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Faculty of Textile Engineering

FILTRATION OF AIR AND LIQUIDS USING ACTIVE SUBSTANCES

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SUMMARY OF THE THESIS

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Abstract

Clean air and water are the foundation of life on our planet. Therefore, the new approaches for the water and air purification should evolve on a par with other fields of the modern science. Unfortunately all problems of water and air contamination cannot be solved within one thesis. So we focused our attention on two important topics: the antibacterial purification of water and air; the air cleaning from harmful gaseous impurities (nitrogen oxides, carbon monoxide).

The filtration materials for the antibacterial purification of water and air and the new methods for the evaluation of the efficiency of filters with antimicrobial properties are presented in the first part of this thesis. The polymer nanofibers were modified in order to impart them antibacterial properties. The most fundamental contribution was done in the investigation of the antimicrobial modification of polyurethane nanofibers by micro- and nanoparticles of copper oxide by the incorporation of modifier into the polymer solution with further electrospinning by Nanospider technique. The influence of different spinning electrodes (rotating electrode with needle surface and thin wire electrode) on the fiberforming of composite nanofibers from the colloidal solutions was studied. It was found out that the nanoparticles of CuO are not appropriate additives for the used modification procedure due to their great tendency to the aggregation resulting in the uneven distribution of modifier into the fibrous structure. But the polyurethane nanofibers with the micro-sized modifier proved their efficiency and stability in the antibacterial purification of water and air. Furthermore, it was found that the microparticles of CuO contribute to the improving of the spinning performance of polyurethane nanofibers. The antimicrobial polyamide nanofibers were also produced and studied as filters for the water purification. The method of cathodic arc deposition of copper on the surface of polyurethane nanofibers was investigated and confirmed as efficient for the production of antibacterial nanofibrous filters. Two methodologies were developed for the studying of antimicrobial properties of the produced materials under the simulated filtration conditions. The first method is intended to test the fixation of antibacterial additives into the structure of nanofibers. The second method allows to evaluate the filtration efficiency and the ability to eliminate trapped bacteria under the conditions of filtration of bacterially contaminated air. Due to the results of these tests our antibacterial filters can be recommended for the systems of water purification and air-conditioning.

In the second part of this thesis our research activity is focused on the air purification from nitrogen oxides and carbon monoxide using the modified nanofibers with the special photocatalytic agents (TiO_2; combined catalyst SnO_2/CrO_2; micro- and nanoparticles SnO_2 doped by NiO). Based on the experimental results, it was found that the polymer nanofibers had not been the suitable carriers of photocatalytic additives. But because of these experiments a new type of photocatalyst (SnO_2/NiO) for the carbon monoxide oxidation was prepared and studied. And we made our contribution into the determination of the influence of water on the photooxidation of CO. This is important, since there is no consensus about the role of water in this reaction. So it was confirmed that the certain amount of the water vapour is necessary for the carrying out of the photocatalytic oxidation of CO. But the excessive humidity promotes the "flooding" of the active sites at the surface of our photocatalyst. The problem of "flooding" was solved by the decrease of particle's size of the catalyst. Our results can be useful for scientists who study the mechanisms of the photocatalytic oxidation of CO.

Keywords: polyurethane nanofibers, copper oxide, nanoparticles, photocatalyst, filtration.

Anotace

Čistý vzduch a voda jsou podstatné pro život na naší planetě. Vzhledem k intenzivnější činnosti člověka je nutné progresivně rozvíjet nové způsoby čištění vzduchu i vody. Pochopitelně nelze řešit všechny problémy kontaminace vody a vzduchu v rámci jedné disertační práce. Téma práce je zaměřeno na oblast, která není v praxi dosud dostatečně řešena. Jedná se o využití chemicky a biologicky aktivních látek při filtraci, konkrétně antibakteriální čištění vzduchu a vody a čištění vzduchu od škodlivých plynů (oxidy dusíku, oxid uhelnatý).

V první části disertační práce je řešeno téma filtrů pro antibakteriální čištění vody a vzduchu a nových metod vyhodnocení účinnosti filtračních vzorků s antimikrobiálními vlastnostmi. Polymerní nanovlákenná vrstva byla využita jako částicový filtr (zachytávající bakterie) a zároveň jako nosič antimikrobiálních látek. Hlavní přínos lze sledovat v antimikrobiální úpravě polyuretanových nanovláken mikročásticemi a nanočásticemi oxidu mědnatého metodou zavedení těchto částic do polymerního roztoku s následujícím elektrostatickým zvlákňováním pomocí metody Nanospider. Byl prozkoumán vliv různých elektrod (rotační elektrody s jehlovým povrchem a strunové elektrody) na zvlákňování kompozitních nanovláken z koloidních roztoků. Bylo zjištěno, že nanočástice CuO nejsou ve srovnání s mikročásticemi vhodným aditivem pro vybraný modifikační postup vzhledem k jejich agregačním tendencím, což vede k nerovnoměrnému rozložení modifikátoru ve vlákenné struktuře. Polyuretanová nanovlákna s mikročásticemi CuO prokázala dobrou účinnost a stabilitu pro antimikrobiální čištění vody a vzduchu. Kromě toho bylo zjištěno, že mikročástice oxidu mědnatého přispívají k zlepšování výkonu zvlákňování polyuretanových vrstev, aniž by zhoršovaly kvalitu nanovláken. Kromě částic CuO v roztoku byla zkoumána i metoda plazmatického naprašování mědi na povrch polyuretanových nanovláken a potvrzená jako efektivní pro výrobu. Dále byly zkoumány možnosti antimikrobiální úpravy polyamidových nanovláken využívaných pro membránové čištění vody.

Pro testování účinnosti antimikrobiálních vlastností bylo nutné vyvinout a optimalizovat nové metody zkoušek antibakteriálních vlastnosti připravených materiálů za simulovaných filtračních podmínek. První metoda je určena k testování fixace antibakteriálních přísad ve struktuře nanovláken. Druhá metoda dovoluje hodnotit filtrační účinnost a schopnost likvidovat zachycené bakterie za podmínek filtrace bakteriálně kontaminovaného vzduchu. Tato metodika byla úspěšně certifikována.

Ve druhé části disertační práce je výzkumná činnost zaměřená na nanovlákenné filtry s aktivními látkami pro katalytické čištění vzduchu od oxidů dusíku a oxidu uhelnatého za běžné teploty (20°C). Nanovlákna byla aktivována fotokatalytickými látkami TiO_2, kombinovaným katalyzátorem SnO_2/CrO_2, mikro a nanočásticemi SnO_2 dopovanými NiO. Na základě experimentálních výsledků bylo zjištěno, že polymerní nanovlákna nejsou velmi vhodným nosičem fotokatalytických aditiv. Nicméně díky těmto pokusům byl připraven a prozkoumán nový typ fotokatalyzátoru (SnO_2/NiO) pro oxidaci oxidu uhelnatého. Kromě toho byl zjištěn a ověřován důležitý vliv vody na fotooxidaci CO. Tento vztah je důležitý, neboť vlhkost čištěného vzduchu se může výrazně lišit a v dnešní době dosud neexistuje jednotný názor na roli vody v této reakci. Bylo potvrzeno, že určité množství vodní páry je nezbytné pro uskutečňování fotokatalytické oxidace CO, nicméně nadměrná vlhkost podporuje "zaplavení" aktivních center na povrchu fotokatalyzátoru. Problém "zaplavení" byl úspěšně vyřešen snížením velikosti částic

katalyzátoru. Naše výsledky mohou být užitečné pro praktickou aplikaci i pro obecné studium mechanismu fotokatalytické oxidace CO.

Klíčová slova: polyuretanová nanovlákna, oxid mědnatý, nanočástice, fotokatalyzátor, filtrace.

Content

I. Nanofibers with antibacterial properties for water and air purification

1. Introduction

This part of the thesis is focused on the antibacterial modification of nanofibrous filters for water and air purification. Micro- and nanoparticles of copper oxides were used for the modification of nanofibers (NFs) in order to impart them antibacterial activity and to evaluate the influence of dimensional characteristics of modifier on the structural and functional properties of nanofibrous layers. Polyurethane (PU) and polyamide 6 (PA 6) nanofibers were modified by incorporation of CuO particles into the polymer solutions (blending method) prior electrospinning. The industrial technique Nanospider was used for the production of composite filters. The rotating spinning electrode with needle surface and the static wire electrode were compared to determine the suitable electrode for the spinning of nanofibers from colloidal solutions. PU nanofibers were also modified by the magnetron sputtering method in vacuum deposition chamber. The fibrous surface was homogeneously coated by copper using the physical vapor deposition. Great attention was paid to the investigation of modifier's fixation at surface of nanofibers. It is important for the studying of durability of antibacterial properties and of safety of the used modification methods in terms of the entering of antimicrobial substances into the environment. One of the perspective application of produced samples is the bacterial filtration of air. Consequently it was necessary to develop an effective method for the estimation of the fibers ability to capture bacteria from the air stream and to eliminate them. The new testing methodology for the evaluation of antimicrobial properties of nanofibrous layers (and other textiles) under the filtration of bacterially contaminated air was developed and successfully certificated.

2. Purpose and aims of the thesis

Briefly our main aims can be described in the following way:

1. Production of the antibacterial nanofibrous materials by the incorporation of modifier into the polymer solutions with further electrospinning and by the magnetron sputtering method:

- comparison of nano- and microparticles of CuO as antibacterial additives for the modification of nanofibers in terms of their influence on properties of polymer solution and on structure of the future samples;
- selection of an appropriate spinning electrode for the fiberforming by the Nanospider technique;
- antibacterial studies of produced composite samples.

2. Development of the testing methodologies to confirm the particle's fixation into the fibrous structure and to study the bacterial filtration efficiency of modified filters under the simulated filtration conditions:

- determination of particle's fixation into the structure of nanofibers by the testing under the simulated conditions of water filtration;
- investigation of the ability of our samples to capture and to eliminate trapped bacteria under the simulated conditions of bacterial air filtration

- selection of the optimum dimensional characteristic (micro or nano) of copper oxide for the modification of polymer nanofibers.

3. Overview of the current state of the problem

The nanoparticles (NPs) of metals and metal's oxides, well known for their highly potent antibacterial effect, include silver (Ag) and gold (Au), iron oxide (Fe_3O_4), titanium dioxide (TiO_2), copper oxide (CuO), zinc oxide (ZnO), calcium oxide (CaO), magnesium oxide (MgO) and others [1]. In order to make possible the use of antibacterial particles for the air and water purification it is necessary to choose a suitable and stable "carrier". One of the way to solve this task is an incorporation of particles of metals or their oxides into the polymer matrices [2]. Polyurethane has been modified by different types of inorganic clusters, such as Ag, CNTs (carbon nanotubes), Zn-Ag bimetallic particles, tourmaline, silica and ZnO [3]. Sheikh et al. have produced PU NFs containing Ag NPs by the electrospinning technique without adding any foreign reducing agents. The next modification procedure was applied: pure PU 10 wt% was prepared by stepwise dissolving in THF and DMF; $AgNO_3$/DMF solutions were prepared and added to the PU sol−gel to have final mixtures; the modified solution was supplied through a glass syringe attached to a capillary tip to be electrospun [4]. In another study we can observe the use of different silver precursors (silver nitrate ($AgNO_3$), silver benzoate ($C_7H_5AgO_2$), and silver behenate ($C_{22}H_{43}AgO_2$)) and reducing agents (water dispersion of zerovalent silver with polyacrylate surface stabilizer, and organic dispersion of 5% silver behenate in N-ethyl-2-pyrrolidone) for modification of PU nanofibers [5]. The interesting method was proposed to prepare the antibacterial polyurethane-g-polyethylene glycol (PEG) nanofiber composite by the anchoring of silver nanoparticles onto nanofibers via the ultrasonication assistance [6]. The fabrication of bimetallic (Zn/Ag) doped PU nanofibers was also presented. Such composite was prepared using blending method prior electrospinning [7].

Copper and copper oxide are also perspective and efficient antimicrobial agents. Copper is a powerful natural antibiotic being used since ancient times for the purpose of manufacturing of drinking water. However there are only few researches about the modification of PU NFs by Cu or CuO NPs. Sheikh et al. produced PU nanofibers containing copper NPs, by using the blending and electrospinning technique (from plastic syringe) without adding of any foreign chemicals. Antibacterial activity of produced nanofibrous substrates was successfully confirmed [8]. But particle's fixation and antibacterial properties under filtration conditions were not studied. In another study CuO particles were also mixed with the polymer solution to produce the composite PU nanofibers by ES from the plastic syringe. The electrical conductivity of the PU/CuO NFs was markedly improved in comparison with pristine PU nanolayers [9].

Despite the fact that nowadays many researchers use and investigate nanoparticles of metals and their oxides for the experiments in different scientific areas, there are still important problems without clear solutions. We are talking about the toxicity of NPs and their tendencies to the aggregation. NPs absorbed into humans or animals by any route may cause cytotoxic effects, which damage DNA and protein synthesis, prevent or hinder the cell division and eventually lead to the cell death [10]. It is proved that NPs exhibit greater toxicity than micro ones with the same composition, and the various-sized NPs induce different levels of cytotoxicity and DNA damage [11]. Moreover, the nanoparticles have a strong tendency to undergo agglomeration followed by

insufficient dispersal in the polymer matrix, degrading the functional properties of the nanocomposites [12].

The problem of nanoparticles penetration to the environment requires the solution. The parsing of control methods of NPs fixation in the structure of nanofibers (which are already proposed in the literature) is particular important. ZnO/carboxymethyl chitosan (CMCS) composite was prepared and deposited on the plasma treated cotton fabric by Wang et al. The laundering durability of the modified cotton fibers was evaluated according to the AATCC 61(2A)-1996 test method. Ultraviolet Protection Factor (UPF) rate and sterilizing rate were determined after 10, 20 and 30 washing cycles in the presence of a non-ionic detergent [13]. But the applied test method AATCC 61(2A)-1996 evaluates color fastness and staining potential of fabrics under accelerated wash conditions that simulate home washings. The testing conditions don't correspond to the filtration conditions when the water (or air) flow passes directly through the sample. In the study [14] CA, PAN and PVC nanofibers were modified by Ag NPs. The stability of antibacterial properties (it also indicates the stability of particle's fixation) was studied by the test with storage. Samples were stored in the refrigerator for six months and then the antimicrobial activity was evaluated. The results showed that antibacterial properties didn't changed after six months of storage. Authors made the conclusion that the Ag NPs assure long-term antibacterial properties. Maybe such test can be demonstrative for another applications of modified NFs but not for filtration. In another research the durable antibacterial Ag/ PAN hybrid nanofibers were also prepared by the electrospinning. In this case authors have provided silver ion release test. For this aim an atomic absorption spectroscopy was used. A small piece of the electrospun nanofibrous mat (approximately 100 mg) was placed in a glass container, and 150 ml of deionized water was added into the container as the release medium. The container was sealed and agitated to insure the complete immersion of the nanofibrous mat, and then incubated at 37°C. The deionized water was collected every 24 h, and the silver ion concentration in the solution was measured using a spectrometer. Finally, these nanofibers were recommended for the long term contact water operations; like antimicrobial water filters [15]. But such recommendation is questionable. The constant consumption of water with silver ions is highly dubious in terms of its positive influence on the human organism. Besides the ion release test is demonstrative and important only for materials for the biomedical application (for example, wound dressing).

4. Materials and methods

4.1. Polyurethane nanofibers with micro- and nanoparticles of CuO

4.1.1. Materials used

In this work, polyurethane (Larithane LS 1086, aliphatic elastomer based on 2000g/mol, linear polycarbonated diol, isophorone diisocyanate and extended isophorone diamine) was used as a polymer. Larithane LS 1086 was dissolved in dimethylformamide. Polyurethane was obtained from Larithane Company. Dimethylformamide and microparticles of copper oxide with a size distribution of 700 nm-1 μm were purchased from Penta. We also used nanoparticles of CuO with an average diameter of 50nm purchased from Sigma Aldrich. Gram-negative (Escherichia coli) and gram-positive (Staphylococcus gallinarum) strains were utilized as model organisms to

check the antimicrobial properties of the produced nanofibres. The bacteria were obtained from the Czech Collection of Microorganisms (Masaryk University in Brno).

PU solutions were prepared at 15% concentration in DMF. Then micro- and nanoparticles of CuO were added to PU to obtain modified solutions with different concentrations of antibacterial agents (5%; 7%; 9.5%; 12 wt%). These colloidal systems were mixed using magnetic stirrers for 12 hours. Rheological properties of solutions were measured using Rheometer HAAKE Roto Visco 1 at 23°C.

4.1.2. Application of ultrasound

Solutions with nanoparticles were treated by the US using Q SONICA sonicator Q500. Probe with a standard diameter ½ " was inserted into the bottle with solution. Pulsations with the amplitudes 20% and 40% were applied for the treatment of solutions with the aim to evaluate the suitable value of this parameter. The effect of ultrasound on solutions was studied in different time intervals (15; 30; 60 and 120s). After US treatment the PU solutions with CuO nanoparticles were electrospun from the rod spinner.

4.1.3. Electrospinning process – the used techniques and electrodes

At the first step we produced NFs from colloidal PU solutions with micro- or nanoparticles of CuO by ES method from the surface of steel rod. This method was used for the quick checking of the spinnability of modified solutions. The roller spinning method with a high voltage power supply was a second method for the production of PU nanofibers with micro- or nanoparticles of CuO. Such technique is applied for the industrial production of nanofibers. The cylindrical rotary electrode with needle surface was used for the fiberforming in this study. This type of electrode was chosen in order to ensure the stirring of colloidal solutions and to prevent the particles aggregation and their deposition at the bottom of dish with PU. Moreover, electrospinning (ES) from a static wire electrode was also used to produce PU nanofibers with antibacterial additives. This technique doesn't provide the continuous stirring of the solution during fiberforming process. ES was carried out by Nanospider laboratory machine NS LAB 500S (from Elmarco s.r.o.) with air conditioning unit.

4.1.4. Structural and functional properties of modified PU filters

The **morphology** of nanofibrous layers was analysed using a scanning electron microscope (TESCAN VEGA3 SEM) and by QUANTA 650FEG scanning electron microscope. The **average diameter of the fibers and the net diameter distribution** of the samples with different CuO concentrations were measured and calculated from SEM photos using Lucie 32G computer software. The elemental composition of the nanofibers and the percentage content of copper oxide were determined using SEM (Carl Zeiss ULTRA Plus with microanalytical system OXFORD Instruments) equipped by an energy dispersive X-ray spectrometer (EDX).

Standard Test Method ASTM E2149[1] was used to determine **antibacterial efficiency** of produced samples. Antimicrobial activity of nanofibers was carried out against gram-negative Escherichia coli (E.coli) and gram-positive Staphylococcus Gallinarum (St.Gal.) bacterial strains. All produced samples were tested under the simulated conditions of water filtration. It was decided to determine **the stability of particles fixation** based on the results of water

filtration test because its conditions are more aggressive than air filtration and the probability of washing-out of bed-fixed particles is higher. Water was passing through each sample at the flow rate 180 l/hod during 8 hours (1440 liters through each sample). Quantitative antibacterial test and EDX analysis of all treated samples were repeated after the water filtration test. It was done with the aim to verify stability of antibacterial properties and fixation of CuO particles in the structure of nanofibers.

Special testing method was developed in order to evaluate the **bacterial filtration efficiency (BFE)** of antimicrobial samples. The BFE of pristine and modified nanofibers was tested using special device AMFIT 13 (Anti-Microbial Filtration Tester). This methodology was officially certificated by the Czech Environment Management Center. AMFIT 13 (Fig. 1) was applied for the verification of extent to which the filter is able to prevent penetration of the aerosolized inoculum with bacteria to the purifying area.

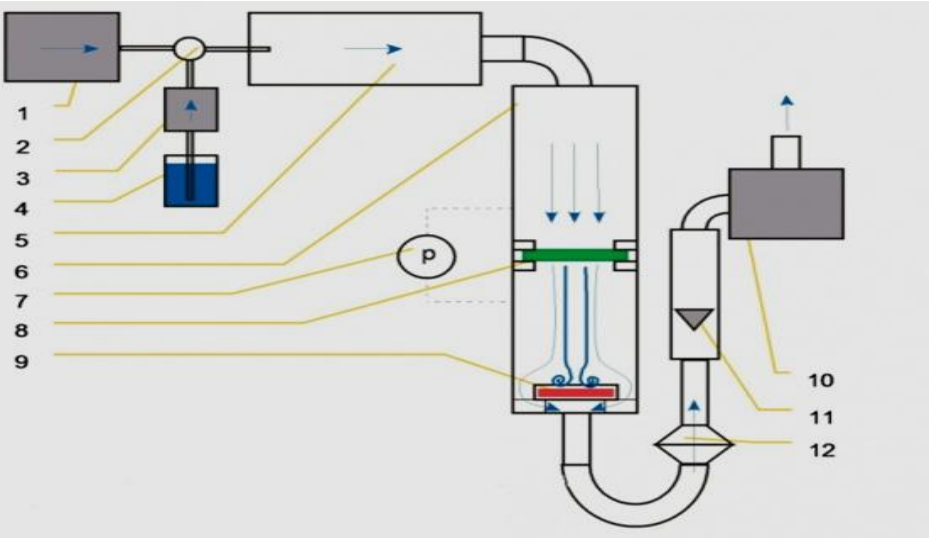

Figure 5. Scheme of AMFIT-13: 1-source of compressed air; 2 - atomizer, 3 - peristaltic pump (dosage control); 4 - reservoir with inoculum; 5 - tube for atomizing; 6 - stabilizing tube with direction of air and aerosol flow before and behind the sample; 7 - pressure gauge sensors; 8 - tested filter; 9 - Petri dish with nutrient agar; 10 - vacuum pump; 11 - float rotameter; 12 - HEPA filter (capture of bacterial aerosol which passed through the tested filter).

The method doesn't determine whether this objective has been achieved by the mechanical capture of bacteria on the filter or by their inhibition due to antibacterial modification of nanofibrous filtration materials. The essence of this measurement is a simulation of a passage of aerosolized contaminated inoculum through the tested sample. The presence of bacteria, which are injected into the testing apparatus and which passed through the filter media, has been analyzed. The Petri dishes with agar were used to determine the amount of bacteria in the device. They were placed at the end of apparatus. Bacteria were captured on the surface of agars and detected after incubation (for 24 hours at 37°C). BFE is defined similarly as in the case of the particulate filtration according to the equation (4):

$$\% \, \boldsymbol{BFE} = \left(\mathbf{1} - \frac{\boldsymbol{n_1}}{\boldsymbol{n_2}}\right) \cdot \mathbf{100} \qquad \textbf{(1)}$$

$\mathbf{n_1}$ - the number of colonies on agar surface when Petri dish is placed behind the tested filter (i.e. amount of bacteria that have not been captured by the filter); $\mathbf{n_2}$- is the number of colonies on agar surface without presence of the filter (i.e. the real amount of bacteria that have been

introduced into the testing apparatus). When the bacterial filtration efficiency was confirmed, the "smear test" was carried out to assess the ability of filters to liquidate captured bacteria.

4.2. PA-6 nanofibers modified by CuO

PA-6 solution was prepared at 12% concentration in the mixture of acetic acid/formic acid (2/1) under heating at 80°C for 5 hours. Then microparticles of CuO (5% wt) were added to PA-6 for obtaining of the modified solution. Modified nanofibers were treated under the influence of temperature, humidity and UV irradiation in order to stabilize copper at their surface. EDS analysis, antibacterial and water filtration tests were provided to prove the rationality of selected stabilization parameters.

4.3. Cathodic arc deposition method for the antibacterial modification of PU NFs

PU nanofibers were used as a substrate for the deposition of copper from pure metallic target. Deposition procedure was carried out in the Radio Frequency Plasma Assisted Chemical Vapour Deposition/Magnetron Sputtering (RF PACVD/MS) chamber. Antibacterial properties of samples and stability of Cu fixation on the surface of nanofibers have been studied.

5. Summary of the results achieved

5.1. Polyurethane nanofibers with micro- and nanoparticles of CuO

5.1.1. Rheological properties

The first step was to compare the viscosities of pristine PU and modified PU solutions with micro- and nanoparticles. It's important because a major increase of viscosity may serve as a first signal to the fact that solution is not suitable for the processing by ES techniques. Starting with concentration 5% the viscosity values of solutions with NPs significantly exceed the corresponding measures of the solutions with microparticles (Fig.2). It may indicate a greater tendency of nanosized additive to the formation of aggregates in the polymer solution.

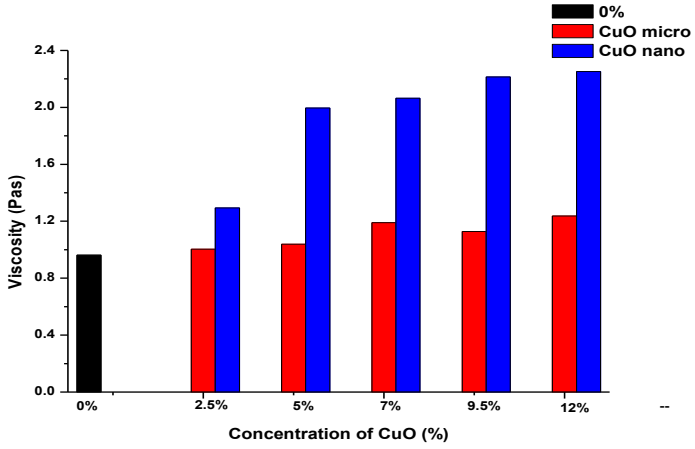

Figure 2. Comparison of average viscosities of pristine PU solution and solutions with micro- and nanoparticles of CuO.

5.1.2. Influence of US treatment on the aggregation of CuO NPs

The spinnability of modified solutions was confirmed by the ES from the rod spinner. Due to SEM analysis it was found out that NPs of CuO had formed quite big aggregates in the structure of nanofibers produced by rod ES. Therefore it was decided to try US treatment of the modified solutions in order to prevent or to decrease the aggregation of NPs. PU solutions were modified by nanoparticles of copper oxide (used concentrations of modifier 2.5; 5 and 7% wt), treated by US and electrospun from the rod spinner. The use of ultrasonication (40% amplitude for 30s) of modified solutions to prevent the aggregation of NPs has been proven as effective only for the solutions with low concentrations (2.5 and 5%) of nanoscale modifier. The attempts to increase duration or amplitude of the ultrasonic treatment led to negative changes in the structure of nanofibrous layers. Therefore no US was applied for the pre-treatment of modified solutions before ES by Nanospider technique.

5.1.3. Modified PU NFs produced by ES from the cylindrical rotary electrode with needle surface

The SEM analysis is enabled to find out the internal morphology of produced mats. In Fig. 3(1) we have an example when NPs aggregate is protected by the nanofibrous web. But in Fig.3(2) we observe an opposite situation. There are large aggregates which aren't covered by fibers. So the stability of such aggregates of NPs in the fibrous structure is unpredictable. And there is no way to control it.

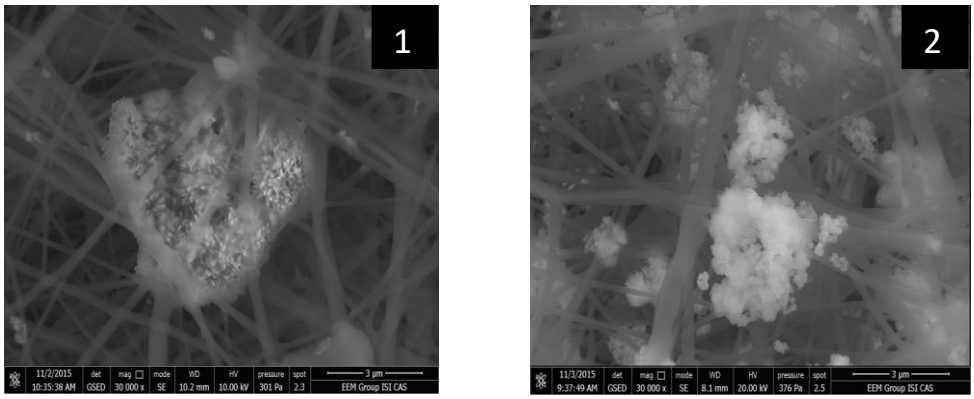

Figure 3. SEM images of PU nanofibers **(1)** with 7% of CuO NPs and **(2)** with 12% of CuO NPs (magnification 30000).

Produced nanofibrous layers have exhibited the smooth surface with diameters distribution in the range 75-650 nm (Tab.1). It can be concluded that in spite of the increase of viscosity of modified solutions and the formation of particles aggregates, the selected concentrations of antibacterial agents do not prevent the electrospinning and have no essential negative impact on the structure of the fibers.

Sample	Number average A_n (nm)	95% Confidence	Weight average A_w, (nm)	Fiber uniformity coefficient K (Aw/An)
Pristine PU	182	5.4	194.5	1.07
PU + 5%CuO μm	226	6.2	239	1.06
PU + 5%CuO nm	228	6.04	239	1.05
PU + 7%CuO μm	278	8.5	298	1.07

PU + 7%CuO nm	262	5.97	270	1.03
PU + 9.5%CuO μm	242	6.9	257	1.06
PU+ 9.5%CuO nm	237	6.1	249	1.05
PU + 12%CuO μm	231	5.7	249	1.08
PU + 12%CuO nm	226	6.9	240	1.06

Table 1. Results of measurement of fibers diameters and calculation of uniformity coefficients.

The SEM-EDX analysis was provided for the confirmation of presence and of approximate percentage content of micro- and nanoparticles of CuO in the structure of nanofibers. Extra peaks responsible for Cu appeared for all samples except pristine PU nanofibers. It was found out (Fig.4) that the detected concentrations of CuO nanoparticles for all samples are higher than the introduced amounts of modifier. It is explained by the tendency to aggregation and corresponds with the high values of viscosity of PU solutions with CuO NPs. This may be reflected in the uneven distribution of the nanoparticles into the structure of the fibers for whole concentration range.

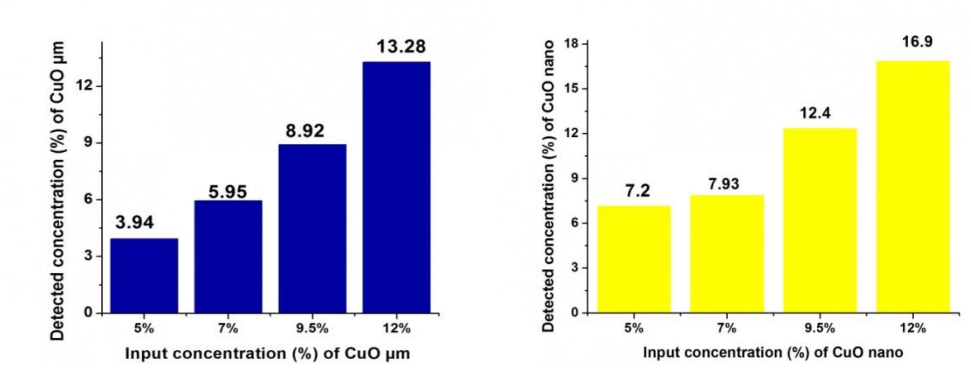

Figure 4. Difference between concentrations of micro- and nanoparticles of CuO in the polymer solutions and in the nanofibrous structures of samples produced from electrode with needle surface.

Micro- and nanoparticles contributed to an increase in the surface density of all of the modified nanofibers in comparison with the pristine PU mat (Tab. 2). The lowest of the selected concentrationы (5%) of CuO MPs provides an almost 5-fold improvement to this characteristic. It is therefore clear that the spinning performance of the polyurethane solution increased with the introduction of the copper oxide. This effect is explained by the well-known conductive properties of copper. The influence of nanoparticles of CuO on the surface density of the fibres is positive but it is not as significant as the influence of the microparticles.

Size and concentration of CuO	Surface density of fibers (g/m²)
PU pristine	2.5
PU + 5% CuO μm	12.28
PU + 5% CuO nm	4.56
PU + 7% CuO μm	13.05
PU + 7% CuO nm	9.89
PU + 9.5% CuO μm	13.93
PU + 9.5% CuO nm	7.41
PU + 12% CuO μm	19.46
PU + 12% CuO nm	5.38

Table 2. Results of surface density measurements for nanofibrous layers produced from rotating electrode with needle surface.

It is possible to observe that the antibacterial activity increased with an increase in CuO concentrations for both sizes of particles (Tab.3). There is no particular difference between the antibacterial properties of the samples with micro- and nanoparticles against the E.coli strain. The test results for the samples with micro- and nanoparticles with Staphylococcus gallinarum are slightly different. Nanofibers with microparticles showed higher activity against the gram-positive strain, but the negative distinction is evident only for the nanofibrous substrate with 5% of CuO NPs.

Sample	Efficiency (%) - **Escherichia coli**		Efficiency (%) - **Staphylococcus gallinarum**	
	µm	**nm**	**µm**	**nm**
PU + 5% CuO	97	96.8	98.8	62.7
PU + 7% CuO	99.7	99.8	100	96.2
PU + 9.5% CuO	100	100	100	98.8
PU + 12% CuO	100	100	100	99.6

Table 3. Antibacterial efficiency of samples prepared from electrode with needle surface against two bacterial strains.

The most important aim of this research was to confirm whether the particles of copper oxide were securely fixed into the structure of the nanofibrous matrix. Therefore, each sample was treated under the simulated conditions of water filtration. Then nanofibers with micro- and nanoparticles after filtration were investigated using the Cornell test to determine their antibacterial efficiency. The change of antibacterial efficiency was not detected in the case of nanofibers modified by microparticles. But as it is shown in Tab.4 a decrease in antibacterial activity was determined for the nano-modified composite mats within the whole concentration range of the nanoparticles against both strains.

Tested sample	Efficiency (%) - **Escherichia coli**		Efficiency (%) - **Staphylococcus gallinarum**	
	before filtration	after filtration	before filtration	after filtration
PU + 5% CuO nm	**96.8**	**86.9**	**62.7**	**30.9**
PU + 7% CuO nm	**99.8**	**91.2**	**98.2**	**80**
PU + 9.5% CuO nm	**100**	**96.8**	**98.8**	**78.3**
PU + 12% CuO nm	**100**	**88.7**	**99.6**	**79.1**

Table 4. Differences of antibacterial activity of samples with nanoparticles of CuO before and after treatment under the simulated conditions of water filtration (experiments with the electrode with needle surface).

The results of the bacterial filtration test correspond to the values of the surface density for all of the prepared samples (Tab.2). As it was mentioned before, the surface density of the nanofibers modified by MPs was higher in comparison with the layers containing NPs of CuO. The samples with 7, 9.5 and 12% of micro-sized CuO demonstrated the highest surface density values, and

these samples showed a100% bacterial filtration efficiency. These results may lead us to the assumption that it is sufficient to use nanofibers with high a surface density for the bacterial filtration and it is not necessary to pay attention to the antibacterial modification of the nanolayers. However, this assumption is erroneous. The capture of bacteria on the surface of the filter is only the first task to be solved. The second important objective is to eliminate the trapped bacteria, and it is at this stage that the antibacterial agents will play a key role.

Sample	Number of bacteria passed through the sample	BFE (%)	Number of survived bacteria after "smear-test"
Inoculum	320	-	-
PU pristine	17	**95**	278
PU + 5% CuO µm	5	**98**	6
PU + 5% CuO nm	15	**95**	13
PU + 7% CuO µm	0	**100**	3
PU + 7% CuO nm	9	**97**	45
PU + 9.5% CuO µm	0	**100**	0
PU + 9.5% CuO nm	11	**96.6**	30
PU + 12% CuO µm	0	**100**	0
PU + 12% CuO nm	11	**96.6**	19

Table 5. Results of the bacterial filtration test and "smear-test" for samples produced from rotating electrode with needle surface.

We can observe in Tab.5 that the results of the “smear test” confirmed the antibacterial activity of all of the modified nanofibers in eliminating the captured bacteria after the bacterial filtration test. The samples with 9.5 and 12% of MPs demonstrated the most impressive results as the complete elimination of trapped bacteria was observed.

5.1.4. Modified PU NFs produced by ES from thin static wire electrode

We can clearly observe in Fig.5 that the structure of nano-modified sample contains a lot of beads. Perhaps some part of NPs aggregates is located inside of these beads.

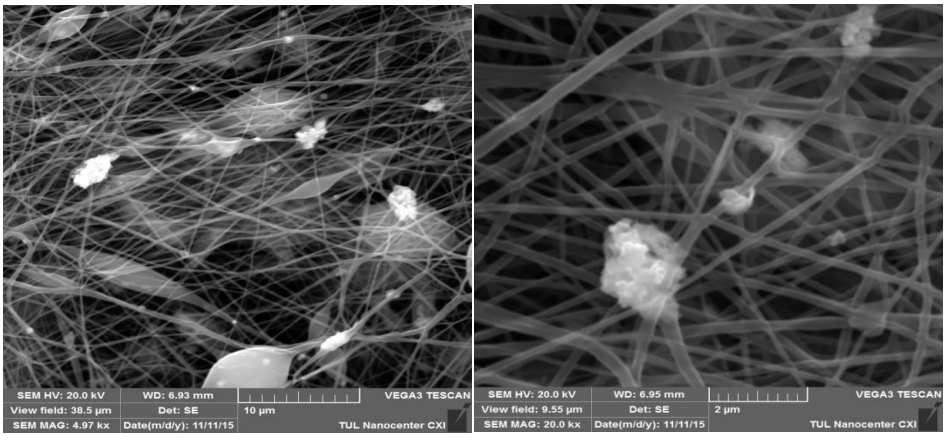

Figure 5. SEM images (magnification 5000 and 20000 respectively) of nanofibers (produced from the wire electrode) with 5% of nanoparticles of CuO.

The EDS analysis confirmed the presence of copper in the structures of all modified layers produced from the wire electrode. In the case with MPs the detected concentration of CuO is much less than the incorporated amount of modifier (Fig.6, red column). It means that microparticles precipitate at the bottom of bath with solution and don’t actively participate in the

ES process together with the solution. Such results of the EDX analysis confirmed our assumption that the rotating electrode with needle surface was obligatory for the efficient electrospinning of colloidal solutions of PU with microparticles of CuO.

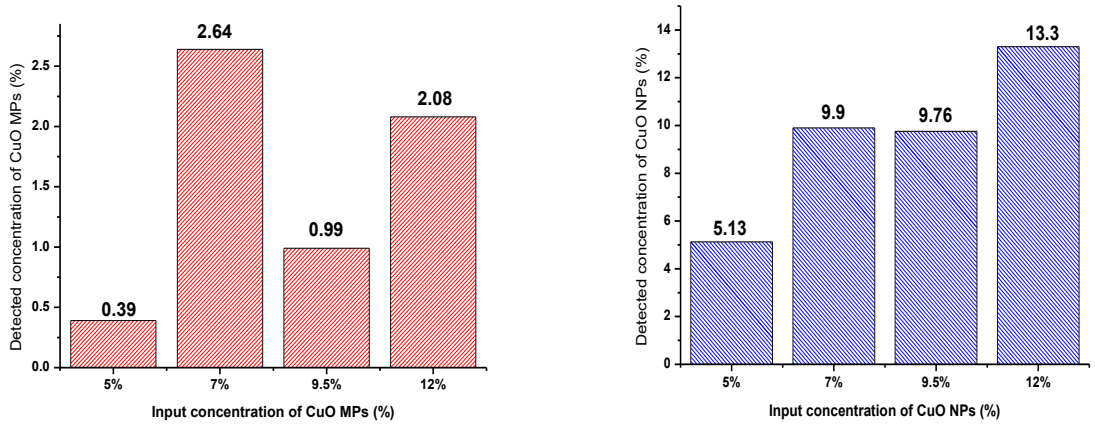

Figure 6. Difference between the concentrations of CuO micro- and nanoparticles in polymer solutions and into the nanofibrous structures of the samples produced from the wire electrode.

The detected amount of NPs into the structure of samples (Fig. 6, blue column) produced from wire electrode corresponds most precisely to the introduced concentrations (5; 7; 9.5 and 12%) in comparison with samples produced from other used electrodes. It may indicate the homogeneous distribution of nanoparticles in the structure of PU fibrous substrates produced from the wire electrode. The results of antibacterial tests will help to confirm or refute such supposition.

According to the results of quantitative antimicrobial tests all composite samples (Tab.6) produced from the wire electrode have significantly lower activity against both tested bacterial strains in comparison with the layers produced from electrode with needle surface. Antibacterial efficiency against Staphylococcus gallinarum is particularly low. In fact we can conclude that such samples are not appropriate for the elimination of this strain.

Sample (produced from wire electrode)	Efficiency (%) - **Escherichia coli**		Efficiency (%) - **Staphylococcus gallinarum**	
	µm	**nm**	**µm**	**nm**
PU + 5% CuO	64	85	0	17
PU + 7% CuO	67	90	23	20
PU + 9.5% CuO	70	89	29	16
PU + 12% CuO	81	96	30	30

Table 6. Antibacterial efficiency of the samples prepared from wire electrode against two bacterial strains.

In case with the micro-modified samples there's no question about their low antibacterial activity. As it was determined by EDX analysis the concentrations of CuO MPs in the structure of PU nanofibers were much lower than the incorporated concentrations. Hence the poor antibacterial properties of samples with MPs were expected. But the samples with NPs don't

demonstrate good antibacterial efficiency (especially against St. Gal.). There are few explanations of such results. Aggregation of NPs was confirmed by SEM images. It can lead to a partial loss of the unique functional properties of NPs. Through the aggregation many nano-scale particles are inside of the clustered formations and they are not available for the contact with bacteria. Moreover there can be the aggregates in the fibrous structure which are not visible for the SEM. A lot of beads in the structure of fibers with NPs was observed in the Fig. 5. If one assumes that these beads are filled with agglomerates of nano-scale CuO, then the low antibacterial activity of these samples can be easily explained.

5.2. PU nanofibers coated by Cu using cathodic arc deposition method

The sample modified by this method demonstrated excellent antibacterial properties (100%) against both strains. Our standard approach was applied for the testing of the stability of antibacterial efficiency and fixation of modifier at the surface of NFs. The sample was tested under the conditions of water filtration with the constant water flow. The concentrations 2.5 and 2.33% of Cu was measured by the EDX analysis before and after water filtration respectively. Such small difference is within borders of permissible error of measurement and doesn't indicate the washing out of Cu from the fibrous surface. Moreover the results of antibacterial tests have confirmed this statement. The difference between antibacterial efficiencies (100% against both strains) of the sample before and after water filtration test wasn't found out. That's why we can conclude that the layer of Cu is firmly attached to PU substrate.

The presented method of modification of PU NFs by the cathodic arc deposition of Cu is very perspective and worth the future experiments. The main advantage of this technology is the homogeneous distribution of modifier onto the surface of modified materials. Moreover the ES process and the structure of future fibers aren't influenced by the adding of extra chemicals for the modification procedure. Deposition process itself is fast. The regulation of thickness of coating layer doesn't cause technological difficulties. And as it was proved by the results of water filtration tests, the well fixed Cu layer had been obtained on the surface of PU NFs.

5.3. PA-6 nanofibers modified by CuO

The production of PA-6 nanofibers with CuO had interesting prehistory. First of all we will discuss so-called "old" and "new" samples. The old samples were produced one year ago. The investigation of these fibers was started one year after their preparation. Excellent and stable antibacterial properties of the "old" samples were determined. Therefore the new batch of the same fibers was produced to continue the experiments. But it turned out that these "new" samples were losing their antibacterial activity after the water filtration test. It means that Cu is in a form of water-soluble salts (acetate and formate) in the structure of NFs. Of course it's not appropriate for the future filtration application. But the behavior of "old" samples from the standpoint of the stability of antibacterial properties was totally different. It means that chemical form of Cu in the structure of PA-6 NFs changed into insoluble during one year of storage. Such chemical transformation could be explained by the involving of Cu into the process of the natural aging of polymer. We've decided to accelerate the aging in order to verify the correctness of such conjecture. Temperature (90°C for 24 hours; 110° for 4 hours), humidity (81% for 35 days) and UV treatment (for 24 hours) were used for the accelerating of aging process. The results of antibacterial tests before and after water filtration (Tab. 7) are the most interesting part of our

experiments with the modification of PA-6 nanofibers by CuO. First of all we can conclude that pristine PA-6 mats didn't inhibit the growth and reproduction of selected bacteria. Modified nanofibers had better antibacterial efficiency against gram-negative strain E.coli. The "old" sample with CuO provided excellent elimination (100%) of E.coli before and after water filtration. The efficiency of "old" NFs against gram-positive strain was also very high before (100%) and after (99.2%) water treatment. "New" sample with CuO without stabilization demonstrated good antimicrobial properties only in its initial form before water filtration. Then (after water treatment) this sample lost its antibacterial activity.

Sample	Efficiency (%) - **Escherichia coli**		Efficiency (%) - **Staphylococcus gallinarum**	
	before filtration	**after filtration**	**before filtration**	**after filtration**
Pristine PA-6	0	0	0	0
PA-6 + CuO, old	100	100	100	99.2
PA-6 + CuO, new	100	15	100	0
PA-6 + CuO, new, T=90°C t=24hours	100	93	100	28
PA-6 + CuO, new, T=110°C t=4hours	100	100	99.2	62
PA-6 + CuO, new, RH=81% 35 days	100	100	95.8	44
PA-6 + CuO, new, UV 24 hod	100	100	98.5	61

Table 7. Changes of antibacterial efficiency of PA-6 nanofibers with CuO before and after water filtration.

The influence of selected parameters for the accelerating of polymer aging had a positive effect on the stabilization of Cu into the fibrous structure of PA-6. As we can see in Tab.7 the antimicrobial efficiencies (100%) of "new" stabilized layers against E.coli aren't changed after water filtration (except one sample - T=90°C for 24hours - 93%). The situation with St. Gal. is worse. But stabilized samples partially preserve their antibacterial activity against St. Gal. after water filtration what cannot be said about the "new" modified NFs without stabilization.

Antibacterial properties of "new" layers after stabilization procedures were significantly improved. We didn't get the same results as for "old" NFs but the selected approach definitely brought positive results. Therefore we can conclude that the results of antibacterial tests of the samples after stabilization procedures confirm our assumption about the positive influence of polymer aging on the stability of Cu in the structure of PA-6 nanofibers.

6. Evaluation of results and new finding

The main goals of this part of thesis were the development of antibacterial filters and the investigation of their properties under the simulated conditions of water and air filtration. To reach these objectives three ways were selected and investigated:

1. Modification of polyurethane nanofibers by micro- and nanoparticles of copper oxide.

The most intensive work has been done in this direction. The selected method of the modification of PU solutions (blending method – incorporation of modifier into the polymer solution with further ES) is simple and does not require making significant adjustments to the fiber forming technology. It was experimentally established that a special spinning electrode must be used for the fiberforming of the efficient antibacterial filters from such solutions. We are talking about the rotating electrode with needle surface. This electrode is required to prevent the precipitation of modifier's particles at the bottom of bath with polymer solution.

An important practical application can find next experimentally established fact. The incorporation of microparticles of CuO contributes to significant improvement of the performance of ES of the polyurethane solution. Therefore, the microparticles of CuO can be used not only for the antimicrobial modification of nanofibers, but also for the improving of electrospinning performance of polyurethane solutions.

As for the antibacterial properties, we found no apparent advantages of nanoparticles in relation to microparticles in terms of future filtration application of our samples. It worth to clarify that microparticles have a slightly higher efficiency (especially against gram-positive strain) than nanoparticles after 24-hours contact with bacterial suspensions. We think that the reason of obtained results lies in the tendency of NPs to aggregation. Due to the formation of big aggregates, nanoparticles lose their major advantage – a larger surface area in relation to the volume. The key indicator of the successful antibacterial modification of filters is the stability of fixation of used antimicrobial substances. The probability of washing-out of poorly fixed particles under the water filtration conditions is higher. For this reason we tested the fixation stability of micro- and nanoparticles in the fibrous structure under the water filtration conditions. This test demonstrated the washing-out of NPs whereas microparticles were securely fastened in the structure of the nanofibers. The nanoparticles at upper layers of aggregates are bound only by physical interaction, so they are washed out by the flow of water. A special device (AMFIT 13) for the determination of BFE was developed and certificated. The samples with microparticles demonstrated higher values of the BFE. Moreover, these samples proved to be more effective in the elimination of captured bacteria than the nanofibers with nanoparticles. Such results are explained by the uneven distribution of NPs in the structure of fibers. So we can conclude that microparticles of CuO are more appropriate additive for the antibacterial modification of PU nanofibers for filtration application than NPs.

2. Modification of PU nanofibers by Cu using the cathodic arc deposition method

It was found out that the used method is also very efficient. The homogeneous distribution of antibacterial layer onto the nanofibrous surface is the biggest advantage of the presented method. Modified samples have good and stable antibacterial properties. They can be recommended as filters for the antibacterial purification of air and water.

3. Modification of PA-6 nanofibers by CuO

"Old" samples of PA-6 with CuO are very efficient and stable filtration materials. We supposed that copper took part in the reactions of polyamide-6 aging (maybe acted as a catalyst of these reactions). With the help of simulation of the aging process of these samples under influence of the elevated temperatures, humidity and UV lights we managed to stabilize copper at the surface

of "new" PA-6 nanofibrous filters. PA-6 nanofibers are known by their good filtration efficiency of particulate matter. Proposed modification procedures make them suitable also for antibacterial water and air purification.

II. Photocatalysts for air purification from NOx and CO

1. Introduction

The process of air purification from dangerous gas emissions and organic compounds can be based on the non-catalytic (adsorption, absorption) and catalytic methods. The catalytic reactions are the most effective tool for the decontamination of pollutants to a level of maximum permissible concentrations [16]. This part of the thesis is focused on the modification of PU nanofibers by the appropriate photocatalytic agents and on studying of the efficiency of the selected catalytic agents. Polyurethane nanofibers were modified by TiO_2 nanoparticles and tested for the photocatalytic oxidation of gaseous products of combustion engine emissions (NO_x and CO). However, the obtained results did not satisfy the presumed expectations. Further, the photocatalytic properties of tin oxide (SnO_2) have been studied both at the surface of nanofibers and as an individual powder. The improvement of photocatalytic efficiency of SnO_2 for the oxidation of carbon monoxide was provided by the doping with another metal oxides. Particular attention was paid on the investigation of influence of tests conditions (especially relative humidity) on catalytic properties of doped SnO_2 in the reaction of CO photooxidation.

2. Purpose and the aims of the thesis

Our objectives in the field of the catalytic purification of air have been changing in the process of experimental work. The results of each experimental stage motivated us to the re-evaluation of the initial objectives and their adjustment. So our initial goals were the production of filtration materials and their modification in order to make efficient for the catalytic oxidation of harmful gases (nitrogen oxides and carbon monoxide) upon contact with the polluted air. Such filters with catalytic properties should serve for the non industrial air-conditioning systems. The main task was to choose an appropriate modifier which would provide high catalytic efficiency to the textile filters. In addition, the question of the determination of catalytic properties of the modified filters also demanded a careful decision. The existing measuring methods and reactors for the catalytic oxidation of gases are oriented on the tests of powder catalysts. Hence, we had to develop an appropriate methodology for the testing of catalytic properties of textile samples.

3. Overview of the current state of the problem

The activation of catalytic reactions requires the large energy inputs. Therefore, most catalytic reactions occur at high temperatures. It becomes immediately clear that the polymer nanofibers are not suitable materials for the use in the conditions of high temperature exposure. In our study we need an alternative source of activation of catalytic reactions at the surface of modified nanofibers. This is a heterogeneous photocatalytic oxidation (PCO). The photocatalytic activity of titanium dioxide molecules is widely studied and utilized in biological, chemical and industrial applications [17]. The study of photocatalytic properties of TiO_2 is usually focused on the powder forms because of its simple preparing technique. But powders are much difficult in

collecting and recycling. Preparation of the photo-catalyst with a certain geometry and such as two-dimensional and three-dimensional is becoming an urgent and critical issue. For example the polypyrrole/polyvinyl alcohol–titanium dioxide (PPy/PVA–TiO_2) composite films were presented as photo-catalysts which had been fabricated by combining the TiO_2 sol with PPy/PVA solution in which PPy was synthesized by in situ polymerization of pyrrole (Py) in the polyvinyl alcohol (PVA) matrix and loaded on glass [18]. There are the examples of immobilization of nanoparticles of TiO_2 into the polymer nanofibers for future catalytic applications in the literature. S. Kedem et al. produced the composite poly(acrylonitrile) (PAN) nanofibers with nanoparticles of carbon nanotubes and titanium dioxide and investigated them as the new photocatalytic reactor elements [19]. In other study the TiO_2 nanoparticles were synthesized and immobilized on PAN based nanofibers by the ES technique. The photocatalytic studies of degradation of methyl orange dye under the UV light irradiation showed that such composite nanofibers were capable of degrading the organic contaminants in water [20]. According to the literature, tin oxide is also very promising photocatalytic material with the rutile-type crystal structure. Tin oxide is an n-type semiconductor with a wide band gap energy of 3.6 eV. But the activity of pure SnO_2 is rather poor. [21,22]. It is necessary to couple SnO_2 with another semiconductors with lower band gaps in order to solve this problem [23]. NiO is a p-type semiconductor with a small band gap. The coupling of SnO_2 with the metal's oxide with lower band gap contributes to easier migration of the photogenerated electrons from SnO_2 to NiO. It provides the separation of photogenerated electrons and holes, what leads to the enhancement of photocatalytic activity [24]. It is known that the tin-oxide based catalysts exhibit good activity towards CO/O_2 and CO/NO reactions. So far the mechanism of photocatalytic oxidation of CO in air was not clearly formulated and verified. There is still a lot of questions about the role of water in this reaction. The electron-hole pairs on the irradiated semiconductor metal oxides react with O_2 to form the active oxygen species. These oxygen species participate in the oxidation reactions. Numerous electron spin resonance (ESR) studies focusing on the characterization of various nano-particulate materials and the identification of transient radical intermediates such as hydroxyl radical (•OH) and reactive oxygen species (O2•−/HO2•, H2O2) in the photocatalytic reactions have recently appeared [25]. In order to identify the reactive species responsible for the CO oxidation, ESR measurement was carried out for the Pt/TiO2 samples. Appeared signal was identified as O_3^-

$$h^+ + O_2^- \leftrightarrow O^- \qquad (1)$$
$$O^- + O_2 \leftrightarrow O_3^- \qquad (2)$$

which possesses a weak covalent bonding between the π electrons of the oxygen molecule and a free electron in O^-. It has been reported that this type of O_3^- was reactive for the

$$O_3^- + CO \rightarrow CO_2 + O_2^- \qquad (3)$$

CO oxidation.

When the irradiation of Pt/TiO2 was carried out in a dry air, the CO conversion and CO_2 formation were very much suppressed showing that the water vapor was indispensable for the CO oxidation. It has been reported that water enhances the photoadsorption of oxygen by trapping of the photogenerated holes and OH^- sites. Therefore, another possible explanation may be that the water vapor inhibits the recombination of photogenerated holes and electrons, and facilitates the formation of stabilized active oxygen species [26]. On the other hand the negative

influence of water vapor on the efficiency of the CO photocatalytic oxidation has been also mentioned in the literature. There is an opinion that the water molecules compete with substrate molecules (with molecules of O_2) for active surface sites. For example Hwang et al. have reported that the OH radicals do not play a significant role in the CO photooxidation on Pt/TiO_2 [27].

4. Materials and methods

4.1. Polyurethane nanofibers with nanoparticles of TiO_2

4.1.1. Materials used

Particles of TiO_2 (Degussa P25, particle's size ≈21nm) were purchased from Evonik. Nanoparticles of the selected catalyst were incorporated into the PU solution. Modified solution with 5% wt of TiO_2 was stirred for 24 hours. Nanofibers were produced by the Nanospider technique.

4.1.2. Measurement of photocatalytic efficiency of sample with TiO_2

The photocatalytic properties of filters were studied in the reactions with exhaust gases produced by the automotive engine. An aspirated inline three-cylinder combustion engine Skoda 1.2 HTP was chosen for the experiment as a source of emissions. An engine of the vehicle was producing the gaseous emissions. The measurement set-up was equipped with an electric asynchronous dynamometer. So it was possible to adjust the operating conditions of the engine and maintain them stable for a long period. The concentration of exhaust gaseous components remained unchanged, because the stable operation mode was achieved and controlled. Finally the concentrations of the exhaust compounds were determined by the system of analyzers which had been capable to determine the concentrations of oxides of nitrogen and carbon monoxide. The first step of the measurement procedure was the determination of initial concentrations of harmful gases before our filter. Then the gaseous flow was switched to the container with filter and the exhaust stream was passing through the nanofibrous layer with nanoparticles of TiO_2 activated by UV lamp. The catalytic efficiency of our sample was calculated as the difference of measured concentrations of gases (NOx and CO) before and behind the filter.

4.2. Polyurethane nanofibers with particles of SnO_2/CrO_2

4.2.1. Materials used

The microparticles of SnO_2 and CrO_2 (99.9% trace metals basis) were purchased from Sigma Aldrich (United Kingdom). The different concentrations (1; 2; 3 and 4%) of SnO_2/CrO_2 (in the ratio 95/5) were incorporated into the solution of polyurethane. The obtained colloid solutions were stirred for 48 hours. The nanofibers from modified solutions were produced by the Nanospider technique.

4.2.2. Catalytic properties of nanofibers with combined catalyst SnO_2/CrO_2

The measurement set-up for the determination of photocatalytic efficiency of produced samples in the reactions with NO_x and CO was used. This testing method was already described in the

sub-chapter 4.1.2. Then the photocatalytic properties of composite nanofibers were also studied under the conditions of CO oxidation in the mixture with pure laboratory air (Fig. 7).

The photooxidation of CO in the presence of O_2 was carried out in a flow-type reactor (7) at the room temperature. UV irradiation was performed by the lamp with the radiation spectrum 350-400 nm (Philips Actinic BL 6W, peak of radiation = 370nm). The flow rates of CO (3) and O_2 (2) were controlled by Brooks microprocessor control & read out unit (9). The concentrations of CO_2 and CO in the gaseous mixture were simultaneously measured by the infrared gas analyzer (8) (Fuji Electric Co., Ltd, type ZSVFGYY1-2AAYY-2YY2BA).

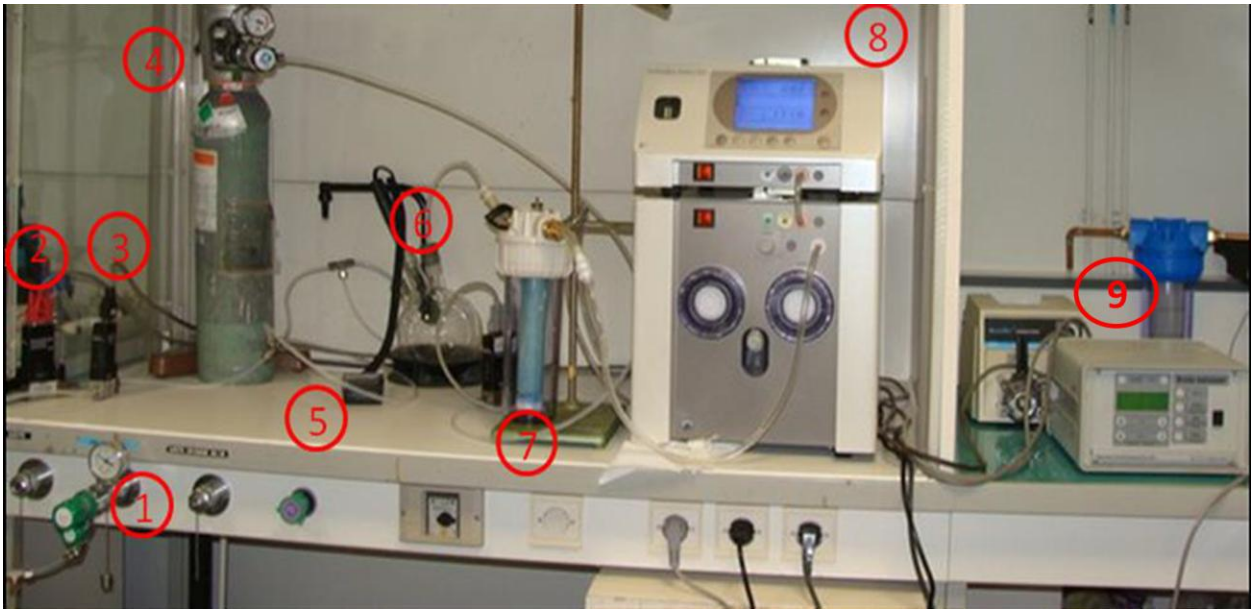

Figure 7. Measurement setup for the determination of photocatalytic activity in the reaction of CO oxidation in air: 1 - feeding of compressed air; 2 - flow meter to control air flow rate; 3 - flow meter to control CO flow rate; 4 - cylinder with CO; 5 - humidity measurement; 6 - mixing of CO with air; 7 - reactor with filter; 8 - infrared gas analyzer, 9 - microprocessor to control the flow rates of CO and O2.

The measurement procedure included three steps: the measurement of initial concentrations of CO and CO_2 without filter in the reactor 7; the measurement of gases concentrations with filter in the reactor 7; control of the stability of detected concentrations of CO and CO_2 again without filter.

4.3. Micro- and nanoparticles of SnO_2 doped by NiO. Modification of PU nanofibers by synthesized particles

4.3.1. Preparation of photocatalysts

The SnO_2/NiO (with components ratios 90/10; 80/20 and 70/30 wt.%) micro- and nanocomposites were obtained by the simple wetness impregnation method. Microparticles of SnO_2 with average diameter 1 μm and nanoparticles of SnO_2 with average diameter 100 nm were used as the substrates for the deposition of NiO. $Ni(NO_2)_3*6H_2O$ was selected as a precursor for NiO formation. The precursor was dissolved in distilled water with a desired molar ratios. The solutions of $Ni(NO_2)_3$ were added drop wise to the particles of SnO_2. This procedure was carried out under the continuous stirring at 80°C for 2 hours. Then the wet precipitates were

dried at 100 °C in air. The obtained dry powders were calcined at 550°C in air atmosphere for 5 hours to get the finalized catalysts.

4.3.2. Measurement of the photocatalytic activity

The laboratory setup for the measurement of the photocatalytic activity was already presented in Fig.7. Typically 0.3g of the catalyst was used for the activity evaluation. The synthesized powders were deposited on the surface of adhesive paper. The adhesive paper with catalyst was fixed at the special frame which was placed into the reactor 7 (Fig. 7). The influence of water vapour contents on the efficiency of microparticles SnO_2/NiO was investigated at 5; 15; 30 and 50% of relative humidity. It was found out that the catalytic activity of microparticles sharply decreased when the humidity had reached 50%. The range of water content was expanded to 70% in the measurement of the catalytic efficiency of synthesized nanoscale catalyst SnO_2/NiO. The water vapour content in the reaction's mixture was stabilized before the beginning of the experiment. The tests were carried out at the flow rates 500 ml/min and 1250 ml/min. Moreover the change of two initial concentrations of CO (20 and 200 ppm) was monitored during the process of measurement.

4.3.3. Modification of PU nanofibers by micro- and nanoparticles of SnO_2 doped by NiO

The synthesized particles of SnO_2/NiO were incorporated into the solution of PU prior electrospinning. The modified solutions with 5% wt of micro- or nanoparticles of the prepared catalyst were stirred for 48 hours. The photocatalytic properties of modified nanofibrous substrates were investigated under the same tests conditions as it was presented in the sub-chapter 4.2.2 (II).

5. Summary of the results achieved

5.1. PU nanofibers with nanoparticles of TiO_2

It was found out that nanoparticles of TiO_2 at the surface of PU nanofibers exhibit some photocatalytic activity and promote the oxidation of NO_x gases. The change of NO_x concentrations in contact with the modified sample is presented in Fig. 8.

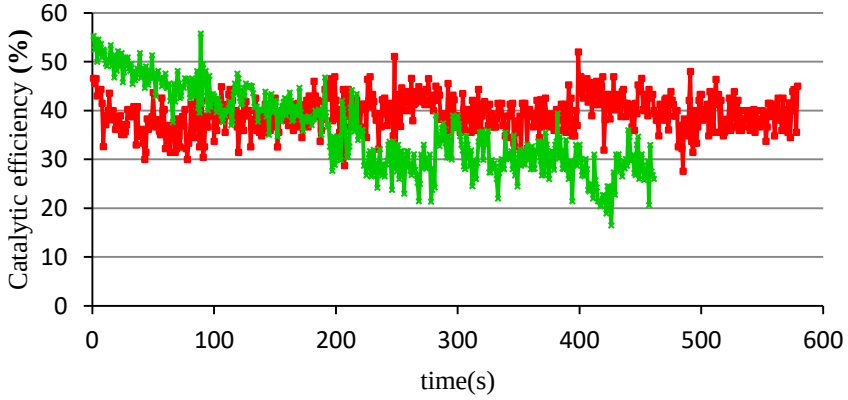

Figure 8. Comparison of photocatalytic efficiency of the pristine PU layer (green curve) and modified PU nanofibers with TiO_2 (red curve).

The catalytic efficiency of PU filter with TiO_2 in the reaction with NO_x isn't high (average value is 37%). Moreover it should be mentioned that the modified nanofibers didn't exhibit photocatalytic efficiency in the reaction with carbon monoxide.

5.2. Modification of PU nanofibers by the combined photocatalyst SnO_2/CrO_2

The results of tests with vehicle engine. The modified samples exhibited good catalytic activity in the reactions of NO_x and CO oxidation. The filter with 3% of modifier provides the best neutralization of the monitored pollutants. We observe a small decrease of the average catalytic efficiency with further growth of SnO_2/CrO_2 concentration to 4 %. Therefore we didn't continue the experiments with the incorporation of higher amounts of catalyst to the polymer solution.

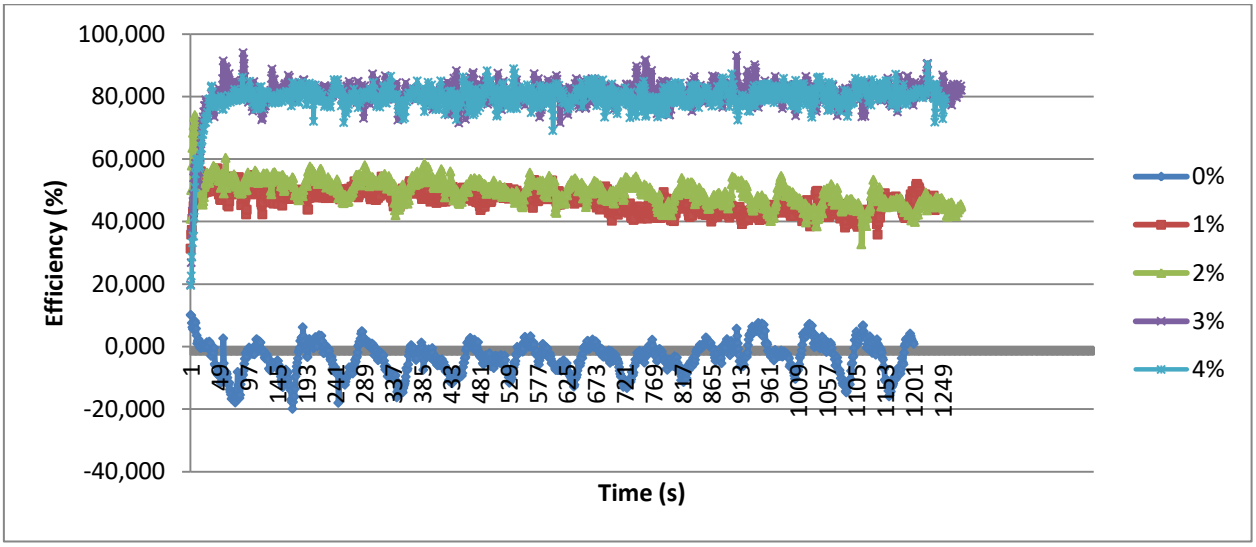

Figure 9. Photocatalytic efficiency of samples in the reaction with CO (test with the exhaust gases).

There is the example of behaviour of the produced samples in contact with CO in Fig.9. The pristine PU nanofibers don't exhibit the photocatalytic efficiency in contact with carbon monoxide. The samples with SnO_2/CrO_2 behave differently. At the beginning of the measurement the catalytic activity gradually increases, reaches a certain value, and then remains constant over time. All samples demonstrated the similar effect in the relation with NO_x.

The results of tests under the model conditions of CO oxidation in the mixture with air. Here we studied the photocatalytic activity of our samples in the reaction of CO oxidation in pure air. The initial concentrations of CO were low (5, 20 and 100 ppm). Our samples didn't exhibit the photocatalytic activity at the low concentrations of CO and in the absence of impurities (NOx, VOC and others) in the reaction mixture.

5.3. Micro- and nanoparticles of SnO_2 doped by NiO

The commercial micro- and nanoparticles of SnO_2 were modified by NiO with different molar ratios of components using simple wetness impregnation method. The microparticles of undoped SnO_2 (without NiO) did not exhibited catalytic properties in the studied reaction (Fig. 10). But the doping procedure of the microsized SnO_2 by NiO had an important influence on the behaviour of our catalyst for all selected combinations of testing parameters (FR= 500ml/min, C(CO) = 20ppm; FR = 500ml/min, C(CO) = 200ppm; FR = 1250ml/min, C(CO) = 20ppm; FR = 1250ml/min, C(CO) = 200ppm). An initial relative humidity for all measurements was 5%. It

was impossible to carry out the experiments in completely dry air because the initial content of moisture in the laboratory air was 5%. The photocatalytic activity of microparticles gradually increased with the addition of moisture content into the gas mixture (Fig. 10). But this tendency remains only up to 30% of the relative humidity. It was found out that doped microparticles had the highest removal efficiency of CO under the RH range 25-30% (Fig. 10). The sharp decrease of the catalytic efficiency to zero values was observed when the relative humidity had enhanced to 50%.

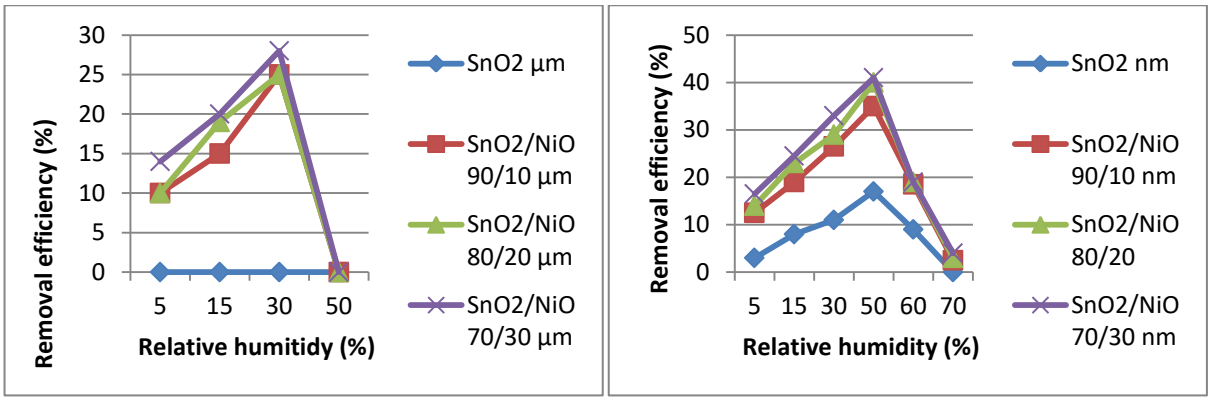

Figure 10. Dependence of the photocatalytic efficiency of micro- and nanoparticles of SnO_2/NiO on the relative humidity under the flow rate 500 ml/min; the initial CO concentration 20 ppm.

The obtained results allow to make a conclusion that the presence of water is a prerequisite for the course of the photocatalytic reaction of carbon monoxide oxidation. However the effect of "flooding" of the catalysts surface was observed at a certain value of humidity. In case of MPs such effect appeared when RH had reached 50%. The nanoparticles of SnO_2/NiO lost their activity when the relative humidity was 70%.

The undoped nanopowder of SnO_2 exhibits some catalytic activity in the investigated reaction. The removal efficiency of nanosized SnO_2/NiO catalyst is higher in comparison with microparticles. The photocatalytic efficiency of doped nanoparticles was similar under all combinations of measurement parameters (flow rate and initial concentration of CO). It is worth to recollect how our particles were fixed in the reactor during the photocatalytic tests. The powders of SnO_2/NiO were deposited at the surface of adhesive paper. So some part of catalysts was closed and could not contact with CO and O_2. So we can suggest that in another reactor where all particles are available for the contact with gas mixture, the activity of our powders will be higher. But the most important conclusion of experiments with the doped nanoparticles relates with influence of the water vapour on their photocatalytic properties. The maximum values of the photocatalytic efficiency of the nanosized photocatalyst in the reaction of CO oxidation were observed when the relative humidity had reached 50%. In case with microparticles it happened when the RH was 30%. So the effect of "flooding" of catalyst's surface under the influence of the water vapour can be avoided due to the application of catalyst in the form of nanopowders. According to the measured values of photocatalytic activity both micro- and nanoparticles of SnO_2/NiO have the highest efficiency at the component ratio 70/30. The experiments with modification of PU nanofibers by SnO_2/NiO in both micro- and nano-sizes were not successful in terms of manifestation of photocatalytic properties.

6. Evaluation of results and new finding

The experimental results of catalytic modification of nanofibers were presented in the second part of this thesis. The polyurethane nanofibers were modified by individual nano-sized catalyst TiO_2 and by two different combined catalysts. The combined catalysts SnO_2/CrO_2 in the form of microparticles and SnO_2/NiO in both dimensional states (micro and nano) were used for the modification procedure. The particles of catalytic agents were incorporated into the polymer solution prior the electrospinning. Such approach proved to be efficient for the antibacterial modification of PU nanofibers. But in the case of incorporation of catalysts it was found out that this method gave controversial results. The availability of active sites and geometry of catalysts at the filter surface with alleged catalytic properties is the first and most important criterion for the effective photocatalytic reaction. Based on the experimental results we can conclude that nanoparticles introduced into the PU solution prior ES don't fulfill these criterion. Nanofibers with TiO_2 nanoparticles exhibited low photocatalytic activity in the reaction of NOx oxidation in the mixture of exhaust gases. Nanofibers with SnO_2/CrO_2 and SnO_2/NiO had no efficiency in the reaction of CO oxidation.

Nevertheless, we have succeeded to obtain the significant results in the investigation of the photocatalytic properties of SnO_2 doped by NiO in the powder form. It was determined that the presence of water strongly influenced the efficiency of the studied photocatalyst. Our results can make a contribution into the explication of the mechanism of CO oxidation. As it's already explained there is no consensus about the role of water in the reaction of photocatalytic oxidation of CO. Our research confirmed the positive influence of water on the studied reaction. According to our results water contributes the adsorption of oxygen (O^-) by the photogenerated holes and provides the presence of OH^- radicals with strong oxidizing properties. Moreover the presented research has the important contribution in terms of practical application. It was determined that presence of water has a positive influence on the photocatalytic activity to a certain value. Then the so-called effect of "flooding" of active sites at the surface of catalysts was observed. And the impact of the "flooding" on the catalytic properties depends on the dimensional characteristic of SnO_2/NiO. The microparticles of this catalyst with the average size 1μm lost their activity when the value of relative humidity was 50%. The same effect of water vapour on the nanoparticles of SnO_2/NiO with average size 100nm was observed under RH 70%. The further decrease of particle's size can help to avoid the "flooding" of active sites. Thus the presented catalyst is a promising material for the low-temperature oxidation of CO, even at high moisture content. The particle sizes of studied catalyst can be selected based on the average values of humidity according to the season or region.

7. References

[1] N. Beyth, Y. Houri-Haddad, A. Domb, W. Khan, R. Hazan, Alternative antimicrobial approach: Nano-antimicrobial materials, Evidence-Based Complement. Altern. Med. 2015 (2015). doi:10.1155/2015/246012.

[2] H. Palza, Antimicrobial polymers with metal nanoparticles, Int. J. Mol. Sci. 16 (2015) 2099–2116. doi:10.3390/ijms16012099.

[3] M.C. Sportelli, R.A. Picca, R. Ronco, E. Bonerba, G. Tantillo, M. Pollini, A. Sannino, A. Valentini, T.R.I. Cataldi, N. Cioffi, Investigation of industrial polyurethane foams modified with antimicrobial copper nanoparticles, Materials (Basel). 9 (2016) 1–13. doi:10.3390/ma9070544.

[4] F. a. Sheikh, N. a. M. Barakat, M. a. Kanjwal, A. a. Chaudhari, I.-H. Jung, J.H. Lee, H.Y. Kim, Electrospun antimicrobial polyurethane nanofibers containing silver nanoparticles for biotechnological applications, Macromol. Res. 17 (2009) 688–696. doi:10.1007/BF03218929.

[5] J. Dolina, T. Jiříček, T. Lederer, Membrane modification with nanofiber structures containing silver, Ind. Eng. Chem. Res. 52 (2013) 13971–13978. doi:10.1021/ie303120j.

[6] H. Shi, H. Liu, S. Luan, D. Shi, S. Yan, C. Liu, R.K.Y. Li, J. Yin, Antibacterial and biocompatible properties of polyurethane nanofiber composites with integrated antifouling and bactericidal components, Compos. Sci. Technol. 127 (2016) 28–35. doi:10.1016/j.compscitech.2016.02.031.

[7] M. Shamshi Hassan, T. Amna, F.A. Sheikh, S.S. Al-Deyab, K. Eun Choi, I.H. Hwang, M.S. Khil, Bimetallic Zn/Ag doped polyurethane spider net composite nanofibers: A novel multipurpose electrospun mat, Ceram. Int. 39 (2013) 2503–2510. doi:10.1016/j.ceramint.2012.09.009.

[8] F.A. Sheikh, M.A. Kanjwal, S. Saran, W.-J. Chung, H. Kim, Polyurethane nanofibers containing copper nanoparticles as future materials, Appl. Surf. Sci. 257 (2011) 3020–3026. doi:10.1016/j.apsusc.2010.10.110.

[9] R. Nirmala, K.S. Jeon, B.H. Lim, R. Navamathavan, H.Y. Kim, Preparation and characterization of copper oxide particles incorporated polyurethane composite nanofibers by electrospinning, Ceram. Int. 39 (2013) 9651–9658. doi:10.1016/j.ceramint.2013.05.087.

[10] T.C. Zhang, R.Y. Surampalli, K.C.K. Lai, Z. Hu, R.D. Tyagi, I.M.C. Lo, Nanotechnologies for Water Environment Applications, 2009. https://app.knovel.com/web/toc.v/cid:kpNWEA000B/viewerType:toc/root_slug:nanotechnologies-water/url_slug:nanotechnologies-water?b-q=Nanotechnologies for Water Environment Applications&sort_on=default&b-subscription=TRUE&b-group-by=true&b-search-type=tech-.

[11] Y. Chang, M. Zhang, L. Xia, J. Zhang, G. Xing, The Toxic Effects and Mechanisms of CuO and ZnO Nanoparticles, (2012) 2850–2871. doi:10.3390/ma5122850.

[12] S. Kango, S. Kalia, A. Celli, J. Njuguna, Y. Habibi, R. Kumar, Surface modification of inorganic nanoparticles for development of organic-inorganic nanocomposites - A review, Prog. Polym. Sci. 38 (2013) 1232–1261. doi:10.1016/j.progpolymsci.2013.02.003.

[13] C. Wang, J. Lv, Y. Ren, Q. Zhou, J. Chen, T. Zhi, Z. Lu, D. Gao, Z. Ma, L. Jin, Cotton fabric with plasma pretreatment and ZnO/Carboxymethyl chitosan composite finishing for durable UV resistance and antibacterial property, Carbohydr. Polym. 138 (2016) 106–113. doi:10.1016/j.carbpol.2015.11.046.

[14] J. Kreuter, Nanoparticles and microparticles for drug and vaccine delivery., J. Anat. 189 (Pt 3 (1996) 503–505. doi:10.1002/bit.

[15] T. Shalaby, O. Mahmoud, A. Al-oufy, Antibacterial Silver Embedded Nanofibers for Water Disinfection, Int. J. Mater. Sci. Appl. 4 (2015) 293–298. doi:10.11648/j.ijmsa.20150405.13.

[16] K.E. Perepelkin, Principles and methods of modification of fibres and fibre materials. A review, Fibre Chem. 37 (2005) 123–140. doi:10.1007/s10692-005-0069-6.

[17] Q.L. Yu, H.J.H. Brouwers, Indoor air purification using heterogeneous photocatalytic oxidation. Part I: Experimental study, Appl. Catal. B Environ. 92 (2009) 454–461. doi:10.1016/j.apcatb.2009.09.004.

[18] S. Cao, H. Zhang, Y. Song, J. Zhang, H. Yang, L. Jiang, Y. Dan, Investigation of polypyrrole/polyvinyl alcohol-titanium dioxide composite films for photo-catalytic applications, Appl. Surf. Sci. 342 (2015) 55–63. doi:10.1016/j.apsusc.2015.02.139.

[19] S. Kedem, J. Schmidt, Y. Paz, Y. Cohen, Composite polymer nanofibers with carbon nanotubes and titanium dioxide particles., Langmuir. 21 (2005) 5600–4. doi:10.1021/la0502443.

[20] P. Nyamukamba, O. Okoh, L. Tichagwa, C. Greyling, Preparation of titanium dioxide nanoparticles immobilized on polyacrylonitrile nanofibres for the photodegradation of methyl orange, Downloads.Hindawi.Com. 2016 (2016). doi:10.1155/2016/3162976.

[21] A. Bhattacharjee, M. Ahmaruzzaman, T. Sinha, A novel approach for the synthesis of SnO2 nanoparticles and its application as a catalyst in the reduction and photodegradation of organic compounds, Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 136 (2015) 751–760. doi:10.1016/j.saa.2014.09.092.

[22] H. Xia, H. Zhuang, T. Zhang, D. Xiao, Visible-light-activated nanocomposite photocatalyst of Fe2O3/SnO2, Mater. Lett. 62 (2008) 1126–1128. doi:10.1016/j.matlet.2007.07.062.

[23] M. Batzill, U. Diebold, The surface and materials science of tin oxide, Prog. Surf. Sci. 79 (2005) 47–154. doi:10.1016/j.progsurf.2005.09.002.

[24] R.M. Mohamed, E.S. Aazam, Photocatalytic Oxidation of Carbon Monoxide over NiO/SnO2 Nanocomposites under UV Irradiation, J. Nanotechnol. 2012 (2012) 1–9. doi:10.1155/2012/794874.

[25] Z. Wang, W. Ma, C. Chen, H. Ji, J. Zhao, Probing paramagnetic species in titania-based heterogeneous photocatalysis by electron spin resonance (ESR) spectroscopy-A mini review, Chem. Eng. J. 170 (2011) 353–362. doi:10.1016/j.cej.2010.12.002.

[26] H. Einaga, A. Ogata, S. Futamura, T. Ibusuki, The stabilization of active oxygen species by Pt supported on TiO2, Chem. Phys. Lett. 338 (2001) 303–307. doi:10.1016/S0009-2614(01)00296-2.

[27] S. Hwang, M.C. Lee, W. Choi, Highly enhanced photocatalytic oxidation of CO on titania deposited with Pt nanoparticles: Kinetics and mechanism, Appl. Catal. B Environ. 46 (2003) 49–63. doi:10.1016/S0926-3373(03)00162-0.

8. List of papers published by the author

8.1. Publications in journals

1. Ganna Ungur, Jakub Hrůza, *Polyurethane nanofibers containing the nanoparticles of metal`s oxides*. In: Workshop pro doktorandy FS a FT TUL – sborník, TUL, September 17-20.2012, Rokytnice nad Jizerou, Czech Republic, pp. 114-119, ISBN 978-80-7372-891-5.

2. Ganna Ungur, Jakub Hrůza, *Nanofibrous filtering materials with catalytic activity*. In: Advanced Materials Letters, Vol. 5, Issue 8, pp. 422-428, 2014.

3. Ganna Ungur, Jakub Hrůza, *Influence of copper oxide on the formation of polyurethane nanofibers via electrospinning*. In: Fibers and Polymers, Vol. 16, Issue 3, pp. 621-628, 2015.

4. Ganna Ungur, Jakub Hrůza, *Modified polyurethane nanfibers as antibacterial filters for air and water purification.* In: European polymer journal, under review, 2016.

5. Ganna Ungur, Jakub Hrůza, Influence of different spinning electrodes on the structure and properties of antibacterial nanofibrous filters. In: Journal of Nanotechnology, under review, 2017.

8.2. Contribution in conference proceeding

Oral presentations

1. Ganna Ungur, Jakub Hrůza, *Polyurethane (PUR) nanofibers containing particles of CuO and TiO2prepared by electrospinning*. In: 9TH International Conference Nanoscience and Nanotechnology, July 3-6.2012, Thessaloniki, Greece.

2. Ganna Ungur, Jakub Hrůza, *Nanofibrous filtering materials with catalytic activity*. In: 13TH AUTEX World Textile Conference, May 22-24.2013, Dresden, Germany.

3. Ganna Ungur, Jakub Hrůza, *Filtering materials based on nanofibers with catalytic properties for air filtration*. In: Advanced Materials Word Congress, September 16-19.2013, İzmir, Çeşme, Turkey.

Poster presentations

1. Ganna Ungur, Jakub Hrůza, *Sub-micron nanofiber membranes*. In: 18TH International Conference Strutex, December 7-8. 2011, Liberec, Czech Republic, ISBN 978-80-7372-786-4.

2. Ganna Ungur, Jakub Hrůza, *Polyurethane nanofibers containing nanoparticles of metal oxides*. In: The Fiber Society Spring 2012 Conference, May 23-25.2012, St. Gallen, Switzerland, ISBN: 978-1-63266-645-1, abstract was published in database Scopus.

3. Ganna Ungur, Jakub Hrůza, *Dual Effect of CuO Particles on Electrospinning Process and Properties of Polyurethane Nanofibers*. In: 4TH International Conference Nanocon, October 23-25.2012, Brno, Czech Republic, TANGER Ltd., pp. 194-199, ISBN:978-80-87294-35-2, article was published in database Thomson Reuters.

4. Ganna Ungur, Jakub Hrůza, *Nanofibers for air filtration with catalytic activity*. In: 19TH International Conference Strutex, December 3–4.2012, Liberec, Czech Republic**.**

8.3. Citations

1. *Nanofibrous filtering materials with catalytic activity* was cited by:

- Wang, Z.; Xu, M.; Shao, L.; et al., *Palladiumimmobilized on chitosan nanofibers cross-linked by glutaraldehyde as an efficient catalyst for the Mizoroki-Heck reaction*, In: Kinetics and Catalysis, Vol. 57, Issue 3, pp. 354-359, 2016.

2. *Influence of copper oxide on the formation of polyurethane nanofibers via electrospinning* was cited by

- Madalina Elena Grigore, Elena Ramona Biscu, Alina Maria Holban, Monica Cartelle Gestal and Alexandru Mihai Grumezescu, *Methods of Synthesis, Properties and Biomedical Applications of CuO Nanoparticles*, In: Pharmaceuticals, Vol. 9, 2016. doi: 10.3390/ph9040075

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Highest level of education attained	Master degree, the topic of master thesis is Influence of additives of copolymer of ethylene with vinyl acetate and carbon nanotubes on the phenomenon of specific fiberforming in the mixture of polypropylene and polyamide.	
Education	January 2011	Technical University of Liberec, Faculty of textile engineering, Department of nonwovens and nanofibrous materials, studying program Textile engineering, field of study Textile techniques, PhD student.
	September 2009- June 2010	Kiev National University of Technologies and Design, master's degree in the field Technology of chemical fibres.
	September 2005- June 2009	Kiev National University of Technologies and Design, bachelor's degree in the field Chemical technology and engineering.
Additional education	September 2013 - January 2015	Course of university pedagogy, degree Ing. Paed. IGIP
Work experience	June - July 2008	Open Joint Stock Company "Kievhimvolokno", work on optimization of lines for secondary raw material (thermoplastic polymers polyethylene and polypropylene) into granules and agglomerates
	September 2014 - October 2015	Technical University of Liberec, Faculty of Mechatronics, Informatics and Interdisciplinary Studies, Institute of New Technologies and Applied Informatics, assistant.
	November 2015	Technical University of Liberec, Institute for Nanomaterials, Advanced Technologies and Innovation, junior researcher.
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Language skills	Ukrainian – native speaker Russian – native speaker English – upper intermediate Czech – intermediate French – elementary	
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Other skills and interests	Reliability, partnership, ability to work in the team; travelling, reading, theatre.	
Achievements	April 2009	All Ukrainian scientific conference for young scientists and students, my report "Ultrathin polypropylene fibers with silica nanoadditives" won the 1st prize in subsection "Technology of chemical fibers"
	May 2009	Student's contest in Russia, St-Petersburg "Nano, micro, macro. Properties, methods of researchs and application of polymer's materials", my scientific work "Nano-filled microfibers" won the 1st prize in a nomination "Innovations in the field of nanomaterials".
	November 2009	Gratitude of The Ministry of education and science of Ukraine for excellent study, active participation in scientifically-experimental work and public life.
	December 2009	The Award and the Certificate of Mayor of Kiev for success in the study and scientific work.
	April 2010	All Ukrainian scientific conference for young scientists and students, my report titled " Influence of additives of copolymer of ethylene with vinilacetate and carbon nanotubes on the phenomenon of specific fiberforming in the mixture of polypropylene and polyamide " won the 1st prize.

Brief description of the current expertise, research and scientific activities

Doctoral studies

Studies	Textile Engineering
	Textile Technics
	Full time
Exams	Macromolecular chemistry 21.11. 2011
	Nanofibers and Nanotechnologies 27.02.2012
	Chemical thermal technology of nonwovens 5.09.2012
	Differential equations 18.04.2014
SDE	State Doctoral Exam completed on with the overall result passed

Teaching activities

Teaching	Industrial textiles, 2012-2014
	Polymers 2013-2014
Leading Bachelors/ Master Students	Galuszková R.: Influence of ultrasound on the electrostatic fiberforming solutions with particles of copper oxide, 2015
	Bc. Polaková L.: Development of methods for nanofibers modification using metals oxides, 2013
	Bc. Mustaeva I.: Fabrication and comparing of nanofibrous filters modified by different methods to impart antibacterial properties, 2014
Research projects	Nanofibers air filters containing active substances for air conditioning and ventilation, ALFA TAČR, participant, 2013
	Development of new methods of nanofibrous modifications by particles of metals and metals oxides in order to improve filtration properties, (Student Grant Competition), investigator, 2012
	Nanofibrous catalytic filters prepared by the method of introduction of metals oxides particles into the polymer solution with further electrospinning (Student Grant Competition), investigator, 2013
	Synthesis of composite catalysts for air purification by methods of wet impregnation and coprecipitation for the treatment of nanofibrous filters, (Student Grant Competition), investigator, 2014
	Nanofibrous composite textiles for special filtration (Ministry of Industry and Trade), participant, 2015
	Active nanofibrous membranes for purification of waste water purification (EPSILON, Technology Agency of the Czech Republic), 2016

Record of the state doctoral exam

TECHNICKÁ UNIVERZITA V LIBERCI
Fakulta textilní

ZÁPIS O VYKONÁNÍ STÁTNÍ DOKTORSKÉ ZKOUŠKY (SDZ)

Jméno a příjmení doktorandky: **Ganna Ungur**

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Doktorský studijní program: **Textilní inženýrství**

Studijní obor: **Textilní technika**

Termín konání SDZ: **10. 9. 2015**

prospěla **neprospěla**

Komise pro SDZ:

		Podpis
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Místopředseda:	prof. RNDr. David Lukáš, CSc.	
Členové:	prof. Ing. Ivan Stibor, CSc.	
	prof. Ing. Josef Šedlbauer, Ph.D.	
	doc. Ing. Luděk Jelínek, Ph.D.	
	Ing. Blanka Tomková, Ph.D.	Tomková

V Liberci dne 10. 9. 2015

O průběhu SDZ je veden protokol.

Recommendation of the supervisor

V Liberci 24.2. 2017

Hodnocení školitele

Zadání práce: Filtration of air and liquids using active substances

Autorka práce: Ing. Ganna Ungur

Hodnocení:
Doktorandka se ve své práci zabývá možností využití nanovlákenných vrstev jako nosiče chemicky a biologicky aktivních látek určených zejména pro filtraci vzduchu a kapalin. Motivem k řešení tohoto tématu je nutnost stále intenzivnějšího čištění vzduchu a vody. V případě vzduchu je třeba řešit jeho kontaminaci nebezpečnými plyny a bakteriemi, kde sebelepší částicová filtrace nestačí. Využití filtru jako nosiče aktivních látek je v současnosti realizováno v oblasti průmyslové filtrace horkých plynů, což neřeší problém kontaminace vzduchu z lokálních topenišť a dopravy. Práce se tedy mimo jiné zabývá možností aktivace katalytických látek za nízkých teplot (<50°C). Antimikrobiální úpravy vzduchových filtrů jsou dnes také částečně realizovány, jejich nevýhodou je však malá životnost. V případě vody je důležité řešit zejména antimikrobiální úpravu filtru, neboť v kapalném prostředí dochází velmi rychle k prorůstání bakterií strukturou filtru a kontaminaci čištěné vody. Zároveň je nutné klást velký důraz na stabilitu uchycení. Antimikrobiální látky uvolněné do vody jsou nebezpečné a poškozují činnost čistíren odpadních vod.

Ganna Ungur řešila problematiku využití nanovlákenných vrstev jako účinného a stabilního nosiče aktivních látek. Svou práci rozdělila na dvě části: Úpravu vzduchu (nebezpečné plyny, bakterie) a úpravu vody (bakterie). Práce je řešena komplexně, zahrnuje výběr vhodného nanovlákenného nosiče, výběr vhodných biologicky a chemicky aktivních látek, způsob jejich aktivace, způsob hodnocení parametrů filtru, vývoj metodiky simulace filtrace bakterií a metodiky určení stability uchycení aktivních látek simulovaným namáháním filtru. Svou činností se aktivně podílela na řešení následujících projektů

- „Nanovlákenné vzduchové filtry s obsahem aktivních látek určené pro klimatizaci a ventilaci“ (TA01011512) ve spolupráci s firmou GEA Heat Exchangers a.s.
- „Filtrační zařízení pro bezpečnou místnost“ (VG20132015126) ve spolupráci s firmou Centrum hydraulického výzkumu spol. s r.o.
- „Aplikace nanomateriálů a progresivních technologií“ (ED3.1.00/14.0295).
- „Aktivní nanovlákenné membrány pro čištění odpadní vody“ (TH01030643) ve spolupráci s firmou BMTO group a.s.

Ganna Ungur své úkoly řeší s nadšením, samostatně a systematicky. Je schopná kooperace při přípravě i komplexním hodnocení funkčních struktur. V rámci výzkumu a vývoje samostatně navrhuje a realizuje řešení jednotlivých problémů. Její činnost přispěla k rozvoji nejen v oblasti aplikovaného výzkumu, ale též v oblasti teoretické (vliv vlhkosti na činnost katalyzátorů, vliv aditiv na výrobnost nanovláken...) a oblasti měřicí techniky. Způsob simulace filtrace bakterií ze vzduchu byl uznán jako certifikovaná metodika v rámci osvědčení vydaného pro antimikrobiální nanovlákenné filtry s obsahem aktivních látek. Publikační činnost Ganny Ungur hodnotím jako velmi uspokojivou. V databázi Scopus lze nalézt 3 konferenční příspěvky a 2 časopisecké publikace. Autorčin H-index je 2.

Navrhuji, aby práce ing. Ganny Ungur byla přijata k obhajobě.

Ing. Jakub Hrůza, Ph.D.

Rewievs of the opponents

Review of the doctoral dissertation
„Filtration of air and liquids using active substances“
by Ing. Ganna Urgur

The submitted dissertation is focused on the preparation and characterization of the filtration materials for water and air purification. It introduces a highly contributive topic in terms of both fundamental research and potential practical use.

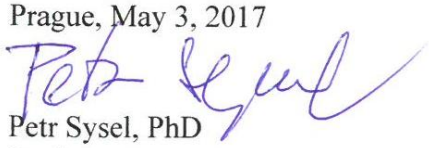
The main aim of this multidisciplinary dissertation was the preparation of the nanofibrous polymeric materials containing metallic modificators and their testing as both antibacterial and air filters. The experiments are described comprehensibly with the possibility to reproduce them. Although some procedures did not yield the expected, favourable findings I think that G. Urgur achieved the main goals in her dissertation and she acquired valuable experimental results and applicable knowledge.

Nevertheless, I believe there are still several points in the dissertation, which G. Urgur should give her attention to during the defence:

(1) The reasons for choosing the polyurethane and polyamide fibrous “matrices” should be more clearly specified.
(2) The basic characteristics (including a molar mass) of these polymeric matrices should be presented in more detail.
(3) If a nanoadditive concentration of 5 – 12 wt% was used, an additive aggregation in the final products was observed. Have you tried to use a lower concentration (e.g. about 1 wt%) of these additives?
(4) The rather different voltage was used for the electrospinning from the rod spinner (27 kV) and the roller spinning method (67 kV). Why?
(5) It is appreciated that the potential toxicity of nanoparticles and nanofibres has been taken into account. Did you take any special precautions to deal with them?
(6) Would it be possible to use the polymer melt as the starting materials (instead of a polymer solution) for any of your experiments?
(7) Two publications (full papers) based on the results of this dissertation have already been issued, and two more manuscripts are under review. What is their current status?
(8) The formal level of this dissertation is decent. However, the pronouns “I”, “me” and “my” should be used instead “we”, “us” and “our”.
(9) The graphical level of this dissertation is fairly good. Nevertheless, the tables together with their headings should occupy the same page (e.g. Table 11 (pages 57 and 58)).

I recommend to accept this doctoral dissertation of Ing. Ganna Urgur for defence.

Prague, May 3, 2017



Petr Sysel, PhD
Professor
Department of Polymers. University of Chemistry and Technology, Prague

Report on PhD thesis by Ganna Urgur entitled

„Filtration of air and liquids using active substances“

The subject of this thesis is related to the research of a very interesting and important process of gas and water purification. The thesis is focused on development and testing of composite filtration materials based on nanofibres, especially for antibacterial purification of air and water and for removing nitrogen oxides and carbon monoxide from air. Different nano and microparticle oxides having catalytic and/or antimicrobial properties and different methods how to incorporate them to the composite filtration materials were studied. From this point of view the subject of thesis appears to be very topical and the results obtained by Ganna Urgur are likely to have a stimulating impact on the next research and development of filtration materials.

The thesis is very voluminous as it consists of two separate parts, actually each of them represents an independent thesis. Both parts have been properly divided into standard chapters. The Theoretical parts, based on up-to-date references, comprise information about fundamentals and state of art in the field of studied filtration and purification processes. The experimental parts comprise essential information on materials, methods, processes and techniques that have been used, focused mainly on techniques of nano fibrous composite filtration materials preparation and methods of their testing.

Both the discussions of obtained results illustrate a very broad scope of the defendant. I am not acquainted with textile techniques and technologies in detail, thus, I don´t feel like to discuss the very details of the experimental work. I assess the thesis as well organized and well done, description and discussion of experiments has been comprehensible. I would like to stress, that reading the thesis was interesting and stimulating. The findings concerning homogeneous distribution of CuO microparticles in PU nanofibres and promising antibacterial activity of composite filters on this base as well as promising achievements in catalytic CO oxidation seem to be very important. As required, the results have been published in two international journals, both papers have been already cited.

My question: how far is the utilization of such filters in an industrial scale?

Conclusion

In conclusion, it can be stated that the subject of thesis is highly relevant and that the candidate achieved the aim using modern experimental and analytical methods. By choosing the approach and method of elaboration Ms. Ganna Urgur manifested her ability of independent a creative scientific work. By a successful solution of a research problem, she brought new findings and showed a good grasp of scientific methods of work. Because Ms. Ganna Urgur thus fulfilled the appropriate conditions, I recommend her thesis for defending. After successful defense, I recommend to confer a scientific degree of PhD upon the candidate.

2017-05-09

Prof. Ing. Jaromír Šňupárek, DrSc.
Faculty of Chemical Technology, University of Pardubice