.

The “cap-pair” effect opens the door to determination of ions of many depolarisers in weak complexing solutions [2] and, indirectly, of catalysing substances.

The effects of ethionine protonation on the kinetics and the mechanism of multi-step process of Bi(III) electroreduction in chlorates(VII) has been studied. The methodology of the study is based on electrochemical methods: DC polarography, square wave voltammetry SWV, cyclic voltammetry CV and electrochemical impedance spectroscopy EIS.

It was concluded that the presence and the protonation of the ethionine have effects on the rate of the multi-step process of Bi(III) electroreduction in the 2 mol dm^{-3} chlorates(VII). The catalytic activity of ethionine increases with increasing amounts of $NaClO_4$ in the basic electrolyte solution. Increased amounts of $HClO_4$ in chlorate(VII) solutions causes a decreased rate of the Bi(III) ion electroreduction process in the presence of ethionine. The mechanism of the catalytic effect of ethionine is associated with the formation of complexes in specific conditions which exist on the surface of the electrode [3]. The active Bi – ethionine complexes facilitate the exchange of electrons between Bi(III) ions and mercury during depolarisation. The various properties of active complexes, due to the change in ethionine protonation, may be the cause of varied catalytic activity of the studied amino acid.

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ANODIC STRIPPING VOLTAMMETRIC DETERMINATION OF Se(IV) FOLLOWING DOUBLE ACTIVATION OF A GOLD MICROELECTRODES ARRAY

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Selenium is an important micronutrient, needful for the proper functioning of organisms and protection from diseases. Selenium deficiency may cause among the others: disorders of the immune system, increased risk of cancer occurrence, damage to the myocardium, symptoms of hypothyroidism and Keshan disease [1]. Selenium occurs in compounds at various oxidation states from –II to +VI. The most widespread forms of this element occurring in the environment are compounds with selenium at +IV and +VI oxidation states. Among them Se(IV) is the form characterized by the highest toxicity. Maximum selenium concentration that can occur in drinking water (10 $\mu g\ L^{-1}$) is strictly restricted by European Union [3]. Due to these facts there is a necessity for monitoring content of this element in various environmental samples at trace level concentrations.

Stripping voltammetry method belongs to the most sensitive analytical methods and can be used for determinations the various forms of the element in the sample including selenium. Stripping voltammetry is competitive analytical method to spectrometric ones because of low cost of instrumentation and possibility of performing field analysis. As a consequence of application the preconcentration step of an analyte on the surface of working electrodes during the measurement procedure, high sensitivity of voltammetric analysis is obtained. Very important issue in the voltammetric method is the selection of the working electrode, wherein the material has an effect on the available range of potential and also on the limit of quantification. For many years selenium have been determined on gold electrodes. In this work array of gold electrodes was used. Among many different voltammetric sensors, microelectrodes undoubtedly offers a lot of benefits. Firstly, microelectrodes provide the opportunity to analyze samples with very small volumes, from diluted solutions and solutions with organic solvent. Due to the spherical diffusion around the surface of the microelectrode, analyte preconcentration can be carried out without a mixing of the solution and, consequently, in-field analyzes can be performed. Next, microelectrodes utilization gives a possibility of miniaturization of measurements arrangement. The crucial role of application of gold electrodes is minimization of background current. The present study demonstrates a novel procedure which combines the advantages of anodic stripping voltammetry with those of the use of an array of gold microelectrodes activated with an application of a double step potential. Such an electrode activation led to an increase of measurement sensitivity and a decrease of background current.

Standard procedure of measurements

A given volume of the sample was transferred into the voltammetric cell and then 200 μL of 1 mol L^{-1} $HClO_4$ was added and adjusted to the volume of 10 mL with purified water. To begin with the first activation step was performed at potential of -1.5 V within 2 s. Then deposition step was performed using ensemble of gold microelectrodes at a potential of -0.2 V for 180 s from stirred solution. Upon completion of this stage the second activation step was performed at the potential of -1.2 V for 1 s. After equilibration time of 2 s at a potential of +0.3 V a differential pulse voltammogram was recorded while the potential was changed in the range from +0.3 to +1.0 V. The frequency, amplitude and step potential were 8 Hz, 50 mV and 4 mV, respectively. After each measurement the potential of +1.0 V was applied within 10 s to working microelectrode to clean electrode's surface from target metals remaining after previous measurement. After each measurement a new sample solution was prepared. The measurements were performed without solution deoxygenation.

Result and discussion

The calibration graph for Se(IV) for an accumulation time of 180 s was linear in the range from 3×10^{-9} to 3×10^{-8} mol L^{-1} and obeyed the equation $y = 0.892x – 1.203$, where y and x are the peak current (nA) and Se(IV) concentration (nmol L^{-1}), respectively. The linear correlation coefficient r was 0.9996. The relative standard deviation (RSD) from seven determinations of selenium at a concentration of 3×10^{-8} mol L^{-1} was 3.5 %. The detection limit estimated from three times the standard deviation at a low Se(IV) concentration and an accumulation time of 180 s was about 1.3×10^{-9} mol L^{-1}. The detection limit of Se(IV) determination obtained in the presented study is lower in comparison to data reported previously in the literature for selenium determination by ASV. It must be mentioned that the decrease of the detection limit might be achieved by prolongation of deposition time.

The interference of foreign ions was studied for a solution containing Se(IV) ions at a concentration of 3×10^{-8} mol L^{-1} and the deposition time of 180 s. Interferences occurring only in the presence of Pb(II) and As(III) excess and can be easily eliminated by omitting the second step of microelectrode activation at potential of -1.2 V within 1 s.

The proposed method is simple, sensitive and allows for Se(IV) determination in natural water samples without complicated sample pretreatment.

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APPLICATION OF MODIFIED ORDERED CARBON MATERIALS FOR ENRICHMENT AND DETERMINATION OF SELECTED TRACE ELEMENTS IN ENVIRONMENTAL SAMPLES BY GF AAS TECHNIQUE WITH SOLID SAMPLE ANALYSIS

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Determination of trace elements in environmental samples by graphite furnace atomic absorption spectrometry technique is often associated with some difficulties: incompatibility of the sensitivity of GF AAS technique with very low content of analytes in studied samples and strong interferences caused by the presence of complex composition of sample matrix. Therefore there is a necessity of addition of preconcentration/enrichment step to the analytical procedure, which can improve the limit of quantification and simplify the sample matrix introduced into graphite furnace. Both reduction of number of steps of analytical procedure and implementation of green chemistry rules in analytical work can be achieved as a result of the application of high resolution GF AAS technique coupled with solid sample analysis for determination of trace elements in real samples. This combined technique is essential in the case of irreversible adsorption of studied analytes onto solid material [1].

Almost from two decades CMK-3 type carbon nanomaterials are the subject of global research related with their potential application as catalyst carriers, materials increasing electrical conductivity (lithium-ion batteries, supercapacitors, electrodes in voltammetry) and efficient adsorbents of heavy metal ions or molecules of different classes of compounds, such as pharmaceuticals or pesticides. These carbonaceous porous solids can be synthesized by nanocasting method. Carbons of CMK-3 type possess large specific surface area, which can be easily chemically modified. In that way it can be obtained the carbonaceous materials having defined adsorption characteristics toward studied adsorbate. Moreover, the structure of CMK-3 consists of highly ordered mesochannels connected with micropores. It can provide fast diffusion rate of adsorbate to surface active sites of carbon material [2].

In this work the results concerning the physicochemical characterization of CMK-3 material both before and after oxidation by H_2O_2 from liquid phase and optimal parameters for Pb(II) and Cd(II) adsorption onto studied oxidized carbon (initial solution pH value, time to establish the adsorption equilibrium and maximum static adsorption capacity) are presented. Carbon denoted as CMK-3 was synthesized by hard-template route, which consisted of four steps: 1) synthesis of SBA-15 silica by sol-gel method, 2) double impregnation of SBA-15 (hard template) by the mixture of aqueous solution of sucrose (carbon precursor) and concentrated H_2SO_4 (catalyst for sucrose polymerization), 3) pyrolysis of obtained solid at 900°C in Ar atmosphere through 3 hours, 4) leaching of the silica template by 1 M water-ethanol solution of NaOH. Obtained carbon nanomaterial was subsequently oxidized by 2.45 M aqueous solution of H_2O_2 at 90°C through 4 hours.

In Tab.1 the physicochemical parameters of pristine (CMK-3_L) and oxidized (Ox_CMK-3_L) nanocarbons are presented. Both nanocarbons possess 2D hexagonally ordered mesopore structure (P6mm), which is related with the presence of three peaks in small angle XRD patterns denoted as (100), (110) and (200). Material denoted as Ox_CMK-3_L has higher specific surface area, mesopore diameter and total pore volume than pristine ordered mesoporous carbon.

Table 1. Physicochemical parameters of CMK-3_L and Ox_CMK-3_L nanocarbons

Symbol of material	S_{BET} [m^2/g]	d_{BJH} [nm]	V_{TOT} [cm^3/g]
CMK-3_L	496	4.2	0.63
Ox_CMK-3_L	562	5.1	0.75

All static adsorption experiments onto Ox_CMK-3_L material were performed by using 20 mg of studied carbon and 5 mL of Pb(II) or Cd(II) water solution at specified concentration of studied element with adjusted pH from 1 to 4. Both initial and equilibrium concentrations of examined metal ions in upper liquid phase were measured by flame atomic absorption spectrometry at 228.8 nm and 217.0 nm for Cd and Pb respectively. In Tab.2 the optimal Cd(II) and Pb(II) adsorption conditions onto Ox_CMK-3_L are presented. The maximum equilibrium adsorption quantity of both studied metal ions onto Ox_CMK-3_L was observed at initial solution pH equal to 3. Moreover, the adsorption equilibrium of Cd(II) and Pb(II) onto Ox_CMK-3_L carbon in studied adsorption systems was established after 60 min, which can be related with uniform mesostructures of examined material ensuring fast diffusion rates of examined metal ions. For optimal adsorption conditions of Cd(II) and Pb(II) onto oxidized ordered mesoporous carbon the respective m aximum static adsorption capacity values: 1.4 mg/g and 3.8 mg/g were estimated.

Table 2. Optimal Cd(II) and Pb(II) adsorption conditions onto Ox_CMK-3_L

Studied metal ion	Initial pH of solution	Time to establish the adsorption equilibrium [min]	Maximum static adsorption capacity [mg/g]
Cd(II)	3	60	1.4
Pb(II)	3	60	3.8

Presented nanocarbon showed fast Cd(II) and Pb(II) adsorption rate but very low maximum static adsorption capacities towards studied metal ions, which could be improved by further chemical modification of examined material.

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STUDIES ON THE POSSIBILITY OF USING MESOPOROUS ORGANOSILICON MATERIALS AS CARRIERS OF BIOLOGICALLY ACTIVE COMPOUNDS CONTAINING NOBLE ELEMENT ATOMS IN THEIR STRUCTURE

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Since 1978, cisplatin has been the most commonly used drug in the treatment of testicular, lung, ovarian and bladder tumors as well as lymphoma, melanoma and myeloma therapy. However, due to unselective binding to proteins, it causes a very serious side effects including nausea/vomiting, gastrointestinal toxicity, renal toxicity, peripheral neuropathy, and ototoxicity, which often does not allow to use it in doses allowing for the complete elimination of tumors. Some hope to reduce side effects and the possibility of administering higher doses of platinum based drugs are associated with a modification of the form of cytostatics introducing into the body. The use of solid carriers for immobilization and partial selective inactivation of platinum complexes can help to reduce side effects. The simplest way of immobilization of anticancer drugs containing in its molecule platinum atom is their adsorption onto solid materials, wherein the solid sorbent used for immobilization of the drug should not be toxic.

In this work the results concerning the adsorption of cisplatin onto modified SBA-15 silica materials are presented.

The modified SBA-15 material was synthesized as follows: 2 g of Pluronic 123 was dissolved in 72 mL of 2 M HCl. The mixture was stirred at 40°C for 8 h, 18 mmol of tetraethoxysilane (TEOS) was dropped. After 15 minutes 2 mmol of thiocyanatopropyltriethoxysilane (TCTES) or (2-cyanoethyl)triethoxysilane (CETES) was added. The mixture was stirred for 24 h at 40°C and aged for 48 h at 100°C. The obtained material was washed with deionized water, filtered and dried at 70°C. Finally, three-time extraction with ethanol at 70°C was carried out.

The two obtained materials were used as sorbents of cisplatin in static conditions; the adsorption systems consisted of 5 mg of sorbent and 5 mL of cisplatin water solution.

In Fig.1. the influence of equilibrium pH on the adsorption of cisplatin onto synthesized materials is presented. As can be seen, for both sorbents the highest value of cisplatin adsorption is obtained in basic environment. The optimal pH value is about 9.8, above this value the adsorption drastically decreases as a result of silica material dissolution. The maximal static adsorption capacity for cisplatin was fixed based on the adsorption isotherms which are presented in Fig.2. The runs of the isotherms are very similar for both materials, the maximal static adsorption capacity was found to be 155 mg/g for TCTES/SBA-15 and 163 mg/g for CETES/SBA-15. However, such high values of adsorption were observed for adsorption arrangements which contains over 200 mg/L cisplatin in the solution in the equilibrium state.

In Fig.3. the influence of time on the adsorption of cisplatin onto TCTES/SBA-15 and CETES/SBA-15 is shown. The adsorption is very slow. After 4 hours of shaking it is equal only about 10 mg/g. In order to reach adsorption equilibrium state 120 hours of shaking are required. However such long-time shaking of the dissolved compound may lead to its decomposition.

In order to investigate the strength of the cisplatin bonding with sorbents desorption studies were carried out. For this purpose thiourea solution, nitric acid and hydrochloric acid of various concentrations were applied. In Fig. 4 the influence of hydrochloric acid on desorption of cisplatin from synthesized sorbents is presented. The desorption efficiency of cisplatin from TCTES/SBA-15 reached in 10 mol/L HCl is about 20%. In the case of CETES/SBA-15 total desorption of cisplatin is possible when at least 6 mol/L HCl is used. Also in the case of application of thiourea and nitric acid cisplatin is more efficiently desorbed from CETES/SBA-15 than from TCTES/SBA-15.

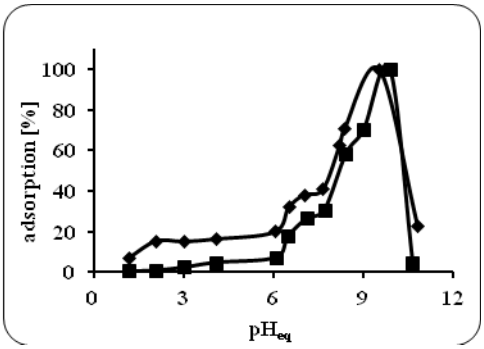

Fig.1. The influence of initial pH on the adsorption of cisplatin onto ■ CETES/SBA-15 and ♦ TCTES/SBA-15 t= 24 h., C_{CisPt}= 149.6 mg/L.

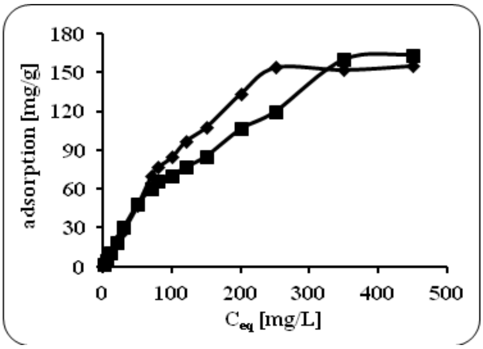

Fig. 2. Cisplatin adsorption isotherms obtained onto ■ CETES/SBA-15 and ♦ TCTES/SBA-15 t= 120 h, pH_{init}=10.3.

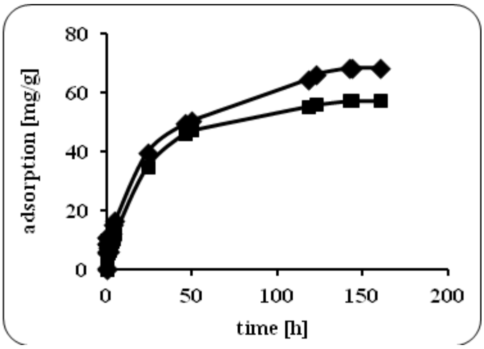

Fig.3. The adsorption kinetics of ciplatin onto ■ CETES/SBA-15 and ♦ TCTES/SBA-15, pH_{init}=10.3, C_{CisPt}= 75 mg/L.

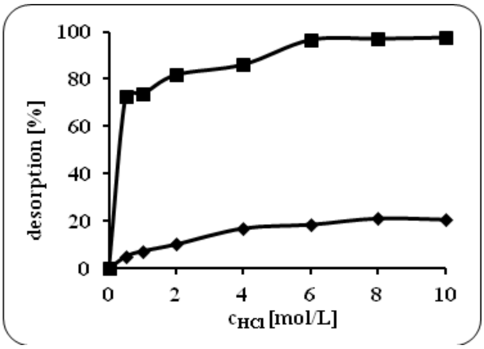

Fig.4. The influence of hydrochloric acid on the desorption of cisplatin from ■ CETES/SBA-15 and ♦ TCTES/SBA-15; V_r= 2 mL, t= 120 h., $A_{TCTES/SBA-15}$= 49.9 mg/g, $A_{CETES/SBA-15}$ = 29.7 mg/g.

SOLUBILIZATION OF ALKYL NAPHTHYL ETHERS IN MICELLES OF ANIONIC SURFACTANTS

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Alkyl naphthyl ethers belong to the family of alkyl aryl ethers - a group of synthetic fragrance raw materials widely used in modern perfumery [1]. Their complex fruity-floral olfactory profile with a dominant orange blossom note, combined with a high chemical stability and resistance to extreme pH values, make them especially useful in perfume blends designed for detergent formulations. However, due to high lipophilicity of alkyl naphthyl ethers, their extensive partitioning into surfactant micelles present in detergent formulations may greatly reduce their volatilization and olfactory performance in this type of formulation. However, data on their interactions with surfactant micelles are very limited [2,3]. It has been shown that appropriate selection of type and composition of surfactants can be used to tune the equilibrium partitioning of perfume raw materials between aqueous and micellar phases with a direct impact on their equilibrium headspace concentrations above aqueous surfactant solutions [4]. Thus, the aim of this study was to quantitatively investigate partitioning of alkyl naphthyl ethers between water and micelles formed by sodium lauryl sulfate (SLS) and sodium lauryl poly(oxyethylene)$_2$ sulfate (SLE2S) by optical spectroscopy. These anionic surfactants were chosen due to their widespread use in consumer products, such as personal and home care products [5]. Furthermore, in order to explain possible differences in alkyl naphthyl ethers solibilization in various surfactant systems, the critical micelle concentrations and aggregation numbers were determined for studied surfactants in order to characterize their aggregation properties in aqueous solutions.

The maximum of a red-edge band of 2-ethoxynaphthalene UV absorption spectrum in water, 0.1M SLS solution and 0.1M SLE2S solution was found at 325.6 nm, 327.6 nm and 328.0 nm, respectively. Similarly, the absorbance ratio at 329.4 nm and 325.6 nm reaches higher value for SLE2S than SLS micelles (Fig. 1.). Both observations implies that stabilization of the molecule in the ground state decreases due to solubilization in SLS micelles and, to a higher extent, in SLE2S micelles. This implies lower polarity of solubilization site and/or weaker hydrogen bonding between water and solute molecules, when solubilized in SLE2S micelles than in SLS micelles [6,7]. Most probably, 2-ethoxynaphthalene molecules are solubilized at the hydrocarbon chain/oxyethylene chain boundary in SLE2S micelles and at hydrocarbon chain/sulfate group boundary in SLS micelles. The differences in solubilization site are reflected in the values of micelle-water partition coefficients, which were determined by fitting experimental values of absorbance ratio $A_{329.4\ \mathrm{nm}}/A_{325.6\ \mathrm{nm}}$ in the pre- and postmicellar region of surfactant concentrations to a mathematical model based on the APN model [8]. The value of micelle-water partition coefficient for SLS micelles was found to be higher (K_{ml} = 890±130 dm^3·mol^{-1}) than for SLE2S micelles (K_{ml} = 594±26 dm^3·mol^{-1}). Similar results were found for other alkyl naphthyl ethers (2-methoxynaphthalene and 2-isobutoxynaphthalene) while the micelle-water partition coefficient increases with an increase of lipophilicity of the molecule. Furthermore, the higher values of K_{ml} for SLS micelles was found to be related to the higher aggregation number of SLS micelles when compared to SLE2S micelles.

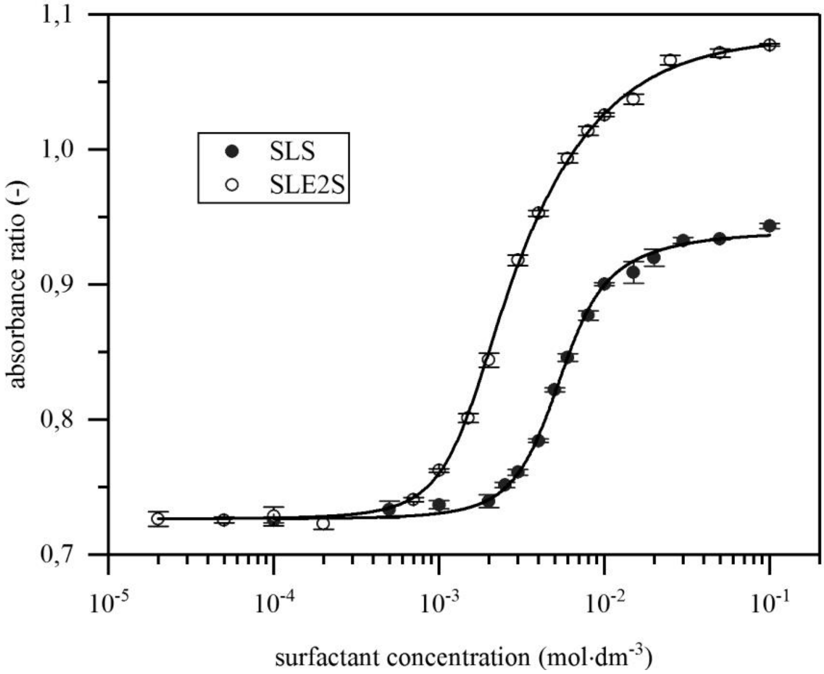

Fig. 1. The effect of surfactant concentration on the absorbance ratio $A_{329.4\ nm}/A_{325.6\ nm}$ of aqueous solution (5·10^{-5} mol·dm^{-3}) of 2-ethoxynaphthalene at 313K. Solid lines are best fits to APN model for monomer and micellar concentrations in surfactant solutions [8].

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CHARACTERISTIC OF TiO_2/BIOPOLIMER CONNECTIONS IN THE DISPERSION SYSTEM AND ON THE SOLID SUPPORT

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Research on properties resulting from natural combinations, biocompatible polymers with inert inorganic substances is a trend in the development of pharmaceutical, medical and cosmetic concerns. The aim of the project is to determine physicochemical parameters of systems containing biopolymers such as chitosan (Ch) and hyaluronic acid (HA) with titanium dioxide (TiO_2).An analysis, among others, of the wettability was made and their hydrophilic-hydrophobic character and effect on the properties of model lipid biological membranes was determined.

Chitosan (Ch)it is a polysaccharide composed of two units: 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-pyranose, containing in the structure amine and hydroxyl groups.This polymer occurs naturally in the shellfish crust, and is also the cell wall component of among others *C. neoformans*and those belonging to the class Zygomycetes,including *Absidiacoerulea*, *Gongronellabutleri*, *Mucorrouxii* and *Rhizopusoryzae*[1-3].However, on an industrial scale, it is obtained as a result of deacetylation of chitin.The popularity of chitosan results from its low cost of production and the ability to create chemical bonds with various inorganic compounds with which it may show a synergistic effect.An example of such a compound is titanium(IV) oxide [4]. Both chitosan and TiO_2, have antibacterial, antifungal and non-toxic properties [5-6]. In addition, these substances are biocompatible and biodegradable in the human body. Due to the unique physicochemical and antibacterial nature, both compounds can be components of skin substitutes. The biocompatibility of mixed systems improves the presence of hyaluronic acid which is the dermal component [7]. Thanks to its excellent moisturizing and anti-aging properties, it occupies an honorable, very high position among the most popular substances used in cosmetic preparations. Therefore, the characteristics of mutual interactions of respective components with cellular membranes are helpful in understanding the processes occurring in the human body.

Investigations of interfacial properties of TiO_2 dispersions with the listed biopolymers and their mixtures in relation to model biological membranes were made using the Langmuir monolayer technique. The main components of biological membranes were used to prepare the model membrane: DPPC phospholipid – 1,2-Dipalmitoyl-*sn*-glycero-3-phosphocholine, DOPC phospholipid – 1,2-Dioleoyl-*sn*-glycero-3-phosphocholine and cholesterol.

Depending on the composition of the membrane and the subphase, the energy of these interactions has changed. However, it was observed that the TiO_2/Ch/HA system and its individual components did not degrade the structure of the model biological membrane. The data resulting from isotherms of the surface pressure as a function of the surface per molecule, which was obtained as a result of phospholipid monolayer compression, was related to free surface energy and its components for lipid films determined on the basis of theoretical approaches. The hydrophilic-hydrophobic properties of the membranes were specified by determining the interactions with liquids of different character, after transferring the subphase to a solid support at a pressure corresponding to the pressure of biological membranes, i.e. 30 and 35 mN/m. At these pressures, phospholipid monolayers formed compact, homogeneous and rigid structuresas confirmed by the images of the Brewster angle microscope (BAM).

The opposite effect occurred in the case of a model bacterial membrane made of DPPG phospholipid – 1,2-Dipalmitoyl-*sn*-glycero-3-phospho-*rac*-(1-glycerol) sodium salt.The presence of Ch, TiO_2 and HA in the subphase influences of the DPPG membrane structure.The greatest changes occur in the presence of TiO_2, which can prove that, the one of mechanisms of antibacterial action of systems containing chitosan, titanium dioxide and hyaluronic acid is probably based on disturbance of bacterial membrane structure.

The variability (or changes) of wettability, chemical composition and surface energy are one of the most important factors helping to specify the interactions between the cell and the surface of the biomaterial, which will allow to achieve the expected response from the biological environment. In addition, determining the synergy of properties of Ch and TiO_2, mainly antibacterial, and additionally the biocompatibility with HA, will help in the skillful control of TiO_2/biopolymer dispersion properties, in order to rationally design safe and effective products used in controlled release of active ingredients, as well as in the production of antibacterial films and even skin substitutes.

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INVESTIGATION OF QUERCETIN AND RUTIN INTERACTIONS WITH NONIONIC SURFACTANTS MICELLES

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Flavonoids are an important element in the human diet. It is estimated that during the day, people should consume about 1g of flavonoid compounds. Despite intense research, the metabolism of flavonoids has not been fully understood. It is believed that almost half of the flavonoids consumed are absorbed unchanged. Flavonoids exhibit in *in vivo* and *in vitro* studies antioxidant, anti-inflammatory, antineoplastic, anti-atherogenic, antiaggregatory, spasmolytic, diuretic, detoxicating, anti-arrhythmic and antihypertensive effects and capillary vessel sealing [1].

Quercetin belongs to the best flavonoids tested so far, however, its solubility in aqueous solutions is small (0.17 - 7.7 μg/ml). Quercetin is a reddish pigment and it is found in many different foods, including in the pigments of the appleskins, in red wine and in red onions. Quercetin has beenlargely investigated for its free radical scavenging andmetal chelating abilities. Particularly, the presence of three hydroxyl groups makes the compound potential free radical scavenger and/or antioxidant. Rutin is the glycoside of quercetin with 3-hydroxyl group blockedby a rutinoside group; it is a bioflavonoid, abundantly present in onions, apples, tea and red wine. A wide variety of biological activities of rutin, including antioxidant, has been reported. It also has poor solubility in aqueous solutions as quercetin. Therefore, much attention is paid to increasing the solubility and the mechanism of transport of these compounds by using for example: microemulsions, nanoparticles, complexes with cyclodextrins or encapsulation using liposomes. It is worth emphasizing that up to now the basis method used for isolation of biologically active substances from raw plant materials is extraction performed under various conditions (hot, cold, assisted by microwave or ultrasonic field, supercritical conditions, etc.). A relatively new method, is the process in which we use surface active compounds (surfactants) for the extraction of active ingredients of plant origin in high concentration. Available literature data mainly concern the study of antioxidant properties of quercetin as well as rutin, moreover they are based on random analysis and unjustified thermodynamic selection of experimental conditions [2, 3].

The aim of the project is to examine the interactions of quercetin and routine with micelles of selected nonionic surfactants. This interactions was determined by testing flavonoids in the aqueous and alcoholic environment without and in the presence of surfactants using measurements of surface tension, both flavonoid solutions and surfactants, spectrophotometric and spectrofluorimetric measurements.

Taking into consideration the results solubilization of quercetin molecules by Tween 80 micelles is much higher than Triton X-114, which is evident from between others from the shape and size of Tween 80 micelles and the influence of quercetin molecules on the water structure around the surfactant chains. Considering the values of the partition coefficient of surfactant-flavonoid and the fixed flavonoid-alcohol bond for the studied systems, it can be concluded that in practical applications, for example in the extraction process, mixtures with the best efficiency should be characterized:

- Tween 80 + Quercetin + propanol
- Triton X-114 + Rutin + ethanol

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STUDY OF VOLUMETRIC PROPERTIES OF NONIONIC KOLLIPHOR SURFACTANTS

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Kolliphor ELP and RH40 are nonionic surfactants obtained by reacting hydrogenated castor oil and ethylene oxide. Kolliphor ELP is used as a solubilizer fat-soluble vitamins A, D, E and K in aqueous solutions for oral and topical administration. Kolliphor RH40 is also used as a solubilizer of fat-soluble vitamins as well as in drug delivery systems [1].

The aim of this project was to determine the volumetric properties of two nonionic surfactants, Kolliphor RH40 and Kolliphor ELP. The research objective will be achieved by performing spectrophotometric and spectrofluorimetric measurements using fluorescent probes with different hydrophobicity, as well as by performing quenching measurements of pyrene fluorescence in aqueous solutions of the tested surfactants in a wide range of their concentration and temperature. On the basis of the obtained research results, the micropolarity and microviscosity the generated micelles will be determined, as well as their number of aggregations.

The first stage of the study was to perform spectrofluorimetric measurements using pyrene as probe. Pyrene is organic compound that consist of four coupled benzene rings. It is commonly used as a fluorescent probe in fluorescence spectroscopy. In the emission spectra of pyrene five characteristic peaks can be distinguished. The intensity of five apices is closely correlated with the surrounding polarity of pyrene monomers in solution. This is very useful in the investigations of solutions of different substances, especially surface active agents (surfactants) [2]. The ratio of the first and third peaks intensity (I_1/I_3 parameter) in the function of concentration of the surfactant allows to determine the critical micelle concentration (CMC). Also from the ratio of excimer to first peak (I_e/I_1) in function of the concentration, CMC also can be calculated.

The aqueous solutions of surfactants, Kolliphor ELP and Kolliphor RH40 ($C = 10^{-8} - 10^{-2}$ M) with the pyrene ($C_{pyrene} = 4\cdot10^{-6}$M) were prepared. The emission spectra of pyrene were recorded on Hitachi FL-2700 spectrofluorimeter. By determining the parameter I_1/I_3 and I_e/I_1 critical micelle concentration of Kolliphor surfactants in aqueous solutions was designated in the presented range of temperature.

On the basis of emission spectra of pyrene in aqueous solutions of Kolliphor ELP and Kolliphor RH40, the values of CMC were calculated and listed below:

Table 1. CMC values [mol/dm^3] for Kolliphor ELP

Parameter	T= 293K	298K	303K	308K	313K	318K
I_1/I_3	$1.22\cdot10^{-5}$	$1.62\cdot10^{-5}$	$2.45\cdot10^{-5}$	$2.69\cdot10^{-5}$	$3.53\cdot10^{-5}$	$4.74\cdot10^{-5}$
I_e/I_1	$6.60\cdot10^{-5}$	$2.04\cdot10^{-5}$	$1.99\cdot10^{-5}$	$2.24\cdot10^{-5}$	$2.04\cdot10^{-5}$	$2.09\cdot10^{-5}$

Table 2. CMC values [mol/dm^3]for KolliphorRH40

Parameter	T=293K	298K	303K	308K	313K	318K
I_1/I_3	$2.45\cdot10^{-5}$	$3.01\cdot10^{-5}$	$3.55\cdot10^{-5}$	$4.26\cdot10^{-5}$	$4.57\cdot10^{-5}$	$6.60\cdot10^{-5}$
I_e/I_1	$6.60\cdot10^{-5}$	$2.04\cdot10^{-5}$	$1.99\cdot10^{-5}$	$2.24\cdot10^{-5}$	$2.04\cdot10^{-5}$	$2.09\cdot10^{-5}$

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STUDY OF THE INFLUENCE OF PHENOLICS EXTRACTION CONDITIONS ON THE RESULT OF THEIR ANALYSIS IN PLANT MATERIAL

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Phenolic compounds belonging to the group of secondary plant metabolites are a group of substances with very diverse structure and properties, including extremely valuable health and healing properties. Unfortunately, these compounds are not synthesized by the human body. Their only source is food, especially plants, fruits and seeds. Among them resveratrol deserves special attention. It is a stilbene representing a group of the phenolic phytoalexins synthesized in plants in response to fungal infections and/or strong stress factor. Resveratrol occurs in two isomeric forms *i.e.* the *cis*- and *trans*- (TR) forms. In addition, it exists as an aglycone and glycosidic forms, which exhibits more hydrophilic properties.

There are many advantageous health properties associated to TR such as antioxidant, anti-cancer, anti-proliferative, anti-inflammatory and anti-angiogenic properties. In the face of so many proven and suggested pro-health activities of TR, it is not surprising that consumer interest in natural products rich in resveratrol is growing. Therefore, more efficient extraction methods, leading to obtain extracts with high TR content, are being sought. It is worth to add that it is not so easy since TR easily degrade/transform to others derivatives, the more that in most cases the long-lasting high-temperature extraction methods are applied, such as extraction in the Soxhlet apparatus or under reflux. The alternative techniques to these classic extraction ones are the so-called assisted extraction techniques *i.e.* pressurised liquid extraction (PLE), ultrasound-assisted solvent extraction (UASE) and microwave-assisted solvent extraction (MASE), which allow for full recovery of compounds from plant samples in a short time. The matrix solid-phase dispersion (MSPD) method or its variant using sand as a dispersing agent (sea sand disruption method - SSDM) is also becoming more and more popular due to a simple and cheap sample preparation procedure involving simultaneous disruption and extraction of various solid and semi-solid materials. The great advantage of the MSPD technique is that it could be perform with high efficiency in low temperatures, what is very beneficial for the isolation of unstable analytes.

The report presents the results of research work on the influence of resveratrol extraction conditions on the evaluation of its actual content in plants. The results obtained using MASE, UASE and PLE were compared to those revealed by MSPD and extraction under reflux. Because the influence of conditions of the selected extraction techniques on resveratrol content may vary depending on the type of matrix extracted, that is why the experiments were carried out on two types of grape matrices, *i.e.* on whole grapes, as well as on grape pulp.

Figure 1 shows the extraction yield of resveratrol obtained applying the UASE, MASE, PLE and MSPD method from the red grapes. Figure 1A and 1B present the yield received from whole grapes and grape pulp, respectively.

Comparing the resveratrol content in the extracts obtained from both matrices, it can be concluded that the whole grapes are characterized by a higher content of this compound than the grape pulp. As to the effect of different extraction conditions on the resveratrol extraction yield from a given matrix, in the whole grapes the highest amount of TR was found in the extract received by the MSPD technique, while the smallest in the MASE technique. In the case of grape pulp the highest TR amount was found in the extract obtained with the PLE technique. It is worth to add that the grape pulp has a more hydrophilic character, which may be related to the preferential presence of more polar TR glycosidic forms. Thus, the higher TR content obtained with the PLE technique than the MSPD may be a consequence of the more destructive nature of the first one and the hydrolysis of the glycosidic forms of trans-resveratrol to the aglycone form.

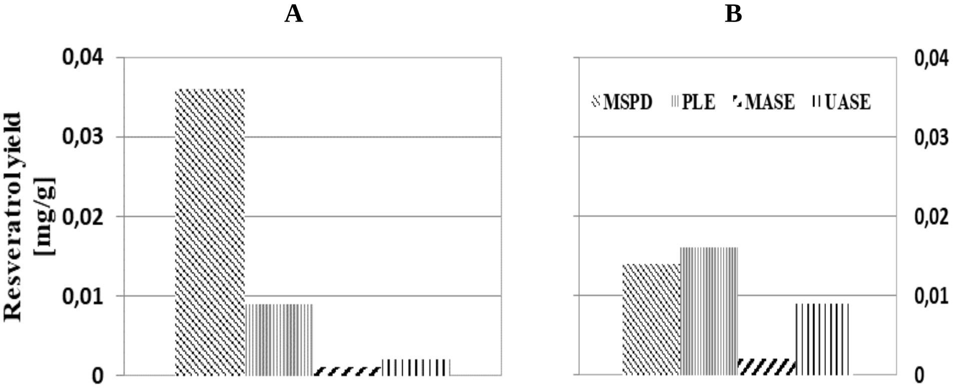

Fig. 1 Yields of resveratrol obtained using MSPD, PLE, MASE and UASE from whole red grapes (A) and grape pulp (B).

During the conducted experiments, the stability of resveratrol standard in simulated extraction conditions was also examined. The simulated extraction conditions were analogous to those used during TR extraction from the whole red grapes and grape pulp. The results are shown in Table 1.

Table 1. Percent residual TR standard after simulated extraction conditions

Extraction technique	**Percentage of the initial quantity [%]**
MSPD	88
UASE	57
MASE	63
PLE	77
Reflux	42

Analysis of the data collected in the table discloses that among the compared extraction techniques, the MSPD technique is characterized by the least destructive nature. The reflux is definitely the most destructive.

Concluding it can be stated that the applied extraction technique differentiates the resveratrol content in the plant extract. This is due to the different extraction power of the compared techniques, as well as the simultaneous transformation and/or degradation of substances that are extracted. Experiments using standards of compounds in simulated extraction conditions are helpful in assessing the degradation degree of compounds during their extraction from plants.

DESIGNING OF FORMULA OF NANOSTRUCTURAL OXIDE CATALYSTS BY USE OF PRECUSORS OF HYDROTALCITE TYPE FOR HYDROGEN PRODUCTION

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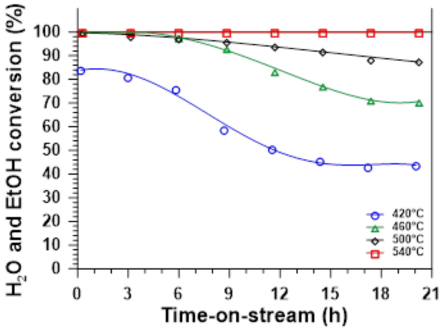
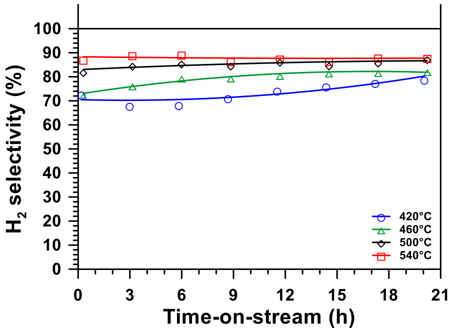
Hydrogen is potentially, a clean energy source for the highly-efficient generation of electricity through fuel cell systems. Among various renewable sources, bio-ethanol produced by fermentation of biomasses seems to represent an excellent candidate owing to its high hydrogen content, availability, low toxicity and ease storage and handling.

The aim of this work was to study the catalytic properties of the cobalt catalyst under steam reforming of ethanol conditions.

The reaction of ethanol conversion with water was carried out under atmospheric pressure in a fixed-bed continuous-flow quartz reactor over the catalyst (0.1 g; 0.15-0.3 mm) reduced in situ with hydrogen at 400°C for 1 hour, prior to the reaction. The aqueous solution of ethanol (H_2O/ethanol=12/1) was supplied to an evaporator (150°C) and the reactant vapours, without diluting with any inert gas, and were fed to the reactor at a flow rate of 100 $mL\times min^{-1}$. The catalytic performance was tested in the temperature range of 390-480°C. The analysis of the reaction mixture and the reaction products (all in gas phase) were carried out on-line by means of two gas chromatographs. One of them, Bruker 450-GC was equipped with two columns, the first filled with a porous polymer Poropak Q (for all organics, CO_2 and H_2O vapor) and the other one—capilary column CP-Molsieve 5 Å (for CH4 and CO analysis). Hellium was used as a carrier gas and a TCD detector was employed. The hydrogen concentration was analyzed by the second gas chromatograph, Bruker 430-GC, using a Molsieve 5 Å, argon as a carrier gas and a TCD detector.





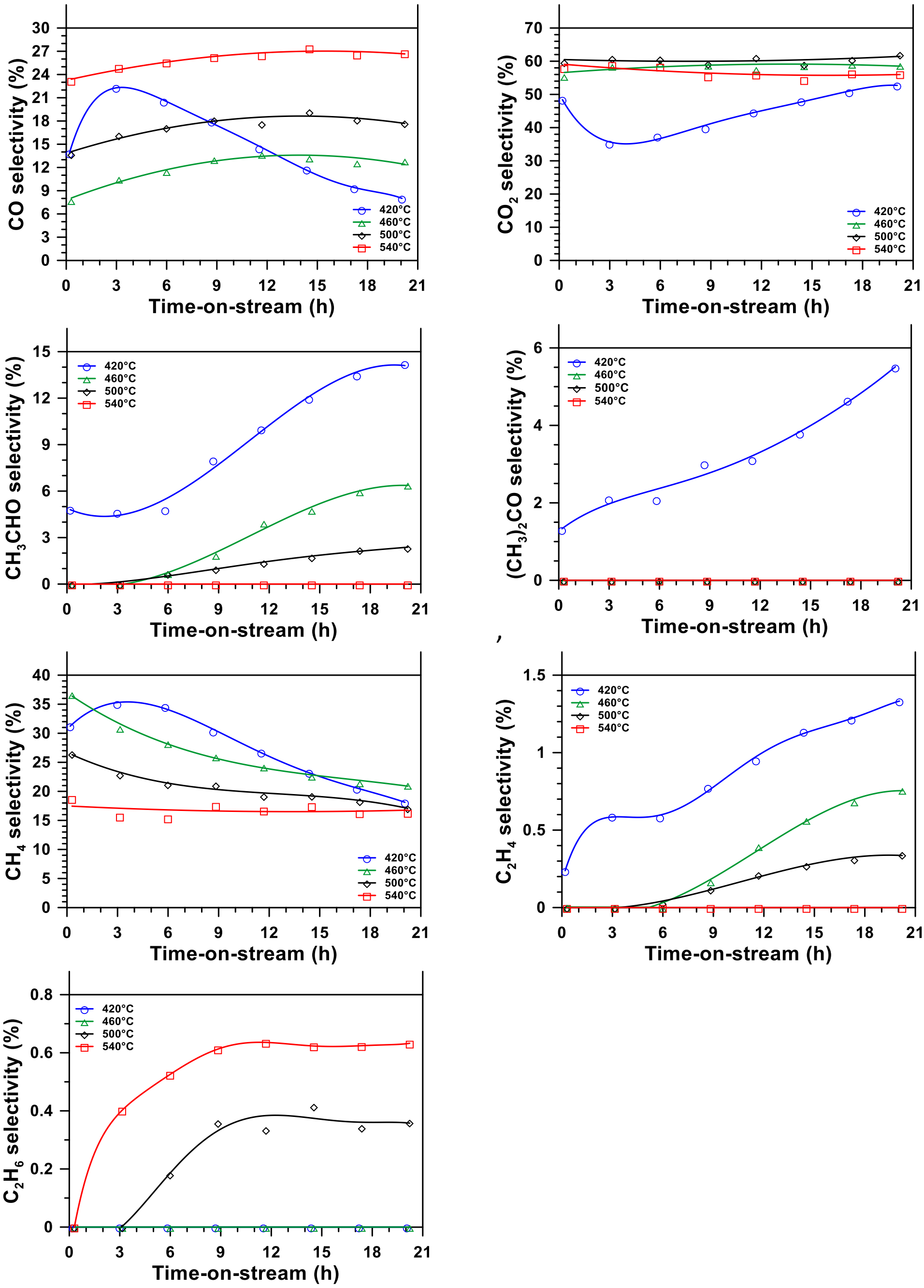


Fig. 1. Effect of the reaction temperature on ethanol and water conversion and selectivity to products over Co-Mg-Al catalyst under SRE conditions.

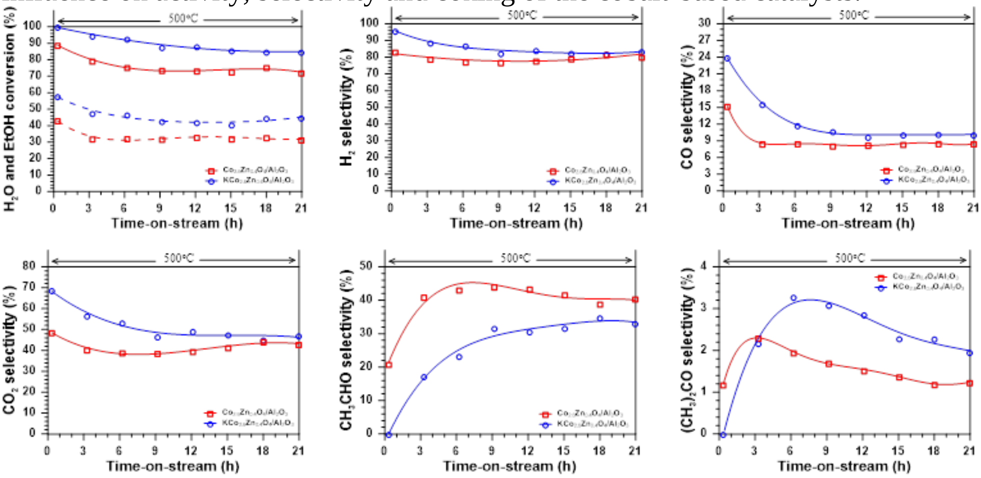
Steam reforming of ethanol (EtOH/H_2O =1/12) over catalyst showed that the temperature of 540°C was the most advantageous for this process. The catalyst indicated the high SRE process selectivity to two most desirable products of reaction, hydrogen and carbon dioxide and amounts of carbon monoxide, methane and acetaldehyde formed in side reactions were much smaller.

ZINC-COBALT OXIDE SPINELS AS CATALYSTS TO HYDROGEN PRODUCTION

Magdalena Greluk
DEPARTMENT OF CHEMICAL TECHNOLOGY

Among the factors which condition the wide range of properties of the oxide spinels at a given chemical composition it is the cationic distribution over the spinel lattice sites that plays a substantial role, especially in clarifying the electric and magnetic properties. Recently, several authors [1-2] have demonstrated that polycrystalline binary oxide spinels $M_xCo_{3-x}O_4$, (M = Cu, Mg, Zn) can be obtained using starting compounds with preset composition and a specific layered structure. Direct methods by solid state reaction of oxides were found not suitable for preparation of such single phase cobalt based spinels due to the low thermal stability of the final product so that alternative techniques have been developed [4]. It is well known that adsorption of alkali promoters on metallic surfaces modifies their electronic properties gauged by the work function. Owing to the exceptionally low ionization potentials of alkali metals, a substantial part of the promotion effect is thought to be related with the charge transfer to the catalyst surface, inducing an electric field gradient at the surface, generated by the resulting dipole moment. Such effects are specially pronounced in the case of heavy alkali atoms because their large ionic radii give rise to large values of the dipole moment and the associated work function changes. Such effect is not exclusive for metal surfaces but has been also reported for molybdenum carbide catalyst, where doping of potassium led to strongly nonmonotonous changes in the work function [5].

The aim of this work was to study the aim of this work was to study effect of potassium promotion on the catalyst performance in SRE reaction and to verify its influence on activity, selectivity and coking of the cobalt-based catalysts.



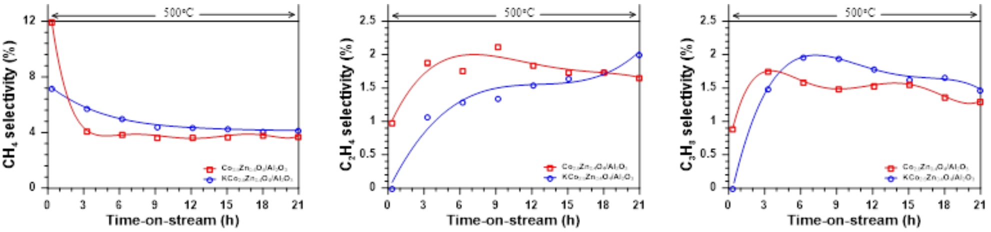


Fig. 1. Effect of potassium on the catalytic properties catalysts in the steam reforming of ethanol at 500°C.

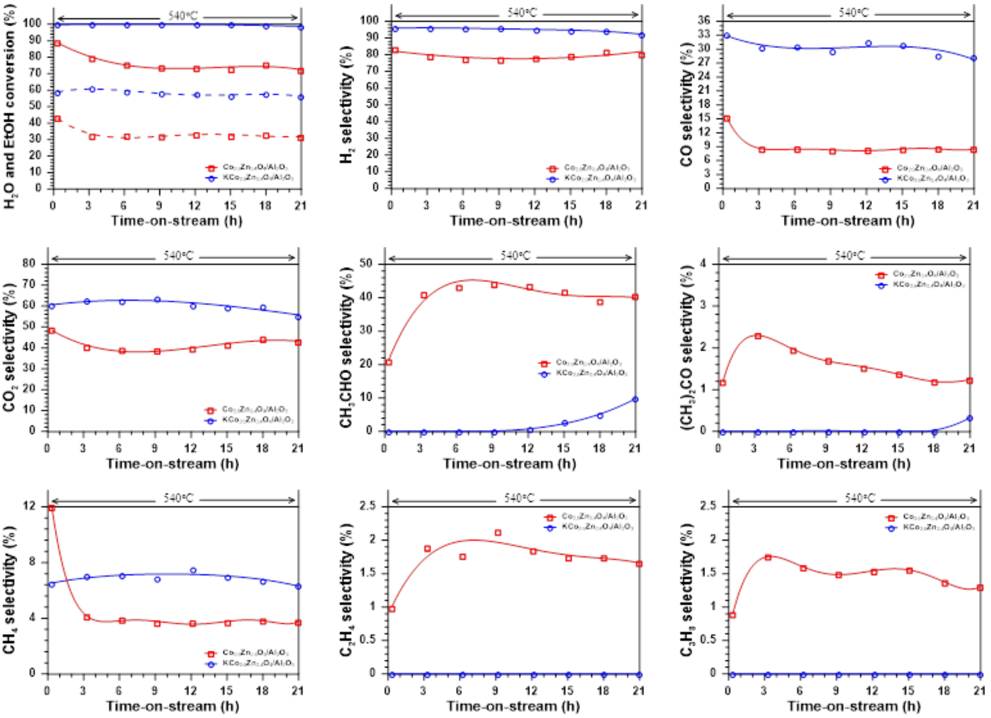


Fig. 2. Effect of potassium on the catalytic properties catalysts in the steam reforming of ethanol at 540°C.

An addition of a small amounts of potassium promoters allows achieve more stable activity measured as ethanol conversion and higher selectivity to two more desirable products of SRE reactions, hydrogen and carbon dioxide. The optimum temperatures of 540 °C is the most advantageous for hydrogen-rich gas production for the SRE performed over studied $KCo_{2.6}Zn_{0.4}O_4/Al_2O_3$ catalyst.

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INFLUENCE OF POTASSIUM PROMOTER ON PHYSICOCHEMICAL PROPERTIES OF NICKEL CATALYST FOR STEAM REFORMING OF ETHANOL

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One of the efficient catalytic processes for obtaining hydrogen is steam reforming of ethanol. A series of reactions (tracks) take part in this process, the proportion of which depends, among other things, on the type of catalyst used. Under the most favorable process conditions, according to the stoichiometric record of the reaction: $C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2$, the maximum hydrogen yield is up to 6 moles with 1 mole of ethanol [1].

Frequently tested heterogeneous catalysts for steam ethanol reforming are catalyst systems based on nickel active phase (usually strongly dispersed on the surface of an inorganic support) that are characterized by high activity, stability, low cost and high selectivity to the most desirable reaction products [2]. In turn, cerium oxide is very often used as a carrier in catalysts intended for reforming steam ethanol. Due to the high oxygen storage and transport properties, CeO_2 has a high activity in various catalytic reactions [3].

Nevertheless, the characteristic disadvantage of nickel catalysts in ethanol conversion is their propensity to create carbon deposits. Therefore, it is important to prevent the formation of carbon deposits, which can be achieved by preventing reactions leading to the formation of carbon. Strategies that lead to the reduction of carbon deposit formation include catalyst modifications by addition of a promoter that would lead to increased catalyst stability in the ethanol steam reforming. The addition of various promoters to catalysts has been extensively studied in ethanol steam reforming. However, promoters with alkaline properties (such as Li, Na, K or Mg) deserve special attention, whose main goal is to limit the formation of carbon deposit or its complete elimination during the reforming of steam ethanol. In addition, the addition of an alkaline promoter can lead to catalyst activity improvement and selectivity to hydrogen and carbon dioxide [4].

The purpose of the research envisaged in the project is to determine the effect of the potassium promoter on the basic parameters of nickel catalyst, such as size and dispersion of crystallites of the active phase, phase composition, reduction and catalytic properties: activity, selectivity and stability in ethanol steam reforming.

The prepared catalysts, based on the nickel active phase deposited on a cerium oxide support, unpromoted and promoted with potassium, were subjected to studies using transmission electron microscopy (S/TEM) combined with EDX spectroscopy, XRD research, hydrogen chemisorption, TPR and catalytic tests.

Presented results showed that the activation (reduction) of the unpromoted catalyst caused decreasing of the nickel crystallites size as compared to the initial nickel oxide crystallites, while potassium promoter increases nickel crystallites during reduction. It was show also that sintering of nickel crystallites is favoured by alkali. Nevertheless, the addition of potassium promoter to the nickel catalyst decreases the temperature necessary for activation of the nickel active phase. Crystallites of metallic nickel were observed in both catalysts after reduction and after SRE. Under applied SRE conditions ($EtOH/H_2O$ = 1/12 mol/mol; 420 °C) nickel crystallites in the unpromoted catalyst increased, while in the potassium-promoted catalyst their average size decreased, in comparison with those in the reduced catalysts. It proves that in the latter catalyst original nickel crystallites underwent defragmentation by growing carbonaceous deposit. In both catalysts fragments of nickel active phase are pushed from the ceria support by carbon deposit produced during the reaction while the rest of nickel still remains on the ceria support surface. Potassium promoter in the oxide and reduced form KNi/CeO_2 catalyst is very good dispersed on the whole catalyst surface.

Catalysts were also characterized after work in the SRE. On the both catalysts, the formation of a carbon deposit was observed. The carbonaceous deposit nature was different in catalysts formed under steam reforming of ethanol. The potassium promoter in the KNi/CeO_2 catalyst does not protect it against formation of carbon deposit and does not improve its stability under SRE conditions. More important in this respect is a high dispersion of the nickel active phase. The results showed that the crystallites size of the active phase has a much greater influence on amounts of the carbon deposit formed during the SRE reaction than the addition of the potassium promoter to the nickel catalyst. The larger crystallites of the active phase cause higher production of carbon deposit and accelerate deactivation of the catalyst in the SRE process, even if the potassium promoter is present in the catalyst. The unpromoted nickel catalyst with smaller nickel crystallites than those in the potassium-promoted catalyst shows better stability in the SRE.

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SIMULTANEOUS STUDIES OF CATALYSTS ACTIVITY AND COKING RATE IN THE REACTION OF HYDROCARBONS CONVERSION WITH APPLICATION OF TAPERED ELEMENT OSCILLATING MICROBALANCE

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Each catalytic reaction carries the risk of deactivating the catalyst, caused by several phenomena. Among them, catalysts poisoning, sintering and coking can be mentioned. Especially coke deposition takes significant share in drop of catalyst activity and can lead to economic losses on large scale in many processes. Therefore, it is reasonable to conduct research on catalysts, which not only be active in specific reaction but also will be resistant to coking.

There are several methods used to determination of catalyst mass change during reaction time. The most widely applied are Thermogravimetric Analysis (TGA) and Thermo-Programmed Surface Reaction (TPSR). Despite their high popularity, methodological objections appear against it, caused by incomplete contact of the reaction mixture (part of the stream flows next to the weighting pan) with the catalyst sample, as well as variation of hydrodynamic conditions. The reservations also concern the lack of assessment of the effects of carbon deposit formation on catalyst activity.

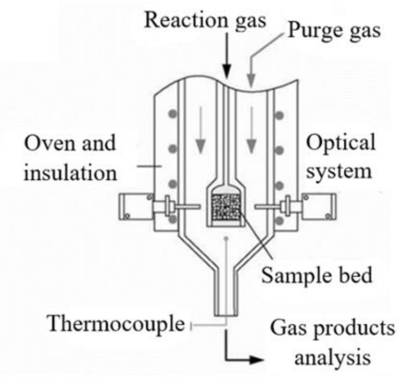

Fig. 1. Scheme of TEOM weighting system

This problems can be solved by application of Tapered Element Oscillating Microbalance (TEOM, Fig. 1). The TEOM microbalance uses the change in oscillation frequency of tapered element to determine mass changes. The use of the oscillating microbalance eliminates the problem of partial washing of the sample by the reaction gas stream and allows the determination of the amount of the carbon deposited on catalyst surface and the composition of the reaction products in a continuous manner. Washing gas (helium) flowing out of the oscillating element directs the reaction products to the microchromatograph (Micro-GC). Thanks to the structure of the constructed reaction and analytical system, it is possible to obtain not only information about the mass change of catalysts (the amount of the coke deposited), but also the full characterization of the process (conversion degree and selectivity to specific gas products).

Possibilities of TEOM application in simultaneous measurements of catalysts activity and resistance to coking were presented during two conferences: 14th Pannonian International Symposium on Catalysis in Stary Smokovec (Slovakia) and LXI Annual Congress of the Polish Chemical Society in Cracow (Poland).

REMOVAL OF RADIOACTIVE SUBSTANCES USING PLANT ORIGINATED LOW – COST ADSORBENTS

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Due to the dangers arising from the presence of radioactive substances of anthropogenic origin in the natural environment, it is important to find potential sorbents that can be effectively used for the radionuclides removal. Concerning the adsorption phenomena of inorganic substances, an low – cost adsorbents (especially wastes from agricultural production) exhibit interesting features. First of all, the mentioned materials are characterized by the great number of the surface functional groups containing oxygen and nitrogen atoms (mainly carboxylic ones) capable of binding ions effectively. Secondly, these solids are easily available constituting waste in many industrial branches. Because they are often not applicable, storage of the large quantities of the plant originated materials can be considered as an serious ecological problem [1]. Moreover, the use of this group of adsorbents decreases process costs, making the adsorption method an attractive alternative to conventional techniques of water and sewage purification.

In the presented studies, two low – cost sorbents: above-ground parts of the *Cladium mariscus* and the oak bark were applied. In both cases, these solids are easily available waste materials. *Cladium mariscus* is a perennial monocot, belonging to the sedge family. It grows up to 3 m height and forms a bulrush at wetland areas. Although the saw sedge is involved in a species protection (in Poland since 2004), for normal growing an annually mowing of leafy parts, connecting with removing of this material, is necessary. However, up till now the removing material has not found any utilization. In turn, the oak bark is a by-product in the wood harvesting and processing industries, but its accumulation in the environment (especially in soil) can provide a serious ecological threat. In addition, the literature data report that it is a promising material in the context of removing cationic pollutants from water and wastewater [2, 3].

The aim of this research project is to determine the sorption mechanism of the selected strontium and caesium radioactive isotopes on the plant based low – cost adsorbents. Due to its anthropogenic origin, high mobility in the environment and the potential negative effects of the emitted radiation on living organisms, an attempts to find efficient, cheap and easily available sorbents able of permanently bind the mentioned nuclides are the research topic of many investigators. Efficiency and the ability to easy control the adsorption process causes that phenomena occurring at the solid – aqueous solution interface are widely used in the various pollution removing processes. Hence initially, it is necessary to determine the impact of various factors (such as the mass of added solid, contact time and the solution pH) on the amount of radioisotopes bounded at the adsorbent surface.

Understanding the relationships affecting the radioactive ions adsorption is crucial to proper optimization of the process conditions. Moreover, an important aim was to investigate the adsorption efficiency not only in the model systems (containing the given radionuclide) but also in the probes comprising the surface active agents of the different chemical nature. These wisely used compounds can migrate into the aqueous environment, which means that impact of their presence on the strontium and caesium ions sorption on the solid surface should be considered. It should be emphasized that the radioisotope adsorption in systems containing interfering substances is not discussed in the literature confirming the novelty of the present research.

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INVESTIGATION OF THE INFLUENCE OF SURFACTANTS OF DIFFERENT CHEMICAL NATURE ON THE STABILIZING PROPERTIES OF SACCHARIDE/OXIDE SYSTEMS

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DEPARTMENT OF RADIOCHEMISTRY AND COLLOID CHEMISTRY

The colloidal systems containing dispersed oxides find a number of interesting applications in different branches of industry [1,2]. However, the limitation of their practical application is that they are not stable in time, what significantly reduces their applicability. The control of the stabilization and flocculation properties of the system requires knowledge not only of the interactions at the solid-solution interface, but also of the changes of the interfaces during the interactions [3].

This project is dedicated to determining stabilization and flocculation properties of ternary dispersed systems containing a surfactant, saccharide and oxide. Its implementation will require the determination of stability of the studied systems, and obtaining information on their adsorption and electrokinetic properties. This information allows to properly describe the mechanisms of stabilization or destabilization in the studied systems. It was decided to use several different research methods. The method used for the determination of stability of the studied systems is UV-Vis spectrometry. To study the adsorption of the polysaccharides on the surface of the oxide in the presence and absence of surfactants the colorimetric Dubois method was used. These data provide information on whether the polysaccharide adsorbs to the surface of the oxide and how the presence of surfactant affects this process. Due to that, the determination of stability or flocculation mechanisms of the saccharide/surfactant/oxide systems is possible. In addition to the above-mentioned methods the determination of the surface charge density of the studied systems is planned. Moreover, important information about stability of the colloidal systems can be obtained by the measurements of electrophoretic mobility converted into the zeta potential. If the value of the zeta potential in water systems is above + 30mV or below -30mV, such system is considered as stable. Further important information on the interactions between surfactants and polysaccharides (range of surfactant concentrations in which the interaction with polysaccharides occurs and polysaccharide/surfactant interaction energy) will be obtained from the conducted tensiometric and microcalorimetric measurements. This information will allow even more detailed description of the stabilization or flocculation mechanisms of the studied systems. It should also be strongly emphasized that there is a lack of literature reports regarding the properties of ternary colloidal systems in which each component can interact with the other two. Perhaps this is due to the fact that the description of such system is a research problem, what is a consequence of the influence of a very large number of factors on the studied systems.

The aim of this research project is to determine the influence of surfactants of the different chemical nature on stabilizing properties of saccharide/oxide systems. The comprehensive studies of such systems will require the use of substances with different properties and chemical nature. In the group of surfactants, substances such as fluorinated surfactants (Capstone FS-91, Chemguard S-106a), silicone surfactants (Silphos A-100, Silquat J2) and biosurfactants (surfactin, rhamnolipids) were chosen. The selection of the polysaccharides planned for use in the research was made on the basis of their properties and possibilities of potential application in many branches of industry. Because of that, it was decided to choose an anionic polysaccharide obtained from marine algae (alginic acid) and a cationic derivative of natural guar gum. Zirconium oxide was chosen as the adsorbent.

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SYNTHESIS OF ACRYLIC DERIVATIVES OF LIGNIN

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Lignin is one of the most abundant natural aromatic polymers on the Earth, which is synthesized by all land plants. This is a constituent of lignocellulosic biomass. Chemically, it is a complex phenolic biopolymer, which contains aromatic alcohols and a lot of polar functionalities. A huge amount of lignin is derived as a waste product from the wood processing in the paper and pulp industry. It is burned to generate mainly energy. However, lignin is characterized by some properties such as: non-toxic nature, very versatile performance, high value potential, being available and inexpensive in huge amounts which makes it increasingly important in numerous biotechnological applications, such as a tanning agent, adhesive, adsorbent of dyes, metal ions, surfactants, organic pollutants like pesticides and phenols. Lignin possesses a lot of very reactive centers which can be modified in chemical, physical and enzymatic reactions, being a huge potential for their exploitation as the industrial raw materials. What is more, lignin contains numerous oxygen (alcoholic and phenolic hydroxyl, ether, methoxyl) functionalities might be responsible for the sorptive capacity. Lignin as one of the lignocellulosic materials can be used as an effective and resistant sorbent for the removal of many different potential pollutants from wastewaters. It is characterized by mechanical resistance, hydrophilic character, easy functionalization and the possibility to be used in different regimes and forms [1-3].

The aim of the research was the modification and application of lignin in the synthesis of new, polymeric, porous and environmentally friendly microspheres, obtained as a result of the suspension-emulsion polymerization of vinyl monomers (divinylbenzene and styrene). As a result of the introduction of lignin into the structure of microspheres, a material was synthesized, having on the surface a number of functional groups derived from lignin (including -SH) and containing environmentally friendly biopolymer [4]. The obtained porous polymer microspheres have been subjected to analyzes confirming their chemical structure, porous structure, morphology and thermal properties. These materials were used as sorbents, among others for removing phenolic compounds from aqueous solutions using the SPE technique.

The ATR/FT-IR spectra of modified and unmodified lignin are presented in Figure 1. The recovery values of phenolic compounds for the sorbent with 1g of lignin is presented in Fig. 2.

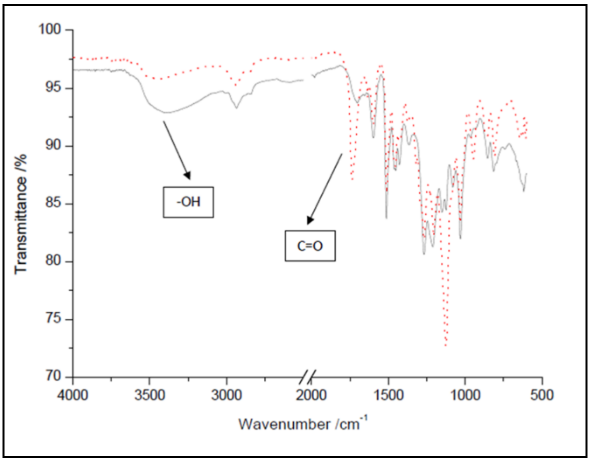

Fig.1.ATR/FT-IR spectra of modified and unmodified lignin.

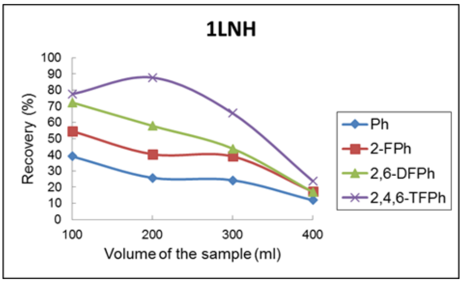

Fig.2. SPE results for the sorbent with 1g of lignin (1LNH). (Ph:phenol, 2-FPh: 2-fluorophenol, 2,6-DFPh: 2,6-difluorophenol, 2,4,6-TFPH: 2,4,6-trifluorophenol).

As follows from these data it can be stated that:
- lignin was successfully modified with methacryloyl chloride,
- the highest recovery values in SPE technique were observed for the sorbent with 1g of lignin (up to 90%). Microspheres with lignin are an effective sorbents for removal of phenolic compounds from aqueous solutions.

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METHACRYLIC DERIVATIVE OF NAPHTHALENE-2-THIOL – SYNTHESIS, STRUCTURE AND POLYMERIZATION

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In the last few years, there has been a growing interest in sulfur-containing polymers, due to their excellent chemical and thermal resistance. Among the sulfur-containing polymers can be distinguish for example: polysulfides, polythioesters, polysulfoxides, polysulfones, polysulfonium salts, polysulfates and others. The variety of the occurrence these polymers provide a wide range of applications. The sulfur-containing polymers may be used as ion-exchange resins, polymeric phase-transfer catalysts, metal ion adsorbents, polymeric reagents, compatibilizers, conducting and photochemical polymeric materials, etc [1, 2].

Nowadays, the thiols are an interesting subject of many studies. Thiols are commonly used as additives in the manufacturing process of several thermoplastics, elastomers or acrylic polymers. Thiols are well-defined chain transfer agents in the free-radical polymerization for such ordinary monomers as styrene or methyl methacrylate [3-5].

This paper presents the synthesis, structure and bulk polymerization of methacrylic aromatic thiol (2-NAF-S-Met). This compound was obtained by reaction of naphthalene-2-thiol (2-NAF-SH) with methacryloyl chloride. The chemical modification of 2-NAF-S-Met was confirmed by ATR/FT-IR method (Fig. 1). Next, the bulk polymerization of 2-NAF-S-Met with commercial monomers - styrene (St) and methyl methacrylate (MMA) was carried out. The amount of monomers used for copolymerization presented in Table 1. The number and mass average molar mass of the obtained 2-NAF-S-Met copolymers were determined by gel permeation chromatography (GPC). Thermal analysis of the obtained materials was also performed using DSC method.

Table 1. The amount of monomers used for copolymerization.

Sulfur monomer	**Co-monomer**	**Copolymerization rates (w/w)**	**Amount of sulfur monomer /g**	**Amount of comonomer /g**	**Initiator (AIBN) (w/w) /%**
2-NAF-S-Met	*MMA* *(or St)*	1:200	0.01	2	0.0201
		1:100	0.02	2	0.0202
		1:50	0.04	2	0.0204
		1:33	0.06	2	0.0206
		1:20	0.1	2	0.0210

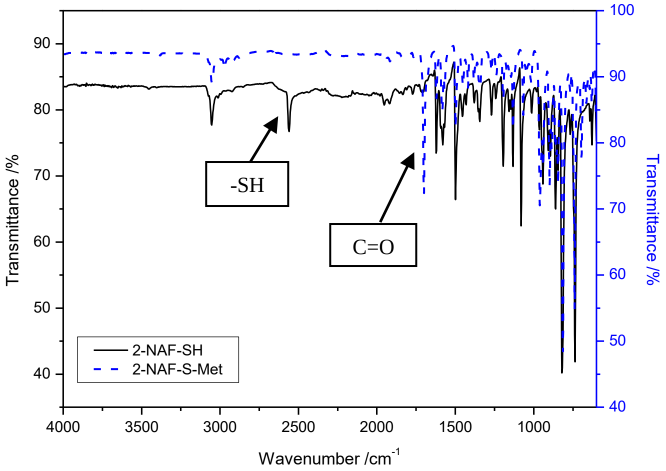

Fig. 1. ATR/FT-IR spectra of naphthalene-2-thiol (2-NAF-SH) and its methacrylic derivative (2-NAF-S-Met).

The use of 2-NAF-S-Met compound as a comonomer in the copolymerization reaction with MMA and St allowed the synthesis of a new group of polymers. DSC measurements indicated that the obtained copolymers possess high thermal resistance, they are stable up to 300°C. The thermal stability of the studied copolymers decreased with the increasing amount of methacrylic monomer. GPC analysis showed that 2-NAF-S-Met comonomer influenced significantly the molecular mass of St+2-NAF-S-Met and MMA+2-NAF-S-Met copolymers. Taking into account the chemical structure, thermal stability and molecular mass of synthesized 2-NAF-S-Met copolymers with St and MMA, and from the other hand the trends in POFs technology, it can be supposed that presented in this study 2-NAF-S-Met monomer can be used as a special additive for polymers used in optical fibres drawing.

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WETTING OF SELECTED SURFACES BY LIQUIDS – COMPUTER SIMULATIONS AND EXPERIMENT

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Wettability studies usually involve the measurement of contact angles as the primary data, which indicates the degree of wetting when a solid and liquid interact. The contact angle of a liquid drop on an ideal solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions: liquid-vapor, solid-vapor, and solid-liquid interfacial tensions, describing by Young's equation. The measurements of this features are very important issue, because research on the properties of the surface layer of different materials is the basis for assessing their characteristics.

The aim of the project is to thoroughly investigate the wetting and wetting process of well-defined, well-characterized surfaces by liquids such as water, diiodomethane and formamide. This goal will be achieved by experimental investigations of wettability of various surfaces using contact angle measurements. Then, these data will be used to develop model systems and force fields for computer simulations of wetting. Additionally, on the basis of experimental and simulation data, the nature of liquid-surface interactions which are used to estimate the value of free surface energy based on different semi-empirical theories will be investigated.

The first stage of the study was to develop a force field for describing behaviour of liquid diiodomethane. Three-site model of diiodomethane molecule (similar to SPC/E water model) based on OPLS-UA (Optimized Potentials for Liquid Simulations – All Atom) force field and one of modification of OPLS-AA (Optimized Potentials for Liquid Simulations – United Atom) force field [1] was developed. All interactions between atoms were described by standard 12-6 Lennard-Jones potential and Coulombic potentials (charged points).

Table. 1. Parameters of the three-center model of diiodomethane.

q [e]	**σ (CH_2)** [A]	**ε (CH_2)** [kcal/mol]	**σ(I)** [A]	**ε(I)** [kcal/mol]	**C-I** bond [A]	**I-C-I** angle [deg]
0.8	3.905	0.118	3.75	0.6	2.182	116.2

It is necessary to determine more physicochemical parameters (not only all surface tension, but also such a enthalpy of vaporization, self-diffusion coefficient, dielectric constant) and compare them with the experimental data in order to carry out a full test of the model. It may shows that more complex model will be required – taking into account the large dipole moment of the molecule (e.g. model with Drude particle).

As it was mentioned above, presented results are the beginning of systematic investigations of wettability and wetting processes of well-defined and well-characterized surfaces by liquids. The results of these studies will be presented in due course.

Some calculations were carried out at the Academic Computer Centre in Gdańsk.

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BS-M-03-002-18-G-01

METHODS OF PREPARATION, PHYSICOCHEMICAL CHARACTERISTICS AND STUDIES ON THE USE OF ADSORBENTS DERIVED FROM WASTE MATERIALS

Małgorzata SĘCZKOWSKA
DEPTARTMENT OF PHYSICOCHEMISTRY OF SOLID SURFACE

Development of industry and agriculture creates the problems related to the necessity of managing biodegradable wastes, sewage sludge and biodegradable fraction of municipal waste in the recovery of matter and/or energy, improving soil properties, limiting the use of mineral fertilizers and plant protection chemicals, reducing greenhouse gas emissions and carbon sequestration in the soil. Therefore, it is necessary to find a common ground to solve these problems in accordance with the principles of sustainable development. Biocarbons production may be the answer to these environmental problems. These materials are obtained through pyrolysis of energy plants, forest waste, agricultural biomass, sewage sludge, organic fraction of municipal waste and residues from agro-food processing. Depending on the starting raw material used, biocarbons have different physicochemical properties and, as a consequence, have different potential applications. Currently, one of the leading directions of utilization of these materials is to obtain cheap and effective adsorbents for toxins removal [1-2].

The main aim of this study was to develop the possibilities of optimizing the parameters of the pyrolysis process, and to determine the physicochemical and adsorption properties of carbon adsorbents obtained from waste materials.

Walnut shells were selected as a row material to obtain biocarbons. The materials were modified by acid impregnation (CH_3COOOH – C2; H_3PO_4 – C3; H_2SO_4 – C4) and then carbonized in a tubular furnace at 600˚C. One sample, for comparative purposes, was pyrolyzed without modification (C1).

The structural properties of the obtained adsorbents were estimated from nitrogen adsorption/desorption isotherms. On the basis of these studies, the specific and external surface area and volumes of pores (total and micropore) were calculated (these parameters are presented in Table 1).

Table 1. Parameters characterizing properties of the obtained carbons.

Active carbon	S_{BET} [m^2/g]	S_{ext} [m^2/g]	S_{ext}/S_{BET} [%]	V_t [cm^3/g]	V_{mic} [cm^3/g]	V_{mic}/V_t [%]
C1	379	53	13.98	0.17	0.13	76.47
C2	450	54	12.00	0.19	0.16	84.24
C3	447	53	11.86	0.19	0.16	84.24
C4	454	63	13.88	0.20	0.16	80.00

In order to determine the adsorptive properties of the obtained materials, the adsorption kinetic and equilibrium measurements were carried out. As the test adsorbates the compounds from the group of typical organic pollutants were selected: 4-nitrophenol (4-NF), 4-chlorophenoxyacetic acid (4-CPA) and methylene blue (MB). The adsorption data obtained were analyzed by using simple kinetic and equilibrium equations and models.

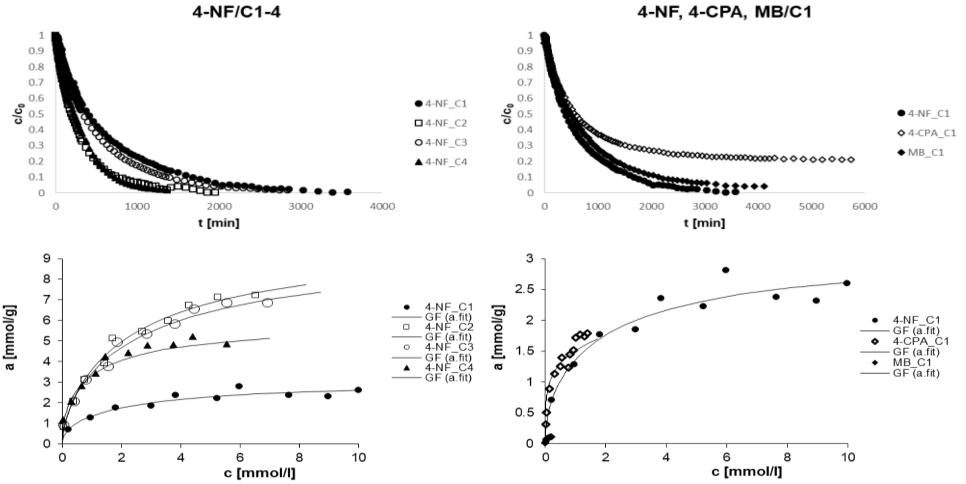

Fig. 1. Comparison of adsorption kinetics (top) and equilibrium (bottom) for 4-NF on C1-4 (left); and 4-NF, 4-CPA and MB on C1 (right).

All kinetic curves were fitted by multi-exponential equation (m-exp). All isotherm data were fitted by the Generalized Freundlich isotherm (GF).

Thermal stability of the received carbonaceous materials were determined from thermal analysis. The studies were performed by using QMS 403D Aeölos equipped with STA449F1 Jupiter mass spectrometer (Netzsch, Germany) and TGA-IR Tensor 27 (Bruker, Germany).

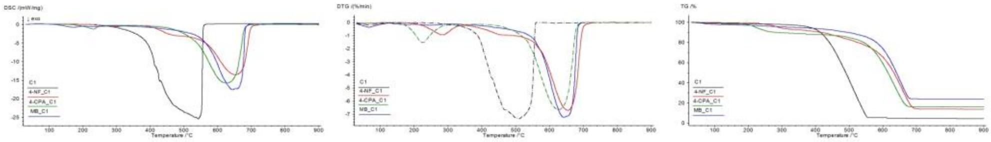

Fig 2. Comparison of DSC (left), DTG (middle) and TG (right) curves for the pure C1 and C1 loaded with 4-NF, 4-CPA and MB.

Based on the analysis of the obtained data, it can be concluded that carbon materials with good adsorptive and thermal properties have been obtained. These adsorbents can be used to remove organic pollutants from waters and wastewaters.

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BIOSTATICITY OF COMPOSITE NANOMATERIALS AS A PRACTICAL DETERMINANT OF APPLICATION POTENTIAL

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DEPTARTMENT OF PHYSICOCHEMISTRY OF SOLID SURFACE

The importance of nanosized metal clusters is well known and appreciated in various sectors of science and modern technology. Noble metal nanoparticles are becoming meaningful components in a wide area of applications, technological solutions, and future developments because of their rare and important physical and chemical properties correlated with their size and morphology [1-3].

Noble metal nanoparticles can be very toxic to bacteria at even low concentrations. In order to preserve this activity, their proper stabilization is required, for example by their incorporation into a solid structure. Immobilization of the nanoparticles by embedding them in common adsorbents may be a means of reducing their number in nature. Increasing problem of the safety of nanomaterials, potential threats in relation to the health of living organisms as well as the natural environment becomes noticeable. Nanocomposites are solid matrices in which nanoparticles are incorporated to provide a material with specific functions such as high barrier, improved mechanical performance, antioxidant capacity, or antimicrobial activity. These nanomaterials act against microorganisms by various mechanisms, which are related to variations in the bacterial cytoplasmic membrane.

The aim of the study was to assess the bactericidal properties and biostatic stability of composite materials containing silver nanoparticles of various sizes and morphologies. In order to comprehensively evaluate the biostaticity phenomenon, various nanomaterials were analyzed using the same bacterial strains and applying the same experimental conditions. The aim of the research was to compare the activity of nanomaterials with the effects generated by systems without nanophases and with the activity of metallic nanoparticles solutions.

Nanomaterials (matrix/AgNP) were tested for antibacterial activity against Gram-negative (Escherichia coli) and Gram-positive (Staphylococcus aureus) bacterial strains. The antibacterial activities of chosen membranes were investigated by a zone inhibition method. The membranes were cut in the form of 5 mm discs and the silver nanoparticles were added in Petri dishes (the volume of AgNP solution was ~1 μl). Membrane discs (3 pieces per plate) were transferred to the dishes containing bacterial strains and incubated for 24 h at 37°C and 32°C, respectively. The zone of inhibition was determined by measuring the diameter of the inhibition area around each disk. Moreover, the membranes without silver nanoparticles and as-synthesized AgNP solution were tested for comparison.

The obtained results suggest, that neither strain showed a significant zone of inhibited growth around in the case of membranes and materials without silver nanoparticles. Even biopolymer materials used as a matrix (chitosan composite) did not exhibit significant limits in the growth of bacteria. The composites with embedded silver nanoparticles gave quite different results, as clear biostatic activity was observed and confirmed by visible changes in the amount of multiplied bacteria. The results show also that the inhibition zone around the discs was two-fold larger for the S. aureus strain than for the E. coli strain (Fig. 1). This observation suggests a difference in the antibacterial effectiveness of AgNP on chitosan nanofibers against Gram-positive (S. aureus) and Gram-negative (E. coli) films. A similar effect was observed previously in the literature [4]. These results confirmed that AgNP in suspension inhibited the growth of bacteria in a dose-dependent manner. The antimicrobial activity increased with the volume of solution used for both the Gram-positive S. aureus, and the Gram-negative E. coli bacteria films. However, again, a slightly higher antibacterial activity was observed against the S. aureus strain than against the E. coli strain.

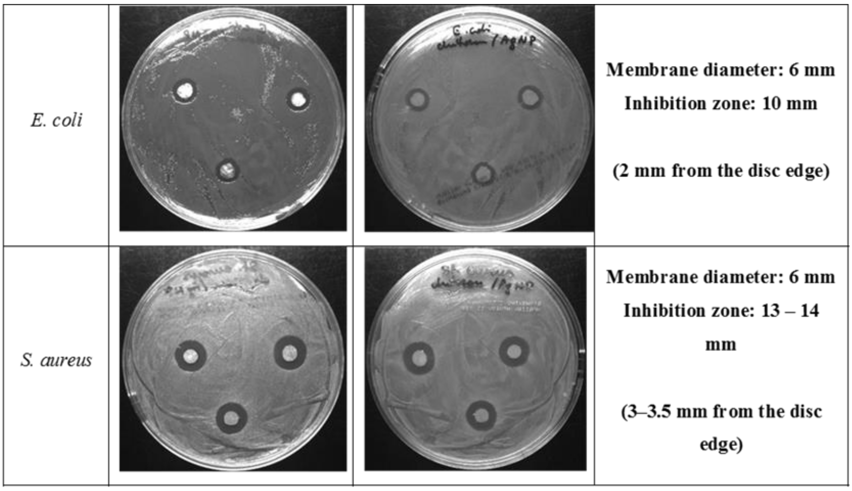

Fig. 1. Photographs of the growth of *E. coli* and *S. aureus* in MHA plates with incorporated Ag/Chitosan/film.

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THE SELECTIVE ADSORPTION PROCESSES OF BIOACTIVE COMPOUNDS ON CARBON AND SILICA-CHITOSAN COMPOSITES.

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Anna DERYŁO-MARCZEWSKA
DEPTARTMENT OF PHYSICOCHEMISTRY OF SOLID SURFACE

The new nanocomposites are an example of the preparation of new functional materials. Among them, nanocomposites based on commercially available materials, as well as natural polymers such as chitosan provides obtaining materials with advanced physicochemical properties and new possible applications. Chitosan-based nanocomposites ensure multi-functionality, biocompatibility, wide range pH stability as well as the activity for these new nanocomposites. The selection and creation of new materials for adsorption purposes should be closely related to the surface chemistry and affinity to the tested adsorbates. The properties and behavior of organic molecules on the surface of a solid body are of fundamental importance in modern applications and developed technologies. Integration of elements from the field such as biological sensors, organic electronics, and integration of bio and nanotechnology is necessary. Although the knowledge of small molecules on the surface is exhaustive, there are still problems understanding the adsorption of larger molecules of biological importance due to their complexity.

In this work, the chitosan/carbon (CS/C) and chitosan/silica (CS/silica) composites were prepared and used as potential adsorbents of sterols (cholesterol). The selected solid matrices have been tested in order to assess their adsorption properties in relation to organic compounds - cholesterol. Cholesterol concentration in experimental samples was determined by chromatographic (HPLC) and spectrophotometric methods. Experimental measurements were performed for the purpose of adsorption efficiency, including the adsorption capacity and the kinetics of this process. On the basis of the obtained results, the relations between the properties of the adsorption system and the efficiency of adsorption processes occurring were determined. The CS/C composites were prepared by impregnation of the activated carbon granules (commercial available RIAA, Norit, n.v., Amersfoort, The Netherlands) in chitosan/acetic acid mixture. CS/silica nanocomposites were synthesized by electrospinning for obtaining the polymer nanofibers. Chitosan solution was prepared by dissolving 2 g of polymer in 70 mL of 70% acetic acid with magnetic stirring at room temperature until a clear solution was obtained. A stable solution of colloidal silica (0.1 g of silica in 20 mL of water) was then added to the chitosan solution. The silica content in the final solutions did not exceed 5%. Finally, 6.68 mL of a 3% PEO solution (10% relative to chitosan) was added to the solution and stirred continuously at room temperature until a homogenous solution was obtained. The electrospinning procedure was carried out using an Elmarco NS LAB 500 (Czech Republic). The polymer solutions were placed in a Teflon cylinder with an active electrode in a parallel position to the collecting electrode.

The obtained experimental adsorption isotherms are presented in Fig. 1 for selected systems. These results suggest the preferred cholesterol adsorption on the chitosan composite.

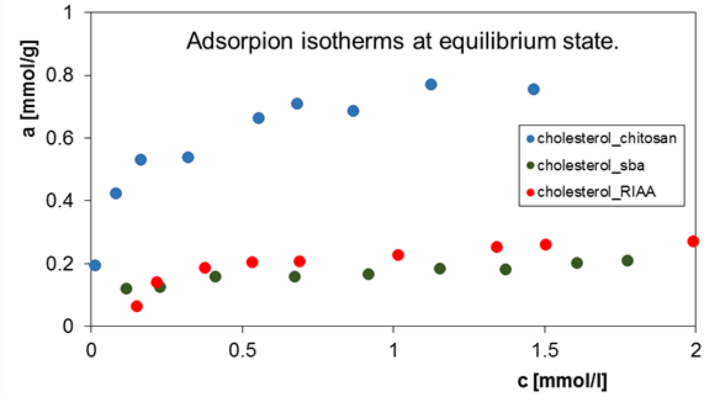

Fig. 1. Cholesterol adsorption isotherms on various materials.

In order to more fully describe the cholesterol adsorption process on selected adsorbents the kinetics of the adsorption process was analyzed. The kinetic curves are presented in the form of changes in adsorbate concentration (C) as a function of time (Fig. 2). The results suggest the preferred adsorption rate also on the chitosan composite.

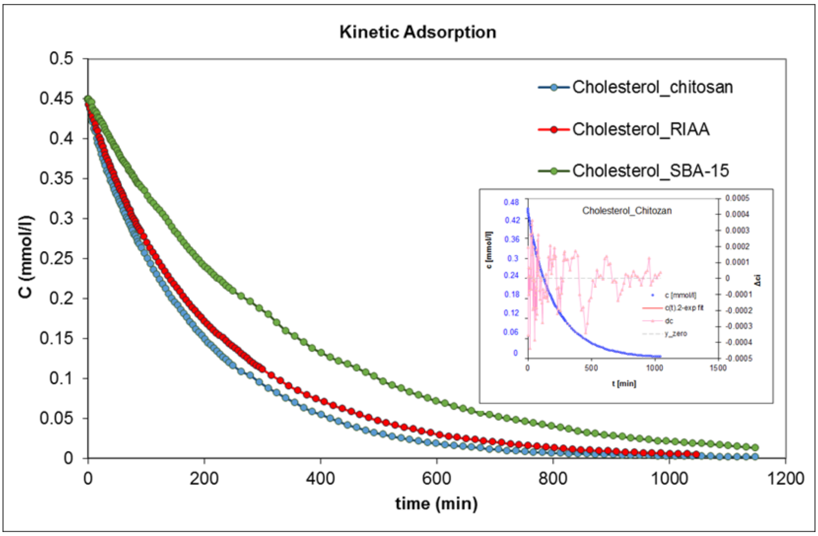

Fig. 2. Kinetic isotherms of cholesterol adsorption on solid materials.