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Filtrace vzduchu a kapalin s pomocí aktivních látek

Disertační práce

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Vedoucí práce:	Ing. Jakub Hrůza, Ph.D.

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Dissertation

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Supervisor:	Ing. Jakub Hrůza, Ph.D.

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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 měďnatého 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 měďnatého 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 měďnatý, nanočástice, fotokatalyzátor, filtrace.

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The last but not least thanks belong to my family, especially my husband and my sister, for supporting me during the thesis processing.

Content

List of symbols

CuO	Copper oxide
EPA	Environmental Protection Agency
WHO	World Health Organization
NPs	Nanoparticles
Ag	Silver
Au	Gold
Fe_3O_4	Iron oxide
TiO_2	Titanium dioxide
ZnO	Zinc oxide
CaO	Calcium oxide
MgO	Magnesium oxide
ROS	Reactive oxygen species
DMF	N,N-dimethylformamide
THF	Tetrahydrofuran
ATP	Adenosine triphosphate
DNA	Deoxyribonucleic acid
UV	Ultraviolet light
NFs	Nanofibers
ES	Electrospinning
PA 6	Polyamide 6
PU	Polyurethane
PE	Polyethylene
PMMA	Poly(methyl methacrylate)
$AgNO_3$	Silver nitrate
PVA	Polyvinyl alcohol
PAN	Polyacrylonitrile
CA	Cellulose acetate

SiO_2	Silicon dioxide
ZrO_2	Zirconium dioxide
PVD	Physical vapor deposition
PP	Polypropylene
HBP	Hyperbranched polymer
CNTs	Carbon nanotubes
$C_7H_5AgO_2$	Silver benzoate
$C_{22}H_{43}AgO_2$	Silver behenate
PEG	Polyethylene glycol
NMs	Nanomaterials
Co_3O_4	Tricobalt tetroxide
Cr_2O_3	Chromium(III) oxide
NiO	Nickel(II) oxide
CMCS	Carboxymethyl chitosan
UPF	Ultraviolet Protection Factor
PVC	Poly(vinyl chloride)
TSB	Tryptone Soya Broth
TSA	Tryptone Soya Agar
P_{max}	Maximum pressure
γ	Surface tension
r	Radius of curvature
US	Ultrasound
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-ray spectrometer
NaCl	Sodium chloride
HEPA	High Efficiency Particulate Air
E.coli	Escherichia coli
St.Gal.	Staphylococcus Gallinarum

CFU	Colony-forming unit
AMFIT	Anti-Microbial Filtration Tester
BFU	Bacterial filtration efficiency
RF PACVD/MS	Radio Frequency Plasma Assisted Chemical Vapour Deposition/Magnetron Sputtering
AA	Acetic acid
FA	Formic acid
RH	Relative humidity
A_n	Number average
A_w	Weight average
K	Fiber uniformity coefficient
NO_x	Nitrogen oxides
CO	Carbon monoxide
VOC	Volatile Organic Compounds
PCO	Photocatalytic oxidation
$e^- h^+$	Electron-hole pair
PPy	Polypyrrole
Ce	Ceria
Ta	Tantalum
ESR	Electron Spin Resonance
•OH	Hydroxyl radical
TEM	Transmission Electron Microscope
TEAB	Tetraethylammoniumbromide
XRD	X-ray diffraction
C	Concentration

I. Nanofibers with antibacterial properties for water and air purification

1. Research objectives

It is well known that the clean air and water is a guarantee of health for the present and future generations. And it is not a secret to anyone that the bacterial contamination of air and water resources is still a potential threat. Therefore we had set for ourselves two main objectives.

The first goal was a development of the efficient antibacterial filters suitable for the air and water purification. To achieve the presented aim we decided to focus on the finding of efficient methods of the antibacterial modification of existing filtration materials. The range of different antibacterial substances is wide. The nanoparticles of metals and their oxides cause an enormous interest in the modern scientific world. However, we want to emphasize that the decision to use the nanoparticles as an antibacterial active substance was made not because of the popularity of investigations in the field of nanomaterials. The real reason was an intention to apply the unique properties of nano-sized materials and to develop the efficient antimicrobial filter. Another motivating factor was an aspiration to verify as far as it is rational to use the nanoparticles as antibacterial materials for the filter's modification.

Some metals and their oxides in the nano-sized state are known by their unique properties including the antibacterial efficiency. The difficulty was to find a safe way for their use in the filtration area. But we had a great chance to combine the unique properties of two different types of nanomaterials owing to the technical facilities of university laboratories and to the outstanding experience of our colleagues in the development of nanofibers. It became clear that it concerned the combination of nanoparticles and nanofibers.

The nanofibers belong to the attractive materials for different advanced applications, including filtration due to their unique properties such as a high specific area, small diameters, highly porous structure with excellent pore interconnectivity. So the successful cooperation of filtration properties of nanofibers with bactericidal properties of nanoparticles means an elaboration of the filter which will be able to capture the bacteria and to ensure their destruction. First of all it was necessary to select the appropriate procedure to modify the nanofibrous layers by nanoparticles. The incorporation of modifier into the polymer solution prior to electrospinning is the simple and cheap method from the technological point of view. The efficiency of this method was already confirmed. Moreover such modification procedure does not require the additional steps, equipment and financial costs (except the cost of modifier).

Despite the well-known antibacterial properties of the nano-sized particles we had some doubts about the propriety to use them for the modification of nanofibers for the filtration application. There are few serious reasons for it. The toxicity of nanoparticles and the tendency to aggregation can cause obstacles to their usage for the filtration aims. From the literature we know that the micro-sized particles of the same chemical composition have less efficiency but less toxicity than nanoparticles. And what is also important, their tendency to aggregate is less. That's why we decided to use the particles of both sizes (nano and micro) for the antibacterial modification of nanofibrous filters and to compare the influence of different dimensional characteristics of modifier on the structure and properties of nanofibers. Two types of polymer materials (polyurethane and polyamide 6) and one type of modifier (copper oxide) in micro- and nano-sized states were used for the production of nanofibrous filters with antibacterial properties. The theoretical and practical justifications of such choice will be presented in the chapter 2 (I). However it worth mentioning that the cathodic arc deposition method was also studied for the modification of nanofibers.

As it was mentioned at the beginning of this chapter we set for ourselves two important goals. The first of them (the development of efficient antibacterial filters) was already presented together with a short description of ways to reach it. Now time has come to reveal the second key objective of this thesis. It was particularly important to develop the appropriate methodologies for the confirmation of stability of particle's fixation into the structure of nanofibers and for the determination of the behaviour of our materials under the real (or close to real) filtration conditions. In case of the antibacterial modification of filters we have to be sure that the modifiers are stably fixed into the structure of materials. It is important from the point of view of lifetime of the antibacterial filtration samples and in terms of permissibility to use such materials in accordance with the environmental regulations. Therefore two developed methodologies will be presented in the chapter 3 (I).

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

1. Production of the antibacterial nanofibrous materials by the incorporation of modifiers into the polymer solution with further electrospinning:

- comparison of nano- and microparticles of CuO as antibacterial additives for the modification of nanofibers in terms of their influence on the properties of polymer solution and on the structure of 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 the 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.

2. Theoretical part

2.1. Current situation of the antibacterial pollution of air and water

Air and water are the fundamental conditions for the existence of life on our planet. Adverse effects of the polluted air on the human health were mentioned in the writings of Hippocrates as early as several centuries ago [1,2]. Most of our life is spent indoors (80 - 95%). Therefore, the indoor air pollution may present a greater risk to the human health. This sub-chapter will focus on one kind of the indoor air pollutant. It will be the airborne microorganisms - bacteria. They are the factors of potential infectious, allergenic and immunotoxic effects. The indoor micro flora is reported to be responsible for the health problems, especially among children [3]. Coughing, shortness of breath, allergic rhinitis, asthma, influenza, malaise, fatigue are often caused by the bioaerosol contamination [1,4]. Possible sources of the biological contamination of indoor air include: people, organic dust, various materials stored in the buildings, and the air inflowing from the ventilation and air conditioning systems [5].

Water isn't less essential for life. The microbial contamination of drinking water remains a significant threat and the constant vigilance is important, even in the most developed countries [6]. The water-borne diseases (i.e., diarrhea, gastrointestinal illness) caused by various bacteria, viruses, and protozoa have been the causes of many outbreaks. There are over 500 waterborne pathogens of the potential concern in drinking water, identified by the US Environmental Protection Agency (EPA) In the developing countries, such as those in Africa, the water-borne diseases infect millions [7,8]. The detected water-borne outbreaks are considered to be just the tip of the iceberg of the total drinking-water-related illness. In fact the actual disease burden in Europe, as in other parts of the world, is difficult to estimate. Most likely it is underestimated [9]. According to the WHO, the mortality of water associated diseases exceeds 5 million people per year [10].

These facts are the strongest motivation to continue the development of effective materials for combating the bacterial contamination of air and water. Let us consider which ways of the solution of this problem are offered by the modern science.

2.2. Antimicrobial activity of metals and metal's oxide nanoparticles

2.2.1. General information

The antibacterial activity is related to compounds that locally kill bacteria or slow down their growth [11]. Metals and metal oxides have been widely studied for their antimicrobial activities [12]. The nanosized state of these substances attracts special attention and interest in the scientific world. The reducing of the particle size of metals and metal oxides significantly changed their physical and chemical properties, sometimes to the extent that completely new phenomenon were established [13]. 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. Most of the nanosized metal's oxides exhibits bactericidal properties through the reactive oxygen species (ROS) generation although some are effective due to their physical structure and the metal ion release [12].

2.2.2. Synthesis of antibacterial NPs

Recent advancements in the field of nanotechnology have provided attractive solutions for the synthesis of nanoparticles. The metallic NPs are usually synthesized by the chemical reduction of suitable metal ions in the solution of sodium borohydride, ascorbates, citrates or carbohydrates. After reduction of metal ions the synthesized nanoparticles are often stabilized by the coating with capping agents. The stability of metallic nanoparticles can be provided by the steric or electrostatic repulsion. The usage of surface active agents such as polymers (e.g.

polyethylene glycol, poly(vinylalcohol), poly(vinylpyrrolidone)) and non-ionic surfactants (e.g., Tween, Triton X-100) ensures the steric stabilization. The electrostatic protection of NPs can be realized by addition of the ionic surfactant (e.g. sodium dodecyl sulfate, cetyltrimethylammonium bromide).

Most of nanoparticle's synthesis methods relies on the use of toxic reducing agents (e.g. sodium borohydride) and harmful organic solvents (e.g. N,N-dimethylformamide (DMF), tetrahydrofuran (THF)). These chemicals represent potential biological and environmental risks. The use of toxic chemicals and solvents forces the scientists to develop more eco-friendly, clean, biocompatible and safe production methods [14]. For instance a novel green source was opted to synthesize silver nanoparticles using the dried roasted Coffea arabica seed extract [15]. Another cost-effective and nonpolluting approach for synthesis of silver nanoparticles (Ag NPs) using the leaf extract of Typha angustifolia was presented [16].

2.2.3. Mechanisms of nanoparticle's antibacterial activity

The precision mechanism of antibacterial activity of ultrafine particles of metals or their oxides is not clear at all. Nowadays, three hypothetical mechanisms obtained wide circulation:
1. Bacterial cell absorbs ions extracted by the metal nanoparticles; ATP and DNA replication is violated.
2. Active oxygen forms generated by nanoparticles and metal's ions are the reason for the oxidative damage of cellular structures.
3. The accumulation of nanoparticles in a bacterial membrane leads to a change in penetration due to the sustained release of lipopolyssacharide, membrane proteins, and intracellular factors [17].

The mechanisms of NPs toxicity depend on composition, surface modification, intrinsic properties, and the bacterial species [11]. A number of studies indicated that the interaction of nanoparticles with a bacterial cell occurred in stages. At the first (physical) stage, the metal nanoparticles are adsorbed at the surface of microorganism due to the resultant electrostatic pressure. After that, nanoparticles get inside. This is confirmed by the submicroscopical researches. At the next stages (molecular and cellular), the cellular membrane is changed: emboly, perforation, and enlargement of cellular wall. The perforation of the cellular wall of microorganism by nanoparticles leads to the discharge of the intracellular matrix.

2.2.4. Types of antibacterial NPs and their characteristics

Ag nanoparticles. According to the literature Ag nanoparticles are the most popular inorganic nano-sized additive used as the antimicrobial agents [17]. Several methods are applied for the preparation of silver NPs, and most of them involves the chemical reduction of silver salts. Nowadays the demand for the green synthesis of silver NPs has been ever increasing. Therefore the biologically active molecules are intensively involved in the synthesis of Ag NPs, especially phytomolecules, which present in the plant extract and often act as functionalizing ligands [18]. Ag NPs are able to interact physically with the cell surface of various bacteria. This is particularly important in the case of Gram-negative bacteria where numerous studies have observed the adhesion and accumulation of Ag NPs to the bacterial surface. Many studies have reported that Ag NPs can damage the cell membranes leading to structural changes, which render bacteria more permeable [19].

ZnO nanoparticles. In the early of 1950s, scientists had already started to investigate ZnO as an antibacterial material [20]. ZnO nanoparticles showed bactericidal effects on Gram-positive and Gram-negative bacteria as well as on spores which are resistant to high temperature and high pressure [17]. The application of ZnO (produced by the wet chemical process) to fabrics such as cotton and polyester may impart beneficial antimicrobial characteristics, enhanced whiteness, resistance to UV radiation and anti-static properties [21].

TiO_2 nanoparticles. Antimicrobial property of TiO2 is related to its crystal structure, shape and size. Photocatalytic properties of the TiO2 nanoparticles help them to efficiently eradicate the bacteria. In fact, TiO2 nanoparticles produce ROS under ultraviolet (UV) light [17]. It is showed that TiO2 is genotoxic, because it interrupts the effects of DNA chains in cells under exposure to light [22].

Cu and CuO nanoparticles. CuO NPs due to their unique biological, chemical and physical properties, antimicrobial activities as well as the low cost of preparation are of the great interest to the scientists [17]. Data of the antibacterial activity of cuprum nanoparticles allowed the United States Committee for Environmental Conservation to confirm their registration as the antimicrobial agent against the malignant bacteria [22]. Application of copper nanocrystals includes antimicrobial, antibiotic and antifungal agents which are incorporated in the coatings, plastics, textiles [23]. CuO NPs have potential for external uses as antibacterial agents in the surface coatings on various substrates to prevent microorganisms from attaching, colonizing, spreading, and forming the biofilms in medical devices [24].

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 [25].

2.3. Nanofibers as efficient filters and carriers of antibacterial substances

Nanofibers (NFs) are a promising variant of polymer matrix which can serve as a carrier of antibacterial agents. Due to their unique properties such as a high specific area, small diameters, highly porous structure with excellent pore interconnectivity the nanofibers belong to attractive materials for different advanced applications [26]. Electrospinning (ES) is the most suitable technique for the production of nanofibers. The advantages include its relative ease, low cost, high speed, vast materials selection and versatility. Additionally, this technique allows the control over the fiber diameter, microstructure and arrangement. Electrospinning will be discussed in details in the chapter 3 (I).

The polymeric nanofibers have been used in a number of commercial air filtration applications over the last 20 years, and hold promise for technical benefits in an expanding field of the filtration application. Compared to conventional filtration microfibers, NFs possess a much smaller diameter thereby offering a higher chance of inertial impaction and interception, i.e., more optimum filtration efficiency. Moreover, the drag force and pressure drop are decreased by virtue of slip flow at the nanofiber surface (for nanofibers with diameters smaller than 500 nm). The slip flow also results in passing more contaminants near the surface of the nanofibers, hence, the inertial impaction and interception efficiencies rise. As a result, the filtration capability of nanofibrous membranes increases for the same pressure drop as compared with conventional fiber mats. Additionally, a very high surface area of the functionalized NFs facilitates adsorption of contaminants from air [27,28].

Nanofibers gradually find its application in the field of water filtration. Engineering of the unique nanomembrane that has almost all required properties for water treatment such as micro- to nano-filtration of particulate impurities, absorption of toxic metal ions, removable of toxic organic molecules (organic dyes), destruction of pathogenic microorganisms, improved antifouling effect, is essential. Composite electrospun fabrics have recently been emerged as an effective membrane for removing of the harmful water-burn contaminants from environment [29]. NFs, or modified nanofibers, have been proposed as potential membranes for applications in separation technology, such as a pre-treatment of water prior to reverse osmosis or as filters or pre-filters minimizing the risk of fouling and contamination prior to ultra- or nanofiltration applications in the water treatment technologies [30]. Functionalized nanofibrous membranes can be beneficial in the disinfection of water. The implementation of substances such as an elemental silver and silver salts, silver-TiO_2 systems, and quaternary ammonium salt-containing cationic polymers can induce good antimicrobial properties to the membranes [28].

In this thesis a particular attention will be focused on two types of polymer nanofibers: polyamide 6 (PA 6) and polyurethane (PU). And here's why. PA 6 has a superior fiber forming ability. It is biodegradable and biocompatible synthetic polymer with good mechanical properties, which are further enhanced by hydrogen bonds. Unlike other polymers, such as polyethylene oxide and polyvinyl alcohol, PA 6 is resistant to both water and humidity. Reports on the properties of electrospun nylon-6 nanofibers showed the PA a particularly attractive material for filtration applications [31]. PU is a polymer known by its excellent elastomeric properties and a broad range of applications [32,33]. The polyurethane electrospun filter media has excellent mechanical properties such as elasticity, tensile strength, durability, and water insolubility [34].

So NFs modified by the particles of metals or their oxides can become perspective multifunctional materials for the water and air purification from the particulate matter and also from the harmful microorganisms. The incorporation of antibacterial modifiers into the nanofibrous structure can be accomplished by the electrospinning of polymer solutions containing the appropriate particles, by impregnation method or by in-situ reduction of metal salts or complexes into the polymeric matrix [35].

2.4. Modifications of electrospun NFs

Various modification techniques have been applied to render nanofiber based materials suitable for a specific application. All modification methods can be divided in two big groups. The first group includes the procedures of modification of polymer solutions prior electrospinning process. We will call this group of methods "Incorporation of modifier in a polymer solution prior ES". The resultant physical morphology and mechanical properties of future fibers vary depending on the polymeric concentration and spinning conditions employed during the process [36]. The most well studied methods of this group are in-situ polymerization and in-situ reduction of metal salts or complexes in the polymer solution, and reactive blending method. The second group includes the methods of modification of already prepared polymer fibers (after electrospinning). This group gets the name "Post-spinning modification of fibers". Post-spinning modification techniques include sol-gel, surface coatings, impregnation procedures and others. Now let us consider both groups with the examples.

2.4.1. Incorporation of modifier in a polymer solution prior ES

In-Situ polymerization and in-situ reduction of metal salts or complexes in the polymer solution. In case of in-situ polymerization, the nanoparticle's dispersion and polymerization occur simultaneously. Abdul Kaleel et al. synthesized polyethylene (PE)/TiO2 nanocomposites using ethylene, metallocene catalysts, and titanium (IV) oxide through *in situ* polymerization. Liu and Su successfully prepared PMMA/ZnO nanocomposites using MMA and oleic acid–modified ZnO nanoparticles with 2,2′-azobis(isobutyronitrile) through the *in situ* solution radical polymerization [37]. There is an example of the in-situ reduction of metal salts or complexes in the polymer solution. In-situ reduction of the silver salt ($AgNO_3$) to Ag NPs was carried out in the aqueous solution of polyvinyl alcohol (PVA). Here, PVA was used as the reducing agent and the stabilizing polymer as well as the electrospinning polymeric matrix for the fabrication of PVA/Ag-NPs nanofibers. Afterwards, hydroxypropyl-beta-cyclodextrin was used as an additional reducing and stabilizing agent in order to control the size and uniform dispersion of Ag NPs [38]. Antibacterial polyvinylpyrrolidone nanofibers containing silver, copper and zinc nanoparticles were also obtained from their corresponding salts by in-situ reduction method [39].

Blending method. It's the simplest and easiest method employed to functionalize polymer nanofibers. It is a physical approach consisting on the addition of blending ligand molecules in the polymer solution and then electrospinning. No chemical bonding or attachments are involved between the polymer material and modifying species. It is a simple mixing of two or more materials that has been proven to be an effective method for the nanofiber modification [40].

Kendouli et al. have applied this method to modify cellulose acetate NFs by Ag NPs with the aim to enhance their thermal stability [41]. In another research Ag NPs were introduced without any chemical or structural modifications into the Poly Lactic-co-Glycolic Acid polymer matrix before ES to form inorganic-organic nanocomposite. Authors recommended the use of obtained nanofibrous mats as antimicrobial agents in biomaterials or water purifying systems [42]. In some studies the special pre-treatment techniques were utilized for the reducing of silver nitrate into Ag NPs before or after ES. Atmospheric helium plasma treatment was used to reduce $AgNO_3$ precursor in PAN pre-electrospinning solution into metallic silver nanoparticles, followed by electrospinning into continuous and smooth nanofibers with Ag nanoparticles embedded in the matrix. The resultant Ag/PAN nanofibers showed excellent antibacterial activity against both Gram-positive and Gram-negative microorganisms. This composite nanofibers have many potential applications including implant scaffolds, chemical and biological protection, medical devices, and biotextiles [43]. Jang et al. produced cellulose acetate (CA) nanofibers containing Ag ions. Fibrous layers were fabricated by the electrospinning with 0.5 or 1wt% of $AgNO_3$. CA nanofibers containing Ag ions/NPs were prepared by UV irradiation of as-spun CA nanofibers [44].

2.4.2. Post-spinning modification of fibers

Sol-gel method. In this method, the nanomaterials are incorporated inside of the polymer matrix in aqueous solution medium. It results in an interpenetration network formation between the inorganic and organic phases at the mild temperatures. This method helps to improve a strong interfacial adhesion between the phases. This is very facile method for the preparation of SiO_2, Al_2O_3, ZrO_2, ZnO, and TiO_2-based polymer nanocomposites at a nanoscale level. In this method, metal alkoxides, coupling agents, and polymer precursors have been employed for the preparation of hybrid polymer nanocomposites [37]. The cellulosic fibers were coated with titanium dioxide nanoparticles, which were obtained from the aqueous titania sol. Titanium isopropoxide was hydrolyzed and condensed in water to obtain the titania sol coating at low temperature. The treated fibers exhibited good antibacterial activity because of the formation of TiO_2 surface on the cellulose substrate [45].

Surface coatings. Physical vapor deposition (PVD) has opened up new possibilities in the modification and functionalization of textile materials. PVD is a process by which a thin film of material is deposited on a substrate. The most promising technique in PVD technology is a sputtering [46]. Magnetron sputtering - cathode sputtering of the target material in magnetron discharge plasma - allows obtaining the thin films and coatings on various supports [47]. The ability to deposit the well-controlled coatings would expand the applications of polymer fibers, based on changes of both physical and chemical properties of fibrous layers. Wei et al. used the sputter coating of copper (Cu) to deposit functional nanostructures on the surfaces of polypropylene (PP) spun bonded nonwovens. The surface conductivity of the produced materials was significantly improved [46]. A magnetron sputter coating was used to deposit the functional zinc oxide (ZnO) nanostructures onto the polyethylene terephthalate nonwoven substrate. The study has explored the surface morphology of polymer fibers treated by the sputter coating [48]. The surface functionalization of PA-6 nanofibers was also done by the reactive sputtering of zinc oxide. The surface conductivity of nanofibers modified by zinc oxide films was significantly improved. The reactive sputter coating of zinc oxide has also enhanced the ultra-violet absorption of PA-6 substrates [49].

Impregnation method. The impregnation of inorganic nanoparticles into the polymer matrix has been synthetically achieved recently. PAN nanofibers were modified by the impregnation in special mixture of hyperbranched polymer (HBP) and solution of $AgNO_3$. HBP has an excellent dispersion and stabilization properties in aqueous medium, so it can be used as a reducer and stabilizer for preparing nanoparticles. The PAN electrospun web was immersed in the Ag/HBP solution at 30°C, 60°C, and 90°C in a water bath for 120 min, respectively. The treated samples were air-dried at the room temperature for the subsequent characterization. Excellent antibacterial and filtration properties of these layers were confirmed [50].

As it was mentioned before we selected two polymer materials (PU and PA 6) for the production of modified nanofibers with antibacterial properties. That's why it is important to consider the current researches with antimicrobial modifications of PU and PA 6 nanofibers which are carried out by another authors.

2.5. Examples of modification of PA-6 and PU nanofibers

PA-6 nanofibers. Polyamide nanofibers made by the electrospinning have been extensively studied. Most of the researches are focused on the influence of different parameters on the obtained materials or on the use of polyamide nanomats in air filtration [51]. In this sub-chapter we will review the examples of modifications of PA-6 NFs for the antibacterial water and air filtration.

Nylon nanolayers with antibacterial properties containing silver nanoparticles were prepared via in situ synthesis of nano-Ag using the reduction of silver nitrate by sodium borohydride in the PA-6 solution prior electrospinning. The produced nylon/Ag NPs composite nanofibers were presented as a good candidate for biomedical applications and for the antibacterial water filtration [52]. Nylon-6/TiO_2 hybrid nanofibrous mats were also prepared by the mixing of TiO_2 NPs with a 20 wt% nylon-6 solution with further ES. The results revealed that the fibers in two distinct sizes (nano and subnano scale) were obtained with the addition of a small amount of TiO_2 NPs. Presence of the selected modifier in PA-6 solution improved the hydrophilicity (antifouling effect), mechanical strength, antimicrobial and UV protecting ability of electrospun mats. It makes them a potential candidate for the future application in water filtration [53]. The researchers did not stop there. Later the silver nanoparticles were successfully embedded into electrospun TiO_2/nylon-6 composite nanofibers through the photocatalytic reduction of silver nitrate solution (impregnation method) under the UV-light irradiation. The results showed that TiO_2/nylon-6 nanocomposite mats loaded with Ag NPs are more effective than composite mats without Ag [54].

There are few interesting researches about the modification of PA-6 by ZnO in different forms. The hydrothermal treatment of zinc acetate/nylon-6 electrospun nanofibers in the presence of suitable reducing agent (bis-(hexamethylene)-triamine) has resulted to the production of nylon-6 nanofibers embedding ZnO flakes [55]. Another study was focused on the forming a spider-wave-like nanonets of nylon-6 decorated with unique mop-brush-shaped ZnO rods. At the beginning the electrospun PA-6 nanolayers containing ZnO nano-seeds were fabricated by the blending of ZnO NPs with nylon-6 solution. Then the electrospun ZnO/nylon-6 composite was hydrothermalized with ZnO precursor solution to grow long ZnO mop-brush-shaped rods on the surface of fibers. Finally the produced modified nanofibers showed good hydrophilicity, photocatalytic properties, and UV-shielding property and could become a potential candidate for the industrial filter application due to their antifouling effect [56].

PU nanofibers. Polyurethane has been modified by different types of inorganic clusters, such as Ag, CNTs (carbon nanotubes), Zn-Ag bimetallic particles, tourmaline, silica and ZnO. Ag is the most commonly used additive to confer the antimicrobial properties to both natural and synthetic fibers (including PU nanofibers) [57]. 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; AgNO3/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; the as-spun fibers were stored for 1 week then vacuously dried for 24 h to remove the residual solvents. PU nanofibers containing silver NPs were presented as a desired candidate for future wound healing agents and for antibacterial filters for water purification systems [58]. 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). But the modification procedure of PU nanofibers remains similar as in the previous example (all components were mixed with polymer solution and spun by ES) [59]. 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. In this case the surface of PU NFs was modified by PEG to lower the toxicity and usage content of NPs. Firstly, the antifouling PEG as a bacteria-repelling component was chemically grafted onto PU nanofibers through the UV photo-graft polymerization to obtain PU-g-PEG nanofibers; then Ag NPs as the bactericidal component were immobilized onto the PU-g-PEG nanofibers under the assistance of ultrasonication. These nanofiber composites performed better antibacterial properties in vitro assays employing gram negative and positive strains, because of the bacterial resistance of the grafted PEG and the bactericidal effect of silver. Such approach has significant potential for the development of the infection-resistant wound dressing [60]. But the above mentioned examples of PU nanofibers modification are very complicated from the point of view of practical application in the filtration area. Described techniques include the multi-step procedures and the usage of additional chemicals.

The easier approach for the modification of PU nanofibers is presented in the next example. Bimetallic NPs composed of two different metal elements have become perspective modifier for the development of antibacterial metal-based composite materials. This is because the bimetallization can improve the properties of the original single-metal and create a novel hybrid property, which may not be achieved by monometallic materials. The fabrication of bimetallic (Zn/Ag) doped PU nanofibers was presented. The bimetallic composite was prepared using blending method prior electrospinning. The utilized colloidal solution was composed of zinc oxide and silver NPs, and polyurethane solution in DMF:THF. The results of antimicrobial test indicated that the combination of different ZnO and Ag nanoparticles embedded in the PU composite had a synergistic bactericidal effect [61].

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 [62]. In another study CuO particles were mixed with the polymer solution to make 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 [63].

2.6. Risks associated with the use of nanoparticles

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. This sub-chapter will be devoted to these topics.

Toxicity of NPs. The unique physicochemical properties and high surface areas of the NPs not only provide the potential to bind and treat toxic pollutants, but also provide the toxic hazards during their application. The direct exposure of nanomaterials (NMs) to human may occur via skin contact, inhalation of atmospheric aerosols, drinking of contaminated water, or ingestion of contaminated vegetables and foodstuffs.

The inhalation of NMs leads to the deposition of NPs in the respiratory tract and lungs, resulting in lung-related diseases such as asthma and bronchitis. The uptake and translocation of NMs also could lead to the accumulation of NPs in the brain. According to a report by the SwissRe, particles < 300 nm can reach the blood stream, while particles < 100 nm are also absorbed in various tissues and organs. NMs 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. [64].

Although the toxicity of the metal oxide NPs has been studied intensively in the past decades, there still remains the question whether the toxicity of the metal oxide NPs originates from the NPs themselves or from the released metal ions. It is generally accepted that the metal oxide NPs have the potential to dissolve in aqueous media, which results in release of toxic metal ions into the surrounding media. Some studies indicate that the released metal ions of the metal oxide NPs are the major, or even the only cause of their toxicity; however, other studies show that the particles rather than the dissolved ions were the major source of toxicity. Wang et al. have investigated the metal ion release of CuO, Fe_2O_3, ZnO, Co_3O_4, Cr_2O_3, and NiO NPs in aqueous media. According to their results the relationships between the metal oxide NPs antibacterial effects and its released metal ions could be divided into three categories: (1) the ZnO NPs antibacterial effect was due solely to the released Zn^{2+}; (2) the CuO NPs antibacterial effect originated from both the released Cu^{2+} and CuO particles; and (3) the antibacterial effects of Fe_2O_3, Co_3O_4, Cr_2O_3, and NiO NPs were caused by the NPs themselves [65]. NPs are able to interact with biomolecules due to their large specific surface area that endows CuO or ZnO NPs by high reactive activity and electronic density. 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 [66].

Aggregation of NPs. Aggregation, a common complex phenomenon for small particles, is problematic in the production and use of many chemical and pharmaceutical products [67]. As it was mentioned before the nanocomposites obtained by the incorporation of inorganic NPs into organic matrix can lead to improvements in several areas, such as optical, mechanical, electrical, magnetic, antibacterial properties. However, the nanoparticles have a strong tendency to undergo agglomeration followed by insufficient dispersal in the polymer matrix, degrading the functional properties of the nanocomposites [68]. If aggregation occurs, the internal structure of aggregates ranges from close-packed clusters to tenuous fractals, depending on the system and preparation [69].

To improve the dispersion stability of nanoparticles in aqueous media or in polymer matrices, it is essential to modify the particle surface by involving of polymer surfactant molecules or other modifiers which generates a strong repulsion between nanoparticles [68]. Different mechanochemical approaches including sonication by ultrasound can be also used for this purpose. However, the scope of such approaches for the dispersing of nanoparticles is limited by the reaggregation of individual nanoparticles and the establishment of an equilibrium state under the definite conditions, which determines the size distribution of agglomerates of dispersed nanoparticles [70].

We can conclude that there are comparatively efficient ways to solve the problems with the aggregation of nanoparticles in the polymer solution (different stabilization methods). However, there is only one approach to prevent the toxic effects of metals and metal's oxides in the nano-sized state on the environment and living organisms. The ingress of nanoparticles into water, air and soil should not be allowed.

2.7. Stability of NPs fixation into the structure of nanofibrous layers

The modification of nanofibrous filters by NPs with the aim to impart them antibacterial properties was studied in this thesis. The results of our investigation will allow to make a conclusion about the usage of such composite filters for antimicrobial purification of air and water. But it is known that NPs are toxic for living organisms. Therefore 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. No significant changes in UPF and sterilization rate before and after washing was observed. It has indicated the excellent laundering durability (what means excellent fixation of modifiers on the fabric surface) of the cotton fabric with the plasma pretreatment and ZnO/CMCS composite finishing [71]. 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. Due to such methodology the specimens can be also evaluated for the abrasion resistance during laundering based on the appearance. We think that this testing method is not the appropriate choice for the evaluating of particles fixation in the fibrous structure for filtration materials. The testing conditions don't correspond to the filtration conditions when the water (or air) flow passes directly through the sample.

In the study [72] CA, PAN and PVC nanofibers were modified by Ag NPs. The next modification procedure was applied: $AgNO_3$ was dissolved in DMF solvent (it provided the spontaneous slow reduction at room temperature); the mentioned polymers were separately added to the solution of $AgNO_3$ in DMF; electrospinning technique was used to produced modified NFs; then nanofibers were irradiated in UV light (400 W) for various time intervals depending upon the type of used polymer. 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. It was found out that the release rate was relatively fast in the first day and then decreased. According to the authors the silver release rate and cumulative release amount indicated that the Ag/PAN nanofibers prepared by electrospinning could release sufficient silver to exhibit a sustained antibacterial activity. Therefore, these nanofibers were recommended for the long term contact water operations; like antimicrobial water filters [73]. 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). It was shown in the next research. Liu et al. have produced CS/PVA/Ag NPs composite nanofibers. In this study the fabricated layers were also tested with the aim to determine the silver ion release behavior by the same method as was described in the previous example. The obtained results were also similar. It is found that the release rate is relatively high in the first few days and then continuously release over time. But in this research the hybrid CS/PVA/Ag NPs nanofibers were recommended for antibacterial biomedical applications [74]. This implies that an effective method for the evaluating of the fixation of antibacterial agents on the filter surface under the real conditions of water or air filtration was not proposed.

In the next sub-chapter we will introduce our vision and ideas for the production and modification of antibacterial nanofibrous filters. The efficient method for the testing of particle's fixation in structure of fibers will be proposed.

2.8. Our approaches to the antibacterial modification of nanofibrous filters

2.8.1. Antibacterial modification of PU nanofibers

Incorporation of CuO in PU solution prior to ES. The goal of our research was to produce bactericidal nanofibrous filters for the air and water purification, to confirm their properties under the simulated filtration conditions and particles fixation into the structure of NFs. Polyurethane was used as a polymer matrix for particles incorporation and for further electrospinning. This polymer is known by its excellent elastomeric properties and a broad range of applications [32,33]. CuO was selected as the antibacterial agent for several reasons. It is easily mixed with PU and relatively stable in terms of both chemical and physical properties. The blending method was used for the modification of PU solution. It means that particles of copper oxide were incorporated directly into the pre-electrospinning polyurethane solution. This procedure is the easiest and the chiepest from technological and economical points of view. Particular attention was paid to the dimensional characteristics of used CuO particles. The NPs of metal oxides can cause toxic effects not only on the bacteria cells but also on the cells of plants, fishes and mammalian [65]. Other problem with utilization of NPs is their tendency to aggregate because of the high surface energy. Our serious fears are caused by the fact that a certain amount of nanoparticles will be placed inside the polymer matrix because the diameter of the nanoparticles is less than the diameters of nanofibers. Consequently some part of the nanosized modifier won't be available for the contact with bacteria. Therefore we used both micro- and nanoparticles of CuO for the modification of PU solutions in order to compare the influence of different dimensions of the additive on antibacterial properties and on the stability of particles fixation into the structure of fibers.

The sonication is a commonly used method to break up the agglomerated NPs which usually performed in a solvent. In this method, the breaking of agglomerates is mainly controlled by the power, time and dispersion volume [75]. The probe sonication method was used in this thesis to prevent the agglomeration of CuO NPs in the PU solution before ES.

As the first step we produced NFs from colloidal PU solutions with micro- or nanoparticles of CuO by the laboratory ES method from the surface of steel rod. This technique was used in order to check the spinnability of modified PU solutions. When the spinnability was proved, the Nanospider technique was used for the production of composite nanofibrous layers. This commercial method for the production of polymeric nanofibers is used in the industrial range. Two type of spinning electrodes were used: the rotating cylinder with needle surface and the thin wire electrode. The rotating cylinder with needle surface was chosen in order to ensure the mixing of colloidal solutions and to prevent the deposition of micro- and nanoparticles of CuO at the bottom of dish with PU. The wire electrode is widely used in the industrial range because it provides the high productivity of ES process. We tried to utilize the wire electrode for the spinning of modified PU solutions in order to bring our laboratory experiments closer to the industrial conditions.

Modification of PU NFs by surface coating. Post-spinning modification of nanofibers has some advantages. ES process and the structure of future nanofibrous layers are not influenced by antimicrobial substances. Consequently morphological and filtration characteristics of NFs won't be affected. The deposition of metallic oxide materials onto the polymers has attracted a lot of attention recently. This technology allows to prepare the coatings of nearly any chemical composition. Moreover surface coatings by the physical vapor deposition provides an environmentally friendly technique to functionalize various materials. In this thesis the layer of Cu was deposited on the surface of electrospun PU nanofibers by the magnetron sputtering method in vacuum deposition chamber.

2.8.2. Antibacterial modification of PA-6 NFs

PA-6 is a biocompatible polymer with good mechanical properties that have extensive application [52]. Electrospun PA-6 mats have been reported as the effective water filtration media [53]. The PA-6 solution was prepared by dissolving the polymer granules in a formic/acetic acid mixed solvent. Then CuO microparticles were incorporated into the solution prior ES.

CuO reacts with acetic and formic acids. The formate and acetate of copper are produced as a result of these reactions. These two compounds are soluble in water. Therefore it was necessary to stabilize the formate and acetate forms of copper to obtain insoluble compounds. This is a required condition for the future application of such nanofibrous substrates as water filters. For this aim the modified PA-6 nanofibers were treated under the influence of high temperature, ultraviolet radiation and humidity.

2.8.3. New approaches to verify the stability of particles fixation and the bacterial filtration properties of NFs

Firstly the content of modifiers in the structure of electrospun mats (by SEM with EDX) and the antimicrobial activity against Gram negative (Escherichia coli) and Gram positive (Staphylococcus gallinarum) bacterial strains were confirmed. But it is only first characteristics we have to determine in order to make a conclusion about further application of composite fibers. As it was mentioned in the sub-chapter 1.7 the stability of particle's fixation in the fibrous structure is particularly important.

Our method to determine the stability of particle's fixation. For this aim the modified nanofibers were tested under the simulated conditions (which corresponded to the real) 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 the air filtration conditions and the probability of washing-out of bed-fixed particles is higher. Then the EDX analysis and antibacterial tests were repeated after the water treatment and compared with the results which were obtained before the water filtration test. This made it possible to assess the stability of the fixation of antibacterial additives in the fibrous structure and, hence the safety of the used modification methods in terms of the entering of toxic substances into the environment.

Bacterial filtration efficiency of NFs. One of the perspective application of produced samples is air bacterial filtration. Consequently it was necessary to develop an effective method for the estimation of the fibers ability to capture bacteria from the air stream and eliminate them. Hence the new testing device for the evaluation of antimicrobial properties of nanofibrous layers (and other textiles) under filtration of the bacterially contaminated air will be introduced in details in the chapter 3 (I).

3. Experimental part

3.1. Incorporation of CuO in PU solutions prior ES

Polyurethane solutions were modified by micro (700 nm - 1µm) and nanoparticles (≈50 nm) of copper oxide (CuO) in order to determine the influence of dimensional characteristics of modifier on the properties of composite filters.

3.1.1. Materials

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). The nutrient medium

Tryptone Soya Broth (TSB) and sterile Tryptone Soya Agar (TSA) from Oxoid CZ s.r.o. were used for the inoculation and the incubation of the bacteria.

3.1.2. Preparation of solutions

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.

3.1.3. Solution properties

The measurements of viscosity, surface tension and electrical conductivity will determine the influence of different dimensions of particles on the PU solution.

Viscosity. The viscosity of the solution has a profound effect on ES and on the morphology of resultant fibers. When viscosity of the solution is too low, the electrospraying may occur and polymer particles are formed instead of fibers. At lower viscosity where generally the polymer chain entanglements are low, there is a higher likelihood that beaded fibers are obtained instead of smooth fibers [76,77]. But in this thesis we could encounter the opposite problem. An introduction of CuO particles into PU solution will probably cause an increase of the solution viscosity. And the high viscosity results in the hard ejection of jets from the solution. Due to the measurement of viscosity we will be able to conclude whether the modified PU solutions are still suitable for the ES. Therefore it is important to estimate and compare the viscous behavior of pristine and modified polyurethane solutions. The comparison of viscosities of solutions modified by micro- and nanoparticles of CuO in order to analyse the influence of dimensional characteristics of our additive on the structure of future electrospun samples is also particularly noteworthy.

Rheological properties of solutions were measured using Rheometer HAAKE Roto Visco 1 at 23°C. It is a rotary viscometer with the so-called free slot. The rotary viscometer is used for the determination of flow curves of non-Newtonian fluids. The device allows measuring of the dependence of shear stress on strain rate. The measuring part of the device consists of rotary disc and stationary plate. The drop of a polymer solution is deposited on the stationary plate. The rotary disc is immersed into the solution. The required force to overcome the resistance to rotation is measured during the disk's rotation. The measured data is processed by the software Haake RheoWin® which consists of two units. The first unit is the Job Manager which controls the device during experiments and stores the results. The second unit is Data Manager which is suitable for the evaluation of experimental data.

Surface tension. It is a primary force opposing the coulomb repulsion and its role in the determining of electrospinnability cannot be overstated. The charges on polymer solution must be high enough to overcome the surface tension of the solution. The bead formation in electrospinning can be induced by the changing of surface tension of the solution. Beaded fibers can be converted into smooth fibers by the reducing of surface tension of the solution It is often that the values of surface tension and viscosity of the solution determine the gap within which a specific polymer/solvent combination can be electrospun [78]. Different solvents may contribute to different surface tensions of one polymer. [76]. We paid attention on the influence of used additives on the surface tension of PU solution in the presented thesis.

The surface tension of pristine and modified solutions was measured by the bubble pressure method. The method is based on the measurement of the maximum pressure (P_{max}) in a bubble growing at the tip of a capillary immersed into the studied liquid. When the bubble grows at the tip of a capillary, its radius of curvature decreases up to a hemisphere, and then increases again. Thus, at the hemispherical size the maximum pressure is measured. After the bubble passes this maximum pressure it grows quickly, separates from the capillary and a new bubble is formed. The surface tension (γ) is calculated via the Laplace equation taking the capillary radius (r) as radius of curvature ($P_{max} = 2\ \gamma/r$). The measurement was provided by a portable bubble tensiometer PocketDyne. It is a device for quick and easy determination of the dynamic surface tension of liquids. The device calculates the surface tension from the measured values of P_{max}. The surface tension also depends on the temperature of the measured liquid, so the temperature sensor is placed behind the capillary.

Conductivity. The solution must gain sufficient charges (such that the repulsive forces within the solution are able to overcome the surface tension of the solution) to initiate the ES process. Subsequent stretching or drawing of the electrospinning jet is dependent on the ability of the solution to carry charges. Solution conductivity is mainly determined by the polymer type, solvent sort, and the salt. The solvents commonly used in electrospinning have conductivities that are much lower than that of even distilled water. The solution conductivity generally increases due to the availability of conducting ionic species (mostly from impurities or additives) from the polymer. The electrical conductivity of the solvent can be increased significantly through the mixing of chemically non-interacting components [76–78]. In our case particles of CuO were added into the solution of PU in DMF. The conductivity of pristine and modified solutions was measured by conductivity meter EUTECH instruments CyberScan CON 510 in order to evaluate the influence of the antibacterial agents on this important parameter.

The first conclusions about the effect of microparticles and nanoparticles of CuO on the properties of PU solution will be done due to the analysis of viscosity, surface tension and conductivity.

3.1.4. Application of ultrasound

A characteristic feature of colloidal solutions is their relatively low stability. This problem is particularly acute for the colloidal solutions containing nanoparticles because of their noticeable surface energy. Stable dispersion systems are capable to withstand against the processes leading to the change of their structure and degree of dispersion. There are two types of stability of colloidal solutions: sedimentation and aggregate. Aggregate stability represents the ability of the system to resist processes that reduce a surface energy of the interface particles of dispersed phase in a dispersion medium, or the ability to maintain the degree of polydispersity of the particles.

The aggregation of NPs can become a serious problem for the future use of modified nanofibers. The structural advantages initiated by small dimensions of nanoparticles as the key to their unique functional properties (including antibacterial) can be lost in the result of aggregation.

Therefore the ultrasound (US) pre-treatment of PU solutions with NPs before ES was used to prevent the aggregation.

Solutions with nanoparticles were treated by the US using Q SONICA sonicator Q500. Popular applications of this device include nanoparticle's dispersion, creating emulsions, cell lysis and homogenization. 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.

3.1.5. Electrospinning process – the used techniques and electrodes

Electrospinning from the rod spinner. 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. As it was mentioned before this method was used for the quick checking of the spinnability of modified solutions. The technique is shown in the Fig. 1. This device belongs to the simplest equipment construction for electrospinning.

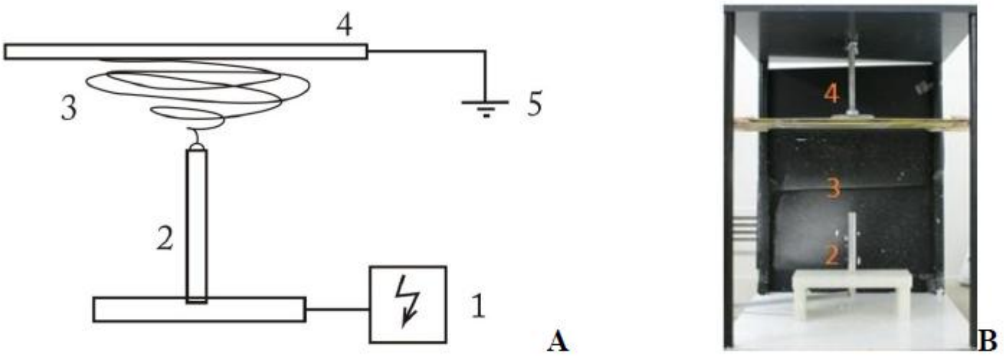


Figure 1. A - schematic illustration of electrostatic fiberforming from the steel rod: 1 - high voltage source; 2 - steel rod with polymer solution; 3 - nanofibers on the way to collector; 4 - collector; 5 - ground connection; B - photo of experimental activity using this method: 2 - steel rod with polymer solution on the top; 3 - nanofibers on the way to collector; 4 - collector.

The droplet of polymer solution is placed on the top of rod spinner. The steel rod is connected to a positive high voltage source. Nanofibers are deposited onto the collector which is positioned at the sufficient distance over the steel rod. The collector is a grounded metal plate. The disadvantage of this method is discontinuity of the process. It is necessary to terminate the process and to replenish polymer after the exhaustion of the volume of the polymer on the top of rod (and exhaustion is very quick) [79]. In our experiments the distance between the rod and the collector was 13 cm and the applied voltage was 27 kV. These parameters were determined experimentally as optimal for the used solutions.

Roller spinning method. The roller spinning method (Fig. 2) with a high voltage power supply was used as a second method to produce PU nanofibers with micro- or nanoparticles of CuO. The method is used for the industrial production of nanofibers. Nanospider consists of the rotating cylinder (spinning electrode) to spin fibers directly from the polymer solution. The cylindrical rotary electrode with needle surface (Fig.3 - 2b) 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. In the present thesis the PU was filled into a polypropylene dish. The spinning electrode was partially immersed into the polymer solution and, as it rotated, a controlled amount of polymer solution was carried to the top parts of the needles on the surface of the cylinder in the electric field where a series of Taylor cones were created.

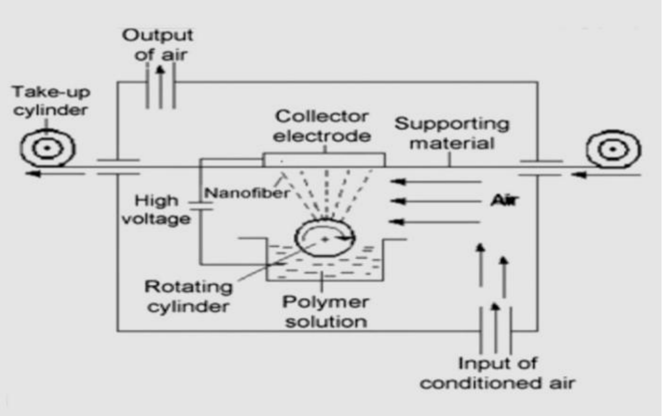


Figure 2. Schematic diagram of Nanospider method.

High voltage was connected to the rotating roller. As the solvent evaporated, the jets of polymer solution were transformed and the solid nanofibers were obtained before reaching to the collector electrode. The nanofibers were collected on the polypropylene spun bond nonwoven antistatic material. The advantages of this method are the continuity of the process and a large productive capacity [79,80].

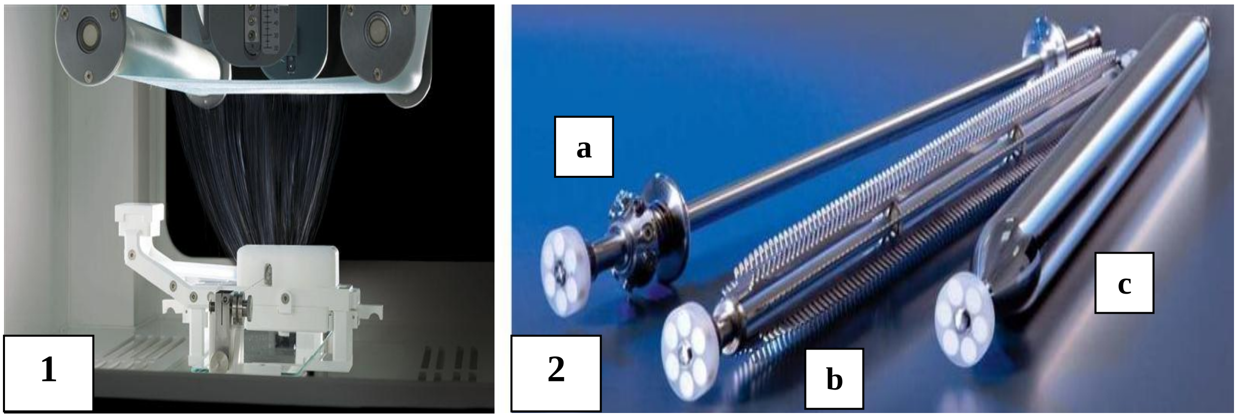


Figure 3. 1 - Free liquid surface ES from static wire electrode; 2 - Types of spinning electrode for Nanospider: a - rotary wire electrode; b - cylindrical rotary electrode with needle surface; c - cylindrical rotary electrode with smooth surface.

The high voltage will induce the necessary charges on the solution and together with external electric field, will initiate the ES process when the electrostatic force in the solution overcomes the surface tension of the solution [76]. All parameters of the electrospinning process of PU modified solutions were determined experimentally and described below:

voltage = 67kV; roller speed = 2.5rpm; speed of collecting material = 0.05m/min; distance between the rotating cylinder and collector electrode = 16cm; temperature (T°C) = 20°C; humidity in the spinning chamber = 22%.

Wire spinning method. Moreover ES from a thin wire electrode (Fig.3, 1) was also used to produce PU nanofibers with antibacterial additives. Electrospinning was carried out by Nanospider laboratory machine NS LAB 500S (from Elmarco s.r.o.) with air conditioning unit. The optimum spinning parameters for modified PU solutions from wire electrode were determined experimentally. They are presented below:

voltage = 60kV; traversing speed of wire = 0.2mm/s; speed of collecting material = 0.05m/min; distance between the wire and collector electrode = 17.5cm; temperature (T°C) = 10°C; humidity in the spinning chamber = 22%.

This technique doesn't provide the continuous stirring of the solution during electrospinning process. So the wire electrode will not prevent the aggregation and precipitation of modifiers at the bottom of bath with colloidal solution. We will be able to estimate the importance of stirring of modified solutions during ES and to select a more appropriate electrode due to the comparison of influence of the rotary electrode with needle surface and static wire electrode on the production of composite NFs.

3.1.6. Structure of produced nanofibers

The morphology of nanofibrous layers was analysed using a scanning electron microscope (TESCAN VEGA3 SEM). The fiber structure was observed from the obtained SEM images with different magnification. Few our samples (PU with 5 and 12% of nanoparticles of CuO) were analyzed by QUANTA 650FEG scanning electron microscope by our colleagues from the team of Environmental electron microscopy from the Institute of scientific instruments of the Czech Academy of Science.

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. Fiber uniformity was determined using number and weight average calculations. The number average is known as an arithmetic mean in mathematics. The method for calculating the uniformity coefficient has the same principle as molar mass distribution in chemistry. We calculated both of these values using the formulas 1 (number average or average diameter) and 2 (weight average), which are given below:

$$A_n = \frac{\sum n_i d_i}{\sum n_i} \quad \textbf{(1)}$$

$$A_w = \frac{\sum n_i d_i^2}{\sum n_i d_i} \quad \textbf{(2)}$$

where d_i - fiber diameter; n_i - fiber number. The fibre uniformity coefficient was determined by the ratio Aw/An and the optimum value should be very close to 1 for fibers with a uniform diameter distribution [80].

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). EDX makes use the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain localized chemical analysis. The qualitative analysis involves identification of lines in the spectrum. The quantitative analysis (determination of concentrations of the presented elements) entails the measuring of line's intensities for each element in sample and for same elements in the calibration Standards of known composition. The surface density of prepared samples was calculated to compare the influence of additives on the spinning performance of polyurethane solution.

3.1.7. Filtration properties of produced composite NFs

The filtration efficiency of pristine and modified PU nanofibers was measured by the Sodium chloride aerosol test equipment (Bench Mounting Rig type 1100P). This device can measure filter efficiency, pressure drop and impact air flow according to the standards: BS 4400 (Method for Sodium Chloride Particulate Test for Respirator Filters-British standard), EN 149 and EN 143 (Respiratory Protective Devices- European standards). The Sodium Chloride aerosol test equipment can be used for testing of high efficient filters such as a HEPA filters. It is possible to estimate classes according to test standards: ASHRAE 52.2, EN 779 and EN 1822. The size of filtered particles of NaCl ranges from 0.02 to 2μm (mean value of particle size = 0.6μm) and the air flow ranges from 10 to 95 l/min. Particles concentration is up to 13 mg/m^3.

This test was done in order to prove that added antibacterial particles didn't have a negative impact on the filtration efficiency of PU nanofibers.

3.1.8. Antibacterial properties of modified nanofibrous layers

Standard Test Method ASTM E2149[1] was used to determine antibacterial efficiency of produced samples. The test quantitatively evaluates the efficiency of samples treated with the antimicrobial agents (fabrics, textiles with non-leaching additives, paper, granular materials, ceramics, plastics, glasses, stoneware) under the dynamic contact conditions between tested samples and bacterial suspension. Antimicrobial activity of nanofibers was carried out against gram-negative Escherichia coli (E.coli) and gram-positive Staphylococcus Gallinarum (St.Gal.) bacterial strains.

The frozen cultures of E.coli and St.Gal. were revived in the Tryptone soya broth in an incubator at 37 °C for 24 hours, then obtained inoculum was diluted to a concentration 10^8 CFU/ml by a pure Tryptone soya broth. Further dilutions were made to get the final concentration of 10^3 CFU/ml (≈ 1000 future colonies). The suspension with E.coli was diluted by a pure physiological solution. In case with St.Gal. the dilution procedure was carried out in physiological solution with addition of bovine serum albumin (0.15%). Such medium supplemented with the nutrients is more appropriate for vital functions and reproduction of Staphylococcus. Pristine and modified samples were sterilized by heat at 80°C in a drying cabinet for 1 hour before the beginning of antibacterial test. The sterilized samples were placed into the test tubes with diluted inoculum (concentration 10^3 CFU/ml). One test tube with inoculum was left without tested filter as a reference sample (hereinafter denotes as a reference). All samples were shaken in dynamic shake tubes in a wrist action shaker to ensure good contact by the constant agitation of test specimen in a bacterial suspension during the test period. 1±0.1 ml of inoculum was withdrawn from each test tube after shaking within 1±0.1 min. This sampling was transferred on agars and incubated at 37°C for 24 hours. The first sampling will be denoted as the sampling at time 0 min in the text below. Then test tubes were placed back to the shaker. Further samplings (1 ± 0.1 ml) were carried out in 60, 120, 180 and 240 min and 24 hours after the start of test. These samplings were also transferred to the TS agars and incubated at 37 ° C for 24 hours. After cultivation the number of grown bacterial colonies on agars was assessed for each sample. So the change of antibacterial activity for each produced nanofibrous layer was monitored over time (from 1 min to 24 hours). The ASTM E2149 method clearly specifies the initial microbial concentration, allowing for a fairly reproducible comparison of different antimicrobial products.

The results are expressed as a percentage (%) of reduction (CFU/ml) after a defined duration of contact between our sample and bacterial suspension (0min; 60, 120, 180, 240 min; 24 hours). Antibacterial efficiency is evaluated according to the following equation (3):

$$\mathbf{E\ (\%) = (B - A)/B\ x100} \qquad \mathbf{(3)}$$

where

A - number of colonies (CFU / mL) for the test tube containing pristine or modified substrate after a specific contact time with bacterial suspension;

B - number of colonies (CFU / ml) for the test tube without sample (reference) which was used to determine "A" after a specific contact time with bacterial suspension.

3.1.9. Stability of particles fixation into the nanofibrous structure

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). The device which was used for the treatment of produced filters under the simulated conditions of water filtration is presented in the Fig. 4.

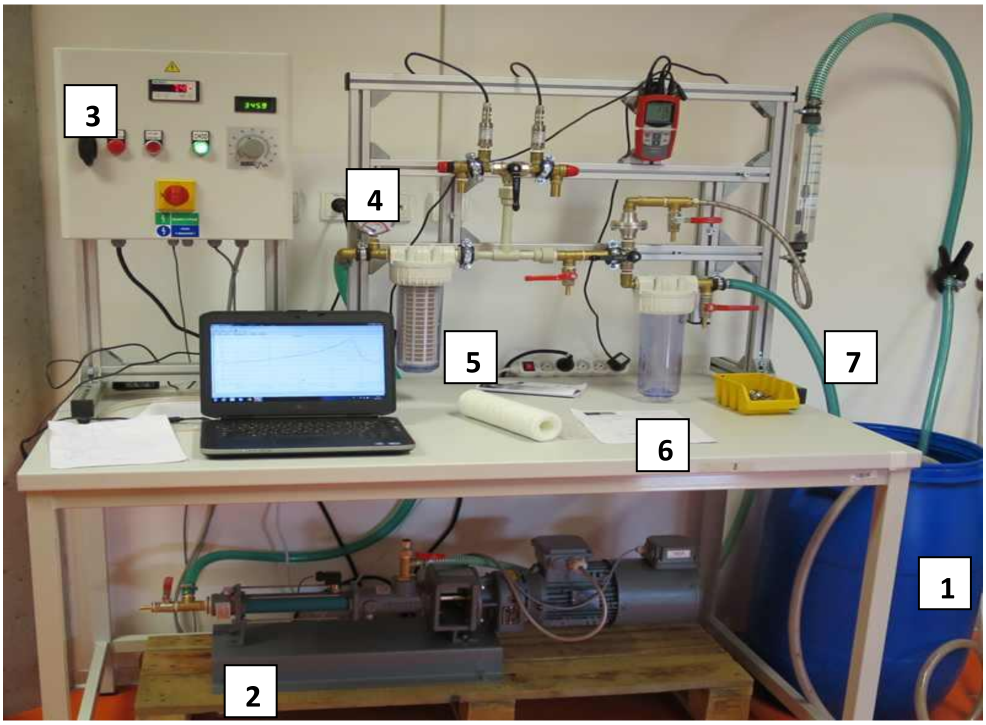


Figure 4. Device for the testing of filters under the simulated conditions of water filtration: 1 - reservoir with distilled water; 2 – water pump; 3 - speed regulator for the water pump; 4 - a pressure gauge; 5 – prefilter; 6 – container for the tested sample; 7 - outflow of water back to the reservoir.

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.

3.1.10. Measurement of bacterial filtration efficiency

This part of the experiment is particularly important from the point of view of valuation of the practical application of our samples under the real conditions of bacterial air filtration. Special testing method was developed in order to evaluate the bacterial filtration efficiency of antimicrobial samples. The bacterial filtration efficiency 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. 5) was applied for the verification of extent to which the filter is able to prevent penetration of aerosolized inoculum with bacteria to the purifying area. 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). Bacterial filtration efficiency (% BFE) is defined similarly as in the case of the particulate filtration according to the equation (4):

$$\% \boldsymbol{BFE} = \left(\mathbf{1} - \frac{n_1}{n_2}\right) \cdot \mathbf{100} \qquad \textbf{(4)}$$

$\mathbf{n_1}$ **-** 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).

The scope of speed of airflow through the filter complies with EN 1822 and EN 779 designated for filtering within building ventilation, as well as the standards EN 143, EN 149 and with others for testing of respirators and personal safety. Evaluation of bacterial filtration efficiency is implemented by a modified ASTM methodology F2101-01.2001 (Test Method for Evaluating the bacterial filtration efficiency of medical mask materials using biological matter). Nonpathogenic bacterial strains from the first class of hazard are recommended for this test. In the presented thesis nonpathogenic form Escherichia coli K-12 (CCM 7929) was used as the test bacterial strain. The using of the non-pathogenic form of bacterial culture is important for this test because the bacterial solutions are aerosolized into the space of the test device. Therefore the possibility of escape of bacteria in the aerosol form into the surrounding environment outside of the test apparatus increases. The using of non-pathogenic forms of the bacteria is the only way to carry out the testing process and to protect environment and personnel against the harmful inhalation of pathogenic bacteria, which are dangerous and can cause health problems.

The functional diagram of the device AMFIT 13 is shown in the drawing (Fig. 5) with numeration of each functional block.

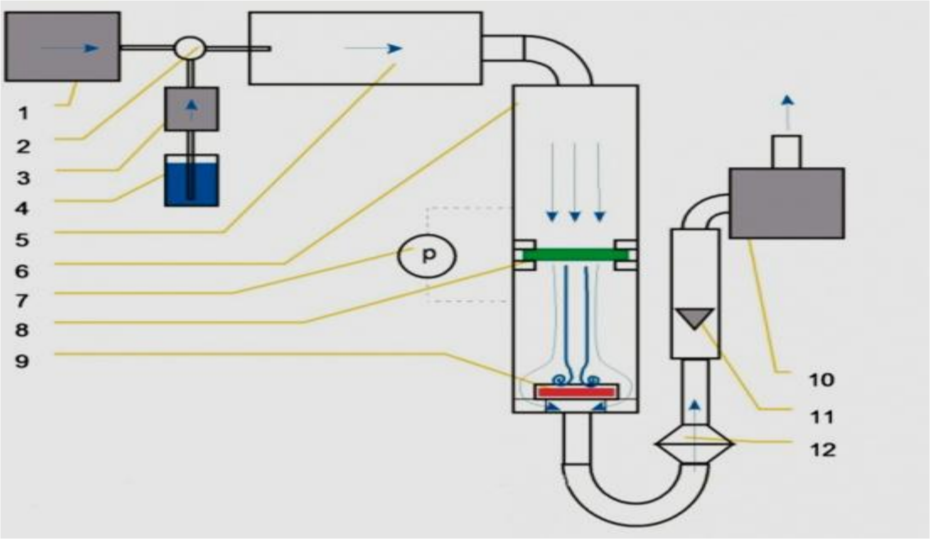


Figure 5. Scheme of AMFIT-13: 1-source of compressed air; 2 - atomizer, 3 - peristaltic pump (dosage control); 4 - reservoir with inoculum; 5 - tube for atomizing; 6 - stabilizing tube with direction of air and aerosol flow before and behind the sample; 7 - pressure gauge sensors; 8 - tested filter; 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 bacterial solution (inoculum) **4** is sprayed (aerosolized) into the main stream of the intake air. The atomizer **2** is driven by the compressed air source (compressor, pressure container, control valve) **1**. The peristaltic pump **3** is dosing a defined quantity of inoculum into the atomizer **2**. The separation of the small aerosol from the larger droplets will occur in the tube **5** for atomizing of inoculum. Aerosol continues its path to the stabilizing tube **6** which also serves as a filter holder. The stabilizing tube **6** consists of three tubes which can slide together easily. The tested filter **8** and Petri dish with agar **9** are fixed by partitions and rubber o-rings inside of the stabilizing tube **6**. Pressure gauge sensors **7** for determining of the pressure drop are placed before and behind the tested filter **8**. The air which passes through the filter is purified using high efficient filter **12** for the enhanced safety. A float rotameter **11** measures the air speed which is sucked by vacuum pump **10**. Air discharged from the vacuum pump **10** is suctioned. The main parts of apparatus (the intake and outlet of air, atomizer, atomizing container and stabilizing tube) are located in the ventilated room for safety reasons. Individual parts of the testing device can be easily disassembled and residues of inoculum deposited on walls of the tubes can be decontaminated using ethanol or UV radiation. Working parameters of AMFIT 13 (Tab. 1) were chosen in order to achieve compatibility with the standards for air filters and to ensure safe and reliable tests in the work with microorganisms in the aerosolized form.

Parameter	**Value**	**Units**
Flow velocity before the filter	5 – 300	cm/sec
Air flow rate	3 – 50	l/min
Filter area	10 – 50	cm^2
Shape of the tested filter	a circular sample; it is required to ensure the tightness of the side walls for bulk materials	
Measurable pressure drop across the filter	1 - 2000	Pa
Amount of spare bacterial suspension	5 - 100	ml
Amount of bacteria at the input	500 - 5000	CFU/ml
Testing time	30 – 1200	sec
Used bacterial strains	E. Coli K-12 (or other bacterial strains of hazard class 1)	
Medium size of bacteria	0,86 ≥	μm
Air pressure in atomizer	0,1	MPa

Table 1. Working parameters of AMFIT 13.

Detailed parameter settings for the currently performed tests are listed in the Tab. 2. These parameters have been found as the most suitable for the standard tests of filtration materials based on the experiments for the optimization of the device. They can be modified according to the special requirements.

Parameter	**Value**	**Units**

Bacterial concentration in inoculum	10^5	CFU/ml
Duration of dosing	3	min
Frequency of pump revs	7	rpm
Dosing speed	1.69	g/min
Air pressure in the atomizer	1.5	bar
Air flow through the filter	1.2	m^3/sec

Table 2. Recommended parameters for the standard measurements at the device AMFIT 13.

When the bacterial filtration efficiency was confirmed, it became necessary to assess the ability of filters to liquidate captured bacteria (we called it "smear test"). "Smear test" was performed in accordance with the procedure described below. 1ml of nutrient medium was inoculated on the surface of new agar. The sample with captured bacteria after bacterial filtration test was placed on this agar with medium. The agar plate with filter was in the incubator with mechanical rotator (for uniform distribution of nutrient medium on the agar surface) for 8 hours at 37°C. An eight-hour time period has been experimentally set as the time required for CuO to manifest its antibacterial properties in full. Then the sample was removed by sterile pincers from the agar surface. As the last step this agar was incubated for next 16 hours at 37°C. The total incubation time was 24 hours. Finally the number of grown colonies was counted.

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

Vapor deposition is a coating process, where the coating material is condensed from vapor phase, forming a thin film, or modifies the surface of the substrate by creating functional groups on the surface. Different types of deposition techniques are used to reach this criterion. Most of these techniques, including vacuum deposition, are used to minimize unwanted reaction with the free space and to shape the film composition easily [81]. Deposition methods have few important advantages. First of all we can easily get a thin homogeneous layer from materials which difficult to melt. The formed layer preserves the composition of the used target. The deposition of homogeneous layers can be provided on the large areas of modified materials.

3.2.1. Used materials

PU nanofibers were used as a substrate for the deposition of copper from pure metallic target. PU solutions were prepared at 15% concentration in DMF. The fibers were produced by Nanospider technology from the static wire electrode (same spinning parameters as were presented in the sub-chapter 3.1.5 I).

3.2.2. Deposition procedure

In this study the deposition was carried out in the Radio Frequency Plasma Assisted Chemical Vapour Deposition/Magnetron Sputtering (RF PACVD/MS) chamber (internal diameter 411 mm and height 393 mm). This device allows the application of few deposition methods: cathodic arc deposition, diode sputtering, pulsed laser deposition and radiofrequency sputtering. In our work the layer of Cu was deposited on the PU nanofibrous substrate at a low temperature by the cathodic arc plasma deposition method. A sample of the nanofibers was placed at the bottom of the vacuum deposition chamber, which was vacuuming to a residual pressure, and then charged with technically pure argon to a pressure of 1 Pa. The metallic Cu (99.99% purity) was used as a cathode target. The deposition of Cu on the surface of PU nanofibers was performed at the room temperature. The sputtered metal condensed on the one side of fibrous material. The thickness of obtained coating was regulated by the deposition time (2.5min).

3.2.3. Structure and antibacterial properties of obtained materials

The morphology of modified nanofibrous layers has been analyzed by scanning electron microscope. The presence of Cu on the surface of PU nanomats was confirmed by SEM equipped by an energy dispersive X-ray spectrometer (EDX).

Antibacterial properties of samples and stability of Cu fixation on the surface of nanofibers modified in the vacuum deposition chamber had been studied by the methods which were already described in sub-sections 3.1.8 and 3.1.9 (I).

3.3. PA-6 nanofibers modified by CuO

Our research in this direction has important prehistory. PA-6 NFs were modified by incorporation of CuO microparticles into the polymer solution and then electrospun. But further experiments with these samples have been postponed. First antibacterial tests were carried out a year after the production of PA-6 nanofibers with CuO. The obtained results showed that we are dealing with very efficient antibacterial samples. The water filtration test confirmed that copper is in stable (insoluble in water) chemical form on the surface of NFs. A new batch of the same PA-6 nanofibers with CuO was prepared one year later. The procedure of preparation and modification of PA-6 solution and the electrospinning process were carried out in the same way and in compliance with all conditions to fully repeat the experiment as it was done a year ago. But it was found out that antibacterial efficiency of new samples greatly decreased after the water filtration test. It means that copper is in water soluble state at the fibrous surface. Probably we are talking about formate and acetate of copper. Such result can be called predictable because CuO reacts with acetic and formic acids in the PA-6 solution. However, then it is not clear why the antibacterial properties of the "old" samples (made a year ago) are not changed after the water filtration test. It indicated that chemical form of copper could be changed during this year due to the process of polymer aging under the influence of environmental conditions. To verify (or refute) this hypothesis, we decided to simulate the aging of modified PA-6 nanofibers by an artificial increase of the influence of environmental factors and thereby reduce the timeframe of the process.

3.3.1. Preparation of modified PA-6 solution and ES process

PA-6 solution was prepared at 12% concentration in the mixture of AA/FA (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. This system was mixed on the magnetic stirrers for 12 hours.

Composite NFs (PA-6 + CuO) were produced from the thin wire electrode by Nanospider technique (laboratory machine NS LAB 500S from Elmarco s.r.o. with air conditioning unit). Spinning parameters are introduced below:

voltage = 60kV; traversing speed of wire = 0.2mm/s; speed of collecting material = 0.05m/min; distance between the wire and collector electrode = 18cm; temperature (T°C) = 22°C; humidity in the spinning chamber = 36%.

3.3.2. Structure and antibacterial properties of produced NFs

The structure of PA-6 nanofibers with the content of Cu was studied by SEM. The content of Cu at the fibrous surface was analyzed by SEM equipped by an energy dispersive X-ray spectrometer (EDX). This method allows the determination of the individual chemical elements but not chemical substances. Therefore we could not observe the difference in the chemical composition between "new" and "old" samples of modified PA-6 NFs.

The same approach was applied for the studying of antibacterial properties and stability of Cu at the fibrous surface as it was described in the sub-chapters 3.1.8 and 3.1.9 (I).

3.3.3. Simulation of the aging of PA-6 nanofibers with CuO

Such environmental parameters as temperature and relative humidity (RH) influence the aging process of polymers. In our experiment the values of these parameters were increased in comparison with the standard values of temperature and humidity to accelerate their influence. Moreover the UV irradiation was also used to speed up the aging of PA-6 NFs with CuO. The list of experimentally selected parameters and their values are represented in the Tab. 3.

Parameter	Values	Exposure time
Temperature	90°C	24 hours
Temperature	110°C	4 hours
Relative humidity	81%	35 days
UV	UV-C lamps 4 x 15W; wave length 254nm	24 hours

Table 3. Parameters for the simulation of the aging process of modified PA-6 NFs.

EDS analysis, antibacterial and water filtration tests were provided after the simulation of aging. The antibacterial test and EDS analysis were repeated after water filtration treatment in order to make a conclusion about the possibility to stabilize Cu on the surface of PA-6 nanofibers by the simulation of the aging of modified layers.

4. Results and discussion

4.1. PU nanofibers modified by micro- and nanoparticles of CuO

Polyurethane nanofibers were modified by micro- and nanoparticles of CuO using the simple blending method. It means that selected antibacterial agents were incorporated directly to the polymer solution prior electrospinning. First samples were produced from the rod spinner to check the spinnability of the modified solutions and to make first conclusions about the influence of additives on the structure of produced nanofibrous layers. So the section 4 (I) will start from the discussion of the results of modified samples produced by the rod ES technique (sub-chapter 4.1.1). Moreover the influence of modifiers on the properties of PU solution will be also discussed in the sub-section 4.1.1.1. Then the composite nanofibers with micro- and nanoparticles of CuO were produced using Nanospider technique. Such approach was selected in order to confirm that the used simple modification procedure is suitable for the application not only within the laboratory facilities but also on the industrial level. Two types of spinning electrodes were used for the production of modified PU NFs by Nanospider technique: the cylindrical rotary electrode with needle surface and the static wire electrode. It was done with the aim to estimate the role of stirring of colloidal polymer systems during the fiberforming and the influence of stirring on the structure and properties of future composite nanofibers. Therefore the sub-chapters 4.1.2 and 4.1.3 are devoted to the results of samples produced from electrode with needle surface and static wire electrode respectively. In the sub-section 4.1.1.4 we will discuss the problem of NPs aggregation and the possibility to prevent it using the US of modified solutions prior ES.

4.1.1. Modified PU NFs produced by ES from the rod spinner

Here we will present and discuss the results of the production of modified PU NFs with micro- and nanoparticles of CuO by ES from the rod spinner which was described in the sub-chapter 3.1.5. We start from the discussion of the effect of different particles sizes and concentrations on the properties of PU solution. It will be important in the analysis of structure and functional properties of samples, regardless of the used ES technique and types of electrode.

4.1.1.1. Influence of micro- and nanoparticles of CuO on the properties of PU solution

Viscosity. The first step was to compare the viscosities of pristine PU solution and modified solutions with micro- and nanoparticles. It's important because a major increasing of viscosity may serve as a first signal to the fact that solution is not suitable for the processing by electrospinning technique.

The first viscosity measurement was done at the low shear rate because of less noticeable time-dependence of the solution at high shear rate. The reason of this fact is an instantaneous orientation of polymer chains at high shear rates. Then the time-dependence of viscosity was measured at constant shear rate (10 1/s) within 10 minutes. It can be concluded that concentrations 2.5 and 5% of microparticles of CuO have no noticeable influence on the behavior of PU solution within time at the low shear rate (Fig.7). However, the viscosity values of modified solutions with higher concentrations of microsized antimicrobial agent (7; 9.5; 12 and 15 wt%) have been significantly changed in comparison with pristine PU solution. The viscosity values increased and the high peaks appeared. Such peaks as we observe for the concentration 15% of MPs of CuO are not typical for the pristine PU solution and for other modified solutions (Fig. 7). Based on this fact it was decided not continue the experiments with such high concentration (15%) of antibacterial additives. There are the results of viscosity measurements under the low shear rate for solutions with NPs of CuO in the Fig. 6. This graph indicates that nanoparticles of copper oxide cause considerable obstacles for the PU solution flow.

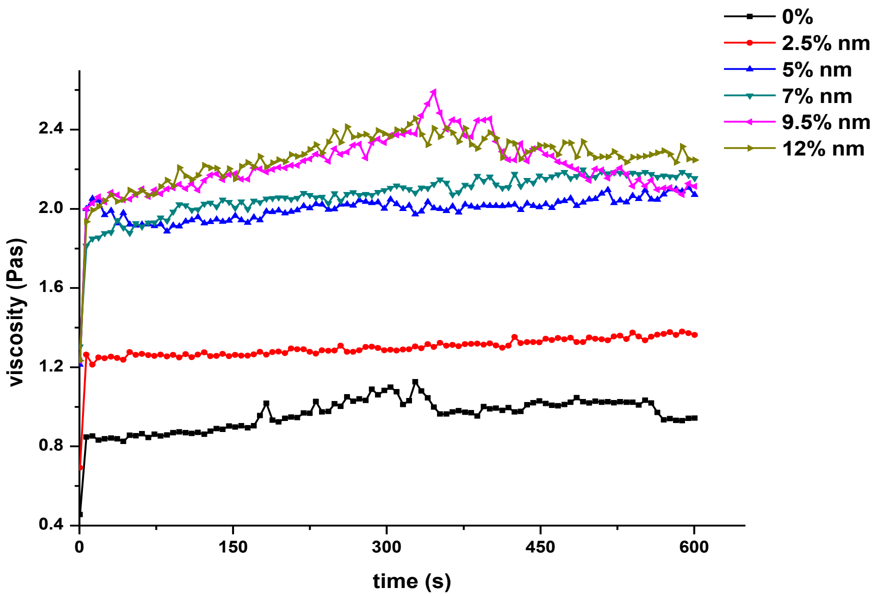


Figure 6. The variation of viscosity within time for polyurethane solution with nanoparticles of CuO at 23°C, shear rate = 10 1/s.

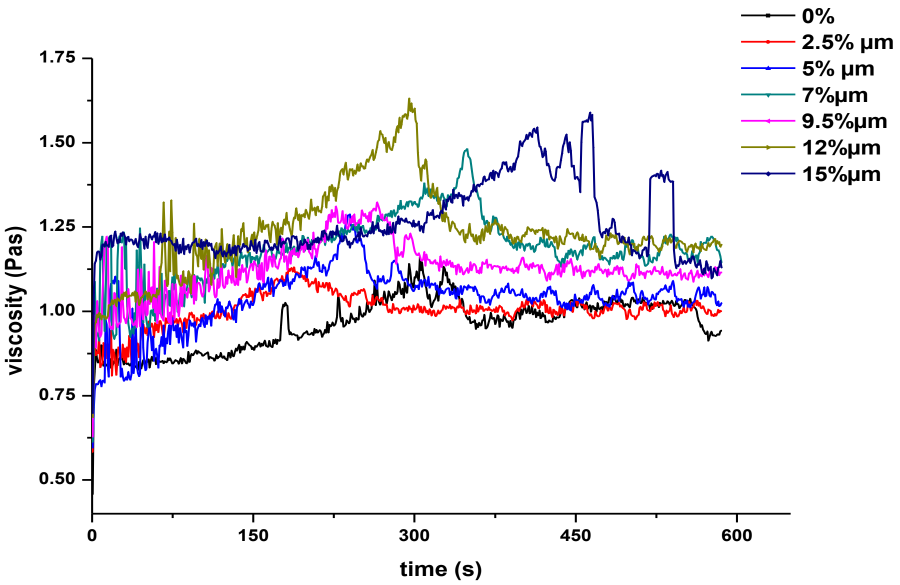


Figure 7. The variation of viscosity within time for polyurethane solution with microparticles of CuO at 23°C, shear rate = 10 1/s.

The average viscosities of solutions with nanomodifiers are higher than the viscosity of non-modified polyurethane solution (first black column in the Fig.8 denoted as 0%). Comparison of the effect of micro- and nanoparticles on the rheological behavior of polymer solutions has a special significance in terms of the influence of these additives on structural and dimensional characteristics of future nanofibers. The concentration 2.5% of NPs doesn't lead to the considerable change of viscosity value in comparison with the solution with microparticles. But starting with concentration 5% the viscosity values for solutions with NPs significantly exceed the corresponding measures for the solutions with microparticles. It may indicate a greater tendency of nanosized additive to the formation of aggregates in the polymer solution. Due to such results our suspicions about the unsuitability of the solutions with NPs for the processing into NFs by the ES method have increased. But running a few steps ahead we can say that despite such high values of viscosities of solutions with NPs the important technological problems with processing of all modified solutions haven't been revealed.

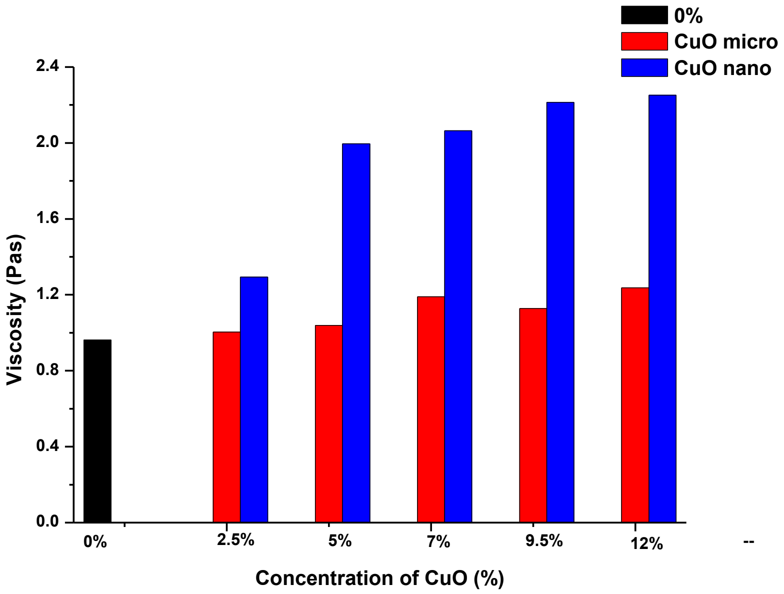


Figure 8. Comparison of average viscosities of pristine PU solution and solutions with micro- and nanoparticles of CuO.

There is a variation of viscosity with shear rate for the solutions with NPs of CuO in the Fig. 9. The experiment was carried out for 5 min and 300 values were measured for each sample. The viscosity values have decreased with increasing of shear rate for pristine PU and for modified solutions with nanoparticles. Similar tendency was observed for solutions with the microsized additive.

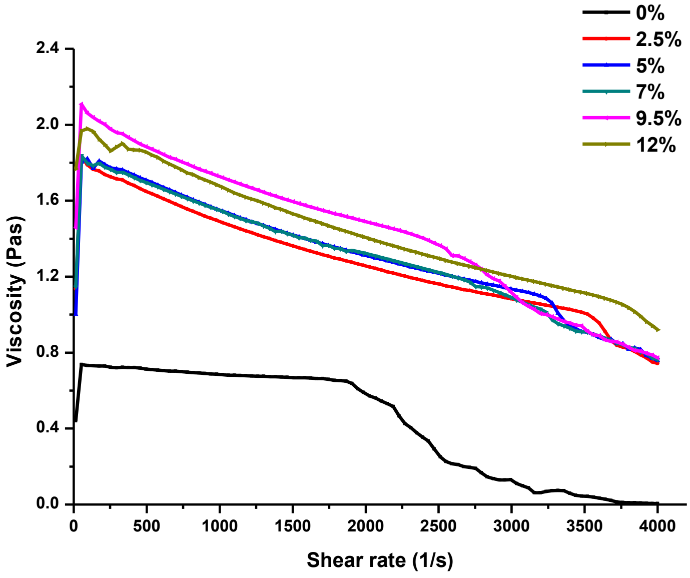


Figure 9. The variation of viscosity with shear rate for PU solutions with NPs of CuO at 23°C.

As a conclusion we can say that MPs of CuO is more appropriate modifier in terms of the influence on the rheological behavior of PU solution. Their incorporation into the polymer solution leads to less noticeable increasing of viscosity values than incorporation of NPs of CuO.

Conductivity and surface tension. The results of measurements of conductivity and surface tension for solutions with MPs and NPs of CuO are presented in the Tab. 4 and 5 respectively.

Solution properties	Concentration of CuO MPs (%)					
	0%	2.5%	5%	7%	9.5%	12%
Conductivity (µS/cm)	436	430	440	450	448	452
Surface tension (mN/m)	70.5	70.7	71.1	68.4	68.1	66.7

Table 4. Values of conductivity and surface tension for solutions with microparticles of CuO.

The conductivity of modified solutions with both sizes of modifier is slightly increased in comparison with pristine PU solution. But a clear dependence of the increase of conductivity with the growth of particle's concentration isn't traced. Such behavior of conductivity values of modified solutions confirms that used additives are chemically stable and don't react with PU.

Solution properties	Concentration of CuO NPs (%)					
	0%	2.5%	5%	7%	9.5%	12%
Conductivity (µS/cm)	436	448	447	452	453	451
Surface tension (mN/m)	70.5	71.3	70.9	66.2	67.8	67.2

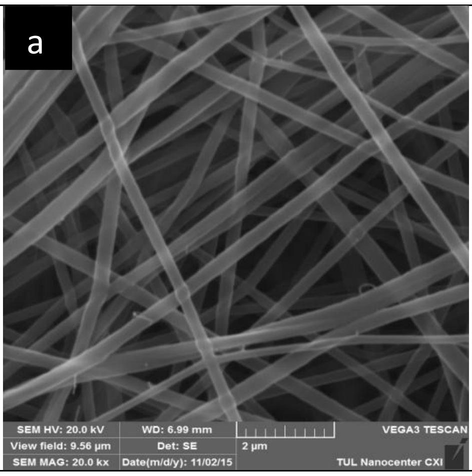
Table 5. Values of conductivity and surface tension for solutions with nanoparticles of CuO.

In case with the surface tension another tendency was observed. Small concentrations of micro- and nanoparticles of CuO (2.5 and 5%) don't have influence on the values of surface tension of PU solution. The further increase of particle's concentrations leads to a small decrease of the surface tension in comparison with pristine solution. But important conclusion is the fact that the introduction of modifiers into PU solution has no significant effect on the change of values of conductivity and surface tension of the modified solutions.

4.1.1.2. Structure of produced composite nanofibers

The Fig. 10 demonstrates that all NFs produced from the rod spinner have a smooth structure without beads or other defects. Particles of antibacterial agents are also well observed in the SEM images. It is clearly seen that micro- and nanoparticles of CuO form aggregates in the structure of fibers. However starting from the concentration 7% there is no noticeable dimensional difference between aggregates formed by MPs and NPs of copper oxide. As we remember the average diameters of used MPs and NPs are around 1 µm and 50 nm respectively. In case of nanoparticles it means that the observed aggregates consist from large numbers of elements. And these elements in the structure of aggregates of nanoparticles are bound only by the forces of intermolecular interaction. So the air or water flow may lead to a "release" of nanoparticles into the environment in case of filtration application. Moreover the aggregation is the first signal that particles in the nanoscale state can also cause serious problems when dealing with modified solutions using Nanospider technique.

Electrospinning from the rod spinner is a short-term process lasting for a few minutes. Therefore it is alarming that nanoparticles form such large aggregates in a short period of time. But MPs also cause problems in case of the rod ES. As we observe in the Fig. 10 the number of micro-sized particles is much less than number of NPs. Moreover it is clearly visible that the amount of MPs is decreased with the increase of CuO concentration (in case of NPs this tendency is opposite). MPs are heavier and it's more difficult to ensure the simultaneous jet formation from PU solution together with microparticles at higher concentrations of this modifier.



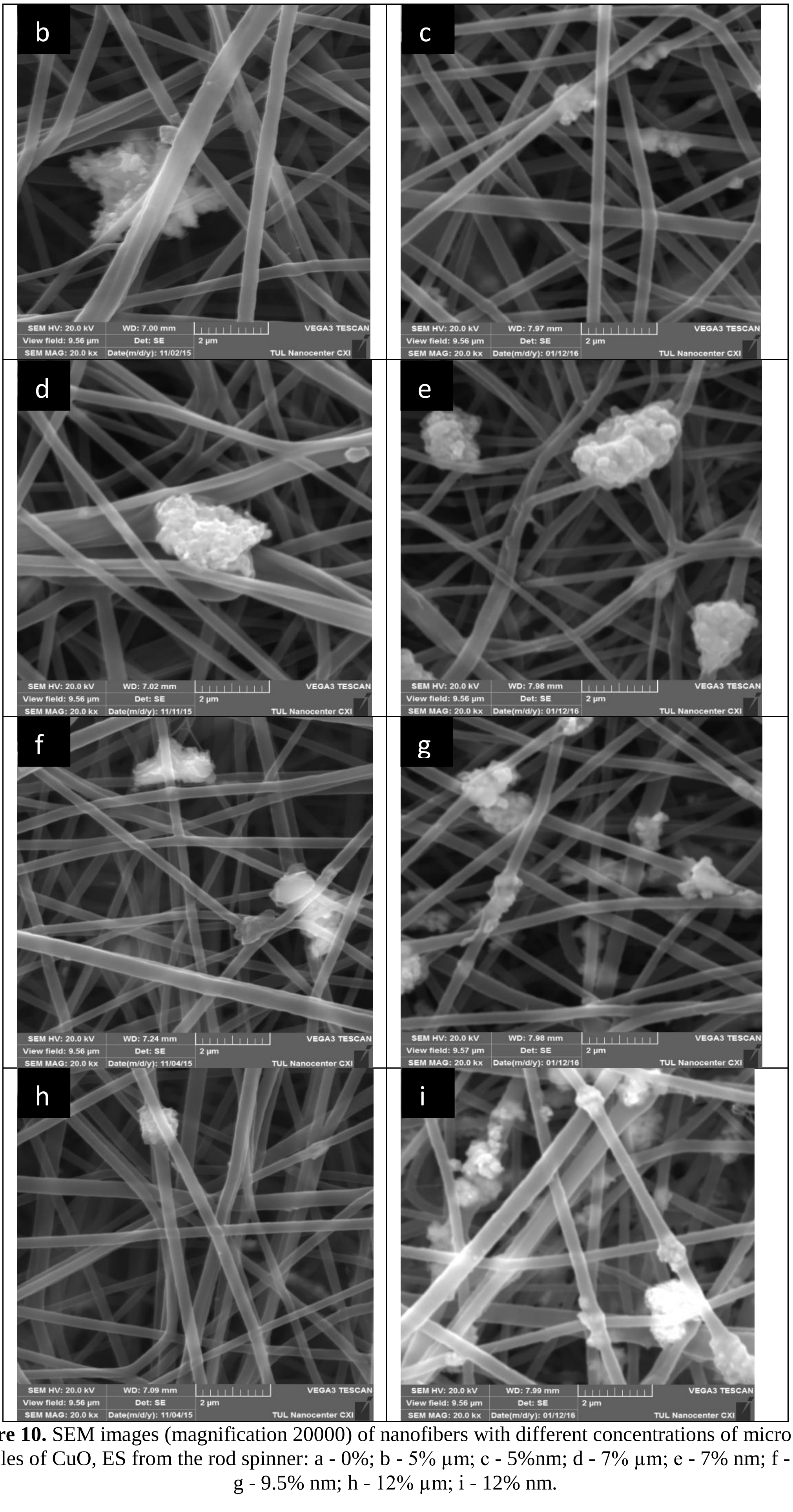


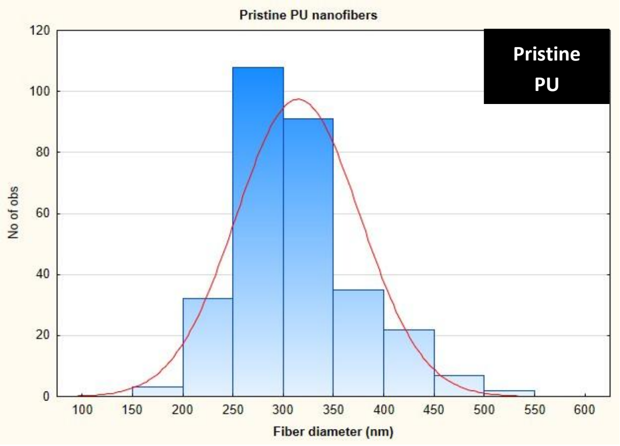
Figure 10. SEM images (magnification 20000) of nanofibers with different concentrations of micro- and nanoparticles of CuO, ES from the rod spinner: a - 0%; b - 5% µm; c - 5%nm; d - 7% µm; e - 7% nm; f - 9.5% µm; g - 9.5% nm; h - 12% µm; i - 12% nm.

There are the results of measurements of diameters and fiber's uniformity coefficients in the Tab. 6. Average diameters of modified fibers are only slightly higher than this index for the pristine PU layer except the samples with 7% CuO nm and 9.5% CuO µm where the opposite tendency is observed. So the selected concentrations of antibacterial substance in micro- and nanoscale forms haven't prevented to the rod ES of modified PU solutions and to the formation of smooth and uniform composite fibers. It is confirmed by SEM images and by values of fiber's uniformity coefficients in the Tab. 6.

Sample	Number average A_n (nm)	95% Confidence	Weight average A_w, (nm)	Fiber uniformity coefficient K (Aw/An)
Pristine PU	314	6.94	326	1.04
PU + 5%CuO µm	371	8.18	386	1.04
PU + 5%CuO nm	347	7.4	359	1.03
PU + 7%CuO µm	352	8.01	367	1.04
PU + 7%CuO nm	296	6.29	306	1.03
PU + 9.5%CuO µm	297	7.61	309	1.04
PU + 9.5%CuO nm	327	7.51	339	1.04
PU + 12%CuO µm	324	6.82	335	1.03
PU + 12%CuO nm	346	8.35	360	1.04

Table 6. The results of measurement of fiber's diameters and calculation of fiber uniformity coefficients for the samples produced by ES from the rod spinner.

Calculated values of the fiber uniformity coefficients are a little higher than 1 for all produced samples. But it's worth noting that the introduction of modifiers didn't influence the indicator of homogeneous diameters distribution of PU nanofibers (1.04 for pristine layer). All produced nanofibers have demonstrated the uniform distribution of diameters (Fig.11). Histograms of the diameter's distribution for another used concentrations are in the Appendix (Fig.1).



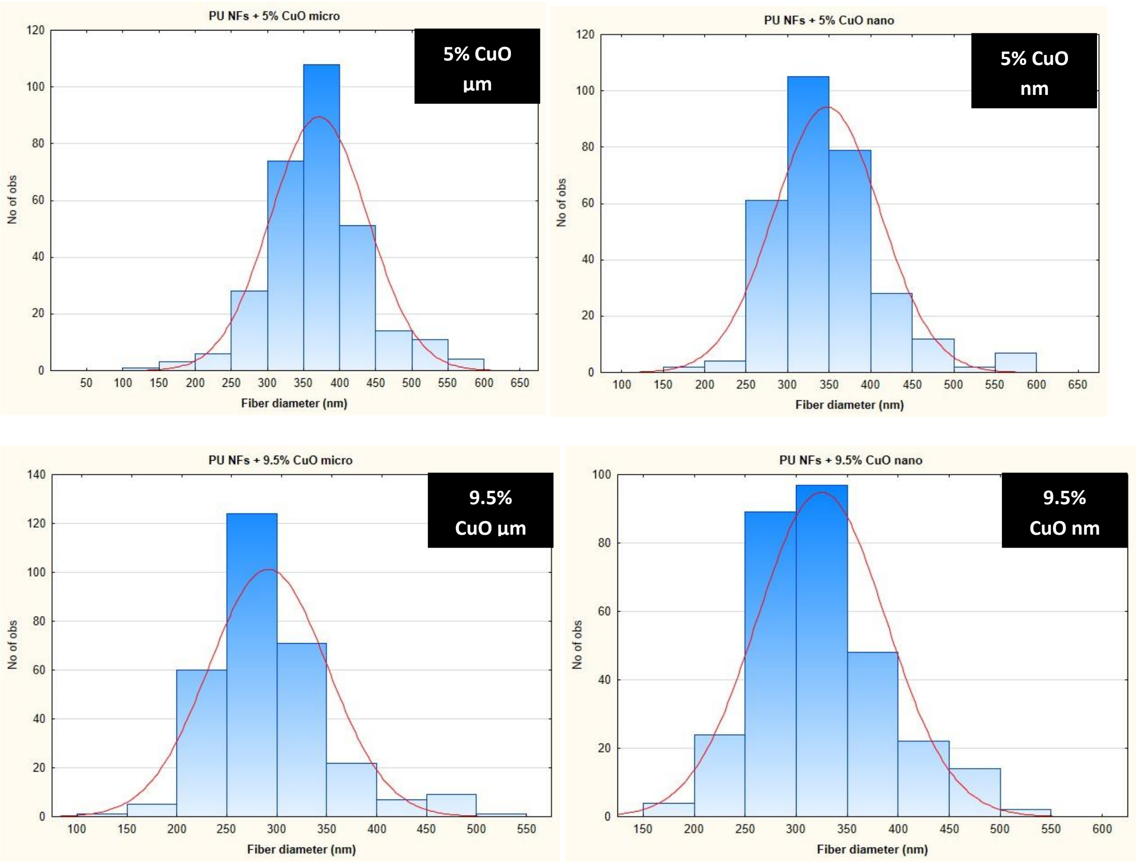


Figure 11. Diameters distribution: pristine PU nanofibers; PU + 5% CuO µm; PU + 5% CuO nm; PU + 9.5% CuO µm; PU + 9.5% CuO nm.

SEM-EDX analysis was provided for the confirmation of presence and for the determination of approximate percentage content of micro- and nanoparticles of CuO in the structure of nanofibers (Fig.12). Extra peaks responsible for Cu appeared for all produced samples except pristine PU nanofibers. There are the EDX areas of the samples with 5% of MPs and NPs of CuO in the Fig. 13 (the spectrums for other samples are in the Fig. 2, the Appendix).

As it's shown in the Fig. 12 the detected percentage ratio of microparticles of CuO at the fiber surface is much less than the amount of particles which was introduced into the solution before electrospinning.

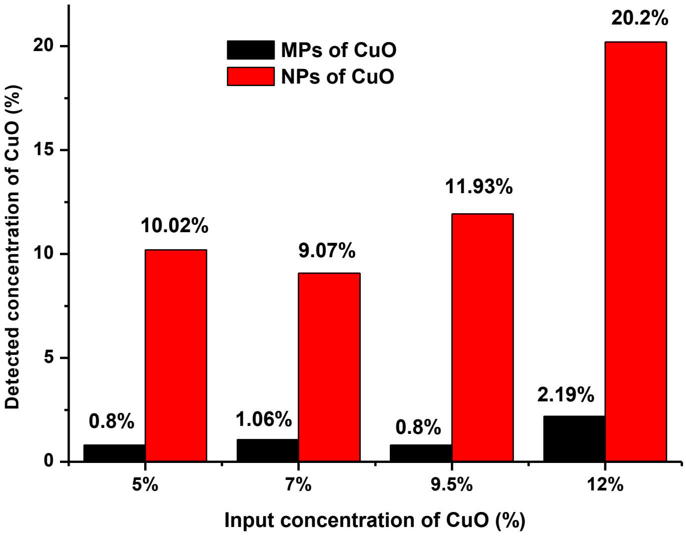
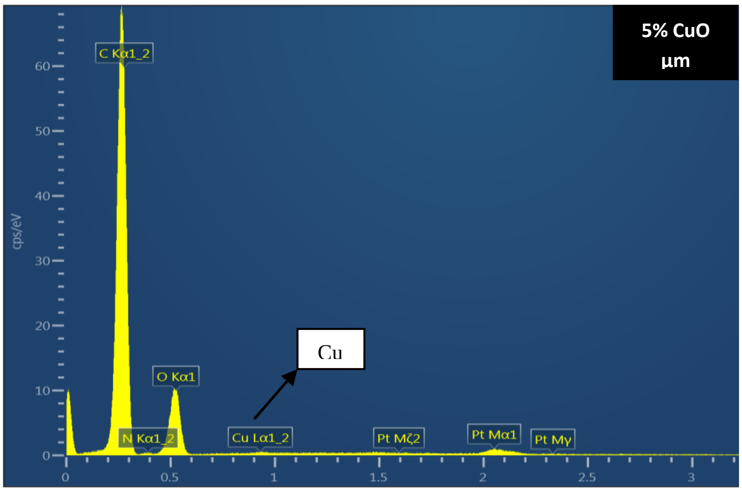


Figure 12. Difference between introduced (input) and detected concentrations of micro- and nanoparticles of CuO.

The detected amount of nanoparticles in the PU fibrous structure exceeded the concentrations which were incorporated for the modification of solutions. Particularly large discrepancy between used and measured concentrations is for the samples with 5 and 12% of CuO NPs. Such difference may indicate uneven distribution of nanoparticles in the fibrous structure. This can affect the antibacterial activity of the samples.



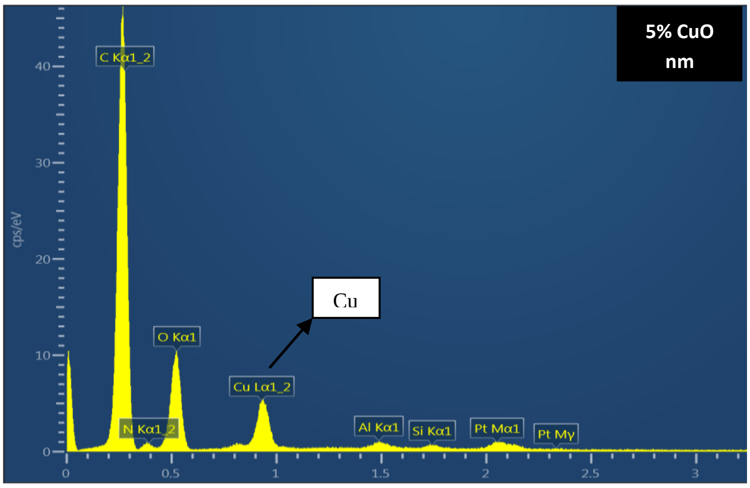


Figure 13. SEM-EDX images: areas of electrospun polyurethane nanofibers with 5% of micro- and nanoparticles of CuO.

Based on the results of EDX analysis it can be concluded that MPs of CuO aren't suitable for the chosen modification method for the PU fibers production from the rod spinner. But it is worth mentioning that the final conclusion can be done only based on the results of the antibacterial tests.

4.1.1.3. Antibacterial properties of composite NFs produced by rod ES

The results of antibacterial tests are the most representative from the standpoint of evaluation of the presence of CuO which is available for the contact with bacteria in the structure of fibers. Also, these results are important in order to draw the conclusions about perspectives of the using of produced composite materials as antibacterial filters. The values of antibacterial efficiency of all samples against two bacterial strains are in the Tab 7. Samples modified by NPs have demonstrated higher antimicrobial activity against both strains than their micro-sized "competitors". But the difference in efficiency is much less noticeable than the difference in percentages of CuO in the fibrous structures with micro- and nanoparticles detected by EDX analysis (Fig. 12). So what do we have? As we know from literature nanoparticles possess higher antibacterial activity (in comparison with MPs) and the detected amount of NPs into the structure of our samples is also considerably higher. But the difference between antibacterial efficiency of samples with MPs and NPs isn't so significant. We think that the explanation is that a large part of the active surface of nanoparticles is "hidden" from the contact with bacteria inside of the micro-sized aggregates formed into the structure of samples with NPs.

Based on the results of antibacterial tests it can be concluded that the concentration 7% of microparticles of CuO is optimal for the modification of PU solution for the rod ES. The sample with 5% of CuO MPs showed low efficiency (especially against St.Gal.). Then the decrease of antibacterial activity is observed for samples with higher concentrations of microparticles (9.5 and 12%) in comparison with the sample PU + 7% CuO MPs. It occurs because the high concentrations of microparticles create difficulties in the simultaneous formation of polymer jet together with micro-scale modifier. The similar tendency wasn't found out for samples with NPs of copper oxide. The concentration range 7 - 12% of nanoscale modifier is appropriate for the modification of PU solution for the production of NFs from the rod ES set-up from the standpoint of antibacterial properties.

Sample (rod ES)	Efficiency (%) - **Escherichia coli**		Efficiency (%) - **Staphylococcus gallinarum**	
	µm	**nm**	**µm**	**nm**
PU+ 5% CuO	64	80	29	64
PU + 7% CuO	96	81	94	96
PU + 9.5% CuO	83	97	66	90
PU + 12% CuO	81	99	88	100

Table 7. Antibacterial efficiency of samples prepared by the rod ES against two bacterial strains (contact time between bacterial solutions and modified samples 24 hours).

The photo documentation of the results of antibacterial tests of composite NFs produced by the rod ES is given in the Fig. 14 - 15 and in the Appendix 1 (Fig.3).

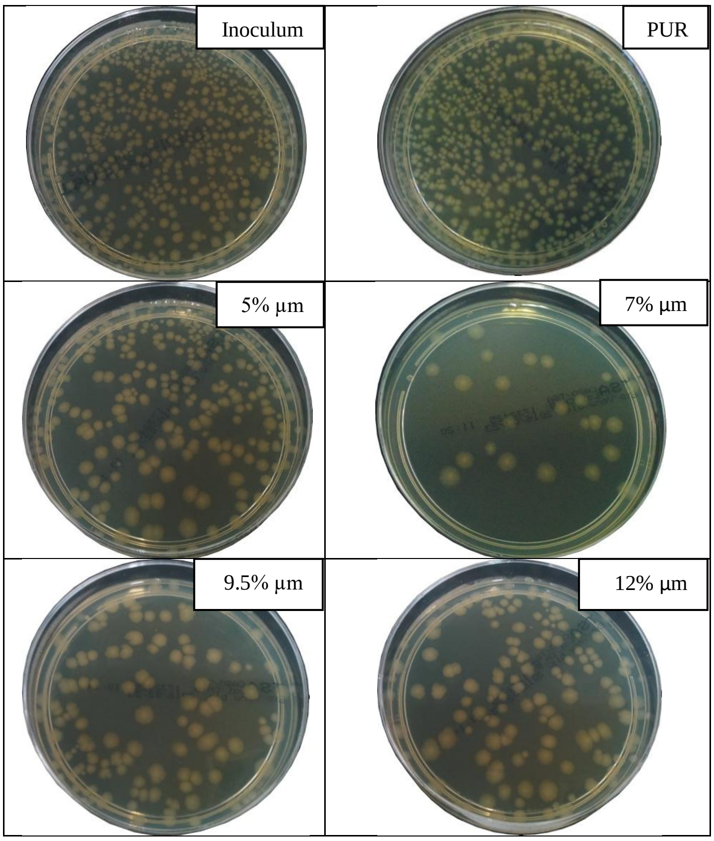
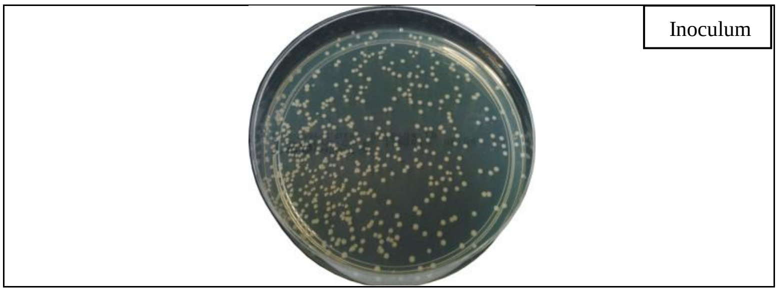


Figure 14. Images of agar plates showing the results of antibacterial test against **E.coli for samples with MPs of CuO - rod ES** (contact time between bacterial solutions and modified samples 24 hours).



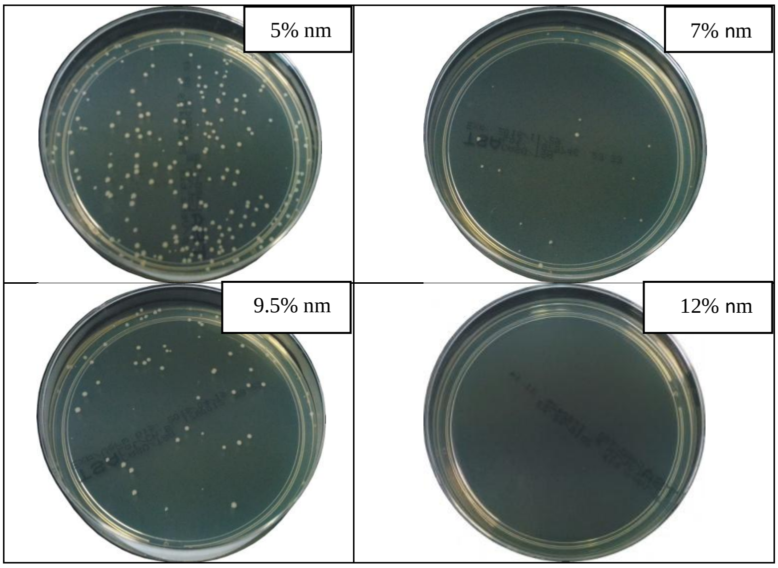


Figure 15. Images of agar plates showing the results of antibacterial test against **Staphylococcus gallinarum for samples with NPs of CuO - rod ES** (contact time between bacterial solutions and modified samples 24 hours).

The nanoparticles of CuO are better antibacterial agent for the modification of PU solution in case of using the rod ES for the production of composite nanofibrous layers. But rod ES set-up isn't appropriate for the production of materials for filtration purposes. This technique was used with the aim to check the spinnability of modified solutions and make a initial insight about possibility to use particles of CuO for the antibacterial modification of PU NFs.

4.1.1.4. Influence of ultrasonication treatment on aggregation of CuO NPs in the structure of PU NFs

As it was confirmed in previous sub-sections the NPs of CuO had formed quite big aggregates in the structure of nanofibers produced by rod ES. We decided to try the US for treatment of 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) and treated by US with pulsation at the amplitude 20%. Duration of ultrasonication was varied. We started from the duration 15s and gradually increased it to 120s (15; 30; 60 and 120s). The most interesting results were obtained for nanofibrous layers with 7% of CuO NPs.

In the Fig. 16 we observe the dependence of average diameters of the samples with 7% of CuO NPs on the durations of US treatment of solutions before ES. It's curious that the average diameters were increased under the duration of US treatment in the range 15 - 60 s in comparison with layer without ultrasonication (Fig.15, 0 s). The diameter of sample with 7% of NPs is decreased when the US duration reaches 120 s. But exactly the same relationship was found out for the viscosities of modified solutions after application of ultrasonication. In other words the viscosity of solutions has been increased under the duration of US exposure in the range 15 - 60 s at the amplitude 20%. When the duration of US treatment had reached 120 s, the viscosity of modified solutions decreased in comparison with untreated modified solutions (without application of US). Viscous behavior of PU solutions after ultrasonication explains the change of diameters of produced nanofibers. It remains to explain the increase of viscosity of solutions in the range of US exposure 15 - 60 s. We think that the phenomenon of formation of cavitation bubbles can cause the observed viscous effect. Ultrasonic waves create small vacuum bubbles or voids in the liquid. When the bubbles attain a volume at which they can no longer absorb energy, they collapse violently. This phenomenon is termed cavitation. The critical size of bubbles before collapsing is known as its resonance size. The resonance size of the bubble depends on the applied frequency of ultrasound field.

According to our assumptions the viscosity of modified solutions was increased after using of US at the amplitude 20% for 15; 30 and 60 s compared to untreated solution because such durations and this frequency of the ultrasonic treatment are not sufficient to collapse the formed cavitation bubbles. In other words, the viscosity was increased due to the presence of uncollapsed cavitation bubbles. And this assumption is confirmed by the fact that viscosity of the treated solutions is decreased when the duration of ultrasonication is enhanced to 120s.

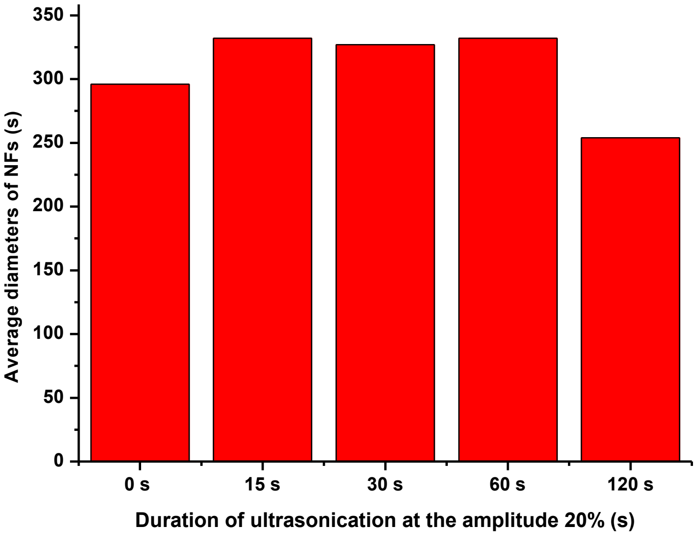


Figure 16. Dependence of average diameters of PU NFs with 7% of CuO NPs on the duration (0; 15; 30; 60 and 120s respectively) of ultrasonication (amplitude 20%) of solutions prior ES.

The equivalent diameters of formed aggregates of CuO NPs in the nanofibrous structure before and after US treatment were measured from the SEM photos using Lucie 32G computer software in order to prove (or to refute) the positive influence of US on the particle's aggregation. The results of this measurement for the sample with 7% of NPs are presented in the Fig. 16. Short durations of US treatment have contributed to the increase of sizes of particle's aggregates. But the increase of the duration of ultrasonication to 120 s hasn't led to the reduction of aggregate's sizes in comparison with the modified NFs without US treatment (Tab.8).

Therefore it was decided to increase the amplitude of US to 40%. At the beginning this frequency of ultrasound waves was used for the treatment of modified solutions for 30s. Such approach was found as appropriate for the samples with low concentrations of CuO NPs (2.5 and 5%). As it's presented in the Tab.8 the equivalent diameters of particle's aggregates of layers with 2.5 and 5% of CuO are decreased in comparison with corresponding NFs without US pre-treatment of the solutions prior ES. Unfortunately with the increase of particles concentration up to 7% the applied frequency (40%) and duration (30 s) of US treatment are no longer sufficient to prevent the aggregation of CuO NPs. The measured equivalent diameters of aggregates for the sample with 7% of NPs are almost identical without and after ultrasonication.

The duration of US treatment under the amplitude 40% was prolonged to 60 s for the sample with 7% of CuO NPs. Due to the SEM analysis it was determined that such parameters of ultrasonication have negative influence on the structure of composite nanofibers. The Fig. 17 demonstrates that there are a lot of defects (large beads and very thick fibers) in the structure of produced layer with 7% of CuO NPs after using of US at the amplitude 40% for 60s. Such combination of frequency and duration of US pre-treatment of modified solutions isn't appropriate in terms of negative influence on the structure and dimensional characteristic of PU nanofibers with NPs of CuO. Shorter duration or lower frequency of the ultrasonication are also not proved to be efficient in combating with the formation of aggregates of NPs into the fibrous structure with 7% of CuO.

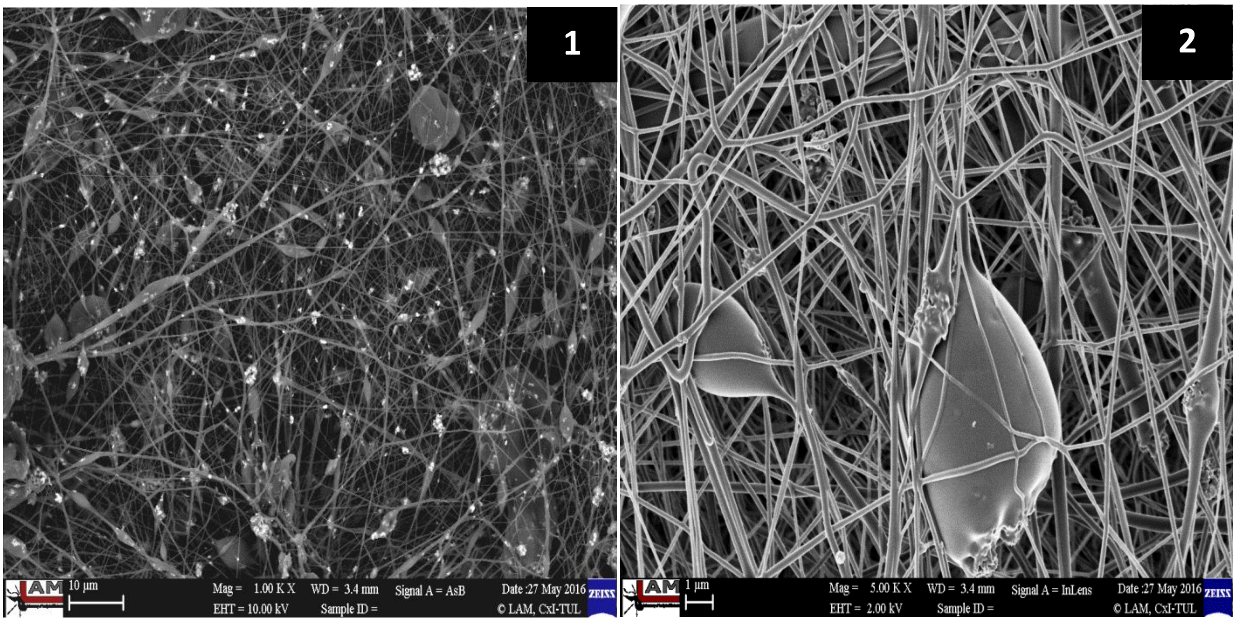


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Figure 17. SEM images of PU nanofibers with 7% of CuO NPs produced from the solution treated by the US at the amplitude 40% for 60 s (1 - magnification ×1000; 2 - magnification ×5000).

The standard deviations in the Tab.8 show that the spread of values of equivalent diameters is wide. Sizes of aggregates of NPs can reach 1µm. The use of nanoparticles can be efficient only in case if their uniform distribution in the structure of modified materials will be achieved. At this stage the micro-sized aggregates of NPs were obtained instead of homogeneously distributed nanoparticles.

Sample	Average equivalent diameters of aggregates (nm)	Standard deviation
PU + 2.5% CuO nm, without US	704	327.71
PU + 2.5% CuO nm, US 20%, 15 s	636	305.44
PU + 2.5% CuO, nm US 20%, 30 s	768	323.75
PU + 2.5% CuO, nm US 20%, 60 s	615	270.96
PU + 2.5% CuO, nm US 20%, 120 s	491	204.3
PU + 2.5% CuO, nm US 40%, 30 s	646	269.43
PU + 5% CuO nm, without US	753	266.29
PU + 5% CuO nm, US 20%, 15 s	641	247.22
PU + 5% CuO nm, US 20%, 30 s	787	319.86
PU + 5% CuO nm, US 20%, 60 s	729	286.43
PU + 5% CuO nm, US 20%, 120 s	579	219.16

PU + 5% CuO nm, US 40%, 30 s	505	198.47
PU + 7% CuO nm, without US	974	227.87
PU + 7% CuO nm, US 20%, 15 s	1058	321.54
PU + 7% CuO nm, US 20%, 30 s	1087	379.4
PU + 7% CuO nm, US 20%, 60 s	1062	300.6
PU + 7% CuO nm, US 20%, 120 s	977	263.44
PU + 7% CuO nm, US 40%, 30 s	979	244.54

Table 8. Average diameters of agglomerates of CuO NPs in the structure of PU NFs without and after US treatment.

The use of US treatment (40% amplitude for 30s) for 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. It's necessary to increase the frequency or duration of ultrasonic exposure in order to discourage the formation of aggregates in solutions with higher concentrations of nanoparticles. The attempts to increase the duration of the ultrasonic treatment have 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 (next step of presented research).

At this stage of our experiments it has been determined that the introduction of modifiers contributes to the increase of viscosity of PU solutions. Such result was expected. However such a big difference (as it shown in the Fig. 8) of viscosities of solutions with micro- and nanoparticles was unexpected. The possibility to produce nanofibers of the desired structure and dimensional characteristics from such viscous colloidal systems was in doubt. But then we experimentally confirmed that all modified solutions with MPs and NPs (concentration range 5 - 12%wt) were suitable for the fiberforming by rod ES set-up.

The using of antibacterial additives hasn't significantly influenced the morphology and size characteristics of obtained NFs. But it was found out that nanoparticles of CuO had formed large aggregates in the fibrous structure. The formation of big agglomerates can lead to the deterioration of the unique functional properties of nanoparticles. At this stage, this apprehension is partially confirmed by the results of antibacterial tests. Antibacterial activity of NFs with the nano-scale CuO don't significantly exceed the corresponding values for samples with microparticles. It can be explained by the fact that a big part of active surface of NPs is hidden inside of agglomerates (and maybe inside of the fibers). Another risk of agglomerate's formation is a possible release of NPs from the upper layers of aggregates (since there is no chemical interaction) and entering into the environment in result of practical application of nano-modified samples as air or water filters. This hypothesis will be considered in the next sub-chapter together with experimental data. Moreover the formation of big amounts of aggregates of NPs may indicate uneven distribution of this antibacterial agent into the structure of fibers. The proof of such assumption is the results of EDS analysis. It was discovered that the measured concentrations of CuO nanoparticles have exceeded the real concentrations used for modification of PU solutions.

Two important tendencies were determined for samples with MPs of CuO. First of them is negative. Detected concentrations of microparticles into the structure of NFs are lower than the real amount of the micro-sized modifier introduced into the PU solution. Consequently MPs due to their initial large sizes don't sufficiently participate in the rod ES process together with polymer solution. Here it should be said about the second noticed tendency which is positive.

Antimicrobial efficiency of the samples with microparticles is relatively high in spite of the low content of the micro-sized additive into the fibrous structure. This suggests that a large part of particles is available (opened) for the contact with bacteria.

In this step the obtained results are quite contradictory. We found out two important problems: NPs form large aggregates (1) and MPs precipitate and don't participate actively in ES process (2). But both problems can be solved in one way. This way is to ensure the stirring of modified solutions during the electrospinning process in order to prevent aggregation and precipitation of antibacterial additives. Moreover we need to use a technique which allows the production of modified filters in the industrial range. So we will focus on Nanospider technique and on the using of rotating electrode with needle surface. This electrode may simplify the work with our colloidal systems, solve the problem with NPs aggregation and prevent the precipitation of MPs. Possibly then MPs will more efficiently participate in formation of the fibrous structure together with PU solution.

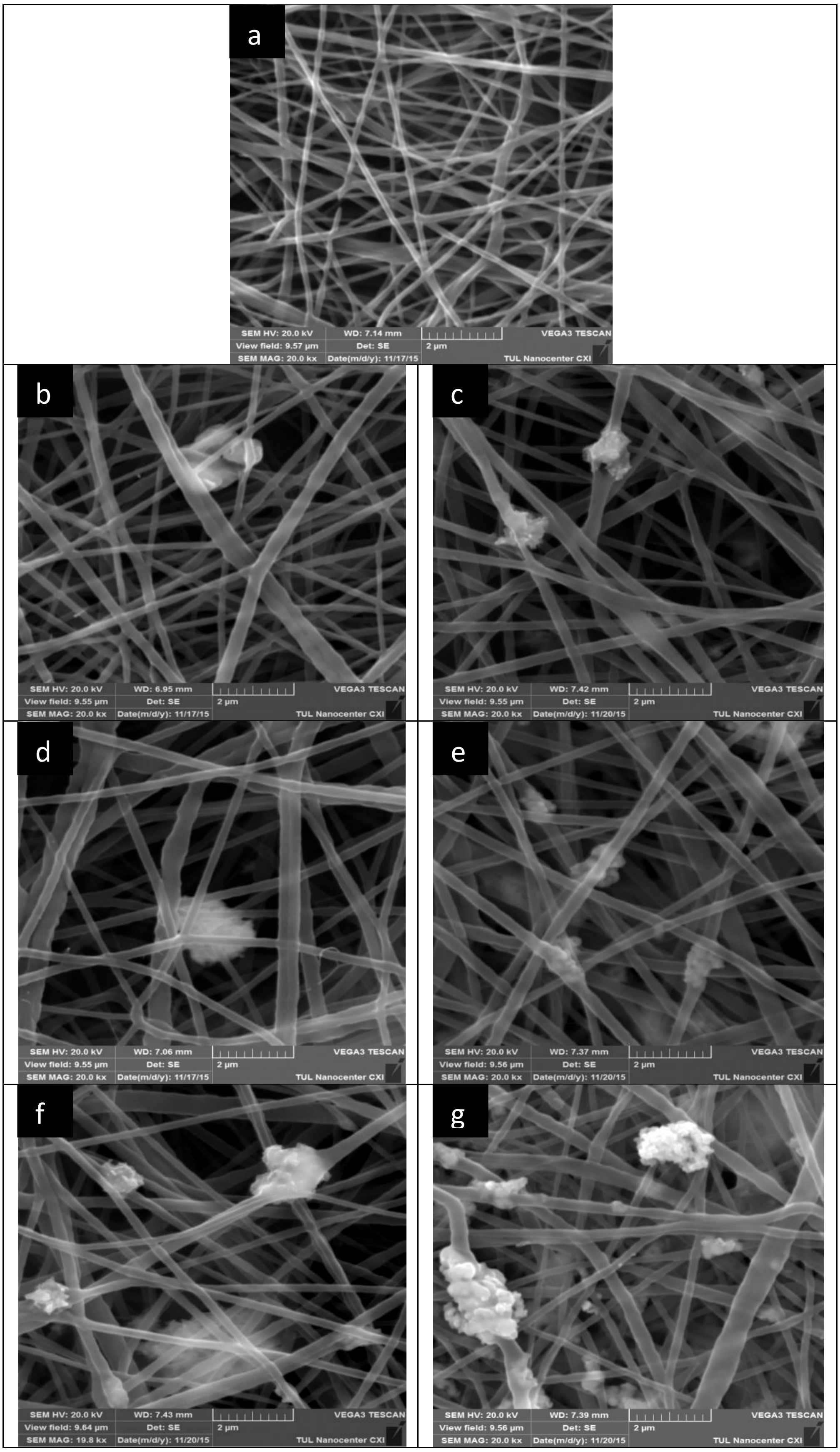
So in the next sub-chapter we will discuss the production of PU NFs with micro- and nanoparticles of CuO by the Nanospider technique using the rotating electrode with needle surface, properties of prepared materials and the rationality of their application as antibacterial filters for air and water purification.

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

The planned application of our composite NFs is antibacterial purification of air and water. The possibility to produce filtration materials in the industrial scale is very important. In fact it has no sense to talk about real practical application of those or other materials if the possibility of their production in the required quantity by affordable and implemented technology hasn't been proved. Therefore we have produced composite polyurethane nanofibers by industrial Nanospider technique using specific spinning electrode which can be appropriate for the ES of colloidal solutions. The electrode with needle surface was selected to prevent aggregation of NPs and precipitation of microparticles at the bottom of bath with the solution during ES process. Micro- and nanoparticles of CuO were added to PU for the obtaining of modified solutions with different concentrations of antibacterial agents (5%; 7%; 9.5%; 12 wt%). Then the composite layers were produced.

4.1.2.1. Structure of produced nanofibers

The SEM analysis is enabled to find out the internal morphology of produced mats. There are images of nanofibers in the Fig. 18. Particular attention should be paid to the photos of fibers with the content of nano-sized form of copper oxide (Fig. 18: c, e, g, i). It is visible that nanoparticles form quite big aggregates. The results for samples with nanoparticles from previous sub-chapter 4.1.1 indicate the same tendency. The unique functional properties of nanoparticles (including antibacterial) are provided by their small sizes (due the extensive surface area). Therefore the formation of aggregates can be an obstacle to the manifestation of antibacterial properties of nanoparticles in full. And experimental results for PU NFs with CuO nanoparticles produced from the rod ES set-up have confirmed this assumption. In addition there are doubts about the stability of such aggregates under further filtration application of samples.



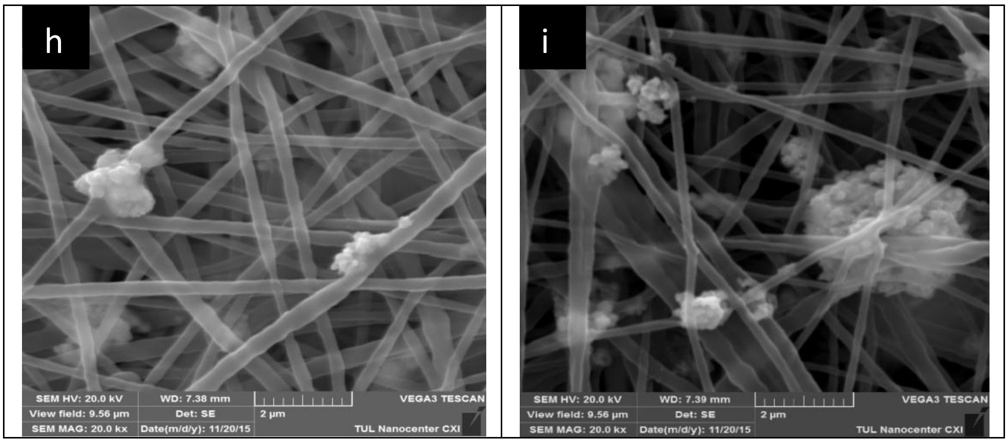


Figure 18. SEM images (magnification 20000) of nanofibers with different concentrations of micro- and nanoparticles of CuO (Nanospider, electrode with needle surface): a - 0%; b - 5% μm; c - 5% nm; d - 7% μm; e - 7% nm; f - 9.5% μm; g - 9.5% nm; h - 12% μm; i - 12% nm**.**

Two samples with nanoparticles (7 and 12%) were analyzed by QUANTA 650FEG scanning electron microscope by our colleagues from the team of Environmental electron microscopy from the Institute of scientific instruments of the Czech Academy of Science. There is an image of sample PU + 7%CuO nm (1 - magnification ×30000; 2 - magnification ×60000) obtained by QUANTA 650FEG SEM in the Fig. 19. It is clearly seen that the nanoparticles form a giant aggregate. It indicates the uneven distribution of nanoparticles in the fibers structure, what can lead to large losses of potential antibacterial "points" for the efficient contact with the bacteria. Another risk is that the nanoparticles can be separated from the big aggregate by the stream of water or air during filtration and get to the environment. In the Figure 19 (2) we have an example when NPs aggregate is protected by the nanofibrous web. But in the Fig. 20 we observe an opposite situation. There are the 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.

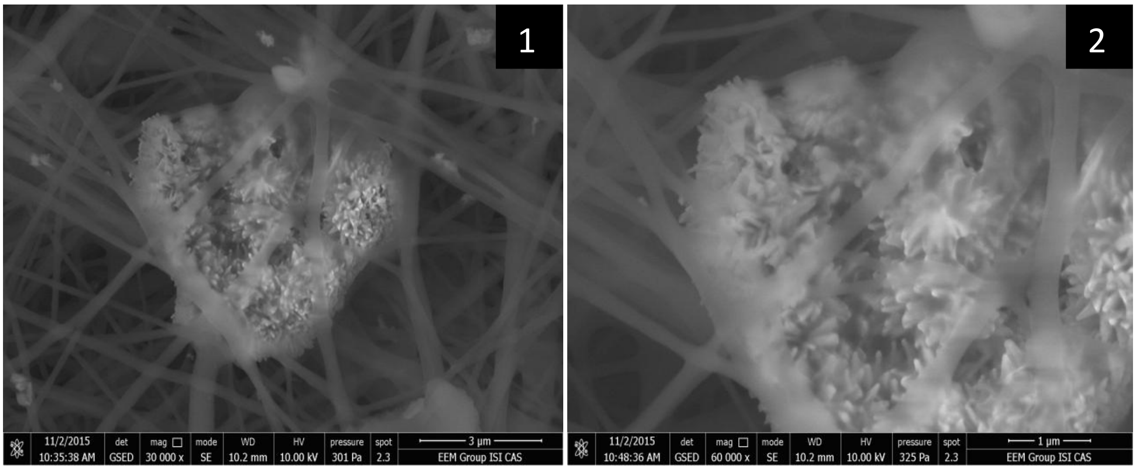


Figure 19.SEM images of PU nanofibers with 7% of CuO NPs (produced from the rotating electrode with needle surface): 1 - magnification ×30000; 2 - magnification ×60000).

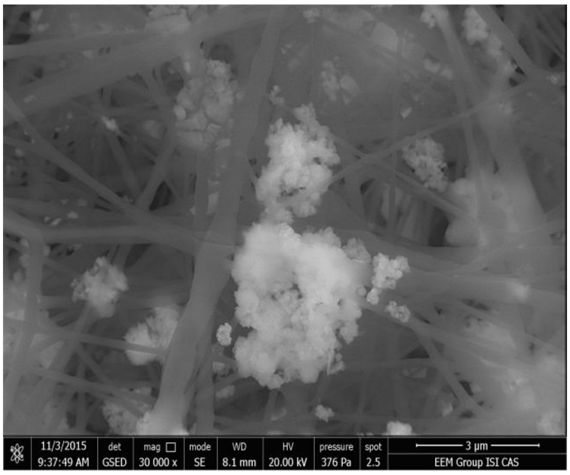


Figure 20. SEM image of PU nanofibers with 12% of CuO NPs produced from the rotating electrode with needle surface (magnification ×30000).

Produced nanofibrous layers have exhibited the smooth surface with diameters distribution in the range 75-650 nm. We observed a visible brown color and it became more intensive with the increase of CuO concentration. Average fiber diameters were calculated for each sample. The using of copper oxide led to the insignificant increase of average diameter of polyurethane nanofibers (Tab. 9). As we remember the incorporation of particles promotes the increase of viscosity of PU solution, so the growth of average diameters of modified samples is expected. The most tangible impact on the increase of the diameters of PU nanofibers was observed for the layer with 7% of CuO. It concerns both micro- and nanoscale additives. But the average diameters of samples with 9.5 and 12% wt of additives decreased. Perhaps the conductivity of CuO plays a greater role in electrospinning of solutions with higher concentrations (9.5 and 12%wt) of selected modifiers. It contributes to a thinning of the fibers and improves the electrospinning performance (it will be discussed later). As it is shown in the Tab. 9 the values of fiber uniformity coefficients didn't increase for modified nanofibers in comparison with pristine PU layer. It indicates the uniform distribution of diameters for all samples regardless of the dimensional characteristics of the modifier.

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 9. Results of measurement of fibers diameters and calculation of uniformity coefficients (experiments with the rotating electrode with needle surface).

The influence of modifiers on uniformity of diameter's distribution of PU nanofibers is clearly shown in the Fig. 20. The largest amount of fibers of the pristine sample lays in the diameter range 100-250 nm (Fig. 21, 1).

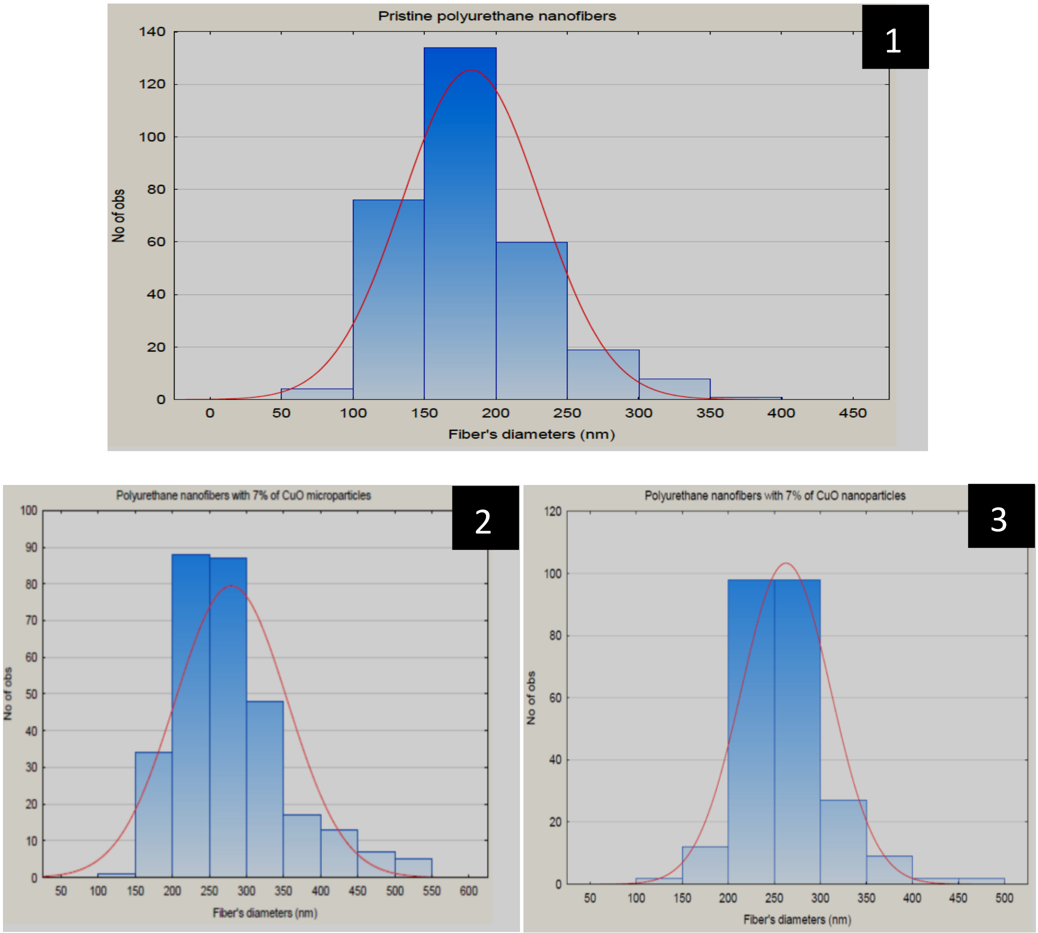


Figure 21. Diameter's distribution of samples produced from electrode with needle surface: 1 - pristine PU nanofibers; 2 - PU + 7% CuO µm; 3 - PU + 7% CuO nm.

The largest number of fibers with NPs lays in the diameter range 200-350 nm (Fig. 21, 3). The situation is slightly changed in case of samples with microparticles and main diameter's range is expanded to 150-350 nm (Fig. 21, 2). 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.

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 (Fig.22 and Appendix 1, Fig. 4).

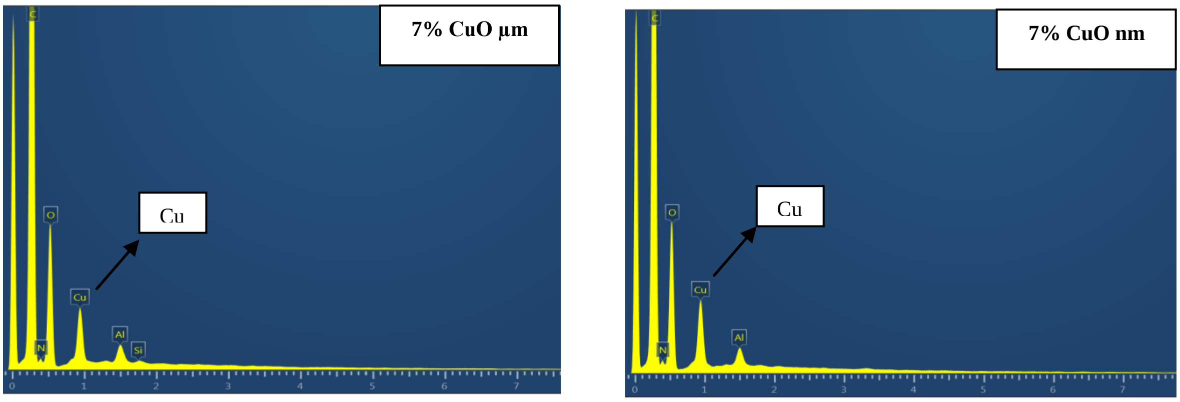


Figure 22. SEM-EDX images: areas of electrospun polyurethane nanofibers with 7% of micro- and nanoparticles of CuO (experiments with rotating electrode with needle surface).

The detected amounts of CuO microparticles correspond with the introduced concentrations (Fig.23). A significant difference was observed for the sample containing 12% of CuO µm. The measured concentration of microparticles was higher (13.28%) than the concentration actually used (12%). It was found out 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.

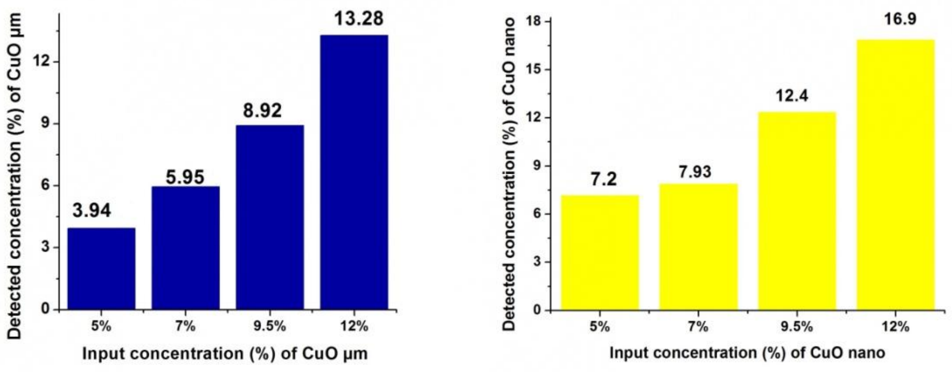


Figure 23. Difference between concentrations of micro- and nanoparticles of CuO in the polymer solutions and in the nanofibrous structures of samples produced from electrode with needle surface.

On the one hand the pursuit of nanosized modifier to aggregation is logically enough from the point of view of their high surface energy. But on the other hand this pursuit may negatively influence their antibacterial properties.

The surface density of prepared nanofibrous layers was calculated to compare the spinning performance depending on the concentration and size characteristics of copper oxide (Tab. 10). The obtained data showed that micro- and nanoparticles contributed to an increase in the surface density of all of the modified nanofibers in comparison with the pristine PU mat. We can observe (Tab. 10) that the lowest of the selected concentrations (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. The positive impact of nano CuO persists to a concentration of 7%. The surface density index of the sample with 12% of CuO NPs decreased and become approximately equal to the respective index of the nanofibrous layer with 5% of nanoscale modifier. Higher concentrations of nanoparticles (9.5 and 12%) lead to the formation of larger amounts and/or sizes of aggregates. This may lead to the deterioration of the properties of the nanoparticles, including their electrical conductivity. Nevertheless, the key conclusion is that micro- and nanoparticles of copper oxide are not merely additives used to impart antibacterial properties but they also contribute to a significant increase in the electrospinning performance during the production of polyurethane nanofibers. Usually, even small concentrations of additives used to improve the productivity of the electrospinning process promote a substantial increase in the diameters of the fibres. However, this was not observed in the case of comparatively high concentrations (5 - 12%) of copper oxide. Therefore, the obtained results have an important practical meaning.

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

The filtration efficiency of all prepared samples was in the range 99-100%. This fact indicates the absence of influence of the selected modifier and the dimensional characteristics of CuO particles on the filtration properties of PU nanofibers.

4.1.2.2. Antibacterial properties of composite nanofibers produced from cylindrical rotary electrode with needle surface

The values of antimicrobial efficiency for all of the modified fibres after 24-hour's contact between the bacterial solutions and tested samples are included in Tab. 11. It is possible to observe that the antibacterial activity increased with an increase in CuO concentrations for both sizes of particles. There is no particular difference between the antibacterial properties of the samples with micro- and nanoparticles against the E.coli strain. We can conclude that all of the produced composite layers with a content of CuO particles in the concentration range from 7 to 12% demonstrated excellent activity against the gram-negative 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 (Tab.11).

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 11. Antibacterial efficiency of samples prepared from electrode with needle surface against two bacterial strains (contact time between bacterial solutions and modified samples 24 hours).

The change of antibacterial efficiency over time (from the minimum contact time between the sample and the bacteria (1 min) to the maximum contact time (24 hours)), is graphically represented in Fig. 24. First of all, we can conclude that pristine PU nanofibers did not exhibit activity after a prolonged contact time. This means that the selected polymeric material without proper modification is inert to bacteria. The second important conclusion is that the nanoparticles started to exhibit their antibacterial efficiency faster (after a 1-hour contact time, Fig.24) than microparticles (after 4 hours, Fig. 24). However, in terms of filtration application there is no fundamental difference if the captured bacteria start to perish within 1 or 4 hours after being captured on the filter. But it is important for the antimicrobial properties of the modified layers with both particles sizes to be almost identical after 24-hour contact between the bacteria and the samples (Tab.11, Fig.24 and 25).

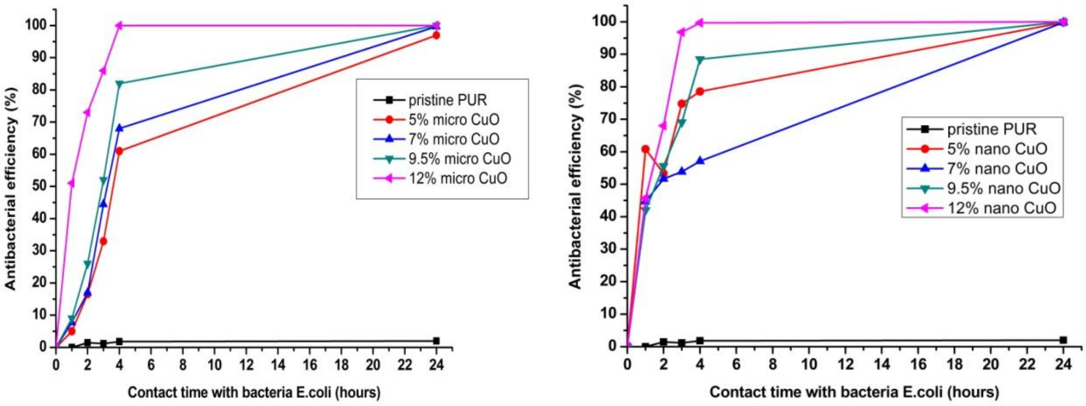


Figure 24. Change of antibacterial efficiency against **E. coli** over time for samples with microparticles and nanoparticles of CuO produced from the rotating electrode with needle surface.

Fig. 25 provides confirmation of the results of the antibacterial test with St. Gal. for samples with 5 and 12% of MPs and NPs of CuO, respectively (contact time 24 hours). The number of grown bacterial colonies for the inoculum (reference test without the sample) and for non-modified fibres is similar. The concentration of 5% of CuO NPs is not sufficient to impart the PU nanofibers with good antibacterial properties against St. Gal. The results with E.coli are presented in Appendix, Fig. 5.

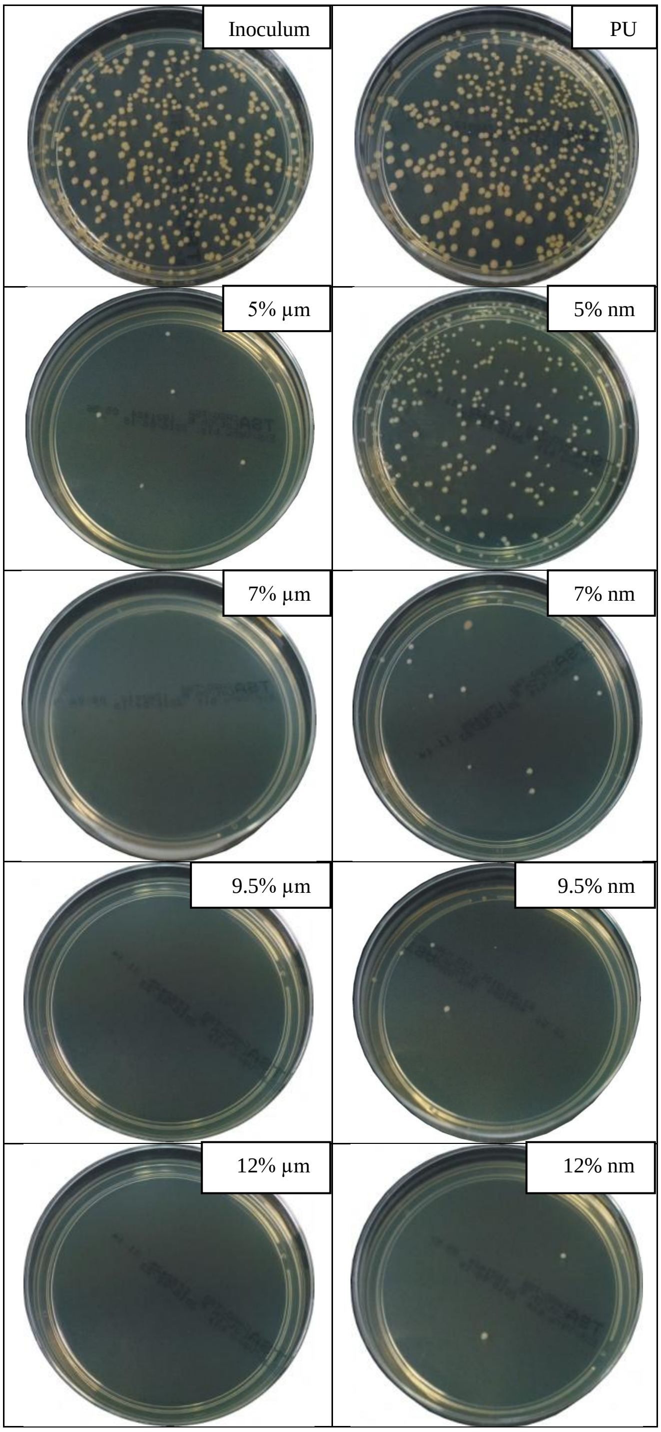


Figure 25. Images of agar plates showing the results of antibacterial test against **Staphylococcus gallinarum** (contact time 24 hours).

The results of viscous measurements and SEM and EDX analysis show that NPs form large aggregates in the polymer solution and in the structure of the fibres. This leads to a loss of the unique properties caused by the nanoscale characteristics of the particles. This statement was confirmed by the results of the antibacterial tests, where the significant advantages of the nanoparticles were not observed.

4.1.2.3. Stability of antibacterial properties of modified nanofibers

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. EDX analysis was repeated to compare the amount of copper on the surface of the fibers before and after the water treatment test.

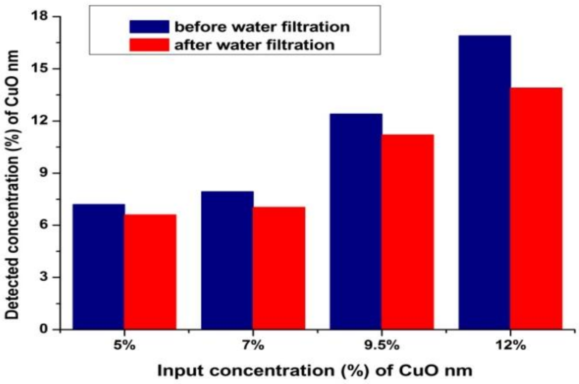


Figure 26. Content of nanoparticles of CuO in the nanofibrous structure before and after treatment under the simulated conditions of water filtration according to the results of EDX analysis (experiments with the electrode with needle surface).

No difference was found between the results of the EDX analysis of composite samples with microparticles before and after the water filtration test. As we can see in the Fig. 26, some number of nanoparticles of copper oxide were poorly fixed into the structure of the produced layers; and as we previously established, the nanoparticles formed sufficiently large aggregates in the fibrous structure. Some particles in the structure of these aggregates are not immobilized inside of the polymer matrix and may only be associated with the neighbouring NPs by physical interaction. This makes it possible to explain the observed tendency of the nano-sized additive to wash out. Nevertheless, the results of the EDX analysis from the standpoint of the percentage ratio of the detected compounds are only approximate. A more demonstrative criterion of particle fixation will be the results of repeated antibacterial tests of the samples, which were used for water filtration. For this purpose, after the test under simulated conditions of water filtration the nanofibers with micro- and nanoparticles were investigated using the Cornell test to determine their efficiency against E.coli and St. Gal.

The change of antibacterial efficiency was not detected in the case of nanofibers modified by microparticles. The results for samples with nanomodifier are slightly different. But as it is shown in Tab. 12 and Fig. 27 a decrease in antibacterial activity was determined for the nano-modified composite mats within the whole concentration range of the nanoparticles against both strains. A significant loss of activity was observed for one sample - PU with 5% of CuO nm - against St. Gal.

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 12. 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 change in the antibacterial properties after the water filtration test is the most important criterion for the selection of an appropriate material for water filtration application. Only filters with stable and long-term antibacterial activity can be considered as being suitable for this use, and PU nanofibers with CuO nanoparticles do not fulfil these requirements. The release of NPs into the environment is potentially dangerous and should be strongly controlled even on an experimental level. We've tried to pay maximum attention to this.

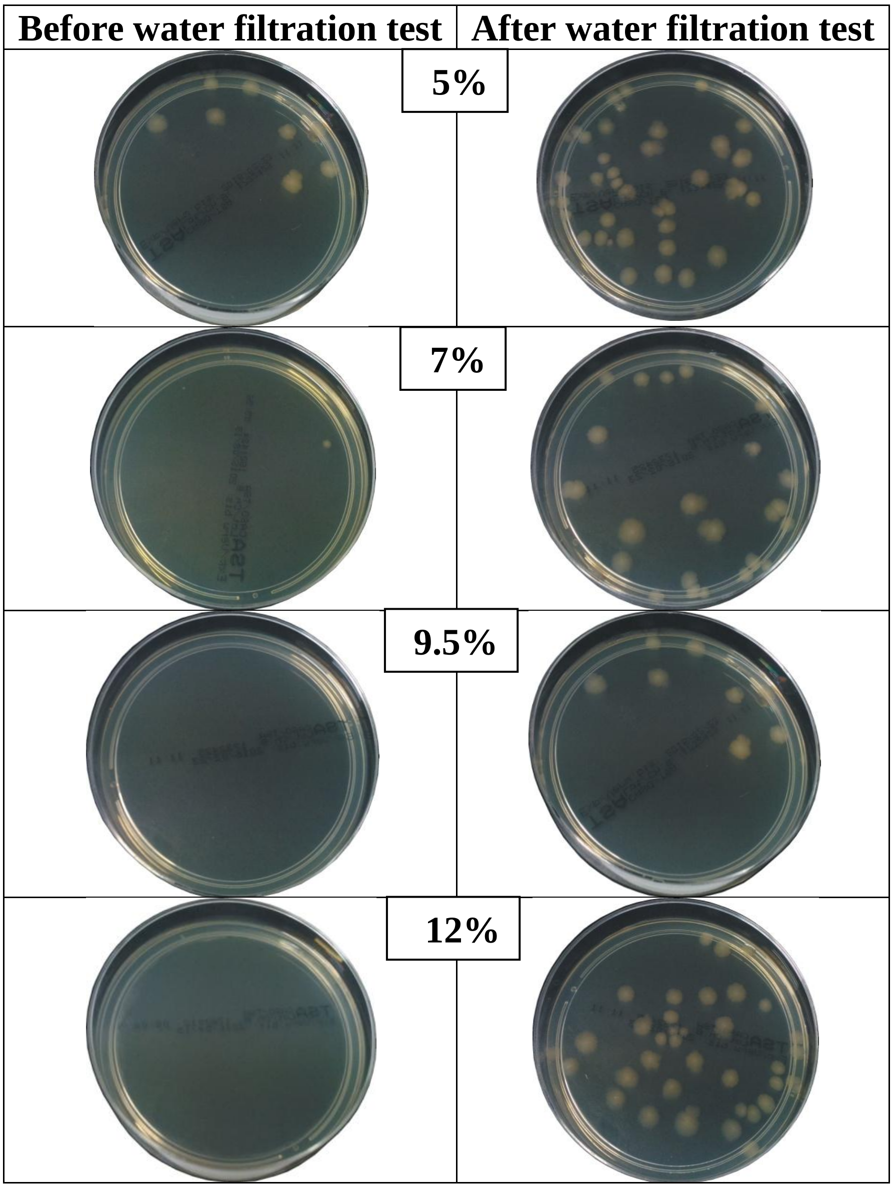


Figure 27. Pictures of agar plates showing the results of antibacterial test against **E.coli** for samples with **nanoparticles** of CuO before and after water filtration test.

However, the deterioration of the antibacterial properties of the samples modified by nanoparticles after the water filtration test leads us to state that a certain amount of nanomodifier is poorly fixed and washes out from the nanofibrous layers. Therefore it can be concluded that the microparticles of CuO are more appropriate additives for the selected modification method (introduction of particles into polymer solution with further electrospinning) of nanofibers.

4.1.2.4. Antibacterial filtration efficiency

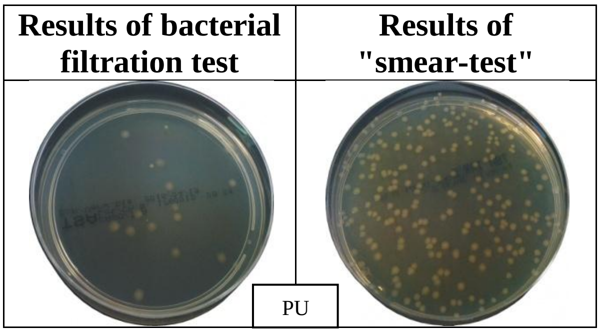
The results of the bacterial filtration test correspond to the values of the surface density for all of the prepared samples (Tab. 13). As it was mentioned before, the surface density of the nanofibres modified by MPs was higher in comparison with the layers containing NPs of CuO. The samples with 7, 9.5 and 12% of micro-sized CuO demonstrated the highest surface density values, and these samples showed a100% bacterial filtration efficiency.

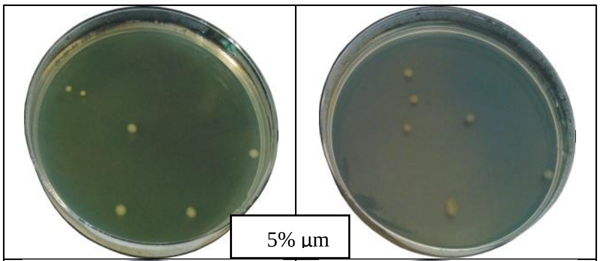
These results may lead us to the assumption that it is sufficient to use nanofibres with high a surface density for the bacterial filtration and it is not necessary to pay attention to the antibacterial modification of the nanolayers. However, this assumption is erroneous. The capture of bacteria on 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.

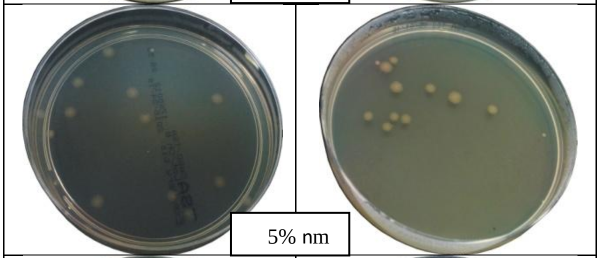
Sample	Number of bacteria passed through the sample	BFE (%)	Number of survived bacteria after "smear-test"
Inoculum	320	**-**	-
PU pristine	17	**95**	278
PU + 5% CuO μm	5	**98**	6
PU + 5% CuO nm	15	**95**	13
PU + 7% CuO μm	0	**100**	3
PU + 7% CuO nm	9	**97**	45
PU + 9.5% CuO μm	0	**100**	0
PU + 9.5%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

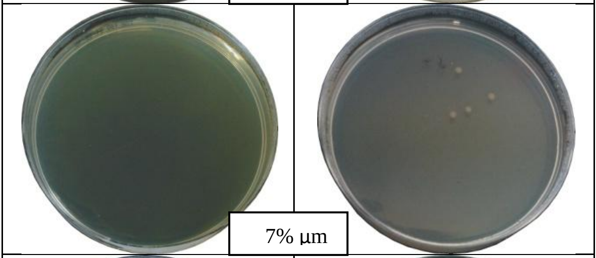
Table 13. Results of the bacterial filtration test and "smear-test" for samples produced from rotating electrode with needle surface.

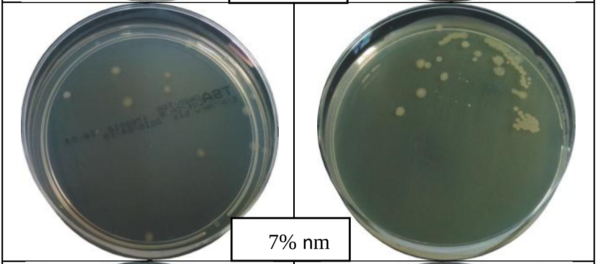
We can observe in Tab. 13 that the results of the “smear test” confirmed the antibacterial activity of all of the modified nanofibers in eliminating the captured bacteria after the bacterial filtration test. The samples with 9.5 and 12% of MPs demonstrated the most impressive results as the complete elimination of trapped bacteria was observed. Fig. 28 is provided to illustrate the difference in the behaviour of the pristine and modified (by 9.5 % of μm and nm CuO) PU layers after bacterial filtration and the “smear” tests.

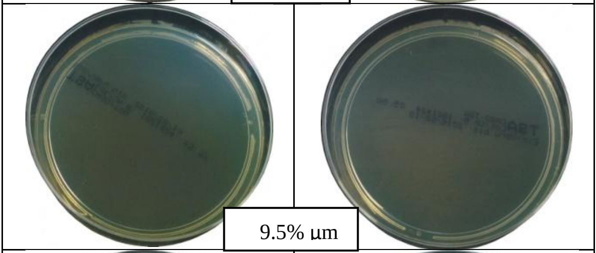


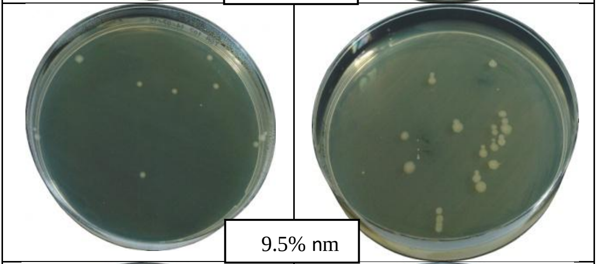

5% µm

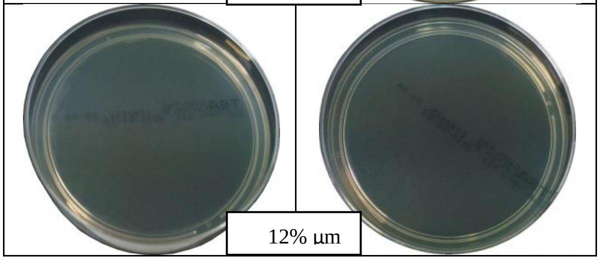

5% nm


7% µm


7% nm


9.5% µm


9.5% nm


12% µm

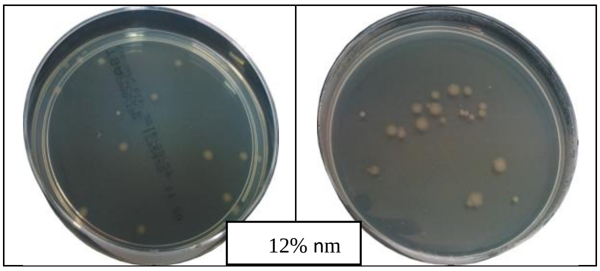


Figure 28. Images of agar plates after the bacterial filtration test and after the "smear-test" for all samples produced from rotating electrode with needle surface.

Nanofibers with a content of CuO microparticles have proven to be more efficient for bacterial air purification. The micro-modified nanofibrous layers are able to capture more bacterial units due to their higher surface density. Moreover the samples with MPs provide better elimination of captured bacteria than nano-modified fibers. This fact proves the homogeneous distribution of microparticles in the structure of our filters.

It was confirmed that composite PU NFs can be produced by the industrial technology Nanospider from modified solutions with the content of micro- and nanosized CuO. At this stage a special spinning electrode with needle surface was used in order to provide the stirring of colloidal solutions during the fiberforming process. According our ideas such approach could prevent the aggregation of NPs and precipitation of MPs of copper oxide.

However it was found out that the selected electrode didn't influenced (at least significantly) the aggregation of NPs. The SEM analysis demonstrated that nanoparticles formed large aggregates in the fibrous structure. The EDX test showed that the detected concentrations of nano-scale copper oxide exceeded the incorporated concentrations. It indicates uneven distribution of CuO NPs into the structure of NFs what is indirect confirmation of the formation of aggregates. In case with MPs, our goals to prevent the precipitation and provide an active participation of this additive in the fiberforming process due the continuous stirring have been reached. The results of EDX analysis of the samples with microparticles produced from the rod ES set-up demonstrated that only a small amount of CuO took part in the ES process. But EDX measurement of the micro-modified samples produced from the electrode with needle surface (Nanospider technique) has proven that the detected concentrations of MPs correspond with the used concentrations.

The using of CuO has a positive effect on the production performance of ES process. The measurement of surface density showed that MPs of CuO contributed to the significant increase of this index (in 4-8 times depending on the concentration). This positive tendency was also observed for the samples with nanoparticles but to a lesser extent. It's important that the increase of productivity isn't accompanied by the perceptible increase of dimensional characteristics of the produced nanofibers (average diameters, uniformity coefficient). It allows to make a conclusion that MPs of CuO can be used not only as antibacterial modifier but also as an additive for the improvement of spinnability of PU solution. As we remember the conductivity of PU solution isn't changed under the influence of CuO. It means that the modifiers don't come into chemical interaction with components of PU solution.

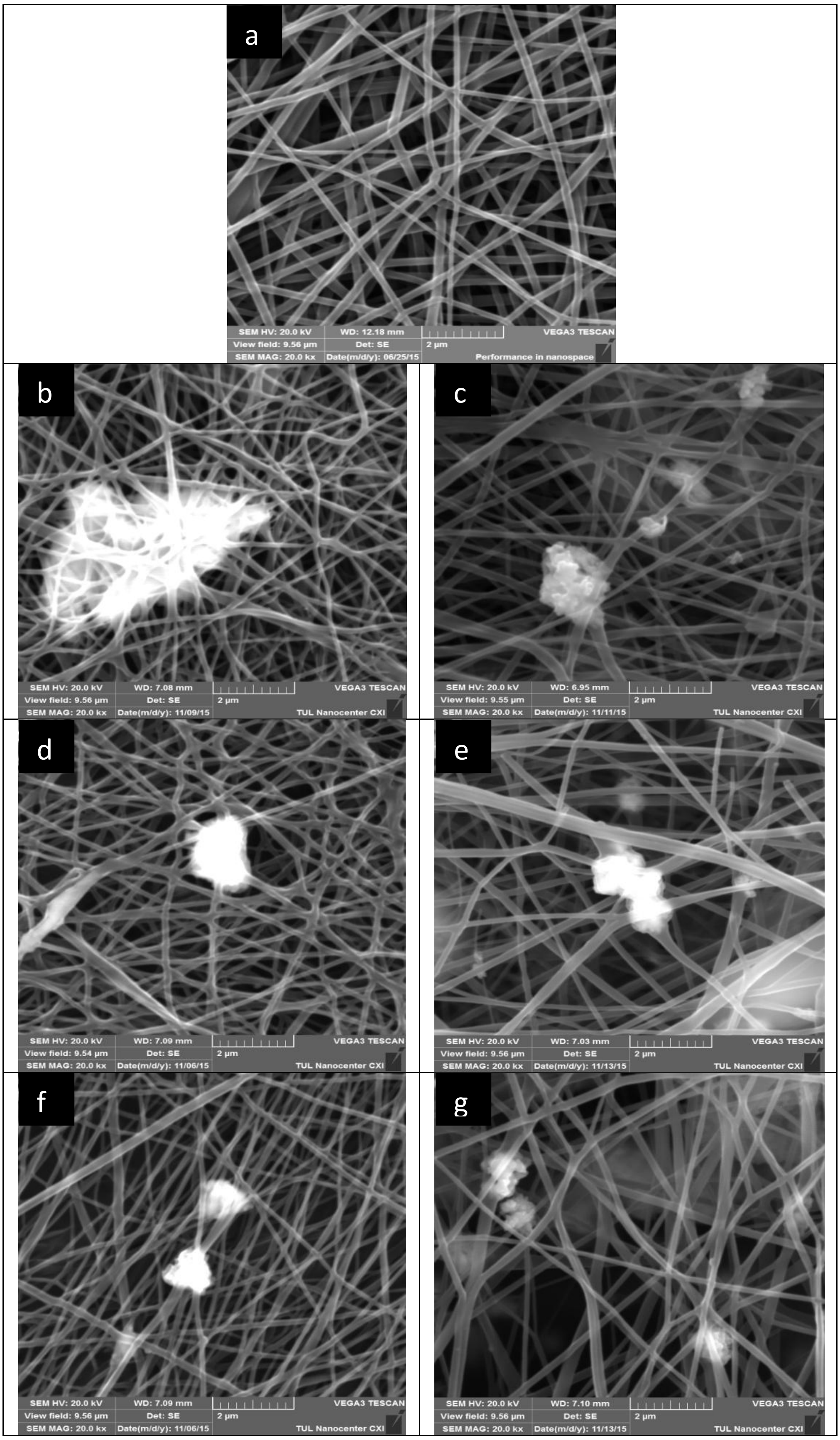
The values of antibacterial efficiency of the samples with micro- and nanoparticles are very similar at 24-hour contact between the modified NFs with bacteria. But it was found that the NPs exhibited their activity quicker. Antimicrobial efficiency of the nano-modified fibers achieved 40-60% depending on the used concentration after one-hour contact with bacteria. MPs need 4 hours to exhibit such activity. But the important objective of this thesis was the production of filters with the stable fixation of antibacterial additives into the fibrous structure. It will provide a long-term application of such materials and a protection of air and water from the ingress of antibacterial agents. From these standpoints MPs are more reliable choice for the modification of PU nanofibers. The results of EDX analysis and antibacterial tests showed that the content of CuO and the values of antibacterial efficiency were not changed after the test under the simulated conditions of water filtration of micro-modified samples. MPs have also proven to be more appropriate modifier according to the results of bacterial filtration tests under the simulated passage of bacterially contaminated air through our samples from the point of view of capturing of aero pulverized bacteria and their liquidation.

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

The wire electrode is widely used in the industrial range of fiber's production because it provides higher performance of ES process. For this reason we decided to try the production of modified PU nanofibers with micro and nanoparticles of CuO by Nanospider technique form the surface of static wire electrode. The structure and properties of prepared samples were investigated according the same experimental approach as had been described in previous sub-chapter 4.1.2 (structure of composite samples, their antibacterial properties; bacterial filtration efficiency). The results of these experiments will be presented below.

4.1.3.1. Structure of composite NFs produced from the wire electrode

SEM images (magnification ×20000) of samples are represented in Fig. 29. The pristine PU layer has a similar structure including dimensional characteristics (Tab. 14) as the respective sample produced from the rotating electrode with needle surface. The samples with MPs of CuO (Fig. 29; b, d, f, h) also have the smooth structure with thin diameters of fibers. But there are visible big aggregates of micro-scale CuO for concentrations 5 and 12% in SEM images (Fig. 29: b and h). We didn't observed such clustered formations of MPs for the samples produced from rod ES set-up and from rotating electrode with needle surface. The rod ES is a short-term process so MPs don't form the aggregates in such short time interval. The ES from electrode with needle surface is a long-term process but it provides the continuous stirring of solution during the spinning process. So such large agglomerates of MPs as in Fig. 29 (b, h) weren’t formed in the previous experiments. It’s explained by the fact that the fiberforming from the wire electrode is long-term and the stirring of modified solutions during ES isn’t ensured. Large aggregates of NPs are also visible in the structure of produced substrates. But such tendency for nano-scale CuO was already mentioned for samples produced from other electrodes. Moreover there are some defects in the structure of PU nanofibers with NPs.


a
SEM HV: 20.0 kV
WD: 12.18 mm
VEGA3 TESCAN
View field: 9.56 µm
Det: SE
2 µm
SEM MAG: 20.0 kx
Date(m/d/y): 06/25/15
Performance in nanospace
b
SEM HV: 20.0 kV
WD: 7.08 mm
VEGA3 TESCAN
View field: 9.56 µm
Det: SE
2 µm
SEM MAG: 20.0 kx
Date(m/d/y): 11/09/15
TUL Nanocenter CXI
c
SEM HV: 20.0 kV
WD: 6.95 mm
VEGA3 TESCAN
View field: 9.55 µm
Det: SE
2 µm
SEM MAG: 20.0 kx
Date(m/d/y): 11/11/15
TUL Nanocenter CXI
d
SEM HV: 20.0 kV
WD: 7.09 mm
VEGA3 TESCAN
View field: 9.54 µm
Det: SE
2 µm
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f
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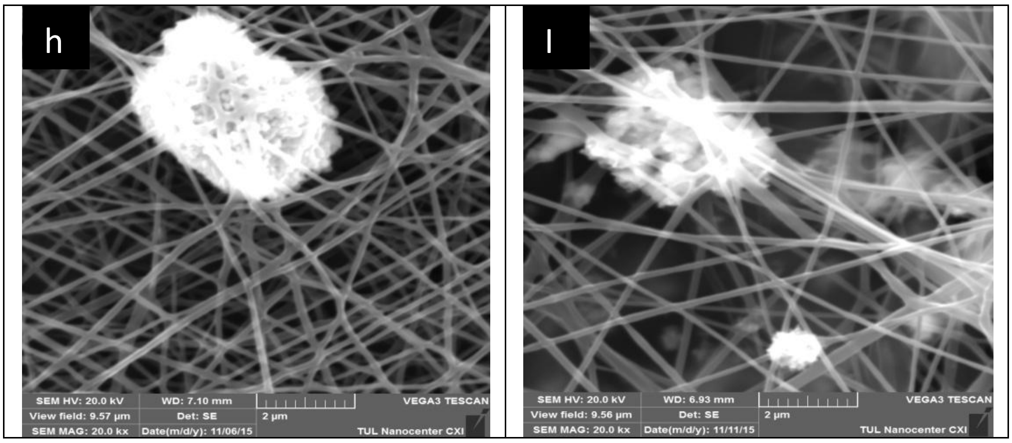


Figure 29. SEM images (magnification 20000) of nanofibers (produced from wire electrode) with different concentrations of micro- and nanoparticles of CuO: a - 0%; b - 5% µm; c - 5%nm; d - 7% µm; e - 7% nm; f - 9.5% µm; g - 9.5% nm; h - 12% µm; i - 12% nm.

There are SEM images of the samples with 5% of micro- and nanoparticles of CuO at smaller magnification (× 5000 times) in Fig. 30. And here we can clearly observe that the structure of nano-modified sample contains a lot of beads. Perhaps some part of NPs aggregates is located inside of these beads.

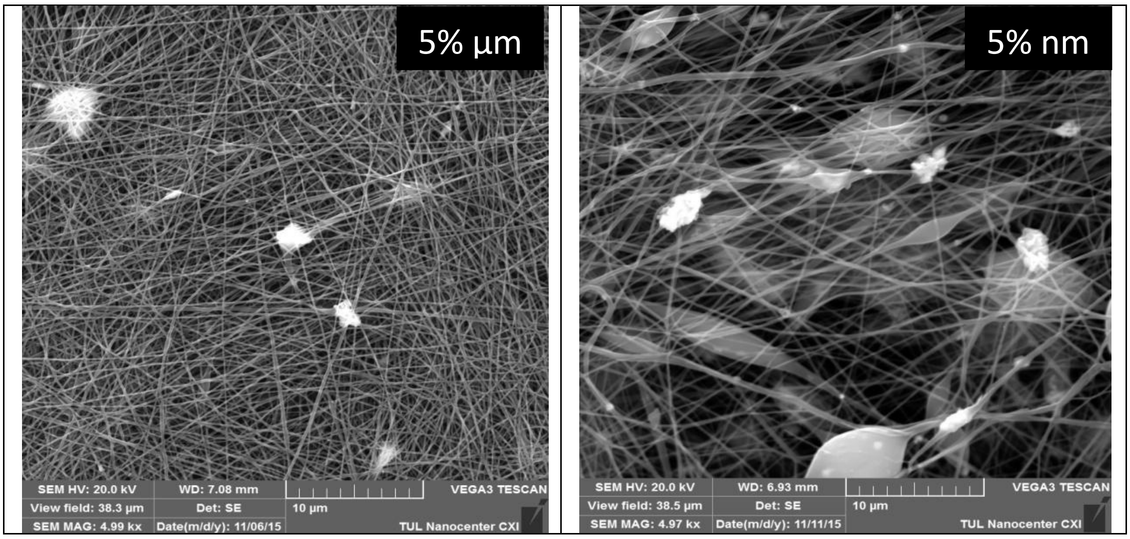


Figure 30. SEM images (magnification 5000) of nanofibers (produced from wire electrode) with 5% of micro- and nanoparticles of CuO respectively.

There are the results of measurements and calculation of dimensional characteristics of the nanofibrous layers produced from wire electrode in Tab. 14. The average diameters of samples with MPs for whole concentration range are less than this parameter for the pristine PU mat. The uniformity coefficients of the micro-modified fibers don't differ (or they are very close) from the values for the pristine substrate. No negative influence of NPs (except the formation of beads) on the dimensional properties of samples was observed. The values of average diameters and uniformity coefficients are similar to non-modified PU. The illustration of diameter's distribution is provided in Fig. 31 (see also Appendix, Fig. 6).

Sample	Number average A_n (nm)	95% Confidence	Weight average A_w, (nm)	Fiber uniformity coefficient K (Aw/An)
Pristine PU	189	5.9	199	1.05

PU + 5%CuO µm	134	4.04	142	1.06
PU + 5%CuO nm	188	6.15	202	1.07
PU + 7%CuO µm	142	3.5	149	1.05
PU + 7%CuO nm	175	5.4	186	1.06
PU + 9.5%CuO µm	125	3.2	132	1.06
PU + 9.5%CuO nm	184	6.3	198	1.08
PU + 12%CuO µm	139	3.3	145	1.04
PU + 12%CuO nm	181	6.1	195	1.08

Table 14. Results of measurement of fibers diameters and calculation of uniformity coefficients of samples produced from wire electrode.

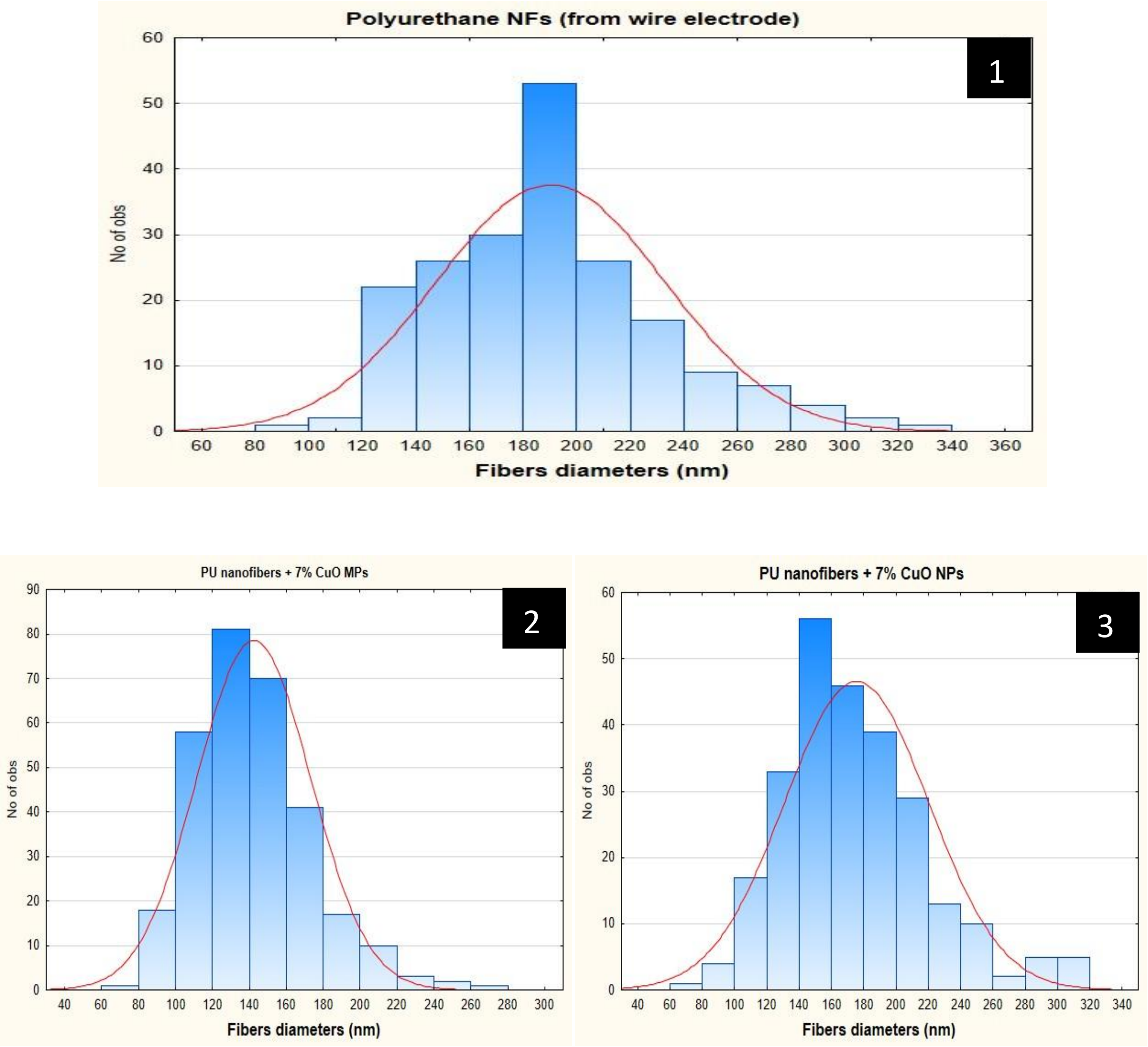


Figure 31. Diameter's distribution: 1 - pristine PU nanofibers; 2 - PU + 7% CuO µm; 3 - PU + 7% CuO nm.

The EDS analysis confirmed the presence of copper in the structures of all modified layers produced from wire electrode (Fig. 32 and 33; Appendix: Fig.7). In case with MPs the detected concentration of CuO is much less than the incorporated amount of modifier (Fig. 32, 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.

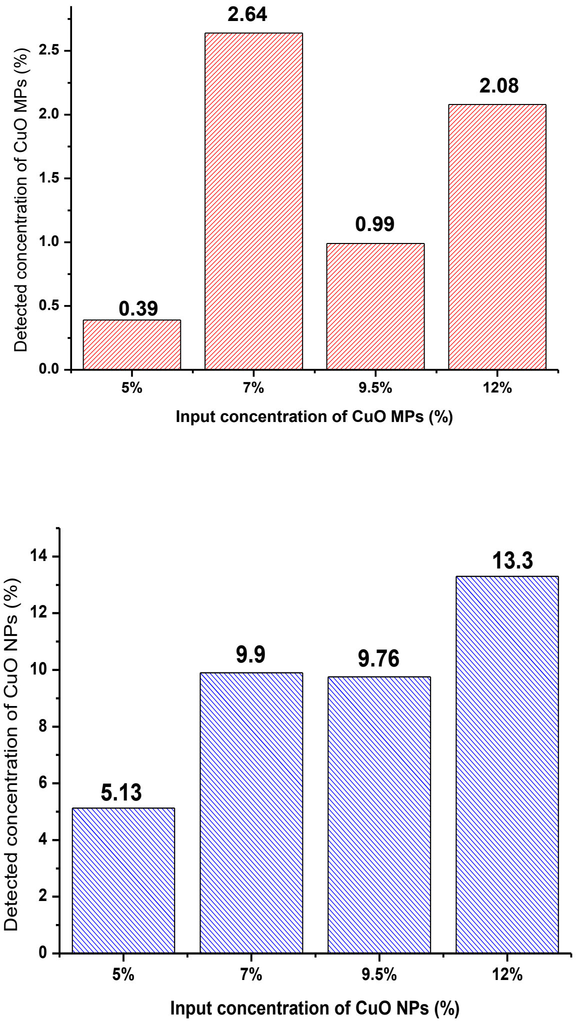


Figure 32. Difference between the concentrations of CuO micro- and nanoparticles in polymer solutions and into the nanofibrous structures for the samples produced from wire electrode.

The detected concentrations of CuO NPs for samples with 5 and 9.5% of CuO correspond with real amounts of modifier introduced to these solutions before ES (Fig. 32, blue column). There is a difference between the measured and incorporated concentrations for layers with 7 and 12% of nanoparticles. Anyway the detected amount of NPs into the structure of samples produced from wire electrode corresponds most precisely to the introduced concentrations (5; 7; 9.5 and 12%) in comparison with samples produced from other tested electrodes. It may indicate more homogeneous distribution of nanoparticles into the structure of PU fibrous substrates produced from wire electrode. The results of antibacterial tests will help to confirm or refute such supposition.

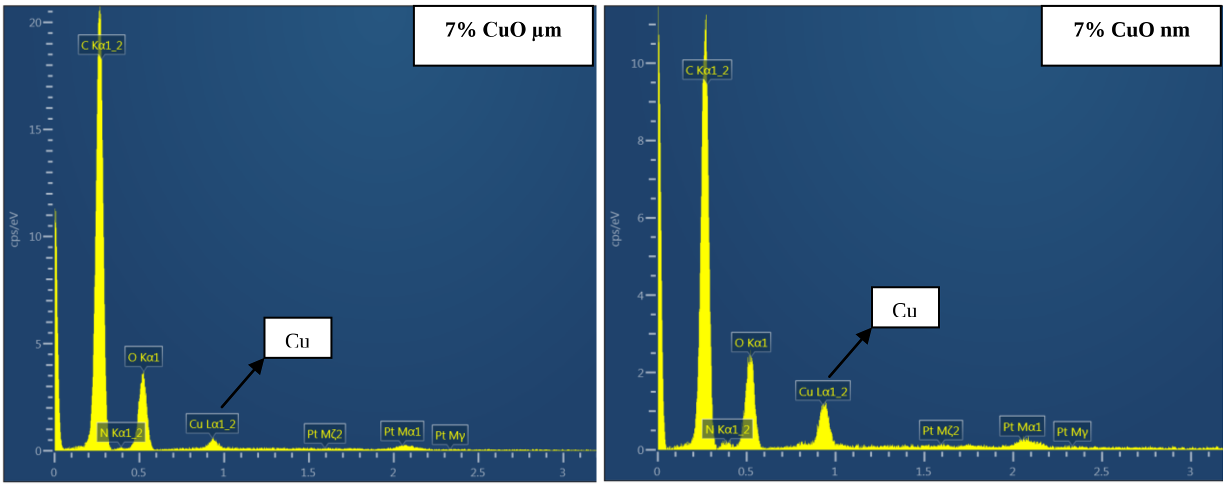


Figure 33. SEM-EDX images: areas of electrospun polyurethane nanofibers with 7% of micro- and nanoparticles of CuO (produced from wire electrode).

The values of surface density of samples produced from wire electrode differ from the respective results of samples from the electrode with needle surface (Tab. 15). The positive tendency of the increase of surface density of PU layers with the incorporation of modifiers is remained. However the degree of modifier's influence on the performance of ES process is decreased for both sizes of CuO particles. It's explained by the difference in construction of spinning electrodes and contact conditions between electrodes and bath with solutions. In case of ES from the rotating electrode with needle surface the charged needles are in continuous contact with modified solutions with CuO. The wire electrode (because it's thin and static) comes into very short interaction with solution in the bath and doesn't provide the stirring.

Size and concentration of CuO	Surface density of fibers (g/m²)
PU pristine	3.43
PU + 5% CuO µm	4.88
PU + 5% CuO nm	3.11
PU + 7% CuO µm	5.31
PU + 7% CuO nm	4.48
PU + 9.5% CuO µm	7.63
PU + 9.5% CuO nm	6.57
PU + 12% CuO µm	7.25
PU + 12% CuO nm	6.18

Table 15. Results of measurements of the surface density of all nanofibrous layers produced from wire electrode.

The filtration efficiency of pristine PU layer and samples with MPs lays in the range 98.5 – 99.9%. This parameter for nanofibrous substrates with nanoparticles changed into a worse side (92 -98%). The lowest filtration efficiency was measured for the sample with highest concentration of CuO NPs (12%). Such deterioration of the filtration efficiency of particulate matter could be predicted from SEM images of nanofibers with the nano-scale modifier where a big number of beads was observed in the fibrous structure.

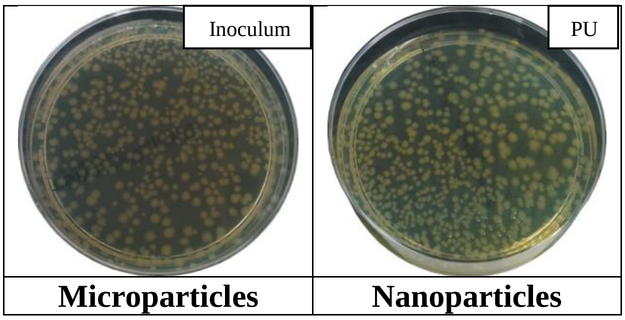
4.1.3.2. Antibacterial properties of modified PU nanolayers produced from wire electrode

According to the results of quantitative antimicrobial tests all composite samples (Tab.16) produced wire electrode have significantly lower activity against both tested bacterial strains in comparison with 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. It was experimentally confirmed that St. Gal. is more resistant than E.coli. Therefore the amount of modifier for liquidation of the colonies of this strain should be higher than for liquidation of E.coli.

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. Moreover microparticles formed the aggregates within fibers produced from wire electrode. Hence the poor antibacterial properties of samples with MPs were expected. The results of EDX measurement of NFs with nanomodifier were opposite. But as we can see in Tab. 16 and in Fig. 34 (see also Appendix: Fig. 8) the samples with NPs don't demonstrate good antibacterial efficiency (especially against St. Gal.). There are two reasons for the explanation of such results. The first reason is again the aggregation of nanoparticles. It's confirmed by SEM images. And as it was described earlier the aggregation led to a partial loss of the unique functional properties of NPs. Through the aggregation many nano-scale particles are inside of clustered formations and they are not available for the contact with bacteria. The second reason is also related with the formation of agglomerates. But here we will talk about aggregates which are not visible for our eyes and for the SEM. As we observe there is a lot of beads in the structure of fibers with NPs in the Fig. 30. 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.

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 16. Antibacterial efficiency against two bacterial strains for the samples prepared from wire electrode (the contact time between bacterial solutions and modified samples was 24 hours).



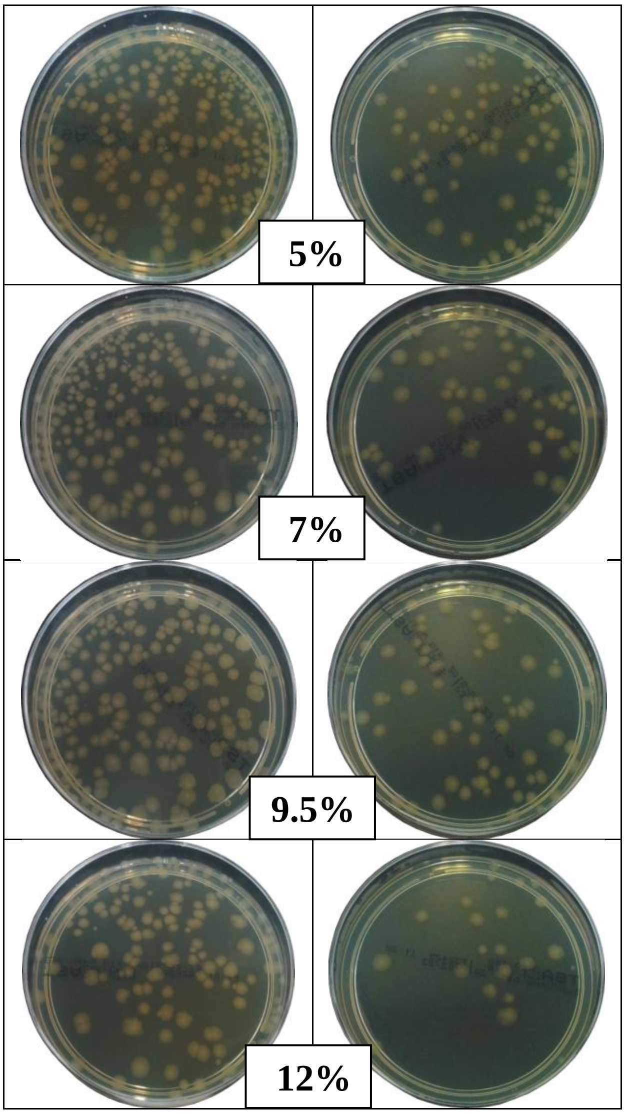


Figure 34. Pictures of agar plates showing the results of antibacterial test against **E.coli** (contact time 24 hours).

4.1.3.3. Bacterial filtration efficiency of samples produced from wire electrode

Bacterial filtration efficiency of composite samples with MPs produced from wire electrode is better in comparison with the pristine PU layer and layers with NPs (Tab. 17). As we remember surface densities of micro-modified substrates is higher. So it plays a key role in the capability of samples to capture bacteria. Moreover the structure of samples with nanoparticles is damaged by the presence of big numbers of beads. The results of smear-test are also in favor of microparticles. But in fact we have to state that all filters produced from wire electrode are not appropriate for the liquidation of bacteria trapped from the filtering medium. The lower elimination abilities to liquidate captured bacteria of nano-modified mats confirm that some part of NPs is hidden inside of fibers or beads.

Sample	Number of bacteria passed through the sample	BFE (%)	Number of survived bacteria after "smear-test"
Inoculum	312	**-**	**-**
PU pristine	23	**93**	303
PU + 5% CuO μm	11	**96**	14
PU + 5% CuO nm	13	**95.8**	52
PU + 7% CuO μm	0	**100**	2

PU + 7% CuO nm	30	**90**	23
PU + 9.5% CuO µm	1	**99.7**	7
PU + 9.5% CuO nm	26	**92**	22
PU + 12% CuO µm	0	**100**	25
PU + 12% CuO nm	75	**76**	43

Table 17. Results of the bacterial filtration test and "smear-test" for samples produced from wire electrode.

The results of measurements of bacterial filtration efficiency and smear-tests have finally proved that the using of wire electrode isn’t suitable for the production of composite antibacterial nanofibers from the modified PU solutions. The absence of continuous stirring of colloidal solutions leads to the aggregation of both dimensional types of modifier, to precipitation of MPs at the bottom of bath and to the formation of agglomerates of NPs inside of polymer beads. Photo documentation with the results of bacterial filtration test is presented in Appendix, Fig. 9.

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

In this thesis few experiments were done for the modification of polyurethane NFs using the deposition method at the special sputtering chamber. The layer of Cu was deposited on the surface of fibrous layer. The thickness of deposited layer is regulated by time of the sputtering procedure. In our case it was 2.5 min. EDX analysis was used to determine the amount of Cu on the surface of nanofibers. The concentration 2.5% of Cu was detected according to the results of this measurement. So it means that approximately 1% of copper is deposited on the fibrous surface during 1 min of sputtering under the chosen parameters (pressure in chamber 1Pa, deposition time 2.5 min).

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 under the constant water flow. The concentration 2.33% of Cu was measured by the EDX analysis after water filtration. As we remember the concentration before water treatment is 2.5%. Such small difference 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.

There is only one special requirement for the using of such modification technique. The availability of special chamber for the deposition procedure is necessary. But all known modification techniques require extra chemicals or equipments.

4.3. PA-6 nanofibers modified by CuO

As it was already mentioned in Experimental part 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) into 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.

4.3.1. Structure and dimensional characteristic of modified PA-6 layers

Polyamide 6 NFs produced by Nanospider technique are known as fibers with thin and uniform diameters. SEM analysis (Fig. 35) confirmed that all PA-6 nanofibrous mats had smooth well-oriented fibers regardless of the addition of CuO.

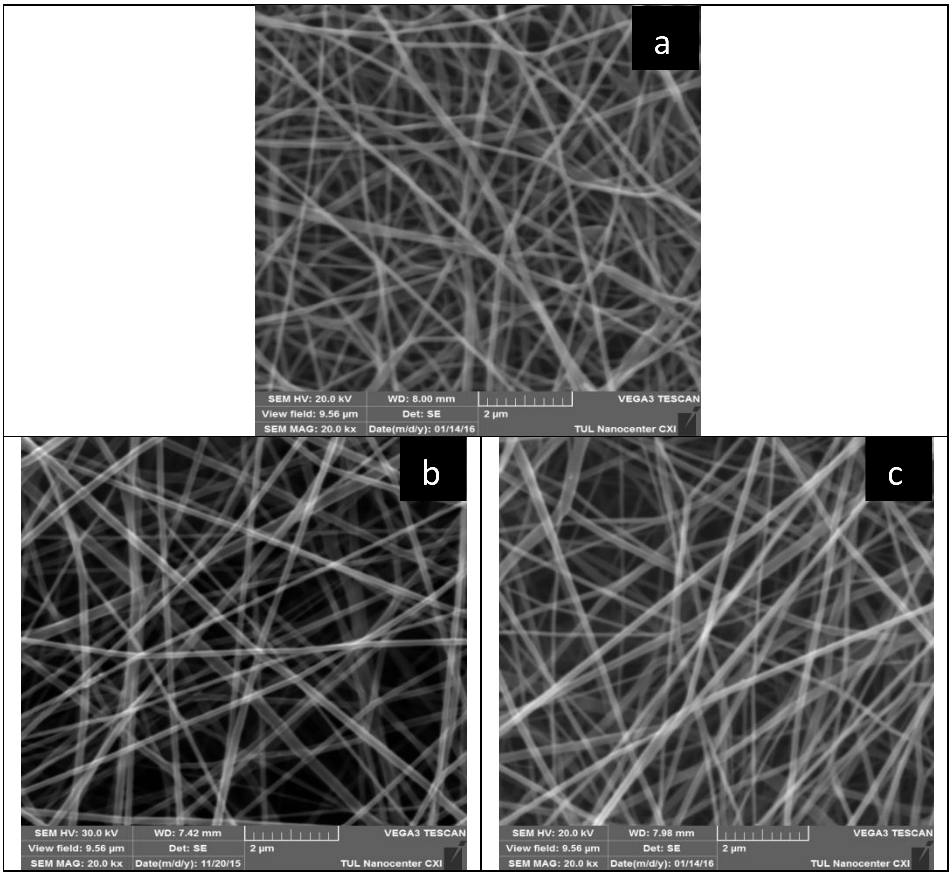


Figure 35. SEM images of PA-6 nanofibers (magnification 20000): a - pristine PA-6 NFs; b - PA-6 with CuO, old sample; c - PA-6 with CuO, new sample.

The optimal parameters for the fast aging of our fibers were determined experimentally. We call the appropriate conditions of temperature, RH and UV treatments as stabilization parameters. So in case of T°C we started from 130°C for 24 hours. As it's presented in Fig. 36 the fibrous structure is destroyed under such combination of stabilization parameters. Then we were gradually decreasing the intensity and time exposure of the temperature. The same principle was used for the determination of the optimal exposure time of UV treatment.

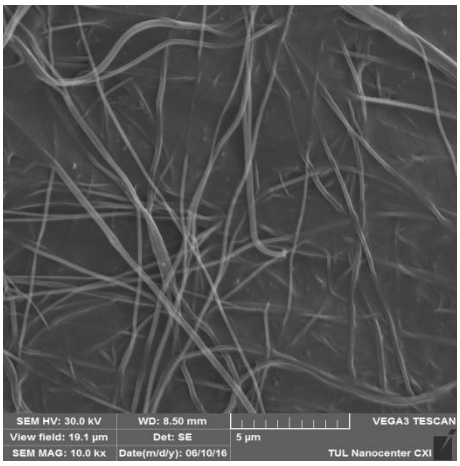


Figure 36. SEM image of "new" PA-6 NFs with CuO after stabilization at 130°C for 24hours.

The incorporation of CuO has insignificantly influenced the dimensional characteristics of nanofibers. As we can observe in Tab. 18 the average diameters of modified layers are slightly higher. The same can be said and about the fiber uniformity coefficients. But it's important that incorporation of the modifier didn't lead to problems with the ES process and to the significant deterioration of structure of produced composite nanofibers.

Sample	Number average A_n (nm)	95% Confidence	Weight average A_w, (nm)	Fiber uniformity coefficient K (Aw/An)
Pristine PA-6	139	4.16	147	1.06
PA-6 + CuO old	146	5.69	158	1.08
PA-6 + CuO new	161	5.83	174	1.08

Table 18. Results of measurement of fibers diameters and calculation of uniformity coefficients of PA-6 nanofibers with CuO.

The difference between distribution of fibers diameters of the pristine sample (1) and "new" modified substrate (2) is presented in Fig. 37.

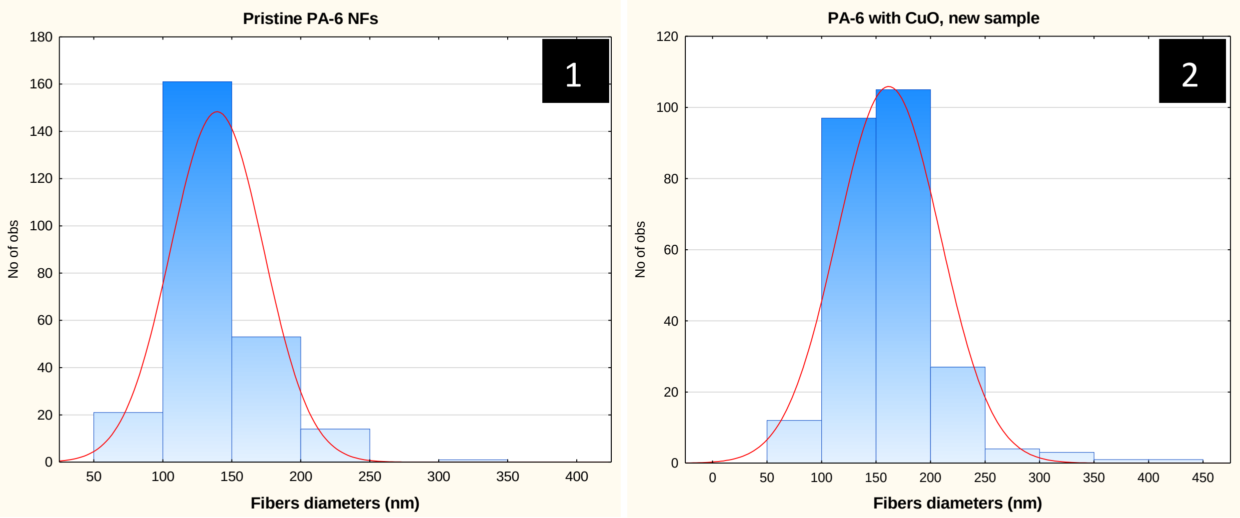


Figure 37. Diameter’s distribution: 1 - pristine PA-6 nanofibers; 2 - PA-6 +CuO, new sample.

4.3.2. Antibacterial properties of PA-6 nanofibers with CuO before and after water filtration test

The results of antibacterial tests before and after water filtration (Tab. 19) 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 19. 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. 19 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.

5. Conclusions

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. We practically confirmed the possibility of using of the colloidal polymer solutions with micro- or nanoparticles of CuO for the production of nanofibers by the Nanospider technique which allowed obtaining the nanofibrous materials in volumes of the mass production. There is only one nuance. It was experimentally established that a special spinning electrode must be used for the fiber forming of the efficient antibacterial filters from such solutions. We are talking about the rotating electrode with needle surface. Such electrode provides a constant stirring of the solutions with particles during the electrospinning. This approach 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 micro- and nanoparticles of CuO contributes to significant improvement of the performance of ES of the polyurethane solution. This phenomenon is explained by the influence of conductive properties of copper under interaction with the charged spinning electrode. It is worth noting that microparticles have a greater impact on the performance improving. Nanoparticles showed their electrical properties to a lesser extent because of their tendency to aggregation. The additives for the improving of ES performance usually contribute to the significant thickening of the diameters of nanofibrous substrates. The use of high concentrations (5 - 12%wt) of our modifier does not affect negatively the structure and dimensional characteristics of produced fibers. 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. The inhibitory effect of nanoparticles appears a little faster. But the aim of antimicrobial modification of filters is the need to ensure the elimination of bacteria which are captured on the surface of filter materials. There is no principal difference if the vital functions of bacteria will be suppressed in an hour or in four hours after the hitting on the surface of filter. Moreover, 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. So the deterioration of their functional properties as a result of aggregation is quite expected.

The key indicator of the successful antibacterial modification of filters is the stability of fixation of used antimicrobial substances. It was necessary to bring closer the tests conditions as much as possible to the real filtration conditions for an objective evaluation of this parameter. 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 into 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. Such behaviour of nanoparticles is also explained by the formation of aggregates. The upper layers of NPs in the structure of aggregates are not incorporated inside of fibers. The nanoparticles at upper layers of aggregates are bound only by physical interaction, so they are washed out by the flow of water.

Besides of tests of particle’s fixation under the water filtration conditions it was also important to evaluate the behaviour of filters under the conditions of air purification. In other words, we had to determine whether our antibacterial filters were able to capture bacteria from air, and what was more important, to eliminate the trapped microorganisms. For this aim a special device (AMFIT 13) was developed. Due to this equipment it became possible to estimate the bacterial filtration efficiency of our samples under the simulated conditions of the filtration of bacterially contaminated air. The samples with microparticles demonstrated higher values of the BFE. It was expected because the surface density of these filters was also higher. However 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. However, in order to make definitive conclusions, this modification method is worth exploring in more details.

3. Modification of PA-6 nanofibers by CuO

Microparticles of CuO were incorporated into the PA-6 solution as in case of PU. The difference is in the fact that components of polyurethane solution are inert in relation to CuO, while the solvents of PA-6 (acetic and formic acids) react with the selected modifier to form salts which are soluble in water. It could be immediately concluded that such samples were not suitable for filtration. But it was found out that the chemical form of copper was changed at the fibers surface as a result of long-term storage. “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 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.

Nevertheless at the end we would like to mention that the most important achievement of this thesis is the developed technology of the production of modified polyurethane nanofibers with particles of copper oxide. Due to the experimental results it was found out that microparticles of CuO are more appropriate candidate for modification of PU fibers for the application in the filtration area. The micro-sized modifier is better fixed into nanofibrous structure. The microparticles are less subject to aggregation, therefore their distribution in the fibrous area is more homogeneous. It provides them better efficiency in the elimination of the captured bacteria.

6. Future perspectives

The blending method can be used for modification of PU nanofibers by another antibacterial agents ($AgNO_3$; ZnO; TiO_2). Comparison of different antimicrobial additives is very important for the practical application of antibacterial filters in order to select the most efficient and stable. The produced nanofibrous layers of PU with particles of CuO are worth to be tested as conductive samples. The magnetron sputtering was less studied then blending method for the modification of nanofibers. But this method (magnetron sputtering) is very perspective for the production of nanofibers with a wide range of functional properties (antibacterial, conductive, catalytic, optical). Proposed testing methodology for the determination of particle's fixation can be used not only for the filtration materials but also for the modified nanofibers for another future application.

II. Photocatalysts for air purification from NOx and CO

1. Research objectives

We were motivated by the fact that the air pollution had not ceased to be an urgent problem, particularly in the developing countries. Nowadays the textile industry offers a wide range of filtration materials for the air purification from dust and another solid impurities. But the problem of air pollution by the harmful gases is no less acute. To solve both problems (the air pollution by solid and gaseous impurities) it's necessary to prepare a filter material with the catalytic properties.

Our objectives in the field of the catalytic purification of air have been changing in the process of experimental work. And 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 the 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.

The polyurethane nanofibers were selected as a filtration material for further catalytic modification. Good filtration properties of PU nanolayers were already described in the first part of this thesis. The choice of catalytic agent for the modification of nanofibers was much more challenging. Such chemical phenomenon as a catalysis usually occurs at very high temperatures required for the formation of the desired active complex which will accelerate a chemical reaction without being consumed as a reactant. The high temperature conditions are incompatible with the conditions under which the polyurethane (or other polymeric) nanofibers can be used. Moreover our objective was to produce the filtration material with catalytic properties for the non industrial air-conditioning systems. Such systems don't include elements for the heating of purified air. So it was necessary to select a catalytic agent which can be activated by another form of energy. It is easy to guess that it can be a photocatalyst. The titanium dioxide (TiO_2) is a well-known semiconductive material that during illumination acts as a strong oxidizing agent lowering the activation energy for the decomposition of organic and inorganic compounds. Thus TiO_2 was selected as the first candidate for the photocatalytic modification of our nanofibers. However, the tests results with this photocatalyst 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. Based on the experimental results the final objectives of this part of the thesis were the improvement of photocatalytic efficiency of SnO_2 for the oxidation of carbon monoxide by doping with another metal oxides and the investigation of the influence of tests conditions (especially relative humidity) on catalytic properties of the selected semiconductor.

The search for a suitable test methodology to determine the photocatalytic activity of the modified nanofibers also occurred in several stages. As a result two testing methods to determine catalytic properties of fibrous and powder materials will be presented in this thesis. The first method was based on the measurement of concentrations of exhaust compounds (NO_x and CO) in the operating mode of the automotive engine. The second method included the determination of CO concentration in the model conditions of the reaction of carbon monoxide oxidation in air.

So in the second part we will present the results of the photocatalytic modification of polyurethane nanofibers by two different agents (TiO_2; SnO_2); the detail investigation of photocatalytic properties of SnO_2 in the reaction of CO oxidation; two different testing methods for the studying of photocatalytic activity of nanofibrous (and not only) materials.

2. Theoretical part

2.1. Problem of air pollution and the ways to solve it

The problems with air pollution are now mostly seen in the big cities of developing countries. Despite the progress in the field of air purification, nitrogen oxides (NO_x), volatile organic compounds (VOC) and photochemical oxidants (connected with the growing traffic) still cause significant damage to the ecological situation [82]. Carbon monoxide is another dangerous pollutant, which is released in the environment due to emissions from automated vehicles, aircraft, natural gas emission, industrial wastage, sewage leaking, mines, etc [83]. Moreover new hazardous compounds, mainly from industry, have been identified with the advanced analytical technique.

The listed contaminants negatively affect the health of all organisms that inhabit our planet. The recent researches suggest that the air pollution contributes to the substantial burden of disease from the acute lower respiratory tract infections to the tuberculosis [82]. The interrelation between the chronic effects of traffic emissions and the respiratory and cardiovascular diseases has been found in the numerous studies [84]. The International Agency for Research on Cancer recently declared the traffic-related air pollution (TRAP) as a Group 1 carcinogen, i.e., a causal agent in human carcinogenesis [85]. Great attention will be paid to the air purification from CO in this thesis. It worth noting that this gas is extremely toxic and often referred to as the “silent killer” since it is colourless, tasteless and odourless [86]. 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 [87].

2.2. Photocatalysis as a method for the air purification

Titanium dioxide. Our initial objective was to use the nanofibers as carriers of the catalytically active metal oxides. So the method (the same as was used for antibacterial modification of nanofibers) of modification of nanofibrous materials by the incorporation of particles of catalysts into the polymer solution prior electrospinning will be presented in this part of the thesis. However, 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). PCO has been studied for several decades and shown as an effective method for air purification. The photocatalytic activity of titanium dioxide molecules is widely studied and utilized in biological, chemical and industrial applications. TiO_2 has many appropriate characteristics: (a) it is inexpensive, safe, very stable, and has a high photocatalytic efficiency; (b) it promotes ambient temperature oxidation of the major indoor air pollutants; (c) no chemical additives are required [88]. The " photocatalytic " ability means the ability of a material to form the electron - hole pairs upon absorbing the electromagnetic radiation. The absorption of electromagnetic radiation by TiO_2 produces the electron-hole pairs ($e^- h^+$) that can be transferred through the material to the surface of the bulk TiO_2. At the surface, the charged electrons (e^-) are spatially separated from the electropositive holes (h^+), thus forming separate reducing and oxidizing centers. The reductive and oxidative abilities of the electron - hole pairs can lead to the production of strong oxidizing agents applicable for many purposes, from chemical to microbial decontamination [89].

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 [90]. 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 [91]. 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 [92]. In the second part of our research we will present the results of experiments of the use of polyurethane nanofibers with TiO_2 nanoparticles for the photocatalytic oxidation of gaseous products of combustion engine emissions (NO_x and CO) . However it was determined that an adsorption of CO on pure TiO_2 is very low. And it is highly detrimental to the CO photooxidation efficiency on the surface of titanium dioxide. It was the reason to continue the search of the effective photocatalyst for the CO oxidation.

Tin oxide. According to the literature, tin oxide is also very promising photocatalytic material with the rutile-type crystal structure. It is known that the tin-oxide based catalysts exhibit good activity towards CO/O_2 and CO/NO reactions. 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. [93,94]. It is necessary to couple SnO_2 with another semiconductors with lower band gaps in order to solve this problem [95]. Tin dioxide has been intensively studied as a support for the noble metal catalysts during last two decades [86]. Combining some semiconductors with different band gaps to form heterojunctions in the photocatalytic systems became a primary focus of researchers. The unique properties of combined semiconductors have appeared because of their interfacial interaction at the nanoscale level [96]. Pt/SnO_2 was presented as an active catalyst in the reactions of low temperature oxidation of CO and CH_4 [97–99]. SnO_2 (and another carriers as Al_2O_3, SiO_2, ZrO_2, TiO_2) with Pd, Ru and Au, are also effective catalysts for the low temperature reaction of the carbon monoxide oxidation [100–102]. Despite of the high efficiency of such composite catalysts there are important disadvantages for their practical application. For example catalysts with Au always suffer from the low thermal stability and water deactivation. Moreover, it is well-known that the precious metals have limited availability around the world and thus have a high price [101].

Therefore the search of new cheap efficient catalysts without using of the precious metals arouses the interest of scientific groups all over the world. The ceria-based catalysts have already drawn much attention as a substitute for the noble metal catalysts. Such materials are perspective due to their low cost and good performance for the oxidation of carbon monoxide and hydrocarbons [103,104]. Sn-Ce-O mixed oxides have an improved activity for the CO oxidation in comparison with the single oxide's components because of the synergistic effect between SnO_2 and CeO_2 [105]. X. Han et al. found out that a small amount of Ta can also significantly promote the activity of SnO_2 for the CO oxidation [106]. The addition of copper, palladium and chromium also increases the total catalytic activity of SnO_2 [95]. Therefore we focused on the preparation of modified PU nanofibers with the combination of two oxides SnO_2/CrO_2. Their properties were confirmed in the reactions of photocatalytic oxidation of the gaseous products of combustion engine emissions. It was done in order to compare the efficiency of TiO_2 and SnO_2/CrO_2 photocatalysts at the surface of nanofibrous materials. Then the photocatalytic properties of nanofibers with SnO_2/CrO_2 were also investigated under the model conditions of CO oxidation in the mixture with air. Unfortunately modified nanofibers with combined catalyst SnO_2/CrO_2 were not active under these conditions.

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 [107]. So the next step of this study was the synthesis of the composite nanoscale catalyst SnO_2/NiO. First of all the photocatalytic activity of the synthesized powder compound was tested under the conditions of the CO oxidation in the mixture with air. When the catalytic efficiency of the composite substance (SnO_2/NiO) was experimentally confirmed, the obtained catalyst was used for the modification of PU nanofibers. It should be noted that one interesting tendency appeared in the course of measurements. The change of humidity strongly influenced the photocatalytic activity of the synthesized catalyst. However it proved difficult to find the explanation for obtained results in the literature.

2.3. The influence of water vapour on the reaction of photocatalytic oxidation of CO

So far the mechanism of photocatalytic oxidation of CO 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

[108]. 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 [109]. 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 [110]. So the role of water vapor has not been clarified yet. But our results confirmed the positive influence of water vapour on photocatalytic efficiency of the composite catalyst SnO_2/NiO in the reaction of CO oxidation in air.

3. Experimental part

3.1. Polyurethane nanofibers with nanoparticles of TiO_2

3.1.1. Production of modified PU nanofibers with the nanoscale particles of TiO_2

The procedure of preparation of the polyurethane solution was described in the sub-chapters 3.1.1 and 3.1.2 (I). 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. The rotating electrode with needle surface was used as a spinning electrode. Detailed description of the electrospinning method and the spinning parameters is in the sub-chapter 3.1.5 (I).

3.1.2. Structure of PU nanofibers with TiO_2

The morphology of composite nanofibers was studied using a scanning electron microscope and transmission electron microscope (TEM - JEOL JEM-2100F). The TEM analysis was provided at the Institute of Physics of Materials (the Czech Academy of Sciences). The average diameter of the fibres with TiO_2 was calculated from the SEM photos using Lucie 32G computer software. The fiber uniformity coefficients were determined according to the same method as it was presented in the sub-chapter 3.1.6 (I). The filtration efficiency of the nanofibrous layer with TiO_2 was investigated by the the Sodium chloride aerosol test equipment (3.1.7 (I)).

3.1.3. Measurement of photocatalytic efficiency of sample with TiO_2

There is no appropriate standardized methodology for the verification of photocatalytic functions of the modified nanofibrous layers. Therefore, it was necessary to find a suitable method for our tests. The photocatalytic properties of filters were studied in the reactions with exhaust gases produced by the automotive engine. The used testing technique will be described in detail. Our filter was wound on the special frame, which was placed into the filtration container. The UV lamp (6) for the initiating of the photocatalytic process was installed inside of the frame with nanofibers (Fig. 38). 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 (1) 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 (Fig.38, point 3 - sampling the gas mixture before the filter). Then the gaseous flow was switched to the container with filter (4). The exhaust stream was passing through the nanofibrous layer with nanoparticles of TiO_2 activated by UV lamp. The analyzers determined concentrations of individual components of emission's mixture that were passing through the filter (Fig. 38, point 7 - sampling the gas mixture behind the filter). The catalytic efficiency of our sample was calculated as the difference of measured concentrations of gases (NOx and CO) before (3) and behind the filter (7). The measurement position (before or behind the filter) was changed during the test by the system of valves. The initial concentrations of CO and NOx in the exhaust were very high (4500 and 4000 ppm respectively). The chemiluminescent and infrared analyzers were used to detect the concentrations of NOx and CO respectively. These analyzers are commonly used for the tests of combustion engines to determine the quantity of different gases in the exhaust sample. The test method MP-04-95 was used to detect the concentration of CO by the infrared analyzer Hartmann-Braun URAS 3E. The second using test method was MPAL 02/95 for the detection of NOx by the chemiluminescent analyzer HORIBA CLA 150.

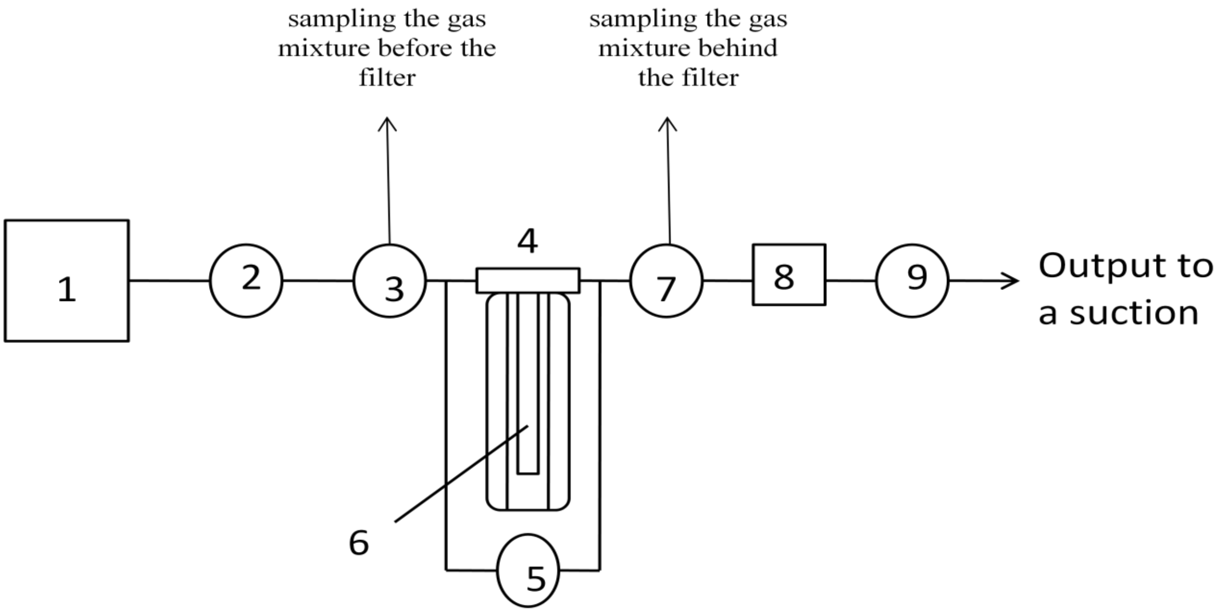


Figure 38. Scheme of the measuring setup: 1- engine; 2 – cooling of emissions gases; 3 – valve for the sampling before the filter; 4 – container with filter; 5 – differential pressure transmitter; 6 – UV lamp; 7 – valve for the sampling behind the filter; 8 – suction pump of exhaust gases; 9 – rotameter.

3.2. Polyurethane nanofibers with particles of SnO_2/CrO_2

3.2.1. Properties of PU solution with the selected combined catalyst

The procedure of preparation of the polyurethane solution was described in the sub-chapters 3.1.1 and 3.1.2 (I). In this experiments tetraethylammoniumbromide (TEAB) was used as an additive to increase the conductivity of polyurethane solution. The particles 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 rheological properties and conductivity of pristine and modified solutions were measured to estimate the influence of used additives on the properties of our polymer solution. The viscosity was investigated using Rheometer HAAKE Roto Visco 1 at 23°C. Conductivity of the solutions was measured by the conductivity meter EUTECH instruments CyberScan CON 510.

3.2.2. Production of polyurethane nanofibrous filters with combined catalyst SnO_2/CrO_2

The nanofibers from modified solution were produced by the Nanospider technique. The rotating electrode with needle surface was used as a spinning electrode. The detail description of the electrospinning method and the spinning parameters are in the sub-chapter 3.1.5 (I).

3.2.3 Structure of nanofibers with SnO_2/CrO_2

The morphology of composite nanofibers was studied using the scanning electron microscope with an energy-dispersive X-ray spectroscopy (SEM with EDS). The surface density of nanofibers layers with different concentrations of catalytic agents was calculated. The average diameters of fibers were measured from the SEM photos using Lucie 32G computer software. The fiber uniformity coefficient was determined according to the same method as it was presented in the sub-chapter 3.1.6 (I). The filtration efficiency of the nanofibrous layer with SnO_2/CrO_2 was studied by the the Sodium chloride aerosol test equipment (3.1.7 (I)).

3.2.4. 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 presented in the sub-chapter 3.1.3 (II). In this case the photocatalytic properties of our materials were measured in the mixture of exhaust gases. Then photocatalytic properties of composite nanofibers were also studied under the conditions of CO oxidation in the mixture with pure laboratory air (Fig. 39).

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).

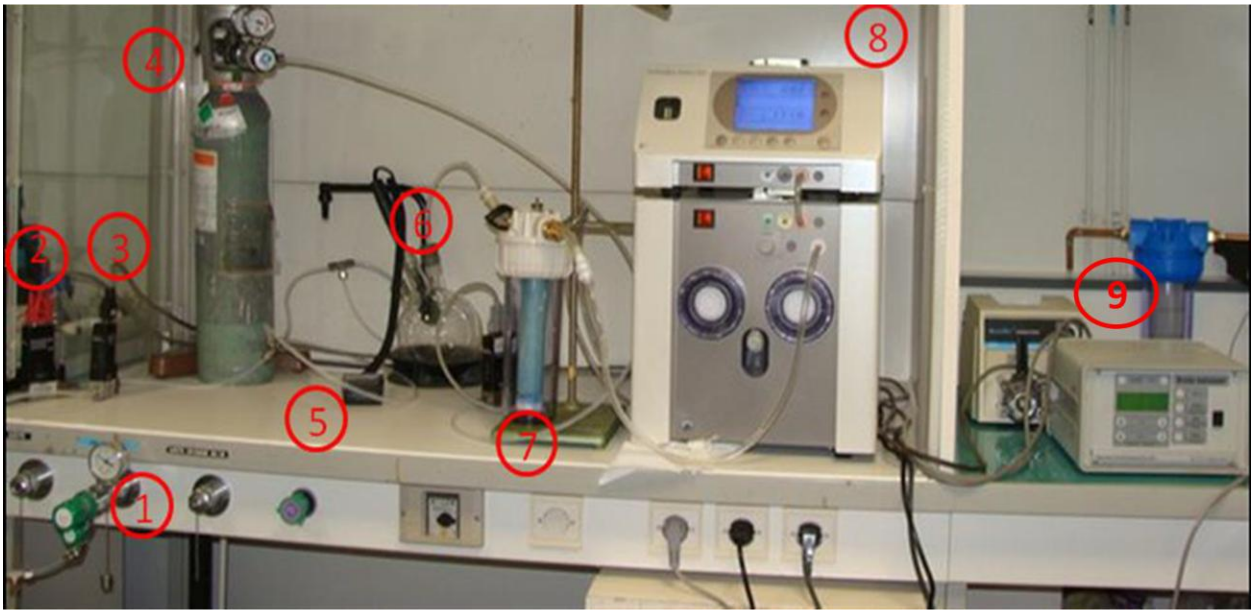


Figure 39. Measurement setup for the determination of photocatalytic activity in the reaction of CO oxidation in air: 1 - feeding of compressed air; 2 - flow meter to control air flow rate; 3 - flow meter to control CO flow rate; 4 - cylinder with CO; 5 - humidity measurement; 6 - mixing of CO with air; 7 - reactor with filter; 8 - infrared gas analyzer, 9 - microprocessor to control the flow rates of CO and O2.

The influence of relative humidity was investigated at the values 5 and 50%. The initial concentrations of CO (5, 20, and 100 ppm) were selected in correspondence with data about the CO content in air. 0.1 ppm - a basic level of CO in the atmosphere; 0.5-5 ppm - an average level in houses and buildings; 100-200 ppm – a level of car exhaust in the centre of megapolises. The Air Quality Directive and the air quality guideline of WHO determined the limit average values of CO for eight-hour (8.7 ppm) and one-hour exposure (26 ppm). The gas flow rates were varied from 0.1 - 2 l/min. The measurement procedure included three steps: the measurement of initial concentrations of CO and CO_2 without filter (for 30 min); the measurement of gases concentrations with filter (for 1 hour); control of the stability of detected concentrations of CO and CO_2 again without filter (for 30 min).

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

3.3.1. Preparation of photocatalysts

All chemicals for this research were obtained from Sigma-Aldrich without further purification. 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.

3.3.2. Catalyst characterization

The structure of the catalysts was examined by X-ray diffraction (XRD) on X'Pert PRO θ-θ powder diffractometer with par focusing Bragg-Brentano geometry using CuK_α radiation (λ = 1.5418 Å, U = 40 kV, I = 30 mA). The intensity data was collected at 25°C over a 2θ range of 5–60°. The morphology and chemical composition of the prepared samples were also examined via a scanning electron microscope with an energy-dispersive X-ray spectroscopy.

3.3.3. Measurement of the photocatalytic activity

The photooxidation of CO in presence of O_2 was carried out with a flow-type reactor at room temperature. The laboratory setup for the measurement of the photocatalytic activity was already presented in Fig.38. 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. 39). The UV lamp for the initiating of the photocatalytic process was installed inside of the frame in reactor. 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. The removal efficiency (E) of CO has been calculated by applying

$$\%E = \frac{Co - C}{Co} \times 100, \qquad (4)$$

where Co (ppm) - concentration of CO in the in-let gas mixture , C - concentration of CO in the out-let gas mixture.

3.3.4. 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 the electrospinning. The modified solutions with 5% wt of micro- or nanoparticles of the prepared catalyst were stirred for 48 hours. Then nanofibers were produced by the Nanospider technique. The rotating electrode with needle surface was utilized as a spinning electrode. The detail description of the electrospinning method and the spinning parameters are in the sub-chapter 3.1.5 (I). The photocatalytic properties of modified nanofibrous substrates were investigated under the same tests conditions as it was presented in the sub-chapter 3.2.4 (II).

4. Results and discussion

4.1. PU nanofibers with nanoparticles of TiO_2

4.1.1. Structure of produced catalytic layers

We can observe big numbers of the agglomerated TiO2 nanoparticles in the TEM images (Fig.40) of modified PU nanofibers. The Fig. 40(2) demonstrates that the nano-sized particles form big aggregates and cover a part of the surface of individual fibers.

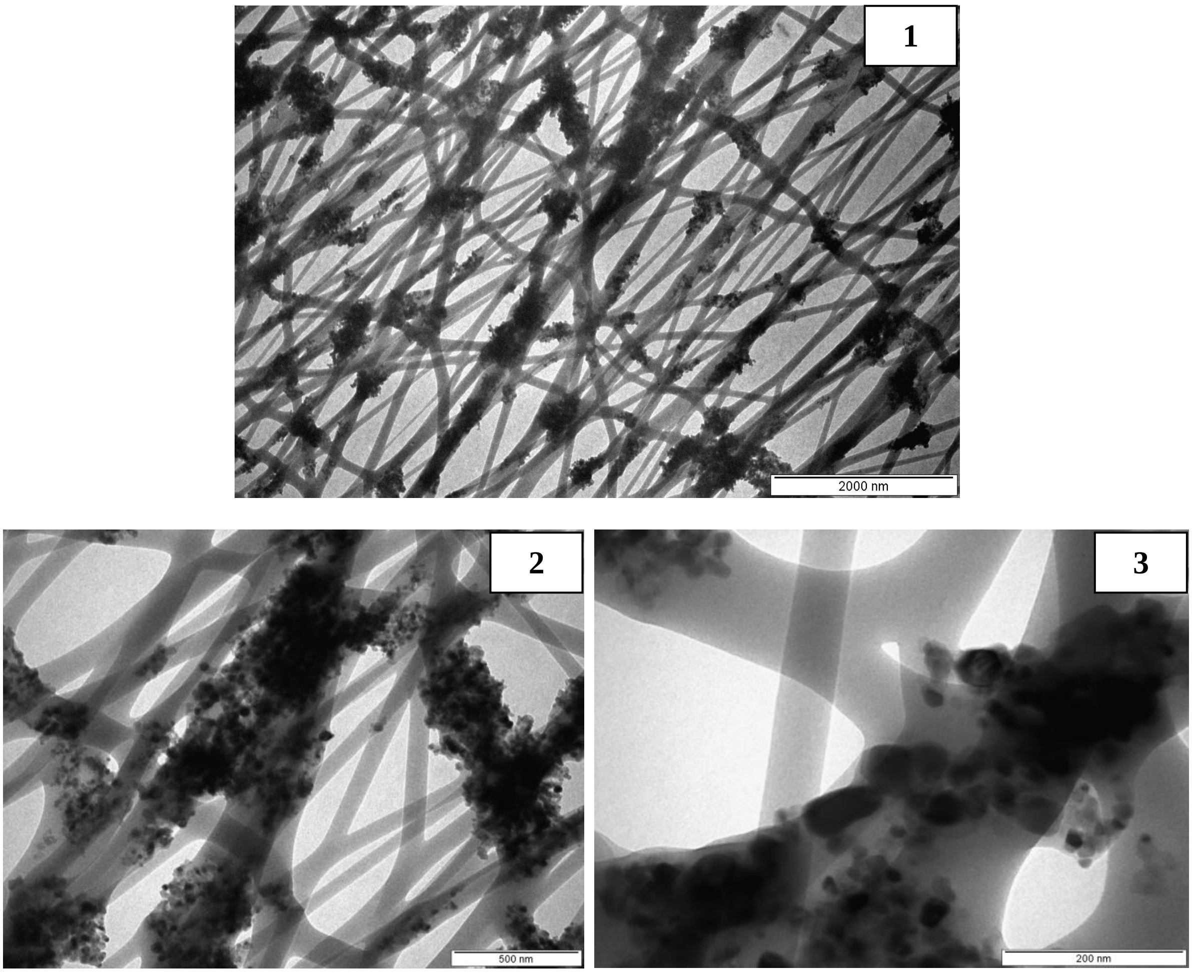


Figure 40. TEM images of the PU nanofibers with 5% of TiO_2 nanoparticles.

The Fig. 40(3) is particularly interesting. This TEM image shows that some particles of TiO_2 are incorporated inside of fibers. They are covered by the polymer layer. It means that some amount of the used catalyst is not available for the contact with the molecules of gases and won't take part in the photocatalytic reactions. The incorporation of the selected nanoparticles contributed to the increase of the average diameters of modified nanofibers in comparison with a pristine PU layer (Tab.20). However the increase of this characteristic doesn't lead to the deterioration of the uniformity of diameters distribution (uniformity coefficient in Tab.20).

Sample	Number average A_n (nm)	95% Confidence	Weight average A_w, (nm)	Fiber uniformity coefficient K (Aw/An)
Pristine PU	196	5.4	210	1.07
PU + 5% TiO_2	306	7.2	324.5	1.06

Table 20. Results of measurement of fibers diameters and calculation of uniformity coefficients.

No significant difference was found in the filtration efficiency of the pristine (99.8%) and modified PU layers (99.6%).

4.1.2. Catalytic properties of nanofibrous layer with titanium dioxide

It was found out that nanoparticles of TiO_2 at the surface of PU nanofibers exhibit photocatalytic properties and promote the oxidation of NO_x gases. The change of NO_x concentrations in contact with the modified sample is presented in Fig. 41. Let's remind that the efficient photocatalytic reaction includes five stages: (1) diffusion of reactants to the catalytic surface, (2) adsorption of reactants onto the surface of catalyst, (3) photocatalytic reaction on the surface of catalyst (semiconductor), (4) desorption of products and (5) diffusion of products from the surface of semiconductor. It is obvious that no catalytic reaction can take place at the surface of nanofibers without catalyst. The green curve (Fig.41) demonstrates the behavior of NO_x concentrations in the presence of pristine layer of PU nanofibers (without TiO_2). The quick diffusion and adsorption of gases occur on the surface of non-modified sample. Then we observe comparatively fast desorption and reverse diffusion of the adsorbed compounds. But the most important stage of the photocatalytic process (reaction on the surface of catalyst) doesn't occur. The red curve shows the behavior of NO_x concentrations at the surface of sample with TiO_2. It is obvious that the absorbed molecules of NOx react with the selected catalyst under the influence of UV lamp because the values of NO_x concentrations decreases and then remains stable during the end of test. So it indicates that all five stages of the efficient photocatalytic reaction take place simultaneously at the surface of PU nanofibers with the nanoparticles of TiO_2.

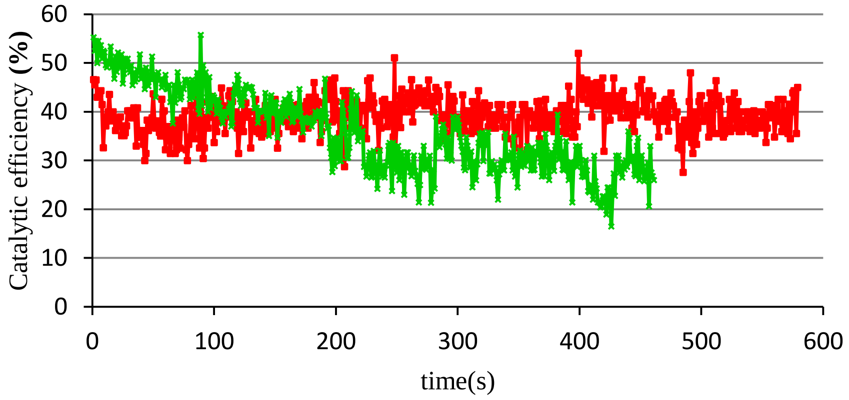


Figure 41. Comparison of photocatalytic efficiency of the pristine PU layer (green curve) and modified PU nanofibers with TiO_2 (red curve).

The catalytic efficiency of PU filter with TiO_2 in the reaction with NO_x isn't high (average value is 37%). The nanoparticles of TiO_2 themselves or at the surface of another carriers with the developed porous structure (silica, alumina, clays, activated carbon) exhibit much higher efficiencies in the photocatalytic reaction with NO_x. As it was presented in Fig. 40(3) some part of the incorporated particles was placed inside of nanofibers. So some amount of the catalyst wouldn't involved in the interaction with harmful gases during catalytic test. It means that we were dealing with the isolated active sites. Moreover it should be mentioned that the modified nanofibers didn't exhibit photocatalytic efficiency in the reaction with carbon monoxide. Therefore we continued the investigations in order to find a suitable catalyst for the modification of PU nanofibers, which would provide photocatalytic activity in reactions with both NO_x and CO. In the next chapter another photocatalyst in the micro-sized state will be presented. Perhaps this approach will help to overcome the problem of the formation of isolated active sites inside of nanofibers.

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

4.2.1. Viscous and conductive properties of modified PU solutions

We determined the changes of surface tension and conductivity of PU solutions with different concentrations of SnO_2/CrO_2 (Tab. 21). We observed the increase of the surface tension of polyurethane solutions with the growth of catalyst concentrations. Some variations appeared in the conductivity of polymer solutions with the incorporation of particles of metal's oxides. The values of conductivity of solutions with SnO_2/CrO_2 reduced compared to the pristine solution.

Solution properties	Concentrations of catalyst				
	0%	1%	2%	3%	4%
Conductivity (µS/cm)	610	486	587	512	478
Surface tension (mN/m)	51.24	55.73	57.09	57.71	62.84

Table 21. Values of surface tension and conductivity of PU solutions with different concentrations of SnO_2/CrO_2.

The average viscosity of PU solution increased with the adding of catalysts (Fig.42,a). The variation of viscosity with the share rate was investigated. The Fig. 42 (b) demonstrates that the viscosity is decreased with the increase of the share rate for all studied solutions.

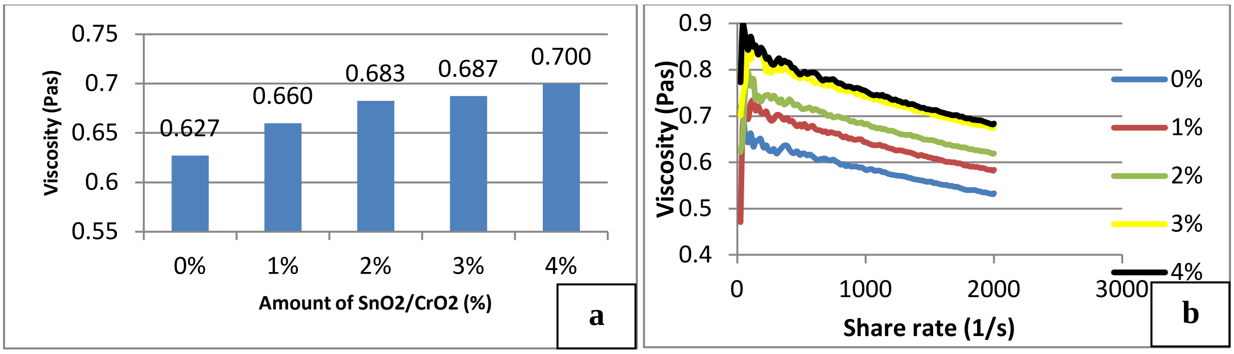
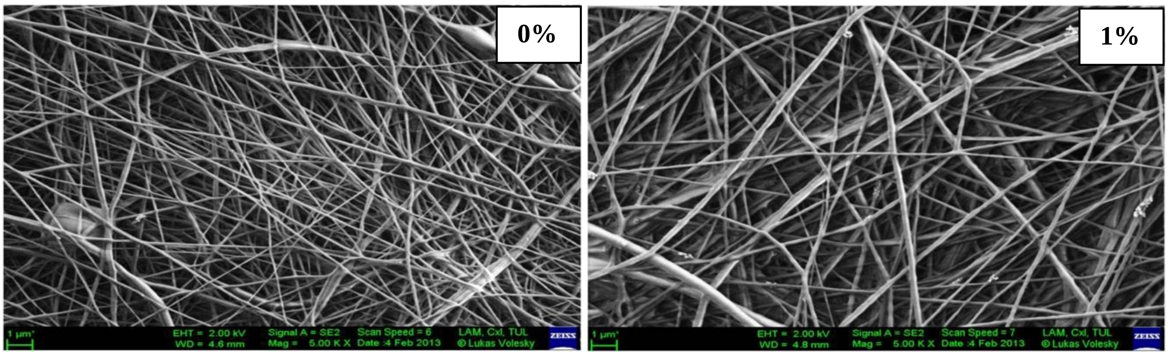


Figure 42. a - dependence of the viscosity of the PU solutions on the concentration of incorporated catalyst; **b** - the change of viscosity with the share rate.

It can be concluded that the incorporation of metal oxides particles influenced the properties of PU solution. But as we will see in the next sub-chapter, this influence has virtually no negative impact on the structural and dimensional properties of the future fibrous layers at the selected concentrations of modifier. So, the use of SnO_2/CrO_2 at certain concentrations for the modification of PU solution does not hinder the process of electrospinning.

4.2.2. Structure of modified nanofibrous samples

There are the SEM images of PU nanofibers containing 0; 1; 3; 4% of SnO_2/CrO_2 respectively in the Fig.43. The well-defined and bead-free nanofibers were obtained by the electrospinning from the colloidal solutions with various amounts of photocatalytic additive. We observed the thickening of diameters of the sample with 1% of the catalytic agent. But there is no increase of the diameters of samples with 3 and 4% of SnO_2/CrO_2 in comparison with pristine PU nanofibers.



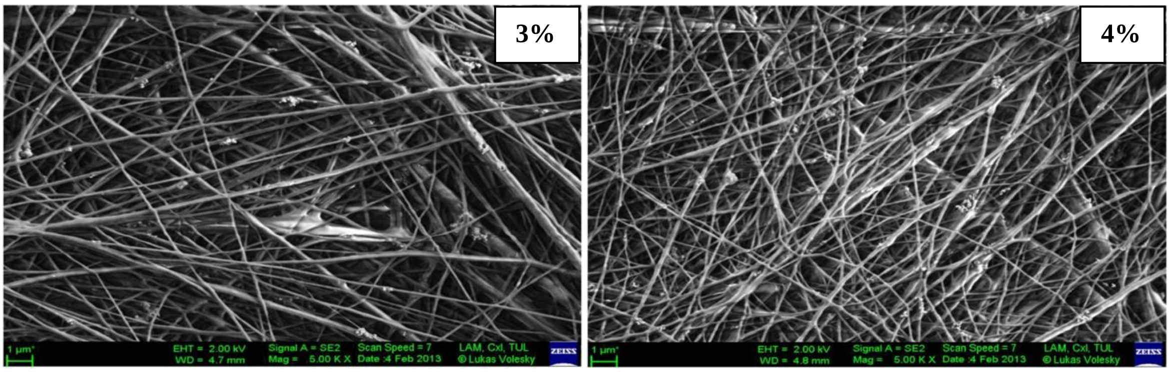


Figure 43. SEM images of the samples of PU nanofibers with various concentrations of SnO_2/CrO_2 (magnification ×5000).

These visual remarks are consistent with the calculations of the average diameters using Lucia 32G computer software. 300 different values were measured for each sample. The effect of catalyst concentrations on the average diameters of polyurethane nanofibers is presented in the Fig. 44. There is one interesting tendency. The small concentrations of catalyst (1 and 2%) lead to the insignificant thickening of diameters of the nanofibers. But the further increase of concentrations of SnO_2/CrO_2 (3 and 4%) has an opposite influence on the dimensional characteristics of modified nanofibers. The average diameters of the samples with 3 and 4% of the catalyst are smaller than the respective characteristic of the pristine PU layer.

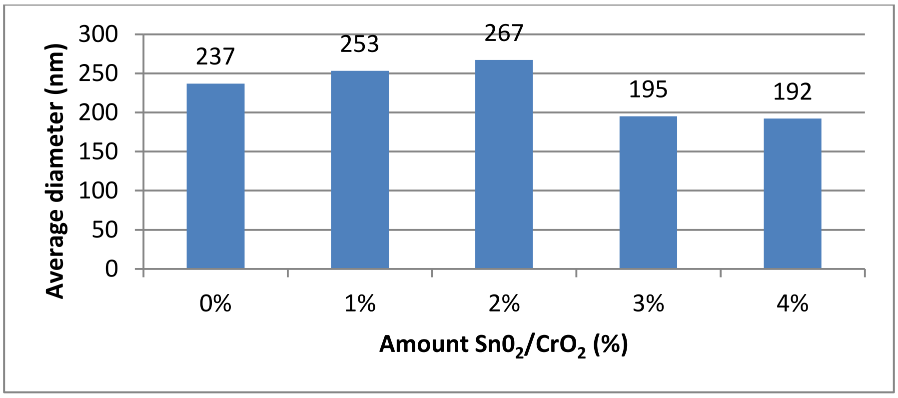


Figure 44. Dependence of the average fiber diameters on the concentrations of SnO_2/CrO_2.

The fiber uniformity coefficients were increased significantly with the adding of SnO_2/CrO_2. Based on the computations in Tab. 22 we can conclude that the produced fibers are fine and uniform; and the incorporation of the selected particles has no significant negative effect on the structure and dimensional charecteristics of modified fibers.

Sample	Number average A_n (nm)	Weight average A_w, (nm)	Fiber uniformity coefficient K (Aw/An)
Pristine PU	237	250	1.05
PU + 1% SnO_2/CrO_2	253	277	1.09
PU + 2% SnO_2/CrO_2	267	289	1.08
PU + 3% SnO_2/CrO_2	195	216	1.1
PU + 4% SnO_2/CrO_2	193	212	1.1

Table 22. Results of measurement of fibers diameters and calculation of fiber uniformity coefficients.

To ensure that the added particles were really presented at the surface of nanofibers, SEM-EDS analysis was carried out with the pristine and modified PU nanofibers (Fig. 45). The detection of C, N, O, Br corresponds with the chemical composition of PU solution with TEAB. The extra peaks responsible for tin were also detected by the EDX analysis. The indicated peaks of Sn confirmed that the catalytic particles were captured by the needles of cylinder body from the dish with polymer solution during the electrospinning process.

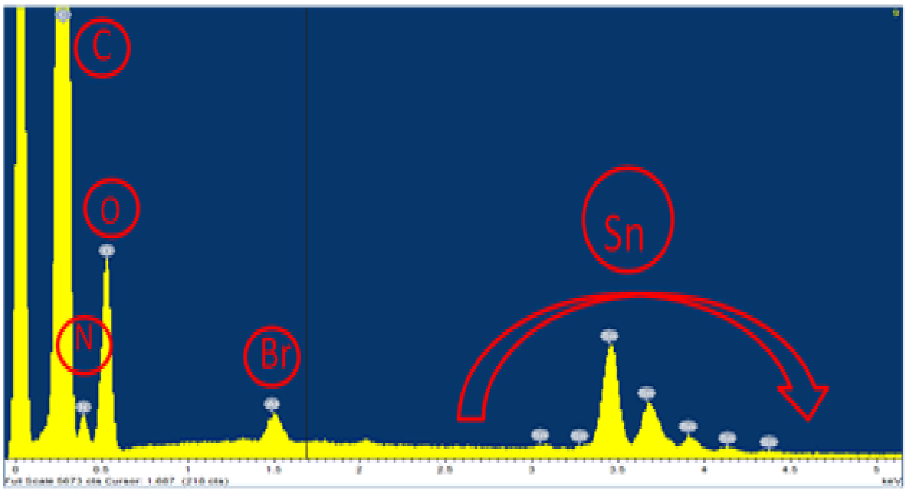


Figure 45. The EDS area of the modified nanofiber mat with 4% SnO_2/CrO_2.

The EDS maps showed the homogeneous distribution of tin particles at the surface of fibrous layers. The location of green points corresponds with the location of the main catalytic agent at the samples with 1 and 4% of SnO_2/CrO_2 in Fig. 46. The uniform particles distribution means that the surface of fibers may provide stable catalytic activity, and the whole surface may be involved into the photocatalytic process.

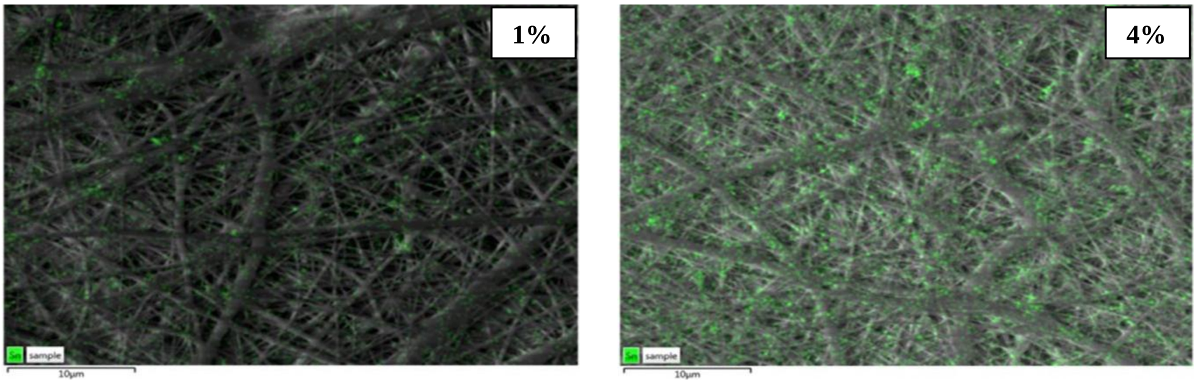


Figure 46. EDS maps of the modified fibers where Sn particles (1 and 4%) are represented in the form of green points.

The surface density of fibrous layers with different concentrations of catalyst was calculated. According to the obtained data the surface density of sample with 0% = 4.5 $\frac{g}{m^2}$; 1% = 3.82 $\frac{g}{m^2}$; 2% = 3.87$\frac{g}{m^2}$; 3% = 4.57$\frac{g}{m^2}$; 4% = 4.54$\frac{g}{m^2}$. So the used modifier didn't contribute to the improving of the spinning performance of PU solutions as it was observed in experiments with micro- and nanoparticles of copper oxide in the first part of thesis.

The filtration efficiency (E) of pristine PU nanofibers was 97%; the measured values of the efficiency for samples with 1 and 2%; 3 and 4% were 95% and 96% respectively. It means that the incorporation of the selected particles doesn't have significant impact on the filtration properties of polyurethane nanofibers.

4.2.3. Photocatalytic properties of nanofibers with SnO_2/CrO_2

The photocatalytic efficiency of modified nanofibers was investigated under the conditions of two different tests. In the first case the photocatalytic properties were measured in the reactions with mixture of exhaust gases produced by the engine vehicle (Fig. 38). The change of concentrations of NO_x and CO was monitored. In the second case the photocatalytic activity of nanofibers with SnO_2/CrO_2 was studied in the model conditions of the CO oxidation in the mixture with pure air.

The results of tests with vehicle engine. The catalytic activity has been calculated as a ratio of the concentrations of measured components before and behind the filter. The sample without catalyst absorbs a small amount of NO_x (Tab. 23). The modified samples exhibit 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.

Sample	CO (%)	NOx (%)
Pristine PU	0	1,5
PU + 1% SnO_2/CrO_2	46	40
PU + 2% SnO_2/CrO_2	49	41
PU + 3% SnO_2/CrO_2	81	73
PU + 4% SnO_2/CrO_2	79	72

Table 23. The average catalytic efficiency of pristine and modified samples with SnO_2/CrO_2.

The changes of CO and NO_x concentrations at the surfaces of pristine and modified nanofibers under the influence of the UV irradiation are presented in the Fig. 47 and 48.

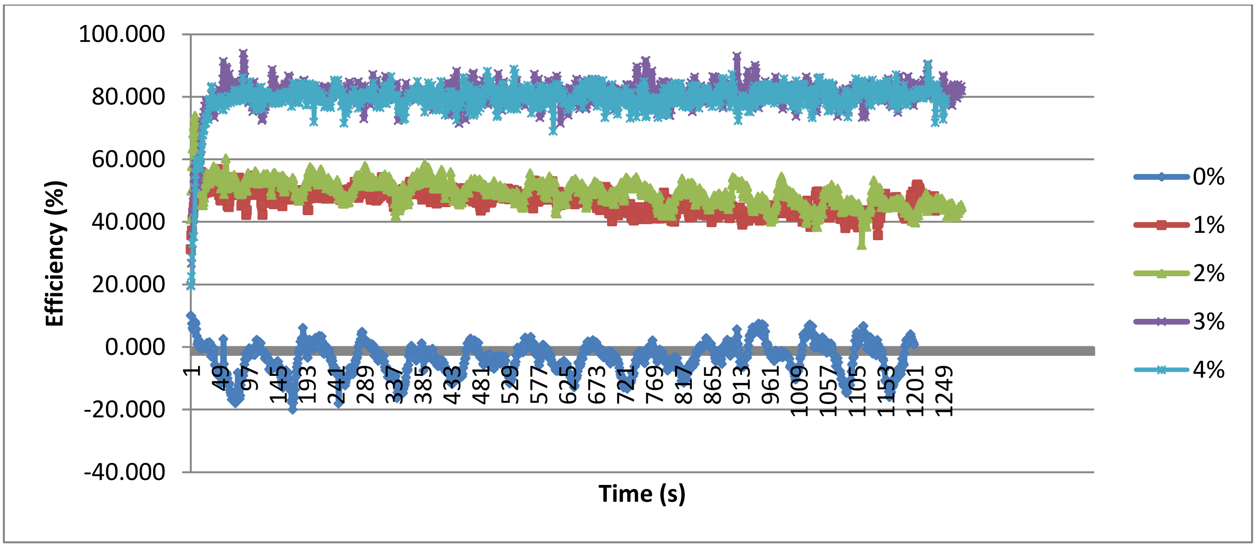
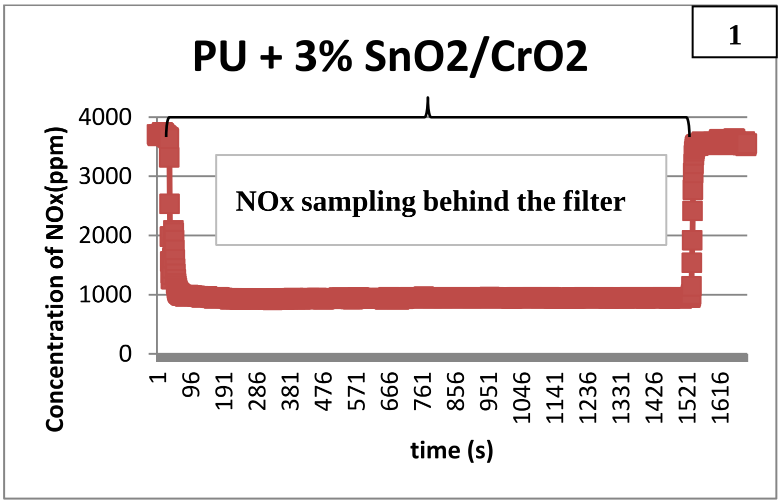


Figure 47. Photocatalytic efficiency of samples in the reaction with CO (test with the exhaust gases).

There is the example of behaviour of the produced samples in contact with CO in the Fig.47. The pristine PU nanofibers don't exhibit the photocatalytic efficiency in contact with CO. 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. There is no significant difference in the photocatalytic efficiency of nanofibers with 1 and 2% of SnO_2/CrO_2. The same conclusions can be done about the samples with 3 and 4% of the additive. So the concentration 3% is more appropriate and can be selected as optimum for the modification of PU nanofibers from the point of view of the photocatalytic efficiency and economic reasons.



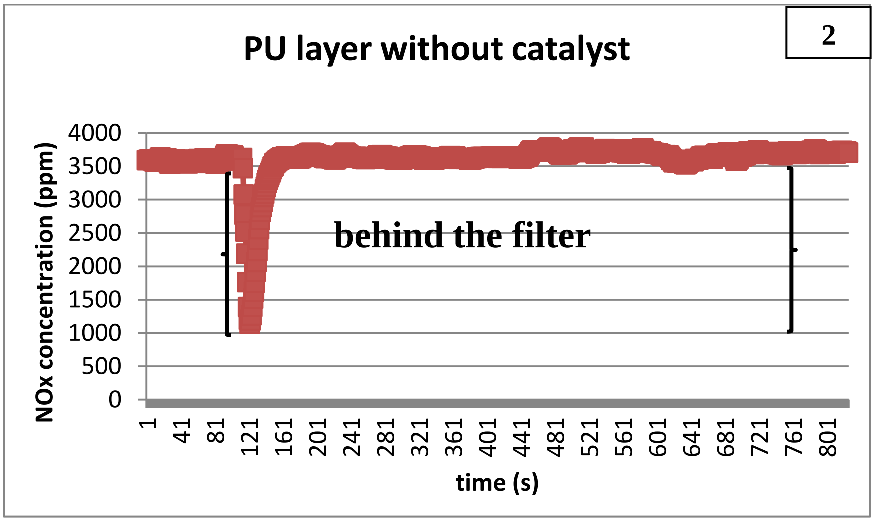


Figure 48. Change of NO_x concentrations in contact with (1) sample with 3% SnO_2/CrO_2 and with (2) sample of pristine PU nanofibers.

The change of NO_x concentrations in contact with the surface of the modified (with 3% of catalyst) and pristine layers is shown in Fig.48 (1 and 2). The sampling of gases behind the pristine nanofibers (Fig. 48 (2)) is marked by two black brackets. We observe the adsorption (sharp decrease of the monitored concentration) of NO_x at the surface of the unmodified sample at the beginning of sampling. But then the desorption process starts and the concentration of NO_x becomes the same as in position "sampling before the filter". So no catalytic reactions take place at the surface of PU nanofibers without SnO_2/CrO_2. The opposite situation is presented in Fig. 47 (1). Here we observe the adsorption of NO_x at the surface of sample with catalyst. An adsorption process is demonstrated as a sharp decrease of NO_x concentration from 3900 ppm to 1000 ppm at the beginning of the measurement in Fig.48 (1). Then the NOx concentration remains stable (around 1000 ppm). In this section of the graph we see the photocatalytic reaction at the surface of nanofibers with 3% of SnO_2/CrO_2 under the influence of UV irradiation. The irreversible desorption process starts when the flow of emission gases is switched to the position "sampling before the filter". And concentration of NO_x turns back to the initial values. According to the experimental results the PU nanofibrous layer with 3% of SnO_2/CrO_2 (95/5) could be offered as a filtering material for the air purification from CO and NOx. Such positive conclusions were done based on the experimental data about the structural and catalytic properties of the sample under the conditions of CO and NOx oxidation reactions in the mixture of exhaust gases. It's obvious that the modified PU nanofibers cannot serve as automotive filters. But the air-conditioning systems are a perspective variant for the application of our materials. However, the used test's conditions with high initial concentrations of CO (≈4500 ppm) and NOx (≈4000 ppm) are not the most appropriate for the testing of filters for air-conditioning systems. A basic level of CO in the atmosphere is 0.1 ppm; an average level in houses and buildings is 0.5-5 ppm; a level of car exhaust in the centre of megapolises is 100-200 ppm. So the efficiency of our modified filters must be confirmed under the testing conditions with lower initial concentrations of harmful gases. The suitable measurement set-up was found at the research centre Mines Ales Centre of Materials (C2MA) of Ecole des Mines d'Ales (EMA) in France (Fig.39).

The results of tests under the model conditions of CO oxidation in the mixture with air. The further experiments with nanofibers modified by SnO_2/CrO_2 were carried out using the measurement set-up which was presented in Fig. 39. 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). Unfortunately 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. In this part of our research we used microparticles of SnO_2 and CrO_2. When we found that the PU nanofibers with the selected combined micro-sized catalyst are not suitable for the photocatalytic oxidation of CO under the desired parameters, we decided to try a slightly different approach to the solving of the assigned task. As it was already mentioned in the chapter Theoretical part the coupling of SnO_2 (3.6eV) with the metal's oxides with lower band gaps contributes to easier migration of the photogenerated electrons from SnO_2 to another semiconductor. NiO is a good candidate for the coupling with SnO_2. It's band gap is 1.8eV.

4.3. 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. Their phase compositions and crystalline structures were studied. All produced powders were tested to determine their ability to eliminate some carbon monoxide from the air flow. When we did the literature analysis in order to understand the mechanism of photocatalytic oxidation of carbon monoxide, one intersting tendency was found out. As it was already mentioned in the Theoretical part, the role of water vapour in the studied reaction is not clear. Some scientists affirm that water enhances the photoadsorption of oxygen by trapping of the photogenerated holes and OH^- sites. Others convinced that water molecules compete with substrate molecules (with molecules of O_2) for the active sites at surface of photocatalyst. Therefore we decided to investigate the effect of water vapor on the photocatalytic oxidation of CO depending on the particle sizes (micro and nano) of the used catalyst and make our own conclusion about the role of H_2O in this reaction. Moreover the synthesized micro- and nanoparticles of SnO_2/NiO were also used for the modification of PU nanofibers in order to impart them photocatalytic activity.

The results of XRD analysis showed that the peak positions of each sample exhibit the rutile type tetragonal structure of SnO_2 which were confirmed from the ICDD card. No other impurities (except NiO peaks) were observed in the XRD pattern showing the single phase sample formation. The crystallinity of SnO_2 was not changed by the adding on nickel and by the use of pretreatment of powders after the synthesis (drying, calcination).

The microparticles of undoped SnO_2 (without NiO) did not exhibited catalytic properties in the studied reaction (Fig. 49 and 50). 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. 49). But this tendency remains only up to 30% of the relative humidity. It was found out that the doped microparticles had the highest removal efficiency of CO under the RH range 25-30% (Fig. 49 and 50). The sharp decrease of the catalytic efficiency to zero values was observed when the relative humidity had enhanced to 50%.

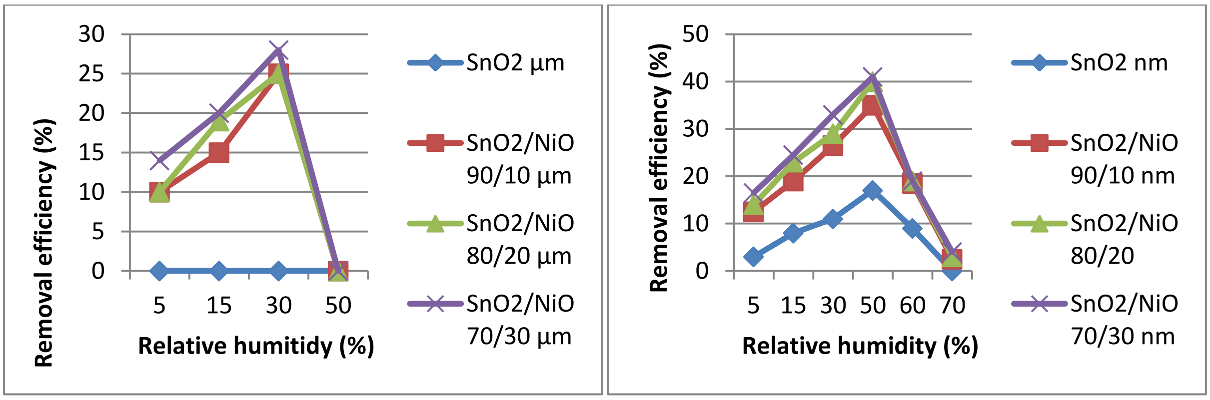


Figure 49. Dependence of the photocatalytic efficiency of micro- and nanoparticles of SnO_2/NiO on the relative humidity under the flow rate 500 ml/min; the initial CO concentration 20 ppm.

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%.

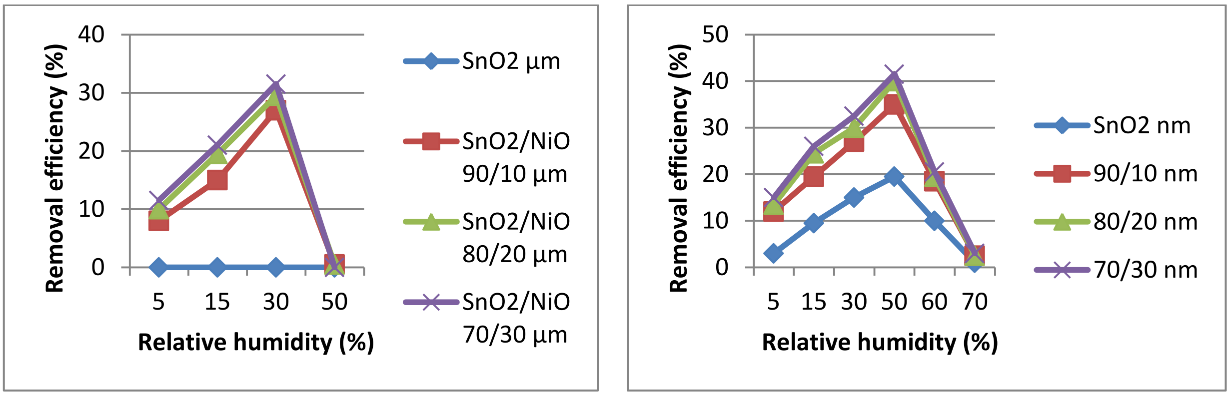


Figure 50. Dependence of the photocatalytic efficiency of micro- and nanoparticles of SnO_2/NiO on the relative humidity under the flow rate 1250 ml/min; the initial CO concentration 200 ppm.

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 measured values of the 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.

5. Conclusions

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 TiO2 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. First of all it was confirmed due to the TEM images that some amount of nanoparticles of TiO_2 was fully trapped inside of fibers. So such isolated particles are not involved in the photocatalytic reaction. Moreover it was also proved that nanoparticles form big aggregates at the surface of our filters. These two observed tendencies (isolation inside of fibers and aggregation) are much more dangerous for the manifestation of catalytic properties than in case of the antibacterial air or water purification. The availability of active sites and their geometry 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/NiO had no efficiency in the reaction of CO oxidation.

Our attempts to use microparticles for the photocatalytic modification of nanofibers were crowned with a little more success. The modified nanofibrous layers with SnO_2/CrO_2 combined catalyst in the micro-sized state exhibited quite good catalytic efficiency in the reaction with NOx and CO. Such results were obtained under tests conditions with high initial concentrations (4000 - 4500ppm) of harmful gases in the mixture of automotive emissions. But our goal was to produce filters with catalytic properties for the air-conditioning systems. Such high initial concentrations and presence of impurities don't correspond with the real content of NO_x and CO in the air. When the nanofibrous layers with MPs of SnO_2/CrO_2 were tested under the small initial concentrations of CO in the model reaction in air, it was found out that our samples have no photocatalytic efficiency under such conditions. The same results were obtained for the filters with particles of SnO_2/NiO. Therefore we can conclude that the used modification method isn't appropriate in order to impart the photocatalytic properties to the nanofibrous filters. The incorporated particles lose a big number of active sites due to the "immersion" into the structure of fibers.

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 the 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 completely 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.

6. Future perspectives

The synthesized powder SnO_2/NiO can be very perspective as a photocatalyst for the oxidation of NO_x. The selection of suitable solid porous carrier (not nanofibers or another textiles) for this photocatalyst is also interesting research topic which can be a continuation of our experiments. Moreover the determined dependence of the efficiency of SnO_2/NiO on the presence of water vapour can find a particular attention of scientists who investigate the mechanisms of photocatalytic reactions.

List of papers published by the author

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.

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**.**

Citations

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

-Wang. Z.; Xu M.; Shao L.;et al., *Palladiumimmobilized on chitosan nanofibers cross-linkes 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 Grigire, Elena Ramona Biscu, Alina Maria Holban, Monica Cartelle Gestal ans Alexandru Mihai Grumezescu, *Methods of synthesis, properties and biomedical applications of CuO nanoparticles*, In: Pharmaceuticals, Vol. 9, 2016. doi: 10.3390/ph9040075

Other results

1. Prototype Air Filter with Catalytic and Antimicrobial Effect (Filter V002), 2013.

2. Certificated methodology for the determination of bacterial filtration efficiency of textile materials (according to EU Environmental Technology Verification). Certificate was obtained from the Czech Environment Management Center.

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Appendix

Antibacterial modification of nanofibers

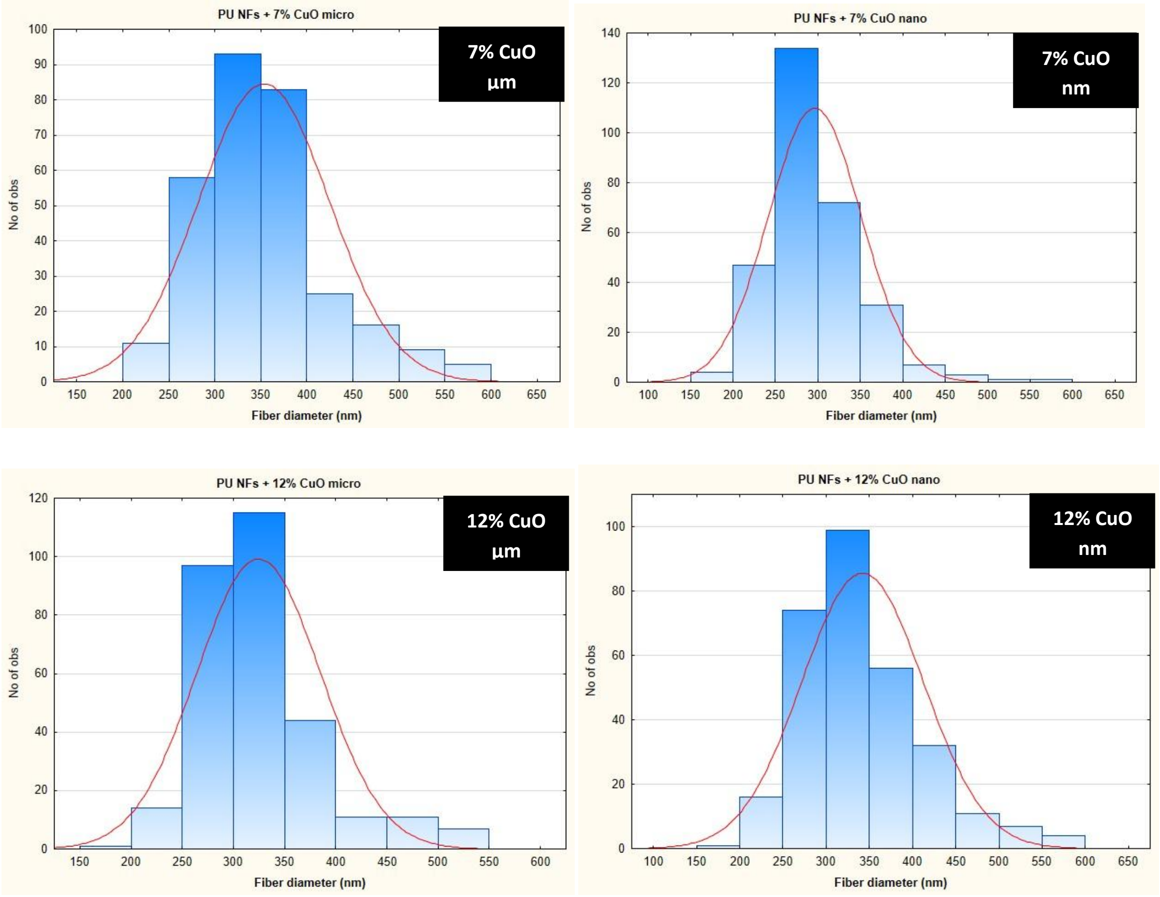
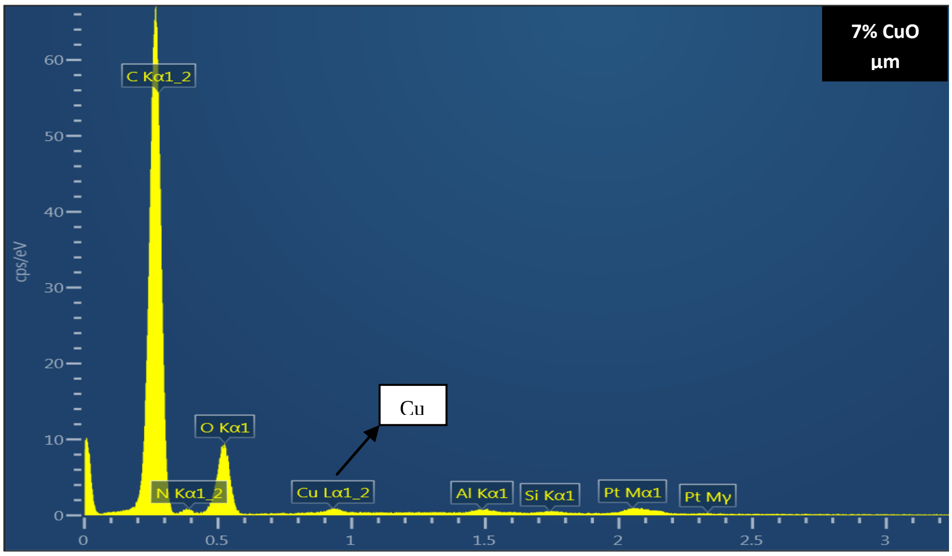
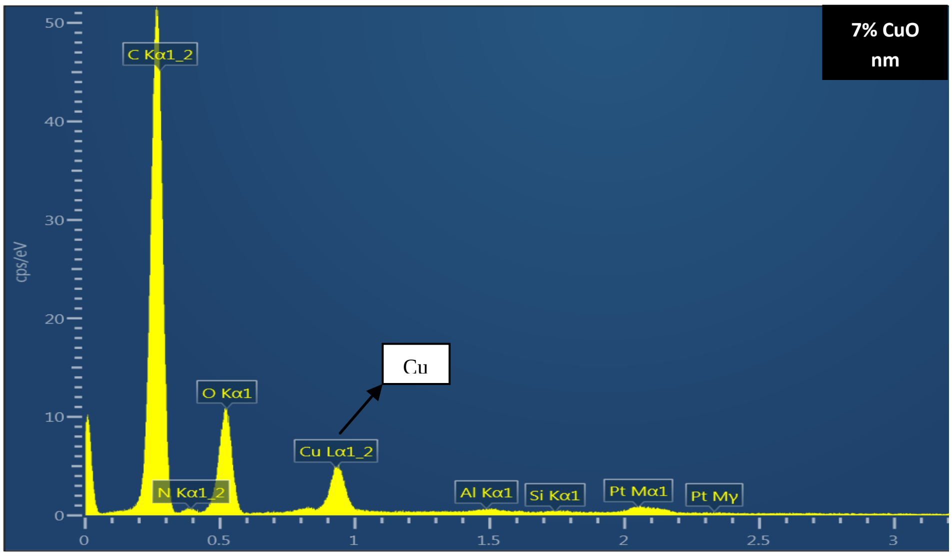
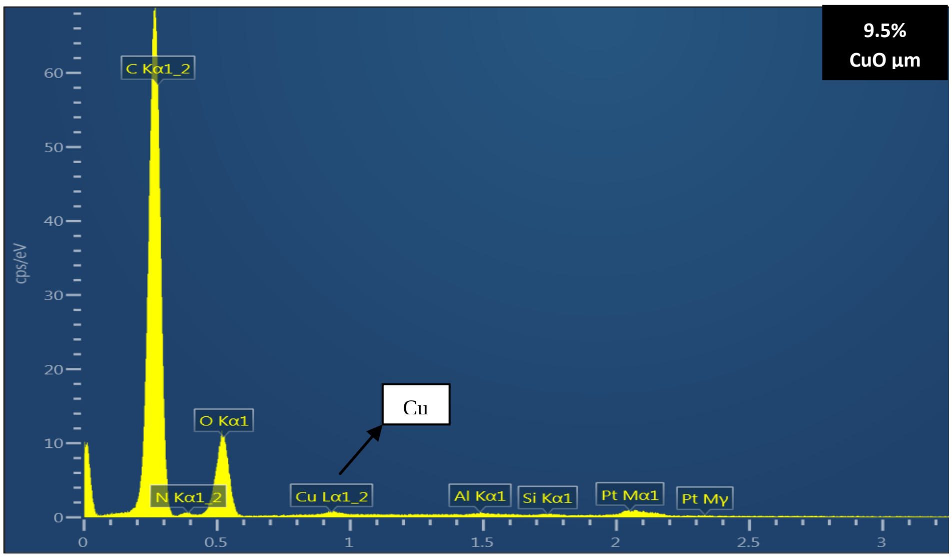


Figure 1. Diameters distribution of fibers produced from the rod ES set-up: PU + 7% CuO µm; PU + 7% CuO nm; PU + 12% CuO µm; PU + 12% CuO nm.




7% CuO
nm
cps/eV
50
40
30
20
10
0
C Kα1_2
O Kα1
N Kα1_2
Cu
Cu Lα1_2
Al Kα1
Si Kα1
Pt Mα1
Pt Mγ
0
0.5
1
1.5
2
2.5
3


9.5%
CuO µm
cps/eV
60
50
40
30
20
10
0
C Kα1_2
O Kα1
N Kα1_2
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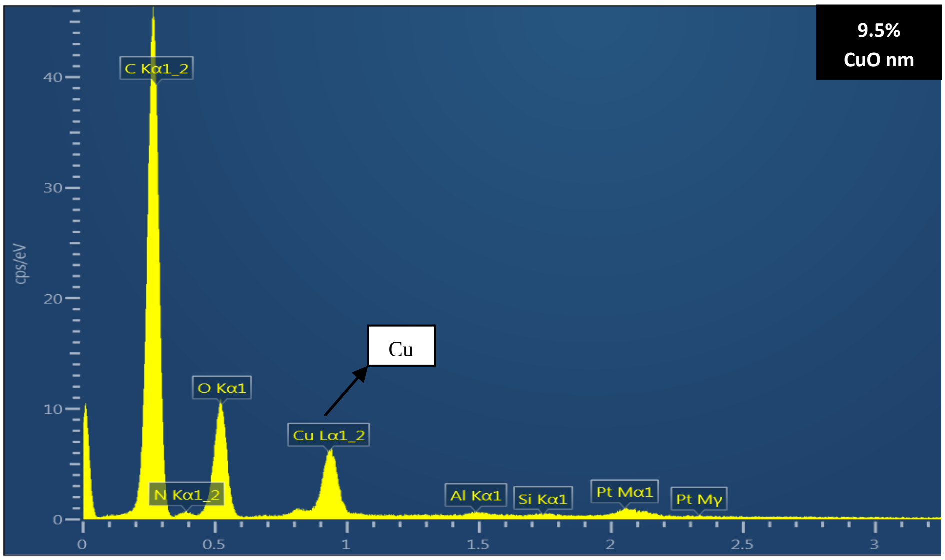
9.5%
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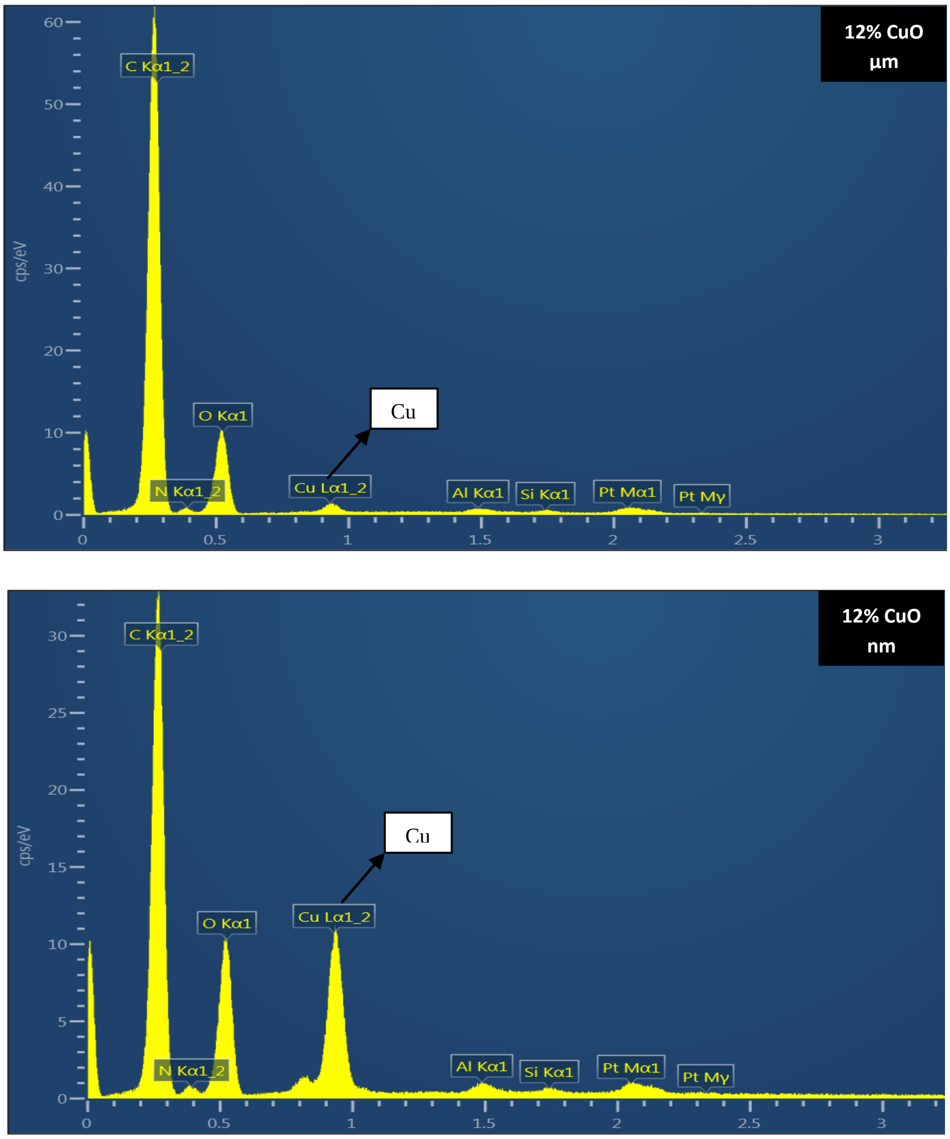
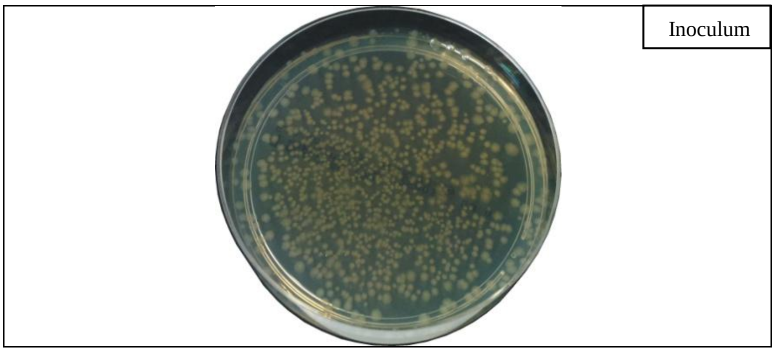


Figure 2. SEM-EDX images: areas of electrospun polyurethane nanofibers with 7; 9.5 and 12% of micro- and nanoparticles of CuO respectively (rod ES).



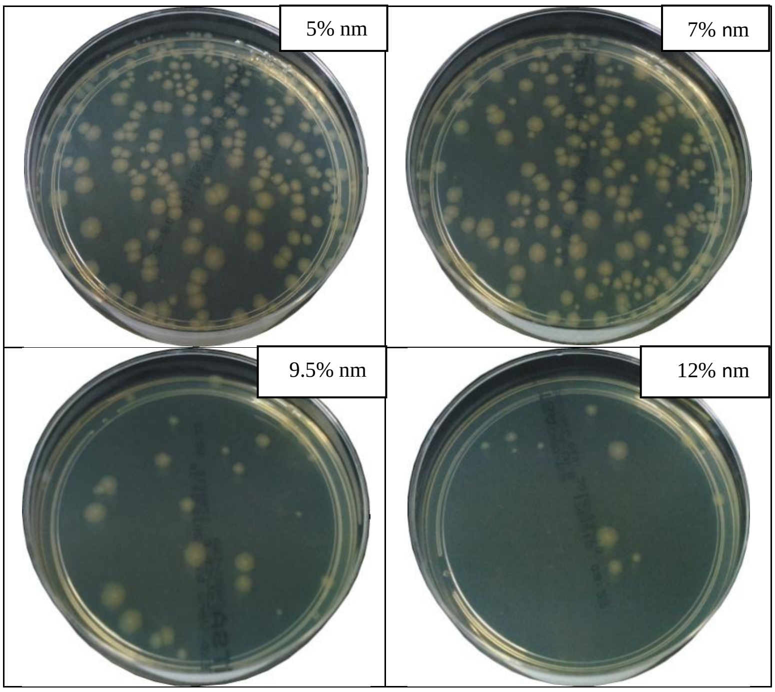
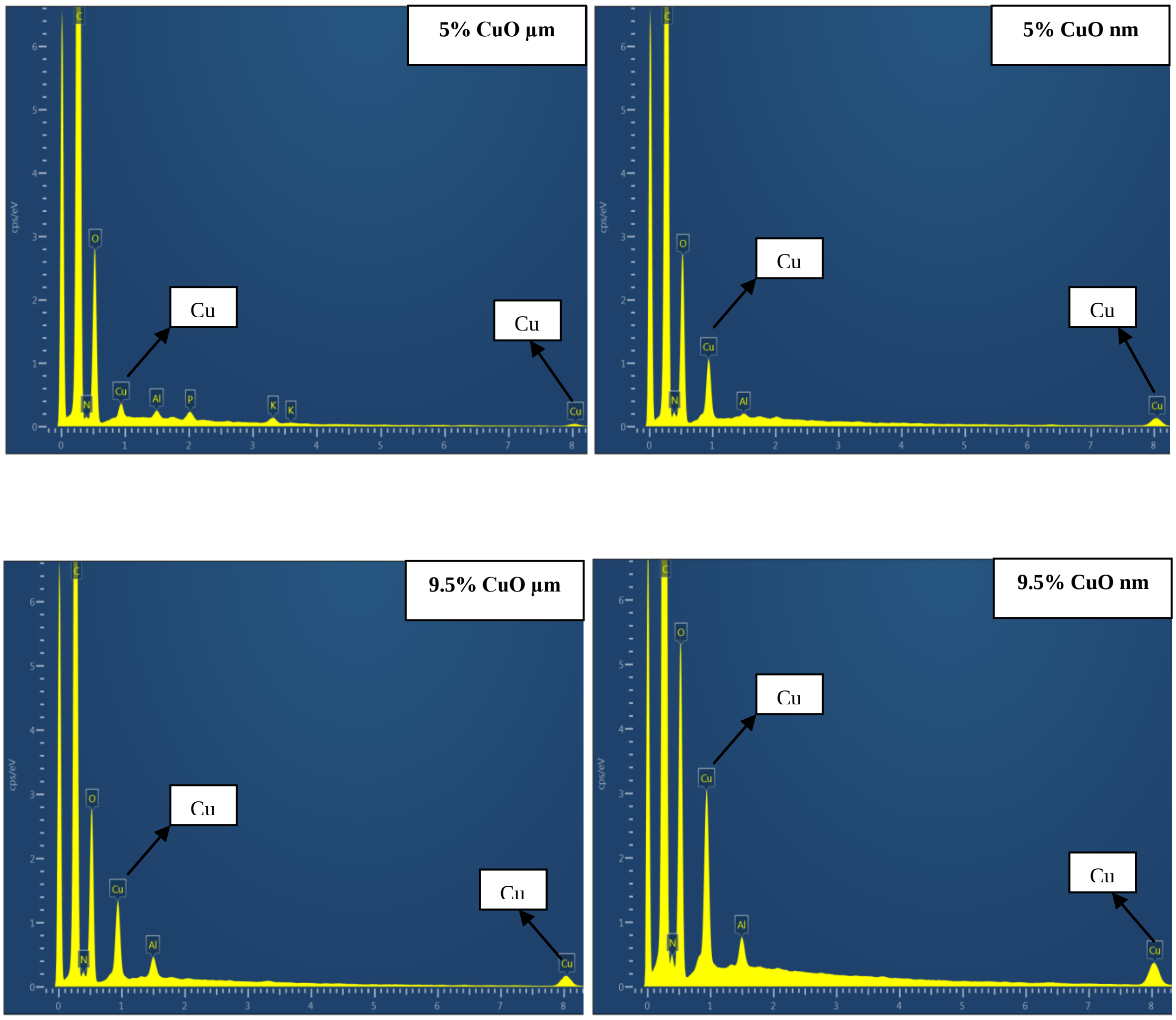


Figure 3. Images of agar plates showing the results of antibacterial test against **E.coli for samples with NPs of CuO - rod ES** (contact time 24 hours).



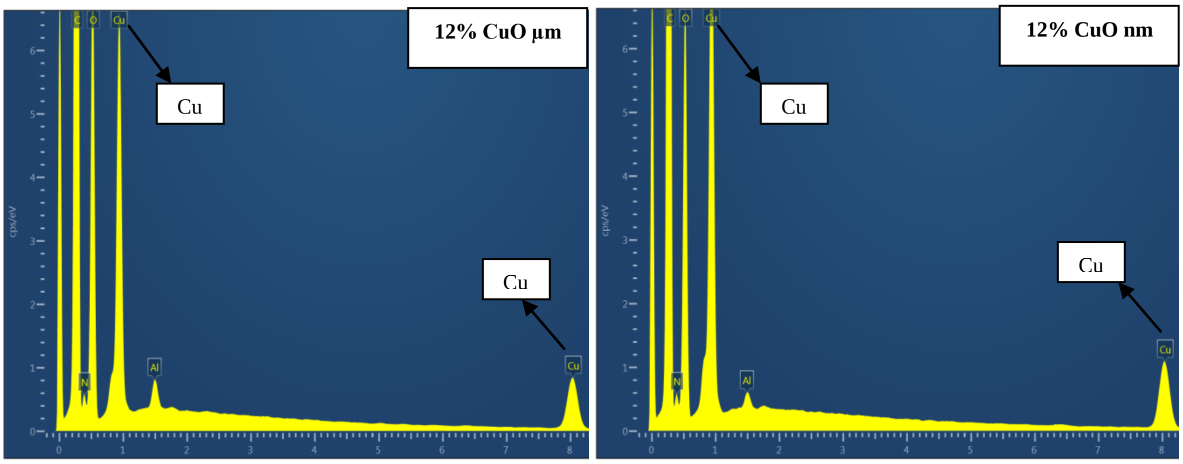
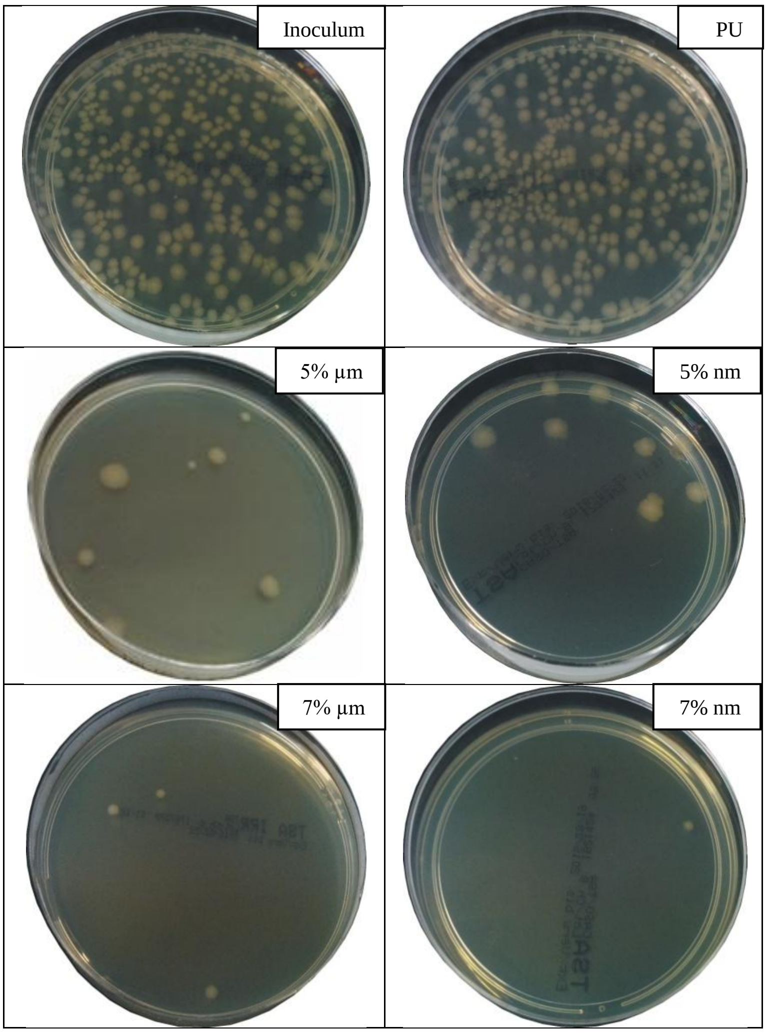


Figure 4. SEM-EDX images: areas of electrospun polyurethane nanofibers with 5; 9.5 and 12% of micro- and nanoparticles of CuO respectively (ES from rotary electrode with wire surface).



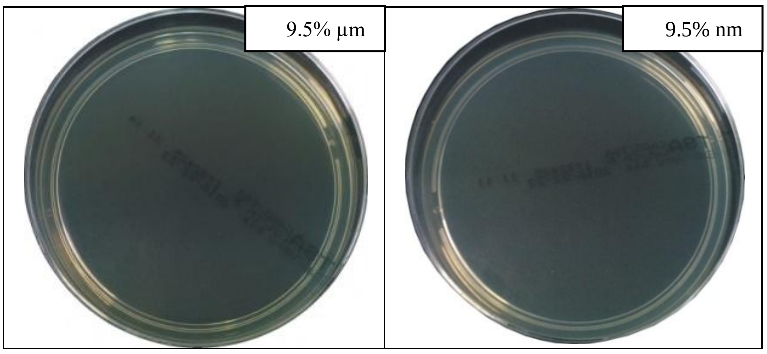


Figure 5. Images of agar plates showing the results of antibacterial test against **E.coli** of samples produced from wire electrod (contact time 24 hours).

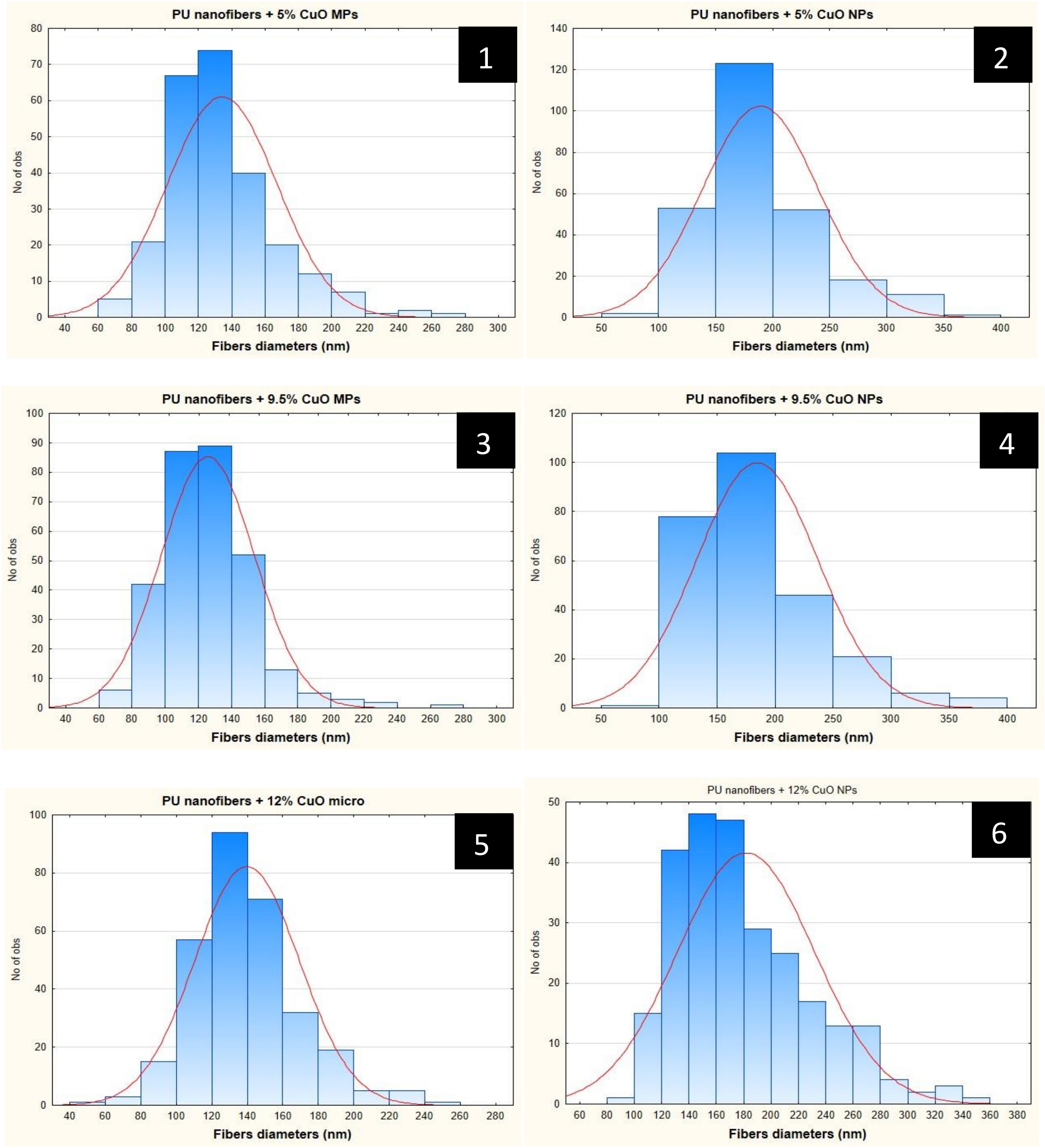


Figure 6. Diameters distribution of fibers produced from the wire electrode: 1 - PU NFs + 5% CuO µm; 2 - PU NFs + 5% CuO nm; 3 - PU NFs + 9.5% CuO µm; 4 - PU NFs + 9.5% CuO nm; 5 - PU NFs + 12% CuO µm; 6 - PU NFs + 12% CuO nm.

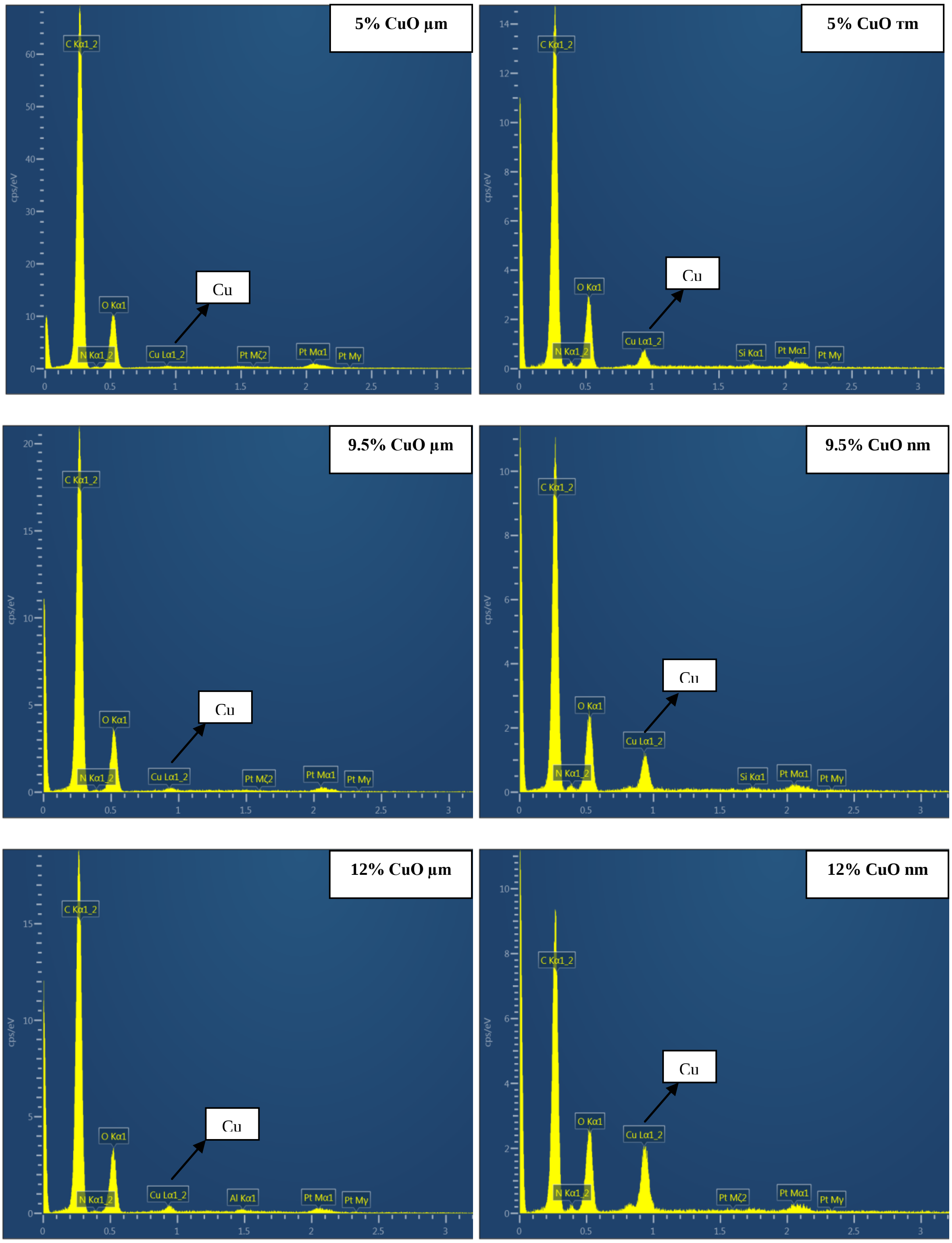


Figure 7. SEM-EDX images: areas of electrospun polyurethane nanofibers with 5; 9.5 and 12% of micro- and nanoparticles of CuO (wire electrode) respectively.

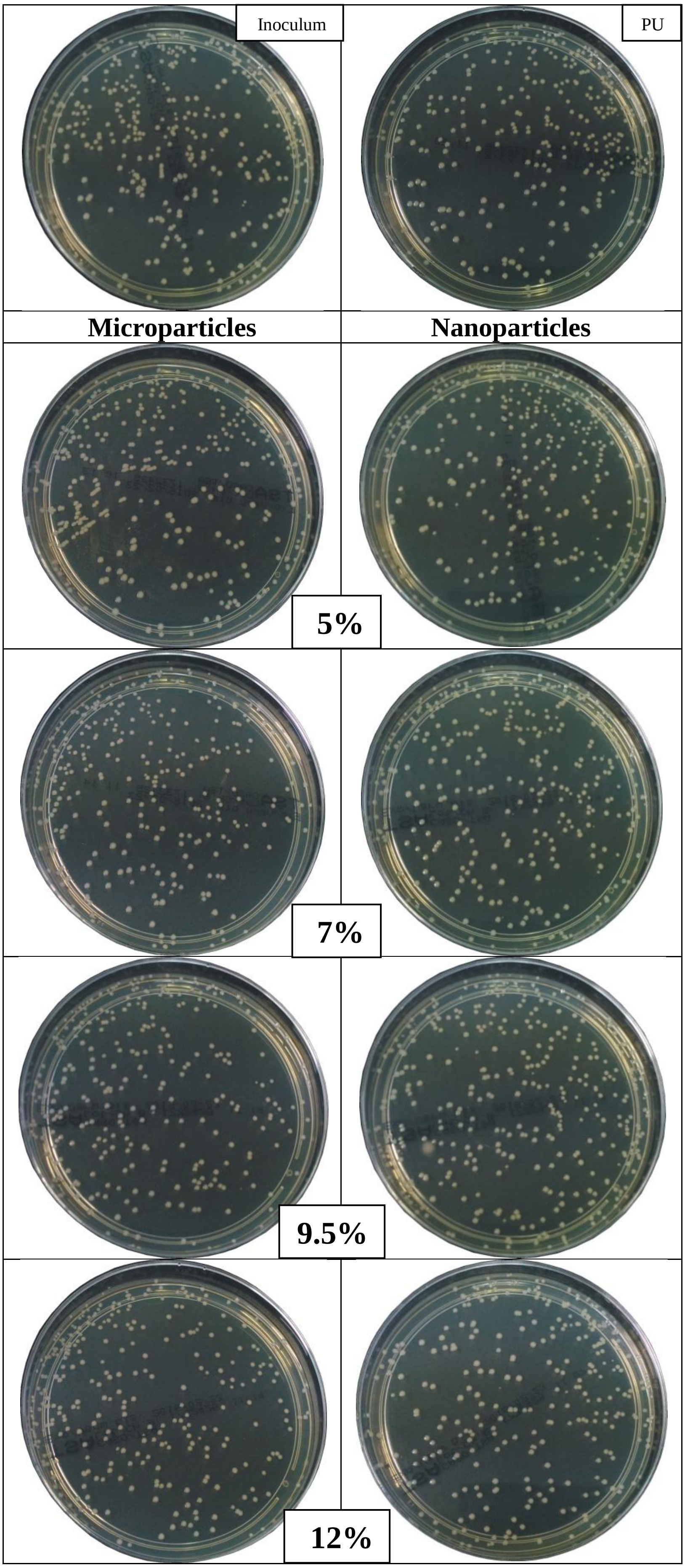
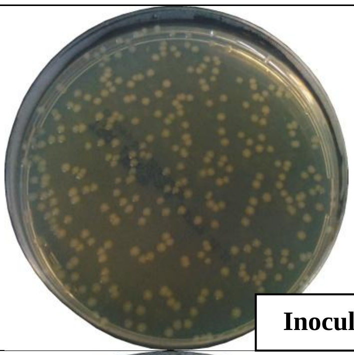
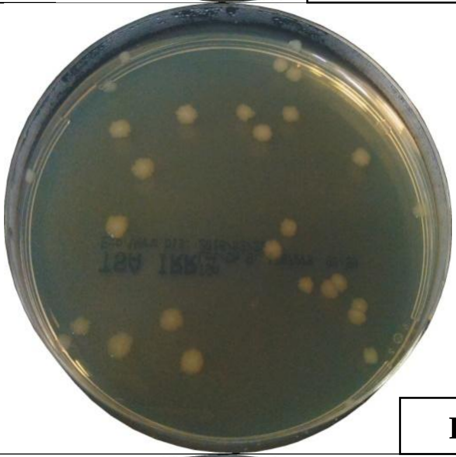
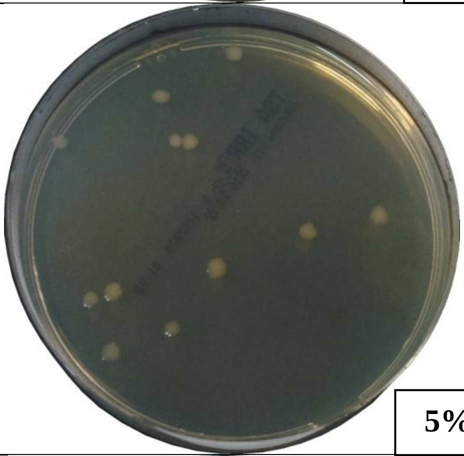
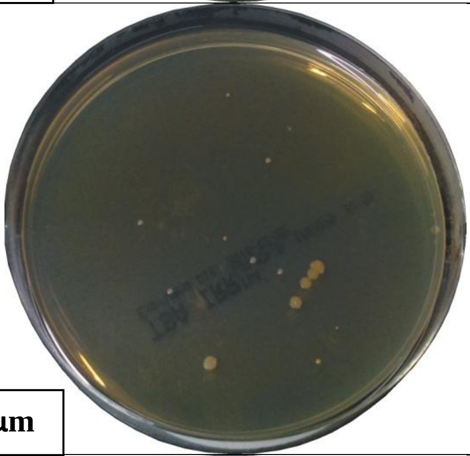
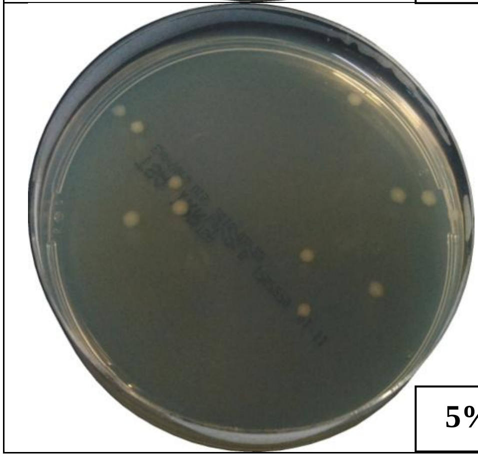
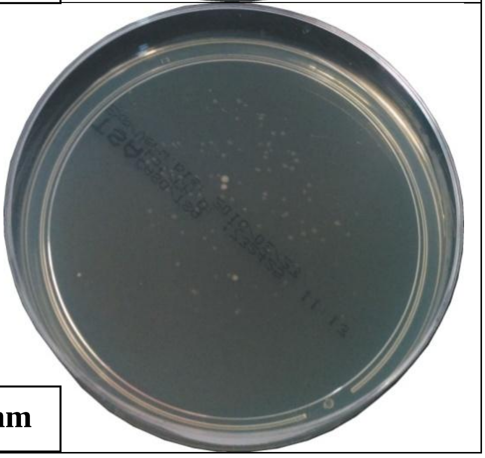
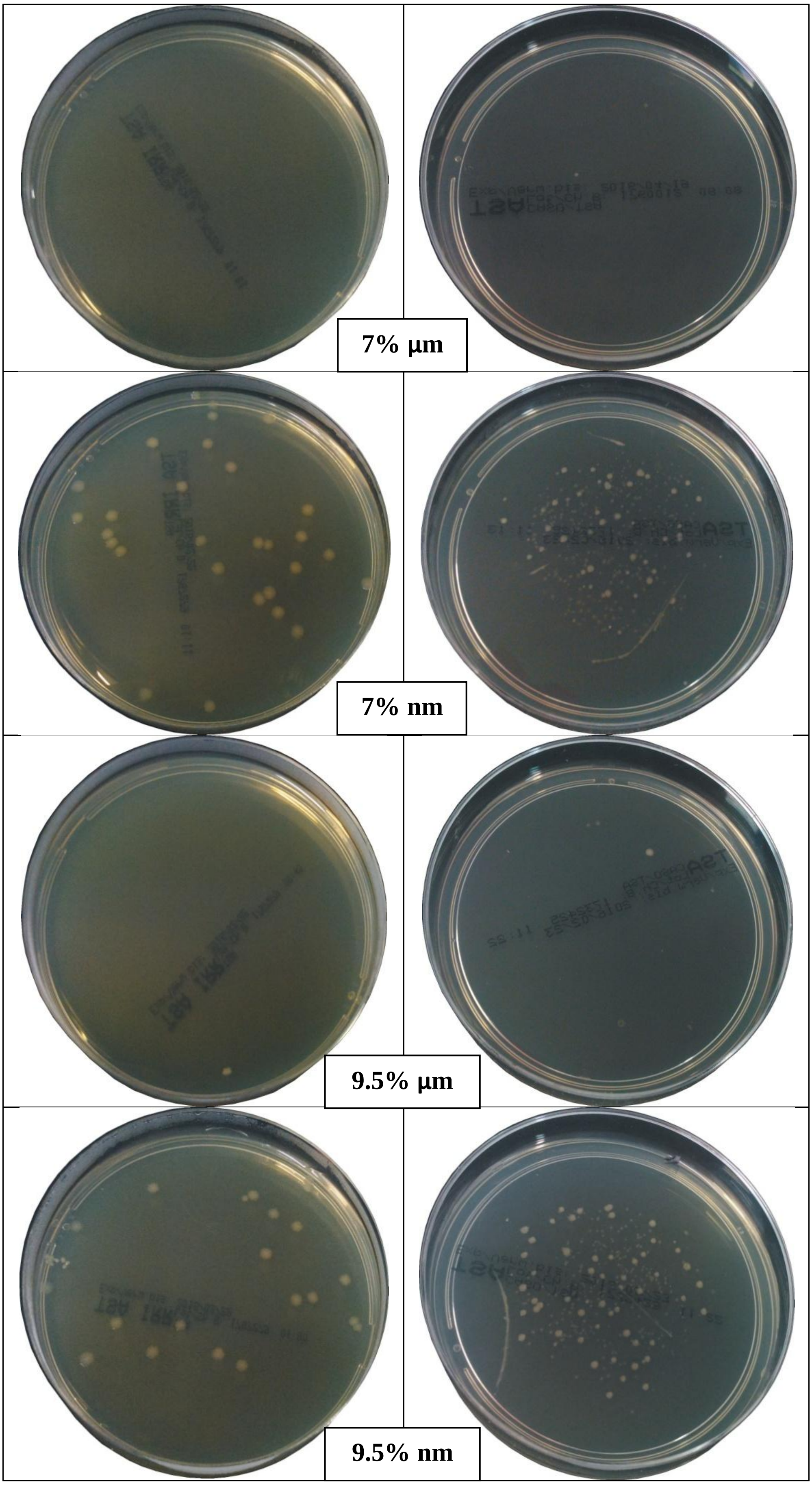


Figure 8. Images of agar plates showing the results of antibacterial test against **Staphylococcus gallinarum** (contact time 24 hours) - samples from wire electrode

Results of bacterial filtration test	Results of "smear-test"
 **Inoculum**	
 **PU**	
 **5% µm**	
 **5% nm**	


7% µm
7% nm
9.5% µm
9.5% nm

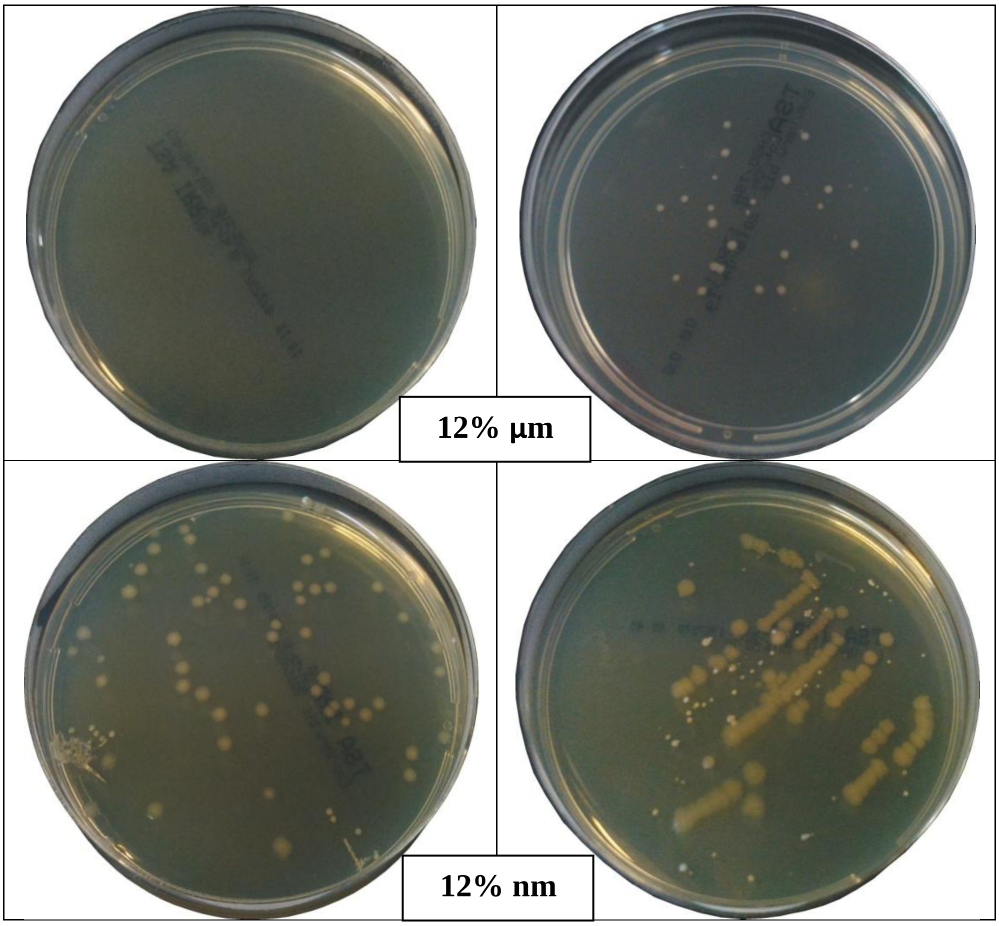


Figure 9. Images of agars after the bacterial filtration test and after the "smear-test" for all samples produced from static wire electrode.