MENDEL UNIVERSITY IN BRNO

FACULTY OF AGRISCIENCES

Department of technology and automobile transport

Use of modified nanotextiles and noparticles for filtration and treatment of contaminated water

Dissertation

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ABSTRACT

Došek M.: Using modified nanotextiles and nanoparticles for filtration and treatment of contaminated water, dissertation, Mendel University in Brno, 2016

Clean water available to all. This is one of the major challenges of the 21st century. With increasing population explosion, which goes hand in hand with industry, increasing demands for food and their production increases the need for water while increasing water pollution. The need for technological innovation in the field of water resources, allowing the efficient treatment of wastewater, along with integrated management, it is more than obvious.

This dissertation is dedicated to the cleaning and treatment of water, especially waste water, and utilizes the latest technologies in the field of water treatment using nanotechnology and nanofiber membranes. At the beginning of the dissertation is briefly introduce the description of the nanotechnology. There are presented general concepts of nanotechnology, imaging methods, history of the field, focusing on the use of cleaning and water treatment. There is also given the current legislation regarding to nanotechnology, especially in relation to wastewater treatment. There are mentioned the benefits and drawbacks which these technologies bring.

The second part focuses on the description of the mechanism of liquid filtration and type of membranes curently used for filtration, including nanofiber membranes. For the treatment and purification of water are used during the experiments mostly nanofiber membranes, which are manufactured using electrospinning methods. These membranes are designed to remove various contaminants from the aqueous medium, or concentrated solutions, depending on the characteristics and purpose membranes. Results to date indicate a wide range of potential uses of nanofiber membranes. Taking their primary purpose to which is focus the experimental part, is the development of membranes for removal of microbial contamination, concentration of activated sludge at sewage treatment plants, sewage tertiary purification, removal of various pollutants and treatment of water for irrigation.

Another option to intensify the functioning of membranes is their modifications. Membranes can be modified for example by adding various elements or antimicrobial additives, additives increasing hydrophobicity, resistance to biofouling and clogging of membranes. These include phthalocyanines, zeolites, chlorohexidine, titanium dioxide and other substances. During the experimental part was designed and proven, several modifications nanofiber membranes, which are together with the results of the filtration experiments described and also evaluated.

The third part is devoted to laboratory experiments that led to the selection of membranes for the next phase of the experiment. During laboratory tests has been selected the most suitable membranes which were subsequently used in the context of pilot plant, designed primarily to filtration and concentration of activated sludge. Pilot unit was placed on sewage treatment plants. Experiments were conducted at the WWTP Letonice, later Brno-Modřice, which took place in the context of long-term testing compared with the best

available type of membranes available on the market: hollow fibre membranes and flat sheet membranes. Results of testing are disclosed herein. In the final part are discussed the experimental results and are compared with the available literature and knowledge of other domestic and foreign authors and are clearly interpreted. Within the discuses is also proposes a number of possible applications in which these technologies can be applied in practice.

This dissertation tries to bring of the professional public issue of nanofiber membranes and nanoparticles. Demonstrates their use on a practical example in the form of a membrane bioreactor on sewage treatment plant. The output of the acquired knowledge were also impacted foreign publications listed below.

Some results presented in this study are based on data obtained from two projects in which the author during the writing of the thesis participated. These projects are: "Suitable materials for nanotechnology applications for purification and treatment of water and air," supported by a grant TA CR TA01010356 and the project "From waste to resources", supported by a grant from the National Agency for Agricultural Research: QJ1320234

Keywords: Nanostructures, Membranes, Nanoparticles, Pollutants, Biofouling, Filtration, Micro-organisms, Waste water, Activated sludge

ABSTRAKT

Došek M.: Využití modifikovaných nanotextilií a nanočástic pro filtraci a úpravu Došek M.: Využití modifikovaných nanotextilií a nanočástic pro filtraci a úpravu kontaminované vody, Disertační práce, Mendlova universita v Brně, 2016

Čistá voda dostupná pro všechny. To je jedna z hlavních výzev 21. století. S rostoucí populační explozí, která jde ruku v ruce s průmyslem, zvyšujícími se nároky na potraviny a jejich produkci vzrůstá i potřeba vody a zároveň se zvyšuje znečištění vodních zdrojů. Potřeba technologické inovace v oboru vodních zdrojů, která by umožnila efektivní čištění odpadní vody spolu s integrovaným managementem, je více než zřejmá.

Tato disertační práce je věnována čištění a úpravě vody, zejména pak vody odpadní, přičemž jsou využity nejnovější technologie v oboru membránového čištění vod s

využitím nanotechnologií, konkrétně nanovláknitých membrán. Na úvod se disertační práce stručně věnuje problematice nanotechnologií. Jsou zde uvedeny obecné pojmy z oboru nanotechnologie, zobrazovací metody, historie oboru se zaměřením na použití k čištění a úpravě vod. Rovněž je zde uvedena současná legislativa, týkající se nanotechnologií a to zejména ve vztahu k čištění odpadních vod. Jsou zde zmíněny přínosy, ale i negativa, jež sebou tyto technologie přináší.

Druhá část práce je zaměřena na popis mechanismu filtrace kapalin a membrán v současnosti k filtracím používaným včetně nanovláknitých membrán, kterým je tato práce z větší části věnována. K úpravě a čištění vody jsou během experimentů využívány nanovláknité membrány, které jsou vyrobeny za pomocí metody elektrospinningu. Tyto membrány jsou následně určeny k odstranění specifických kontaminantů z vodného prostředí a zahuštění roztoků, v závislosti na vlastnostech a účelu použití. Dosavadní výsledky poukazují na široké spektrum možného využití nanovláknitých membrán, přičemž jejich primární účel, na který se v experimentální časti disertační práce zaměřuje, je vývoj membrán určených k odstranění mikrobiální kontaminace a zahuštění aktivovaného kalu na čistírnách odpadních vod, terciární dočištění odpadní vody, odstranění specifických polutantů a úprava vody k závlaze.

Jedna z možností, jak intenzifikovat funkčnost membrán je jejich modifikace. Membrány lze modifikovat například přidáním různých částic nebo aditiv s antimikrobiálním účinkem, aditiv zvyšující hydrofobicitu, odolnost proti biofoulingu a clogingu membrán. Jedná se například o všeobecně známé částice stříbra a oxidu titaničitého, dale pak ftalocyaniny, zeolity, chlorhexidine a další látky. Během experimentální části bylo navrženo a ozkoušeno několik modifikací nanovláknitých membrán, které jsou zde spolu s výsledky filtračních experimentů také z části popsány.

Navazujicí část práce se věnuje systematicky laboratorním a poloprovozním experimentům, které vedly k selekci membrány vhodné pro dlouhodobé testování v membránovém bioreaktoru (MBR). Během těchto testů byly ozkoušeno značné množství membrán a jejich modifikací. Nejperspektivnější z nich které prošly selekcí byly použity v rámci poloprovozní jednotky s MBR určené primárně k filtraci a zahuštění aktivovaného kalu. Poloprovozní jednotka byla umístěna postupně na dvou čistírnách odpadních vod. Experimenty probíhaly v aktivační nádrži na ČOV Letonice a poté na ČOV Brno-Modřice. Zde proběhlo v rámci testování dlouhodobé porovnání s komerčními MBR typu: holow

fiber membranes a flat sheet membranes. Výsledky testování jsou zde zveřejněny v takové podobě, aby nebylo ohroženo know-how. V závěrečné části, jsou pak experimentální výsledky diskutovány a konfrontovány s dostupnou literaturou a poznatky ostatních, domácích i zahraničních autorů a jsou srozumitelně interpretovány. Je navrženo několik možných aplikací, kde se tyto technologie mohou uplatnit v praxi.

Disertační práce se pokouší přiližit odborné veřejnosti problematiku nanovlákenitých membrán a nanočástic. Demonstruje jejich použití na praktickém příkladě v podobě membránového bioreaktoru na čistírně odpadních vod. Výstupem získaných poznatků byly i impaktované zahraniční publikace, citované dále v textu.

Disertační práce čerpá data ze dvou projektů, na jejichž řešení se autor během psaní práce podílel. Jedná se o projekty: „Vhodné materiály pro nanotechnologické aplikace pro čištění a úpravy vody a vzduchu“, podpořený grantem TA ČR: TA01010356 a projekt: „Z odpadů surovinami“, podpořený grantem Národní agentury pro zemědělský výzkum: QJ1320234

Klíčová slova: Nanostruktury, Membrány, Membránový bioreactor, Nanočástice, Polutanty, Biofouling, Filtrace, Mikroorganismy, Mikrofiltrace, Odpadní voda, Aktivovaný kal, Nanovlákna

ACKNOWLEDGMENT

Došek M. .: The use of modified nanotextile and nanoparticles for filtration and treatment of contaminated water. Dissertation, Mendel University in Brno, 2016

Clean water available to all. This is one of the major challenges of the 21st century. With increasing population explosion, which goes hand in hand with industry, increasing demands for food, and their production and increasing water demand, while increasing water pollution. The need for technological innovation in the field of water resources that would enable efficient treatment of wastewater, along with integrated management, it is more than obvious.

This thesis is devoted to the purification and treatment of water particularly waste water, combining the latest technologies in the field of membrane water treatment using nanotechnology, specifically nanofibrous membranes.

The introduction describes briefly problematics of nanotechnology. There are presented general concepts of nanotechnology, imaging methods, the history of the field, focusing on the use of nanotechnology in the segment of water treatment. Also describe current legislation regarding to the use of nanotechnologies especially in relation to wastewater treatment. There are mentioned benefits, but also negatives which these technologies bring.

The second part focuses on the description of the mechanism of liquid filtration and membranes currently used for this purpose, including nanofibrous membranes. For the experiments were used nanofiber membranes, which were manufactured using electrospinning methods. These membranes were designed to remove specific contaminants from aqueous solutions and to make sludge more concentrating. The current results indicate a broad spectrum of potential uses nanofibrous membranes. In the experimental part of the dissertation focuses on the development of membranes designed to eliminate microbial contamination and concentration of activated sludge wastewater treatment plants, tertiary purification of waste water, removal of specific pollutants and the treatment of water for irrigation.

One possibility how to intensify the functioning of the membranes is their modifications. Membranes can be modified for example by adding various particles or antimicrobial additives, additives increasing hydrophobicity, resistance to biofouling and membrane clogging. These include well-known silver particles and titanium dioxide, as well as phthalocyanines, zeolites, chlorhexidine and other substances. During the experimental part was designed and proven, several modifications nanofibrous membrane, which are together with the results of the filtration experiments also partially described.

Following part is devoted to systematic laboratory and pilot plant experiments that led to the selection of membranes suitable for long-term testing in a membrane bioreactor (MBR). During these tests has been proven, large amount of membranes and their modifications. The most promising of them have passed selections were used in the pilot plant with MBR primarily intended for filtration and concentration of activated sludge. Pilot unit was positioned sequentially at two wastewater treatment plants. Experiments

conducted in the activation tank WWTP Letonice and then WWTP Brno-Modřice. Part of testing was also the long-term comparison with commercial MBR type: holow fiber membranes and flat sheet membranes. The test results are presented here in the form that it would not jeopardize know-how. In the final part, the experimental results are discussed and compared with the available literature and knowledge of other domestic and foreign authors and are clearly interpreted. It proposes a number of possible applications in which these technologies can be applied in practice.

Dissertation attempts to approach the issue of nanofibrous membranes and nano particles to professional public. Demonstrating their use on a practical example in the form of a membrane bioreactor located at the wastewater treatment plant. The output of the lessons learned were also impacted foreign publications, cited in the text below.

Dissertation draws data from two projects in which was the author during the writing of work involved. These projects are: "Suitable materials for nanotechnology applications for the purification and treatment of water and air", supported by a grant TA CR TA01010356 and the project "From waste to materials", supported by a grant from the National Agency for Agricultural Research: QJ1320234

Keywords: Nano Structures, Membranes, Membrane bioreactor, Nanoparticles, Pollutants, Biofouling, Filtration, Microfiltration, MicroorganismsWaste water, Activated sludge, Nanofibers

PODĚKOVÁNÍ

S postupem času a blížícím se koncem doktorského studia jsem stale vice zjišťoval, že ačkoliv bych po skončení studia měl být již odborníkem na danou problematiku, stále je přede mnou mnoho neznámých a vynořují se další a další otázky, jejiž zdpovězení je nezbytné nejen pro dokončení této disertační práce.

Vědecká práce je v dnešní době, kdy jsou mnohé vědecké obory tolik rozsáhlé, že není možné aby je obsáhnul jediný člověk, často prací do jisté miry kolektivní. Za dobu svého studia a práce ve firmě ASIO spol. s.r.o., která mi umožnila tuto disertaci vypracovat, jsem potkal celou řadu zajímavých lidí, kteří mě do problematiky zasvětili a pomohli mi dělat první krůčky v mé vědecké kariéře. Rád bych jmenoval alespoň některé z nich, kteří přispěli k tvorbě této disertační práce a tímto jim poděkoval za jejich úsilí.

Zejména bych rád poděkoval svému kolegovi, Ing. Jaroslavu Lvovi Ph.D., který mě vytvořil prostor pro mé doktorské studium na Mendelově universitě a zasvětil mě do problematiky nanovláknitých materiálů a membránové filtrace. Během mé práce mě metodicky vedl a směroval, rovněž mi poskytl celou řadu materiálů, bez kterých by tato práce jen stěží vznikla. Mé díky take patří mému školiteli, doc. Ing. Michal Černý, CSc., který mi byl mentorem během mého doktorského studia na Ústavu techniky a automobilové mechanizace a dokázal mě vždy vhodně motivovat k dalšímu kroku směrem za dokončením mého stuida.

Velké díky patří i kolegům z firmy ASIO spol. s.r.o., konkrétně Ing. Marku Holbovi Ph.D a Ing. Ondřeji Škorvanovi za jejich rady a technologický dozor během experimentů s nanovláknitými materiály. Také děkuji lidem z firmy SPUR a.s. Zlín, zejména Ing. Dušanu Kimmerovi, CSc, kteří ochotně připravovali velké množství testovacích materiálů. Bez jejich úsilí by se nepodařilo vyvinout dostatečně kvalitní membrány pro vývoj inovativního MBR reaktoru.

V neposlední řadě děkuji sehranému týmu z laboratoří mikrobiologie Mendelovy university kolem Ing. Libora Kalhotky, Ph.D., kteří neúnavě analyzovali veškeré dodané vzorky odpadních vod a filtrátů.

Mé díky patří samozřejmě i mé rodině, která byla během psaní této práce poněkud méně na výsluní. Děkuji za trpělivost přítelkyni Báře Jiřikovské a dvěma svým dcerkám, Agátě a Alici.

Na závěr patří poděkování dvěma grantům, které se podíleli na získání dat pro tuto práci. Jedná se o projekty: „Vhodné materiály pro nanotechnologické aplikace pro čištění a úpravy vody a vzduchu“, podpořený grantem TA ČR TA01010356. Dále pak projekt: „Z odpadů surovinami“, podpořený grantem Národní agentury pro zemědělský výzkum: QJ1320234

CONTENTS:

INTRODUCTION

Water, water resources, air and nature in its entirety have been from time immemorial but the man who is on planet earth relatively short time, has on the quality and condition of resources on planet earth major impact. With the increasing progress of human society, it is necessary to focus not only on economic growth but also on the sustainability of growth and the preservation of basic resources such as water, on planet earth. Human society is facing at the beginning of the 21st century major challenges. Drinking water for all and basic hygiene. The basis of the success of this promise should be sufficient waste water to a level to avoid further pollution of water resources and especially to clean, fresh water available for all inhabitants of the planet. But this is no easy task. Hand in hand with the population explosion is increasing the need for water resources, mineral resources, increasing food production. None of this would be impossible to sustain, without enough clean water. It is important to remember that our bodies are composed largely of water. It is therefore hard to believe that at the beginning of the 21st century does not have access to clean and safe drinking water and basic sanitation 780 million people. [1]

Figure 1: *Cuyahoga "Burning River" several times in its history flared* up *due to heavy soiling. Last time in 1969 (source: wkipedia.com)*

Human society, particularly those from developed, industrialized countries, is at the forefront of technological progress. Over the last decade created numerous new technologies, applicable even in wastewater treatment. This covers nanotechnology, which uses miniaturization, the current trend of many technologies. These new technologies have great potential, since they allow to purify water from various sources, even where it was previously very difficult or impossible. Increasing pressure on water resources forcing look where it previously was not necessary. This is the recycling of grey water (water from households), rainfall, brackish water, water containing heavy metals, etc. Although they are often highly sophisticated technology has the potential to use even in developing countries. Providing clean water is associated with basic human needs. Unsafe drinking water, inadequate availability of water for hygiene, and lack of access to sanitation together contribute to about 88% of deaths from diarrheal diseases. [2]

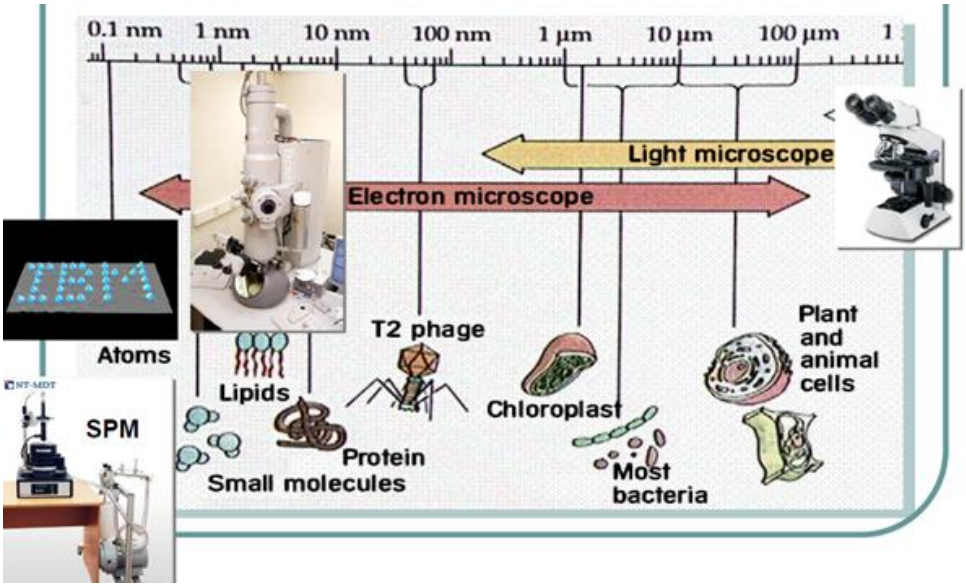
People often invest in other modern technologies, computers, cell phones, automobiles, but they forget to invest in the basic and essential, to clean water. It would then have to remember especially government officials in the allocation of subsidies. It is clear that investments in technologies related to security of clean water are not interesting for investors because they have a long recovery, but we must not forget their importance and not to take clean water for granted. In many visionary predictions have been told that the next world war will be just about water and other essential raw materials.

1 NANOTECHNOLOGY

A typical definition of nanomaterials, characterizes them as materials of less than 100 nm in at least one dimension. [3] These are particles of less than 10-9 m. Other definition characterize the "nanoworld" using interval range, where the materials have values in intervalu1-100 nm. With these dimensions often acquire new properties and conditions for the use of technology, which larger particles do not have the same composition. Some have already been applied in the field of wastewater treatment, particularly due to a number of specific benefits such as surface area, solubility, high reactivity, or sorption properties. Many of them, however, has been proven, yet only in laboratory scale. Nanotechnology is certainly possible to define interdisciplinary. In human society, the concept of nanotechnology began using in the second half of the 20th century. But in reality it is nothing new. Nanoparticles are around us since time immemorial. The air in a normal room can contain 10,000 to 20,000 nanoparticles/cm-3[4]

Renaissance ceramic glazes contain particles of copper and silver with a diameter of 5 to 100 nanometres and meet the criteria for classification of nanomaterials. The procedure for the preparation of such glazes are preserved in the book by Italian author Ciprian Piccolpassa of 1557. The salts of copper and silver mixed with vinegar potters, and besides clay.

Figure 2: *A comparison of small formations*



(Source: Presentation: Nanotechnology and its applications, Doc. RNDr. Roman Kubínek CSC, Regional Centre of Advanced Technologies and Materials, 2014)

1.1 Nanohazard, health risk

Nikola Tesla already in r. 1905 complained: "In our world today, revolutionary ideas and inventions instead help and support from the outset encounter obstacles and intrigues that they intend selfish interest, pedantry, stupidity and ignorance, they are facing assault and ridicule. "It's always easier to reject or criticize than to study and try to understand the new. It is also politically lucrative lifted above the crowd flag against heretics rather than try to open the soul of people to new ideas. The situation is similar in relation to nanomaterials

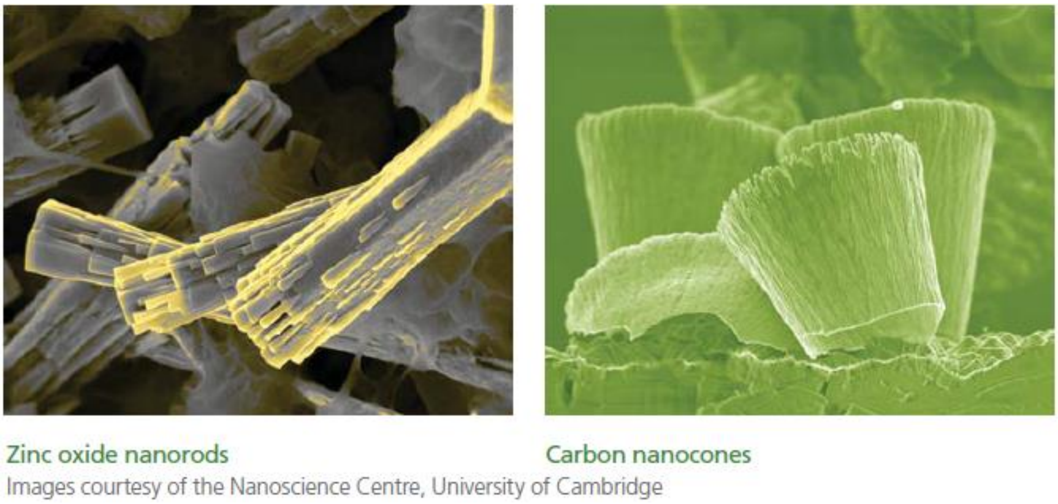
Although it has been said that the nanoparticles are found in nature since time immemorial, they can still pose some environmental and health risks. Many of the materials and structures, were created by human. Examples are well known carbon nanotubes. History of nanotechnology is relatively short and therefore is difficult to predict how organisms cope with the increased accumulation and deposition. Of course, it is made with new material before putting into practice a number of Eco toxicological, toxicological and other tests. But you can´t guarantee 100 % safety of materials in the long run. Probably the biggest risk is the inhalation of nanoparticles.

One of the factors hazard is simply their size. Because they are less than 100 nm, can substantially freely move through living organisms. Another risk factor is the fact that the properties of nanoparticles can be varied in shape and size. For example, gold nanoparticles can have different colours from blue to purplish red, depending on the particle size. Therefore, it is also very complicated regulatory measures. There is also a problem with placing nanoparticles. It is immaterial whether they are free or bound to other structures. Most technical applications gravitating to the second variant. (Composite materials, chips, colour,....) Once attached, it is necessary to assess their bioavailability and risk release to the environment management.

The greatest danger is therefore a risk in places of production of nanomaterials or after the end of their useful life during recycling. On the other hand it must be said that the nanoparticles are in many cases highly reactive, they tend to agglomerate or immobilized. At present (2014) there are no universally valid and grounded rules for assessing the hazards of nanoparticles. Where products are associated with nanoparticles, usually are tested based on the standards valid in specific country.

Finally, it should be noted that nanoparticles are found everywhere around us. One source is currently smog from burning fossil fuels. Nanoparticles also have approximately the same size as the chemical and biochemical molecules, or cellular structure. It should be divided among the newly prepared and already existing particles in the environment.

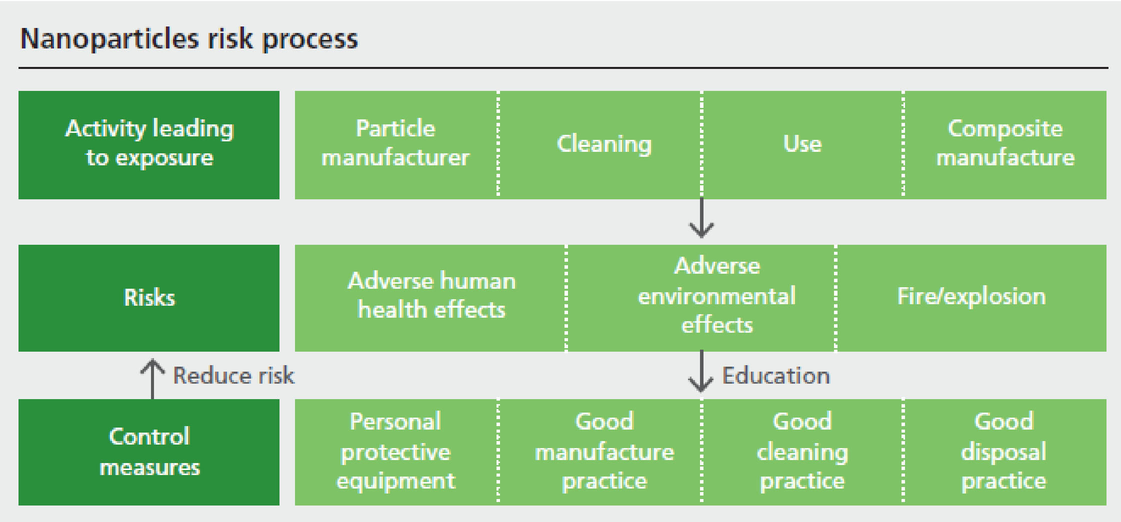
Figure 3: *Example of the nanoparticles (Carbon and Zinc)*



1.2 Legislation in relation to the use of nanomaterials

We can note that the above described risks have been captured by governments around the world, like GMOs, at an early stage, which can be any risk and minimize damage. For example, the report of the Royal Society in London in 2007, just balances the potential benefits of nanotechnology cost or risk. The European Union is sponsoring numerous research projects aimed at understanding and quantification of risk involving so-called: IT'S NANO technology. As an example of risk assessment process is given the following chart. [5]

Table 1: *Nanoparticles risk process*



In connection with research hazard of nanomaterials, we can mention, for example, large-scale projects RIP-oN. The two RIP-oN projects (RIP-oN2 and RIP-oN3) are independent projects funded by the Institute for Health and Consumer Protection (IHCP) of the European Commission's Directorate General Joint Research Centre (JRC) to a consortium led by SAFENANO (link is external) (Institute of Occupational Medicine), and including the Nanotechnology Industries Association.

For example, studies of the health impact of airborne particles Generally Shown That for toxic materials, Smaller particles are more toxic. This is due in part to the Fact That, given the same mass per volume, the dose in terms of particle numbers increases as particle size decreases.

The International Council on Nanotechnology maintains a database and Virtual Journal of scientific papers on environmental, health and safety research on nanoparticles.[3] The database currently has over 2000 entries indexed by particle type, exposure pathway and other criteria.

The European Union has formed a group to study the implications of nanotechnology called the Scientific Committee on Emerging and Newly Identified Health Risks [7], which has published a list of risks associated with nanoparticles. [8] Consequently, manufacturers and importers of carbon products, including carbon nano-tubes will have to submit full health and safety data within a year or so in order to comply with REACH. [9]

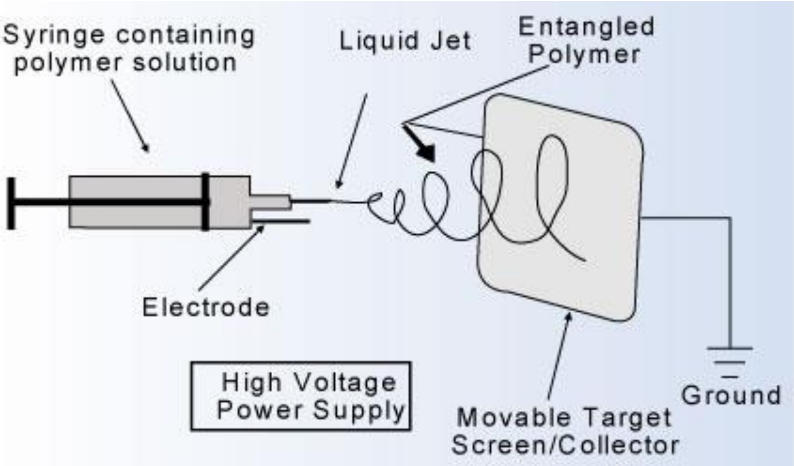
1.3 Nanofibers and their history

History of nanofibers is already quite long. In fact dates back to 1914. In that year describes the technology shaping the nanofiber Czech-Americans, John Zelený. He worked as a physicist at the University of Michigan. His preparation technology is based on electro hydrodynamic jetting (electro-hydrodynamic jetting). [11] Some patents, ranging even up to 1902. [10] In the years 1934 to 1944 followed by a series of patents Formals company also describes an experimental procedure for producing polymer fibres using electrostatic forces. The turn followed in 1971, when Maumgarten [11] constructed an apparatus for spinning of acrylic fibres with a diameter within 0.05 to 1.1 microns. The spinning was used stainless steel capillary into which the solution was fed infusion pump. On these and some other researchers then followed up research prof. Oldřich Jirsák, who worked at the Technical University in Liberec. [12] In cooperation with Elmarco in 2004, he has developed and patented technology electrostatic fiberized nanospider which has compare to competing technologies great advantage due to high production of nanofibers of different materials and is thus suitable for industrial production. [10]

The process of nanofibers spun by the aid of an electrostatic field is called electrospinning. In this process, a high voltage is used to create a stream of electrically charged polymer solution or melt, wherein the high voltage electrode is connected directly with the polymer solution. Thanks to its high electrical voltage between the tip of the capillary and a grounded collector is formed a so called. Taylor cone at the tip of the capillary from which they are produced submicron fibres. The fibres became after evaporation of the solvent solidified and form the fibrous layer on the surface of the collector. In this way can produce 0,1 - 1 g/hour -1. This technology uses capillaries it is suitable for laboratory processes. Due to its performance data, which is a limiting factor for the industrial production

Figure 4: *Scheme of preparation of nanofibers using jet*

(Source: Magazine- Nanofiber technology for tissue engineering)



Techniques for nanofibers producing:

According to the spinning process manufacturing technology can be divided into three basic techniques:

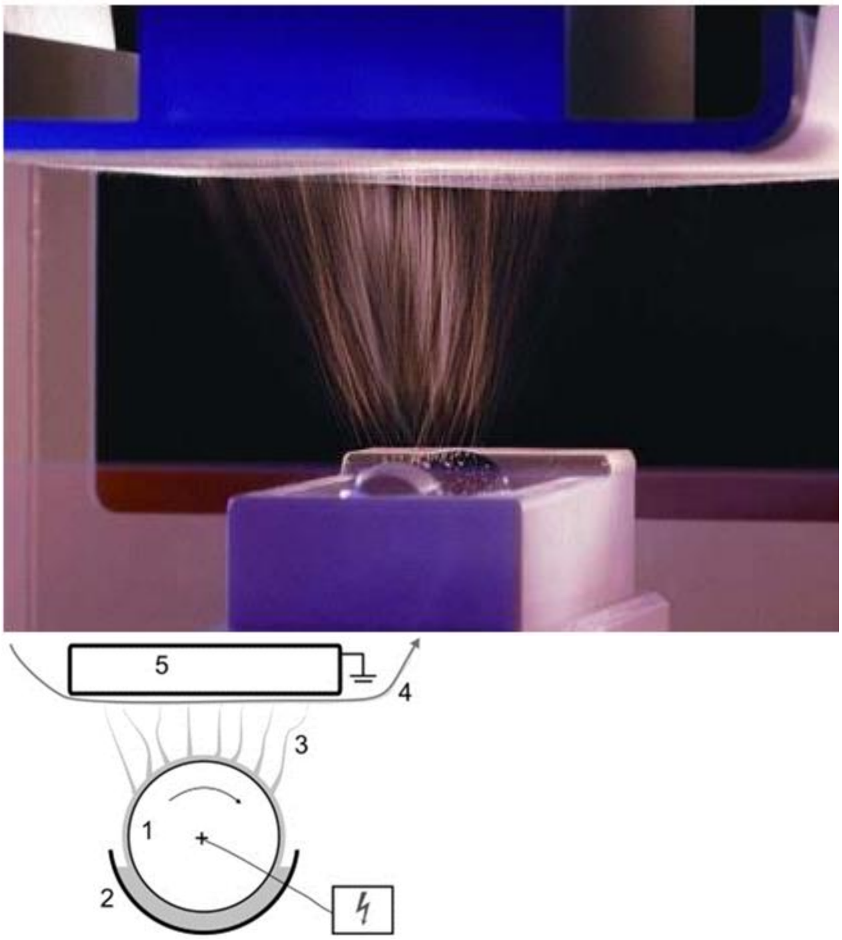
- Spinning using a nozzle
- Spinning by roller rotating in the polymer
- Spinning bubbles from the free surface

1.3.1 Technology nanospider

Productive method of production, called NANOSPIDER, was developed by a team of prof. Jirsak at the Technical University in Liberec [12]. Nanospider don´t use for creation of fibres nozzles or capillaries, but drum partially immersed in a polymer solution (Fig. 5).

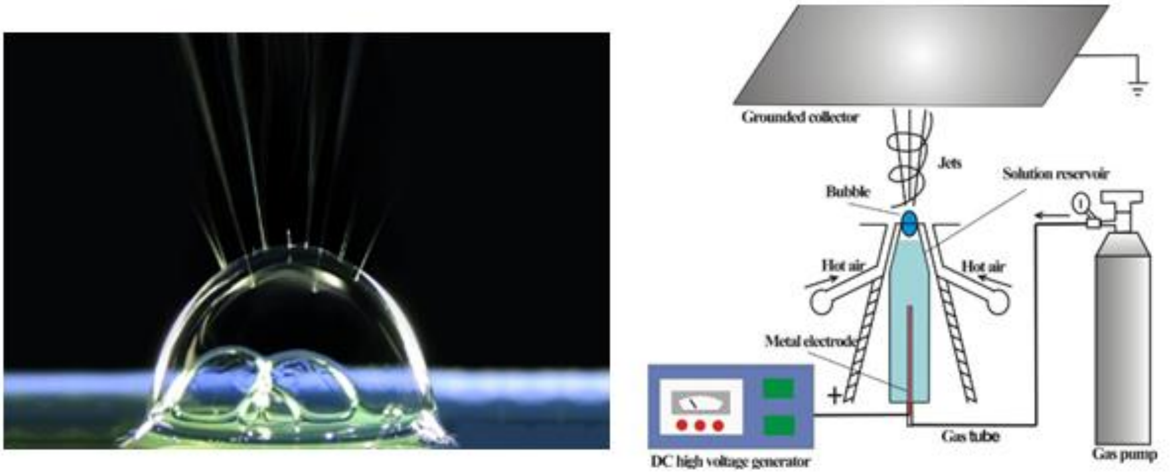
The cylinder rotates around its axis and on its surface with a thin film of polymer solution. In the upper dead centre of the rotary movement of the cylinder, which is also the place with the lowest distance from the collector - opposing electrodes, this result of the maximum electric field strength will create foci multiple Taylor cones, which further results in a spinning process. Taylor cones and then mass flows are generated in a dense network covering the top of the cylinder. This achieves a high production capacity spinning head nanospider (1-5 g.min-1.m-1 working width). Streams of the polymer solution are then freed from the solvent and become fixed nanofibers just before they reach the collector.

Figure 5: *Technologies nanospider in process [13]*



On the figure 5 it is presented the diagram of preparation of nanofibers by a roller rotating in a dissolved polymer - NanospiderTM Technology: 1 - a metal cylinder (positively charged); 2 - Tray polymer solution; 3 - in the direction of forming nanofibers; 4 - nonwoven substrate (base material for forming nanofibers); 5 - grounded collector.

__Figure 6:__ bubble-electrospinning process [22]



1.4 Nanotextiles

Nanotextiles are a promising material that is applied in many areas of human activity. Nano-structure can be compared to a nonwoven fabric made of very fine fibres - nanofibers. The fibre diameters are in the range from 50 to 500 nm. Process for producing nanofibers by electrostatic spinning is called electrospinning. These nanofibers are core structural material nanofibers membranes, which have been used for experiments in this work. [10] The layer of nanofibers is mostly applied to the carrier material (PP, nonwoven viscose, paper, etc.) that enable safer handling of a fine layer nanofibers. The advantage of this technology is the high stability of the spinning process. The electrodes are mechanically simple and has no parts that could be easily clogged (in comparison with the electrospinning nozzle). Another advantage is the ease of application of additives influencing the properties of the nanofiber layer, in dissolved or molten material] (e.g., antibacterial agents ..). This technology is already quite commonly used and commercially available for industrial production nanotextiles. High productivity process contributes to lower operating expenses. Price per square meter nano is in the order of up to tens of euros. The cost depends on the thickness of the nanofiber layer, the characteristics of the spun material, and any other special treatments.

Electrostatic spinning technology and Nanospider can produce organic, inorganic and biopolymer nanofibers. Number of materials that it is possible using electrospinning to spin nanofibers, continues to grow. At present, there is already over 50 kinds of polymers suitable for fibrillation process. Overview of commonly

Table 2: *Commonly used materials for the production of nanofibers by NANOSPIDER [14]*

Organic materials	Anorganic materials	Biopolymers
PA6 (Nylon 6)	TiO_2	Gelatin
PA 6/12 (Polyamid)	SiO_2	Chitosan
Polyaramid	Al_2O_3	
PUR (Polyurethane)	ZnO	
PES (Polyethylsulfide)	$Li_4Ti_5O_{12}$	
PVA (Polyvinylacohol)	ZrO_2	
PAN (Polyakrylnitril)	$MgAl_2O_4$	
PEO (Polyethyleneoxide)		
PS (Polystyrene)		
PVDF (Polyvinylidenfluoride)		
PVP (Polyvinylpyrrolidone)		
PVP – I (Povidone-iodine)		

At present, we can say that the method of spinning is not engaged in a lab and university, but also the whole series Afire, whose products are commercially available. Some of them are listed in the table below:

Table 3: *Selection of commercial suppliers of electro spun nanofiber-based.*

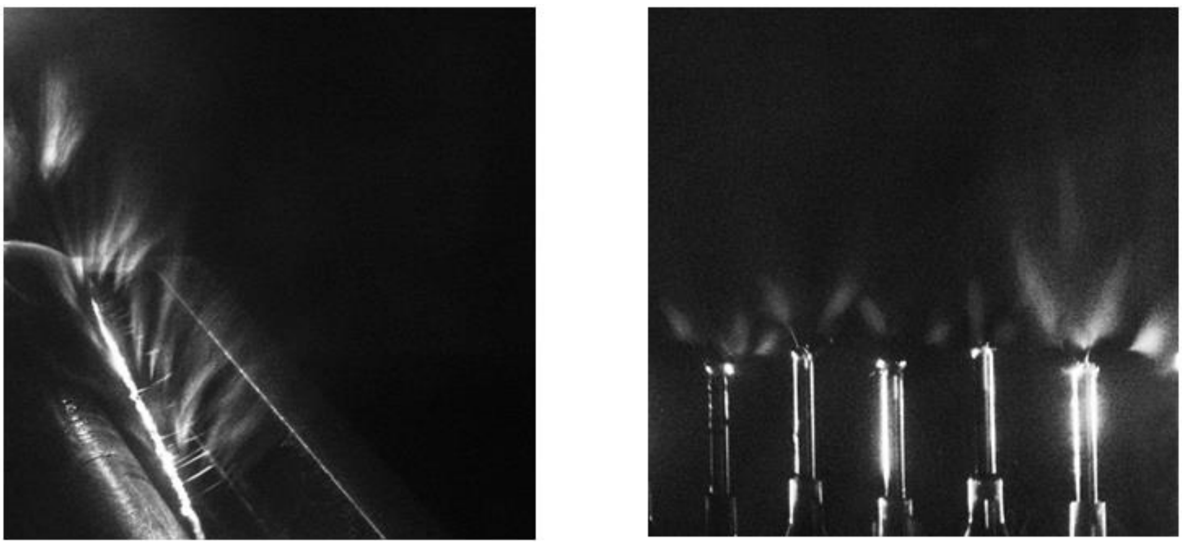
	Company Name	Country of origin	Website
1	Donaldson Company Inc.	USA	http://www.donaldson.com/
2	Espin Technologies Inc.	USA	http://www.espintechnologies.com/
3	US Global Nanospace	USA	http://www.usgn.com/
4	Finetex Technology	Republic of Korea	http://www.finetextech.com/
5	Nanoval GmbH and Co. KG	Germany	http://www.nanoval.de/
6	Japan Vilene Company Ltd.	Japan	http://www.vilene.co.jp/
7	Toray	Japan	http://www.toray.com/
8	Elamarco	Czech Republic	http://www.elmarco.cz/
9	Hills Inc.	USA	http://www.hillsinc.net/
10	Esfil Tehno	Republic of Estonia	http://www.esfiltehno.ee/

One of the major companies, which are engaged in production of nanofiber materials and in particular by the development, the Czech company SPUR a.s from Zlín.

Figure 6: *Unit on producing nanofiber textiles, Spin Line 120, Manufacturing width 1400 mm. (Source: SPUR a.s., Zlín)*

This unit also works on the principle of electrospinning. Is able to monitoring more than 20 variables (c, χ, U, D, collecting substrate, speed of shift nanofiber collecting substrate, rotational electrode speed, spinning electrodes etc.) It is equipped with rotating electrode with cord spinning elements - Jets.

Figure 7: *Rotating electrode with cord spinning elements (Photo: SPUR a.s, Zlín)*



1.5 Nanofibers for nanotextiles

In some cases it may be during the production of nanofibers during fibrillation added other inorganic material, in the form of differently sized particles. Alternatively, nanofiber layer can be further treated with a fine powder. This may in practice be used e.g. for production of electronic components and semiconductor photoactive layers.

1.5.1 Additives for nanofibers modifications

For specific applications can be incorporated into the nanofiber layers other additives to improve or create new properties of the prepared materials, e.g., biocidal effects, photocatalytic, absorption properties and the like. Additives may be mechanically anchored into the porous structures between the nanofibers, or in the case of multilayer materials between layers. This method is suitable for anchorage additives e.g. in the form of powders. The disadvantage is the possible leaching of particles during operation. Another option is to dissolve additives or chemically coupled to the polymer from which they are produced nanofibers. Binding of additives is more reliable compared to the previous method, there is however a loss of active surface anchoring in nanofibers, and in some cases may cause partial loss of activity. As the additive most frequently used biocide elements or compounds of Ag, Cu. For the preparation of photocatalytic materials are used, then compounds of the metals Ti, Zn, Ag.

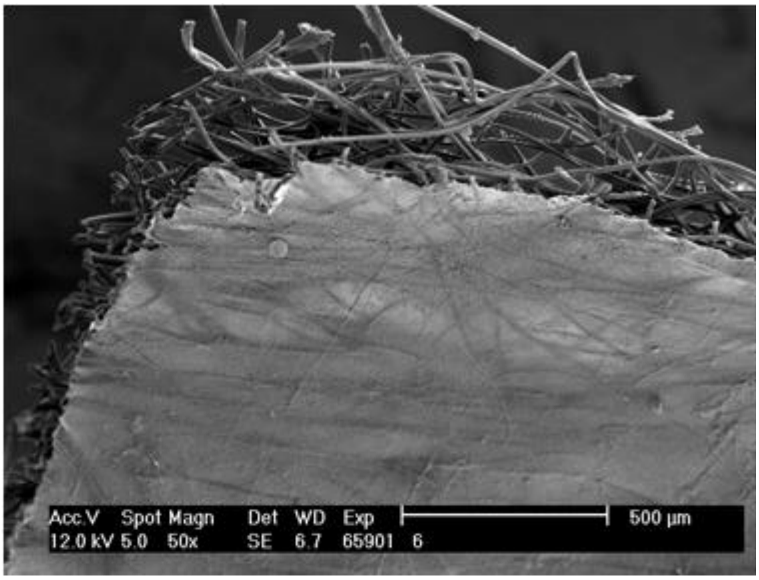
1.5.2 Characteristics of nanofiber layers

The nonwoven web layer forms nanotextiles materials with specific properties. The resulting structure has a very low density, high specific surface area, small pore size, high porosity and excellent mechanical properties in proportion to their weight. Because of the random orientation of the nanofibers, the size of the pores in the structure mainly influenced by the morphology of the fibres, fibre diameters (nm) and the thickness of the layer, characterized by layer basis weight (given in g / m2). Commonly used nano have an average diameter of nanofibers around 200 nm, for special applications are produced nanofibers with a diameter of 80 nm or less. According to the requirements to function nanotextiles the basis weight ranges from tenths of a gram to a few tens of grams per square meter. The pore size is read from the frame structures, where pore sizes are measured resulting overlapping fibres. These values are determined by the pore size range of the produced material. To improve mechanical properties and to guarantee the filter parameters may nanofibrous structure composed of several layers of nanofibers from the same or a different kind of polymer.

1.5.3 Carrier media for nanofibers:

Due to the extremely fine structure of the nano, low basis weight, etc. are usually directly in the manufacture of nano placed on a carrier material, which ensures easier handling of the prepared layers of nanofibers and strengthens the resulting product. As carrier media according to the purpose of use, generally a nonwoven fabric of viscose or polypropylene. Electrospinning technology is however also possible to coat nanofibers on another carrier different structure and shape. Nanofibers can also be applied to the individual yarns of the fabric or flat woven of various materials. The fibres are bound to the surface only by weak van der Waals forces. For the layers with low grammage e.g. for air filtration, this anchorage sufficient. For layers with greater weights can be consistency on the substrate is problematic. If it is necessary to securely anchor the nanofibrous layer on the substrate, various techniques are used to increase adhesion. It is used e.g. mechanical reinforcement layers or compression bonding. Layer with a basis weight of 10 g/m2 is already sufficient mechanical properties and can be used without a carrier material.

Figure 8: *Layer of polymeric fibres on a substrate of a nonwoven fabric of PP fibres. (Photo: SPUR a.s., Zlín)*



1.6 The application of nanotechnology in water management

As was already mentioned, the first mention of nanotechnology is credited with US scientists Richard Feynman in r. 1959, when in his visionary lecture There's Plenty of Room at the Bottom predicted the emergence of the field as we know it now. Nanotechnology boom hit in the scientific sphere, particularly in the 80s and 90s of the last century and it is gratifying that this is one of the few disciplines where the Czech Republic does not play second fiddle.

The application of nanotechnology in water management can be observed mainly in the following three areas:

- Cleaning and remediation.
- Scanning and detection.
- Protection against contamination.

As for the cleaning and remediation, so there nanotechnology contribute to long-term water quality, availability and quality of water resources, such as. The use of advanced filtration materials, which contribute to enhance water reuse, recycling and desalting. Development of new and advanced sensors at the nanoscale conversely helps detect biological and chemical contaminants already in low concentrations in any environment, including water.

In terms of the scope of this dissertation is probably the most interesting filtration. Concretely applications of nanofiber structures in water filtration, use of biocidal preparations to remove unwanted microbial recovery in water and application of advanced nanomaterials for clean water and wastewater.

1.6.1 Using nanotextiles materials for water treatment

The high porosity, small pore size, and other properties nanotextiles provide good conditions for the production of filter materials for gases and liquids. In the case of filtration of gases / air mass are compared with the filtration of liquids, placed such high demands on the mechanical resistance, allowing faster application, and there are already a number of commercial applications.

Nanotextiles materials are for water filtration far less used. However, there are already a number of studies that describe the wider possibilities of application themselves nanofibers or functionalized nanofiber e.g. to remove microbiological contamination.

Studies have been verified and compared with silver filtration efficiency PA nanofibers functionalized with PA nanofibers without modification. Tests were carried out with real microbial contaminated water from hospitals, rain water and water from the water tank. After filtration of said microbial contaminated water has been achieved by reducing the number of bacteria 2 to 3 log CFU/ mL in the case of non-functionalised nanotextiles PA, and 3.9 - 4 log CFU/mL. The conclusions of this study show a great potential for applications, in particular functionalized nanofibers material and elimination of microbial contamination from water. For the development of filter materials useful in real operation, however, a need for further functionalization and improvement of finding a method for cleaning and regeneration of the filter material.

One of the first applications is the use of silver functionalized nanofiber structures together with activated carbon, to produce so called: Tee bag. This filter is inserted in a special attachment, which is screwed onto the bottle with polluted water. Filtered water meets the requirements for drinking water. Filtering and antibacterial effects functionalized nanofibers is eliminated microbial contamination, for absorption of chemical substances serve activated carbon. This inexpensive solution has been used for preparation of drinking water in developing countries. In this case, the disposable nanotextiles materials, therefore there are no problems with the disposal or regeneration of clogged filters or overgrown, which is often a major problem in long-term operations.

Mentioned findings of these studies, the first practical applications show a high potential for using nanofiber structures in the field of water treatment. For real applications, however, still need to be resolved optimum composition nanofibrous structures biocidal additives and their mechanical resistance, cleaning and regeneration systems.

2. LIQUID FILTRATION

One of the basic methods for obtaining the pure compounds using simple physical or chemical principles is crystallization and of course also filtration. Especially filtration done for the last time a big step forward. Filtration is the removal of suspended particles from a fluid performed by a filter medium, septum, cloth or bed of solids. These techniques are already widely used in practice. We can mention for example separation toilets. Filtration is commonly encountered in chemistry laboratories on a Buchner funnel and within the kitchen during the making of filter coffee. It is a very important industrial process as it is often a key stage in product recovery. The increasing number of technologies based on “nano” was also reflected in the world by filtration and crystallization. We can also observe this phenomenon in membrane filtration.

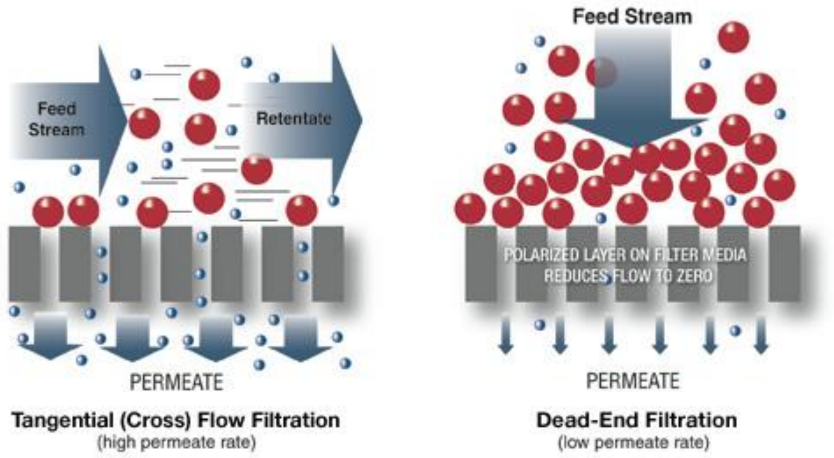
Currently, during filtration we focus not only to liquids, but with use of this technic we are able to remove even the smallest particles from the air, to prepare and isolate the various drugs on molecular basis. Current membrane technologies are capable to purify the substance up to about 1 micrometre, in some cases, molecules or ions. For example, we designate application of biogas cleaning, which is based on methane separation. Among other industrial applications, which are the most common is it production of drinking water in the desalination of seawater or wastewater. In the automotive industry are found by protecting sensitive device of the engine, fuel filters.

2.2 Membrane filtration

Membrane filtration is very wide. Membranes usually possess a thin filtering surface, which may be supported by a much thicker structure. Documents that describe the best available technology in the field of so-called. BAT, membrane filtration is often reported as one of the best solutions at all in terms of obtaining pure liquids or rare materials.

The semi-permeable membrane acts as a barrier which retains larger particles, while allowing smaller molecules to pass through the membrane into the permeate. Molecules naturally move from areas of high concentration to low concentration. By applying external pressure, molecules can then flow from areas of low concentration to high concentration. The pressure difference on both sides of the membrane will cause the permeate to cross the membrane at a steady state. This allows the final product, permeate or retentate to be have higher overall yields.

***Figure 9**: Conventional vs Cross flow filtration [19]*



There are a wide number of membranes characteristic, properties of membranes and their internal structure and methods of their definition. For example, the size and the pore size distribution further shape pore, total porosity (e.g. volume percent), the inner connecting pores (interconnectivity). If we use for the filtration membrane, regardless of the material composition of the membrane, separation process is divided by the pore size of the membrane.

- **Microfiltration:**

In the context of particle technology, the most appropriate membrane filtration process is microfiltration (MF). Microfiltration removes particles higher than 0,08-2 µm and operates within a range of 7-100 kPa. [15] Microfiltration is used to remove residual suspended solids (SS), to remove bacteria in order to condition the water for effective disinfection and as a pre-treatment step for reverse osmosis. Relatively recent developments are membrane bioreactors (MBR) which combine microfiltration and a bioreactor for biological treatment.

- **Ultrafiltration:**

Ultrafiltration removes particles higher than 0,005-2 µm and operates within a range of 70-700kPa. [15] Ultrafiltration is used for many of the same applications as microfiltration. Some ultrafiltration membranes have also been used to remove dissolved compounds with high molecular weight, such as proteins and carbohydrates. In addition, they are able to remove viruses and some endotoxins

- **Nanofiltration:**

Nanofiltration doesn´t mean that we use for filtration nanofibers. Is derived, as in previous cases, the dimensions of the pores of the membrane Nanofiltration is also known as “loose” RO, is a pressure process using membranes for the separation of particles larger than 1 nm. Application spectrum Nanofiltration is between reverse osmosis and ultrafiltration. While the application potential of reverse osmosis is used in a commercial scale especially for desalination of seawater, and ultrafiltration process which usually serves as a pre-treatment before directed reverse osmosis, whether in the case of sea water desalination, as well as with regard to pre-treatment of industrial wastewater. The ultrafiltration is currently often encountered when applying the membrane separation in municipal wastewater treatment plants, where the pores of the membrane moves in the order of hundredths of a micron to prevent passage of bacteria and most viruses,

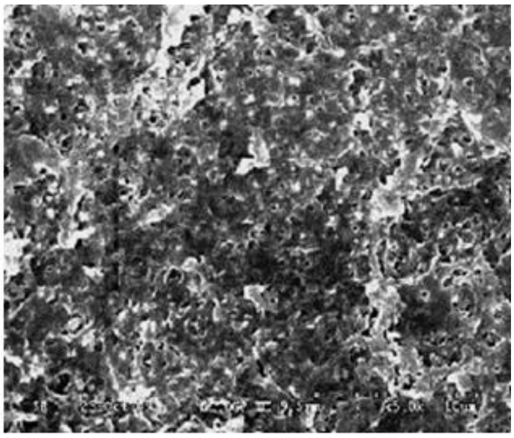
Nanofiltration is used for the removal of selected dissolved constituents from wastewater. NF is primarily developed as a membrane softening process which offers an alternative to chemical softening. The main objectives of NF pre-treatment are: [16]

Nanofiltration is successfully used for the removal of various pollutants Membranes are produced in the range of 150 to 300 Da. Nanofiltration membranes began to be produced in the 70s of the last century as an alternative to reverse osmosis with a lower rejection and meaningful flux of at significantly lower pressures. In the literature, therefore, may be found with terms such as lossy reverse osmosis or reverse osmosis open. The first real nanofiltration membrane started to be used ca. before 20 to 25 years. The main application of nanofiltration membranes is a water softening, brackish water purification, effluent treatment and reuse, the separation of valuable raw materials in the industry, and recycling salts recently desalination and, when not used as the last step of reverse osmosis, but the two stage nanofiltration.

- minimize particulate and microbial fouling of the RO membranes by removal of turbidity and bacteria,
- prevent scaling by removal of the hardness ions,
- lower the operating pressure of the RO process by reducing the feed-water total dissolved solids (TDS) concentration.
- water softening, brackish water purification
- separation of valuable raw materials in the industry

The first material, used for the production of nanofiltration membrane was cellulose acetate, which unfortunately has a limited sphere of application and therefore the advent of nanofiltration began to develop other membrane materials, such as polyamides (PA), polyethersulfone (PES), polysulfone (PS), chlorinated PVC or polyvinylidene fluoride (PVDF). Inorganic membranes are based mostly based on alumina, zirconia or titania. Most membrane is charged, negatively charged, and nanofiltration membranes are therefore preferably removed anions. Characterisation of nanofiltration membranes is done mostly through their morphological and performance parameters and parameters according to the charge, the most important are the surface charge, porosity, resistance, roughness, chemical composition, hydrophobicity and zeta potential, e.g. morphological characteristics are examined under the microscope most, i.e. TEM (Transmission Electron Microscope), SEM (Scanning Electron Microscope), and ATM (atomic force microscopy).

Figure 10: *Surface structure nanofiltration membranes SEM (Photo: ASIO spol. Ltd.)*



- **Reverse and forward osmosis:**

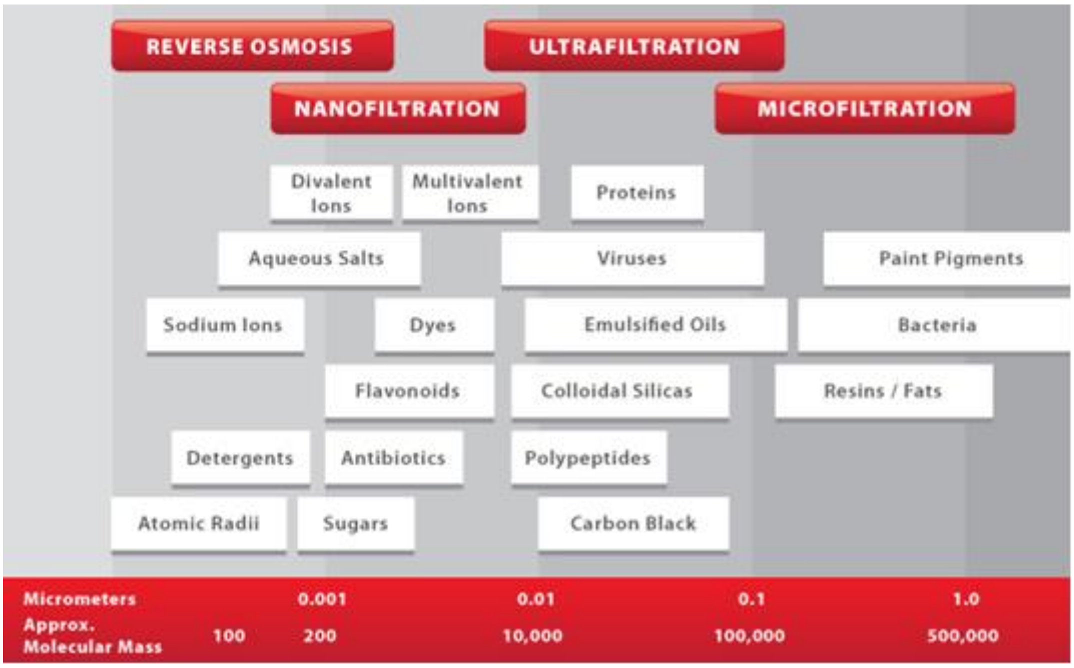
Reverse osmosis is commonly used for desalination. As well, RO is commonly used for the removal of dissolved constituents from wastewater remaining after advanced treatment with microfiltration. RO excludes ions but it requires high pressures to produce deionizer water (850-7000 kPa).

Forward osmosis is an osmotic process that, like reverse osmosis (RO), uses a semi-permeable membrane to effect separation of water from dissolved solutes. The driving force for this separation is an osmotic pressure gradient, such that a "draw" solution of high concentration (relative to that of the feed solution), is used to induce a net flow of water through the membrane into the draw solution, thus effectively separating the feed water from its solutes. In contrast, the reverse osmosis process uses hydraulic pressure as the driving force for separation, which serves to counteract the osmotic pressure gradient that would otherwise favour water flux from the permeate to the feed. Hence significantly more energy is required for reverse osmosis compared to forward osmosis. [17]

The most commonly used modules are used for nanofiltration spiral wound, plate, tubular, hollow fibre, or ceramic capillary. To select a suitable membrane frequently we take into account the energy requirement, and flux control fouling (clogging by deposits of biological origin) and scaling (fouling by deposits of inorganic origin - mainly calcium and magnesium salts in combination with carbonates).

The global market for nanofiltration membranes reached in 2006 89.1 miles. USD with the assumption of 310.5 miles. USD in 2012, which should 210.7 miles. USD feel just applications associated with water management. [21]

Figure 11: *Types of Membrane filtration processes based on membrane pore sizes. [19]*



Current possibilities for displaying pores (250 nm optical microscope, SEM and AFM useful magnification 103-104, resolution up to 1 nm) allow study pores MF and UF membranes, but not enough for the NF and RO membranes, which are divided inorganic molecules and ions because size ionic radii ranging from 30 pm (0.3 Å) to 200 microns (2 Å = 0.2 nm). Beautiful AFM spatial image bacteria whose size is in the range of hundreds of nm. (At high magnification, resolution 77 pm) are already AFM images but few meaningful). To study NF and RO membrane structures have been developed two new alternative methods by which scientists reported on NSRRC Taiwan 2 is a method suitable for NF membranes - NTXM - nano-transmission X-ray microscopy, with the possibility of displaying units> 2 nm and a suitable method for RO membranes - PALS - positron annihilation lifetime spectroscopy, with display units <2 nm, reportedly up to 0.1 nm. From the acquired image can be reconstructed spatial arrangement of pores and watch the interconnectivity and thus clogging of small pores. The disadvantage is still a high price range. [18]

Commercial MF/UF membrane material

As a basic material for the manufacture of membranes is currently used relatively large amounts of substances. Some of the most common are listed below. [62]

CA – Cellulose acetate

PS – polysulfone

PES – Polyether sulfone

PAN – Polyacrilonitrile

PVDF – Polyvinylidiene fluoride

PP – Polypropylene

PE – Polyethylene

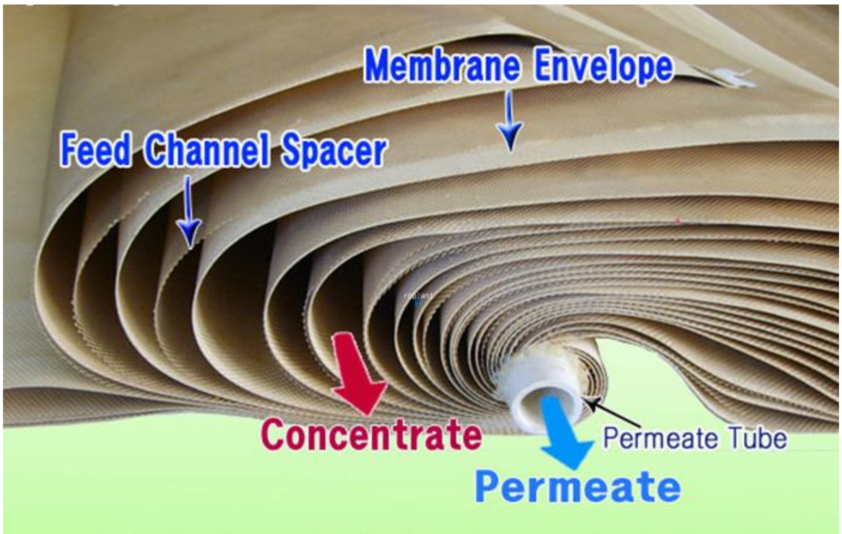
PVC – Polyvinyl chloride

2.2.1 Membrane Configurations

Membranes come in four basic configurations. Each is configured differently, both in packaging and in the types of materials used, to address the range of physical characteristics found in process fluids. There are distinct advantages that come with each configuration, allowing you to manage your process needs effectively.

- **Spiral wound** where a flexible permeate spacer is placed between two flat membranes sheet which allows produced water to flow. A flexible feed spacer is added and the flat sheets are rolled into a circular configuration. Mesh spaces are made from polypropylene; it promoted the transmission of substances and decreases density polarization. Spiral-wound module is the most widely used system because it's the most compact and cheapest. It can adapt to various environments and process as it does not have certain type of settled forms. In actual processes, 2~6 of Spiral-wound modules are connected to pressure vessels in series.

Figure 12: *Spiral-Wound membrane, function scheme [23]*



• **Hollow fiber** membranes consists of a bundle of hundreds to thousands of hollow fibres. The entire assembly is inserted into a pressure vessel. The feed can be applied to the inside of the fibre (inside-out flow) or the outside of the fibre (outside-in flow). The hollow-fibre e.g. ultrafiltration membranes operate at relatively low pressures, have high filtering surfaces and ensure a high quality of water.

Figure 13: *Hollow fibre configuration [20]*

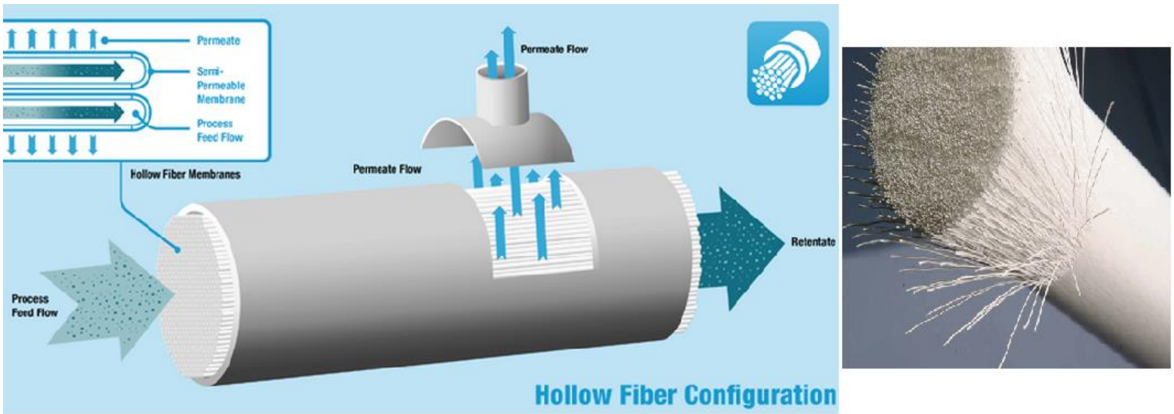
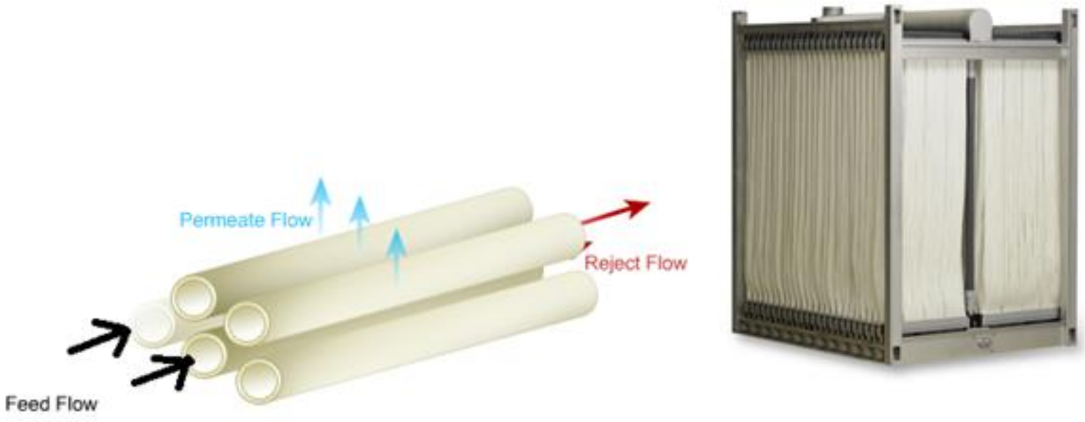
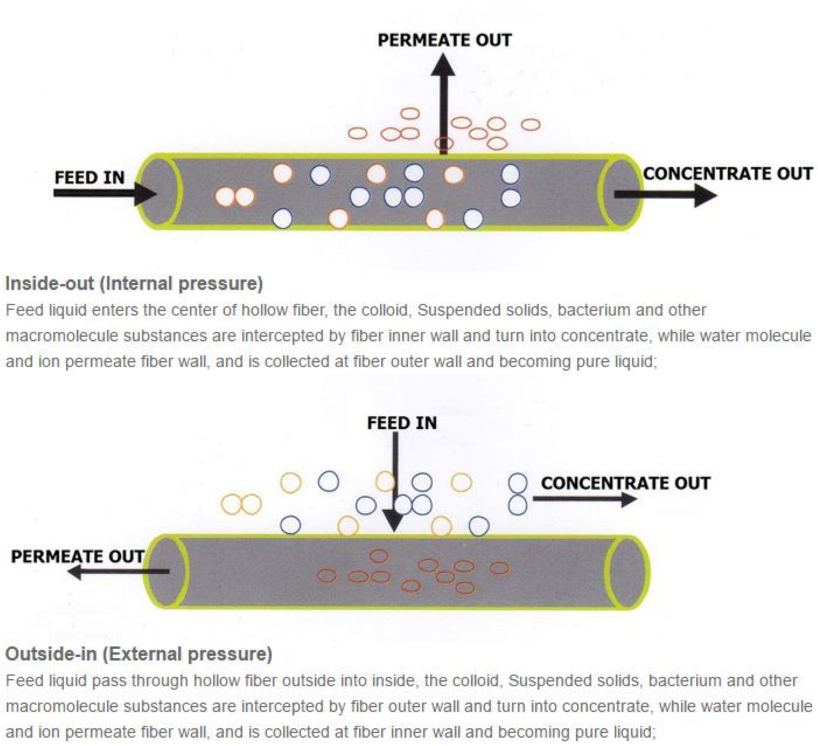


Figure 14: Tubular membrane, scheme of the filtration process and module



For tubular membranes and also other types of membrane technology those are in general two main possibilities of filtration directions with respect to the direction of passage of the liquid through membrane wall. It is either configuration from the outside in or the inside out. The difference between this two is shown in the figure below. Each type has its own advantages and disadvantages, and it is therefore necessary to distinguish what kind of application and the nature of the liquid has to be filtered.

Figure 15: *Difference between two UF filtration methods [61]*



- **Tubular module**

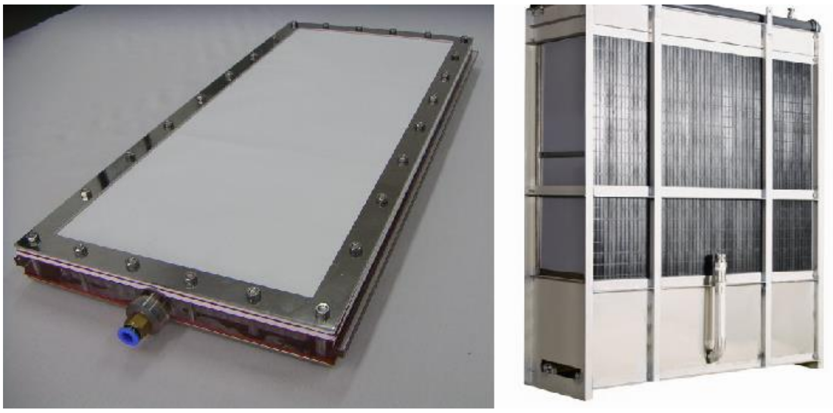
It is composed of various membrane elements that look like pipes within the internal pressure instrument. Mostly it is driven with inner pressure and cleansed with sponge balls. The density of membranes is low; however, sections in the membranes are big enough to apply to liquids with big sized molecules.

Figure 15: *Tubular Type Module Ceramic Membrane & PES and PVDF)*

Tubular devices are primarily used in micro and ultrafiltration applications because of their ability to handle process streams with high solids and high viscosity properties, as well as for their relative ease of cleaning.

- **Flat sheet** (plate and frame) consist of a series of flat membrane sheets and support plates. The water to be treated passes between the membranes of two adjacent membrane assemblies. The plate supports the membranes and provides a channel for the permeate to flow out of the unit module.

Figure 16: *Flat sheet membrane module*



Each membrane configuration is differently in packaging density and in the types of materials used. There are distinct advantages that come with each configuration, allowing to manage certain filtration process needs effectively.

2.3 The modified membranes and use of nanoparticles

Application of membrane technology water purification faces a major problem, and that is primarily biological and microbiological fouling of the membrane surface, which causes a decrease in permeability, i.e. a decrease of hydraulic power system. After a certain operating time, the membrane must be removed from the system and subject it to physical and chemical cleaning. This discontinuity is operational and application of chemical agents, especially chlorine compounds and organic and inorganic acids, which may pose certain environmental risks.

There are however a number of substances or nanoparticles, which may extend the life of the membrane. The most famous are probably the silver nanoparticles. They exhibit an extraordinary activity against a wide range of bacteria, yeasts and fungi with very low values of minimum inhibitory concentrations. The activity of silver nanoparticles often exceeds the effectiveness of commercial example antifungals. Suitable anchoring silver nanoparticles may lead to self-cleaning of membranes and filters, and thus to a considerable streamlining of these technologies. In contrast, natural biofilms are promising wastewater treatment technologies with a specific type of pollution.

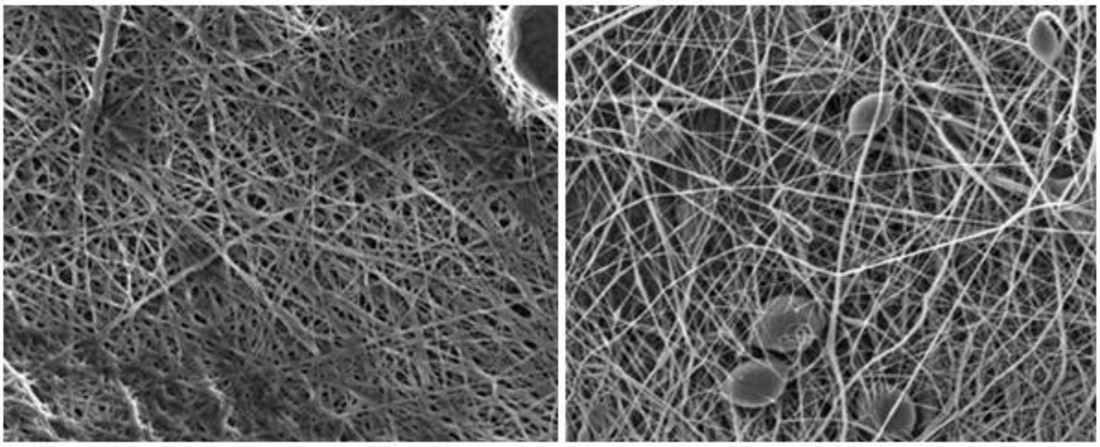
2.3.1 Biofouling and clogging

Biofouling is generally undesirable for many applications. This is the accumulation of unwanted biological matter on surfaces, with biofilms created by micro-organisms and macroscale biofouling (simply called macro fouling) created by macro-organisms. In addition to biofouling, inorganic fouling is composed of deposits from corrosion, crystallization, suspended particles, oil and ice. The term fouling describes both biofouling and inorganic fouling. [24] The type and extent of fouling depend on the local environment, inorganic deposits and organisms; this varies significantly between medical, marine and industrial applications. In general, medical biofouling includes only the biofilm, whereas marine and industrial biofouling generally include a combination of biofilm, macro fouling and inorganic fouling.[25]

In terms of membrane filtration is biofouling big complication Especially two types of fouling include biofouling from organism colonization and inorganic fouling from non-living particles.

Nature offers many solutions to control fouling through various physical and chemical control mechanisms. Examples include low drag, low adhesion, wettability (water repellence and attraction), macrotexture, grooming, sloughing, various miscellaneous behaviours and chemical secretions. A survey of nature's flora and fauna was taken in order to discover new antifouling methods that could be mimicked for engineering applications. Antifouling methods currently employed, ranging from coatings to cleaning techniques, are described. New antifouling methods will presumably incorporate a combination of physical and chemical controls.

Figure 17: *Example of the antibiofouling treatment using silver nanoparticles shown under electron microscope. Left membrane without Ag, right with Ag membranes. (Photo: SPUR a.s.)*

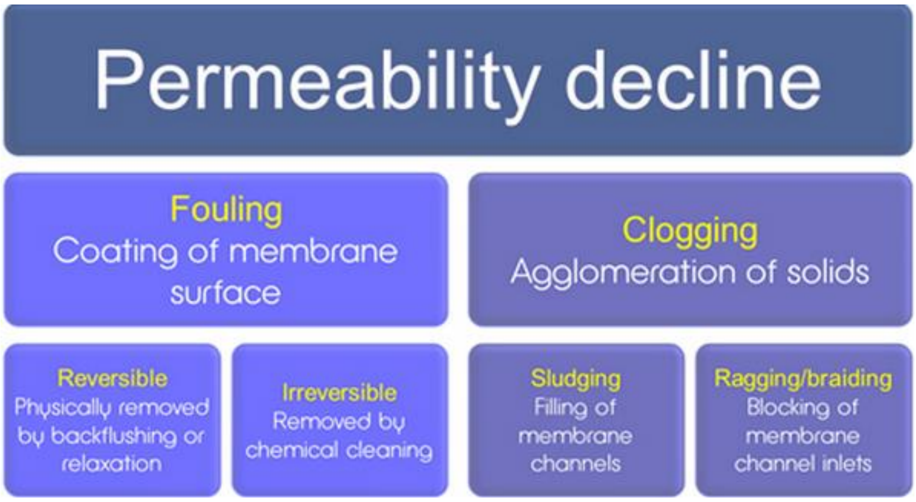


While most scientific articles about MBR systems suggest membrane surface fouling as being the main operational limitation for the technology, it is widely recognised by practitioners that clogging phenomena – possibly related to inefficient pre-treatment – are at least as important. Filter clogging can occur primarily because of molecular aggregation and can result in deterioration of product quality and longer processing times and thus, loss of plant capacity.

It is also recognised that clogging takes different forms. 'Sludging' refers to the filling of membrane channels with sludge solids and depends on process design (membrane module and aerator, pre-treatment). ‘Ragging’ (or ‘braiding’) is the blocking of membrane channels with particles agglomerated as long rag-like particles [28].

Filter clogging can occur primarily because of molecular aggregation and can result in deterioration of product quality and longer processing times and thus, loss of plant capacity.

Figure 17: *Permeability decline causes [27]*



TMP = trans membrane pressure

TMP = (Pf + Pc)/2 – Pp

Pf = feed pressure

Pc = concentrate pressure

Pp = permeate pressure

2.3.2 Nanoparticles as additives for membranes

Biofouling nowadays succeeds in limiting using some of additives, which are applied to the membrane. Or incorporated directly into the supporting fibres (nanofibers case membranes). This is a modification of nanofibers to achieve further significant characteristics of the filter layers and the biocide, antibacterial (elimination of live microorganisms, prevent their growth, affect biofouling etc.)

Generally known applications (references to the effects of nanoparticles in the literature) today e.g.:

- Nanoiron - zerovalent iron effects are associated with it´s strong reducing properties that is used to remove chlorinated hydrocarbons, heavy metals, arsenic, pesticides, radionuclides, and others.
- Nanosilver - silver in a humid environment emits ions Ag^{+}, which are the cause of its antimicrobial properties. Ag^{+} ions are aggressive towards Gram-negative and Gram-positive bacteria, interrupt important vitally important functions in the organism, and without these functions are either suppressed the growth of bacteria or microorganism is frequently death. Oligodynamic effects described for other metals e.g. for copper and zinc.
- Nano forms of metal oxides - e.g. ZnO, TiO_2 - known as the oxidation, and antimicrobial properties based photodynamic effect, when the interaction of the light quanta of a certain wavelength (in this case, the UV region) with an appropriate metal oxide generated from diatom oxygen reactive oxygen forms which have a strong oxidizing properties and are highly reactive. Among the reactive oxygen forms belong e.g. hydroxyl radicals, superoxide's, singlet oxygen and other. Photosensitive characteristics of ZnO and TiO_2 is used by photo oxidation phenol based pollutants, disinfection and can also be used in air purification.

Within this doctoral thesis has been made experiments with nanoparticles of these materials:

- Phthalocyanines
- Zeolites
- TiO2,
- Ag, AgNO3

Testing nanofibers filters have been focused on the development of the technology of immobilization of nanoparticles of metallic silver, the material characterization of materials prepared for subsequent laboratory and pilot tests. At the Mendel university were tested the filter materials in the laboratory in terms of mechanical and hydrodynamic properties, filtration characteristics and tests biocidal properties. Company SPUR also develops nano- and microfibrous biomass-carrier filter material with immobilized enzymes for cleaning micro pollutants and filtration membranes for membrane bioreactors, and verified their efficiency in laboratory. The role of Botanical Institute of the Czech republic consisted of screening potential enzymatic activities and their determination as well as in the selection of suitable microbial strains for natural immobilization. Botanical Institute of the Czech republic and the Mendel University also involved in microbiological testing "nanosilver" modified materials which were prepared by the University Palackého (UPOL).

The results of this testing, however, determined as confidential and can´t be in this phase of the research and the work published. Therefore, they are mentioned only marginally, as part of a comprehensive doctoral thesis.

2.3.2.1 Titanium dioxide (TiO_2)

Titanium dioxide in the crystalline state exists in three modifications, which correspond to three different minerals - rutile, anisate and bookie. Titanium dioxide is approaching its photocatalytic properties almost ideal material. It is relatively inexpensive, chemically stable molecule and TiO_2 as such, is almost non-toxic (Fujishima et al., 2000). Recently titanium dioxide is used primarily for water treatment, the degradation of organic substances, for the production of self-cleaning coatings and disinfection. TiO_2 is added to the water in suspension (titanium oxide is insoluble in water), or is applied as a coating.

The most promising appears to be the use of TiO_2 in anatase form, wherein after irradiation of a suitable wavelength (under 385 nm) and by interaction with molecular oxygen leads to formation of (* OH) radicals, or superoxide radical (O_2 * -). In other reactions may then occur in the formation of other reactive oxygen species such as singlet oxygen, perhydroxyl radical or hydrogen peroxide. All of these extremely reactive species interact with near-occurring organic molecules or organisms. Hydroxyl radicals are usually referred to as the main agent responsible for the bactericidal effects of photocatalytic materials. Their formation occurs degradation of organic substances, bacteria, algae, cyanobacteria, fungi or viruses.

2.3.2.2 Phthalocyanines

In connection with problems of treatment and purification of water and air, it was decided to try out also phthalocyanines photosensitizers whose photo-oxidation and anti-microbial effects based photodynamic effect, are known and were reported many times. Phthalocyanines unlike the aforementioned titanium oxide and zinc interact with light quanta in the visible rays to produce singlet oxygen from oxygen diatom whose presence is necessary for the progress of the reaction.

Phthalocyanines (FTC) are planar aromatic molecules, synthetic analogues of porphyrins. The first industrial application of phthalocyanines was determined by their optical properties and utilized primarily for dyeing in the textile industry. Its greatest advantage is that they can, after irradiation by light radiation to produce reactive oxygen species like the photoactive titanium oxide. Moreover, without any further treatment can leverage (unlike TiO2) as UV light and radiation in the visible spectrum of light. Thanks to these properties are used for example for the treatment of malignant tumours, the degradation of some pollutants, destruction of microorganisms. In addition, various modifications can phthalocyanines. Major sites of modification are mainly central atom which may be formed of aluminium type metals, copper, manganese, zinc, tin and the like. The phthalocyanines can also establish another molecule and the functional group of molecules that can significantly affect their properties such as the production of singlet oxygen or the charge on the peripheral portion.

Phthalocyanines toxicity to aquatic organisms are relatively poorly understood. The only exceptions are studies of a few writers who tested phthalocyanines against algae, cyanobacteria or daphnia. The result of this work shows that it always depends on specific structural variation of the properties of phthalocyanines and phthalocyanines cannot be generalized in the sense that they are toxic or non-phthalocyanines. Phthalocyanines can exhibit both relatively high toxicity (up to hundredths FTC milligrams per litter of water) and low toxicity (acute adverse effect on the body has not been detected at a concentration of 50 mg/L).

Nowadays are phthalocyanines used for limiting the development of various types of bacteria and microscopic fungi. They may be applied as aqueous solutions, anchored on carriers of various types of appropriate coatings. Phthalocyanines are capable of inhibiting growth of the following organisms: *Mycobacterium smegmatis, Escherichia coli, Staphylococcus aureus, Tritrichomonas foebus, Synechococcus nidulans* and others.

2.3.2.3 Zinc Oxide

Among other nanomaterials exhibiting photocatalytic reaction include zinc oxide. Thermal stability, light resistance and flexibility in the creation of nanostructures make the zinc oxide material suitable for production of photodetectors, UV nano laser, gas sensors, biosensors and the like. As in the case of other materials can be combined zinc oxide with nanostructures of various polymers to achieve the necessary properties

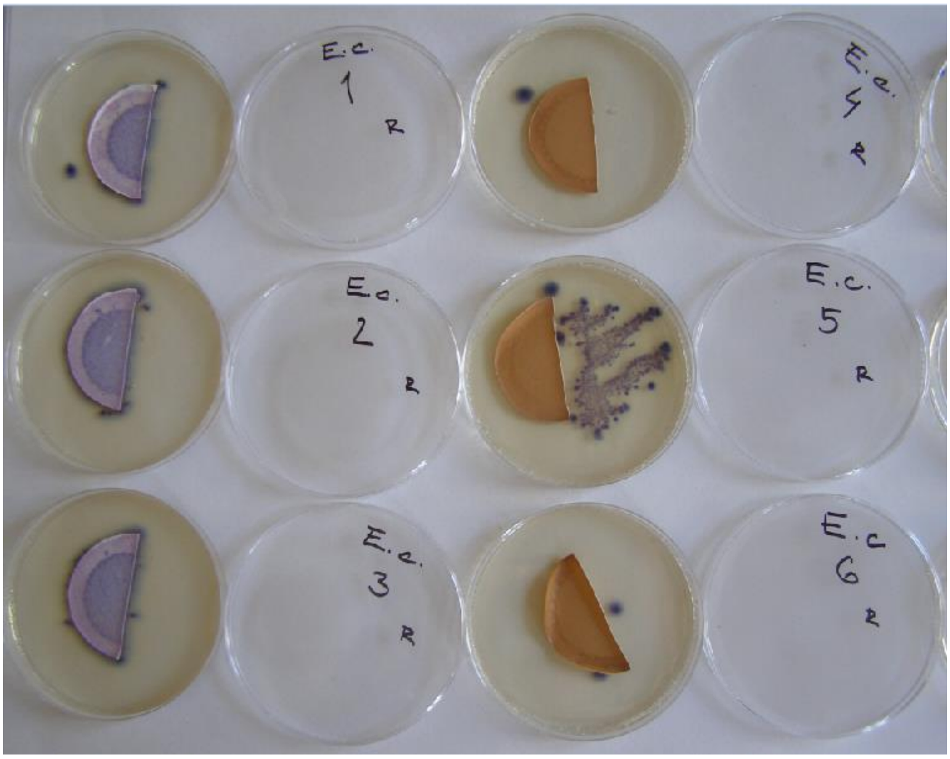
2.3.2.4 Nanosilver

Nanosilver has like the previous materials strong antimicrobial properties. On the other hand, light activation for its effect is not as important as in the case of titanium dioxide, phthalocyanines or zinc oxide. Although the properties of nanosilver known for decades, it is still not exactly documented their effects on microorganisms.

Silver is used both to water and to air filters. Although silver is often water running from the eluted carriers, there are ways to prevent this process. In the publication of Pradeep Jain, [29] raised the possibility of nanosilver by the polyurethane foam, thereby achieving stability of silver plus its elution was limited, probably due to interaction with nitrogen atoms polyurethane. Another possibility is the use of nanoparticles for binding carbon nanofibers, [30] or ceramic filters (Oyanedel-Craver and Smith, 2008).

It is reported that in everyday life, the nanoparticles are applied in more than one hundred product types [31]. At random, we can choose application against to the occurrence of mold where the particles are contained in paints, coatings for kitchen against the development of microorganisms used in the textile industry, in addition to clothing, deodorants, sunscreens, water purification (Aquapure®, Kinetico®, and QSI-Nano®) and so on [31].

Figure 18: *The picture shows testing of anti- biofouling modified membranes doped with silver nanoparticles, engaged by a covalent bond.*



Illustrative image coming from the experiment when filtration of the model solution with high concentrations of *E. coli* was carried out. In conventional materials, modified by silver nanoparticles occurs washout of nanoparticles during washing or using material. Eventually loses the ability to act anti-microbial. Using the latest findings was created prototype of membranes in cooperation with Palackého university and the company SPUR as. Zlín. Silver is bound by a covalent bond and this is prevention against washout. This was confirmed by experiment. On washed membranes and after filtering the solution with E. coli bacteria colony were growing and observed after colouring just on the membrane without nanosilver particles. Brown membranes are with additive of silver, which betrays their colour.

3 OBJECTIVE OF WORK

The dissertation topic was chosen with regard to the current rapid development of nanotechnology in the world and in the Czech Republic. Nanotechnology can be used for many intensification of the process of which one is for our future very important and it is pure water.

Nowadays, there are technologies that enable the production of nanofibers in industrial scale. We can generate a variety of structures, membranes, adding additives and thus completely change the position of the membrane filtration in the market. Thanks to all the opportunity to transfer technology of the "future" from the lab into the practice, and to ordinary users.

This dissertation is focused on the use of knowledge for producing nanofibers in combination with established techniques for water treatment. Within a few years of research, which was connected with the project NANAPL (Suitable materials for nanotechnology applications in the purification and treatment of water and air) is solved in the framework of the ALFA Technology Agency of the Czech Republic in the years 2011 - 2014. The main objective of the project was an extension of nanotechnologies and nanomaterials in the purification and treatment of water and air.

At present, it is clear that neither the existing BAT technologies aren´t in some cases able to ensure "the good quality of waters", and therefore the discovery of new technologies are needed and desired - especially if they will lead to economic solutions. Currently, more and more foreign companies are engaged in the use of nanotechnology for water and air treatment. It is therefore necessary to capture this trend and through protected procedures and appropriate promoting to secure a position on the European market as well as export options to other non-European countries.

The research team consisted of five members - two representatives of academia (The Institute of Botany of the ASCR and the Mendel University in Brno "MENDELU"), a research centre "COC" (Centre of Organic Chemistry s.r.o. Rybitví), and two application companies, producer of plastic products and nanofiber structures (SPUR a.s. Zlín) and ASIO, spol. s r.o., which has a role of coordinator in this consortium. Currently, in the field of water and air purification the nanotechnology and nanomaterials are becoming more frequent. Their use, however, can greatly increase the effectiveness of existing treatment processes such as adsorption or catalytic oxidation, due to increase the usability of the surface per unit volume, e.g. use of titanium dioxide for catalytic oxidation of organic materials acquires a completely different meaning by using nanotechnology and even in the case of disinfection - destruction of viruses and bacteria. The technologies applicable only marginally for its relatively low performance and efficiency (for example, using of titanium dioxide) may come to the forefront and may even completely replace the current technology due to the vast increase in the area and thus of intensification. Nanotechnology can replace in the process of treatment and purification of water and air many of the classic technologies - ion exchangers, reverse osmosis, coagulation and sorption, under more favourable conditions than those technologies provided and without some limitations of these technologies - without excess of sludge production, without increasing salinity, with lower costs, etc.

A utility model or prototype of equipment for disinfection of water using the biocidal effects of nanotechnology (demonstrating the utility of nanotechnology in this field) was planned as the output of the NANAPL project. Based on the results of this project were built up, this PhD thesis. The specific form of the output is decided upon laboratory testing of multiple options and evaluation of economic advantages (utilization of nanosilver, nanoiron, or other substances which comes into consideration). Also the prototype of nanofiber layer suitable polymer, active ingredients, structure of nanofibers, and the overall composition of the filtration layer to filtration of surface waters in order to capture bacteria.

During the project, a number of promising nanomaterials has been already prepared, which are now being tested for use in purification of water and air. For example, the polymer nanofiber structures for filtration of bacterial contamination or photoactive biocidal nanoparticles based on phthalocyanines. Currently, not only functional properties of these materials and technologies useful in the practice are tested, but also the potential negative effects on human health and the environment. Thereby potential risks are eliminated which may arise from the use of new, previously unused materials.

In subsequent years of the solution it is expected to transfer of laboratory results to pilot models and verify the properties of manufactured materials in real conditions. Continuous measurement results and acquired experience have been already presented in many national and international conferences and seminars.

Besides the main objective, namely to develop a device that will be able to effectively and quickly clean and appropriate sanitation and water were determined as well as certain other objectives:

Milestones in the process of dissertation can be formulated as follows:

- Create an overview of the application of nanotechnology in the field of water management with emphasis to the water filtration
- With regard to the specific properties of nanofibers, more precisely identify a segment of wastewater, wherein the filtration with nanofibers suitable and competitive solutions.
- On the basis of cooperation with the manufacturer of nanofibers to develop the most suitable material and test them in the laboratory and small scale unit
- Experimentally verified theoretical assumptions using the pilot plant at the selected location
- Evaluate data and suggest possible improvements.

4 EXPERIMENTAL VERIFICATION OF THE FILTRATION PROPERTIES OF NANOTEXTILE MATERIALS

Fibbers having a diameter of several tens nanometres were from the beginning developed mainly for the production of filter materials. Materials with a high porosity while having little pore sizes are ideal for the production of filters. Nanofibers are therefore very quickly applied especially in the filtration of air/gas, where they exhibit good results and are already commonly used. Due to their lower mechanical resistance, has not been applications nanotextiles for liquid filtration devoted as much attention as air filtration. But one can assume that nano slowly beginning to find application in the filtration of liquids, which is evidenced by the increased professional publications in recent years. After consultation with experts focused part of the work on the experimental verification of the use nanotextiles for water and liquids in general.

To test was chosen rather lengthy process designed to ensure the selection of the best possible material for applications. Due to technical difficulties and time demands have not undergone all potentially successful materials by this procedure. Nevertheless, several materials have been selected, which during the test proved to be very promising. For the selection and testing of the materials was chosen sequence:

- Testing on laboratory filtration device (flow rate and filtration efficiency)
- Testing in semi-laboratory conditions using filter frames
- Testing with the real water in a smaller scale
- Testing in pilot plant conditions

During the project, several laboratory, then the larger laboratory devices and then the pilot plant units were constructed. Experimental verification of the data was divided into several stages but testing has been linked. For easier understanding of the interdependence key stages of the project are shown in a table with their brief description and goals.

Shortcuts: HF = hollow fibres, FS = flat sheet, NFS = nanofibrous flat sheet

Table 4: *Dividing of the experimental phase of the project into different stages.*

Phase	Time period	Main goal	Place of instala-tion	Type of the membrane
Suitable material for membrane testing.	10/2011 – 6/2012	Verification of the hypothesis Manufacturability tests	Lab.	Different types of small flat sheets
Laboratory samples and devices, semi-pilot plant	7/2012 – 5/2013	Check laboratory efficiency of selected materials	Lab.	Small Flat sheet modules
Pilot - MBR testing	7/2013 – 5/2014	Verification under real conditions, optimization	WWTP Letonice	NFS
Pilot – MBR comparison	9/2014 – 2/2015	Comparison of the conventional flat sheet membrane with nanofiber membranes and hollow fibres	WWTP Modřice	FS NFS HF
MBR comparison	8/2015 – 9/2015	Tests of the modified NFS module against Commercial FS	WWTP Modřice	NFS FS

Within the phase: Suitable material for membrane testing, were performed experiments focusing on material properties of produced nanotextiles materials and was selected area for experimental verification of their properties. The hypothesis assumed that due to the large number of pores will be this new material excellent in the filtration rate and still be able to compete with the mechanical properties of competitive membranes. Although filtration is used in a variety of fields, from industry to the food industry, we have chosen the path filtering of wastewater. The aim was to develop new membrane and this objective was systematically followed during experimenter.

The following stage describe chronological experiments conducted in cooperation with other colleagues and participating research institutions that participated in the development of materials, construction and designs of operational models and evaluation tests. Those experiments were performed mostly In laboratory using laboratory scale and semi laboratory scale devices for filtration. The aim was to choose best material for pilot testing and eliminate potential operational problems.

The part: Pilot MBR testing is related to the construction of the first pilot plant membrane bioreactor. This was installed after several months on the treatment plant Letonice. This phase brought invaluable operational experience and gave suggestions for optimization and future adjustments of the pilot plant.

Following an experiment on bypass of the wastewater treatment plant Modřice. Here, the operation of membrane modules was divided to several partial experiments that has certain characteristics. The first phase, when there was a rupture of the nanofibrous membranes is omitted from the evaluation. In this part of the dissertation is evaluated data segment from 7 October 2014 to 15 February 2015.

The last phase of the table: MBR comparison, is dedicated to the subsequent testing. It was a period of optimization and implementation of new membranes design and manufacturing techniques. In the dissertation, this period is mentioned only marginally. One reason is that this experimental phase, which began 8/2015 is actually still running. (Today: 6 September 2016).

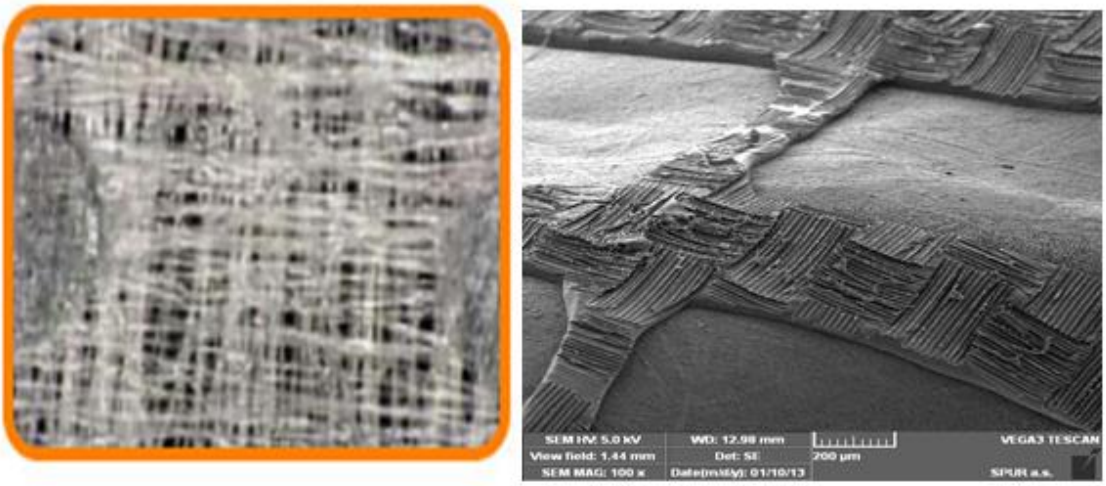
Some parts of the dissertation can´t go too much into details in order to protect know-how and technology of the project consortium.

4.1 Construction of membranes

There were many possibilities of constructions and material options for fixing the substrate with nanofibers and types of nanofiber material production. In the first part it was necessary to test large amount of various materials and choose the direction in which further development will proceed. For experimental verification of the proposed material was created methodology of comparing the properties of various materials nanotextiles filter materials. This method will be described in detail in the following chapters.

The main objective of the design of the filter membrane with nanofibers is to achieve a sufficient resistance and in doing so significantly negatively without affecting the flow rate. During this work, we examined several stiffening adhesive systems:

Figure 19: *Adhesive PE/PP nets: CLAF fi. Nippon (fibres 200 – 500 µm), weigh: 16 – 100 g/m². (Photo: SPUR a.s.)*

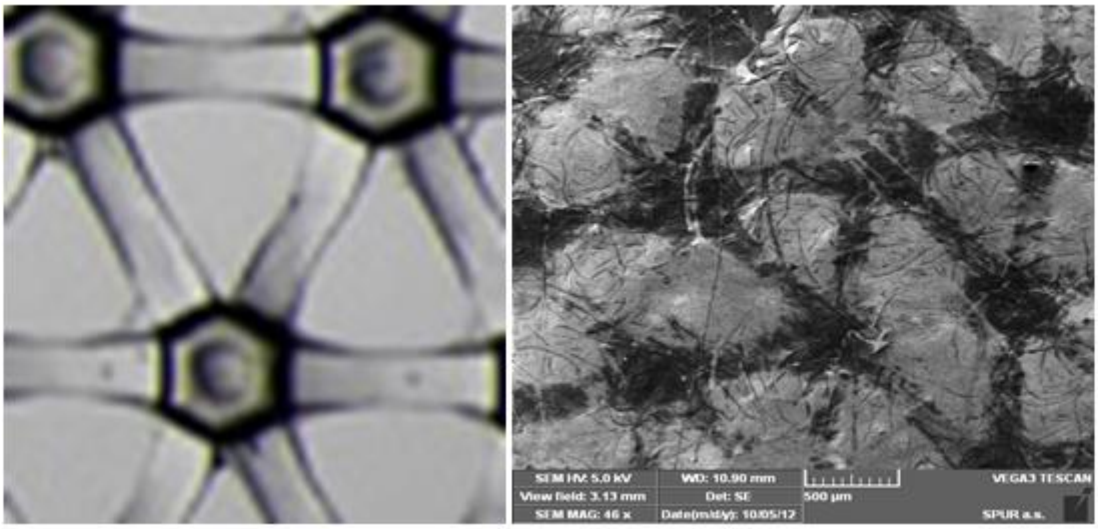


This microscope image SEM (right image) shows an adhesive connection with the network as NNT, and underlying microfiber cloth - on the fibre mesh is visible imprint microfibers.

4.2 Filtering water through nanotextiles membranes

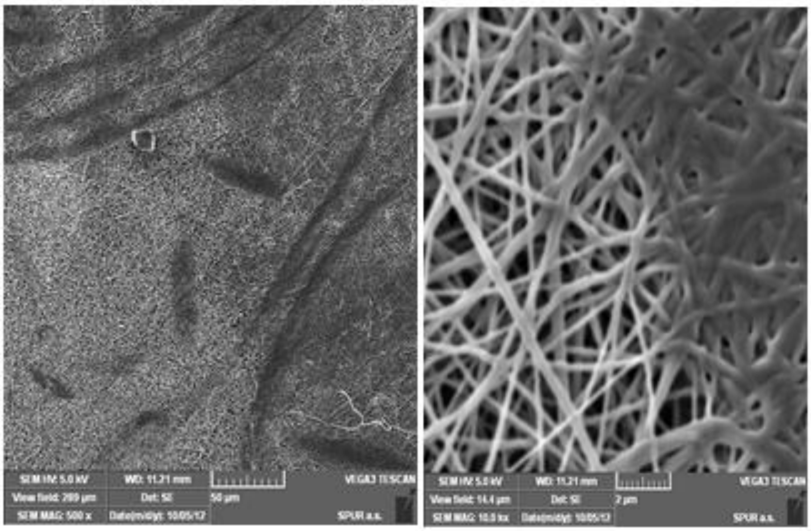
When evaluating membranes designed to filter water were considered two major quantifiable indicators. Results of porometric measurement (measurement of the pore size by means of flow porosimetry), and flow rate at the membrane with pure water at ambient conditions, the driving force (pressure drop expressed on the membrane). Although these two parameters is essential and used in practice, require specific properties of nanofibers also monitor other parameters, to some extent subjective appreciable, and thus mechanical strength of the membrane. Taking into account the results in the previous period and on our knowledge and experience of nanofibers destined for membranes to filter water were selected NNT polyurethane (PU) and NNT of polyvinylidene fluoride (PVDF).

Figure 20: *PE network melting ionomer layer, Smith & Nephew (fibres 100 mA) and 9 grammage 15 g / m². (Photo: SPUR a.s.)*



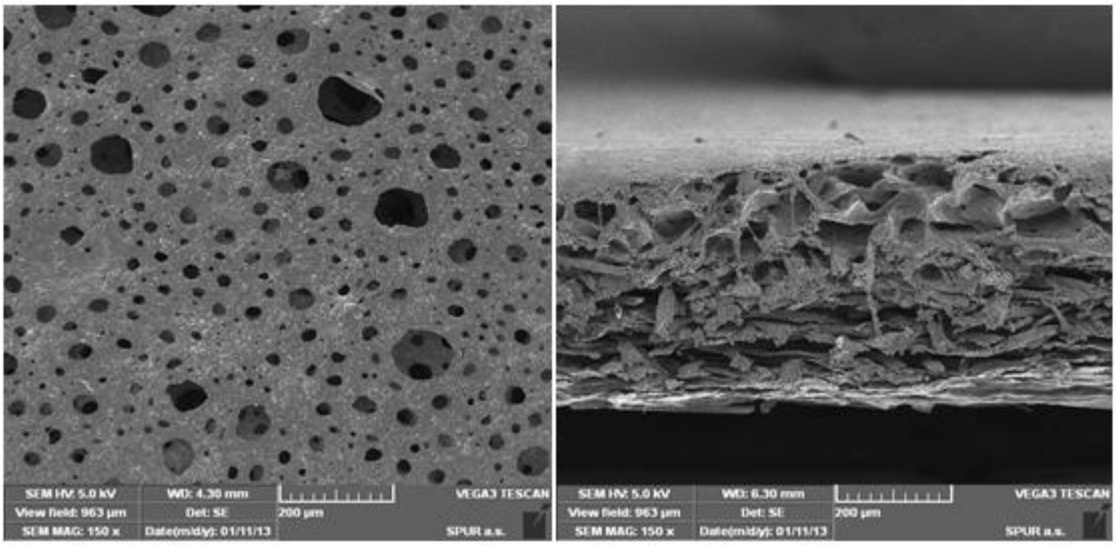
SEM (picture right) shows the penetration ionomer network structure nNT.

Figure 21: *The adhesive web-based Copolyamide fy Protechnic (20 µm fiber) weight of 6,8 and 12 g/m².(Photo: SPUR a.s.)*



SEM (pictures right) shows the penetration of the adhesive layer of nNT site.

Fig 22: *Open PU foam is applied to the substrate textiles (Photo: SPUR a.s.)*



Left image shows the open surface of PU foam, right image shows a section of open-cell foam into which the front side is pressed nNT.

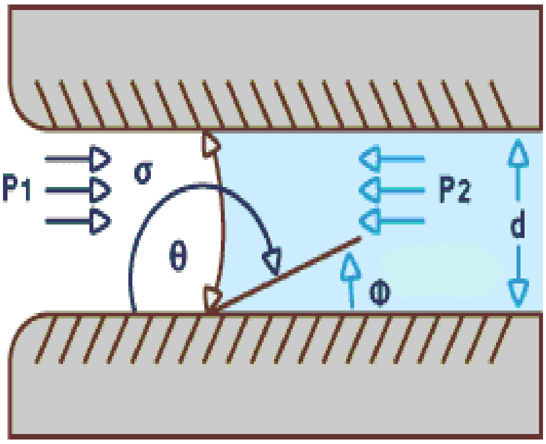
All four systems are promising for real use, because nNT maintain permeability even though it is to some degree influenced. Fundamentally solves the mechanical properties of nNT, their gripability and usability for the filtration of of liquids. Specific application still will be preceded by a series of experiments.

4.2.1 Porosimetry

Generally recognized method of determining pore size filter membranes is the American standard ASTM F316 - 03, which is defined by the flow porosimetry.

Principle of the method is very simple and is based on force balance (equilibrium) of the pores of the wetted membrane, which act against each other from one side of the force given by the air pressure on the pore surface and the second side of the force given by the surface tension of wetting liquid is applied along the circumference of the pores.

Figure 23: *Scheme of the balance of forces in the pore wetting liquid*



The result of this balance is the relationship determining pore diameter for a given pressure

$d = \sigma\ 4k\ \cos\theta\ /\ P$

P = "bubble point" pressure

d = pore diameter

k = correction factor shaped pore

$\cos\theta$ = wetting angle of the liquid-solid

σ = surface tension of wetting liquid

Porometric measurement is performed so that the dependence of the air flow follows the membrane at atmospheric pressure at first, the dry membrane, and the membrane subsequently wetted with a wetting liquid. Examine called dry and wet test, from which it is possible using the above equation to calculate pore size (corresponding to the air pressure) and the proportional representation of the pore size and thus statistical distribution of pores according to their size.

Porometric measurement results are shown in the following two graphs:

Fig 24: *The dependence of flow-pressure dry and wet test*

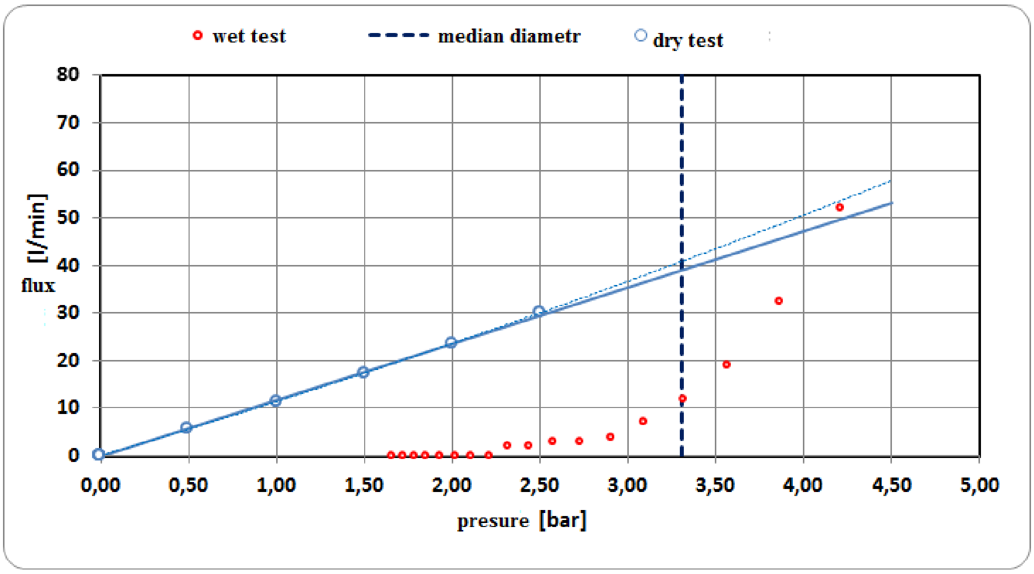
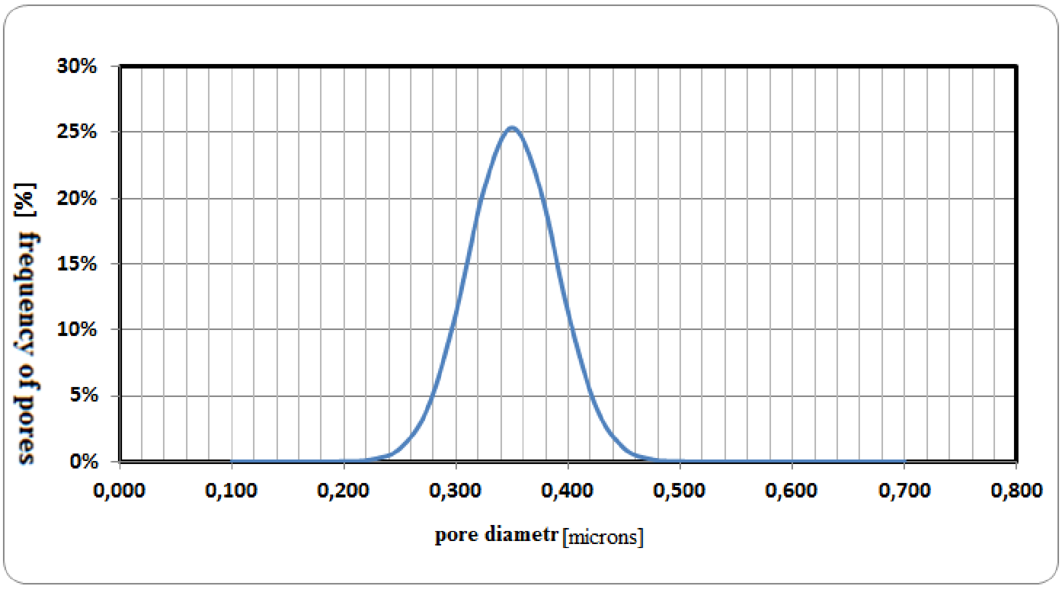


Fig 25: *Frequency function f (d) - the relative abundance of pores of different diameters*



In order to intensively devote the issue and understand the specifics of layers based on nanofibers were prepared porometric apparatus, based on the above American standards and takes into account the characteristics of very fine structures nNT.

Fig 26: *Scheme of the porosimeter*

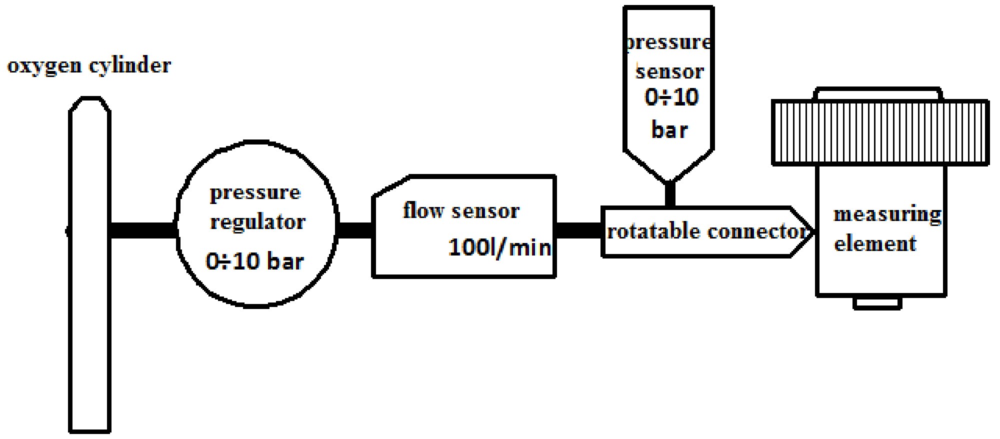


Fig 27: *The assembled apparatus for measuring pore sizes and variances, SPUR a.s*

4.2.2 Measuring the flow rate of the membranes

The flow rate of the membranes was measured, first at low pressure drop of 0.075 bar the liquid level of the water column above the diaphragm, and also at a higher pressure (0.5, 1 and 2 bar) the regulated pressure of air above the surface. Measuring the flow rate at Δp 0,075 bar: 106 mm diameter filter surface. The height of the water column 750 mm ~ 7.5 kPa, provided the overflow. It was measured volumetric flow rate depending on the time of filtration.

Fig. 28: *Measuring the flow rate of the membranes at a constant pressure drop of 7.5 kPa*

4.2.3 Laboratory device for membranes testing

Within the project was designed and constructed at first laboratory device for measuring the permeability of filter materials of pure water at a given height of the water column from the column height was then simply derived pressure on the test material. Using the measured values may be captured by the velocity of flow depending on the pressure of the liquid over the filter. Acquired parameters used to determine the parameters produced nanotextiles materials. Measurement methodology has been designed according to ČSN EN ISO 11058 - Geotextiles and geotextile-related products - detection of water permeability characteristics normal to the plane, without load. [32].The device itself is the subject of Utility Model no. 26795: Filter and devices for cleaning liquid.

4.2.3.1 Material and technology of production

The device was designed for the filtration of liquids - water, oil, beverages, liquid agricultural products and the like. On the basis of these requirements, the material selected for the manufacture of the individual components.

Stainless steel the ČSN 17240, which is usually used for the manufacture of tanks and pipelines in the food industry. This material provides sufficient chemical, thermal and mechanical resistance. The individual parts of the device are assembled from standard, mass-produced blanks, control and measuring elements. Components were associated fittings, sealed with Teflon tape, complicated parts welded with TIG (titanium inert gas - welding titanium electrodes under inert gas).

4.2.3.2 Constructional solutions

Construction of the first laboratory equipment, which were tested also in the laboratory produced membranes were as follows:

The filtration device was designed as a pressure tank, mechanically very resistant. This was attached to a sturdy bracket. The upper part of the pressure tank was equipped with a funnel diameter of 20 mm and flange. It was closed ball valve.

The flange is fixed to the tank 8 bolts. This ensures that sufficient unison pressure on the rubber seal. Additionally, the system allows easy removal and cleaning. From the side it is applied to the compressed air conduit of 15 mm diameter. Compressed air supply is provided with a pressure sensor, check valves, control valve, air filter and ending couplings. Here it is possible to bring the pressurized air from the cylinder or of the pressurized air supply. The equipment enables the use of other gases than air pressure, e.g., inert gases, nitrogen, carbon dioxide and the like. In the lower part of the device is located drain pipe connection to a pressure sensor (connection to PC), a drain valve, and the filter material holder.

Figure 29: *The first version of the filter device (left) and third version (right). (Photo: Došek M.)*

4.2.3.3 Technical parameters

The device is designed for the pressure to 2.5 bar using the barometer of the above range may be increased (estimated to 10 bar). The device can be equipped with accurate pressure sensor - ready fitting to drain the drain valve, can be connected to PC. Pressure vessel capacity is about 1.5 litters (possibility of modification connecting the fluid supply to filling valve - constant stream of the media).

4.2.3.4 Principle and function of the facilities

The device is especially designed for monitoring filter efficiency, but can also be used to monitor other material parameters of different filters in the laboratory, respectively pilot plant conditions. Filtration can be performed as dead end (all liquid is forced through a filter), or cross-flow (the fluid flows around the filter portion of the liquid residue is filtered and circulates in the circulation)

Dead-end filtration:

Before starting the filtration is necessary to assemble the device, according to the size of the used filters. The device allows you to use filters on sizes 48 and 100mm. For connecting the filter diameter 48 must be used to reduce the clamp flanges corresponding dimensions. Before the filter attachment is always necessary to incorporate the butterfly valve size. After closing the drain claque (flap above the filter) may be impregnated with the liquid for filtering.

Contaminated liquid is poured or pumped into the pressure vessel filling opening in the upper part of the device. After closing the dispensing valve can be fed through the pressure regulating valve compressed air. Control valve can be set to a constant pressure of 10 bar. There must be observed regardless of the connected Barometer (range may be smaller and may overload).

To start filtering process, just open the drain valve above the filter. Thanks to the pressure above the filter leads to liquid filtration and filter clogging. By tracking the flow can be traced Speed clogging. Both the original and the filtered liquid are subjected to analysis and is calculated filtration efficiency of the material.

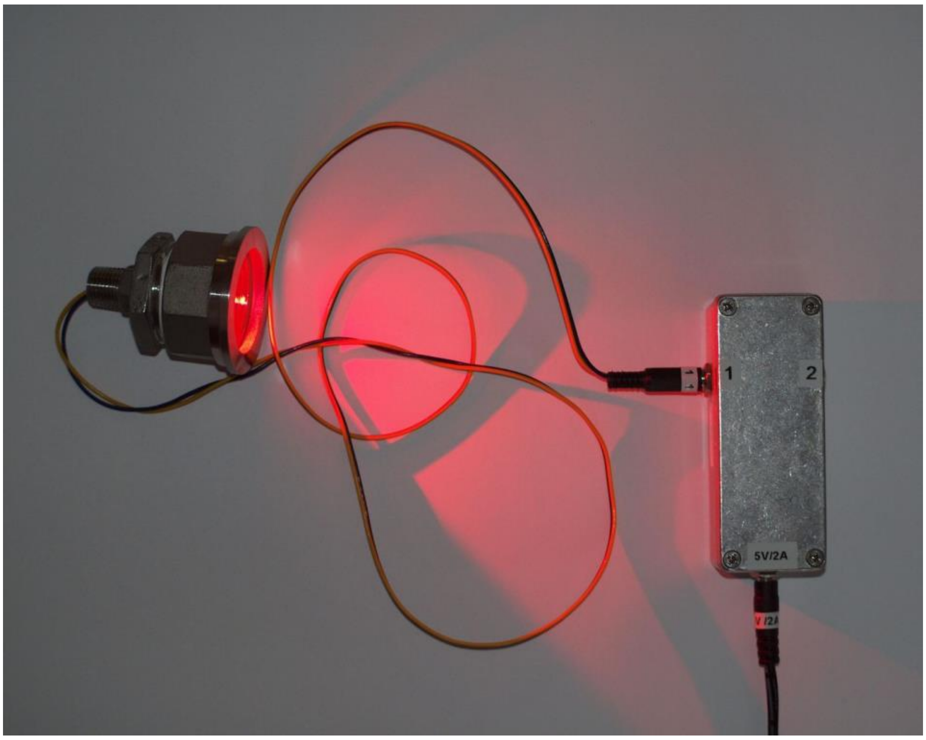
Cross-flow filtration:

For cross flow filtration system must be completed with pump and storage tank. Before starting the filtration is necessary to assemble the device, according to the size of the used filters. The device allows you to use filters on sizes 48 and 100mm. For cross flow filtration I recommend the use of larger filters, as smaller filters are designed for smaller volumes. Before the filter attachment is always necessary to incorporate the butterfly valve size. After closing the drain claque (flaps over the filter) can be impregnated with liquid.

From the storage tank the liquid is pumped by pump into a pressure tank from which it is filtered through the filter portion, and part is diverted through the choke valve back to the reservoir. Throttle valve can set the required positive pressure above the filter. Both the original and the filtered liquid is subjected to analysis and is calculated the filtration efficiency of the material.

In case that were used for nanofibrous membrane with additive of photoactive substances, it was possible to attach the lighting adapter.

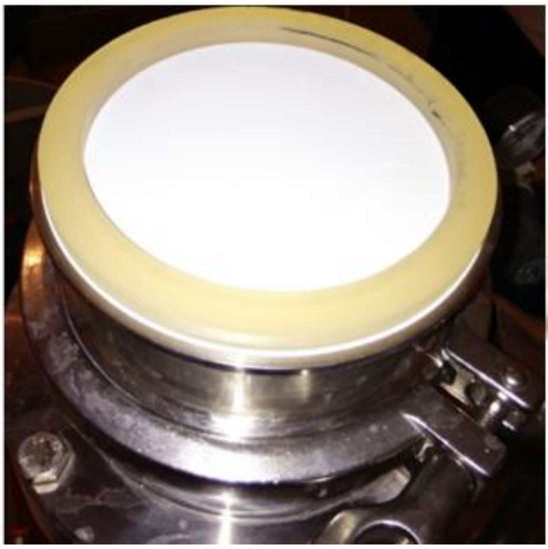
Figure 30: *Detail of the lighting adapter for illumination of filtration membranes with red spectrum diode, suitable for activation of phthalocyanines. (Photo: M. Došek)*



4.2.3.5 Preparation of the nanotextiles samples for filtration

From rolls of nanotextiles materials, were punch through samples for filtration with a punch of own construction. Samples had a diameter 48 mm or 100 mm. Accordingly, the filtration apparatus which has been selected. The punch consists of a holder and a removable attachment embossing. Punching howled done using a rubber mallet. As a basis for stamped was used Teflon pad.

Figure 31: *Punch through membrane, diameter 100 mm, placed on the filtration device (left) Sample preparation for testing. (right)*



4.3 Membrane testing using a model microbial pollution

Water is one of the basic conditions for the biosphere. The consequence of a growing human population, increasing pollution of water sources and climate changes that can degrade or destroy the water resources in the near future may become particularly high-quality drinking water is scarce.

Even today, in some developing regions, drinking water normally available. Estimates of the World Health Organization (WHO) is talking about 1.2 billion people lack access to clean drinking water. They represent a problem with polluted water bacteria and viruses that also cause serious health problems, which may result in death. 3.4 million people, mostly children, die annually from water-related diseases [33].

To remove microbiological contamination from water can be used a number of conventional method such as membrane separation, ozone, peroxide, chlorine or UV radiation. New productive technologies of electrostatic spinning polymer nanofibers provide a source of new materials with specific properties that have the potential to be an alternative or complementing existing technologies abolition of microbiological contamination. Bacteria vary in size, and may be as long as 20 μm or as short as 0.5 μm. Coccus = 0.5 μm, Spiral = 15 μm [34].

The pore size of the nonwoven nanofibrous structure is in the tens or hundreds of nanometres. Such differences sized dimensions predict nanotextiles ability to capture the microbiological pollution and other contaminants. By verifying these assumptions experimental measurements are explored in this chapter.

4.3.1 *E. coli* as a model microbial pollution for laboratory experiments

To evaluate optimal filtration properties of materials suitable nanotextiles to remove bacteria from the liquid was used water pollution model. Experiments were performed with sterile distilled water artificially contaminated *E. coli* bacteria.

4.3.2 Material and Methods

For the experiment were used materials produced by nanotextiles electrospinning with different fibres diameters and the basis weight of the nanofiber layer thickness representing. It has been tested several dozen samples of materials. Therefore, are not listed by name. Based on this first experiment were then selected materials for further test series. A sample of nano always had a circular diameter of 48 mm. Clamping of the sample to the filtration holder was functional part reduced to a diameter of 38 mm, which corresponds to an area 1134 mm2 (11.34 cm^2). Sterilization was performed by UV radiation for 4 hours.

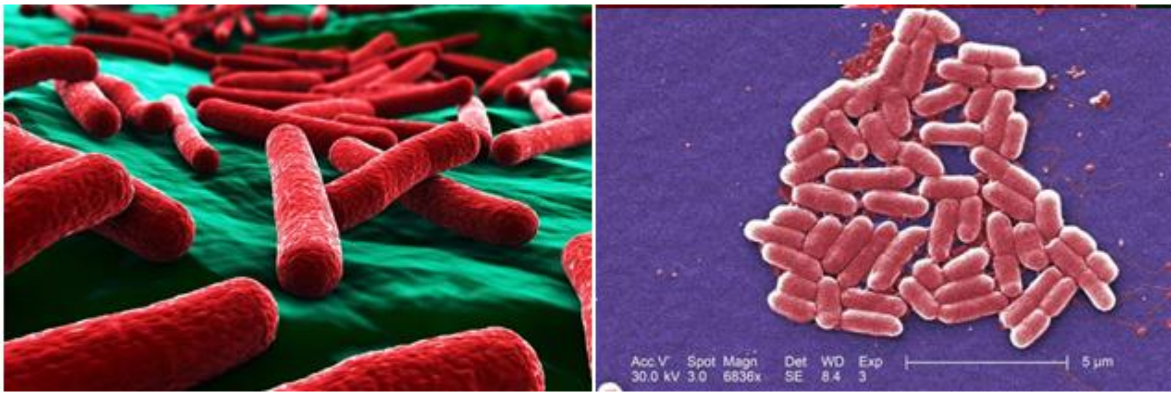
Table 5: *Example of the evidence of used nanotextiles for one series of filtration tests.*

material identification	nanofibers material	Basis weight of the nanofiber layer [g/m^2]
SpurTex M167	PVDF	1.36
SpurTex M168	PVDF	2.72
SpurTex 018	PVDF	2.56
SpurTex M173	PUR	0.99
SpurTex M174	PUR	1.98
SpurTex M175	PUR	2.97
SpurTex 015	PUR	3.60
SpurTex M176	PUR	3.96

4.3.2.1 Escherichia coli as a model bacterium

For simulating bacterial contamination were used Escherichia coli CCM 2024. These bacteria are a major indicator of the faecal contamination of water. Contents these microorganisms in the waters is particularly monitored because they can cause serious health problems. Escherichia coli has a size diameter: 1,1–1,5 x 2- 6µm [36]

Figure 31: *Escherichia coli [35]*



Before filtration, it was necessary to prepare a solution with the bacteria. The procedure was in accordance with the Czech national standard ČSN 75 7835 (757835), Water quality - Determination of Thermotolerant coliforms and Escherichia coli. [37]

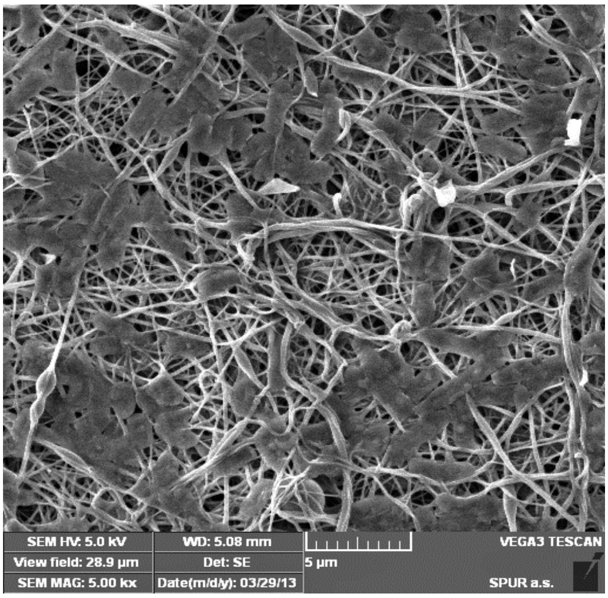
The procedure was as follows. Sterile TSB (Biokar Diagnostics, France) were inoculated with the bacterium Escherichia coli and cultured at 37 C for 18-24 hours. The bacterial culture was centrifuged for 20 min. at 3000 rev. / min. and resuspended in sterile saline solution and centrifuged again. After completion of the centrifugation, the supernatant was resuspended and prepare the filter for the solution of a concentration of about 106 E. coli. The solution was poured through the filler valve into the sterile filter unit. In the bottom of the filtration apparatus was attached manometer through which he was set to 105 Pa overpressure. Nanotextiles material was anchored in sterile variable head in the bottom of the apparatus. The control valve the solution flow through the material and nanotextiles filtrate of 100 ml was collected into a graduated cylinder. During the experiment, the filtration time was recorded. The filtered and unfiltered solution was subjected to microbiological analysis. As the nutrient medium was chosen VRBL agar (Biokar Diagnostics, France) and the plates incubated at 37 C for 24 hours. After the time of culture, the Petri dishes grown colonies counted and converted to CFU / ml. On the basis of the number of bacteria before and after the filtration was assessed antimicrobial material ability of the selected nanotextiles.

Table 6: *Example of recording and evaluation from measurement of filtration efficiency of the model pollution with E.coli using nanofibrous materials.*

Matrial identification	Nanofibers material	Basis weight	Bacteria after filtration		Removal efficiency	Log removal
		[g/m^2]	[KTJ/mL]	[log KTJ/mL]	[%]	[log KTJ/mL]
SpurTex M167	PVDF	1.36	2909	3.46	99.925	3.12
SpurTex M168	PVDF	2.72	1314	3.12	99.966	3.47
SpurTex 018	PVDF	2.56	0	0.00	100.000	6.59
SpurTex M173	PU	0.99	8545	3.93	99.779	2.66
SpurTex M174	PU	1.98	1423	3.15	99.963	3.43
SpurTex M175	PU	2.97	591	2.77	99.985	3.82
SpurTex 015	PU	3.6	273	2.44	99.993	4.15
SpurTex M176	PU	3.96	190	2.28	99.995	4.31
Model contamination before filtration (anticipated pollution 106 CFU / mL)			3863636	6.58		

Selected samples of the filtration membranes were analysed using of the scanning electron microscope PHILIPS XL30li.

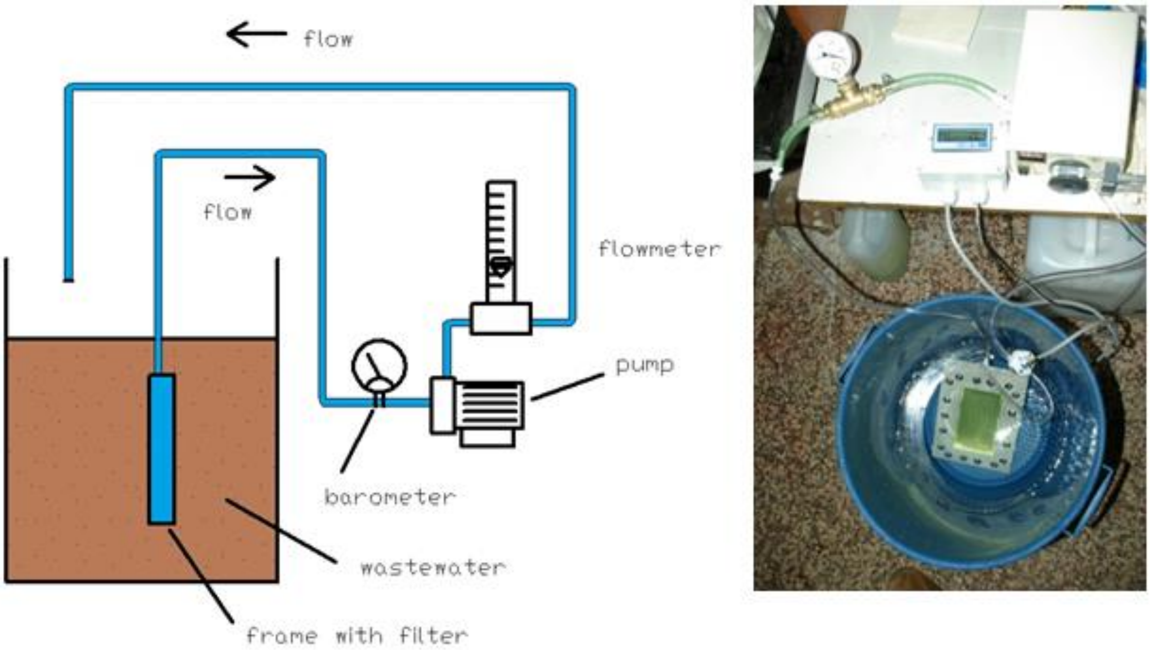
Figure 32: *The image of the filter material after filtration, SpurTex M176, E. coli contamination (Photo: SPUR a.s.)*



4.3.3 Semi-laboratory device

In the first stage it was tested several tens of materials supplied by SPUR. Within these tests were selected best nanofibrous membranes. During next phase was necessary to test membranes at more realistic conditions. Therefore, it was designed and constructed device for semi laboratory measurement. The aim was to test the filtering properties of the membrane of a larger membrane area and test material resistance of the membranes in semi pilot conditions. Using this device have been tested nanofiber membrane materials produced and supplied from company SPUR a.s.

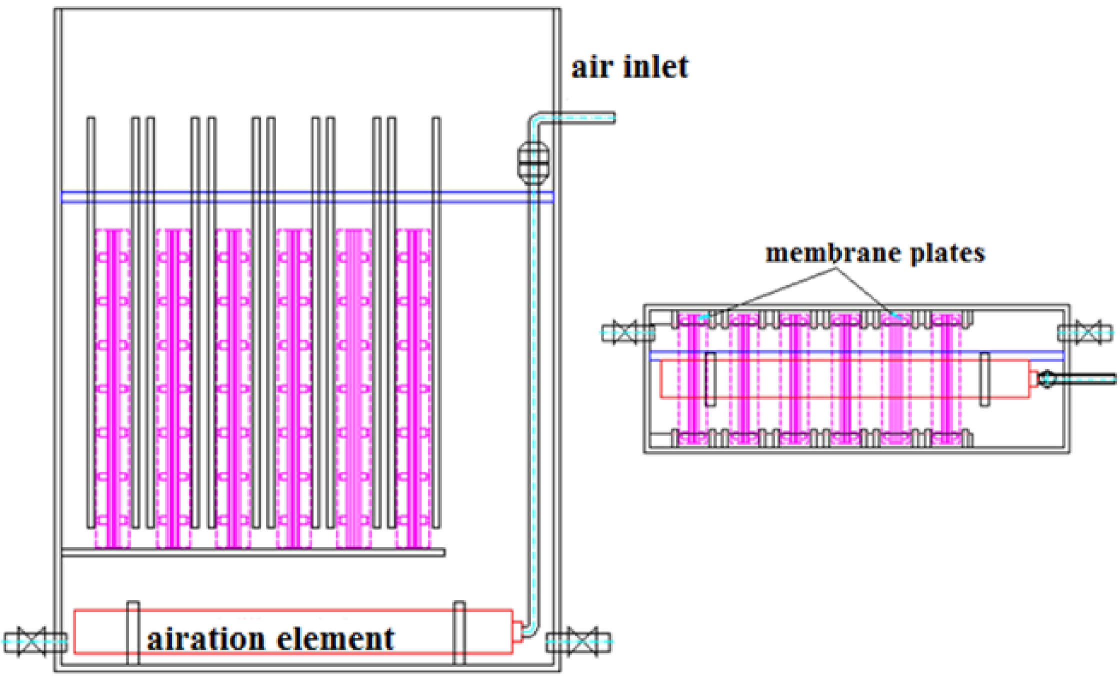
Figure 33: *Connection diagram of semi laboratory device and photo from experiment*



The device serves in particular for testing the flow of filter material, wherein the medium was initially demineralized water, then the model contamination by *E. coli* bacteria. From these tests determine the optimum pumping rate (of the negative pressure or overpressure to the filter plate).

For the pilot test was constructed tank, into which were installed several filter plates. Beneath the plate was mounted aeration element for cleaning plates with air bubbles. This system was mounted into the small tank, which was submerged in activated sludge. Part of the filtered water was accumulated and was subsequently use for back flushing of the filter plates.

Figure 34*: Schematic diagram (Lev, 2013)*



4.3.4 Description of the experiments

Verification of parameters of selected membranes took place at several levels. These are described in brief below. All selected materials haven´t been tested in its entirety especially for reasons of time and also because the experiments were often accompanied by technical difficulties.

Laboratory testing:

Before long-term tests were always performed experiments in a laboratory to verify the membranes parameters. The aim was to eliminate costs that are associated with large scale testing.

For this experiments was used filtration device called the "rocket". Samples of material with diameter of 48mm (functional 38 mm), were tested using filtration. Medium for filtration was physiological solution of volume 100 mL and with certain concentration of the *E. coli*.

During the first stage of experiment was measured also the flow rate during the filtration with demineralized water in the laboratory condition. For this experiment were used membrane samples with diameter 80 mm. The dependence of the height of the water column was considered to the calculation of fluid flow.

Materials that successfully passed these tests were subjected to further laboratory-pilot plant testing with a larger membrane area. Parts of these selective tests were obviously also analysis of filtration efficiency.

Laboratory-pilot plant testing was carried out as follows:

- Testing of the nanotextiles throughput clamped in the frame of the functional filtration area 100 x 200 mm.

- Test of the flow rate with demineralised water, graphical evaluation of dependence of negative pressure [bar] to flux [L/min].

Was performed also calculation of flux [L/m-2* hod^{-1}].

- Testing nanofiber layer adhesion to the base material.

- Testing backwash with demi water - monitoring of possible defects of the membranes and separation of nanofibers from the support material.

- Testing of the filtration properties on the model waste water with E. coli, Filtration of the model solution of *E. Coli* about the concentration

100 CFU/mL. For several test was used also real waste water from runoff of wastewater treatment plant.

- Before every testing was performed apparatus sterility control by the analysis of a sample of water from the flush of the apparatus.

- Monitoring of the filtration efficiency during the filtration time. Record volume flow at times: 1,5,10,20,30,45,60 min. Subsequent microbiological analysis of used membrane samples on Petri dishes and under the microscope. Comparison with the analysis of the original water in the tank prior to filtration and water in the tank after filtration (difference values contamination of the water in the tank before and after filtration should be bacteria that adhere to the filter)

- Testing of backwash on the basis of values obtained from previous measurements - determining the optimum time to begin backwashing (recorded during the flow time)

- Testing a reduction of clogging of the filter via aeration. Testing by filtration of activated sludge - measuring filtration efficiency testing influence of backwash and sparing. Testing of filtration in tanks with a capacity of about 50 L of activated sludge, where treated water is returned to the tank.

After these tests, if the results point to the good quality of the material in all directions it was an indicator that the tested material is mechanically strong, has good filtering ability and that the process of filtration and backwashing is in synergy and material is capable of long-term operation, only then was the material submitted for further testing

4.3.5 Semi-pilot testing of the nanotextile membrane filters

With selected membranes were conducted tests on a larger scale. For this test were made filter frames into which the membranes were clamped. Permeability test with nanotextiles clamped in the frame of the functional membrane area was about 200 x 500 mm [100 cm^2]

At the first stage were performed test of the flow rate with demineralised water. They were evaluated by graphical dependence of negative pressure [bar] on flux [L/min^{-1}] and the calculation of flux [$L/m^{-2}.hod^{-1}$] based on results from filtration of 50 L demineralised water.

- It was also observed nanofiber layer adhesion to the base material. That was performed also by testing backwash under the different condition and pressure with demi water. It was examined with the naked eye and under the microscope possible defects, separation of nanofibers from the support material.
- Testing the effectiveness of the filter for the filtration of activated sludge (volume up to 500 L)

After this testing of the functionality was prepared fully automated experiment with record of the flux, recording pressure changes and auto-start backwashing.

During the experiment were performed extensive analysis of water for the physical, chemical, and microbial. Microbiological culture analyses were performed by flow cytometry and PCR. As an indicator microorganisms was determined to monitor a typical representatives: E. coli Thermotolerant coliform, Intest. enterococci and the number of total bacteria CPM at 22°C and 36°C, yeasts, molds, eventually other types of bacteria and BOD, COD.

Sampling the filtrate and the activated sludge in reservoir tank took place immediately after the launching the pilot in a time period of 1, 5, 10, 20, 30, 45, 60 min. Then after 2, 4, 6, 12, 24 hours.

4.4 Experimental part, the partial results

It was collected large amounts of data. The amount is so broad that it would exceed the purpose and scope of this work. Therefore, there are only partial results for better understanding gradual development and illustration. More important are the later stages of the experiment and data from the operation of the pilot plant unit.

4.4.1 Comparison of the nanotextile material with the commercial membrane material

The next logical step was to confirm the hypothesis comparing filtration properties of our new nanofiber membrane with the filtration properties of commercial materials. As a representative of the commercial material was selected, in wastewater treatment widely used, membrane from company Microdine Nadir, ultrafiltration membrane UP 150. For this the experiment was selected nanotextile membrane marked: 148 BC PP 30 / c + XLI press, size of filter plates 500x200 mm

Table 7: *Example of the measured values. Flow rate depending on the negative pressure*

Material	Nanotext. 148 BC PP 30/c + XLI lis
Negative pressure [bar]	Flux [L/min]
0.7	15.1
0.6	14
0.5	12.6
0.4	11
0.3	9.4
0.2	7.7
0.15	6.8
0.68	15.9
0.6	14.6
0.5	13.3
0.4	11.7
0.3	10
0.2	8.1
0.14	6.91

Material	UP150
Negative pressure [bar]	Flux [L/min]
0.5	1
0.5	1.1
0.45	1.1
0.3	0.5
0.35	0.71
0.4	0.75
0.55	1.09
0.4	0.73

Material	Nanotext. 148 BC PP 30/c + XLI lis
Negative pressure [bar]	Flux [L/min]
0.2	8.3
0.3	10.4
0.4	11.8
0.5	13.4
0.6	14.5
0.68	15.7

The measured data were interpreted using a graphical representation of a comparison of flow with distilled water through the commercial and nanofiber membrane.

Figure 35: *Graphic processing, comparison of the flux with distilled water between nanotextile membrane and UP150*

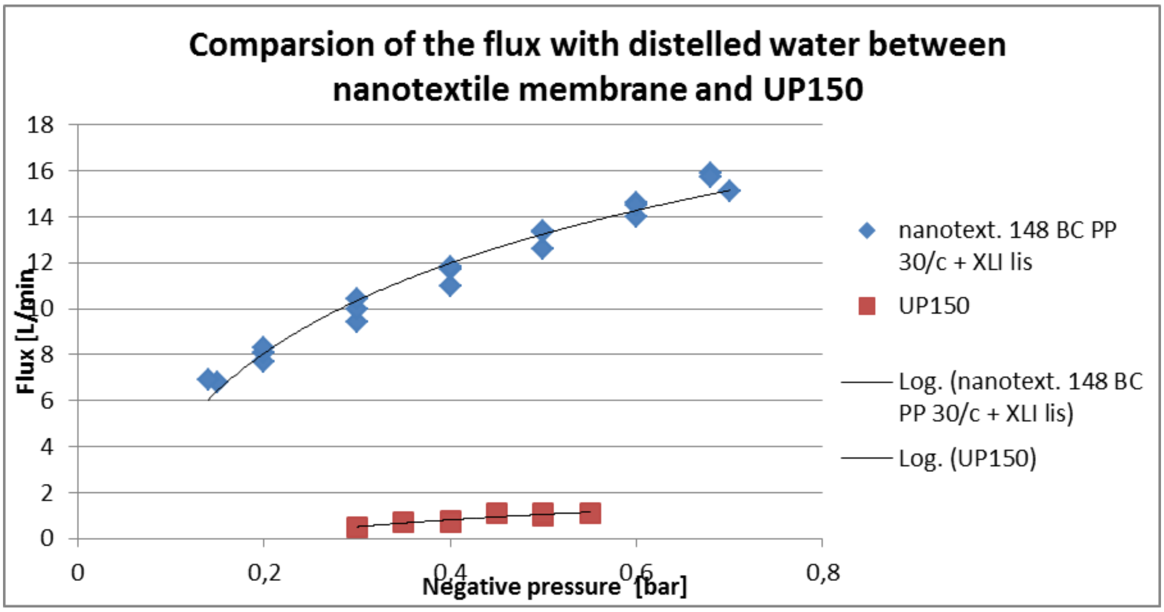
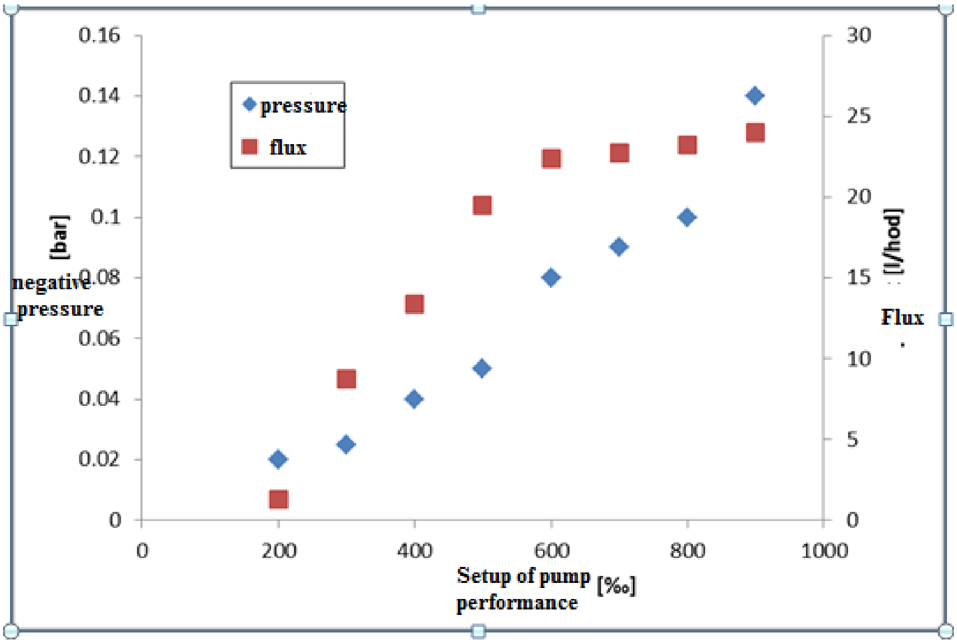


Table 8: *Record from testing nanofiber membranes. Monitoring the flux and negative pressure with increasing pump performance*

Negative pressure [bar]	Flux [L/hour]	Setup of pump performance [‰]	Flux [L/h/m^2]
0.02	1.25	200	62.5
0.025	8.72	300	436
0.04	13.4	400	670
0.05	19.5	500	975
0.08	22.4	600	1120
0.09	22.7	700	1135
0.1	23.2	800	1160
0.14	24	900	1200

The below shown chart proves that, due to its increased porosity, the membrane is able to filter water faster than commercially available membrane UP150. However, it was performed only a short test with only pure distilled water. This was insufficient to assess the material. Therefore experiment was followed by tests with model pollution and innovative nanofibers material Spurtex.

Figure 37: *Illustration of the flow chart when changing setup of pump performance depending on the negative pressure.*

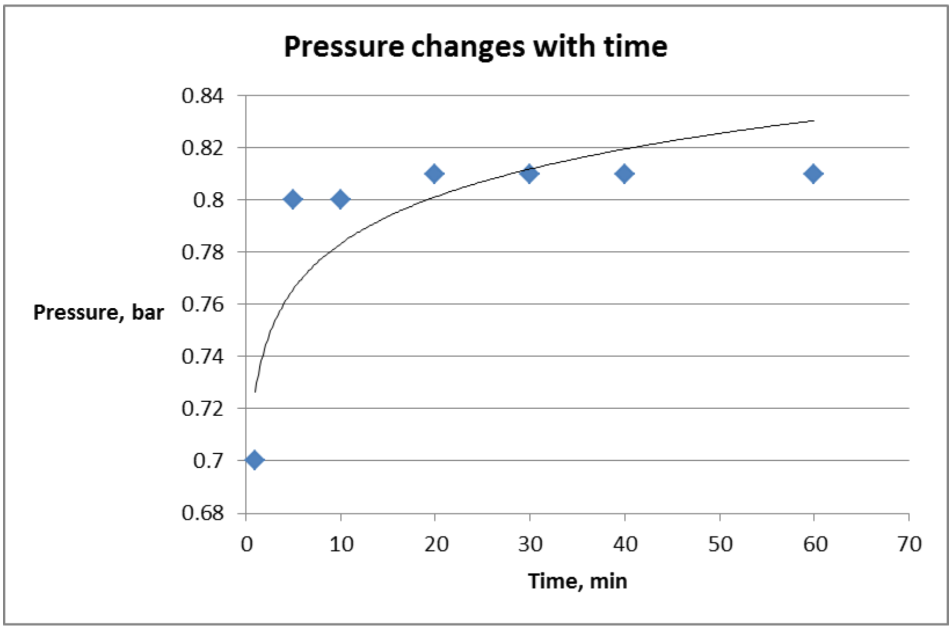


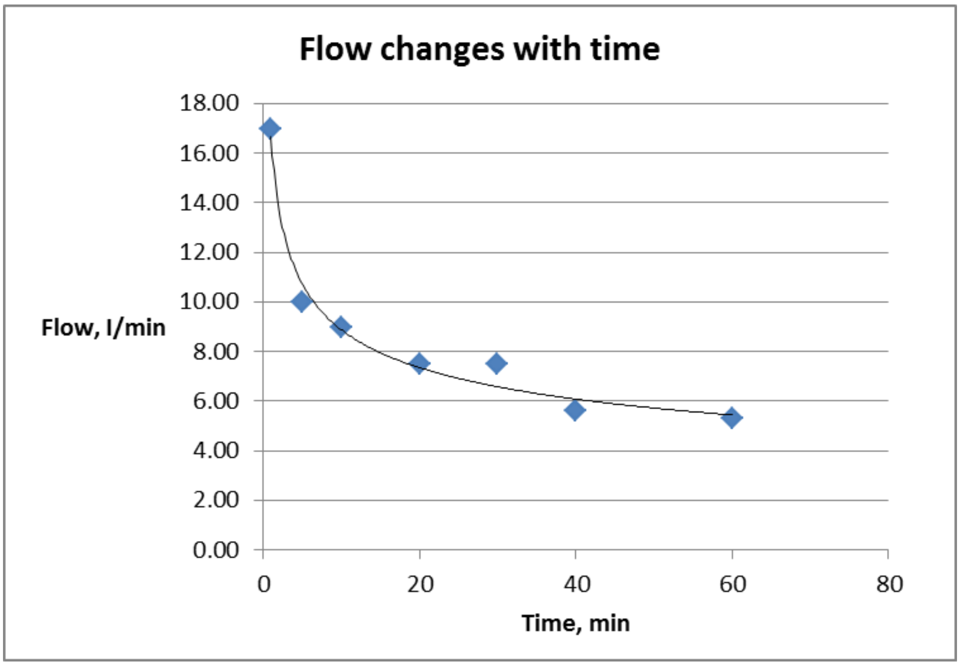
Similar results were realized during the following describe test. This was focused on water sanitation and hygienisation. The purpose of the experiment was to simulate the function of membranes in the effluent of sewage treatment plant at the tertiary waste water purification. Model contamination was simulated again using *E.coli*.

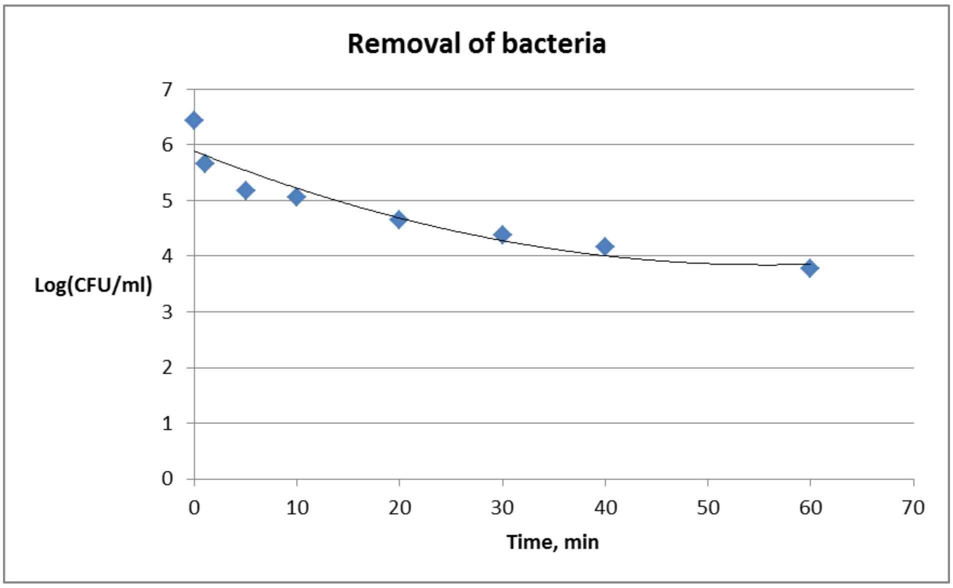
Table 9: *Testing the effectiveness of filtration mat. SPURTEX on a model E. coli bacteria contamination, Date 11/7 2013, Test. water + E. coli, 50 l volume*

		Clean water							
	Medium	Amount of bacteria CFU/mL	Log [KTJ/ml]	Time, [min]	Sample volume, [L]	Tank volume, [L]	Flow , [l/min]	Energy cons. [W]	Neg.pressure, [bar]
1	pure water	0	0	0	0.10	49.90	21.20	261	0.6
2	pure water after pump	0	0	1	0.10	49.80			
		Clean water + bacteria							
no.				time, min	sample volume, L	tank volume , L	flow , L/min	Energy cons,W	neg. pressure, [bar]
3	water with bacteria	2704545	6.432094212		0.1	49.70			
4	filtrate after 1 min	456818	5.659743208	1	0.10	49.60	17.00	262	0.7
5	filtrate after 5 min	147200	5.16790781	5	0.10	49.50	10.00	250	0.8
6	filtrate after 10 min	116000	5.064457989	10	0.10	49.40	9.00	250	0.8
7	filtrate after 20 min	44805	4.651326482	20	0.10	49.30	7.50	257	0.81
8	filtrate after 30 min	24350	4.386498966	30	0.10	49.20	7.50	258	0.81
9	filtrate after 40 min	14400	4.158362492	40	0.10	49.10	5.60	241	0.81
10	filtrate after 60 min	5927	3.772834927	60	0.10	49.00	5.30	236	0.81
11	water with bacteria 60 min	14091	4.148941815	60	0.10	48.90			
12	initial suspenzion with bacteria E. coli	494090909	8.693806863						

Figure 38: *The following graphs show the change of flow, pressure and the removal of bacteria while filtering liquids with a model pollution during the time, using material SPURTEX*







At first glance, it is evident that the removal efficiency of the bacteria is good. From initial *E. Coli* concentration log 8,69 CFU/mL. It was reached concentration around 4 log CFU/mL. However, if the membrane should be use in practice, the bacteria should not pass through a membrane. If bacteria pass through the membrane, so the maximum number of units.

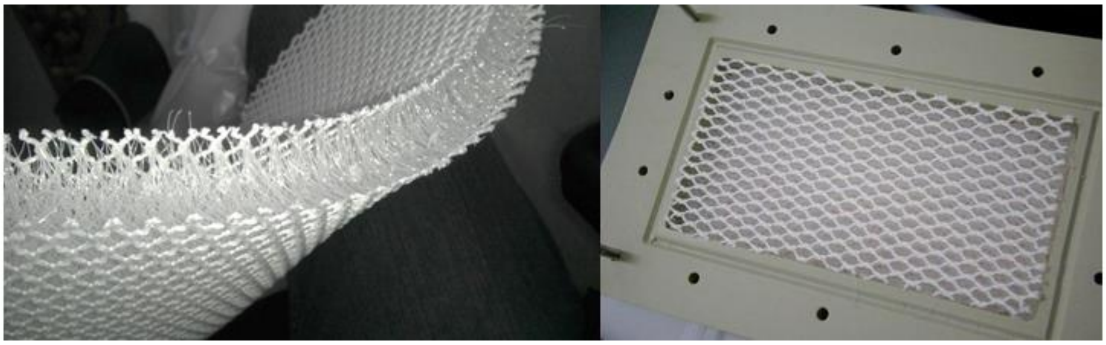
Figure 39: *Testing of the flow rate of filter plate 200 x 100 mm with material labelled as: n. 94*

4.4.2 Measuring of the effectiveness of the filter mat. 93 with a model pollution *E. coli* bacteria and backing support layer mat.: Tylex 20 mm

Previous experiment with filter plate wasn´t structurally well designed. Mechanical properties wasn´t sufficient. Due to previous problems with rupture of the membrane filter plate was improved also the space between the membranes sides. This space was filled with backing layer. Among the filters in the filter plates were inserted material Tylex®. Highly porosive material with good resistance to compression. The purpose was to prevent bursting of the filter inner parts together thereby causing the reduction of flow rate and lifting of the filter. This was used also to avoid rupture. During the suction phase, both sides of the membrane are sucked together. Deflection of membranes could lead than to disruption of membrane because of construction frame.

However, it was necessary to determine what affects will have this Tylex® layer to filtration properties.

Figure 40: *Background material, Tylex® 20 mm serving as support for nano-fabric filter*.



Simple experiment was prepared as follows:

- measuring of the filtration efficiency
- Initial suspension about volume 30 L with *E. Coli* concentration of 10 E6

Samples for Analysis:

- The initial suspension (1 sample)
- A sample from the tank after mixing the solutions (1 sample)
- Water from flushing the pump before adding bacteria - sterility control apparatus (1 sample)

- The filtrate after 1,5,10,20,30,45,60 min, then back flushing filtrate after 5, 10, 20, 30 (11 samples)
- Water from the tank after filtering (1 sample)
- A total of 15 samples for analysis

Table 10: *Record from experiment with support material Tylex®.*

sample	identifikation	CFU/mL	log
1	sample from feed pump	0	
2	initial bac. suspension	2E+07	7.36
3	solution with bacteria	309091	5.49
4	filtrate 2 min	56364	4.75
5	filtrate 5 min	346545	5.53
6	filtrate 10 min	292727	5.46
7	filtrate 20 min	255455	5.40
8	filtrate 40 min	305000	5.48
9	filtrate 60 min	345000	5.53
10	tank after 20 min backflush	1E+06	6.7
11	filtrate 5 min	11500	4.6
12	filtrate 10 min	475000	5.67
13	filtrate 20 min	587272	5.76
14	filtrate 30 min	867273	5.93
15	tank after end	1E+06	6.11

4.4.3 Partial technical findings

While numerous attempts in the stage before pilot testing that was approaching real conditions. It was a relatively frequent phenomenon of mechanical damage to the used filter materials, which in laboratory conditions have not been previously reported. A frequent cause was separating the nanofiber layer from the carrier medium, thus produced composite loses its mechanical properties and subsequently causes perforation of the filter. This was caused by using a larger size filter material and by the pressure in both directions through the filter (when using back flushing). This problem was solved by the development of materials with a covering layer of nanofibers, which supported a nanotextile layer during fluid flow in the opposite direction

4.5 A pilot plant for waste water treatment and hygienisation

In previous experiments were designed and manufactured simple device for sanitary water treatment and was obtained functional sample and utility model. The device used the nanofibrous membrane structure for removal of microbial contamination from water. The goal of the project and hence the thesis was to develop a long-term test devices in real conditions in order to obtain experience with long-term operation. In previous experiments, there were tested in various types of filtration nanofibrous materials, their methods of anchoring elements on plate etc.

4.5.1 Membrane bioreactor (MBR)

One of the objectives was to develop a material which would be suitable for membrane bioreactor. Membrane bioreactor (MBR) is the combination of a membrane process like microfiltration or ultrafiltration with a suspended growth bioreactor, and is now widely used for municipal and industrial wastewater treatment. Membrane bioreactor technique is one of the new yet swiftly maturing technologies in the waste water treatment industries. MBR reactors using biological processes, as in the existing biological treatment plants, but are supplemented by a separation unit which separates the active sludge, fine particles and bacteria.

These technologies achieve higher quality clean water and allow its further use. Conventional ubiquitous technologies are estimated to be replaced by MBR systems in the coming years, owing to low operation and maintenance costs of MBR systems. MBR sales are being driven by increasingly strict legislation concerning discharge quality and recycling levels [38].

Nations, especially in developed countries are pushing for better sanitation and water resource rehabilitation through effective wastewater treatment and reclamation means. Growing popularity of MBR system applications is likely to boost the product demand over the forecast period. In terms of volume, the municipal wastewater treatment application market is likely to grow at a CAGR (Compound Annual Growth Rate) 21.7% from 2013 to 2019 [38,39].

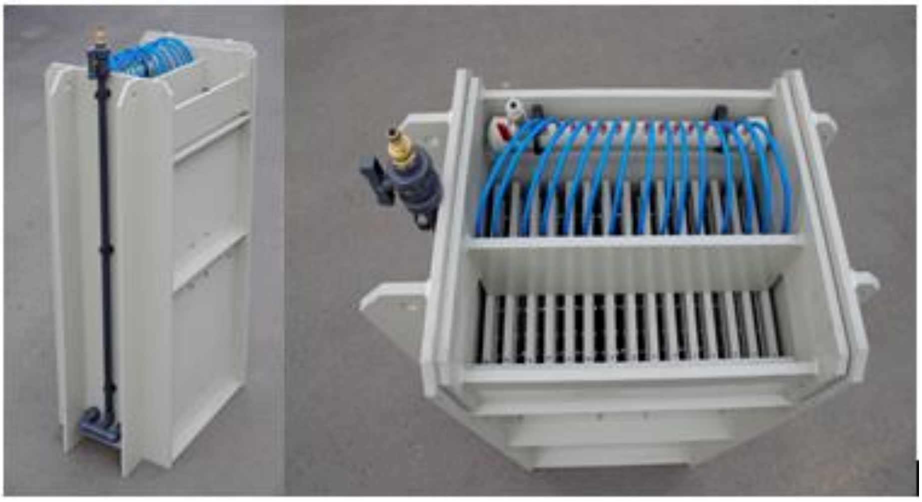
In connection with the growing interest in MBR systems is the development of new filter materials, which would still improve the properties of existing technologies. Promising areas represent nanostructured materials. One of these materials can be electrostatically spun polymer nanofiber structure (electrostatic nanofibers structures). These structures have a high porosity with small pore size [40, 41, 42].

Manufacturing method of electrospinning is currently experiencing a great development, and nanofiber structures are becoming more common and affordable. In several earlier studies were conducted laboratory and pilot plant tests with nanofiber materials and proven usefulness in the field of water treatment [43,44].

These studies and previous experiments, are used to design MBR reactor for the company ASIO. MBR. This part of thesis presents the design of MBR test module and tests carried out in the field. The aim of the study is to evaluate the applicability of the produced nanofiber material for the production of modules for membrane bioreactors. A pilot plant was assembled on the basis of these findings. The function of this device for hygienisation of water is based on the use of the high separation capability nanofibrous structures that are clamped to the filter plates in parallel concatenated into larger units. Compared to current materials have an advantage particularly in higher flow rate (a lower pressure drop). From the filter plates, the filtrate is extracted by common pump. Part of the filtered water is used to clean plates by backflush. To reduce fouling is mounted under filtration plates an aeration elements.

This device was tested during the year 2014 on water from the activation tank of the wastewater treatment plant situated in Letonice, south Moravia region. The pilot test unit is shown in Fig. 41.

Figure 41: *Pilot unit (only membrane module) for testing the nanofibers membrane materials*



4.5.2 Materials used during the test

During the experiment was used newly manufactured membrane, which was the previous mechanically resilient. Type: 1110-2. This is a membrane based on PU nanofibers immobilized on the open PU foam. Basis weight PU nanofibers is 2 g / m^2, of which 1 g / m^2 electrospinning was directly applied to PU foam and the second layer of nanofibers has been transferred from PP SB device Fulard (company INOTEX). Fixation layers NNT to PU foams was carried out under the following conditions - pressure rubber roll by cold pressure of 70 kN/cm^2 and fixing in a hot tunnel dryer at a temperature of 100^0C, all at a speed of 5 m/min.

4.5.2.1 Membranes for pilot unit, wastewater treatment plant Letonice, characteristics of membrane 1110-2

For the pilot test at WWTP Letonice was selected nanofiberous microfiltration membrane with following parameters.

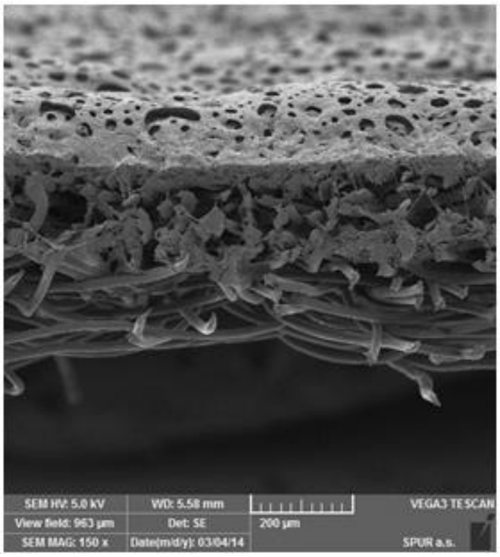
Table 11: *Parameters of used material membrane 1110-2*

Membrane material	PU[1)]
Support material	PET[1)]
Nominal pore size [µm]	0.3 ± 0.10
Water flux [L/(m²·h)]	> 500 [2)]
Thickness [µm]	250 - 300
Area weight of nanofibers layer [g/m^2]	2.82

PU – polyurethane, PET – Polyethylene terephthalate

Test conditions: after 1 hour of distilled water filtration at 7.5 kPa, 23 °C

Figure 42: *SEM of the Membrane 1110. Open PU foam, cross sectional view of a front face, (photo: SPUR a.s.)*



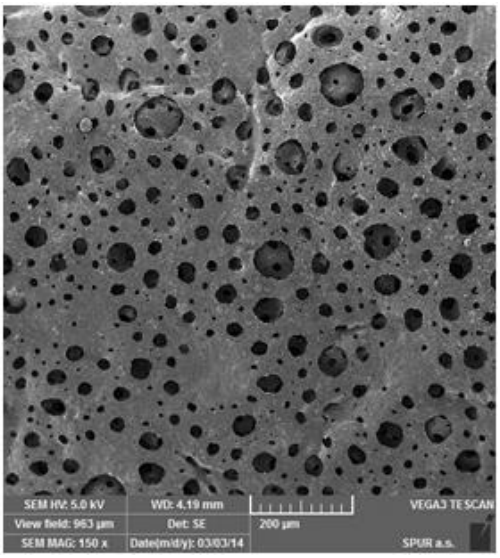
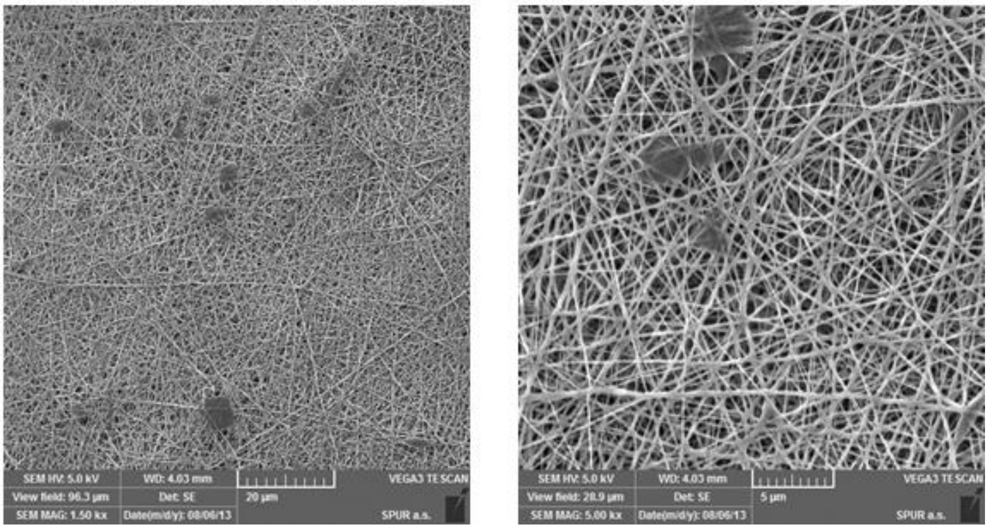


Figure 43: *SEM of the membrane: 1110-2, front side, magnification 1500x and 5000x*



4.5.2.2 Preparation and characterization of electro spun nanofibrous membrane

Nanofiber layers were prepared from the polymeric solutions via commercially available SpinLine 120 equipment (SPUR a.s., Zlín, Czech Republic) using nanofibers forming jets. The experimental conditions were as follows: 28% relative humidity, 23 °C temperature, 75 kV voltage applied to the PU solution, 210 mm distance between electrodes and speed of supporting textile collecting nanofibers 0.3 m/min. The nanofibers were collected on surface treated polyester fabric with weight 50 g/m2.

Nanofiber-based filter prepared by the electrospinning process was characterized by a scanning electron microscope (SEM, Vega 3, Tescan, Czech Republic). Pore size distribution, average pore size value and maximum pore size measurements were analysed in accordance with ASTM F316 – 03 [11]. Parameter of used material is summarized in Table below.

Figure 44: *Porometric measurement, wetting liquid POREFIL (γ 16 mN / m)*

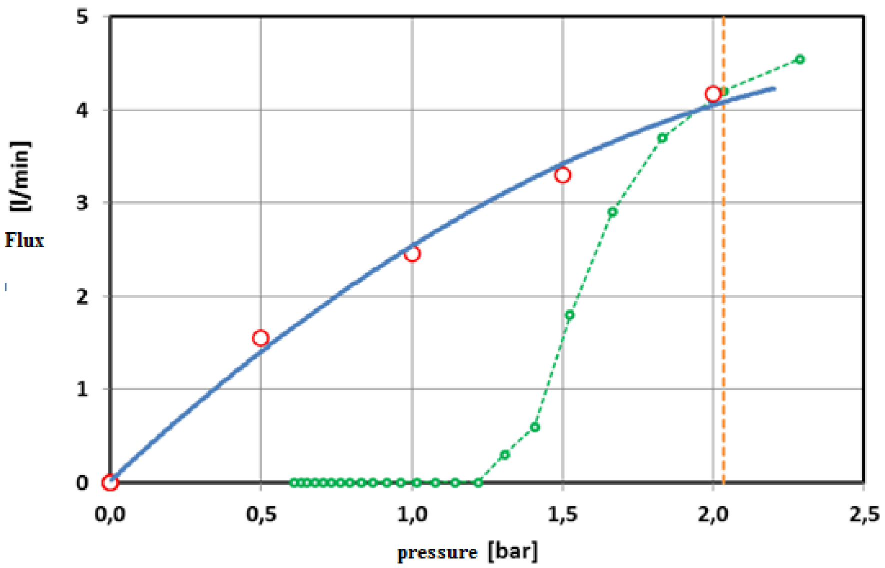


Figure 45: *The result of porometric measurements of the membrane number: 1110-2, frequency distribution of pore sizes.*

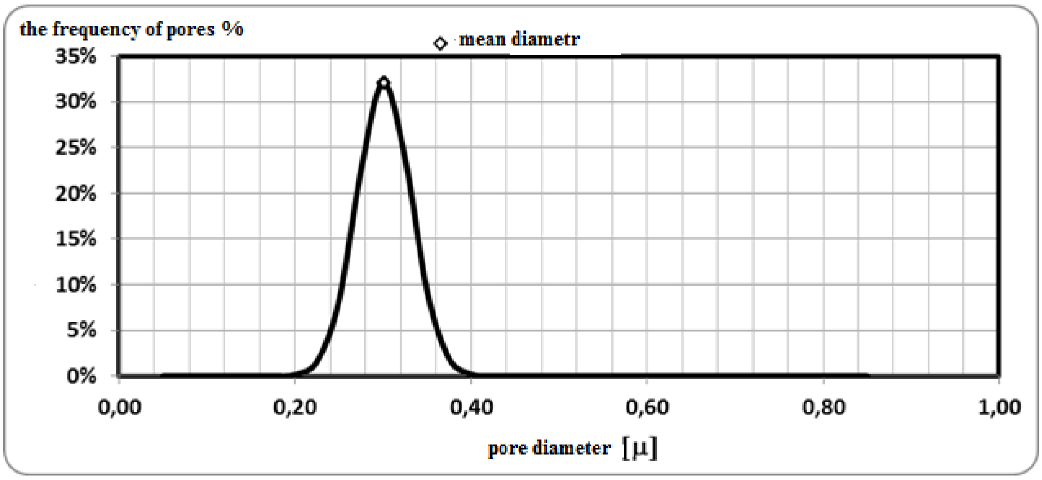
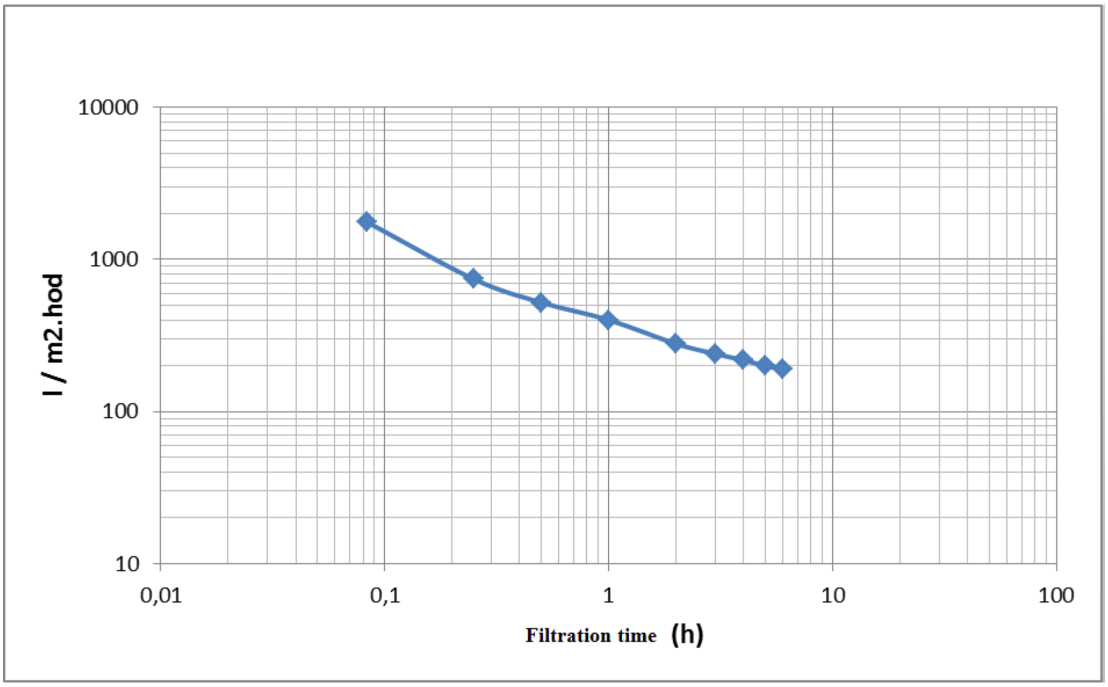


Table 12: *Statistical evaluation of porometric measurements on membrane 1110-2*

average pore diameter d:	0,3	+/-10%	µ
95% confidence interval:	0,28	< d. <	0,33
maximum pore diametr:	0,4	+/-8%	µ
width frequency function:	0,2	µ	

__Figure 46:__ Flux parameters, M 1110-2, distilled water, 7,5 kPa



4.5.3 Membrane module specification

Membrane module was composed from 15 flat sheet membranes with nanofibrous material. The membrane was glued and screwed to the frame. All the membrane outlets are directed into one common output. Aerating elements serving to scour the membranes are placed at the bottom of the module. The assembled membrane module is shown on Fig.41, the module parameters are given in table below.

***Table 13**: Membrane module specification*

Membrane module dimensions H x W x D [m]	1.17 x 0.76 x 0.48
Dimensions of membrane H x W [m]	0. 6 x 0. 2
Number of membranes [pcs]	15
Total membrane area [m^2]	0.24
Total membrane module area [m^2]	3.6

4.5.4 Experimental setup

Before running test was apparatus sterilized by NaClO solution. Pilot testing membrane module was carried out in the reservoir of the activated sludge sewage 1100 PE. The membrane module was anchored in the aeration tank. Permeate was pumped through a membrane pump (RM-ECO P10-2.3, 24V) to the backwash tank. Filtrate was recycled from the backwashing tank into the overflow tank.

It was measured intake manifold pressure and flux. Values were recorded using a PLC (programmable logic controller) to the memory card. To increase the effect of sanitation of the filtrate was irradiated with UV-C (Atman UV-9W). To reduce fouling system was used backwashing every 5 minutes. Suction pump was turned off and opens the three-way valve, which ceded portion of the filtrate from the storage tank back into the intake system and membranes. The amount of liquid used for back flushing flow was recorded via flow meter BONEGA TA/13. Membrane relaxation break among pumping was set to 2 minutes and the backwash lasted 30 seconds in never-ending loop.

Figure 47: *launching MBR module into the tank with activated sludge, WWTP Letonice*

The amount of permeate used for flushing was measured and recorded. Samples of 100 mL of the filtrate prior to UV irradiation and after the UV irradiation and from the storage tank were collected and subjected to microbiological analyses. Samples were taken at weekly intervals.

The cultural microorganisms at 22 ˚C and 36 ˚C were enumerated by inoculation in a PCA (Biokar diagnostics, France) for 48 and 72 hours (EN ISO 6222:1999) [45].

Escherichia coli were detected and enumerated in a Endo Agar (HiMedia, India) at 37 °C for 72 hours. Every sample was duplicated. The culturable microorganisms were enumerated by inoculation in nutrient agar culture medium. Intestinal enterococci grown on Slanetz Bartley agar (Merck KGaA, Germany) for 72 h at 36 ˚C (ČSN EN ISO 7899-2) [46], Thermotolerant coliform bacteria on m-FC agar (Merck KGaA, Germany) for 18-24 h at 44 ˚C (ČSN 75 7835) [47].

The duration of the experiment was 84 days. Wiring diagram with nanofibre membrane module is shown in Figure 42.

Figure 48: *Scheme of the pilot test apparatus*

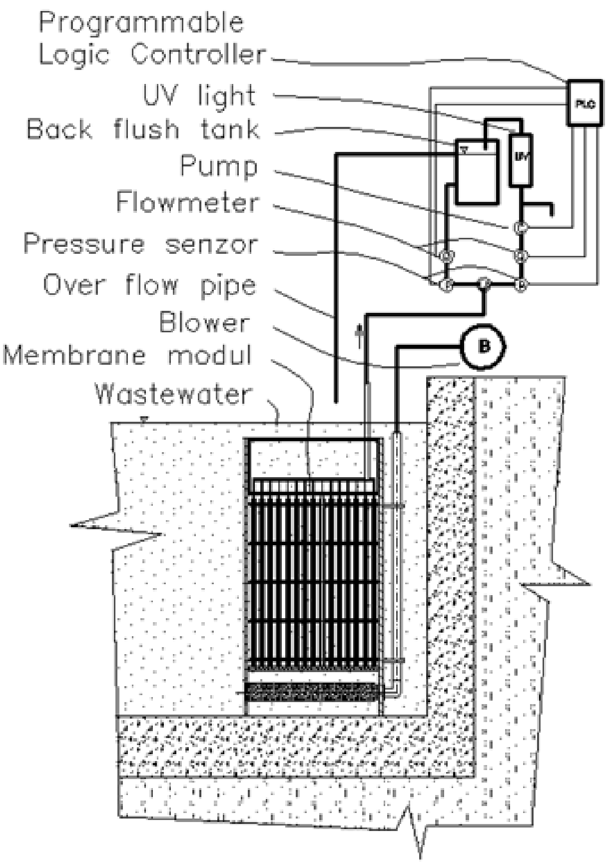


__Figure 49:__ Membranes in the relaxation phase. Need the wetting of before use

At the beginning (left photo) sludge was a very unusual and it was observed flotation instead sedimentation. It confirmed the presence of filamentous bacteria which cause sludge bulking. For filtration unfortunately not optimal operating conditions.

Figure 50: *The photo shows measuring of the sludge index in Letonice*.

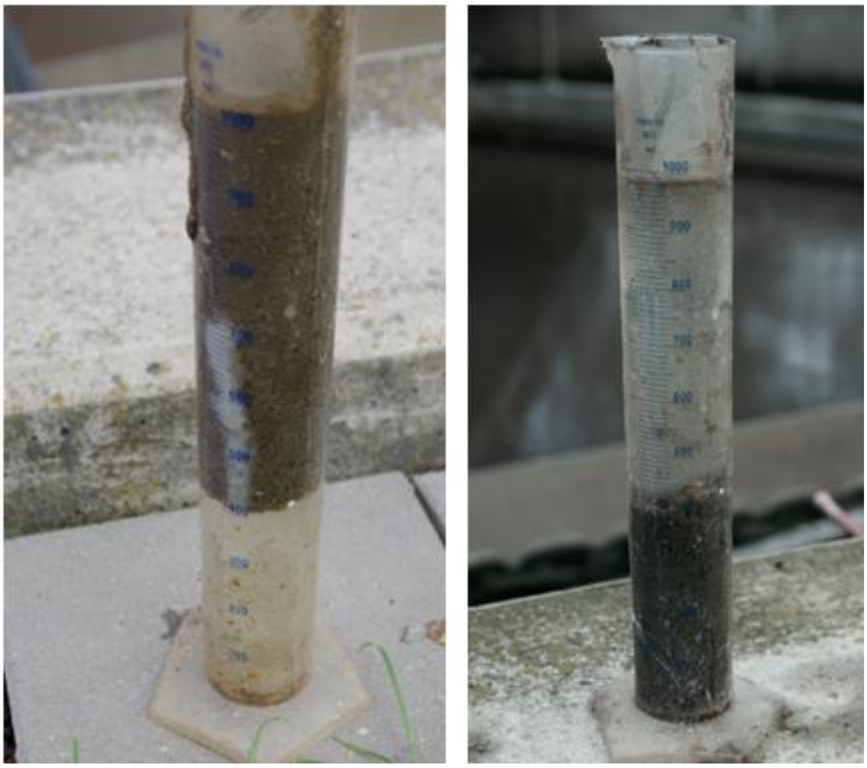
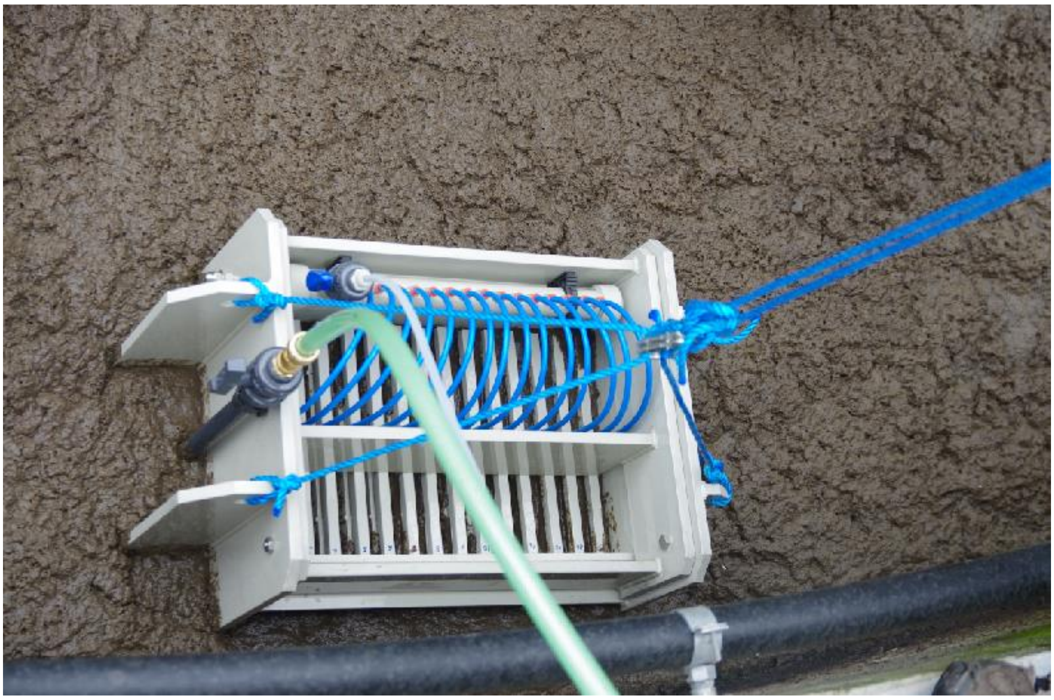


Figure 51: The photo shows the immersion of the membrane module into the activation tank with sludge.



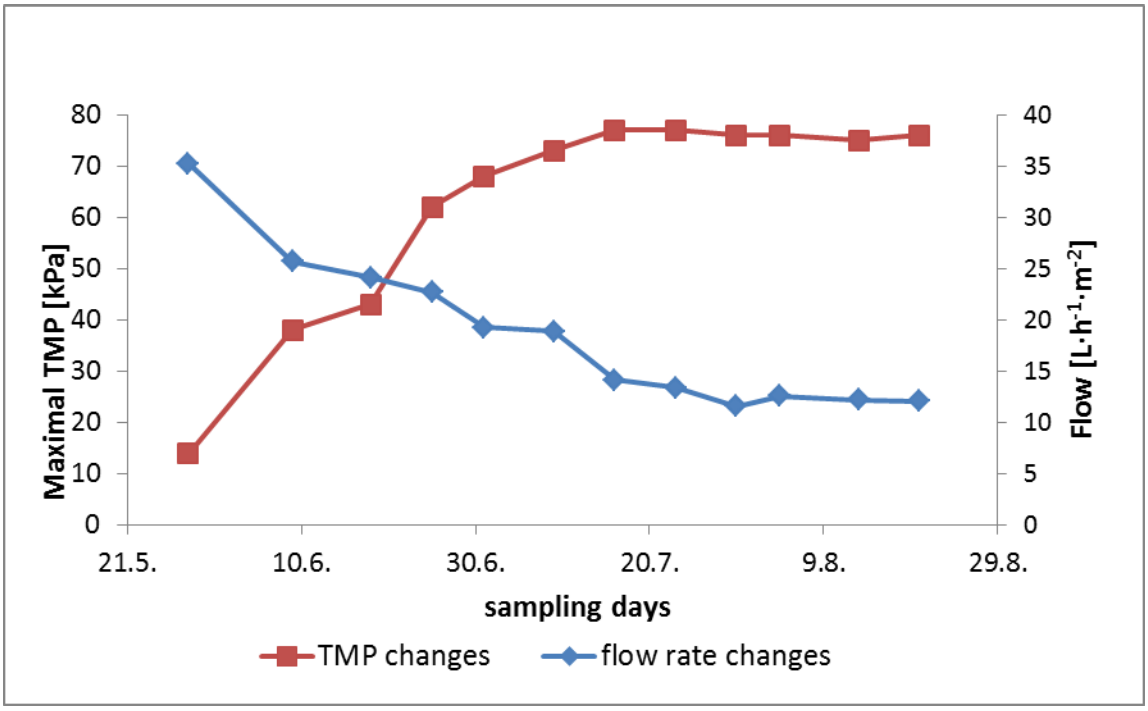
4.6 Partial findings and outcomes

The experimental part at the wastewater treatment plant Letonice follows on previous laboratory and semi-pilot tests that showed good filtering capabilities of nanofiber layers [44, 48, 49]. The tests described in this part of thesis were conducted to evaluate usability of nanofiber materials for wastewater treatment in a membrane bioreactor.

Operating parameters (pressure on the membrane, flow) and quality of treated water were monitored during the tests. Figure below. shows the progress of trans membrane pressure (TMP) and flow membrane module during the experiment.

During the reporting period (84 days) was observed gradual clogging of the filter material. The initial conditions of flux 35 [L/(h*m2)] at 14 kPa TMP decreased to 12 [L/(h*m^2)] and TMP increased up to 0.76 kPa. There was a presumption that the main cause of reduced flow was biofouling, due to the clogging of nanofiber structures with small particles [50].

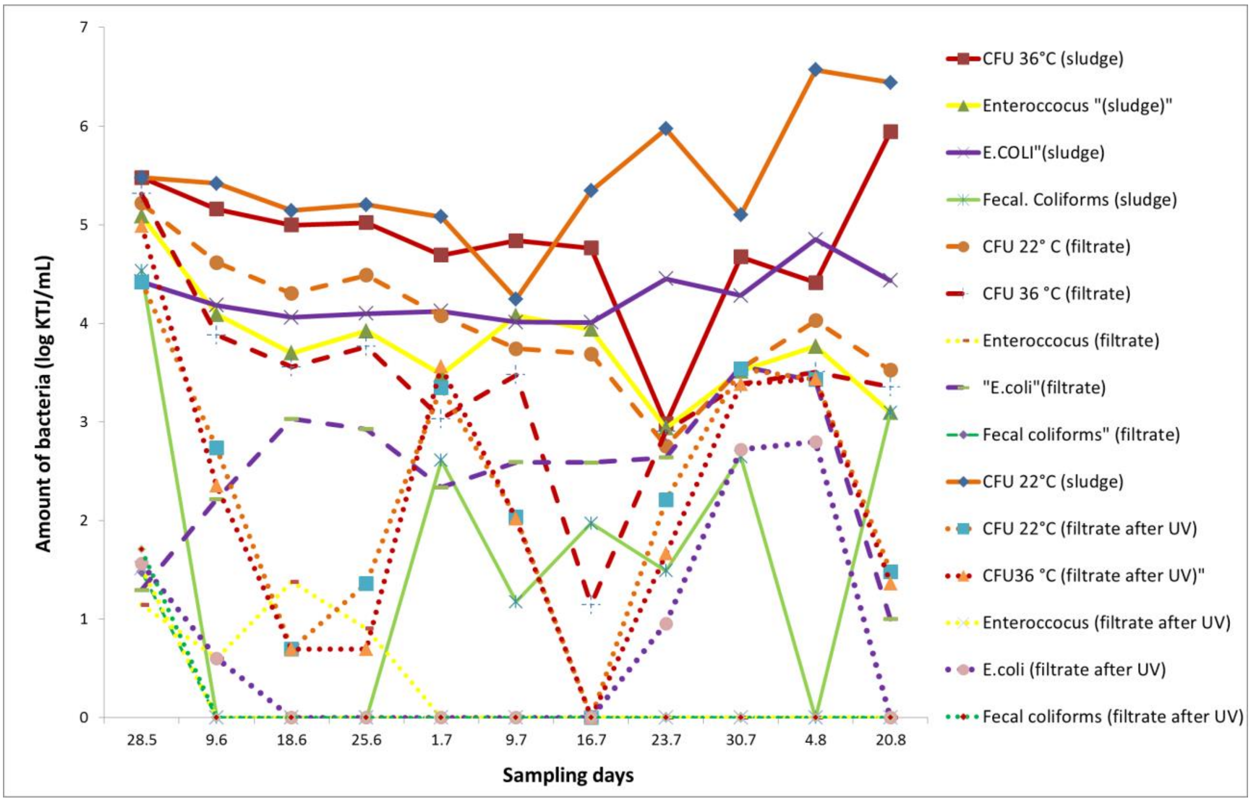
Fig. 52: *Pressure and filtration velocity changes during pilot run*



In a similar study by Hyun-Chul Kim [51], was experimentally tested membrane module with 15 pcs PMMA-PVDF membrane microfiltration nanofibre materials with mean pore size of 0.45 micron was used, for pilot testing refining wastewater [49]. The authors achieved a constant flux of 30 L/m2/h TMP increase from the initial value of 7 kPa to 23 kPa after 18 days of operation without backwashing. In our case occurred after 20 days of TMP increase to about 40 kPa despite the backwash. High TMP causes faster fouling, especially in conditions with higher mixed liquor suspended solids (MLSS). The literature indicates that the MBR are suitable for MSLL in the maximum range 10 to 15 $g{\cdot}L^{-1}$ [52].The concentration MLSS in the activated sludge tank WWTP Letonice during the experiment was 16-20 $g{\cdot}L^{-1}$.

The quality of the treated water was continuously monitored in the filtrate, the filtrate treated with UV and waste water. Values of microbial contamination of the filtrate, the filtrate after UV and wastewater are shown in Fig.53.

Fig. 53: Monitoring of the microorganisms in activated sludge and in filtrate



There has been a decrease of 1-3 CFU/mL log removal after filtration. These results are comparable to our previous values of the semi-pilot testing in activated sludge [53].

Similar values when using microfiltration PA (Polyamide) nanofiber membranes with a mean pore size of 0.4 micron in laboratory tests indicate Bjorge [54] the log removal of 2.24 CFU/mL of culturable organisms at 37 ° C and Daels [55] log removal 1.3- 3.2 CFU/mL S. aureus with nanofibre membranes. Higher values were achieved only after functionalization with different functionalizing agents.

UV light was used to increase microbial purity of the filtrate and to evaluate possible water reuse. The reductions of bacterial contamination is show Fig. 5. If comparing activated sludge to the filtrate, values of the bacterial contamination are reduced by 2 log removal CFU/mL, and in some case such a faecal coliform, enterococcus, E. coli, to zero.

Comparison with the legislative requirements in the Czech Republic showed, that the average value of microbial contamination meet the government regulation on indicators and values of acceptable waste water pollution and the details of the permit to discharge waste water into groundwater number 416/2010 [52] (500 CFU/mL E. coli, 400 CFU/mL Enterococcus).

Our pilot tests confirmed the usefulness of nanofiber membrane systems in full-scale. Average flow rate 30 L·h-1 was measured with a MBR module (membrane area 3.6 m2) at the end of the experiment. It means 720 litters per day, which corresponds approximately to the needs of the 5 members household.

Figure 54: *The filtrate of activated sludge, backwash reservoir*

In the photo above is captured the backwash reservoir for filtrate storage. The filtrate (permeate) from the membranes was largely recycled back to the activated sludge tank, after passing through the flow meter. Part of the filtrate was drained into the backwash reservoir. That was placed in the rear side of the cabin. During the relaxation phase, the membranes were backwashed by this water at predefined intervals.

Backwash reservoir also served as one of the sampling points. Since was isolated from the environment by sealing cover with a HEPA filter in the upper part. HEPA filter was placed there due to movement of air in the reservoir during the inflow of the filtrate.

Despite these efforts, with time on the walls of the tank formed biofilm of a greenish-brown colour. Smear and its subsequent analysis showed that it is a single-celled algae whose spores probably not came from the filtrate, but from the external environment during the sampling.

On the figure are seen membrane plates of module after removal from the activation tank. The module has been blasting the flow of clean pressurized water. At first sight there is no visible rupture. At the beginning of the experiment, there were concerns that because of its porous structure, it will be difficult to prevent fouling and clogging of the membranes. Impurities could penetrate easier to the structure of the membrane and stuck deeper. This is obviously inferior for membrane regeneration.

Figure 55: *One of the membranes after the end of the experiment, regeneration process*

During the experiment were the membrane plates regenerated by continuous flow of medium coarse bubbles. A part of the membrane module were two aeration elements, which was fed from the air blower. The first membrane module, which was placed in Letonice wastewater treatment plant, wasn´t probably equipped with a sufficiently strong aeration module. Aeration was not uniform for all the sections. The figure shows that in the lower zone of the membrane plate was sludge more cumulated. It was also evident that at the beginning and end of the module was peripheral membranes more clogged, because aeration intensity here was lower. After membrane clogging experiment was stopped. The membranes were lifted from the module. The first stage regeneration is spraying with clean water.

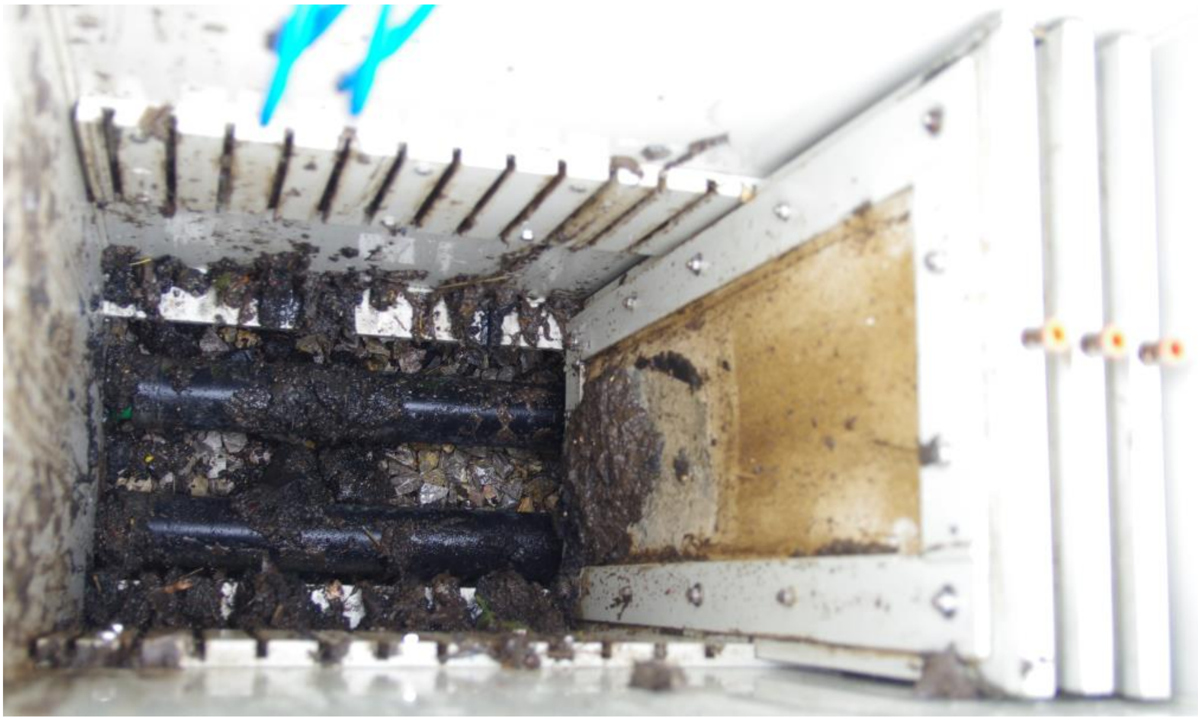
Figure 56: *The first stage regeneration is spraying with clean water*

Due to this experiment it was found that the gap distances among the membrane plates play an important role as well as the density and characteristic of the sludge. For optimum filtration is better concentrated sludge with a higher dry matter content.

Table 14: *Results of testing of the flux of each membranes plates after the end of the experiment*

Plate number	č. 1:	č.2	č.3	č.4	č.5	č.6	č.7	č.8	č.9	č.10
Pressure loss [bar]	0,43	0,44	0,41	0,39	0,43	0,42	0,38	0,37	0,373	0,38
Volume [mL]	260	250	385	420	275	280	315	355	350	350
Time [s]	300	300	300	300	300	300	300	300	300	300
Flux [l/hod/m2]	12,98	12,48	19,22	20,97	13,73	13,98	15,72	17,7	17,47	17,47
Avarage flow [m3/hod/m2]	0,013	0,012	0,019	0,021	0,014	0,014	0,016	0,02	0,017	0,017
Permeability/pressur [m3/hod/m2/bar]	0,0302	0,028	0,047	0,054	0,032	0,033	0,041	0,05	0,047	0,046

Figure57: *Aeration elements were conducted in the lower part of the membrane module.*



4.7 Experimental comparison of commercially available membrane modules with nanofibrous flat sheet membrane module

MBRs are operated at higher biomass concentrations with resulting high metabolic rates, MBRs produce a more hygienic effluent and since hydraulic and solid (biomass) retention times are independent of each other, MBRs offer an additional degree of freedom for process control. MBR process disadvantages include investment costs, complicated equipment and increased demands on quality maintenance and service.

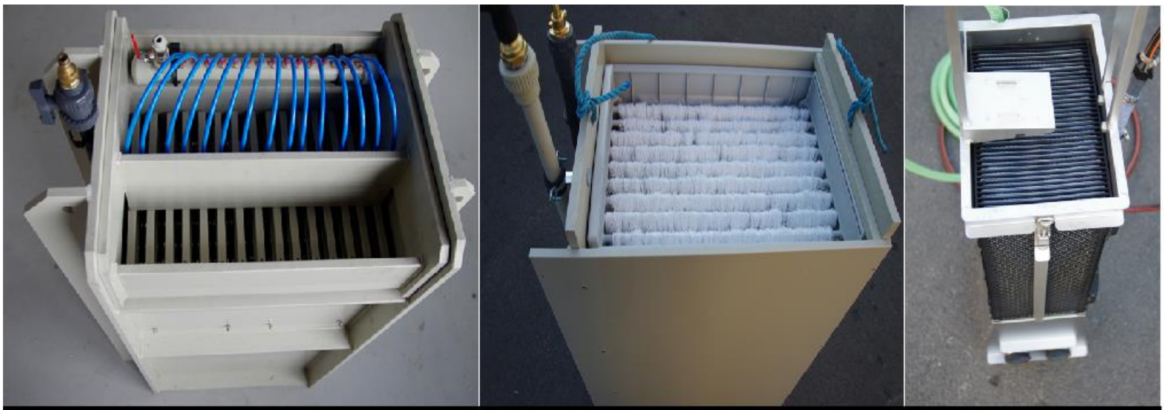
After the end of the experiment at the wastewater treatment plant in Letonice was proposed similar experiment situated on the waste water treatment plant in Brno city, Modřice (513 000 EO).

The aim of this experiment was to test membrane modules immersed in pilot tank situated on WWTP Modřice, next to the activation section. This tank was charged with activated sludge from the aeration zone of the municipal WWTP. Small tank for activated sludge was supposed to simulate conditions in the activation tank, but allow better measurement and control of the experiment. Large WWTP should provide a more stable environment for the experiment.

One of the findings, which was unveiled at the Letonice WWTP experiment was a little resistant of the used seal during long-term loads. In terms of production, if successful, also appeared this manufactory as unsatisfactory. Competitive manufacturer of membrane modules, company Martin Systems AG, puffed on a similar principle uses a technique for welding the plastic frame of the membrane together with membrane.

One of the goals of this experiment was modified, in cooperation with company SPUR a.s, nanofiber membrane so that it can be welded to the plastic frame of module and at the same time, keep good mechanical properties against mechanical damaged.

Figure 58: Tested MBR modules



F.S. MBR with nanofibrous membranes *SpurTex®*	Hollow fiber MBR, company Hyflux	Flat sheat MBR, company MS

The following chapters are focused on the preparation of the experiment, which had the following objectives:

1) Modifying of the nanofiber membrane which was used in Letonice, so that it can be welded on polypropylene frame without the use of seals.

2) Long-term monitoring operation of the membrane module in the filtration of activated sludge.

3) Compare this module with commercially available modules.

4) Confirm or disprove the hypothesis that nanofiber microfiltration membranes are comparable with ultrafiltration membranes

4.7.1 Description of the experiment and experimental setup

Experimental testing of membrane modules were conducted at the wastewater treatment plant in Brno in Modřice. This plant is designed for a capacity of 513 000 EO. The experiment was designed for the filtration of activated sludge. Pilot unit was situated within the section of sludge management, which is further described below.

At the WWTP Modřice, wastewater after mechanical cleaning is piped to the pumping station, from where it is pumped to activation. Activation is divided into two lines, each with two single tracks, which can be operated separately or together. Water is fed first into the anaerobic tank with the function of defosfatation, subsequently to the circulation anoxic tank with the function of pre-denitrification. The last degree of the aerobic part of activation zone which is divided by fine course aeration into aeration and non-aeration zone. Air is supplied from the blowers. Reversible sludge is fed back from settling tanks to achieve effective defosfatation deprived of nitrate by denitrification in the anoxic tank located in the first part of the activation. Degradation of phosphorus is provided by either a biological process or ferric sulphate dosing to achieve the required results. [60]

Figure 59: *General view to the area WWTP Modřice. [60]*

4.7.1.1 Key parameters and monitoring of the pilot

During the experimental part in Modřice wastewater treatment plant was needed to monitor a wide range of variables. Most of them were recorded continuously by the control unit. Some of them had rather subjective (immeasurable) character.

The main limitation for the widespread application of MBRs lies in membrane fouling that reduces the filtration performance and thus increases investment and operating costs. [57,58,59]. Depending on external conditions, after some time the membrane clogged and rapidly reduce their permeability. Then it is necessary to regenerate the membrane module. The marginal value of permeability, indicating a need for regeneration of membranes (flat sheet) is about the value of $\mu = 500$. (Based on personal experience)

In such cases, following regeneration of the membrane, which requires a careful chemical cleaning. Typically, using strong oxidants e.g. (sodium hypochlorite) to remove organic substances. Following regeneration of the organic acid (e.g. citric acid) coupled with mineral acid.

Having regard to this facts was designed experiment at Modřice. Part of the testing were the following tasks:

- Permeability test of nanotextiles clamped in a frame, the functional part of 100x200 mm or 200 x 500 mm, eventually were assembled smaller units of frames with several filter plates.

- Performed flow rate test with demineralised water in the water column, calculate flux ($L/m^2/h^{-1}$) * Filter area (m^2)

- Testing nanofiber layer adhesion to the base material - testing backwash with demi water - monitoring for possible defects, separation from the background material

- Testing on real water from runoff and activation. Analysis of the filtering efficiency and sterility of the control apparatus (a sample of water from the flush pipe, the detection of environmental cleanliness for comparison with the filtrate).

- Microbiological analyses of water and the filtrate before filtration, the total number of microorganisms CPM (microbiological culture analysis, by flow cytometry and PCR), E. coli, Thermotolerant coliform bacteria, intestinal enterococci, the number of bacteria cultivated at 22° and 36° C (ratio of the contamination of water in the tank before and after filtration determine filtration efficiency, reducing the degree of contamination).

- Testing of backwash on the basis of values obtained from previous measurements - determining the optimum time to begin backwashing (recorded during the flow-time)
- Testing a reduction of clogging of the filter backwash and bubbling (flow-course record time)
- Testing nanofiber layer adhesion to the base material - testing backwash with demi water - monitoring for possible defects, separation from the substrate
- Testing the effectiveness of the filter for the filtration of activated sludge (fully automatic operation, recording of the flow, negative pressure, auto-start backwashing)
- Monitoring of the speed of irreversible clogging of the filters.
- After long trials testing the regeneration of the filter - dry cleaning

Figure 60: *View to the tank with activated sludge, from which was pumped the sludge to a smaller experimental tank. (photo: author)*

5.9.2 Membranes and modules used for the experiment in Modřice

On site was carried out testing of the nanofiber membrane module in real conditions. Using this module, there is a separation of activated sludge and most microorganisms and suspended solids. In the tank are also other membrane modules for an objective comparison of operating parameters in operation. Properties of these membranes and modules are described below.

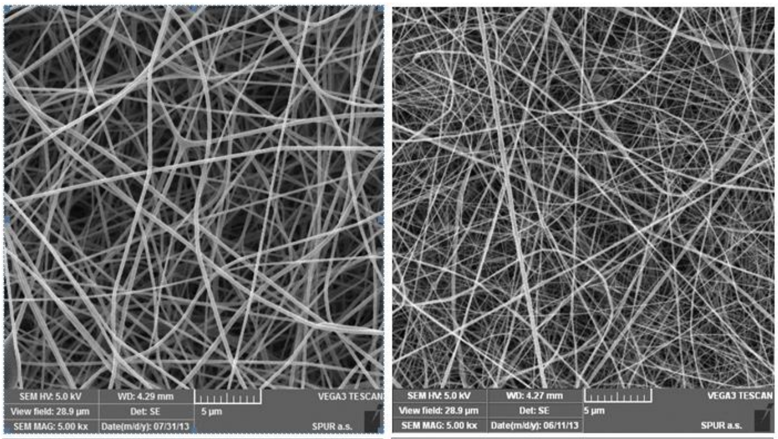
For the experiment in Modřice been chosen membrane SpurTex® MF RF. Modified polyurethane solution in dimethylformamide (DMFA) for electrostatic spinning was prepared from diisocyanate, polyesterdiol, 1,4-butanediol and phthalocyanine containing amino or hydroxyl group at the temperature of 90 °C for a time period of 6 hours. Per parts method of synthesis was used. The solution was diluted with DMFA to a viscosity of 1.3 Pa.s and conductivity was increased to 150 µS/cm.

This membrane is based on nanofiber of PVDF-HFP total basis weight of 6 g/m². These are two of three grams layers nNT, which were successively fixed to the open-cell foam polyurethane molding lines on a heated roll Hofman Schwabe first coating under conditions 165^{0}C and second coating at 170^{0}C, gap setting between the rolls of 0.1 mm and the draw-off speed 1.5 m / min.

Table 15: *Nanofiber Membrane module specification*

Membrane module dimensions H x W x D [m]	1.17 x 0.76 x 0.48
Dimensions of membrane H x W [m]	0. 6 x 0. 2
Number of membranes [pcs]	15
The average pore size membrane [µm]	0.3
Total membrane module area [m^2]	3.795

Figure 61: *SEM of the membranes, magnification 5000x. (source: SPUR a.s.)*



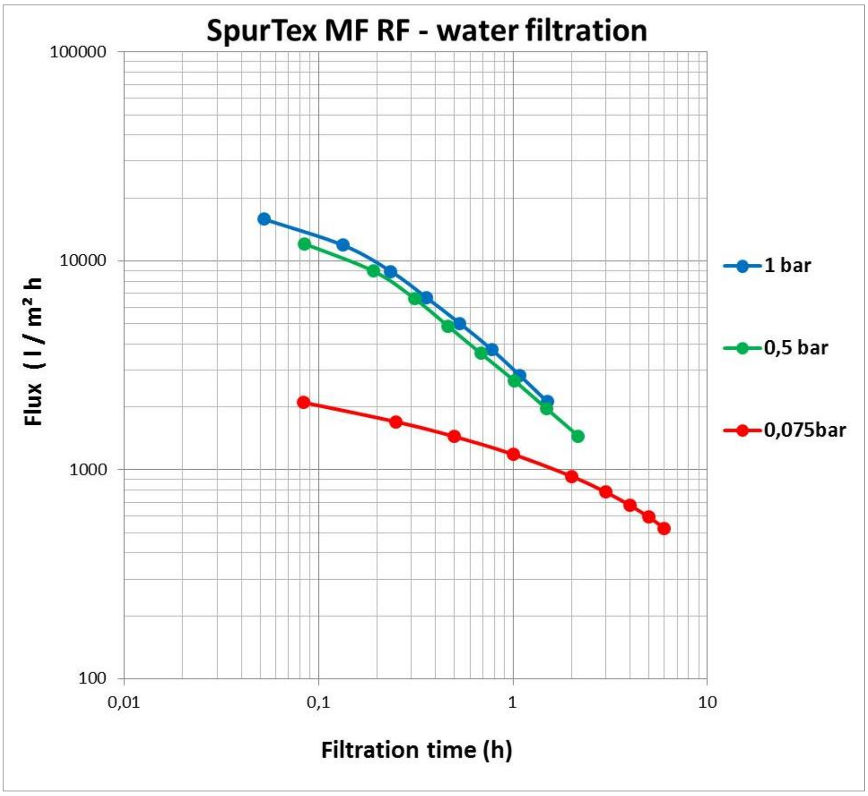
PU nanostructured membrane surface, magnification 5 000x

PVDF nanostructured membrane surface, magnification 5 000x

Table 16: *Membrane properties*

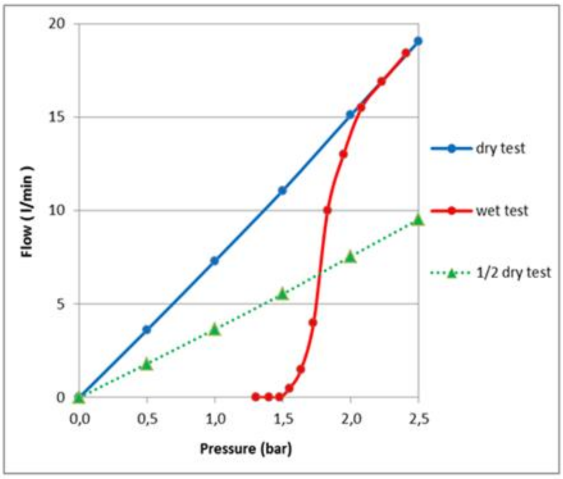
Membranes Properties		Conditions
Average pore size	250 nm	ASTM F316-03
Initial water flux	> 2 000 l/m^2h	23°C; 0,075 bar; distillated water
Operating pressure	< 3 000 mbar	
Back washing pressure	< 1 000 mbar	Usual cleaning processes are recommended
pH applicability	3 - 12	
Max. operating temperature	60°C	

Figure 62: *chart shows flux through SpurTex microfiltration membrane based on PVDF nanostructure placed on microporous open cell material*



Left chart display the wet and dry test for membrane filter pore size characteristics by bubble point and mean flow pore test (ASTM F316-03). Right chart display pore size distribution of SpurTex MF RF membrane filter. Small pores scattering is one of the essential characteristics of good membrane. Only in this way can guarantee the filtering parameters.

Figure 63: *Membrane filter pore size characteristics*



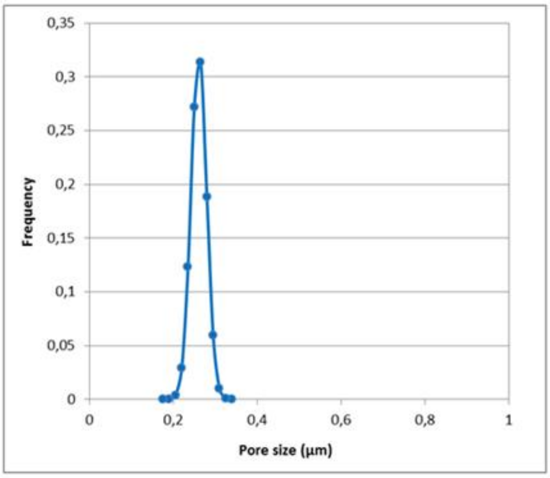


Table 17: *Statistical evaluation of porometric measurements of the membrane*

Mean pore diametr d_m :	**0,3**	**+/-11%**	**µ**
95% confidence interval:	**0,28**	**< dm <**	**0,32**
Maximum pore diametr:	**0,4**	**+/-8%**	**µ**
Width of frequency function:	**0,2**	**µ**	

The membrane was of course tested under the system introduced in earlier stages and adequately proven in terms of filtering distilled water. Although this was a pure distilled water filtration, membrane sample exhibited during prolonged testing flow reduction as if the membrane clogging. It was verified that this clogging is possible on a small scale always observed. Distilled water is not completely free of the impurities. Of course there was also checking quality of the distillation apparatus and distilled water. In tests showed the reduction in the flow rate also commercial membrane purchased from Martyn system.

4.7.2 Competitive membrane modules characteristics used for this study.

Hyflux membrane module:

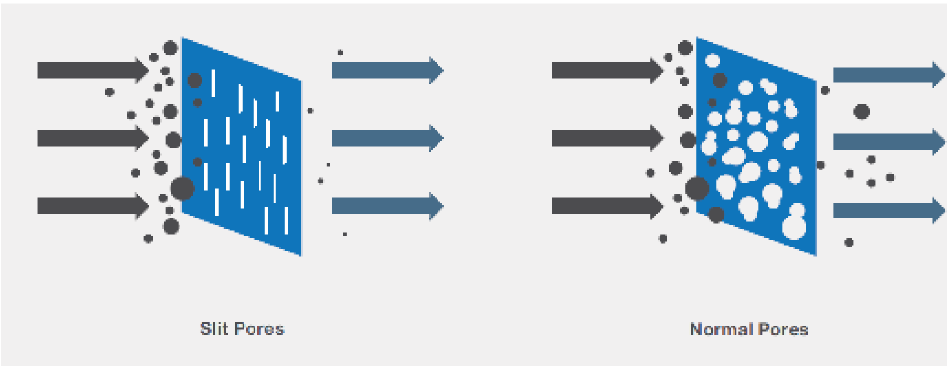
Was manufactured and assembled in Singapore by technology PoroCep® Hollow Fibre Submerged Membrane For MBR Systems. are made from high-density polyethylene (HDPE), a non-toxic, non-leaching material with excellent tensile strength as well as strong pH and oxidation resistance to be used in Membrane Bio-Reactor (MBR) systems. Each hollow fibre membrane is produced through environmentally friendly processes such as melt-spinning and stretching which do not use harmful chemicals. [63]

Table 18: *Basic data about the membrane and MBR from company Hyflux [63]*

PoroCep® Membrane Specifications	
Material	HDPE
Type	Hollow fibre
Pore structure	Asymmetric slit pore
Nominal pore size (micron)	0.1
Outer diameter (mm/inch)	0.4 / 0.016
Inner diameter (mm/inch)	0.3 / 0.012
Wall thickness (mm/inch)	0.05 / 0.002
Tensile strength (MPa)	80
Chlorine resistance (ppm-hrs)	1,000,000
PoroCep® Unit Box Specifications	
Overall dimensions: length x width x height (mm/inch)	345 x 500 x 1,000 / 13.6 x 19.7 x 39.4
Box material	PVC
Membrane elements per box	10
Membrane area per box (m^2)	85
Permeate outlet diameter (inch)	1.5
Specific membrane area per box (m^2/m^3)	493
Dry weight (kg/lbs)	19 / 42

The membranes are housed in unit boxes that are in turn mounted on a skid that comes with its own air diffusing module. Unlike conventional wastewater treatment systems, MBR systems require a smaller footprint, produce less sludge and allow for a higher mixed liquor suspended solids (MLSS) content with a shorter hydraulic retention time. The compact design of the PoroCep® skid allows a higher packing density to be achieved within a MBR. With its high filtration capacity and superior performance efficiency [63]

Figure 64: *rejection provided by slit pores compare to normal pores [63]*



Martin system membrane module MS 611:

Organic polymer membranes, flat-sheet (Martin Systems - Germany) with commercial membrane module with ultrafiltration membranes (filters manufactured by the company Microdine nadir under the designation UP150).

For module construction was used high-grade plastics (PP) and stainless steel components (SS 304, SS 316 optional). [64]

Figure 65: MS 611[64], and MS 611 characteristic [64]

Membrane modul characteristics	
Material	Organic polymer, PES
Cut-off limit	Ultrafiltration
MWCO	150 kDalton
Nominal pore size	approx. 35 nm
Maximum pore size	0.1 µm
Membrane area	6,25 m2
Size of the modul (L*W*H)	423*289*805
Dry weight (kg)	14
Max. flux (m3/h)	0,17
Avarage flux (m3/day)	2,73

4.7.3 Experimental Conditions

The goal was to test the hypothesis that the nanofiber membranes are useful in the MBR, comparable to or better than membrane systems from Martin and Hyflux company (equivalent or superior permeability, durability, resistance to biofouling, sanitation, electricity consumption). They were adapted to the conditions of operation.

The aim was to demonstrate in particular long-term stability and functionality nanofiber membranes for treatment of waste water in the MBR. Demonstrate the competitiveness of nanofiber membranes compared to UF board and hollow fiber and fiber MF membranes in the test under the same input conditions.

Figure 66: *Photo on the left is a cabine with switchboard and PLC control unit with a record. The left image shows the membrane modules during the relaxation phase before starting the test. (Photo, M. Došek)*

To the PLC is recorded flow through membranes, water temperature, the negative pressure suction, overpressure during backwash, the flow from the backwash, the volume of water pumped out of the membrane, the volume of water used for flushing, the total volume of water utilized.

In addition, behind the behind the membrane from the nanofibers was installed UV lamp to reduce microbial contamination. (Samples were collected before and after UV and tank backwash). From experience, it appears that the actual waste water treatment filtration using microfiltration nanofibrous materials is not sufficient for water sanitation. Using UV assume security (disposal) of microbial contamination on the parameters of the decree (the use of water for irrigation, bathing, etc.).

Each membrane module was before starting the test 24 hours soak in clean water. The membranes were placed in a common tank into which was pumped activated sludge from the activation section. The overflow was drain to the sewer (control for optimal sludge dry matter). To ensure a constant dry weight of the sludge during the test was necessary to set the filling sludge in the tank depending on the rate of outflow of filtrate.

As a quality monitoring filtration samples were taken for microbial analysis *E.coli*, T. coliforms, enterococci, CFU 22 and 36 °C and also BOD, COD. Samples were taken mostly weekly. Samples were taken from several connection points and were transported in a cool box.

Flushing apparatus with water (before the first measurement, the apparatus for determining the pollution)

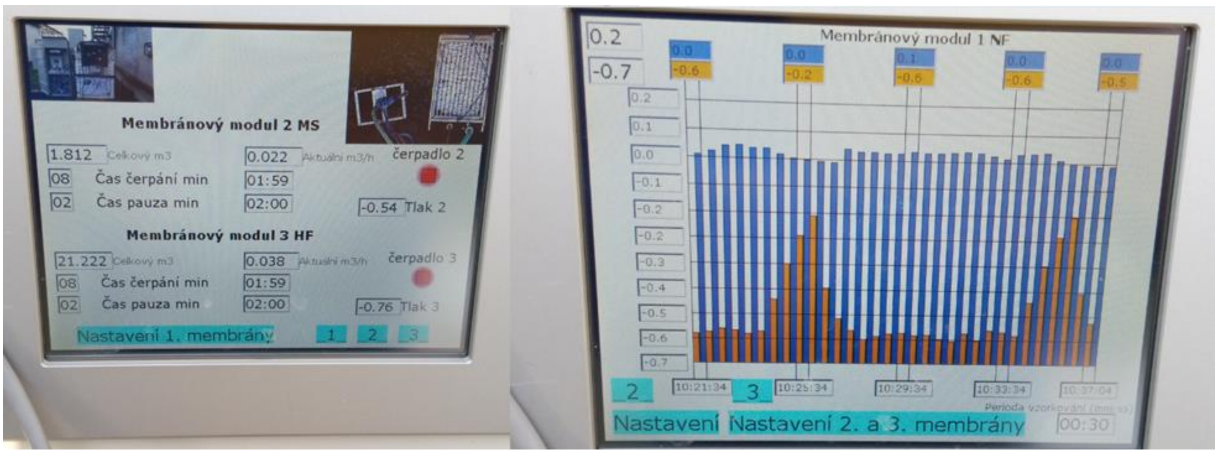
The filtrate before UV after UV filtrate, filtrate from the backwash tank, activated sludge. The evaluation of the results was used comparison of the overall pumped water relative to the surface of the membranes, the water quality (microbiological purity), the pressure on the membrane fouling rate (recovery method). Water consumption to backwash pressure intensity.

Pumping permeate from modules

In order to evaluate the differences between modules, it was necessary to set the mode for pumping all identical modules. The conditions were adjusted as follows:

NV module: 8 min pumping, 2 min. delay backflush (flow rate was set at 100 L/hour). MS module: 8 min pumping, 2 min. Delay (adjust the flow to 100 L/hour). HF module: 8 min pumping, 2 min. delay (the manufacturer's recommendations for the operation of the module 7-10 min drawdown delay 1-3 min) adjusting the flow 1600 L/hour. There has been zeroing energy consumption meters (PLC) for pumps and blowers, gauges in the PLC and the recording (photographing) the state of the analogy dials water meters. Turning pumping of all modules takes place simultaneously. Before the first sampling 2 min. leave running, then sampling.

Figure 67: *The photo is captured display PLC, which allowed to adjust settings on the site of the pilot. Pictured on the left is seen setting modules and the current status. Photo right shows the graphic evolution of negative pressure during pumping, backwashing and relaxation.*



4.7.4 Methodology for microbiological analysis of water samples, sediments and active filters

In the samples of water, activated sludge and filtrate from long-term experiments examined for the presence of certain bacteria by law and standards: intestinal enterococci on Slanetz-Bartley agar (Merck, Germany) at 37 °C for 72 h, coliforms ENDO agar (Merck, Germany) at 37 ° C for 72 hours, the microorganisms can be cultivated at 22 and 36 ° C PCA agar (Biokar Diagnostics, France) at 22, respectively 36 ° C for 72 resp. 48 h. were determined Thermotolerant coliform counts mFC agar (Merck, Germany) at 44 °C for 24 hour, counts of *E.coli* chromogenic soil (MILCOM as, Czech Republic) at 37 °C for 24 h .

The samples of waste water before filtration and after filtration were prepared a series of decimal dilutions, followed by 1 ml of the appropriate dilution of the sample or pipetted into Petri dishes and sealed breeding ground. The plates were then incubated in a thermostat upside at the above temperatures and for the time indicated. Accrued characteristic colonies were counted and the results were recorded in CFU/mL

Figure 68: *Samples for analysis were collected every week.*

Samples of influent, sedimentation tank output, permeate (effluent from membrane module - treated water) and activated sludge were taken every week.

4.7.5 Comparing the measured values with the legislation of the Czech Republic

The results of microbiological analysis were compared with the limits under Directive 2006/7 / EC concerning the management of bathing water quality, emission standards for the use of water for water supply purposes (in accordance with Section 31 of the Act 254/2001 on water and bathing water (under Section 34 of the Act 254/2001 Coll., on Waters) Government Regulation 61/2003 Coll., the quality requirements and quality of water intended for human consumption specified in Directive 98/83 / EC, Regulation 252/04 Sb. setting hygiene requirements for drinking and hot water and the frequency and scope of drinking water control and water quality requirements, designed to irrigate landscaped CSN 757143.

4.7.6 Operational problems and end of the experiment

Monitoring and evaluation of the data from this experiment was terminated for operational reasons in December 2014. In fact, whole experiment has been shut down in February 2015.

During the first phase of testing, there were several problems. Some were technical, others were caused from the lack of experience regarding the operation of the MBR. Tests were planned for the warmer summer and fall.

One of the reasons why the test was delayed was an imperfect membrane welding technology for plastic supporting frames. The technology was tested for the first time just before starting the pilot plant. After 14 days from the start of the experiment, due to the increasing negative pressure some of the membrane broke away of the supporting frames. The experiment had to be discontinued. Welding technology has been modified.

Figure 69: The photo shows the membrane detached from the supporting frame

After starting the next phase of the experiment, which deals with the final passage (7.10- 24.12.2014) were expected complications associated with outdoor conditions. The pilot device was placed outside, not isolated. The temperature of the activated sludge in climatic conditions of the Czech Republic is the whole year above zero. However in terms of a small tank and with tubing of narrow diameter occurred freezing. The experiment was interrupted.

Figure 70: *Frozen pilot unit, end of the experiment*

5 RESULTS AND DISCUSSION

During the first stage (7.10.2014 – 24.12.2015), clogging of membranes were observed in a relatively short time compared to expectations. This, however, relate to all types of test membrane modules. It is highly probable that microscopic, colloid or high-molecular particles in influent together with biofouling cause preterm clogging of the membrane. WWTP Modřice was chosen particularly because its size should provide stable conditions. During the experiment were monitored parameters of activated sludge (influent). Especially with regard to the dry weight of the sludge.

The table shows the average values of analysis of the activated sludge and permeate during the period 7.10.2014 – 15.2.2015.

Table 19: *Analyses of the activated sludge and permeate from tested MBR*

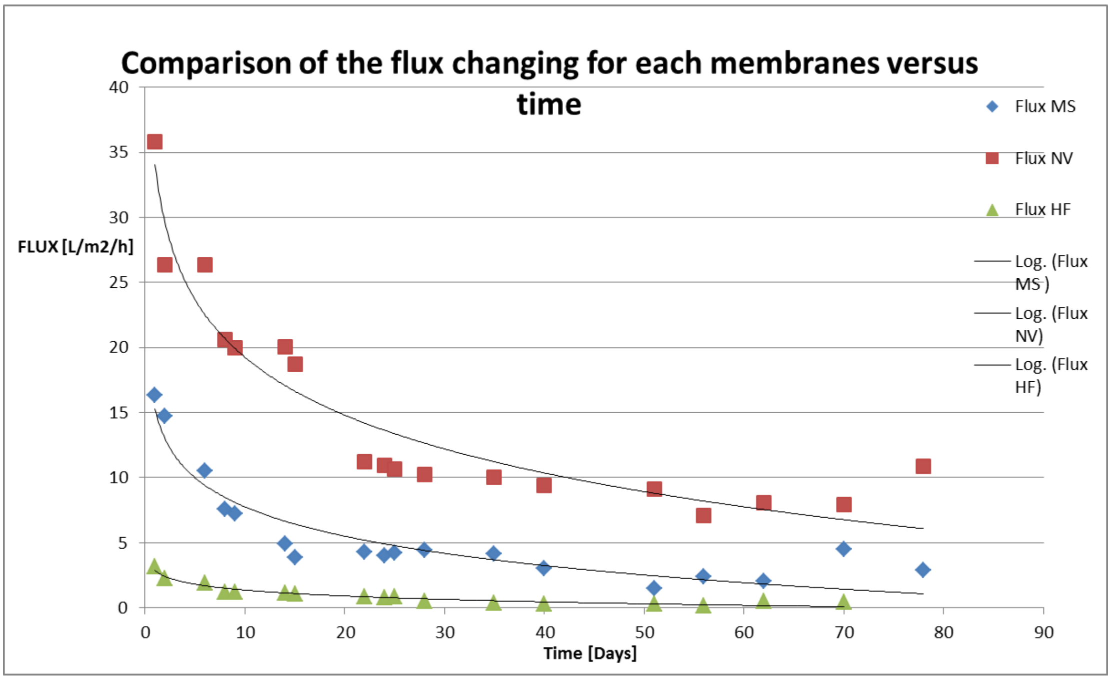
	Influent	Permeate		
Indicators	**avarage [mg/L]**	**NV [mg/L]**	**MS [mg/L]**	**HF [mg/L]**
COD	6010	53,6	51,8	49,6
BOD5	1511	5,3	5,9	26,7
SS	4665	10	10	20
Dry matter	25,137			

The activated sludge solids are moved relatively normal. The average value of six measurements was 4.66 g/L. This value is normal for activated sludge. However, for the membrane treatment plants is important to set different operating conditions. Typical mixed liquor suspended solids (MLSS) concentrations are 1,500 mg/L to 5,000 mg/L. Typical MLSS concentrations in MBR systems are 10,000 mg/L to 12,000 mg/L. [65]

Higer MLSS of the sludge liquor in the membrane section prevent clogging of the membrane. In some cases the membrane was run at 30 mg/L. (Colsen 2016), but at the cost of frequent regeneration.

Despite these problems, pilot testing of newly developed nanofibrous membrane module demonstrated long-term stability of the filtration process in activated sludge in real conditions at the wastewater treatment plant and showed the potential for further development and testing. The hypothesis that due to its extreme porosity membrane modules reached higher flow rates was also confirmed. The experiment results confirmed a graphical representation of the measured values.

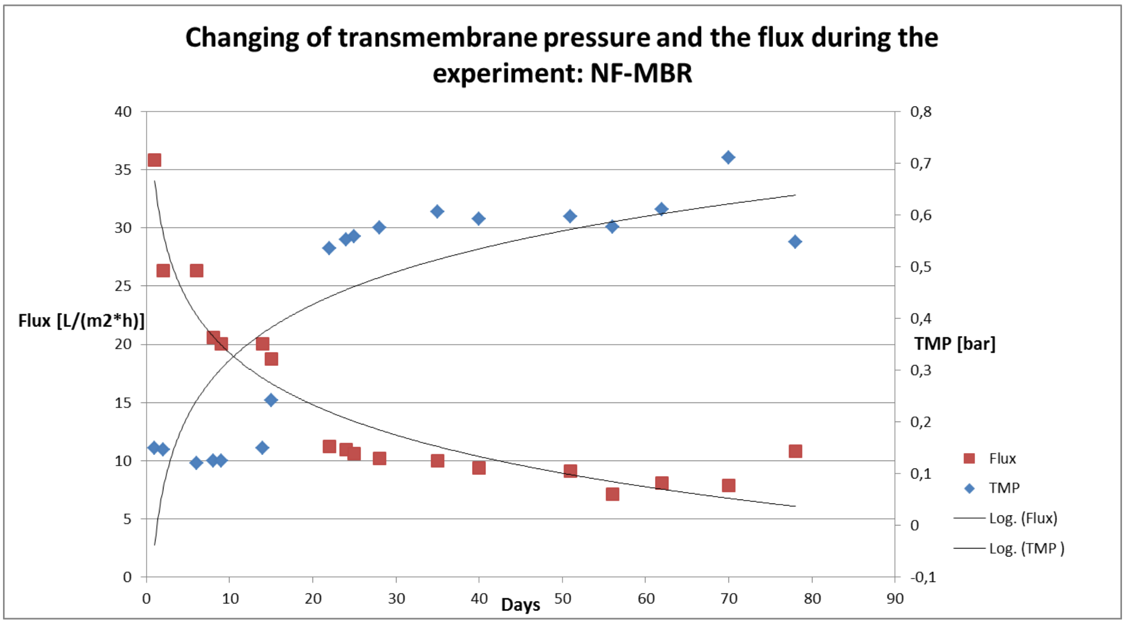
Figure 71: *Comparison of the flux changing of each membranes versus time*



The upper graph shows, the progression of the flux [L/m^2/h] changes during the time. The flow is converted to a square meter. The chart clearly shows that during the first days of the experiment nanofibrous membrane has once more higher flux than Martin system MBR. When pulling out the flow per unit area lags well hollow fibres module. The permeate flux was measured in all membrane modules. The flat sheet membrane modules (NF and MS), has different initial values of permeate flux. For NF it was 36 L/(m^{-2}* h $^{-1}$) and MS 16,5 L/(m^{-2}* h $^{-1}$) for the hollow fibre it was 3,2 L/(m^{-2}* h $^{-1}$). It is not possible to say, that during the whole period of the operation showed modules relatively stationary fluxes as they should have in practice. The flux reduction was very fast. Flow (L/h) were obviously different, because of different membrane area and "packing density" of each module. MS = 102 L/h, NF = 136 L/h, HF = 272 L/h. Assessing the effectiveness we must consider also this packing density. If we compared the filtration efficiency relative to the area needed for installation, hollow fibres will always have the advantage.

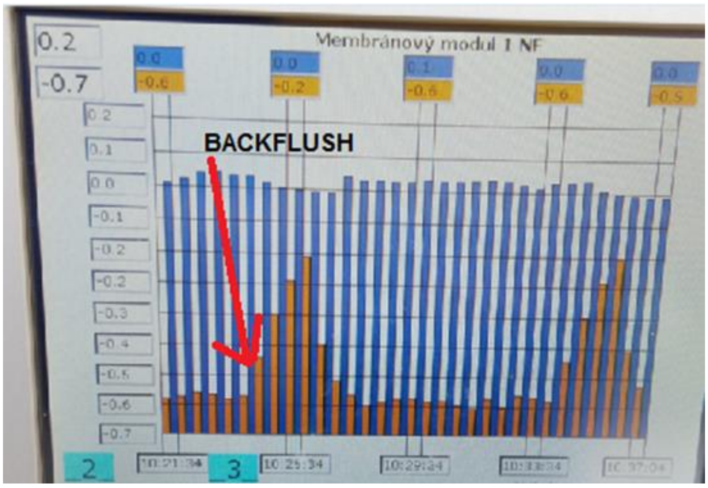
Since plant start-up, there was observed a slow, almost immediate and continuous TMP increase (Fig. 72). One of the reason could be the fact, that the membrane was operated at relatively high flow rate, which was set at 100 L/hour (for flat sheet) but this value was recommended by the membrane supplier.

Figure 72: Changing of TMP and the flux during the experiment with NF-MBR



During the experiment, in spite of the continuous maintenance operations which are essential for the sustainable and long term operation of the MBR (i.e. air scouring and backwash), was observed TMP trend which showed the typical two-stage behaviour with an initial slow pressure increase followed by a rapid rise with an exponential trend, according to the well-documented theory of the local critical flux concept [66, 67]. Membrane cleaning by back flush using permeate from reservoir helped achieve a significant improvement of the measured TMP.

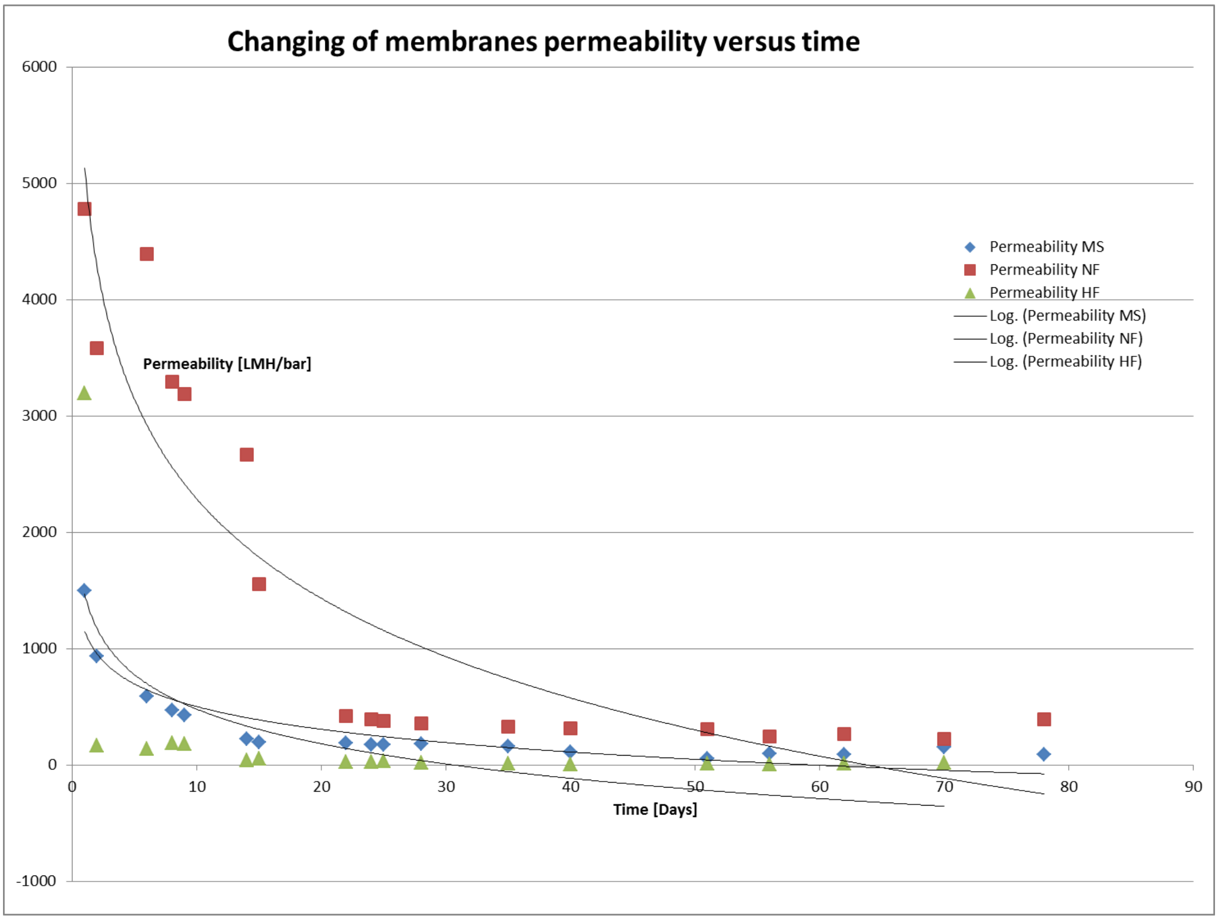
Figure 73: *Record from the PLC influence of backwash on the membrane pressure.*



.

Due to the different nature of the membrane configuration it was necessary to supplement the comparison by calculating of the permeability. The values are shown in the chart below. The tank was equipped with a temperature sensor in order to determine the sludge temperature for permeability calculation. Unfortunately, during the experiment several times broke down the temperature sensor. The measured temperature couldn´t be use for calculation. For calculating of the permeability was used than normalized temperature 20 °C. Permeability (K20) showed similar trends (although symmetric) to TMP. Using relatively low (adequately) fluxes and TMP usually applied in MBRs, should ensure "clean" membranes and keep them operable in the pressure controlled region. When pressure controls the flux, constant permeability should be observed. This fact wasn´t detected during the experiment.

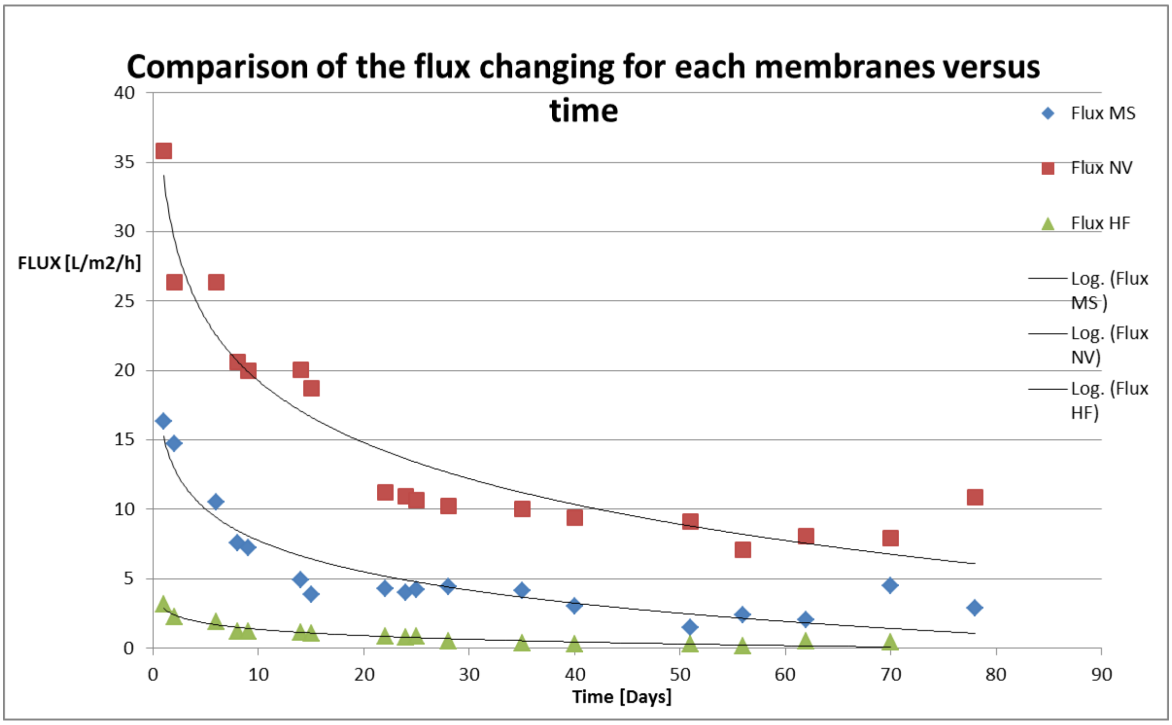
Figure 74: *Changing of membranes permeability versus time*



Permeability should provide information regarding the occurrence of the fouling process, even if different fluxes were applied for the filtration. Thereafter, with the membrane operation progress, the permeability decreased above the unity indicating the occurrence of fouling phenomena that can be explained also by the rise of the operating TMP.

The hypothesis that the nanofibrous membranes are far more porouse than conventional membranes confirmed their permeability. The initial value of permeability of the membrane SpurTex MF RF was around K = 4800. Whereas Martin system MBR with membrane MS 611 from company Microdyn-Nadir, started on the permeability value of K = 1500. Nanofibrous membrane reached the same permeability as was the initial value of MS membrane until 15 days from the start of the experiment. During trial operation was reported a similar pattern as observed in laboratory and pilot plant experiments in the earlier stages. Nanofiber membranes showed at the beginning a much greater permeability. But this permeability persists only first few weeks. During this time decreases rather rapidly. After a steady decline its further course corresponds to the course of what we know from other commercially available membranes. It can be assumed that this benefit lasts until such time as it is formed on the membrane fouling.

Figure 75: *Comparison of the flux changing for each membranes versus time.*



5.1.1 Runoff sanitation, monitoring of the microorganisms in activated sludge and filtrate

The aim of the study was to assess capability of membranes to ensure hygienisation of runoff from wastewater treatment plant. There were tested filtration properties of various membranes. From the results were drawn appropriate conclusions.

There has been a decrease of 1-3 CFU/mL log removal after filtration for nanofibrous MBR. These results were comparable to our previous values obtained from the semi-pilot testing in activated sludge [53]. Similar values when using microfiltration PA (Polyamide) nanofiber membranes with a mean pore size of 0.4 micron in laboratory tests indicate Bjorge [68] the log removal of 2.24 CFU/mL of culturable organisms at 37 ° C and Daels [69] log removal 1.3- 3.2 CFU/mL S. aureus with nanofibrous membranes. Higher values were achieved only after functionalization with different functionalizing agents. Compare to results with others MBR is similar to the Martin system but better compare to the ultrafiltration Hyfflux MBR. There was almost zero CFU/mL log removal compare to the values obtained from the analysis of the sludge. When monitoring the indicator Enterococus and, E. coli, was found a reduction of concentration of 2-3 CFU/mL log removal after filtration for both nanofibrous microfiltration MBR and Martin system ultrafiltration MBR. When monitoring the indicator enterococci, E. coli, was found a reduction of concentration of 2-3 CFU/mL for both nanofiber microfiltration and ultrafiltration membranes and Martin MBR system. In contrast, the ultrafiltration membrane type hollow fibres from the company Hyflux showed almost no reduction of CFU/mL log removal after filtration. There has been no decrease in the average one order of magnitude.

Table 20: *Microbial indicators of the raw activated sludge (inlet)*

Raw sludge (inlet)												
Days	T. coli [CFU/mL]	log	CFU_{36} [CFU/mL]	log	CPM_{22} [CFU/mL]	log	ENT. [CFU/mL]	log	E. coli [CFU/mL]	log	Coliform [CFU/mL]	log
1	0		88636	4,95	94109	4,97	5236	3,72	0		0	
8	0		1322	3,12	9094	3,96	1222	3,09	0		7505	3,88
14	4	0,6	498	2,7	123392	5,09	9164	3,96	120	2,08	1673	3,22
22	2	0,3	34036	4,53	305455	5,48	1225	3,09	0		0	
27	0		78941	4,9	123055	5,09	2793	3,45	0		0	
34	44	1,64	60028	4,78	279864	5,45	3568	3,55	0		0	
55	19	1,28	21207	4,33	117818	5,07	22	1,34	2880	3,46	0	

Table: *Microbial indicators of the permeate from the Hyflux hollow fibres MBR.*

Hyfflux Holow fiber MBR												
Days	T. coli [CFU/mL]	log	CFU_{36} [CFU/mL]	log	CPM_{22} [CFU/mL]	log	ENT. [CFU/mL]	log	E. coli [CFU/mL]	log	Coliform [CFU/mL]	log
1	0		215	2,33	109091	5,04	4450	3,65	0		0	
8	105	2,02	815	2,91	19847	4,3	1	0	59	1,77	0	
14	0		24836	4,4	16219	4,21	9164	3,96	136	2,13	44	1,64
22	0		52	1,72	1345	3,13	2009	3,3	256	2,41	218	2,34
27	0		749	2,87	1984	3,3	5353	3,73	12	1,08	0	
34	0		539	2,73	15450	4,19	0		0		0	
55	0		66	1,82	255	2,41	22	1,34	*22*	1,34	6	0,78

Table: *Microbial indicators of the permeate from the MS flat sheet MBR.*

Martin system -MBR											
Days	T. coli [CFU/mL]	CFU_{36} [CFU/mL]	log	CPM_{22} [CFU/mL]	log	ENT. [CFU/mL]	log	E. coli [CFU/mL]	log	Coliform [CFU/mL]	log
1	0	1677	3,22	18536	4,27	0		0		0	
8	0	85	1,93	136473	5,14	0		10	1	0	
14	0	9616	3,98	9159	3,96	0		140	2,15	0	
22	0	5	0,7	71	1,85	0		3	0,48	0	
27	1	14	1,15	1545,5	3,19	1	0	1	0	1	0
34	0	43	1,63	630	2,8	0		1	0	0	
55	0	4	0,6	164	2,21	0		6	0,78	3	0,48

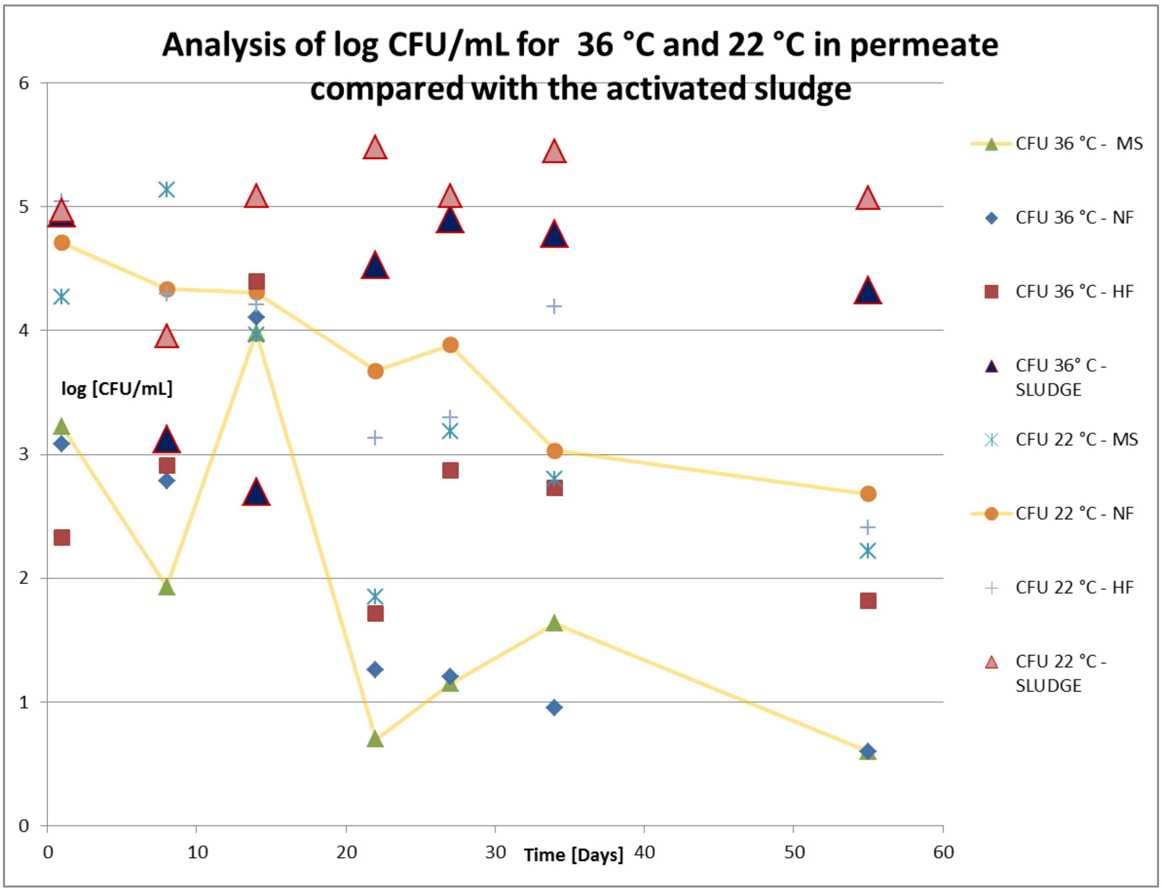
Table: *Microbial indicators of the permeate from the Nanofibrous flat sheet MBR.*

Nanofibrous MBR									
Days	T. coli [CFU/mL]	CFU_{36} [CFU/mL]	log	CPM_{22} [CFU/mL]	log	ENT. [CFU/mL]	E. coli [CFU/mL]	log	Coliform [CFU/mL]
1	0	1209	3,08	51181	4,71	0	0		0
8	0	607	2,78	21679	4,34	0	100	2	0
14	0	12804	4,11	20345	4,31	0	45	1,65	0
22	0	18	1,26	4738	3,68	0	1	0	1
27	0	16	1,2	7614	3,88	0	1	0	0
34	0	9	0,95	1070	3,03	0	0		1
55	0	4	0,6	481	2,68	0	5	0,7	0

The quality of the treated water was continuously monitored in the filtrate and wastewater. Values of microbial contamination of the filtrate and wastewater are summarised and shown for all MBR in upper tables.

UV light was used to increase microbial purity of the filtrate at the outlet of the nanofibrous MBR and to evaluate possible water reuse. The reductions of microbiological contamination for CFU/mL of culturable organisms at 37 ° C, when comparing the values obtained from microbial analysis of the sludge, filtrate and UV treated filtrate, were monitored. Contamination was reduced by 2 log removal CFU/mL, compared permeate and sludge and in some case such a faecal coliform, enterococcus, E. coli, to zero. But between permeate and permeate after UV light was no different. Probably because of incorrect design for UV, there was propose relatively short retention time with flow, which didn´t correspond to power of the UV light. Thus evaluation of additional post hygienisation using UV light was not in this case performed. ´

Figure 76: Monitoring of the log CFU/mL cultivated at 36 and 22 °C, in raw sludge compare to outlet from MBR´s modules.



These results supported our assumptions about suitability of nanofibrous membranes for membrane bioreactors. The quality of the treated water was continuously monitored in the filtrate and waste water. Values of microbial contamination of the filtrate and wastewater for the indicator CFU/mL of culturable organisms at 37 ° C and 22 °C are shown in the chart above.

It was managed to preliminarily demonstrate the suitability of nanofibrous membranes for use in practice. They can be used for example to increase the throughput capacity of wastewater treatment systems without increasing the physical size of the old WWTP, and thus still be able to meet tough discharge regulations, if t install nanofibrous MBR.

6 CONCLUSION

Our pilot tests confirm the usefulness of nanofiber membrane systems in full-scale. Average flux 15, 2 ($L/m^2/h$) was measured with a MBR module (membrane area 3.795 m^2). That's 3 times higher than Martin system and 15 times more than Hyflux MBR. It means 365 litters per day, which corresponds approximately to the needs of the 3 members household. Membrane modules was able to remove COD (as much as 88, 8%) and more than 99% of suspend solids in the long-term operation without activated sludge removal. Using the obtained dataset, permeability (K) was calculated according to the following equation. K = Flux/TMP, where TMP and K were then normalised to the reference temperature of 20 ° C in order to take into account the influence of permeate viscosity on the processes. The results obtained within online measurement of appropriate parameters served for the monitoring of TMP, permeability, fouling behaviour and sludge fouling potential, using newly developed nanofibrous membrane SpurTex® MF RF in MBR. The permeability of nanofibrous membrane measured during initial phase of the experiment was K = 4778,2 - 1553,5. it is already above the level required for process of sludge filtration.

It was clearly confirmed that this newly developed nanofibrous microfiltration membranes SpurTex® MF RF, even though it was the very first specimen, used in a membrane bioreactor of own production, can be compared with the best commercial membranes (MBR´s) on the market: Hyfflux hollow fibre membrane module and Martin system flat sheet membrane module, that they are even a class above with regard to filtration efficiency. Our nanofibrous MBR achieved even better hygienisation of runoff than the Hyfflux MBR. This confirmed that one of the assumptions of our hypothesis. This says that for the hygienisation of the effluent from wastewater treatment plant are sufficient in most cases microfiltration membranes. Hygienisation effect is after short time the same as if using ultrafiltration membranes, because on the surface of the membrane and along the fibbers, there will occur cake layer formation profiles. But the porous structure of the nanofibrous membrane also allows during the initial phase of filtration significantly higher flows at lower pressure loss, which is energetically advantageous.

After withdrawing the membrane module of the sludge tank and its disassembly into individual filter plates was obvious the positive effect of additional external aeration of membrane modules. It was evident that there is still space for optimization. The far plates were more clogged. Regeneration, optimization and antifouling surface treatment will be another step to increase the competitiveness of nanofiber membranes for water treatment.

Besides the technical problems (numerous clogging of membrane and ice-up of feeding pipes), can be experiment considered as beneficial to further development of this type of membranes. Pilot testing of membrane module with nanofiber membranes in Letonice and in Modřice, demonstrated long-term stability of the filtration process in activated sludge even with sludge, which was not typical, because has had a lower concentration of solids than is suitable for treating sludge with membrane bioreactors. Despite this fact showed membranes the applicability in real-world conditions at the wastewater treatment plant. Microbial contamination of samples of the filtrate reached log removal 1-3 CFU/mL after filtration. Filtration in combination with UV irradiation didn´t resulted in a reduction of microbial contamination.

Nevertheless, it was only initial testing of new nanofibers material and results led to the impression that they are suitable for further optimization for application in membranes bioreactor. In practice is still need to verify long-term reliability and durability of nanofiber materials. It is also necessary to compare the results more in detail with commercial membranes, their parameters and also to test the possibility of regeneration after clogging. These experiments and testing of antifouling modifications of membranes will be part of our future work.

7 ACKNOWLEDGEMENTS

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9 LIST OF FIGURES

10 LIST OF TABLES

11 LIST OF ABBREVIATIONS/SEZNAM ZKRATEK

CFU	Colony-forming unit
CPM	Celkový počet mikroorganismů
HEPA	High Efficiency Particulate Air filtr
HF	Hyflux membrane module
KTJ	Kolonie tvořící jednotky
MBR	Membrane bioreactore
MPPS	Most Penetrating Particle Size
MS	Martiny system mebrane module
NF	Nanofibrous membrane
nNT	Nanovlákenná textilní vrstva
PCA	Živné médium, obchodní název Plate Count Agar
PET	Polyetylentereftalát
PU	Polyuretan
PVDF	Polyvinylidenfluorid
SEM	Skenovací elektronový mikroskop
VS	Viskóza

12 APPENDIX

Certificate/material list of the membrane SPURTEX MF RF which was developed within this thesis and performed by the company SPUR a. s. Zlín.

SPUR

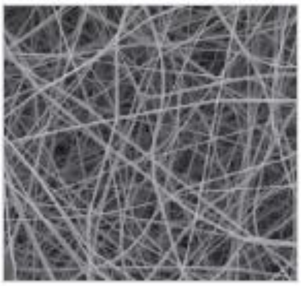
NANOTECHNOLOGIES
We understand today and think about tomorrow.

SpurTex MF RF

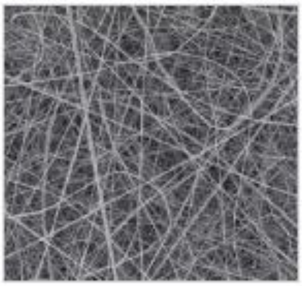
reinforced multilayer cleanable nanostructured filtration material for microfiltration on liquids

- excellent retention of bacteria and fine solids
- increased performance (higher flux and nanostructure reinforcing)

Materials	
Filtration layer	Polyurethane, Polyvinylidene fluoride nanostructure
Drainage	Microporous open cell materials
Support layers	Polyester woven textile or Polypropylene nonwoven textile or glass paper



PU nanostructured membrane surface, magnification 5 000x



PVDF nanostructured membrane surface, magnification 5 000x

Membranes properties		Conditions
Average pore size	250 nm	ASTM F316-03
Initial water flux	> 2 000 l/m²h	23 °C; 0,075 bar; distillated water
Operating pressure	< 3 000 mbar	
Back washing pressure	< 1 000 mbar	Usual cleaning processes are recommended
pH applicability	3 – 12	
Max. operating temperature	60 °C	

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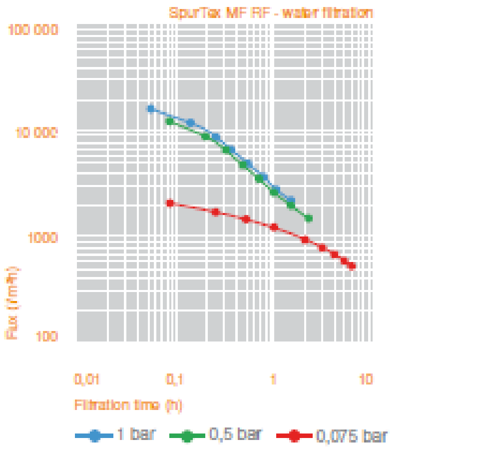
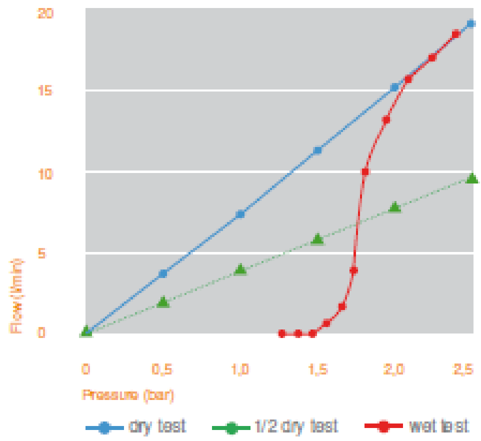
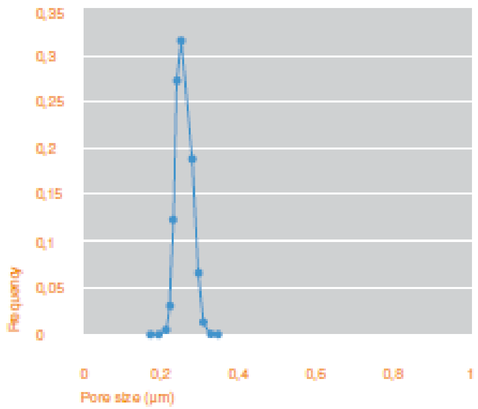


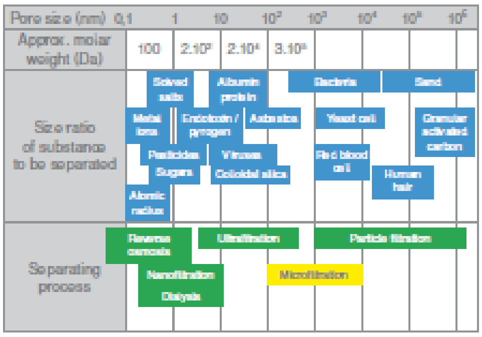
Flux through SpurTex microfiltration membrane based on PVDF nanostructure placed on microporous open cell material



Wet and dry test for membrane filter pore size characteristics by bubble point and mean flow pore test (ASTM F316-03)



Pore size distribution in SpurTex MF RF membrane filter



Pore size of filtration materials, sizes of eliminated particles and adequate separating processes