Development of cellulose-based photoactive nanohybrid membranes for water purification

Theses Booklet

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Introduction

Water is an essential compound in our daily life activities and for the environment. Water makes up 60-75% of human body weight, and a loss of 15% of total body water can be lethal. Although 71% of the Earth's surface is covered with water, only 0.2% is suitable for drinking, and its distribution is very inhomogeneous, as 98% is salty, and 1.8% is frozen in glaciers. The quality of most resources we rely on is being drastically reduced and exhausted due to rapid population growth, climate change, global warming, agriculture activities, etc. [1,2]. Freshwater is necessary for human survival but also serves as a primary raw material for numerous industries. Almost 70% of the world population could be under water-deficit conditions, and millions of people will be suffering from absolute water deficiency by 2025, as predicted by the United Nations [3,4]. Based on these alarming forecasts, the number of people who will experience water deficiency is expected to reach 7 billion by 2050 [3,5]. Given this situation, massive efforts are being initiated throughout the world to prevent this emerging crisis.

The reuse, recycling, and recovery of water have proven fruitful in creating a new and reliable water supply while not compromising public health, and this can be achieved by improving wastewater treatment plants and related technologies such as membrane filtration, UV disinfection, treatment with activated carbon, ozone, and advanced oxidation to remove the contaminants present in water [6]. Membrane filtration is recognized as one of the most promising and extensively used processes for cleaning wastewater, seawater, and brackish water [7]. However, the use of conventional materials in water treatment processes such as activated carbons and petroleum-based polymers have a large carbon footprint associated with their production and application [8]. Thus, it is critical to employ low-cost, environmentally friendly green alternatives with superior performance and lower carbon footprints for a sustainable future. In this context, adsorption properties, photocatalytic activity, and electrostatic interactions are the most major useful, attractive and clean technologies for water treatment, virus removal, and antibacterial properties [9].

Recently bio-based nanomaterials, such as bacterial cellulose (BC), cellulose nanocrystals (CNC), cellulose nanofiber (CNF), referred to as cellulose nanomaterials (CNs), have been investigated for the water treatment process and virus removal since cellulose is recognized as one of the most abundant biopolymers used as a reinforcing material for fiber composite materials [10] and represents one of the most inexhaustible sources of raw material for the growing need for biodegradable and biocompatible products [11,12]. The advantages of cellulose and cellulose derivatives are that they are environmentally friendly, non-toxic, renewable, biocompatible, sustainable, and cost-effective sources of carbon-based composites and support material for the development of hybrid nanocomposite materials [13,14]. However, the application of cellulose has largely been limited in food packaging due to its lack of antibacterial activity [15,16]. Functional nanomaterials are widely used to enrich cellulose with antibacterial properties [17,18,19,20]. Cellulose is used as a support material for carbon derivates, metal nanoparticles, and metal oxides such as TiO_2, ZnO, Fe_2O_3, CuO, Ag, Cu, while multi-walled carbon nanotubes (MWCNT) have also attracted much attention in the past decade [21,22,23]. Because of their high surface area, water suspendability, and reductive surface functional groups, CNs are attractive supports for carbon derivatives such as MWCNT, metal NPs, and metal oxides. The incorporation of CNs inside polymer matrices – similar to the addition of carbon nanotubes – modifies the membrane characteristics even at very low weight percentages [24]. The most remarkable property enhancement is the large improvements in membrane tensile strength obtained from small weight additions of CNs [25,26]. Other beneficial characteristics include changes to membrane surface hydrophilicity, more superior permeability, higher selectivity, and improved resistance to biofouling [27].

This dissertation focuses on the synthesis of novel cellulose reinforced nanohybrid membranes for application in the removal of bacteria (such as *E. coli*) and organic dyes (such as methylene blue). In addition, the catalytic hydrogenation of n-butene is also investigated. The overall objectives of this dissertation are as follows:

a) Preparation of composites (ZnO-MWCNT) that are used as additives to improve the adsorption and photocatalytic properties of as-prepared hybrid membranes. The preparation was performed following two different methods: impregnation and the solvothermal method. The mechanical and chemical properties of the composite were investigated intensively using different analytical techniques. The photocatalytic activity of the as-prepared ZnO-MWCNT nanocomposite additives was examined through the decomposition of acetaldehyde.

b) Synthesis of photoactive BC-ZnO-MWCNT hybrid membranes, using bacterial cellulose as matrix material and ZnO-MWCNT composites as additives. Two types of ZnO-MWCNT additives with different morphologies were used in a wide concentration range from 0% to 90% for BC-based hybrid membranes produced by filtration. The interaction between BC and ZnO-MWCNT and the effect of concentration and morphology of additives on properties such as zeta potential, hydrophilicity, and electrical conductivity were studied.

Furthermore, the as-prepared membranes were characterized by the use of scanning electron microscopy (SEM), focused-ion beam scanning electron microscopy (FIB-SEM), energy-dispersive X-ray spectroscopy (EDAX), X-ray powder diffraction (XRD), and surface area measurement (BET).

c) The performance of the hybrid photoactive membranes in the adsorption and photocatalytic degradation of methylene blue (MB) under UV irradiation and the removal of *Escherichia coli (E. coli)* was investigated.

Knowledge gap

As can be seen and concluded from the literature review, many reports and scientific papers have investigated the synthesis as well as the application of MWCNT composites; however, the effect of solvent conditions on the preparation of ZnO-MWCNT composites on the photocatalytic activity performance has not yet been investigated. Furthermore, no study has yet compared the influence of solvothermal and impregnation methods on the structural, optical, morphological properties, and photocatalytic activity of the ZnO-MWCNT composites. The preparation and investigation of NC-based composites in the field of water treatment towards various contaminant species present in contaminated water have been reported, and numerous semiconductor materials (TiO_2, ZnO, graphene oxide, CdS, and Fe_2O_3) have been added to NC in order to improve the photocatalytic degradation as well as the adsorption capacity of NC towards different organic pollutants present in contaminated water. Although several studies have reported the fabrication and application of BC, CNC, or CNF with different organic-inorganic materials, including photocatalysts such as TiO_2, ZnO, CuO, Fe_2O_3, or MWCNT, the fabrication, the antibacterial properties and the photocatalytic activity of BC-ZnO-MWCNT nanohybrid membranes have not been studied so far.

Objectives

The current work's primary objective is to create an efficient water treatment solution derived from sustainable and abundant renewable resources at low cost and fabricated through a facile preparation synthesis. Therefore, a stable and self-supported BC-ZnO-MWCNT membrane constituted of MWCNT as a material with high adsorption capacity, ZnO as a photocatalyst, and BC as a support material with high mechanical strength and high hydrophilicity properties was produced. The adsorption capacity, the photocatalytic degradation, and the antibacterial activity of the as-prepared hybrid membranes were investigated.

1- The preparation was performed in the following two phases:
   a) The first phase is the synthesis of the ZnO-MWCNT composites, which was achieved by two preparation methods, the impregnation method, and the solvothermal synthesis.
   b) In the second phase, the BC-ZnO-MWCNT hybrid membranes were produced using a papermaking technique that involves passing the prepared suspension through a microfiltration apparatus under vacuum, then pressing the prepared membranes slightly.

2- The as-prepared ZnO-MWCNT composites and the hybrid membranes were extensively characterized utilizing different analytical techniques: XRD, BET, SEM, FIB-SEM, Raman spectroscopy, contact angle measurements, zeta potential measurements, etc.

3- Subsequently, the photocatalytic activity of the ZnO-MWCNT composites was investigated towards the degradation of acetaldehyde, and the efficiency was compared based on the solvent conditions in which the composites were prepared. Finally, the BC-ZnO-MWCNT hybrid membranes were applied as adsorbent materials and photocatalysts for the decomposition of methylene blue; furthermore, the antibacterial activity was studied towards the removal of *E. coli* as Gram-negative bacteria.

Summary

The experimental results obtained during this Ph.D. work could be summarized in the following conclusions:

- The surface of SDS modified MWCNT were successfully coated with ZnO nanoparticles by a noncovalent impregnation method. The synthesis was successful in each case, although the resulted ZnO-MWCNT composites' structure was different. By applying the TEM technique, different layer construction and morphology were observed using EtOH and H_2O as solvents. The impregnation method's products were ideal candidates as starting material in photocatalytic measurements due to the partially covered MWCNTs, which are involved in the adsorption process during photocatalysis. The as-prepared ZnO-MWCNT nanocomposites exhibit enhanced photocatalytic degradation property of acetaldehyde (AA), caused by electron transfer processes from the attached ZnO MWCNT, in which MWCNT plays a role of an electron acceptor while ZnO is considered as a good electron donor. The synthesized ZnO-MWCNT nanocomposite prepared in EtOH showed the highest photocatalytic efficiency (71%) during the UV irradiated degradation of AA.

- The synthesis of ZnO-MWCNT composite materials was made using two different preparation methods. These were the impregnation, and the solvothermal synthesis techniques. We reported that these synthesis ways were successful, but the structure of composites and the size of the ZnO particles formed were different. Using the scanning electron microscopy technique, it was verified that different layer construction and morphology could be obtained by varying the applied synthesis techniques. Moreover, Raman measurements confirmed the presence of ZnO crystallites on the surface of MWCNT and the interaction between them. Using the impregnation surface of MWCNT was not completely covered with ZnO nanoparticles, while in hydrothermal synthesis, micrometer size ZnO particles formed. The differences observed between the two types of synthesis could be explained by the disparity of nanocrystallite size of ZnO. The results made it clear that the best wrappings were obtained using solvothermal synthesis. The biggest advantage of the hydrothermal method is that by changing the reactant's concentration, the coverage of ZnO particles on the surface of MWCNTs can be controlled easily.

- A new type of bacterial cellulose-based hybrid membrane (BC-ZnO-MWCNT) was developed and characterized. We showed that by choosing the appropriate synthesis method of ZnO-MWCNT composite additive (such as impregnation or solvothermal), the physical parameters of the as-prepared membranes could be tailored to specific applications. Zeta potential and contact angle data proved that the surface properties of hybrid membranes were modified significantly in a controllable way by the preparation method and concentration of the ZnO-MWCNT composite additive. The Zeta potential is positive for the SOLVO 80 and SOLVO 90 membranes over the pH range of drinking water. Furthermore, these membranes have the highest surface area value. Similarly, the differences in conductivity values of membranes also confirmed the importance of the synthesis method, and the SOLVO membranes showed higher conductivity over the IMP membranes. Raman spectroscopy confirmed that the intensity and position of the D- and G- bands of MWCNT in the composite were changed in comparison to those in the pristine nanotube. Thus, based on the results of Raman measurements, the formation of a chemical bond between BC fibers and MWCNT-based inorganic additive can be described as an interaction between two nanometric supra-molecular structures. The uniform structure of ZnO-MWCNT additives and the favorable MWCNT-BC matrix interaction led to excellent mechanical properties and flexibility.

- The adsorption, photocatalytic and antibacterial properties of the cellulose-ZnO-MWCNT hybrid membranes were presented. The as-prepared membranes were characterized by SEM, CT, and MIP equipment. The photocatalytic degradation of MB and the removal efficiency and antibacterial properties against Gram-negative *E. coli* bacteria of the as-prepared hybrid membranes were studied. By comparing the results, it was found that SOLVO 80 membrane showed outstanding properties during these experiments. Both the photocatalytic degradation of MB and the *E. coli* removal efficiency was achieved 92% in the case of SOLVO 80. Moreover, SOLVO membranes showed much better mechanical stability under UV-irradiation and in the filtration experiments. In contrast, IMP membranes were damaged during both photocatalysis and filtration experiments due to their lower tensile strength parameter. Thus, the application of BC-ZnO-MWCNT-SOLVO membranes containing ZnO particles in a micrometer range could offer further advantages and potential application alternatives such as a field of photocatalyst-based water treatment technology.

New scientific results

1st thesis: The effect of solvent on the formation of ZnO-MWCNT nanocomposites

It was verified that the emerging morphology of ZnO-MWCNT inorganic nanocomposites and the proportion of segregated ZnO nanoparticles observed in the as-prepared samples are fundamentally determined by the material quality such as the polarity of the solvent used.

1.1. ZnO-MWCNT composites were prepared under two different solvent conditions, water and EtOH. The impact of the applied solvent on the morphological, structural, optical properties was verified by transmission electron microscopy (TEM) and X-ray powder diffraction (XRD), and the photocatalytic degradation of acetaldehyde (AA) was explored by gas chromatography (GC). TEM images showed that inorganic particles formed and adhered onto the surface of MWCNT using both of EtOH and water solvents. However, separated aggregates of ZnO nanoparticles were also observed under EM investigations.

1.2. By applying EtOH as solvent the amount of segregated ZnO particles were reduced in the ZnO-MWCNT nanocomposite. Due to the different polarities of the applied solvents (EtOH and water), the surface coverage of the MWCNT was different due to competitive adsorption occurred on their surface. Presumably, the formation of the ZnO nanoparticles begins at the defect sites of MWCNT formed during the CVD process. Comparing the as-prepared ZnO-MWCNT nanocomposites, in general it can be concluded that those prepared by using EtOH as solvent produced morphologically more uniform structure.

1.3. Moreover, it was found that using EtOH the degradation of acetaldehyde was found to be 71% in photocatalytic test reactions. This is also related to the impact of the surface tension of the solvent used.

2nd thesis: The effect of synthesis method on the formation of ZnO-MWCNT nanocomposites

It was proved that the formation of the morphologies of the ZnO-MWCNT composites can be affected by the applied synthesis methods. Using the impregnation technique, MWCNT covered with ZnO nanoparticles formed, while applying solvothermal method, micro-sized hexagonal ZnO particles with built-in carbon nanotubes were observed.

2.1. The preparation of ZnO-MWCNT nanocomposites was carried out successfully applying both the impregnation and solvothermal synthesis methods. Although, it was found that by changing the synthesis method, the morphology of the ZnO-MWCNT composites changed as well. Using impregnation, carbon nanotubes covered with ZnO nanoparticles formed, while applying solvothermal treatment, micro-sized hexagonal ZnO particles with built-in carbon nanotubes were observed which was also proved by the focus ion beam scanning electron microscopy (FIB-SEM) analysis. From the preparation of nanocomposites with different weight ratios, it was concluded that by choosing the appropriate synthesis route (impregnation technique or solvothermal method) the structure of the as-prepared ZnO-MWCNT nanocomposite can be easily controlled.

3rd thesis: Preparation of BC-ZnO-MWCNT hybrid membranes

I certified that flexible self-supported bacterial cellulose (BC) based hybrid membranes can be synthesized by a simple and cheap papermaking method. Furthermore, it was confirmed that the physical parameters of the as-prepared hybrid membranes can be tailored by the synthesis method and the weight ratios of ZnO-MWCNT composite additives.

3.1. As is well-known, the MWCNT has high specific surface area and excellent adsorption properties, ZnO a semiconductor material with a bandgap of 3.2 eV allowing it to have a good photocatalytic activity toward the pollutants present in water, and bacterial cellulose is an ideal candidate as a cheap and environmentally benign matrix material in order to fabricate a self-supported and flexible membrane. Self-supported and flexible bacterial cellulose (BC) based hybrid membranes were synthesized and decorated with ZnO-MWCNT composite additives in order to modify and tune their surface and bulk properties. Two types of ZnO-MWCNT additives with different morphologies were used in a wide concentration range from 0 wt % to 90 wt% for BC-based hybrids produced by filtration.

3.2. To prepare novel hybrid membranes containing BC and ZnO-MWCNT composite additives, a simple and cheap so-called papermaking method was applied. It was shown that by choosing the appropriate synthesis method (such as impregnation or solvothermal), and the usage of adequate weight ratios (from 20 wt % to 80 wt %) of ZnO-MWCNT composite the physical parameters of the as-prepared membranes can become affectable. The uniform structure of ZnO-MWCNT composite additives and the favourable MWCNT-BC matrix interaction led to excellent mechanical properties and flexibility for most of the weight ratios applied.

3.3. Based on my investigations, I verified that the BC-based hybrid membranes containing higher amount of MWCNT-ZnO composite additive (50 wt% and 80 wt%) prepared by the solvothermal method can emerge as versatile materials for future applications in various areas.

4th thesis: Application of BC-ZnO-MWCNT hybrid membranes

It was found that ZnO particles with a micrometer size have played a significant role during the retention processes of bacteria and organic dyes as bigger photoactive centers. I proved that SOLVO 80 membrane - containing micrometer sized ZnO particles in large quantity - showed the highest photocatalytic efficiency (92%) and antibacterial retention (92%) in filtration experiments.

4.1. The as-prepared BC-ZnO-MWCNT hybrid membranes were tested in removal experiments of organic dyes and bacteria in order to prove their usability and efficacy towards contaminants present in water. The methylene blue (MB) was chosen as a model for dyes, and E. *Coli* was selected as the model of bacteria. Comparing the results of both types of membranes, impregnated (IMP) and solvothermal (SOLVO), I verified that SOLVO 80 membrane - containing micrometer size ZnO microparticles - showed the highest photocatalytic efficiency (92%) and antibacterial retention (92%).

4.2. Moreover, SOLVO membranes (SOLVO 50 and 80) have considerable mechanical stability than IMP membranes under UV-irradiation and in the filtration experiments. I confirmed by X-ray micro-computed tomography (μCT) analysis that, ZnO particles in the micrometer range - prepared by SOLVO method - have significantly higher volume (from 5×10^{-8} mm^3 to 1.16×10^{-6} mm^3) than ZnO nanoparticles synthesized by IMP technique, which explains the increased photocatalytic performance of SOLVO membranes. These ZnO microcrystals act as an effective trap in the retention processes of bacteria and organic dyes, as bigger photoactive centers.

4.3. Thus, the application of BC-ZnO-MWCNT-SOLVO membranes containing ZnO particles in the micrometer range could offer further advantages and potential application alternatives in the field of photocatalyst-based water treatment technology.

List of Publications

Articles connecting the dissertation:

1. **B. El Mrabate,** E. Szőri-Dorogházi, M. A. Shehab, T. Chauhan, G. Muránszky, E. Sikora, Á. Filep, N. Sharma, L.Nánai, K. Hernadi, Z. Németh
Widespread applicability of bacterial cellulose-ZnO-MWCNT hybrid membranes.
ARABIAN JOURNAL OF CHEMISTRY – accepted article
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2. **B. El Mrabate,** M. Udayakumar, E. Csiszár, F. Kristály, M. Leskó, L. Somlyai-Sipos, M. Schabikowski, Z. Németh
Development of bacterial cellulose-ZnO-MWCNT hybrid membranes: a study of structural and mechanical properties.
ROYAL SOCIETY OPEN SCIENCE 7 (2020) 200592.
IF: 2.647 (D1)

3. **B. El Mrabate**, M. Udayakumar, M. Schabikowski, Z. Németh
Comparative Electron Microscopy study of the ZnO/MWCNT nanocomposites prepared by different methods.
CIRCULAR ECONOMY AND ENVIRONMENTAL PROTECTION 3(1) (2019) 16-24.
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4. E. Bartfai, K. Nemeth, **B. El Mrabate**, M. Udayakumar, K. Hernadi, Z. Nemeth
Synthesis, Characterization and Photocatalytic Efficiency of ZnO/MWCNT Nanocomposites Prepared Under Different Solvent Conditions.
JOURNAL OF NANOSCIENCE AND NANOTECHNOLOGY 19:1 (2019) 422-428.
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Other publications:

1. M. Udayakumar, **B. El Mrabate,** T. Koós, K. Szemmelveisz, F. Kristály, M. Leskó, Á. Filep, R. Géber, M. Schabikowski, P. Baumli, J. Lakatos, P. Tóth, Z. Németh
Synthesis of activated carbon foams with high specific surface area using plyurethane elastomer templates for effective removal of methylene blue.
ARABIAN JOURNAL OF CHEMISTRY – accepted article
IF: 4.762 (Q1)

2. **B. El Mrabate,** Á. Prekob, L. Vanyorek, E. Csiszár, F. Kristály, M. Leskó, Z. Németh
Catalytic hydrogenation of n-butene with nanosized Pt/NBCNT hybrid membranes einforced with bacterial cellulose.
JOURNAL OF MATERIALS SCIENCE 56 (2021) 927-935.
IF: 3.553 (Q1)

3. L. Vanyorek, Á. Prekob, E. Sikora, G. Muránszky, **B. El Mrabate**, M. Udayakumar, P. Pekker, B. Viskolcz, Z. Németh
Development of N-doped bamboo-shaped carbon nanotube/magnesium oxide nanocomposites.
JOURNAL OF COMPOSITE MATERIALS 54(6) (2019) 857-863.
IF: 1.972 (Q2)

4. M. Udayakumar, **B. El Mrabate**, T. Koós, K. Szemmelveisz, J. Lakatos, L. Vanyorek, Z. Németh
Preparation and investigation of carbon foams from waste polyurethanes.
CIRCULAR ECONOMY AND ENVIRONMENTAL PROTECTION 3:1 (2019) 5-15.
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Conference presentations:

1. **B. El Mrabate**, M. Udayakumar, Z. Németh
Influence of the preparation technique on the properties of MWCNT/ZnO used as additives for BC hybrid membranes.
9TH VISEGRAD SYMPOSIUM ON STRUCTURAL SYSTEMS BIOLOGY
Szilvásvárad, Hungary (2019)
Poster Presentation

2. M. Udayakumar, **B. El Mrabate**, T. Koós, K. Szemmelveisz, J. Lakatos, L. Vanyorek, Z. Németh
Effective recycling of polyurethane wastes with enhanced CO_2 reduction.
9TH VISEGRAD SYMPOSIUM ON STRUCTURAL SYSTEMS BIOLOGY
Szilvásvárad, Hungary (2019)
Poster Presentation

3. **B. El Mrabate,** Z. Németh
Design of photoactive bacterial cellulose-based hybrid membranes.
3rd INTERNATIONAL CONFERENCE ON MEMBRANE SCIENCE AND TECHNOLOGY
Barcelona, Spain (2019)
Oral Presentation

4. M. Udayakumar, **B. El Mrabate**, T. Koós, K. Szemmelveisz, J. Lakatos, L. Vanyorek, Z. Németh
A comparative study of carbon foams prepared from waste polyurethanes under different pyrolysis conditions.
18TH AUSTRIAN CHEMISTRY DAYS
Linz, Austria (2019)
Poster Presentation

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References

[1] N. Mohammed, N. Grishkewich and K. C. Tam, Cellulose nanomaterials: promising sustainable nanomaterials for application in water/wastewater treatment processes, *Environ. Sci.: Nano*, **2018**, 5, 623–658.

[2] C. Santhosh, V. Velmurugan, G. Jacob, S. K. Jeong, A. N. Grace and A. Bhatnagar, Role of nanomaterials in water treatment applications: A review, *Chemical Engineering Journal*, **2016**, 306, 1116–1137.

[3] S. Kar, R. C. Bindal and P. K. Tewari, Carbon nanotube membranes for desalination and water purification: Challenges and opportunities, *Nano Today*, **2012**, 7, 385–389.

[4] D. Zhou, L. Zhu, Y. Fu, M. Zhu and L. Xue, Development of lower cost seawater desalination processes using nanofiltration technologies — A review, *Desalination*, **2015**, 376, 109–116.

[5] P. S. Goh, A. F. Ismail and B. C. Ng, Carbon nanotubes for desalination: Performance evaluation and current hurdles, *Desalination*, **2013**, 308, 2–14.

[6] Jordi Lladó Valero, Adsorption of organic and emerging pollutants on carbon materials in aqueous media. Environmental implications, *PhD thesis*, Universitat Politècnica de Catalunya, **2014**.

[7] X. Qu, P.J.J. Alvarez, Q. Li, Applications of nanotechnology in water and wastewater treatment, *Water Res.*, **2013**, 47, 3931–3946.

[8] M.M. Pendergast, E.M. V Hoek, A review of water treatment membrane nanotechnologies, *Environ. Sci*. ,**2011**, 4, 1946–1971.

[9] G. Zhu, H. Xu, A. Dufresne and N. Lin, High-Adsorption, Self-Extinguishing, Thermal, and Acoustic-Resistance Aerogels Based on Organic and Inorganic Waste Valorization from Cellulose Nanocrystals and Red Mud, *ACS Sustainable Chem. Eng.*, **2018**, 6, 7168–7180.

[10] M. Gouda, A. Hebeish and A. Aljafari, Synthesis and characterization of novel drug delivery system based on cellulose acetate electrospun nanofiber mats, *Journal of Industrial Textiles*, **2013**, 43, 319–329.

[11] P. Bazant, I. Kuritka, L. Munster and L. Kalina, Microwave solvothermal decoration of the cellulose surface by nanostructured hybrid Ag/ZnO particles: a joint XPS, XRD and SEM study, *Cellulose*, **2015**, 22, 1275–1293.

[12] N. A. Ibrahim, B. M. Eid, E. Abd El-Aziz and T. M. Abou Elmaaty, Functionalization of linen/cotton pigment prints using inorganic nano structure materials, *Carbohydr Polym*, **2013**, 97, 537–545.

[13] A. Jiménez and R. A. Ruseckaite, Binary mixtures based on polycaprolactone and cellulose derivatives, *J Therm Anal Calorim*, **2006**, 88, 851–856.

[14] S. B. Khan, K. A. Alamry, E. N. Bifari, A. M. Asiri, M. Yasir, L. Gzara and R. Z. Ahmad, Assessment of antibacterial cellulose nanocomposites for water permeability and salt rejection, *J Ind Eng Chem*, **2015**, 24, 266–275.

[15] S.-W. Zhao, C.-R. Guo, Y.-Z. Hu, Y.-R. Guo and Q.-J. Pan, The preparation and antibacterial activity of cellulose/ZnO composite: a review, *Open Chemistry*, **2018**, 16, 9–20.

[16] E. Csiszár and S. Nagy, A comparative study on cellulose nanocrystals extracted from bleached cotton and flax and used for casting films with glycerol and sorbitol plasticisers, *Carbohydrate Polymers*, **2017**, 174, 740–749.

[17] F. Cheng, J. W. Betts, S. M. Kelly, D. W. Wareham, A. Kornherr, F. Dumestre, J. Schaller and T. Heinze, Whiter, brighter, and more stable cellulose paper coated with antibacterial carboxymethyl starch stabilized ZnO nanoparticles, *J. Mater. Chem. B*, **2014**, 2, 3057–3064.

[18] L. Jiao, J. Ma and H. Dai, Preparation and Characterization of Self-Reinforced Antibacterial and Oil-Resistant Paper Using a NaOH/Urea/ZnO Solution, *PLoS ONE*, **2015**, 10, e0140603.

[19] S. Azizi, M. B. Ahmad, M. Zobir Hussein, N. A. Ibrahim and F. Namvar, Preparation and properties of poly(vinyl alcohol)/chitosan blend bionanocomposites reinforced with cellulose nanocrystals/ZnO-Ag multifunctional nanosized filler, *Int J Nanomedicine*, **2014**, 1909.

[20] O. M. El-Feky, E. A. Hassan, S. M. Fadel and M. L. Hassan, Use of ZnO nanoparticles for protecting oil paintings on paper support against dirt, fungal attack, and UV aging, *Journal of Cultural Heritage*, **2014**, 15, 165–172.

[21] M. A. Hubbe, O. J. Rojas, L. A. Lucia, and M. Sain, Cellulosic nanocomposites: a review. *BioResources*, **2008**, 3, 929-980.

[22] X. Xu, Y.-Q. Yang, Y.-Y. Xing, J.-F. Yang and S.-F. Wang, Properties of novel polyvinyl alcohol/cellulose nanocrystals/silver nanoparticles blend membranes, *Carbohydrate Polymers*, **2013**, 98, 1573–1577.

[23] Q. Cheng, D. Ye, C. Chang and L. Zhang, Facile fabrication of superhydrophilic membranes consisted of fibrous tunicate cellulose nanocrystals for highly efficient oil/water separation, *Journal of Membrane Science*, **2017**, 525, 1–8.

[24] A. W. Carpenter, C.-F. de Lannoy and M. R. Wiesner, Cellulose Nanomaterials in Water Treatment Technologies, *Environ. Sci. Technol.*, **2015**, 49, 5277–5287.

[25] R. E. Abouzeid, R. Khiari, D. Beneventi and A. Dufresne, Biomimetic Mineralization of Three-Dimensional Printed Alginate/TEMPO-Oxidized Cellulose Nanofibril Scaffolds for Bone Tissue Engineering, *Biomacromolecules*, **2018**, 19, 4442–4452.

[26] H. Zhu, S. Jia, T. Wan, Y. Jia, H. Yang, J. Li, L. Yan and C. Zhong, Biosynthesis of spherical Fe_3O_4/bacterial cellulose nanocomposites as adsorbents for heavy metal ions, *Carbohydrate Polymers*, **2011**, 86, 1558–1564.

[27] V. K. Thakur and S. I. Voicu, Recent advances in cellulose and chitosan-based membranes for water purification: A concise review, *Carbohydrate Polymers*, **2016**, 146, 148–165.