National Ministry of Education

National University of Science and Technology Politehnica Bucharest

Faculty of Chemical Engineering and Biotechnologies

PhD Thesis

PhD student:

Eng. Mădălina OPREA

Scientific coordinator:

Prof. Dr. Eng. Habil. Ioan Ștefan VOICU

BUCHAREST

2023

Polymeric materials for applications in hemodialysis and osseointegration

PhD student:

Eng. Mădălina OPREA

Scientific coordinator:

Prof. Dr. Eng. Habil. Ioan Ștefan VOICU

Table of contents

Chapter I: Introduction

1. **Introduction into membrane technology**
   - **1.1. A brief history of polymeric membranes**
   - **1.2. Principles behind the phase inversion process**
   - **1.3. Methods for optimizing membranes properties and performances**
2. **Polymers used for membrane synthesis**
   - **2.1. Natural polymers – Cellulose acetate**
   - **2.2. Synthetic polymers – Polysulfone**

Chapter II: Nanocomposites based on functionalized bacterial cellulose and poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

1. **Introduction**
2. **Materials and methods**
   - **2.1 Materials**
   - **2.2 Functionalization of BC surface**
   - **2.3 Synthesis of the nanocomposite sponges**
   - **2.4 Characterization techniques**
3. **Results and discussion**
   - **3.1 PHBV uptake into the sponges**
   - **3.2 ATR FT-IR**
   - **3.3 TGA, DTG**
   - **3.4 Kinetic analysis**
   - **3.5 DSC**
   - **3.6 DMA**
   - **3.7 SEM**
   - **3.8 Swelling degree in PBS**
4. **Partial conclusions**

Chapter III: Zinc-loaded cellulose acetate membranes for potential biomedical applications

1. **Introduction**
2. **Materials and methods**

2.1 Synthesis of the hybrid membranes
2.2 Characterization techniques
3. Results and discussion
3.1 ATR FT-IR
3.2 TGA, DTG
3.3 DSC
3.4 SEM
3.5 EDS
3.6 Swelling degree
3.7 Antibacterial activity
4. Partial conclusions

Chapter IV: Crown ether functionalized cellulose acetate membranes with potential applications in osseointegration

1. Introduction
2. Materials and methods
2.1 Materials
2.2 Functionalization of the membranes surface with AB15C5
2.3 Biomineralization of the functionalized membranes
2.4 Characterization techniques
3. Results and discussion
3.1 ATR FT-IR
3.2 Raman
3.3 XPS
3.4 TGA, DTG
3.5 Tensile tests
3.6 Biomineralization studies
4. Partial conclusions

Chapter V: A new generation of membranes based on crown ether functionalized polysulfone and reduced graphene oxide with potential applications in hemodialysis

1. Introduction
2. Materials and methods
2.1 Materials

2.2 Functionalization of rGO-NH_2 with CE

2.3 Synthesis of the PSF/rGO-NH_2-CE composite membranes

2.4 Testing of the metal ions retention efficiency

2.5 Characterization techniques

3. **Results and discussion**

3.1 Characterisation of functionalized rGO-NH_2

3.2 Characterization of PSF/rGO-NH_2-CE composite membranes

4. **Partial conclusions**

Chapter VI: General conclusions

Chapter VII: Original contributions and scientific achievements in the field of research

References

List of scientific publications

Chapter I was partially published as:

Oprea, M.; Voicu, S.I. Recent advances in composites based on cellulose derivatives for biomedical applications. Carbohydrate Polymers 2020, 247, 116683.

Oprea, M.; Voicu, Ş.I. Recent advances in applications of cellulose derivatives-based composite membranes with hydroxyapatite. Materials 2020, 13(11), 2481.

Oprea, M.; Voicu, Ş.I. Cellulose-based composites with graphene for tissue engineering applications. Materials 2020, 13(23), 5347.

Oprea, M.; Panaitescu, D.M. Nanocellulose hybrids with metal oxides for biomedical applications, Molecules 2020, 20(18), 4045.

Chapter II was fully published as:

Oprea, M., Panaitescu, D. M., Nicolae, C. A., Gabor, A. R., Frone, A. N., Raditoiu, V., Trusca, R.; Casarica, A. Nanocomposites from functionalized bacterial cellulose and poly (3-hydroxybutyrate-co-3-hydroxyvalerate). Polymer degradation and stability 2021, 179, 109203.

Chapter III was fully published as:

Oprea, M.; Ficai, A.; Ilie, C.; Trusca, R.; Oprea, O.C.; Serbanescu, O.S.; Voicu, S.I. Zinc-loaded cellulose acetate membranes with potential biomedical applications. UPB Scientific Bulletin 2022, 84(2), 15-30.

Chapter IV was fully published as:

Oprea, M.; Pandele, A.M.; Nicoara, A.I.; Nicolescu, A.; Deleanu, C.; Voicu, S.I. Crown ether-functionalized cellulose acetate membranes with potential applications in osseointegration, International Journal of Biological Macromolecules 2023, 230, 123162.

Chapter V was fully published as:

Pandele, A.M.; Oprea, M.; Dutu, A.A.; Miculescu, F.; Voicu, S.I. A Novel Generation of Polysulfone/Crown Ether-Functionalized Reduced Graphene Oxide Membranes with Potential Applications in Hemodialysis. Polymers 2022, 14, 148.

Chapter I

Introduction

The aim of the polymeric materials modification methods developed in this thesis consists in improving their stability in the physiological environment, conferring an antibacterial character, increasing the *in vitro* biomineralization capacity for applications in osseointegration as well as improving the retention capacity of heavy metals for applications in hemodialysis.

Due to its importance, novelty and topicality, this subject is prioritized among the international and national concerns of researchers. The research hypothesis consists in obtaining functionalized polymeric materials and composites for applications in hemodialysis and osseointegration having as objectives to be solved within the scientific research: the synthesis and characterization of nanocomposites based on functionalized bacterial cellulose and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with improved stability in the physiological environment, synthesis and characterization of zinc-loaded cellulose acetate membranes with antibacterial properties, synthesis and characterization of crown ether functionalized cellulose acetate membranes with increased biomineralization capacity, and synthesis and characterization of composite membranes based on polysulfone and reduced graphene oxide functionalized with crown ether with high potential for heavy metal retention.

The research objectives are met by developing some revolutionary and easy methods for modifying the selected polymeric substrates. Initially, the polymeric substrate was bacterial cellulose (BC) that was functionalized by amination (BCA) and then modified by impregnation with a solution of bacterial polyester, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), to improve its chemical stability and mechanical properties so that the obtained nanocomposite material is suitable for biomedical applications, especially for osseointegration. Although the results obtained were favorable, the main disadvantages of bacterial cellulose are the high production price and low volumetric yield as well as the lack of large-scale production capacity. Therefore, the transition was made to a more economically efficient cellulosic substrate, specifically cellulose acetate. The first studies focused on introducing an antibacterial character to cellulose acetate, because both in the hemodialysis process and in the osseointegration process, bacterial contamination is a major problem that can cause systemic complications such as septicemia. For this purpose, hybrid materials were prepared by in situ synthesis of zinc-based compounds on the surface of cellulose acetate (CA) membranes, using a simple method

based on impregnation with zinc salts and alkaline precipitation. Further, the aim was to increase the biomineralization capacity of cellulose acetate membranes for applications in osseointegration. In this study, the surface of commercial cellulose acetate membranes was functionalized with 4'-aminobenzo-15-crown-5 ether using a covalent binding approach. The final study aimed to extend the covalent surface functionalization approach to a filler material (reduced graphene oxide), with the functionalized material then being used for the synthesis of polysulfone-based composite membranes. Polysulfone was chosen as a polymeric substrate in this case because the synthesized materials have as an application the detoxification of the body in case of heavy metal poisoning through the "one-day hemodialysis" process, and, according to literature studies, polysulfone shows increased hemocompatibility and does not produce a substantial immune response compared to cellulose-based membranes. Synthetic polysulfone membranes were modified with reduced graphene oxide functionalized with crown ether, an organic compound with high metal ion complexation capacity.

The results of the studies showed that the polymeric materials modified by the methods developed in this thesis showed high stability in the physiological environment, extended antimicrobial activity against Gram negative (*Pseudomonas aeruginosa*) and Gram positive (*Staphylococcus aureus*) bacteria, increased biomineralization capacity *in vitro* and improved metal ion adsorption capacity.

1. Introduction into membrane technology

Membranes can be defined as thin, semi-permeable filter media that act as a barrier between two distinct phases and allow the passage of specific molecules only when exposed to a driving force such as a pressure or concentration gradient. From the point of view of

separation capacity, membranes can be classified into microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO) and nanofiltration (NF) membranes (Fig. 1) [4].

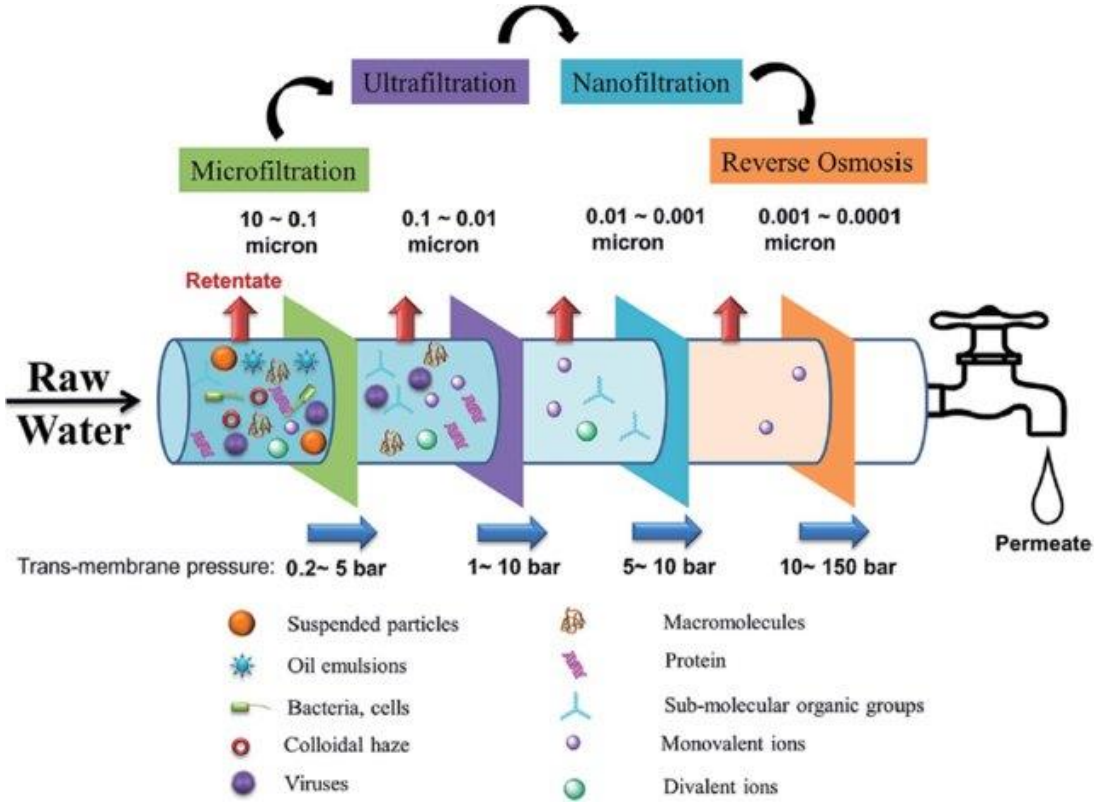

Figure 1. Schematic representation of different types of membrane filtration processes, from 100 nm (microfiltration) to 0.1 nm (reverse osmosis) [7].

1.1 A brief history of polymeric membranes

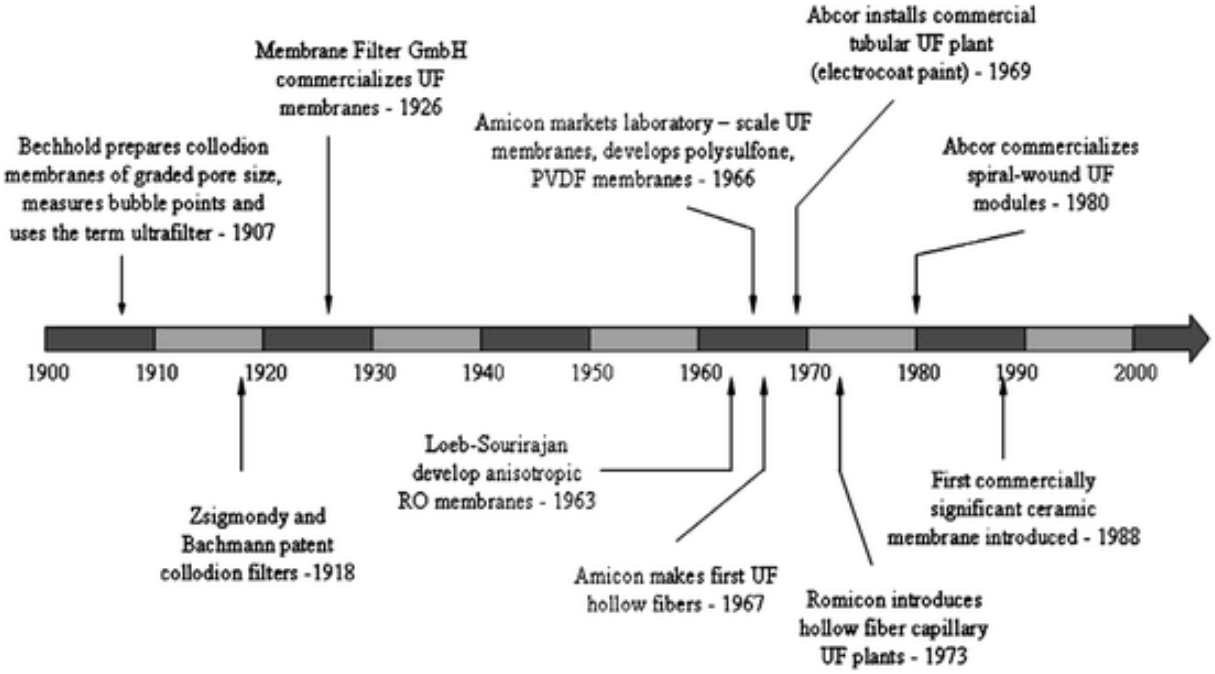

Figure 2. Important moments in the history of polymeric membranes [15].

1.2 Principles behind the phase inversion process

The principle behind the phase inversion method is a liquid-liquid demixing of a polymer solution into a polymer-rich and a polymer-poor phase, followed by solidification of the phase with the highest polymer concentration [21]. Depending on the factor that initiates the demixing process, phase inversion can be divided into precipitation by immersion, thermally induced phase separation, vapor induced phase separation and evaporation induced phase separation (Fig. 3) [22].

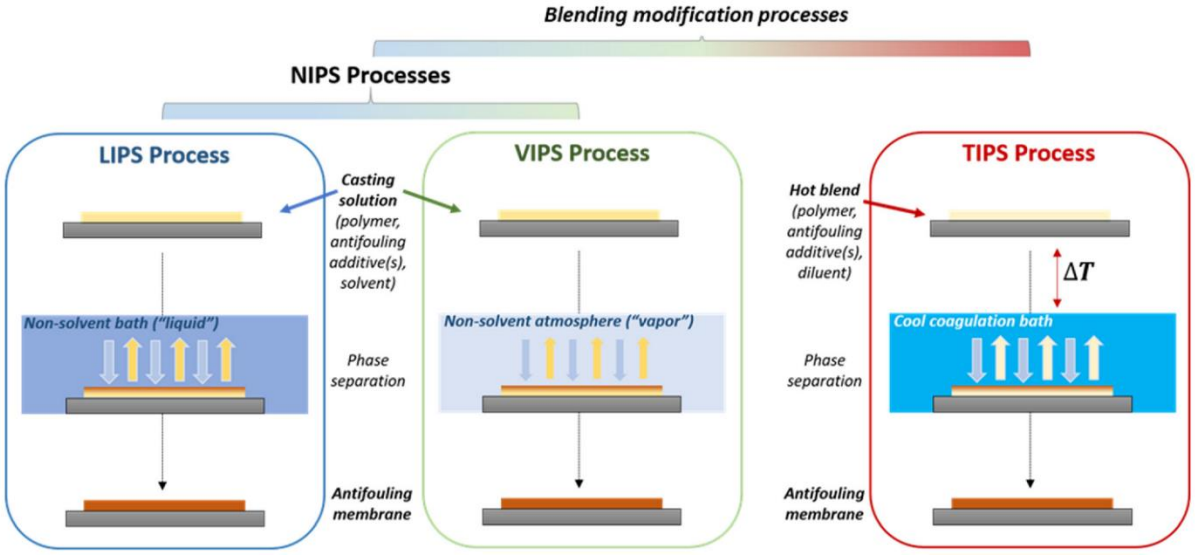

Figure 3. Schematic representation of different types of phase inversion [23].

All variations of the phase inversion process produce membranes whose structures are formed due to a combination of phase separation and mass transfer and are based on similar thermodynamic principles. These thermodynamic aspects of membrane formation can be described using a ternary phase diagram constructed by theoretical calculations of the binodal and spinodal limits based on the Flory-Huggins theory for three-component systems [27, 28].

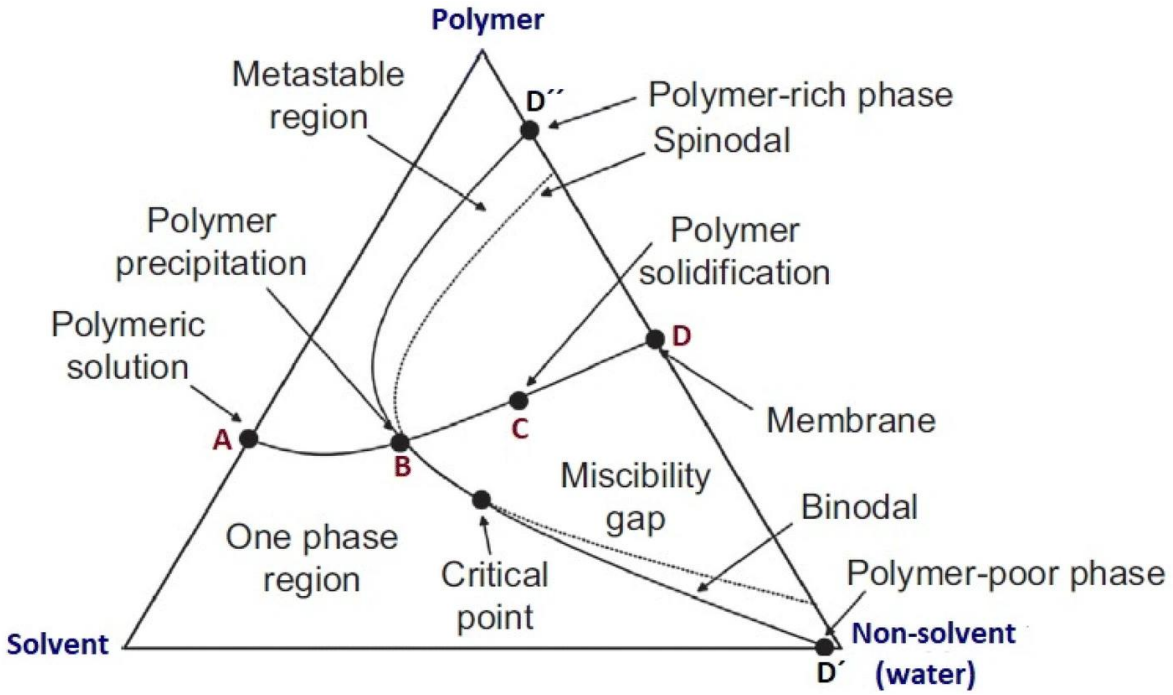

Figure 4. Schematic representation of the ternary phase diagram of a polymer/solvent/non-solvent system [29].

The adaptability of the immersion precipitation method allows the use of a wide range of polymers for membrane fabrication. However, polymers such as cellulose acetate, polysulfone and polyethersulfone are more commonly encountered in this field due to their favorable thermal and mechanical properties and also due to their good film-forming ability and solubility in a wide range of solvents [45].

1.3 Methods used to optimize membrane properties and performances

Most of the polymeric membrane materials used in the biomedical field exhibit these basic characteristics, however, to obtain new properties and improved performance, the development of membrane modification techniques is mandatory [46, 16].

One strategy involves the incorporation of functional fillers into the polymer structure, thus resulting in a synergistic performance between the organic matrix and the inorganic filler [42]. These types of hybrid membranes are one of the fastest growing classes of materials due to the flexibility they offer in terms of adapting the material properties according to the application requirements.

Another modification technique is represented by surface functionalization which can be achieved by mixing polymers, physical adsorption, or covalent immobilization. Among all these methods, covalent immobilization is the most effective because it allows a stable, highly selective binding between the functional groups of the polymeric substrate and those of the functionalizing agent [51].

2. Polymers used for membrane synthesis

2.1 Natural polymers - Cellulose acetate

Cellulose acetate (CA) is a cellulose ester obtained by acetylation of the free hydroxyl groups from the anhydroglucose units (AGU).

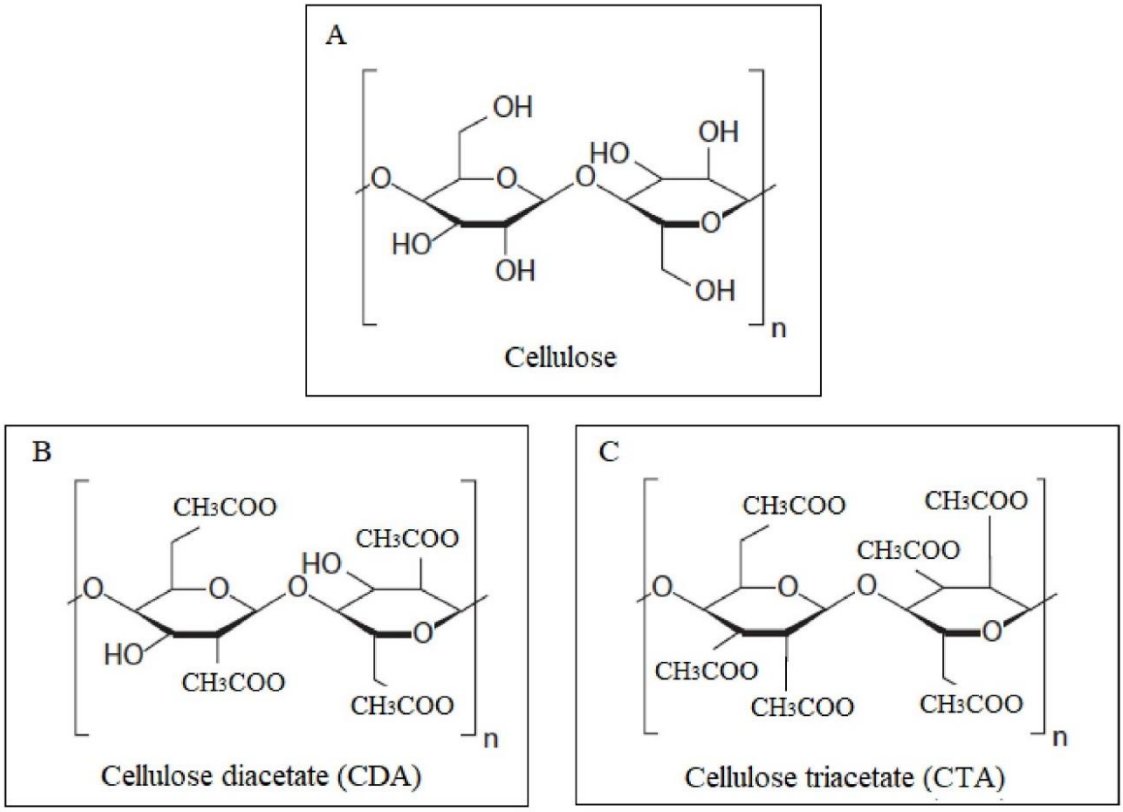

Figure 5. Molecular structures of cellulose (A), cellulose diacetate (B) and cellulose triacetate (C) [59].

Cellulose acetate is still used to produce a variety of consumer goods, including textiles, photographic film, personal care products, and cigarette filters [70], but its chemical resistance, flexibility, and reasonable mechanical properties [71], together with low susceptibility to fouling and hydrophilic nature [72], recommend this polymer especially for the production of membranes with water purification and biomedical applications. Studies have shown that cellulose acetate is a suitable material for osseointegration due to its high biocompatibility and non-toxicity. The degradation products of cellulose acetate in the human body are glucose fragments and acetyl groups that do not induce cytotoxicity, their only effect being a slight acidification of the environment at the implantation site. Membranes based on cellulose acetate were among the first materials used for hemodialysis purposes, however, their selectivity and hemocompatibility still require improvement for superior results in this field [46]. The dialysis performances of cellulose acetate membranes can be improved by the integration of functional fillers such as nanoparticles or organic molecules. For this purpose, clay silica nanowires [48], mixtures of carbon nanotubes and graphene [42] or sulfated polysaccharides from fungi [87] have been successfully used, all synthesized materials showing a non-cytotoxic character, high flow rates and capacity high protein binding.

3.2 Synthetic polymers - Polysulfone

Polysulfones are a group of high-performance thermoplastic polymers consisting of repeating units containing a sulfone group and additional alkyl or aryl groups [88]. Depending on the additional functional group, three main types of polysulfone can be distinguished - polysulfone (PSU), polyethersulfone (PES/PESU) and polyphenylene sulfone (PPSU) (Fig. 7) [89].

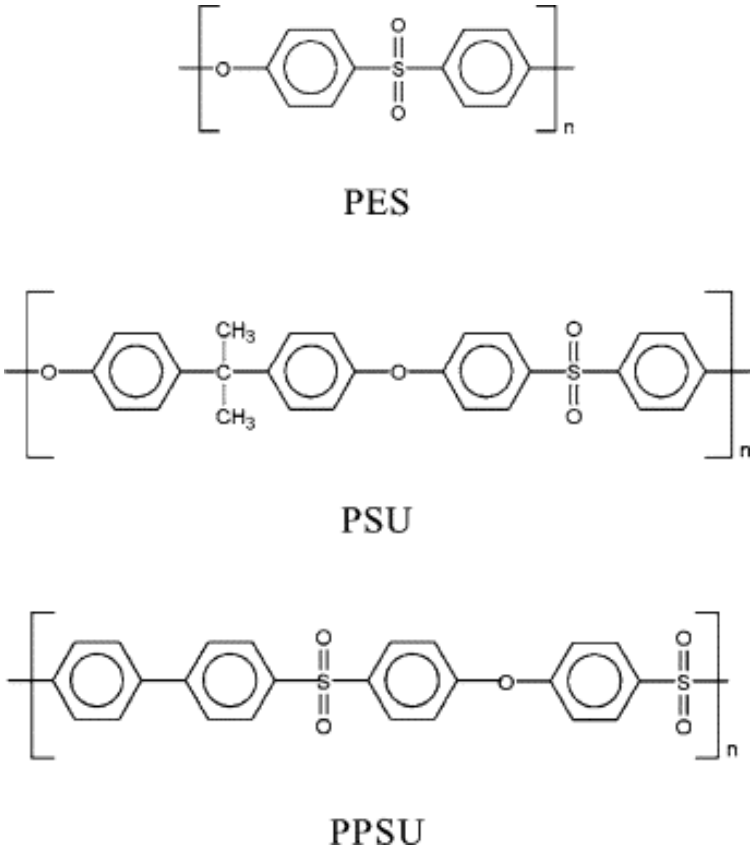

Figure 6. The main types of commercial polysulfone [89].

The chemical structure of polysulfones is responsible for their excellent thermal and mechanical properties. High thermal stability is ensured by the diphenylene sulfone group which provides high mechanical properties, high oxidation resistance and excellent flame retardancy, but makes the polymer rigid. The flexibility of the polymer chain is ensured by the ether bonds that also contribute to thermal stability [90].

Polysulfone is an ideal choice for the development of membranes with biomedical applications, especially in the field of hemodialysis, due to its intrinsic biocompatibility and low cytotoxicity provided by the alkyl or aryl sulfone chemical groups in its structure, high permeability to low molecular weight proteins, high retention capacity of endotoxins and high resistance during sterilization. Various membrane modification methods have been proposed, most of them focusing on increasing the hydrophilicity of the membrane [93]. Polysulfone

membranes can be modified by incorporating nanometric fillers or macromolecules into the polymer matrix or by functionalizing the membrane surface to control the microstructure. thereby improving flow and anti-fouling properties.

Chapter II
Nanocomposites based on functionalized bacterial cellulose and poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

Abstract: Bacterial cellulose (BC) sponges are valuable materials for tissue engineering and regenerative medicine due to their biocompatibility and nano-sized fiber network with interconnected open porosity. However, their instability in the physiological environment and poor mechanical properties are the main problems that need to be solved to obtain suitable three-dimensional scaffolds for tissue regeneration. In this work, a bacterial polyester, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and a simple impregnation method were used to improve the properties of BC sponges for biomedical applications. The highly hydrophilic surface of BC was functionalized by amination (BCA) to improve its affinity towards PHBV. PHBV uptake in BC and BCA sponges depended on PHBV concentration and was confirmed by Fourier transform infrared spectroscopy and density increase after impregnation. SEM investigation showed that PHBV was deposited on the BC nanofibrous network, under some conditions forming a three-dimensional ordered honeycomb structure with uniform micrometric pores. Thermogravimetric and kinetic analyzes revealed a delay in thermal degradation for BCA nanocomposite sponges compared to BC ones and an increase in degradation activation energy compared to pure PHBV. Better compressive strength was obtained for the BCA/PHBV nanocomposite sponges due to the increased interactions between the polymer and the aminated cellulose substrate. Swelling tests showed that BC and BCA sponges did not withstand and completely disintegrated within 90 min of incubation in phosphate-buffered saline, but good stability was achieved in this simulated physiological environment after impregnation with PHBV. The degree of swelling varied between 1200% and 2400% for BC/PHBV and between 700% and 1200% for BCA/PHBV sponges, the values being high enough to allow water diffusion and nutrient transport. Therefore, these easily

obtained BC/PHBV and BCA/PHBV nanocomposite sponges with improved properties could be a promising option for tissue engineering scaffolds.

2. Materials and methods

2.1 Materials

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) powder (2% hydroxyvalerate) was purchased from Goodfellow (Cambridge Ltd. UK) and chloroform (99%) from Chimreactiv (Romania). Bacterial cellulose membranes were produced in static culture by the bacterial strain Gluconacetobacter Xylinus DSM 2004 (Leibniz Institute DSMZ, German Collection of Microorganisms and Cell Cultures) under the conditions mentioned in a previous study [137]. Defibrillation of BC membranes was first performed with a blender for 15 min resulting in a gel, then using a recirculating vertical colloid mill for 2 h and finally in an LM20 Microfluidizer (Microfluidics, USA) for 10 passes. (3-Aminopropyl)triethoxysilane (APS, 99%) from Sigma Aldrich (Germany), ethanol (99%) and glacial acetic acid (99%) from Chimreactiv (Romania) were used without purification to graft amino groups onto the surface BC. Analytical grade NaCl, Na2HPO4, KCl and KH2PO4 were purchased from Sigma Aldrich (Germany).

2.2 BC surface functionalization

The chemical modification of the BC surface was carried out in three main steps: (i) APS (1%) was dispersed under magnetic stirring in a mixture of ethanol and water (90/10) and the pH was adjusted to 4 by addition of glacial acetic acid; (ii) an amount of 100 g of BC suspension in water (1%) was added and the components were homogenized under magnetic stirring for 2 hours at room temperature; (iii) the homogenized mixture was kept at 100 ◦C for 2 h under reflux to functionalize the BC surface. The heat treatment initiated the formation of covalent bonds between the silanol groups in APS and the hydroxyl groups on the BC surface. BC grafted with amino groups was denoted as BCA.

2.3 Synthesis of nanocomposite sponges

Suspensions of BC and BCA in water were lyophilized for 72 h using a FreeZone 2.5 L equipment (Labconco, USA). Freeze-drying is an environmentally friendly method, widely used in the food and pharmaceutical industry, being a standard practice in the industrial processing of penicillin, hormones, blood plasma and vitamins [138, 139]. The obtained BC

and BCA sponges (Fig. 1 a) had an average density of 0.021 and 0.019 g/cm^{-1}. PHBV solutions were prepared by dissolving the polymer powder in chloroform under magnetic stirring for 90 min at 80 ◦C. Chloroform is the optimal choice for dissolving PHB or PHBV and is widely used to obtain scaffolds or materials for biomedical use [140, 141]. The cellulose sponges were immersed in the PHBV solutions (Fig. 1 b) for different time intervals and then dried in a vacuum oven at 40 ◦C for 30 min to completely remove the solvent. PHBV solutions with a concentration of 0.1, 0.2 and 1% were used for impregnation, resulting in BC and BCA nanocomposite sponges. They were denoted as BC/PHBV0.1, BC/PHBV0.2 and BC/PHBV1 and similarly for BCA nanocomposites.

Chapter III

Zinc-loaded cellulose acetate membranes for potential biomedical applications

Abstract: This study presents the successful synthesis of zinc-loaded cellulose acetate membranes with antibacterial properties and potential biomedical applications. The main aim of this work was to obtain hybrid materials by in situ synthesis of zinc-based compounds on the surface of polymer membranes, using a simple method based on impregnation with zinc salts and alkaline precipitation. FT-IR and SEM analyzes were used to reveal the morpho-structural characteristics, and the thermal stability was investigated by TGA and DSC. The degree of swelling and antibacterial properties were also studied to determine whether the obtained membranes are suitable for use in wound healing.

1. Materials and methods

1.1 Sinthesys of the hybrid membranes

Three solutions of zinc salts were prepared by dissolving different percentages (1, 2 and 5%) of zinc acetate dihydrate (Lach Ner, Czech Republic) in distilled water under magnetic stirring at room temperature. Commercial cellulose acetate membranes (Prat Dumas, France) were placed in Petri dishes containing 10 ml of the corresponding zinc acetate solution or distilled water in the case of the neat sample. Dilute ammonium hydroxide (28–30%, Sigma Aldrich) was uniformly sprayed over the membranes to initiate the precipitation of zinc

compounds and ensure the deacetylation of cellulose acetate, thus favoring the interactions between the cellulosic matrix and the zinc compounds formed by alkaline precipitation. After 24 h of impregnation, the modified membranes were dried at 80°C in a laboratory vacuum oven to remove excess moisture and residual solvents.

Chapter IV

Crown ether functionalized cellulose acetate membranes with potential applications in osseointegration

Abstract: Due to its inherent properties and wide availability, cellulose acetate is a highly competitive candidate for the production of polymeric membranes. However, for the best results in certain applications, membrane modification is required to minimize unwanted interactions and introduce new characteristics to the polymer. In this study, the surface of commercial cellulose acetate membranes was functionalized with 4'-aminobenzo-15-crown-5 ether using a covalent binding approach. The main goal was to improve the biomineralization capacity of the membranes, thus making them prospective materials for bone regeneration applications. The proposed reaction mechanism was confirmed by XPS and NMR analyses, while the presence of functionalizing agents in the membrane structure was evidenced by ATR FT-IR and Raman spectra. The effects of the functionalization process on the morphology, thermal and mechanical properties of the membranes were studied by SEM, TGA and tensile tests. The obtained results showed that cellulose acetate membranes were successfully functionalized with crown ether and provided a good understanding of the interactions that occurred between the polymer and the functionalizing agents. Moreover, promising results were obtained during Taguchi biomineralization studies. SEM images, EDS mapping, and XRD spectra indicated that the CA-AB15C5 membranes exhibit a superior Ca^{2+} ion retention capacity, which leads to an enhanced deposition of calcium phosphate on the modified polymer fibers compared to the pristine CA membrane.

2. Materials and methods

2.1 Materials

Commercial cellulose acetate membranes (diameter 47 mm, porosity 0.45 µm) were supplied by Prat Dumas France. Sodium hydroxide (98%, Sigma Aldrich), ethanol (96%, Chimreactiv), acetic acid (99%, Chempur), ethanolamine (99%, Sigma Aldrich), glutaraldehyde (25%, Sigma Aldrich) and 4'-ether aminobenzo-15-crown-5 (97%, Sigma Aldrich) were used without further purification for membrane functionalization. Calcium chloride (94%, Roth), hydrochloric acid (37%, Sigma Aldrich), tris(hydroxymethyl)aminomethane (99.8%, Sigma Aldrich) and anhydrous disodium phosphate (99%, Sigma Aldrich). The water used in all experiments was distilled water.

2.2 Surface functionalization of membranes with AB15C5

The first step consisted of partially deacetylating the cellulose acetate membranes using a 5% NaOH solution. The membranes were immersed in the NaOH solution for 24 h at room temperature. Then the surface of the membranes was functionalized with ethanolamine (6 hours, 40 °C) and glutaraldehyde (2 hours, 40 °C); both reactions were performed under magnetic stirring in NaOH medium. Functionalization with AB15C5 was performed in mildly acidic ethanolic medium under magnetic stirring for 2 h at 40 °C. After each step, the membranes were rinsed thoroughly with distilled water to remove any unreacted compounds. The samples were dried for 72 hours at room temperature before characterization.

2.3 Biomineralization of functionalized membranes

Biomineralization studies were performed using the alternative soaking method described by Taguchi et al. [234]. The samples were first incubated in a 200 mM $CaCl_2$ solution at 37 °C for 24 h. The pH of the solution was adjusted to 7.4 using HCl and Tris base. The membranes were then rinsed with distilled water and incubated for an additional 24 h in a 120 mM Na_2HPO_4 solution at 37 °C. The cycle was repeated twice. Finally, the membranes were rinsed with distilled water and dried for 72 h at 37 °C before characterization.

Chapter V

A new generation of membranes based on crown ether functionalized polysulfone and reduced graphene oxide with potential applications in hemodialysis

Abstract: Heavy metal poisoning is a rare health condition caused by the accumulation of toxic metal ions in the soft tissues of the human body that can be life-threatening if untreated. In the case of severe poisoning, hemodialysis is the most effective method for a rapid removal of metal ions from the bloodstream, therefore, the development of hemodialysis membranes with superior metal ion retention capacity is of great research interest. In the present study, synthetic polysulfone membranes were modified with crown ether functionalized reduced graphene oxide, an organic compound with high metal ion complexation capacity. The physicochemical characteristics of the composite membranes were determined by FT-IR, Raman, XPS and SEM analyses, while their efficiency in retaining metal ions was evaluated by ICP-MS analysis. The obtained results showed that the thermal stability of reduced graphene oxide was improved after functionalization with crown ether and that the presence of carbon filler influenced the morphology of the membranes in terms of pore sizes and membrane thickness. Moreover, the retention capacity of Cu^{2+} ions from the synthetic feed solution was up to three times higher for the composite membranes compared to the neat ones.

1. Materials and methods

2.1 Materials

Polysulfone with an average molecular weight of 35,000 g/mol and pellet form was purchased from Sigma Aldrich (St. Louis, MO, USA) and used as the base polymer in the membrane casting solution. N,N-Dimethylformamide (DMF) of 99.8% analytical purity was purchased from Sigma Aldrich and used as a solvent. Tetraethylene-pentamine-reduced graphene oxide (rGO-NH2) (Nanoinnova) was used as a functional filler for membrane modification. Cyanuric chloride (CC) and 4'-aminobenzo-15-crown-5 ether (CE), used for rGO-NH2 functionalization, were obtained from Sigma Aldrich. All substances were used as received without prior purification.

2.2 Functionalization of rGO-NH_2 with CE

Tetraethylenepentamine-reduced graphene oxide was chosen for this experiment because it contains highly reactive amino (NH_2) groups on its surface, thus facilitating the functionalization procedure. First, rGO-NH_2 was dispersed in DMF by low-amplitude sonication for 30 min in an ice bath to prevent overheating. After a uniform dispersion was obtained, cyanuric chloride was added to the mixture under magnetic stirring and the temperature was set to 40 °C. Under the influence of temperature, the chlorine atoms in the cyanuric chloride react with the amino groups on the rGO-NH_2 surface forming amino bonds. In order to increase the effectiveness of the reaction, the solution was kept under these conditions for 2 hours. Subsequently, the temperature was increased to 70 °C and the crown ether was added to the mixture. The reaction mechanism between the crown ether and cyanuric chloride is similar to that described previously, more precisely, the amino groups in the structure of the crown ether react with the chlorine atoms in the cyanuric chloride forming amino bonds. The theoretical mechanism of the functionalization reaction is illustrated in Scheme 1. After 2 h, the dispersion was filtered using a Teflon membrane (0.4 µm pore diameter) and dried in a laboratory vacuum oven for 48 h at 40 °C. The resulting fine, black powder was further characterized to demonstrate that the functionalization was successful.

2.3 Synthesis of PSF/rGO-NH2-CE composite membranes

The first step consisted of dissolving PSF pellets in DMF under magnetic stirring for 3 h at 50 °C to obtain a 12% PSF solution. After complete dissolution of the polymer, a small amount of functionalized rGO (1 %) was added and the solution was sonicated for 10 min in an ice bath to ensure uniform dispersion of the filler. The ultrasound was performed at low amplitude to prevent breaking the bonds formed between the reduced graphene oxide and the crown ether. Membranes were then prepared by phase inversion. The phase inversion procedure consisted of pouring the cooled polymer solution onto a glass plate and immersing the plate in a coagulation bath containing a non-solvent, in this case distilled water. Due to the exchange of solvent and non-solvent, precipitation of the polymer occurred, and an asymmetric membrane was formed. The same procedure was followed to prepare the neat PSF membrane and both resulting membranes were kept in distilled water before characterization.

Capitolul VI

General conclusions

Chapter I presents the motivation for choosing the theme for this thesis, its importance, novelty and topicality, as well as its inclusion in international and national concerns. The research hypothesis is formulated and the scientific objectives to be solved within the research are highlighted. The content of the paper is briefly presented, highlighting the results obtained. Also the history of polymer membranes, the principles behind the phase inversion method, methods used to optimize membrane properties and performance, and the main polymers used in membrane technology are presented.

Chapter II presents the synthesis and characterization of nanocomposites based on functionalized bacterial cellulose and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and the following conclusions can be drawn:

- Nanocomposite materials based on PHBV and BC or BC aminated (BCA) were obtained using a simple impregnation method.
- The additional peaks in the FT-IR spectra, observed after the addition of PHBV, confirm the formation of a nanocomposite structure; corroborating these results with the SEM images, it can be said that a chemically stable double layered structure was formed by the two polymers.
- An improved thermal stability was observed for BCA/PHBV: the onset degradation temperature of BCA was shifted from 284 °C in the case of BC to 325 °C and kinetic analysis showed a higher degradation activation energy for BCA/PHBV compared to PHBV.
- The double-layered structure of the BC/PHBV and BCA/PHBV nanocomposite sponges and their low hydrophilicity led to greater stability in the simulated physiological environment, the disintegration of the nanocomposite sponges being prevented during swelling in the PBS medium.

Chapter III presents the synthesis and characterization of zinc-loaded cellulose acetate membranes for potential biomedical applications, and the following conclusions can be drawn:

- An easy method to modify cellulose acetate membranes based on impregnation with zinc salt solution followed by alkaline precipitation was developed.

- FT-IR, SEM and EDS analyzes revealed the successful loading of zinc-based antibacterial compounds, especially zinc hydroxide, tetraamine zincate complex ions and zinc oxide, and their homogeneous distribution in the membrane structure.
- From the antibacterial evaluations, it can be concluded that zinc-loaded CA membranes have good antibacterial activity against Gram-positive and Gram-negative bacterial strains, with higher zinc content resulting in more pronounced inhibition of microbial growth.

Chapter IV presents the synthesis and characterization of crown ether functionalized cellulose acetate membranes with potential applications in osseointegration and the following conclusions can be drawn:

- A method was developed for the covalent functionalization of cellulose acetate membranes with 4'-aminobenzo-15-crown-5 ether, using ethanolamine as a modifying agent and glutaraldehyde as a linker molecule.
- The additional peaks present in the FT-IR and Raman spectra of the functionalized membranes confirmed the presence of modifying agents in the membrane structure.
- The success of the functionalization reaction and the validation of the proposed reaction mechanism was ensured by XPS and NMR analyses, more precisely by the appearance of a new C=N peak at 400.4 eV in the N1s spectra and an aromatic carbon peak at 285.52. eV in the C1s spectra of CA-AB15C5 as well as in NMR analysis.
- Following the biomineralization studies, it was observed from the SEM, EDS and XRD analyzes that the functionalized membranes have a superior capacity to retain Ca2+ ions, this causes an increased deposition of hydroxyapatite on the modified polymer fibers compared to the neat CA membrane.

Chapter V presents the synthesis and characterization of membranes based on polysulfone and reduced graphene oxide functionalized with crown ether with potential applications in hemodialysis and the following conclusions can be drawn:

- PSF/rGO-NH_2-CE composite membranes for heavy metal retention were obtained during this study. Initially, reduced graphene oxide was functionalized with crown ether, a compound with a high capacity to complex metal ions.
- Functionalized reduced graphene oxide was observed to have higher thermal stability due to the thermal shielding effect of the benzene ring in the attached crown ether structure.
- rGO-NH_2-CE was identifiable in the PSF structure, an aspect confirmed by the new FT-IR peaks at 1651 cm^{-1} and 1735 cm^{-1} attributed to the N–H and C=O bonds in the

functionalized rGO structure and also by the presence of D (1350 cm^{-1}) and G (1580 cm^{-1}) bands in the Raman spectra of the composite membranes.

- The results obtained in the ICP-MS analysis showed that the PSF/rGO-NH_2-CE composite membranes showed a metal ion adsorption capacity up to three times higher compared to those of pure PSF.

Chapter VII

Original contributions and scientific achievements in the field of research

The most important aspects of originality are:

- The use of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) to improve the stability of cellulose-based materials in the physiological environment.
- The use of the ethanolamine linker molecule as an economically viable alternative to conventionally used aminosilanes for the functionalization of cellulose-based materials and studying the reaction mechanism between ethanolamine and the cellulosic substrate.
- Development of easy methods to modify cellulose-based materials in order to confer antibacterial properties and improve the biomineralization capacity in vitro for applications in osseointegration.
- Testing the versatility of the developed modification methods by applying them also to a filler (reduced graphene oxide) in order to increase the retention capacity of metal ions for hemodialysis applications.

References

1. Laciak, D.V.; Langsam, M. Gas separations with polymer membranes, in Encyclopedia of Separation Science, Wilson, I.D. Editor. 2000, Academic Press Oxford, p. 1725-1738.
2. Jarvis, P.; Carra, J.; Jafari, M.; Judd, S.J. Ceramic vs polymeric membrane implementation for potable water treatment. Water Res. 2022, 215, 118269.
3. Kaldis, S.P.; Pantoleontos, G.T.; Koutsonikolas, D.E. Membrane technology in IGCC processes for precombustion CO2 capture, in Current Trends and Future Developments on (Bio-) Membranes, Basile, A.; Favvas, E.P. Editors. 2018, Elsevier, p. 329-357.
4. Van der Bruggen, B. Microfiltration, ultrafiltration, nanofiltration, reverse osmosis, and forward osmosis, in Fundamental Modelling of Membrane Systems, Luis, P. Editor. 2018, Elsevier, p. 25-70.
5. Miller, D.J.; Dreyer, D.R.; Bielawski, C.W.; Paul, D.R.; Freeman, B.D. Surface modification of water purification membranes. Angew. Chemie Int. Ed. 2017, 56(17), 4662-4711.
6. Sagle, A.; Freeman, B. Fundamentals of membranes for water treatment. University of Texas at Austin, 2004, 2(363), 137.
7. Selatile, M.K.; Ray, S.S.; Ojijo, V.; Sadiku, R. Recent developments in polymeric electrospun nanofibrous membranes for seawater desalination. RSC Adv. 2018, 8(66), 37915-37938.
8. Zulkarnaev, A. A brief history of the study of diffusion and osmosis in the context of dialysis, in Nephrology dialysis transplantation. 2017, Oxford Univ Press, p. 2-6.
9. Robeson, L.M. Polymer membranes, in Polymer Science: A Comprehensive Reference. Matyjaszewski, K.; Möller, M. Editors. 2012, Elsevier Amsterdam, p. 325-347.
10. Maex, R. Nernst-Planck equation, in Encyclopedia of Computational Neuroscience. Jaeger, D.; Jung, R. Editors. 2013, Springer New York, p. 1-7.
11. Olaru, M.; Bordianu Antochi, I.; Simionescu, B. Polymers in membrane science, in Systems Membranes - Complex Roadmaps Towards Functional Devices and Coupled Processes. 2010, Printech, p. 191-240.
12. Pierce, H.F. Nitrocellulose membranes of graded permeability. J. Biol. Chem. 1927, 75(3), p. 795-815.
13. Venault, A.; Chang, Y.; Wang, D.-M.; Bouyer, D. A review on polymeric membranes and hydrogels prepared by vapor-induced phase separation process. Polymer Rev. 2013, 53(4), 568-626.
14. Tewari, P.K. Membrane technology, in Nanocomposite Membrane Technology. 2015, CRC Press, p. 6-15.
15. Fane, A.G.; Wang, R.; Jia, Y. Membrane technology: past, present and future, in Membrane and Desalination Technologies. Wang, L.K. Editor. 2011, Humana Press: Totowa, p. 1-45.
16. Oprea, M.; Voicu, S.I. Recent advances in applications of cellulose derivatives-based composite membranes with hydroxyapatite. Materials 2020, 13(11), 2481.
17. Baker, R.W. Overview of membrane science and technology, in Membrane Technology and Applications. 2004, John Wiley and Sons LTD, p. 1-14.
18. Rozelle, L.T.; Cadotte, J.E.; Corneliussen, R.D.; Erickson, E.E. Phase inversion membranes, in Encyclopedia of Separation Science. 2000, Academic Press, p. 3331-3346.
19. Loeb, S. The Loeb-Sourirajan membrane: how it came about, in Synthetic Membranes. 1981, American Chemical Society, p. 1-9.
20. Muralidhara, H.S. Challenges of membrane technology in the XXI century, in Membrane Technology. Cui, Z.F.; Muralidhara, H.S. Editors. 2010, Butterworth-Heinemann: Oxford, p. 19-32.
21. Ismail, A.F.; Yean, L.P. Review on the development of defect-free and ultrathin-skinned asymmetric membranes for gas separation through manipulation of phase inversion and rheological factors. J. Appl. Polym. Sci. 2003, 88(2), 442-451.
22. Hołda, A.K.; Vankelecom I. Understanding and guiding the phase inversion process for synthesis of solvent resistant nanofiltration membranes. J. Appl. Polym. Sci. 2015, 132(27), 42130.
23. Geleta, T.A.; Maggay, I.V.; Chang, Y.; Venault, A. Recent advances on the fabrication of antifouling phase-inversion membranes by physical blending modification method. Membranes 2023, 13(1), 58.
24. Gohil, J.M.; Choudhury, R.R. Introduction to nanostructured and nano-enhanced polymeric membranes: preparation, function, and application for water purification, in Nanoscale Materials in Water Purification. Thomas, S. Editor. 2019, Elsevier, p. 25-57.
25. Tekin, F.S.; Çulfaz-Emecen, P.Z. Controlling cellulose membrane performance via solvent choice during precursor membrane formation. ACS Appl. Polym. Mat. 2023, 5(3), 2185-2194.

26. Zhang, M.; Ni, F.; He, J.; Liu, Y. Evaluation of the formation and antifouling properties of a novel adsorptive homogeneous mixed matrix membrane with in situ generated Zr-based nanoparticles. RSC Adv. 2021, 11(15), 8491-8504.
27. Ebrahimpour, M.; Safekordi, A.A.; Mousavi, S.M.; Nasab, A.H. Phase separation analysis in the ternary system of poly (butylene succinate) /1,1,2,2,-tetrachloethane/non-solvent in relation to membrane formation. Bulgarian Chem. Commun. 2016, 49, 389-395.
28. Ayman, E.; Heba, A.; Sahar, S.A. Construction of ternary phase diagram and membrane morphology evaluation for polyamide/formic acid/water system. Australian J. Basic Appl. Sci. 2012, 6, 62-68.
29. Díez, B.; Rosal, R. A critical review of membrane modification techniques for fouling and biofouling control in pressure-driven membrane processes. Nanotech. Environ. Eng. 2020, 5(2), 15.
30. Tang, Y.; Lin, Y.; Ford, D.M.; Qian, X.; Cervelle, M.R.; Millet, P.; Wang, X. A review on models and simulations of membrane formation via phase inversion processes. J. Membr. Sci. 2021, 640, 119810.
31. Tiwari, R.R.; Jin, J.; Freeman, B.D.; Paul, D.R. Physical aging, CO2 sorption and plasticization in thin films of polymer with intrinsic microporosity (PIM-1). J. Membr. Sci. 2017, 537, 362-371.
32. Zhou, H.; Tao, F.; Liu, Q.; Yang, W.; Cao, X.; Jin, W.; Xu, N. Microporous polyamide membranes for molecular sieving of nitrogen from volatile organic compounds. Angew. Chem. Int. Ed. 2017, 56(21), 5755-5759.
33. Zhou, H.; Jin, W. Membranes with intrinsic micro-porosity: Structure, solubility, and applications. Membranes 2019, 9(1), 3.
34. Serbanescu, O.S.; Pandele, A.M.; Miculescu, F.; Voicu, S.I. Synthesis and characterization of cellulose acetate membranes with self-indicating properties by changing the membrane surface color for separation of Gd (III). Coatings 2020, 10(5), 468.
35. Raicopol, M.D.; Andronescu, C; Voicu, S.I.; Vasile, E.; Pandele, A.M. Cellulose acetate/layered double hydroxide adsorptive membranes for efficient removal of pharmaceutical environmental contaminants. Carbohydr. Polym. 2019, 214, 204-212.
36. Thakur, V.K.; Voicu, S.I. Recent advances in cellulose and chitosan based membranes for water purification: A concise review. Carbohydr. Polym. 2016, 146, 148-165.
37. Satulu, V.; Mitu, B.; Pandele, A.M.; Voicu, S.I.; Ktavets, L.; Dinescu, G. Composite polyethylene terephthalate track membranes with thin teflon-like layers: Preparation and surface properties. Appl. Surf. Sci. 2019, 476, 452-459.
38. Rana, A.K.; Gupta, V.K.; Saini, A.K.; Voicu, S.I.; Abdellattifand, M.H.; Thakur, V.K. Water desalination using nanocelluloses/cellulose derivatives based membranes for sustainable future. Desalination 2021, 520, 115359.
39. Pandele, A.M.; Iovu, H.; Orbeci, C.; Tuncel, C.; Miculescu, F.; Nicolescu, A.; Deleanu, C.; Voicu, S.I. Surface modified cellulose acetate membranes for the reactive retention of tetracycline. Sep. Purif. Technol. 2020, 249, 117145.
40. Savaş-Alkan, A.; Çulfaz-Emecen, P.Z. Solvent recovery from photolithography wastes using cellulose ultrafiltration membranes. J. Membr. Sci. 2022, 647, 120261.
41. Voicu, Ş.I.; Dobrica, A.; Sava, S.; Ivan, A.; Naftanaila, L. Cationic surfactants-controlled geometry and dimensions of polymeric membrane pores. J. Optoelectron. Adv. Mat. 2012, 14, 923-928.
42. Ioniță, M.; Crica, L.E.; Voicu, S.I.; Dinescu, S.; Miculescu, S.; Costache, M.; Iovu, H. Synergistic effect of carbon nanotubes and graphene for high performance cellulose acetate membranes in biomedical applications. Carbohydr. Polym. 2018, 183, 50-61.
43. Voicu, Ş.I.; Pandele, M.A.; Vasile, E.; Rughinis, R.; Crica, L.; Pilan, L.; Ionita, M. The impact of sonication time through polysulfone-graphene oxide composite films properties. Dig. J. Nanomat. Biostruct. 2013, 8, 1389-1394.
44. Stamatialis, D.F.; Papenburg, B.J.; Girones, M.; Saiful, S.; Betthalli, S.N.M.; Schmitmeier, S.; Wessling, M. Medical applications of membranes: Drug delivery, artificial organs and tissue engineering. J. Membr. Sci. 2008, 308(1), 1-34.
45. Mulder, M. Membrane preparation - Phase inversion membranes, in Basic Principles of Membrane Technology. 2000. Kluwer Academic Publishers, p. 3331-3346.
46. Oprea, M.; Voicu, S.I. Recent advances in composites based on cellulose derivatives for biomedical applications. Carbohydr. Polym. 2020, 247, 116683.
47. Ionita, M.; Vasile, E.; Crica, L.E.; Voicu, S.I.; Pandele, A.M.; Dinescu, S.; Predoiu, L.; Galateanu, B.; Hermenean, A.; Costache, M. Synthesis, characterization and in vitro studies of polysulfone/graphene oxide composite membranes. Compos. Part B Eng. 2015, 72, 108-115.

48. Corobea, M.C.; Muhulet, O.; Miculescu, F.; Antoniac, I.V.; Vuluga, Z.; Florea, D.; Vuluga, D.M.; Butnaru, M.; Ivanov, D.; Voicu, S.I.; Thakur, V.K. Novel nanocomposite membranes from cellulose acetate and clay-silica nanowires. Polym. Adv. Technol. 2016, 27(12), 1586-1595.
49. Ionita, M.; Crica, L.E.; Voicu, S.I. Pandele, A.M.; Iovu, H. Fabrication of cellulose triacetate/graphene oxide porous membrane. Polym. Adv. Technol. 2016, 27(3), 350-357.
50. Miculescu, M.; Thakur, V.K.; Miculescu, F.; Voicu, S.I. Graphene-based polymer nanocomposite membranes: A review. Polym. Adv. Technol. 2016, 27(7), 844-859.
51. Oprea, M.; Pandele, A.M.; Nicoara, A.I.; Nicolescu, A.; Deleanu, C.; Voicu, S.I. Crown ether-functionalized cellulose acetate membranes with potential applications in osseointegration. Int. J. Biol. Macromol. 2023, 230, 123162.
52. Thakur, V.; Guleria, A.; Kumar, S.; Sharma, S.; Singh, K. Recent advances in nanocellulose processing, functionalization and applications: a review. Mater. Adv. 2021, 2(6), 1872-1895.
53. Ulbricht, M. Advanced functional polymer membranes. Polymer 2006, 47(7), 2217-2262.
54. Ozdemir, M.; Yurteri,C.U.; Sadikoglu, H. Physical polymer surface modification methods and applications in food packaging polymers. Crit. Rev. Food Sci. Nutr. 1999, 39(5), 457-77.
55. Goddard, J.; Hotchkiss, J.H.M. Polymer surface modification for the attachment of bioactive compounds. Progr. Polym. Sci. 2007, 32, 698-725.
56. Serbanescu, O.S.; Voicu, S.I.; Thakur, V.K. Polysulfone functionalized membranes: Properties and challenges. Mater. Today Chem. 2020, 17, 100302.
57. Radu, E.R.; Voicu, S.I. Functionalized hemodialysis polysulfone membranes with improved hemocompatibility. Polymers 2022, 14(6), 1130.
58. Niaounakis, M. The problem of marine plastic debris, in Management of Marine Plastic Debris. Niaounakis, M. Editor. 2017, William Andrew Publishing, p. 1-55.
59. Holtzapple, M.T. Cellulose, in Encyclopedia of Food Sciences and Nutrition (Second Edition), Caballero, B. Editor. 2003, Academic Press: Oxford, p. 998-1007.
60. McGath, M.; Movery, S.J.; Pollei, M.; Heslip, S.; Baty, S. Cellulose acetate lamination: A literature review and survey of paper-based collections in the united states. Restaurator Int. J. Preserv. Library Archiv. Mater. 2015, 36, 333-365.
61. Akim, E.L. On the mechanism of cellulose acetylation. Pure Appl. Chem. 1967, 14(3-4), 475-480.
62. Das, A.M.; Ali, A.A.; Hazarika, M.P. Synthesis and characterization of cellulose acetate from rice husk: Eco-friendly condition. Carbohydr. Polym. 2014, 112, 342-349.
63. Ebrahim, S.; Morsy, A.; Kenwy, E.; Abdel-Fattah, T.; Kandil, S. Reverse osmosis membranes for water desalination based on cellulose acetate extracted from Egyptian rice straw. Desalin. Water Treat. 2015, 57, 1-11.
64. Araújo, D.; Castro, M.C.R.; Figuiredo, A.; Vilarinho, M.; Machado, A. Green synthesis of cellulose acetate from corncob: Physicochemical properties and assessment of environmental impacts. J. Clean. Prod. 2020, 260, 120865.
65. Loo, M.M.L.; Hashim, R.; Leh, C.P. Recycling of valueless paper dust to a low grade cellulose acetate: effect of pretreatments on acetylation. Bioresources 2012, 7(1), 1068-1083.
66. Rustemeyer, P. History of CA and evolution of the markets. Macromol. Sympos. 2004, 208(1), 1-6.
67. Strathmann, H.; Scheible, P.; Baker, R.W. A rationale for the preparation of Loeb-Sourirajan-type cellulose acetate membranes. J. Appl. Polym. Sci. 1971, 15(4), 811-828.
68. Lee, K.P.; Arnot, T.C.; Mattia, D. A review of reverse osmosis membrane materials for desalination - Development to date and future potential. J. Membr. Sci. 2011, 370(1), 1-22.
69. Cellulose acetate world market report (MCP-2035). 2020. Available from: https://www.strategyr.com/market-report-cellulose-acetate-forecasts-global-industry-analysts-inc.asp.
70. Puls, J.; Wilson, S.; Hölter, D. Degradation of cellulose acetate-based materials: A review. J. Polym. Environ. 2011, 19, 152-165.
71. Wsoo, M.A.; Shahir, S.; Bohari, S.P.M.; Nayan, N.H.M.; Razak, S.I.A. A review on the properties of electrospun cellulose acetate and its application in drug delivery systems: A new perspective. Carbohydr. Res. 2020, 491, 107978.
72. Dobos, A.M.; Filimon, A.; Bargan, A.; Zaltariov, M.-F. New approaches for the development of cellulose acetate/tetraethyl orthosilicate composite membranes: Rheological and microstructural analysis. J. Molec. Liq. 2020, 309, 113129.

73. Neacsu, P.; Staras, A.; Voicu, S.I.; Ionascu, I.; Soare, T.; Uzun, S.; Cojocaru, D.; Pandele, A.M.; Croitoru, S.M.; Miculescu, M.; Cotrut, C.M.; Dan, I.; Cimpean, A. Characterization and in vitro and in vivo assessment of a novel cellulose acetate-coated Mg-based alloy for orthopedic applications. Materials (Basel) 2017, 10(7), 686.
74. Voicu, S.I.; Condruz, R.M.; Mitran, V.; Cimpean, A.; Miculescu, F.; Andronescu, C.; Miculescu, M.; Thakur, V.K. Sericin covalent immobilization onto cellulose acetate membrane for biomedical applications. ACS Sust. Chem . Eng. 2016, 4(3), 1765-1774.
75. Pandele, A.M.; Neacsu, P.; Staras, A.I.; Miculescu, F.; Iordache, A.; Voicu, S.I.; Thakur, V.K.; Toader, O.D. Cellulose acetate membranes functionalized with resveratrol by covalent immobilization for improved osseointegration. Appl. Surf. Sci. 2018, 438, 2-13.
76. Zhang, Q.-Y.; Tan, J.; Huang, K.; Nie, R.; Feng, Z.-Y.; Zou, C.-Y.; Li, Q.-J.; Chen, J.; Sheng, N.; Qin, B.-Q.; Gu, Z.-P.; Liu, L.-M.; Xie, H.-Q. Polyphenolic-modified cellulose acetate membrane for bone regeneration through immunomodulation. Carbohydr. Polym. 2023, 305, 120546.
77. Pandele, A.M.; Comanici, F.E.; Carp, C.A.; Miculescu, F.; Voicu, S.I.; Thakur, V.K.; Serban, B.C. Synthesis and characterization of cellulose acetate-hydroxyapatite micro and nano composites membranes for water purification and biomedical applications. Vacuum 2017, 146, 599-605.
78. Shaban, N.Z.; Kenawy, M.Y.; Taha, N.A.; El-Latif, M.M.A.; Ghareeb, D.A. Cellulose acetate nanofibers: incorporating hydroxyapatite (HA), HA/berberine or HA/moghat composites, as scaffolds to enhance in vitro osteoporotic bone regeneration. Polymers 2021, 13(23), 4140.
79. Dascălu, C.-A.; Maidaniuc, A.; Pandele, M.A.; Voicu, S.I.; Pisu-Machedon, T.; Stan, G.E.; Cimpean, A.; Mitran. V.; Antoniac, I.V.; Miculescu, F. Synthesis and characterization of biocompatible polymer-ceramic film structures as favorable interface in guided bone regeneration. Appl. Surf. Sci. 2019, 494, 335-352.
80. Maidaniuc, A.; Miculescu, F.; Voicu, S.I.; Andronescu, C.; Miculescu, M.; Matei, E.; Mocanu, A.C.; Pencea, I.; Csaki, I.; Pisu-Machedon, T.; Ciocan, L.T. Induced wettability and surface-volume correlation of composition for bovine bone derived hydroxyapatite particles. Appl. Surf. Sci. 2018, 438, 158-166.
81. Esmaeili, E.; Arshaghi, T.E.; Hosseinzadeh, S.; Elahirad, E.; Jamalpoor, Z.; Hatamie, S.; Soleimani, M. The biomedical potential of cellulose acetate/polyurethane nanofibrous mats containing reduced graphene oxide/silver nanocomposites and curcumin: Antimicrobial performance and cutaneous wound healing. Int. J. Biol. Macromol 2020, 152, 418-427.
82. de Faria, A.F.; de Moraes, A.C.M.; Andrade, P.F.; da Silva, D.S.; do Carmo Goncalves, M.; Alves, O.L. Cellulose acetate membrane embedded with graphene oxide-silver nanocomposites and its ability to suppress microbial proliferation. Cellulose 2017, 24, 781-796.
83. Corobea, M.S.; Albu, M.G.; Ion, R.; Cimpean, A.; Miculescu, F.; Antoniac, I.V.; Raditoiu, V.; Sirbu, I.; Stoenescu, M.; Voicu, S.I.; Ghica, M.V. Modification of titanium surface with collagen and doxycycline as a new approach in dental implants. J. Adhes. Sci. Technol. 2015, 29(23), 2537-2550.
84. Ruggiero, R.; de Almeida Carvalho, V.; da Silva, L.G.; de Malghaes, D.; Ferreira, J.A.; de Menezes, H.H.M.; de Melo, P.G.; Naves, M.M. Study of in vitro degradation of cellulose acetate membranes modified and incorporated with tetracycline for use as an adjuvant in periodontal reconstitution. Ind. Crops Prod. 2015, 72, 2-6.
85. Azhar, O.; Jahan, Z.; Sher, F.; Niazi, M.B.K.; Kakar, S.J.; Shahid, M. Cellulose acetate-polyvinyl alcohol blend hemodialysis membranes integrated with dialysis performance and high biocompatibility. Mater. Sci. Eng. Part C 2021, 126, 112127.
86. Athira, V.B.; Mohanty, S.; Nayak, S.K. Preparation and characterization of porous polyethersulfone (PES) membranes with improved biocompatibility by blending sulfonated polyethersulfone (SPES) and cellulose acetate (CA) – A comparative study. Mater. Today Commun. 2020, 25, 101544.
87. Peng, L.; Li, H.; Meng, Y. Layer-by-layer structured polysaccharides-based multilayers on cellulose acetate membrane: Towards better hemocompatibility, antibacterial and antioxidant activities. Appl. Surf. Sci. 2017, 401, 25-39.
88. Nalesso, F.; Claudio, R. Selecting a dialyzer: technical and clinical considerations, in Handbook of Dialysis Therapy (Fifth Edition). Nissenson, A.R.; Fine, R.N. Editors. 2017, Elsevier, p. 227-238.
89. McKeen, L.W. Binders, in Fluorinated Coatings and Finishes Handbook. McKeen, L.W. Editor. 2006, William Andrew Publishing: Norwich, NY, p. 45-58.
90. Chen, Y.; Lin, B.; Qiu, Y. Modification of polysulfone and the biomedical application of modified polysulfone. Int. J. Polym. Mater. Polym. Biomater. 2023, 72(3), 224-242.
91. Ida, S. PES (Poly(ether sulfone)), Polysulfone, in Encyclopedia of Polymeric Nanomaterials, Kobayashi, S. Müllen, K. Editors. 2015, Springer Berlin Heidelberg, p. 1528-1534.

92. Price, J. History of the development and application of whey protein products, in Whey Proteins. Deeth H.C.; Bansal, N. Editors. 2019, Academic Press, p. 51-95.
93. Wenten, I.G.; Aryanti, P.T.P.; Khoiruddin, K.; Hakim, A.N.; Himma, A.F. Advances in polysulfone-based membranes for hemodialysis. J. Membr. Sci. Res. 2016, 2(2), 78-89.
94. Mamah, S.C.; Goh., P.S.; Ismail, A.H.; Suzaimi, N.D.; Yogarathinam, L.T.; Raji, Y.O.; El-badawy, T.H. Recent development in modification of polysulfone membrane for water treatment application. J. Water Proc. Eng. 2021, 40, 101835.
95. Kamal, N.; Ahzi, S.; Kochkodan, V. Polysulfone/halloysite composite membranes with low fouling properties and enhanced compaction resistance. Appl. Clay Sci. 2020, 199, 105873.
96. Mukherjee, R.; De, S. Preparation of polysulfone titanium di oxide mixed matrix hollow fiber membrane and elimination of long term fouling by in situ photoexcitation during filtration of phenolic compounds. Chem. Eng. J. 2016, 302, 773-785.
97. Homayoonfal, M.; Mehrnia, M.R.; Rahmani, S.; Mojtahedi, Y.M. Fabrication of alumina/polysulfone nanocomposite membranes with biofouling mitigation approach in membrane bioreactors. J. Ind. Eng. Chem. 2015, 22, 357-367.
98. Onbattuvelli, V.P.; Onbanttuvelli, P.; Enneti, R.K.; Simonsen, J.; Kate, K.H.; Balla, V.K.; Atre, S.V. Structure and thermal stability of cellulose nanocrystal/polysulfone nanocomposites. Mater. Today Commun. 2020, 22, 100797.
99. Nechifor, G.; Voicu, S.I.; Nechifor, A.C.; Garea, S. Nanostructured hybrid membrane polysulfone-carbon nanotubes for hemodialysis. Desalination 2009, 241(1), 342-348.
100. Zambianchi, M.; Khaliha, S.; Bianchi, A.; Tunioli, F.; Kovtun, A.; Navacchia, M.L.; Salatino, A.; Xia, Z.; Brinas, E.; Vazquez, E.; Paci, D.; Palermo, V.; Bocchi, L.; Casentini, B.; Melucci, M. Graphene oxide-polysulfone hollow fibers membranes with synergic ultrafiltration and adsorption for enhanced drinking water treatment. J. Membr. Sci. 2022, 658, 120707.
101. Park, H.M.; Jee, K.Y.; Lee, Y.T. Preparation and characterization of a thin-film composite reverse osmosis membrane using a polysulfone membrane including metal-organic frameworks. J. Membr. Sci. 2017, 541, 510-518.
102. Ghasempour, A.; Pajootan, E.; Bahrami, H.; Arami, M. Introduction of amine terminated dendritic structure to graphene oxide using Poly(propylene Imine) dendrimer to evaluate its organic contaminant removal. J. Taiwan Institute Chem. Eng. 2017, 71, 285-297.
103. Zhang, X.; Wang, Z.; Tang, C.Y.; Ma, J.; Liu, M.; Ping, M.; Chen, M.; Wu, Z. Modification of microfiltration membranes by alkoxysilane polycondensation induced quaternary ammonium compounds grafting for biofouling mitigation. J. Membr. Sci. 2018, 549, 165-172.
104. Shahkaramipour, N.; Tran, T.N.; Ramanan, S.; Lin, H. Membranes with surface-enhanced antifouling properties for water purification. Membranes (Basel) 2017, 7(1), 13.
105. Balakrishna Prabhu, K.; Saidutta, M.B.; Isloor, A.M.; Hebbar, R.; Zhang, Z. Improvement in performance of polysulfone membranes through the incorporation of chitosan-(3-phenyl-1h-pyrazole-4-carbaldehyde). Cogent Eng. 2017, 4(1), 1403005.
106. Moreno Madrid, A.P.; Vrech, S.M.; Sanchez, M.A.; Rodriguez, A.P. Advances in additive manufacturing for bone tissue engineering scaffolds. Mater. Sci. Eng. Part C 2019, 100, 631-644.
107. Frerich, S.C. Biopolymer foaming with supercritical CO2 thermodynamics, foaming behavior, and mechanical characteristics. J. Supercrit. Fluids. 2015, 96, 349-358.
108. Kang, J.; Hyunjoon, G.; Ranjoo, C.; Seok, I.Y. Fabrication and characterization of poly(3-hydroxybutyrate) gels using non-solvent-induced phase separation. Polymers 2016, 104, 61-71.
109. Raza, Z.A.; Abid, S.; Banat, I.M. Polyhydroxyalkanoates: characteristics, production, recent developments and applications, Int. Biodeterior. Biodegrad. 2018, 126, 45-56.
110. Freier, T.; Kunze, C.; Nischan, C.; Kramer, S.; Sternberg, K.; Sass, M.; Hopt, U.T.; Schmitz, K.- P. In vitro and in vivo degradation studies for development of a biodegradable patch based on poly(3-hydroxybutyrate). Biomaterials 2002, 23, 2649-2657.
111. Chen, G.-Q.; Wu, Q. The application of polyhydroxyalkanoates as tissue engineering materials. Biomaterials 2005, 26, 6565-6578.
112. Volova, T.G.; Shumilova, A.A.; Nikolaeva, E.D.; Kirichenko, A.K.; Shishatskaya, E.I. Biotechnological wound dressings based on bacterial cellulose and degradable copolymer P(3HB/4HB). Int. J. Biol. Macromol. 2019, 131, 230-240.

113. Bergstrand, A.; Uppstrom, S.; Larsson, A. Permeability of porous poly(3- hydroxybutyrate) barriers of single and bilayer type for implant applications. Int. J. Polym. Sci. 2014, 958975.
114. Panaitescu, D.M.; Lupescu, I.; Frone, A.N.; Chiulan, I.; Nicolae, C.A.; Tofan, V.; Stefaniu, A.; Somoghi, R.; Trusca, R. Medium chain-length polyhydroxyalkanoate copolymer modified by bacterial cellulose for medical devices, Biomacromolecules 2017, 18, 3222-3232.
115. Chiulan, I.; Panaitescu, D.M.; Frone, A.N.; Teodorescu, M.; Nicolae, C.A.; Casarica, A.; Tofan, V.; Salageanu, A. Biocompatible polyhydroxyalkanoates/bacterial cellulose composites: preparation, characterization, and in vitro evaluation. J. Biomed. Mater. Res. 2016, 104(10), 2576-2584.
116. Srithep, Y.; Ellingham, T.; Peng, J.; Sabo, R.; Clemons, C.; Turng, L.-S.; Pilla, S. Melt compounding of poly (3-hydroxybutyrate-co-3-hydroxyvalerate)/nanofibrillated cellulose nanocomposites. Polym. Degrad. Stab. 2013, 98, 1439-1449.
117. Panaitescu, D.M0.; Frone, A.N.; Chiulan, I.; Nicolae, C.A.; Trusca, R.; Ghiurea, M.; Gabor, A.R.; Mihailescu, M.; Casarica, A.; Lupescu, I. Role of bacterial cellulose and poly (3-hydroxyhexanoate-co-3-hydroxyoctanoate) in poly (3-hydroxybutyrate) blends and composites. Cellulose 2018, 25, 5569-5591.
118. Jiang, L.; Morelius, E.; Zhang, J.; Wolcott, M.; Holbery, J. Study of the poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/cellulose nanowhisker composites prepared by solution casting and melt processing. J. Compos. Mater. 2008, 42, 2629-2645.
119. Panaitescu, D.M.; Frone, A.N.; Chiulan, I. Nanostructured biocomposites from aliphatic polyesters and bacterial cellulose. Ind. Crops Prod. 2016, 93, 251-266.
120. Klemm, D.; Heublein, B.; Fink, H.-P.; Bohn, A. Cellulose: fascinating biopolymer and sustainable raw material. Angew. Chem. Int. Ed. 2005, 44(22), 3358-3393.
121. Torres, F.G.; Arroyo, J.J.; Troncoso, O.P. Bacterial cellulose nanocomposites: an all-nano type of material. Mater. Sci. Eng Part C. 2019, 98, 1277-1293.
122. Barud, H.G.O.; Silva, R.R.; Barud, H.S.; Tercjak, A.; Gutierrez, J.; Lustri, W.R.; Oliveira Jr., O.B.; Ribeiro, S.J.L. A multipurpose natural and renewable polymer in medical applications: Bacterial cellulose. Carbohydr. Polym. 2016, 153, 406-420.
123. Sharma, C.; Bhardwaj, N.K. Bacterial nanocellulose: present status, biomedical applications and future perspectives. Mater. Sci. Eng Part C. 2019, 104, 109963.
124. Roman, M.; Haring, A.P.; Bertucio, T.J. The growing merits and dwindling limitations of bacterial cellulose-based tissue engineering scaffolds. Curr. Opin. Chem. Eng. 2019, 24, 98-106.
125. Ye, S.; Jiang, L.; Su, C.; Zhongjie, Z.; Yanyi, W.; Wei, S. Development of gelatin/bacterial cellulose composite sponges as potential natural wound dressings. Int. J. Biol. Macromol. 2019, 133, 148-155.
126. Ul Islam, M.; Subhan, F.; Ul Islam, S.; Khan, S.H.; Shah, N.; Manan, S.; Ullah, M.W.; Yang, G. Development of three-dimensional bacterial cellulose/chitosan scaffolds: analysis of cell-scaffold interaction for potential application in the diagnosis of ovarian cancer. Int. J. Biol. Macromol. 2019, 137, 1050-1059.
127. Helenius, G.; Backdahl, H.; Bodin, A.; Nannmark, U.; Gatenholm, P.; Risberg, B. In vivo biocompatibility of bacterial cellulose. J. Biomed. Mater. Res. 2006, 76(A), 431-438.
128. Yin, N.; Stilwell, M.D.; Santos, T.M.A.; Wang, H.; Weibel, D.B. Agarose particle template porous bacterial cellulose and its application in cartilage growth in vitro. Acta Biomater. 2015, 12, 129-138.
129. Li, Z.; Ramay, H.R.; Hauch, K.D.; Xiao, D.; Zhang, M. Chitosan alginate hybrid scaffolds for bone tissue engineering. Biomaterials 2005, 26, 3919-3928.
130. Oliveira Barud, H.G.; da Barud, S.H.; Cavicchioli, M.; do Amaral, T.S.; de Oliveira Jr., O.B.; Santos, D.M.; de Oliveira Almeida Petersen, A.L.; Celes, F.; Borges Matos, V.; de Oliveira, C.; de Oliveira, P.F.; Furtado, R.A.; Tavares, D.C.; Ribeiro, S.J.L. Preparation and characterization of a bacterial cellulose/silk fibroin sponge scaffold for tissue regeneration. Carbohydr. Polym. 2015, 128, 41-51.
131. Panaitescu, D.M.; Frone, A.N.; Ghiurea, M.; Chiulan, I. Influence of storage conditions on starch/PVA films containing cellulose nanofibers. Ind. Crop. Prod. 2015, 70, 170-177.
132. Zheng, T.; Li, A.; Li, Z.; Hu, W.; Shao, L.; Lu, L.; Cao, Y.; Chen, Y. Mechanical reinforcement of a cellulose aerogel with nanocrystalline cellulose as reinforcer. RSC Adv. 2017, 7(55), 34461-34465.
133. Pircher, N.; Veigel, S.; Aigner, N.; Nedelec, J.M.; Rosenau, T.; Liebner, T. Reinforcement of bacterial cellulose aerogels with biocompatible polymers. Carbohydr. Polym. 2014, 111, 505-513.
134. Karageorgiou, V.; Kaplan, D. Porosity of 3D biomaterial scaffolds and osteogenesis. Biomaterials 2005, 26, 5474-5491.

135. Zhijiang, C.; Chengwei, H.; Guang, Y. Poly(3-hydroxubutyrate-co-4-hydroxubutyrate)/bacterial cellulose composite porous scaffold: preparation, characterization and biocompatibility evaluation. Carbohydr. Polym. 2012, 87(2), 1073-1080.
136. Kirdponpattara, S.; Khamkeav, A.; Sanchavanakit, N.; Pavasant, P.; Phisalaphong, M. Structural modification and characterization of bacterial cellulose-alginate composite scaffolds for tissue engineering. Carbohydr. Polym. 2015, 132, 146-155.
137. Panaitescu, D.M.; Frone, A.N.; Chiulan, I.; Casarica, A.; Nicolae, C.A.; Ghiurea, M.; Trusca, R.; Damian, C.M. Structural and morphological characterization of bacterial cellulose nano-reinforcements prepared by mechanical route. Mater. Des. 2016, 110, 790-801.
138. Bhatta, S.; Stevanovic Janezic, T.; Ratti, C. Freeze-drying of plant-based foods. Foods 2020, 9(1), 87.
139. Renteria Gamiz, A.G.; Dewulf, J.; De Soete, W.; Heirman, B.; Dahlin, C.J.; Krebser, U.; De Meester, S. Freeze drying in the biopharmaceutical industry: an environmental sustainability assessment. Food Bioprod. Proc. 2019, 117, 213-223.
140. Almeida Neto, G.R.; Barcelos Valinhos, M.; Ribeiro, M.E.A.; Folly, M.M.; Rodriguez, R.S.J. Formulation and characterization of a novel PHBV nanocomposite for bone defect filling and infection treatment. Mater. Sci. Eng. Part C 2019, 104, 110004.
141. Bakare, R.; Hawthrone, S.; Vails, C.; Gugssa, C.; Karim, A.; Stubs, J.; Raghavan, D. Antimicrobial and cell viability measurement of bovine serum albumin capped silver nanoparticles (Ag/BSA) loaded collagen immobilized poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) film. J. Colloid Interf. Sci. 2016, 465, 140-148.
142. Liu, Y.F.; Xu, Q.Q.; Cai, P.; Zhen, M.Y.; Wang, X.Y.; Yin, J.Z. Effects of operating parameters and ionic liquid properties on fabrication of supported ionic liquid membranes based on mesoporous g-Al2O3 supports. J. Membr. Sci. 2018, 545, 176-184.
143. Calisto, J.S.; Pacheco, I.S.; Freitas, L.L.; Santana, L.K.; Fagundes, W.S.; Amaral, F.A.; Canobre, S.C. Adsorption kinetic and thermodynamic studies of the 2, 4 edichlorophenoxyacetate (2,4-D) by the [CoeAleCl] layered double hydroxide. Heliyon 2019, 5, 02553.
144. Feng, J.; Nguyen, S.T.; Fan, Z.; Duong, H.M. Advanced fabrication and oil absorption properties of super-hydrophobic recycled cellulose aerogels. Chem. Eng. J. 2015, 270, 168-175.
145. Oprea, A.M.; Profire, L.; Lupusoru, C.E.; Ghiciuc, C.M.; Ciolacu, D.; Vasile, C. Synthesis and characterization of some cellulose/chondroitin sulphate hydrogels and their evaluation as carriers for drug delivery. Carbohydr. Polym. 2012, 87, 721-729.
146. Fernandes, S.C.M.; Sadocco, P.; Alonso-Varona, A.; Palomares, T.; Eceiza, A.; Silvestre, A.J.D.; Mondragon, I.; Freire, C.S.R. Bioinspired antimicrobial and biocompatible bacterial cellulose membranes obtained by surface functionalization with aminoalkyl groups. ACS Appl. Mater. Interfac. 2013, 5, 3290-3297.
147. Gayathri, G.; Srinikethan, G. Bacterial cellulose production by K. saccharivorans BC1 strain using crude distillery effluent as cheap and cost effective nutrient medium. Int. J. Biol. Macromol. 2019, 138, 950-957.
148. Andrade, F.K.; Morais, J.P.S.; Muniz, C.R.; Nascimento, J.H.O.; Vieira, R.S.; Gama, F.M.P.; Rosa, M.F. Stable microfluidized bacterial cellulose suspension. Cellulose 2019, 26, 5851.
149. Panaitescu, D.M.; Ionita, E.R.; Nicolae, C.A.; Gabor, A.R.; Ionita, M.D.; Trusca, R.; Lixandru, B.E.; Codita, I.; Dinescu, G. Poly(3-hydroxybutyrate) modified by nanocellulose and plasma treatment for packaging applications. Polymers 2018, 10, 1249.
150. Masood, F.; Aziz, M.; Haider, H.; Shakil, O.; Yasin, T.; Hameed, A. Biodegradation of gamma irradiated poly-3-hydroxybutyrate/sepiolite nanocomposites. Int. Biodeter. Biodegrad. 2018, 126, 1-9.
151. Frone, A.N.; Panaitescu, D.M.; Chiulan, I.; Nicolae, C.A.; Casarica, A.; Gabor, A.R.; Trusca, R.; Damian, C.M.; Purcar, V.; Alexandrescu, E.; Stanescu, P.O. Surface treatment of bacterial cellulose in mild, eco-friendly conditions. Coatings 2018, 8, 221.
152. Kissinger, H.E. Reaction kinetics in differential thermal analysis. Anal. Chem. 1957, 29, 1702-1706.
153. Moliner, C.; Badia, J.D.; Bosio, B.; Arato, E.; Kittikorn, T.; Stomberg, E.; Teruel-Juanes, R.; Ek, M.; Karlsson, S.; Ribes-Greus, A. Thermal and thermo-oxidative stability and kinetics of decomposition of PHBV/sisal composites, Chem. Eng. Commun. 2017, 205, 226-237.
154. Aoyagi, Y.; Yamashita, K.; Doi, Y. Thermal degradation of poly[(R)-3-hydroxybutyrate], poly[e-caprolactone], and poly[(S)-lactide]. Polym. Degrad. Stab. 2002, 76, 53-59.
155. Kim, K.J.; Doi, Y.; Abe, H. Effects of residual metal compounds and chain-end structure on thermal degradation of poly(3-hydroxybutyric acid). Polym. Degrad. Stab. 2006, 91, 769-777.

156. Cichosz, S.; Masek, A. Cellulose structure and property changes indicated via wetting-drying cycles. Polym. Degrad. Stab. 2019, 167, 33-43.
157. Khankari, R.K.; Law, D.; Grant, D.J.W. Determination of water content in pharmaceutical hydrates by differential scanning calorimetry. Int. J. Pharm. 1992, 82, 117-127.
158. Oner, M.; Çol, A.A.; Pochat-Bohatier, C.; Bechelany, M. Effect of incorporation of boron nitride nanoparticles on oxygen barrier and thermal properties of poly(3-hydroxybutyrate-cohydroxyvalerate). RSC Adv. 2016, 6, 90973-909811.
159. Wang, L.; Du, J.; Cao, D.; Wang, Y. Recent advances and the application of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) as tissue engineering materials. J. Macromol. Sci. 2013, 50(8), 885-893.
160. Czerniecka, A.; Magon, A.; Schliesser, J.; Woodfield, B.F.; Pyda, M. Heat capacity of poly(3-hydroxybutyrate). J Chem. Thermodyn. 2014, 73, 76-84.
161. Shang, L.; Fei, Q.; Zhang, Y.H.; Wang, X.Z.; Fan, D.D.; Chang, H.N. Thermal properties and biodegradability studies of poly (3-hydroxybutyrate-co-3-hydroxyvalerate). J. Polym. Environ. 2012, 20(1), 23-28.
162. Hatakeyama, T.; Matsumoto, Y.; Asano, Y.; Hatakeyama, H. Glass transition of rigid polyurethane foams derived from sodium lignosulfonate mixed with diethylene, triethylene and polyethylene glycols. Thermochim. Acta 2004, 416(1), 29-33.
163. Hameed, N.; Guo, Q.; Tay, F.H.; Kazarian, S.G. Blends of cellulose and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) prepared from the ionic liquid 1-butyl-3-methylimidazolium chloride. Carbohydr. Polym. 2011, 86(1), 94-104.
164. Barham, P.J.; Keller, A.; Otun, E.L.; Holmer, P.A. Crystallization and morphology of a bacterial thermoplastic: poly-3-hydroxybutyrate. J. Mater. Sci. 1984, 19, 2781.
165. Nakayama, A.; Kakugo, A.; Gong, J.P.; Osada, Y.; Takai, M.; Erata, T.; Kawano, S. High mechanical strength double-network hydrogel with bacterial cellulose. Adv. Funct. Mater. 2004, 14, 1124-1128.
166. Martoïa, F.; Cochereau, T.; Dumont, P.J.J.; Orgeas, L.; Terrien, M.; Belgacem, M.N. Cellulose nanofibril foams: links between ice-templating conditions, microstructures and mechanical properties. Mater. Des. 2016, 104, 376-391.
167. Quintana-Quirino, M.; Morales Osorio, C.; Ramirez Vigueras, G.; Vasquez-Torres, H.; Shirai, K. Bacterial cellulose grows with a honeycomb geometry in a solid-state culture of Gluconacetobacter xylinus using polyurethane foam support. Process Biochem. 2019, 82, 1-9.
168. Hamedi, S.; Shojaosadati, S.A.; Najafic, V.; Alizadeh, V. A novel double-network antibacterial hydrogel based on aminated bacterial cellulose and schizophyllan. Carbohydr. Polym. 2020, 229, 115383.
169. Kozlowska, J.; Kaczmarkiewicz, A. Collagen matrices containing poly(vinyl alcohol) microcapsules with retinyl palmitate e structure, stability, mechanical and swelling properties. Polym. Degrad. Stab. 2019, 161, 108-113.
170. Shi, X.; Cui, Q.; Zheng, Y.; Peng, S.; Wang, G.; Xie, Y. Effect of selective oxidation of bacterial cellulose on degradability in phosphate buffer solution and their affinity for epidermal cell attachment. RSC Adv. 2014, 4, 60749-60756.
171. Shin, E.J.; Choi, S.M.; Singh, D.; Zo, S.M.; Lee, Y.H.; Kim, J.H.; Han, S.S. Fabrication of cellulose-based scaffold with microarchitecture using a leaching technique for biomedical applications. Cellulose. 2014, 21, 3515-3525.
172. Dhandayuthapani, B.; Yoshida, Y.; Maekawa, T.; Sakthi Kumar, D. Polymeric scaffolds in tissue engineering application: A review. Int. J. Polym. Sci, 2011, 290602.
173. Nugraha, B. CelluSponge™ and Go Matrix as innovative three-dimensional cell culture platforms, in Technology Platforms for 3D Cell Culture: A User's Guide. Przyborski, S. Editor. 2017, John Wiley & Sons, p. 250-283.
174. Aslam, B.; Wang, W.; Arshad, M.I.; Khurshid, M.; Muzammil, S.; Rasool, M.H.; Nisar, M.A.; Alvi, R.F.; Aslam, M.A.; Qamar, M.U.; Salamat, M.K.F.; Baloch, Z. Antibiotic resistance: a rundown of a global crisis. Infect. Drug Resist. 2018. 11, 1645-58.
175. Oprea, M.; Panaitescu, D.M. Nanocellulose hybrids with metal oxides nanoparticles for biomedical applications. Molecules (Basel) 2020, 25, 4045.
176. Muhulet, A.; Tuncel, C.; Miculescu, F.; Pandele, A.M.; Bobirica, C.; Orbeci, C.; Palla Papavlu, A.; Voicu, Ş.I. Synthesis and characterization of polysulfone–TiO_2 decorated MWCNT composite membranes by sonochemical method. Appl. Phys. A 2020, 126, 233.
177. Tariq, S.; Wani, S.; Rasool, W.; Shafi, K.; Bhat, M.A.' Prabhakar. A.; Shalla, A.H.; Rather, M.A. A comprehensive review of the antibacterial, antifungal and antiviral potential of essential oils and their chemical constituents against drug-resistant microbial pathogens. Microb. Pathog. 2019, 134, 103580.

178. Sharma, C.; Bhardwaj, N.K. Fabrication of natural-origin antibacterial nanocellulose films using bio-extracts for potential use in biomedical industry. Int. J. Biol. Macromol. 2020, 145, 914-25.
179. Liu, F.; Li, X.; Wang, L.; Yan, X.; Ma, D.; Liu, Z.; Liu, X. Sesamol incorporated cellulose acetate-zein composite nanofiber membrane: An efficient strategy to accelerate diabetic wound healing. Int. J. Biol. Macromol. 2020, 149, 627-38.
180. Ullah, A.; Ullah, S.; Khan, M.Q.; Hashmi, M.; Nam, P.D.; Kato, Y.; Tamada, Y.; Kim, I.S. Manuka honey incorporated cellulose acetate nanofibrous mats: Fabrication and in vitro evaluation as a potential wound dressing. Int. J. Biol. Macromol. 2020, 155, 479-89.
181. Sun, D.; Babar Shahzad, M.; Li, M.; Wang, G.; Xu, D. Antimicrobial materials with medical applications. Mater. Technol. 2015, 30, B90-B5.
182. Bakhsheshi-Rad, H.R.; Hadisi, Z.; Ismail, A.F.; Aziz, M.; Akbari, M.; Berto, F.; Chen, X.B. In vitro and in vivo evaluation of chitosan-alginate/gentamicin wound dressing nanofibrous with high antibacterial performance. Polym. Test. 2020, 82, 106298.
183. Naseri-Nosar, M.; Ziora, Z.M. Wound dressings from naturally occurring polymers: A review on homopolysaccharide-based composites. Carbohydr. Polym. 2018, 189, 379-98.
184. Moeini, A.; Pedram, P.; Makvandi, P.; Malinconico, M.; Gomez d'Ayala, G. Wound healing and antimicrobial effect of active secondary metabolites in chitosan-based wound dressings: A review. Carbohydr. Polym. 2020, 233, 115839.
185. Du, H.; Liu, W.; Zhang, M.; Si, C.; Zhang, X.; Li, B. Cellulose nanocrystals and cellulose nanofibrils based hydrogels for biomedical applications. Carbohydr. Polym. 2019, 209, 130-44.
186. Oprea, M.; Voicu, S.I. Cellulose composites with graphene for tissue engineering applications. Materials 2020, 13, 5347.
187. Voicu, S.I.; Thakur, V.K. Aminopropyltriethoxysilane as a linker for cellulose-based functional materials: New horizons and future challenges. Curr. Opin. Green Sustain. Chem. 2021, 30, 100480.
188. Palla-Papavlu, A.; Voicu, S.I.; Dinescu, M. Sensitive materials and coating technologies for surface acoustic wave sensors. Chemosensors 2021, 9, 105.
189. Mohd, N.; Syed Draman, S.F.; Salleh, M.S.N.; Yusof, B. Dissolution of cellulose in ionic liquid: A review. AIP Conf. Proceed. 2017, 1809, 020035.
190. Zizovic, I.; Senerovic, L.; Moric, I.; Adamovic, T.; Jovanovic, M.; Krusic, M.K.; Misic, D.; Stojanovic, D.; Milovanovic, S. Utilization of supercritical carbon dioxide in fabrication of cellulose acetate films with anti-biofilm effects against Pseudomonas aeruginosa and Staphylococcus aureus. J. Supercrit. Fluids. 2018, 140, 11-20.
191. Chen, J.C.; Soden, K.J. Anti-adhesion cellulose acetate wound dressing. Google Patents 2002, CA2246992C.
192. Almoudi, M.M.; Hussein, A.S.; Abu Hassan, M.I.; Mohamad Zain, N. A systematic review on antibacterial activity of zinc against Streptococcus mutans. Saudi Dent. J. 2018, 30, 283-91.
193. Artifon, W.; Pasini, S.M.; Valério, A.; González, S.Y.G.; de Arruda Guelli Ulson de Souza, S.M.; de Souza, A.A.U. Harsh environment resistant - antibacterial zinc oxide/Polyetherimide electrospun composite scaffolds. Mater. Sci. Eng. Part C. 2019, 103, 109859.
194. Ahmed R, Tariq M, Ali I, Asghar R, Noorunnisa Khanam P, Augustine R, et al. Novel electrospun chitosan/polyvinyl alcohol/zinc oxide nanofibrous mats with antibacterial and antioxidant properties for diabetic wound healing. Int. J. Biol. Macromol. 2018, 120, 385-93.
195. Holt BA, Gregory SA, Sulchek T, Yee S, Losego MD. Aqueous Zinc Compounds as Residual Antimicrobial Agents for Textiles. ACS Applied Mater. Interfac. 2018, 10, 7709-16.
196. Goswami M, Das AM. Synthesis and characterization of a biodegradable Cellulose acetate-montmorillonite composite for effective adsorption of Eosin Y. Carbohydr. Polym. 2019, 206, 863-72.
197. Ahmed, F.; Ayoub Arbab, A.; Jatoi, A.W.; Khatri, M.; Memon, N.; Khatri, Z.; Kim, I.S. Ultrasonic-assisted deacetylation of cellulose acetate nanofibers: A rapid method to produce cellulose nanofibers. Ultrason. Sonochem. 2017, 36, 319-25.
198. Luo, Z.; Cheng, W.; Chen, H.; Fu, X.; Peng, X.; Luo, F.; Nie, L. Preparation and properties of enzyme-modified cassava starch-zinc complexes. J. Agric. Food Chem. 2013, 61(19), 4631-4638.
199. Katepetch, C.; Rujiravanit, R.; Tamura, H. Formation of nanocrystalline ZnO particles into bacterial cellulose pellicle by ultrasonic-assisted in situ synthesis. Cellulose 2013, 20, 1275-1292.
200. Thein, M.; Pung, S.; Azizan, A.; Itoh, M. The role of ammonia hydroxide in the formation of ZnO hexagonal nanodisks using sol–gel technique and their photocatalytic study. J. Exp. Nanosci. 2014, 10, 1-15.

201. Kołodziejczak-Radzimska, A.; Markiewicz, E.; Jesionowski, T. Structural characterisation of ZnO particles obtained by the emulsion precipitation method. J. Nanomater. 2012, 65653.
202. Sajó, E.; Kótai, L.; Keresztury, G.; Gács, I.; Pokol, G.; Kristóf, J.; Soptrayanov, B.; Petrusevski, V.M.; Timpu, D.; Sharma, P.K. Studies on the Chemistry of tetraamminezinc(II) dipermanganate ([Zn(NH3)4](MnO4)2): low-temperature synthesis of the manganese zinc oxide (ZnMn2O4) catalyst precursor. Helv. Chim. Acta 2008, 91, 1646-58.
203. Kayani, Z.; Iqbal, M.; Riaz, S.; Zia, R.; Naseem, S. Fabrication and properties of zinc oxide thin film prepared by sol-gel dip coating method. Mat. Sci. Poland 2014, 33, 515-520.
204. Moafi, H.F.; Shojaie, A.F.; Zanjanchi, M.A. Photocatalytic self-cleaning properties of cellulosic fibers modified by nano-sized zinc oxide. Thin Solid Films 2011, 519, 3641-6.
205. De Campos, E.; Campos, S.; Roos, A.; Souza, B.; Schneider, J.; Uliana, M.B.; de Oliveira, R.C. Titanium dioxide dispersed on cellulose acetate and its application in methylene blue photodegradation. Polym. Polym. Compos. 2013, 21, 423-30.
206. Lin, C.-C.; Li, Y.-Y. Synthesis of ZnO nanowires by thermal decomposition of zinc acetate dihydrate. Mater. Chem. Phys. 2009, 113, 334-7.
207. Exner, M.; Bhattacharya, S.; Christiansen, B.; Gebel, J.; Goroncy-Bermes, P.; Hartemann, P.; Heeg, P.; Ilschner, C.; Kramer, A.; Larson, E.; Merkens, W.; Mielke, M.; Oltmans, P.; Ross, B.; Rotter, M.; Schmithausen, R.M.; Sonntag, H.-G.; Trautman, M. Antibiotic resistance: What is so special about multidrug-resistant Gram-negative bacteria? GMS Hyg. Infect. Control 2017, 12, Doc05.
208. Shiohara, A.; Prieto-Simon, B.; Voelcker, N.H. Porous polymeric membranes: fabrication techniques and biomedical applications. J. Mater. Chem. B 2021, 9(9), 2129-2154.
209. Medical membranes market by material (PTFE, PVDF, PP, PSU & PESU), Process technology (UF, MF, NF), application (Pharmaceutical filtration, hemodialysis, drug delivery, IV infusion & sterile filtration), Region-global forecast to 2022. Available from: https://www.marketsandmarkets.com/Market-Reports/medical-membrane-advanced-technologies-and-global-market 86.html?gclid=CjwKCAjwoZWHBhBgEiwAiMN66fTqTw2oL6Yswu8O1GOlejtZkj7i9EHp2oIFU2_4tCv4Npvek-XY-RoCtAwQAvD_BwE.
210. Gopi, S.; Balakrishnan, P.; Chandradhara, D.; Poovathankandy, D.; Thomas, S. General scenarios of cellulose and its use in the biomedical field, Mater. Today Chem. 2019, 13, 59-78.
211. Jazini, F.; Karimi, M.; Azari, S. Tuning the pore features of cellulose acetate/cellulose triacetate membranes via post-casting solvent treatment for forward osmosis. Carbohydr. Polym. 2021, 255, 117348.
212. Alenazi, N.A.; Hussein, M.A.; Alamry, K.A.; Asiri, A.M. Modified polyether-sulfone membrane: a mini review. Design Monom. Polym. 2017, 20(1), 532-546.
213. Irfan, M.; Shah, S.M.; Baig, N.; Saleh, T.A.; Ahmed, M.; Naz, G.; Akhtar, N.; Muhammad, N.; Idris, A. Hemodialysis performance and anticoagulant activities of PVP-k25 and carboxylic-multiwall nanotube composite blended polyethersulfone membrane. Mater. Sci. Eng. Part C 2019, 103, 109769.
214. Waheed, H.; Hussain, A. Fabrication of cellulose acetate/polyaziridine blended flat sheet membranes for dialysis application. BioNanoSci. 2019, 9, 256-265.
215. Filimon, A.; Dobos, A.M.; Musteata, V. New perspectives on development of polysulfones/cellulose derivatives based ionic-exchange membranes: Dielectric response and hemocompatibility study. Carbohydr. Polym. 2019, 226, 115300.
216. Waheed, H.; Minhas, F.T.; Hussain, A. Cellulose acetate/sericin blend membranes for use in dialysis. Polym. Bull. 2018, 75(9), 3935-3950.
217. Raharjo, Y.; Fahmi, Z.; Wafiroh, S.; Widati, A.A.; Amanda, E.; Ismail, A.; Othman, M.H.; Santoso, D. Incorporation of imprinted-zeolite to polyethersulfone/cellulose acetate membrane for creatinine removal in hemodialysis treatment. J. Teknol. 2019, 81(3), 1-17.
218. De Pascale, M.; De Angelis, M.G.; Boi, C. Mixed matrix membranes adsorbers (MMMAs) for the removal of uremic toxins from dialysate. Membranes 2019, 12(2), 203.
219. Hayder, A.; Hussain, A.; Khan, A.N.; Waheed, H. Fabrication and characterization of cellulose acetate/hydroxyapatite composite membranes for the solute separations in hemodialysis. Polym. Bull. 2018, 75(3), 1197-1210.
220. Dumitriu, C.; Voicu, S.I.; Muhulet, A.; Nechifor, G.; Popescu, S.; Ungureanu, C.; Carja, A.; Miculescu, F.; Trusca, R.; Pirvu, C. Production and characterization of cellulose acetate – titanium dioxide nanotubes membrane fraxiparinized through polydopamine for clinical applications. Carbohydr. Polym. 2018, 181, 215-223.

221. Lee, J.; Moon, J.Y.; Lee, J.C.; Hwang, T.I.; Park, C.H.; Kim, C.S. Simple conversion of 3D electrospun nanofibrous cellulose acetate into a mechanically robust nanocomposite cellulose/calcium scaffold. Carbohydr. Polym. 2021, 253, 117191.
222. Mousa, H.M.; Hussein, K.H.; Sayed, M.M.; Abd El-Rahman, M.K.; Woo, H.M. Development and characterization of cellulose/iron acetate nanofibers for bone tissue engineering applications. Polymers 2021, 13(8), 1339.
223. Hatamie, S.; Mohamadyar-Toupkanlou, F.; Mirzaei, S.; Ahadian, M.M.; Hosseinzadeh, S.; Soleimani, M.; Sheu, W.-J.; Wei, Z.H.; Hsieh, T.-F.; Chang, W.-C.; Wang, C.-L. Cellulose acetate/magnetic graphene nanofiber in enhanced human mesenchymal stem cells osteogenic differentiation under alternative current magnetic field. SPIN 2019, 09(02), 1940011.
224. Ignat, S.-R.; Lazăr, A.D.; Şelaru, A.; Samoilă, I.; Vlăsceanu, G.M.; Ioniţă, M.; Radu, E.; Dinescu, S.; Costache, M. Versatile biomaterial platform enriched with graphene oxide and carbon nanotubes for multiple tissue engineering applications. Int. J. Molec. Sci. 2019, 20(16), 3868.
225. Salazar, J.R.; Monserate, J.J. Electrospun polylactic acid (PLA)-nanosilica (nSiO2)-cellulose acetate nanofiber composite: A potential biomaterial bone tissue scaffold. Asia Life Sci. 2018, 27, 481-495.
226. Abdelaziz, D.; Hefnawy, A.; Al-Wakeel, E.; El-Fallal, A.; El-Sherbiny, I.M. New biodegradable nanoparticles-in-nanofibers based membranes for guided periodontal tissue and bone regeneration with enhanced antibacterial activity. J. Adv. Res. 2021, 28, 51-62.
227. Ko, S.W.; Lee, J.Y.; Rezk, A.I.; Park, C.H.; Kim, C.S. In-situ cellulose-framework templates mediated monodispersed silver nanoparticles via facile UV-light photocatalytic activity for anti-microbial functionalization. Carbohydr. Polym. 2021, 269, 118255.
228. Cifuentes, A.; Borrós, S. Comparison of two different plasma surface-modification techniques for the covalent immobilization of protein monolayers. Langmuir 2013, 29(22), 6645-6651.
229. Potopnyk, M.A.; Jarosz, S. Nitrogen-containing macrocycles having a carbohydrate scaffold, in Advances in Carbohydrate Chemistry and Biochemistry. Horton, D.; Editor. 2014, Academic Press, p. 227-295.
230. Davis, F.; Higson, S. Crown ethers, cryptands and other compounds, in Macrocycles: Construction, Chemistry and Nanotechnology Applications 2011, p. 34-76.
231. Anitua, E.; Prado, R.; Orive, G.; Tejero, R. Effects of calcium-modified titanium implant surfaces on platelet activation, clot formation, and osseointegration. J. Biomed. Mater. Res. A 2015, 103(3), 969-80.
232. Anitua, E.; Cerqueira, A.; Romero-Gavilán, F.; García-Arnáez, I.; Martinez-Ramos, C.; Ozturan, S.; Azkargorta, M.; Elortza, F.; Gurruchaga, M.; Goñi, I.; Suay, J.; Tejero, R. Influence of calcium ion-modified implant surfaces in protein adsorption and implant integration. Int. J. Implant Dent. 2021, 7(1), 32.
233. Koju, N.; Sikder, P.; Ren, Y.; Zhou, H.; Bhaduri, S.B. Biomimetic coating technology for orthopedic implants, Curr. Opin. Chem. Eng. 2017, 15, 49-55.
234. Tetsushi, T.; Akio, K.; Mitsuru, A. Hydroxyapatite formation on/in poly(vinyl alcohol) hydrogel matrices using a novel alternate soaking process. Chem. Lett. 1998, 27(8), 711-712.
235. Mohamed, M.; Norharyati, W.; Jaafar, J.; Mohd Asri, S.E.A.; Ismail, A. Physicochemical properties of “green” nanocrystalline cellulose isolated from recycled newspaper. RSC Adv. 2015, 5, 29842-29849.
236. Oprea, M.; Panaitescu, D.M.; Nicolae, C.A.; Gabor, A.R.; Frone, A.N.; Raditoiu, V.; Trusca, R.; Casarica, A. Nanocomposites from functionalized bacterial cellulose and poly(3-hydroxybutyrate-co-3-hydroxyvalerate). Polym. Degrad. Stab. 2020, 179, 109203.
237. Rosa, M.F.; Medeiros, E.S.; Malmonge, J.A.; Gregorski, K.S.; Wood, D.F.; Mattoso, L.H.C.; Glenn, G.; Orts, W.J.; Imam, S.H. Cellulose nanowhiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behavior. Carbohydr. Polym. 2010, 81(1), 83-92.
238. Chen, L.; Zhu, X.; Huang, D.; Xu, Z.; Shen, J.; Zhang, W. Polystyrene/poly(dibenzo-18-crown-6) composite nanofibers for the selective adsorption of plasma catecholamines. RSC Adv. 2017, 7, 13263-13271.
239. Sánchez-Márquez, J.; Fuentes-Ramirez, R.; Cano-Rodríguez, I.; Gamino Arroyo, Z.; Rubio-Rosas, E.; Kenny, J.; Rescignano, N. Membrane made of cellulose acetate with polyacrylic acid reinforced with carbon nanotubes and its applicability for chromium removal. Int. J. Polym. Sci. 2015, 320631.
240. Yan, X.; Xu, T.; Chen, G.; Yang, S.; Liu, H.; Xue, Q. Preparation and characterization of electrochemically deposited carbon nitride films on silicon substrate. J. Phys. Part D: Appl. Phys. 2004, 37(6), 907.
241. Velásquez-Rojas, M.M.; Contreras-Torres, F.F.; Meza-Laguna, V.; Álvarez-Zauco, E.; Farías, M.H.; Basiuk, V.A.; Basiuk, E.V. Solvent-free functionalization of graphene oxide powder and paper with aminobenzo-crown ethers and complexation with alkali metal cations. Mater. Chem. Phys. 2021, 260, 124127.

242. Kujawa, J.; Rynkowska, E.; Fatyeyeva, K.; Knozowska, K.; Wolan, A.; Dzieszkowski, K.; Li, G.; Kujawski, W. Preparation and characterization of cellulose acetate propionate films functionalized with reactive ionic liquids. Polymers 2019, 11(7), 1217.
243. Asiri, A.M.; Petrosino, F.; Pugliese, V.; Khan, S.B.; Alamry, K.A.; Alfifi, S.Y.; Marwani, H.M.; Alotaibi, M.M.; Algieri, C.; Chakraborty, S. Synthesis and characterization of blended cellulose acetate membranes, Polymers 2022, 14(1), 4.
244. Hou, J.; Wang, Y.; Xue, H.; Dou, Y. Biomimetic growth of hydroxyapatite on electrospun CA/PVP core-shell nanofiber membranes, Polymers 2018, 10(9), 1032.
245. Yamaguchi, K.; Prabakaran, M.; Ke, M.; Gang, X.; Chung, I.M.; Um, I.C.; Gopiraman, M.; Kim, I.S. Highly dispersed nanoscale hydroxyapatite on cellulose nanofibers for bone regeneration. Mater. Lett. 2016, 168, 56-61.
246. Ogiwara, T.; Katsumura, A.; Sugimura, K.; Teramoto, Y.; Nishio, Y. Calcium phosphate mineralization in cellulose derivative/poly(acrylic acid) composites having a chiral nematic mesomorphic structure. Biomacromol. 2015, 16(12), 3959-69.
247. Qi, P.; Ohba, S.; Hara, Y.; Fuke, M.; Ogawa, T.; Ohta, S.; Ito, T. Fabrication of calcium phosphate-loaded carboxymethyl cellulose non-woven sheets for bone regeneration. Carbohydr. Polym. 2018, 189, 322-330.
248. Rodríguez, K.; Renneckar, S.; Gatenholm, P. Biomimetic calcium phosphate crystal mineralization on electrospun cellulose-based scaffolds. ACS Appl. Mater. Interfac. 2011, 3(3), 681-689.
249. Joshi, M.K.; Tiwari, A.P.; Maharjan, B.; Won, K.S.; Kim, H.J.; Park, C.H.; Kim, C.S. Cellulose reinforced nylon-6 nanofibrous membrane: Fabrication strategies, physicochemical characterizations, wicking properties and biomimetic mineralization. Carbohydr. Polym. 2016, 147, 104-113.
250. Ruiz-Hitzky, E.; Ariga, K.; Lvov, Y.M. Bio-inorganic hybrid nanomaterials: strategies, synthesis, characterization and applications. 2008, John Wiley & Sons.
251. Du, Y.; Li, Y.-J.; Wu, T. A superhydrophilic and underwater superoleophobic chitosan–TiO_2 composite membrane for fast oil-in-water emulsion separation. RSC Adv. 2017, 7, 41838-41846.
252. Li, W.; Walz, J.Y. Porous nanocomposites with integrated internal domains: application to separation membranes. Sci. Rep. 2014, 4(1), 4418.
253. Lai, C.; Zhang, S.J.; Wang, L.Q.; Sheng, L.Y.; Zhou, Q.Z.; Xi, T.F. The relationship between microstructure and in vivo degradation of modified bacterial cellulose sponges. J. Mater. Chem. B 2015, 3(46), 9001-9010.
254. Gong, J.; Li, J.; Xu, J.; Xiang, Z.; Mo, L. Research on cellulose nanocrystals produced from cellulose sources with various polymorphs. RSC Adv. 2017, 7, 33486-33493.
255. Azwar, E.; Chan, D.J.C.; Kasan, N.A.; Rastegari, H.; Yang, Y.; Sonne, C.; Tabatabaei, M.; Aghbashlo, M.; Lam, S.S. A comparative study on physicochemical properties, pyrolytic behaviour and kinetic parameters of environmentally harmful aquatic weeds for sustainable shellfish aquaculture. J. Hazard. Mater. 2022, 424, 127329.
256. Rimal, V.; Shishodia, S.; Srivastava, P. Novel synthesis of high thermal stability carbon dots & nanocomposites from Oleic acid as an organic substrate. Appl. Nanosci. 2019, 10, 455-464.
257. Raia, R.Z.; Iwakiri, S.; Trianoski, R.; Andrade, A.S.D.; Kowalski, E.L.; Effects of alkali treatment on modification of the Pinus fibers. Materia (Rio J.) 2021, 26(01), e12936.
258. Chandrasekaran, A.; Suresh, S.; Dakshanamoorthy, A. Synthesis and characterization of nano-hydroxyapatite (n-HAP) using the wet chemical technique. Int. J. Phys. Sci. 2013, 8, 1639-1645.
259. Tchounwou, P.B.; Yedjou, C.G.; Patlolla, A.K.; Sutton, D.J. Heavy metal toxicity and the environment. Exp. Suppl. 2012, 101, 133–164.
260. Alissa, E.M.; Ferns, G.A. Heavy metal poisoning and cardiovascular disease. J. Toxicol. 2011, 2011, 870125.
261. Singh, R.; Gautam, N.; Mishra, A.; Gupta, R. Heavy metals and living systems: An overview. Indian J. Pharmacol. 2011, 43, 246–253.
262. Mondal, S.; Kumar Majumder, S. Fabrication of the polysulfone-based composite ultrafiltration membranes for the adsorptive removal of heavy metal ions from their contaminated aqueous solutions. Chem. Eng. J. 2020, 401, 126036.
263. Balali-Mood, M.; Naseri, K.; Tahergorabi, Z.; Khazdair, M.R.; Sadeghi, M. Toxic mechanisms of five heavy metals: mercury, lead, chromium, cadmium, and arsenic. Front. Pharmacol. 2021, 12, 643972.
264. Ronco, C.; Clark, W.R. Haemodialysis membranes. Nat. Rev. Nephrol. 2018, 14, 394–410.
265. To, N.; Sanada, I.; Ito, H.; Prihandana, G.S.; Morita, S.; Kanno, Y.; Miki, N. Water-permeable dialysis membranes for multi-layered microdialysis system. Front. Bioeng. Biotechnol. 2015, 3, 70.
266. Yamashita, A.C.; Sakurai, K. Dialysis membranes physicochemical structures and feacture, in Updates in Hemodialysis. Suzuki, H..; Editor. 2015, IntechOpen, London.

267. Eduok, U.; Abdelrasoul, A.; Shoker, A.; Doan, H. Recent developments, current challenges and future perspectives on cellulosic hemodialysis membranes for highly efficient clearance of uremic toxins. Mater. Today Commun. 2021, 27, 102183.
268. Clark, W.R.; Hamburger, R.J.; Lysaght, M.J. Effect of membrane composition and structure on solute removal and biocompatibility in hemodialysis. Kidney Int. 1999, 56, 2005–2015.
269. Poppelaars, F.; Faria, B.; Gaya da Costa, M.; Franssen, C.F.M.; van Son, W.J.; Berger, S.P.; Daha, M.R.; Seelen, M.A. The complement system in dialysis: a forgotten story? Front. Immunol. 2018, 9, 71.
270. Bouré, T.; Vanholder, R. Which dialyser membrane to choose? Nephrol. Dial. Transplant. 2004, 19, 293–296.
271. Jørstad, S.; Smeby, L.C.; Balstad, T.; Widerøe, T.E. Generation and removal of anaphylatoxins during hemofiltration with five different membranes. Blood Purif. 1988, 6, 325–335.
272. Zhong, D.; Wang, Z.; Zhou, J.; Wang, Y. Additive-free preparation of hemodialysis membranes from block copolymers of polysulfone and polyethylene glycol. J. Membr. Sci. 2021, 618, 118690.
273. Wang, C.; Lin, B.; Qiu, Y. Enhanced hydrophilicity and anticoagulation of polysulfone materials modified via dihydroxypropyl, sulfonic groups and chitosan. Colloids Surf. Part B 2022, 210, 112243.
274. Abidin, M.N.Z.; Goh, P.S.; Said, N.; Ismail, A.F.; Othman, M.H.D.; Abdullah, M.S.; Ng, B.C.; Hasbullah, H.; Sheikh Abdul Kadir, S.H.; Kamal, F.; Mansur, S. Polysulfone/amino-silanized poly (methyl methacrylate) dual layer hollow fiber membrane for uremic toxin separation. Sep. Purif. Technol. 2020, 236, 116216.
275. Qi, X.; Yang, N.; Luo, Y.; Jia, X.; Zhao, J.; Feng, X.; Chen, L.; Zhao, Y. Resveratrol as a plant type antioxidant modifier for polysulfone membranes to improve hemodialysis-induced oxidative stress. Mat. Sci. Eng. Part C 2021, 123, 111953.
276. Yang, N.; Jia, X.; Wang, D.; Wei, C.; He, Y.; Chen, L.; Zhao, Y. Silibinin as a natural antioxidant for modifying polysulfone membranes to suppress hemodialysis-induced oxidative stress. J. Membr. Sci. 2018, 574, 86–99.
277. Mahlicli, F.; Altinkaya, S. Immobilization of alpha lipoic acid onto polysulfone membranes to suppress hemodialysis induced oxidative stress. J. Membr. Sci. 2014, 449, 27.
278. Tu, M.-M.; Xu, J.-J.; Qiu, Y.-R. Surface hemocompatible modification of polysulfone membrane via covalently grafting acrylic acid and sulfonated hydroxypropyl chitosan. RSC Adv. 2019, 9, 6254–6266.
279. Ibrahim, G.P.S.; Isloor, A.M.; Inamuddin; Asiri, A.M.; Ismail, A.F.; Kumar, R.; Ahamed, M.I. Performance intensification of the polysulfone ultrafiltration membrane by blending with copolymer encompassing novel derivative of poly (styrene-co-maleic anhydride) for heavy metal removal from wastewater. Chem. Eng. J. 2018, 353, 425–435.
280. Benkhaya, S.; Lgaz, H.; Alrashdi, A.A.; M'Rabet, S.; El Bachiri, A.; Assouag, M.; Chung, I.-M.; El Harfi, A. Upgrading the performances of polysulfone/polyetherimide ultrafiltration composite membranes for dyes removal: Experimental and molecular dynamics studies. J. Mol. Liq. 2021, 331, 115743.
281. Kim, K.; Lee, K.; Cho, K.; Park, C. Surface modification of polysulfone ultrafiltration by oxygen plasma treatment. J. Membr. Sci. 2002, 199, 135–145.
282. Refaat Alawady, A.; Ali Alshahrani, A.; Ali Aouak, T.; Mohamed Alandis, N. Polysulfone membranes with CNTs/Chitosan biopolymer nanocomposite as selective layer for remarkable heavy metal ions rejection capacity. Chem. Eng. J. 2020, 388, 124267.
283. Sherugar, P.; Naik, N.S.; Padaki, M.; Nayak, V.; Gangadharan, A.; Nadig, A.R.; Déon, S. Fabrication of zinc doped aluminium oxide/polysulfone mixed matrix membranes for enhanced antifouling property and heavy metal removal. Chemosphere 2021, 275, 130024.
284. Ionita, M.; Pandele, A.M.; Crica, L.; Pilan, L. Improving the thermal and mechanical properties of polysulfone by incorporation of graphene oxide. Compos. Part B Eng. 2014, 59, 133–139.
285. Serbanescu, O.; Pandele, A.; Oprea, M.; Semenescu, A.; Thakur, V.K.; Voicu, Ș.I. Crown ether-immobilized cellulose acetate membranes for the retention of Gd (III). Polymers 2021, 13, 3978.
286. Voicu, S.; Thakur, V.K. Graphene-based composite membranes for nanofiltration: Performances and future perspectives. Emerg. Mater. 2021, 1–13.
287. Pandele, A.M.; Constantinescu, A.; Radu, I.C.; Miculescu, F.; Ioan Voicu, S.; Ciocan, L.T. Synthesis and characterization of PLA-micro-structured hydroxyapatite composite films. Materials 2020, 13, 274.
288. Chiulan, I.; Heggset, E.B.; Voicu, Ș.I.; Chinga-Carrasco, G. Photopolymerization of bio-based polymers in a biomedical engineering perspective. Biomacromolecules 2021, 22, 1795–1814.
289. Du, J.; Cheng, H.-M. The fabrication, properties, and uses of graphene/polymer composites. Macromol. Chem. Phys. 2012, 213, 1060–1077.

290. Zhang, T.; Xue, Q.; Zhang, S.; Dong, M. Theoretical approaches to graphene and graphene-based materials. Nano Today 2012, 7, 180–200.
291. Pei, S.; Cheng, H.-M. The reduction of graphene oxide. Carbon 2012, 50, 3210–3228.
292. Banerjee, A.N. Graphene and its derivatives as biomedical materials: Future prospects and challenges. Interf. Focus 2018, 8, 20170056.
293. Guo, Z.; Chakraborty, S.; Monikh, F.A.; Varsou, D.-D.; Chetwynd, A.J.; Afantitis, A.; Lynch, I.; Zhang, P. Surface functionalization of graphene-based materials: biological behavior, toxicology, and safe-by-design aspects. Adv. Biol. 2021, 5, 2100637.
294. Bandehali, S.; Moghadassi, A.; Parvizian, F.; Zhang, Y.; Hosseini, S.M.; Shen, J. New mixed matrix PEI nanofiltration membrane decorated by glycidyl-POSS functionalized graphene oxide nanoplates with enhanced separation and antifouling behaviour: Heavy metal ions removal. Sep. Purif. Technol. 2020, 242, 116745.
295. Petrescu, S.; Avramescu, S.; Musuc, A.M.; Neatu, F.; Florea, M.; Ionita, P. Crown-ether functionalized graphene oxide for metal ions sequestration. Mater. Res. Bull. 2020, 122, 110643.
296. Nisola, G.M.; Parohinog, K.J.; Cho, M.K.; Burnea, F.K.B.; Lee, J.Y.; Seo, J.G.; Lee, S.-P.; Chung, W.-J. Covalently decorated crown ethers on magnetic graphene oxides as bi-functional adsorbents with tailorable ion recognition properties for selective metal ion capture in water. Chem. Eng. J. 2020, 389, 123421.
297. Seetharaman, S.; Raghu, S.C.; Velan, M.; Ramya, K.; Mahabadi, K.A. Comparison of the performance of reduced graphene oxide and multiwalled carbon nanotubes based sulfonated polysulfone membranes for electrolysis application. Polym. Compos.2015, 36, 475-481.
298. Song, L.; Huo, J.; Wang, X.; Yang, F.; He, J.; Li, C. Phosphate adsorption by a Cu (II)-loaded polyethersulfone-type metal affinity membrane with the presence of coexistent ions. Chem. Eng. J. 2016, 284, 182–193.
299. Wang, Y.; Liu, Z.; Luo, F.; Peng, H.-Y.; Zhang, S.-G.; Xie, R.; Ju, X.-J.; Wang, W.; Faraj, Y.; Chu, L.-Y. A novel smart membrane with ion-recognizable nanogels as gates on interconnected pores for simple and rapid detection of trace lead (II) ions in water. J. Membr. Sci. 2019, 575, 28–37.
300. Jin, C.; Liu, G.; Wu, G.; Huo, S.; Liu, Z.; Kong, Z. Facile fabrication of crown ether functionalized lignin-based biosorbent for the selective removal of Pb (II). Ind. Crops Prod. 2020, 155, 112829.
301. Kazemzadeh, H.; Karimi-Sabet, J.; Towfighi Darian, J.; Adhami, A. Evaluation of polymer inclusion membrane efficiency in selective separation of lithium ion from aqueous solution. Sep. Purif. Technol. 2020, 251, 117298.
302. Liu, C.; Walter, D.; Neuhauser, D.; Baer, R. Molecular recognition and conductance in crown ethers. J. Am. Chem. Soc. 2003, 125, 13936–13937.
303. Korchowiec, B.; Trojan, S.; Joly, J.-P.; Korchowiec, J.; Beley, M.; Rogalska, E. The interaction of an amphiphile crown ether with divalent metal ions. An electrochemical, Langmuir film, and molecular modeling study. Thin Solid Films 2019, 683, 49–56.
304. Wan, W.; Zhao, Z.; Hu, H.; Gogotsi, Y.; Qiu, J. Highly controllable and green reduction of graphene oxide to flexible graphene film with high strength. Mater. Res. Bull. 2013, 48, 4797–4803.
305. Sharma, M.; Rani, S.; Pathak, D.K.; Bhatia, R.; Kumar, R.; Sameera, I. Temperature dependent Raman modes of reduced graphene oxide: Effect of anharmonicity, crystallite size and defects. Carbon 2021, 184, 437–444.
306. Pandele, A.M.; Ionita, M.; Lungu, A.; Vasile, E.; Zaharia, C.; Iovu, H. Porous chitosan/graphene oxide biocomposites for tissue engineering. Polym. Compos. 2017, 38, 363–370.
307. Eigler, S.; Dotzer, C.; Hirsch, A. Visualization of defect densities in reduced graphene oxide. Carbon 2012, 50, 3666–3673.
308. Olsen, G.; Ulstrup, J.; Chi, Q. Crown-ether derived graphene hybrid composite for membrane-free potentiometric sensing of alkali metal ions. ACS Appl. Mater. Interf. 2016, 8, 37–41.
309. Pandele, A.M.; Andronescu, C.; Vasile, E.; Radu, I.C.; Stanescu, P.; Iovu, H. Non-covalent functionalization of GO for improved mechanical performances of pectin composite films. Compos. Part A Appl. Sci. Manuf. 2017, 103, 188–195.
310. Ayiania, M.; Smith, M.; Hensley, A.J.; Scudiero, L.; McEwen, J.-S.; Garcia-Perez, M. Deconvoluting the XPS spectra for nitrogen-doped chars: An analysis from first principles. Carbon 2020, 162, 528–544.
311. Mironova, M.; Makarov, I.; Golova, L.; Vinogradov, M.; Shandryuk, G.; Levin, I. Improvement in carbonization efficiency of cellulosic fibres using silylated acetylene and alkoxysilanes. *Fibers* 2019, *7*, 84.
312. Ficai, D.; Ficai, A.; Voicu, G.; Vasile, B.; Guran, C.; Andronescu, E. Polysulfone based membranes with desired pores characteristics. Mater. Plast. 2010, 47, 24–27.
313. Alkhouzaam, A.; Qiblawey, H. Novel polysulfone ultrafiltration membranes incorporating polydopamine functionalized graphene oxide with enhanced flux and fouling resistance. J. Membr. Sci. 2021, 620, 118900.

314. Sharma, N.; Sharma, V.; Jain, Y.; Kumari, M.; Gupta, R.; Sharma, S.K.; Sachdev, K. Synthesis and characterization of graphene oxide (go) and reduced graphene oxide (rGO) for gas sensing application. Macromol. Sympos. 2017, 376, 1700006.
315. Kabsch-Korbutowicz, M.; Winnicki, T. Application of modified polysulfone membranes to the treatment of water solutions containing humic substances and metal ions. Desalination 1996, 105, 41–49.
316. Molinari, R.; Gallo, S.; Argurio, P. Metal ions removal from wastewater or washing water from contaminated soil by ultrafiltration–complexation. Water Res. 2004, 38, 593–600.