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Review

Cellulose Acetate-Based Materials for Water Treatment in the Context of Circular Economy

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Abstract: Water, one of the most important resources that the planet offers us, cannot be used without meeting certain quality parameters which are increasingly difficult to achieve due to human activities such as deforestation, improper industrial and agricultural waste management, maritime traffic and fuel spillages. Cellulose-based materials or membranes are among the most important candidates to water treatment processes in the actual context of sustainable processes due to the chemical versatility of this cellulose derivative and also due to its large availability This review aims to present the use of functionalized or composite cellulose acetate membranes in water reuse processes in the context of the circular economy. The synthesis methods, process performances, and limitations of these membranes are presented, and the main future directions are thoroughly discussed at the end of the manuscript.

Keywords: cellulose acetate; membranes; water treatment; circular economy

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1. Introduction

Until the end of the nineteenth century, the use of water exactly as it was found in nature was not a problem, mainly due to the minimal impact that humans had on its quality. The main sources of pollution were represented by household or domestic activities, and the only methods used for water purification were sand filtration (used in stations that supplied water to large cities) and distillation (used specially to produce very pure water for the medical and pharmaceutical field). However, the development of cities and industry lead to a constant growth of water pollution and, therefore, the need for fast and effective filtering methods. Therefore, in 1804, Robert Thom designed the first municipal water treatment station in Scotland. The use of polymer membranes for water filtration and purification became a necessity after the Second World War. In Germany, the newly founded the Millipore company, through the Marshall Plan of the United States, transformed huge quantities of nitrocellulose (used as an explosive powder for bomb production) into microfiltration and ultrafiltration membranes [1]. It should be noted that until the appearance of the first water treatment station in 1804, for almost 1 million years of human existence, in the current evolutionary form, a large-scale filtration method to obtain drinking water was not required, and, in the next 150 years, it was necessary to go from sand filtration to polymer membrane filtration through micro and ultrafiltration processes. In another 50 years (from 1950 to 2000), installations with high capacity for microfiltration and desalination with high energy consumption, working pressures and increased material requirements were also needed, due to a drastic decrease in the size of the species to be removed [2–5].

Filtering processes also experienced certain changes throughout time. At the beginning, it was necessary to filter some chemical species in the field of microns, such as colloidal aggregates or large particles [6]. Over time, the dimensions decreased more and more (e.g., pesticides, drugs, dyes and metal ions) and, according to the size of the species that need to be filtered, the main classification of membranes appeared—microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes [7–10]. These processes are represented in Figure 1.

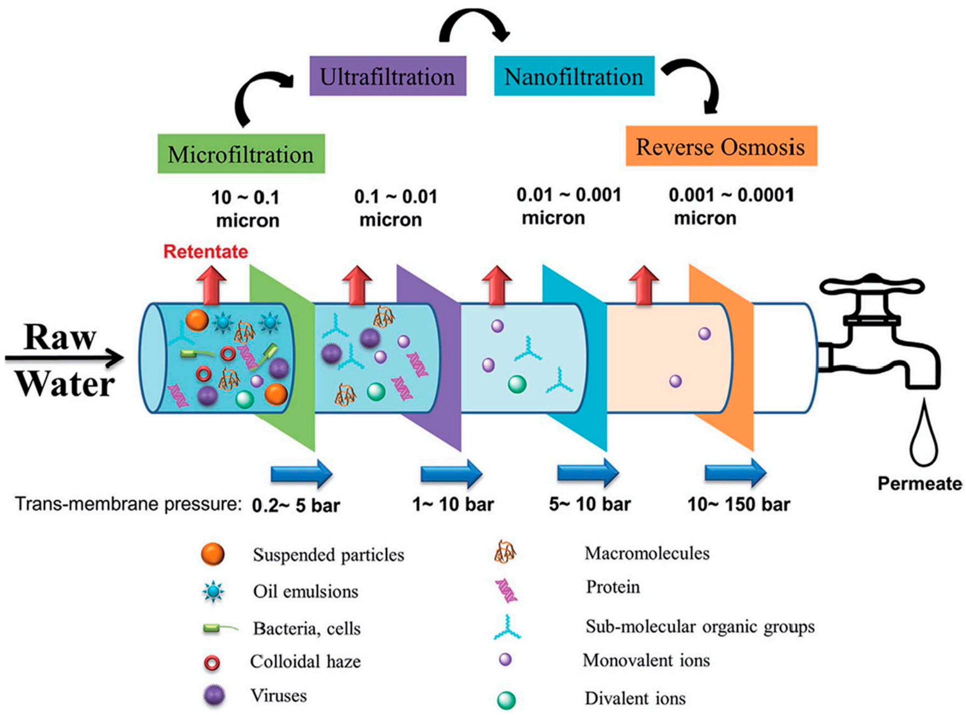

Figure 1. Schematic representation of a membrane-based water treatment system [11].

The main polymers used for water filtration were cellulose derivatives (especially nitrocellulose) [12]. In the early 1960s, along with the appearance of technical polymers, a transition was made from cellulose to polysulfone [13], polyamide [14], polyether ether ketone [15], etc. The advantages of polysulfone, in particular, were superior mechanical and thermal resistance, high versatility regarding the phase inversion process and implicitly a much more precise control of the membranes active layer's properties [16–21]. In recent years, two different philosophies led to the emergence of new trends in water filtration. The first one is related to the use of environmentally friendly polymers for the preparation of membranes. This trend appeared due to the fact that most synthetic polymers are petroleum based and tend to accumulate in nature. This, correlated with the biodegradability of these polymers which is practically zero on the scale of our lives and even in a few tens of generations, led to the need for finding solutions, from the material point of view, for the manufacture of membranes [22–25]. The second philosophy is related to the availability of water sources used to generate both water for industrial use or agriculture, and also drinking water with certain quality parameters [26–28]. In the context of the new concepts regarding the circular economy as well as the sustainability of processes and chemicals, an elegant and common solution was found for both challenges—the replacement of synthetic polymers with natural ones and the reuse of water [28–31].

The main natural polymers are cellulose and cellulose derivatives, gum, pectin, chitin and chitosan, alginate and starch [32,33]. All these polymers belong to the general class called polysaccharides (Figure 2a), and have as main characteristics, high abundance in nature, renewability, biocompatibility, surface versatility for chemical reactions at the hydroxyl (cellulose and derivatives by hydrolysis), carboxyl (pectin) or amino (chitin or chitosan) groups and last but not least, high biodegradability (Figure 2b).

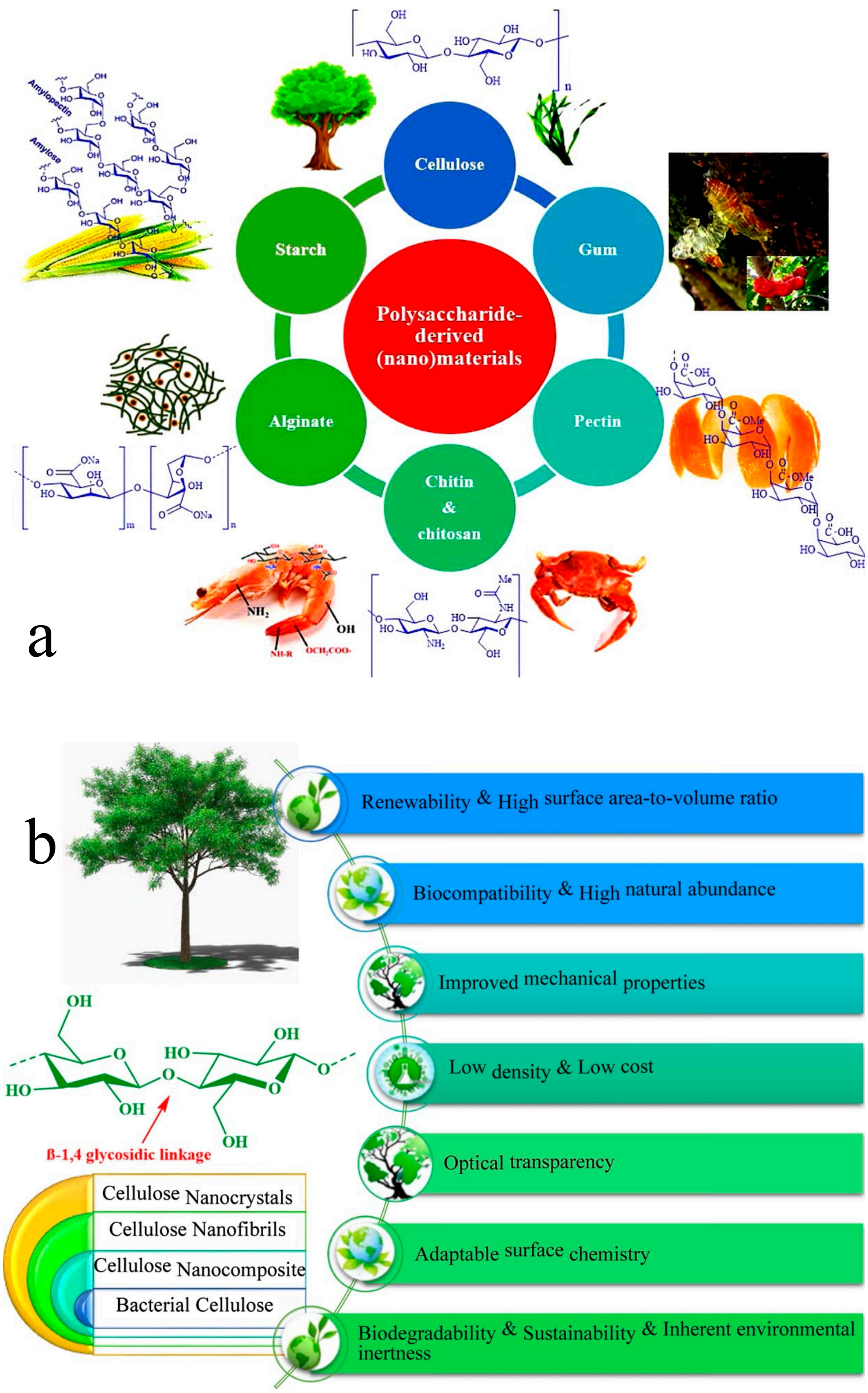

Figure 2. Different examples of environmentally friendly polysaccharides and their provenience source (**a**); chemical structure of cellulose and its main properties (**b**) [33].

Out of all these polysaccharides, the most important ones are cellulose and its derivatives. Cellulose, as such, is difficult to use for membrane synthesis because it is soluble only in very toxic solvent mixtures, therefore, the use of cellulose derivatives is preferred. From the multitude of cellulose derivatives, cellulose acetate (CA) was especially noted for a multitude of applications in the industrial and biomedical fields [34,35]. Due to the high biocompatibility as well as the bioresorbable properties, it was used for the preparation of membranes for osseointegration, either by functionalization with various molecules that induce osteoconductive properties (such as resveratrol or sericin), or by the synthesis of composite membranes with hydroxyapatite [36–40].

This review aims to show to what extent cellulose acetate can be used as a precursor for the synthesis of water purification membranes, and the possibility of reusing it in the context of circular economy. The main classes of compounds that can be removed with the help of cellulose acetate membranes are presented as well as the main challenges related to the limitations of this polymer. Moreover, the future prospects are discussed in length at the end of the manuscript. The methodology used for this literature study was made on Scopus database, with searched years 2018–2023 under the following keywords: 'cellulose acetate membranes' and 'heavy metals' or 'pharmaceutics' or 'dyes'. There were chosen papers that presented one single research topic on the field paying attention to separative properties of synthesized material and also to the type of material—composite or functionalized. Based on this methodology, the main sections of the manuscript have been presented as 'Removal of heavy metals from water using cellulose acetate membranes' and 'Removal of pharmaceutics from water using cellulose acetate membranes', respectively, 'Removal of dyes from water using cellulose acetate membranes. The review especially presents materials or membrane materials based on cellulose acetate for water treatment. The term 'wastewater' which describes more complex systems with interferences was kept in the manuscript from original works previously published.

2. Cellulose Acetate Membranes in the Context of Circular Economy

The circular economy is a sustainable economic model that targets the reuse and recycling of products in order to reduce the consumption of natural resources and minimize waste creation. Currently, in the water treatment field, the economic model is mainly linear, with the filtering membranes being discarded once their water flux rates decrease under certain values or when the filtered water does not reach the desired quality parameters [41]. Considering that the annual membrane replacement percentage varies between 10 and 20% and the water purification technology is in continuous growth, the result is a non-stop accumulation of discarded filtration membranes, which are managed according to each country's environmental regulations, but most commonly end up in landfills [42].

In this context, in the field of water treatment, polymeric membranes play a crucial role. Their separation ability is still inferior in comparison with other high porosity adsorbents such as activated carbon obtained from biomass [43] or, for example, biochar derived from non-customized matamba fruit shell [44], but despite this, this fact presents the highest advantage of being used in continuous flux with minimum maintenance and easy replacement at end-life cycle [45,46]. Moreover, in the context of the circular economy, the type of polymer that is used for making membranes represents a big challenge. The most abundant polymer on earth is a naturally sourced one—cellulose [47]. However, cellulose is very difficult to manipulate in order to obtain membranes due to its solubility in a mixture of solvents, usually very toxic [48]. This is the main reason that cellulose derivatives are preferred, the most representative being nitrocellulose, cellulose acetate, carboxy-methylcellulose and carboxy-propyl-cellulose [49,50]. Among these, cellulose acetate is preferred due to its solubility in a wide range of polar aprotic solvents, which permits high versatility for membranes synthesis and also due to the advantage of multiple possibilities for functionalization given by the presence of acetyl groups and their multiple possibilities for a wide variety of reactions [51–54].

A solution to move the membrane industry towards a more circular economic model is represented by the use of biodegradable membrane materials and the improvement of membrane process performances in order to maintain them as long as possible within the value chain. Cellulose acetate is an appropriate candidate for the achievement of these goals since it is highly biodegradable both in soil and seawater by means of acetyl esterase and cellulase enzymes action, which convert it into environmentally neutral products such as water and carbon dioxide [55]. An issue related to the biodegradability of cellulose acetate is the lack of UV-light absorbing chromophores, leading to reduced photo-degradability under sunlight influence. Nevertheless, the incorporation of photoactive fillers, particularly TiO_2, within the membranes structure showed good results in terms of degradation enhancement under outdoor exposure, with the mention that the filler particles size should be comprised between 0.01 and 1 μm to render a more biodegradable material [56].

The chemistry of cellulose acetate allows for a variety of modification techniques to be performed in order to improve membrane properties and extend their lifespan. For example, the enhancement of a membrane's antifouling ability is one of the most effective techniques to extend its longevity. Studies showed that hydrophilic materials have a low fouling tendency, this behavior being related to the adsorption of water molecules on their surface which form a protective layer that prevents the retention of fouling agents [57]. Therefore, a strategy for the production of cellulose acetate membranes with high antifouling character is the incorporation of fillers such as metals (e.g., Ag, Au, Pt), metal oxides (e.g., ZnO, TiO_2 and SiO_2), metal-organic frameworks (e.g., ZIF-8), clay-based (e.g., montmorillonite, halloysite) or carbon-based (e.g., graphene oxide, nanodiamonds and carbon nanotubes) nanoparticles within the polymer matrix. Furthermore, by preventing surface fouling, these fillers can also improve mechanical, thermal and antibacterial properties [58]. Another strategy is based on the preparation of blended polymer membranes. Cellulose acetate was blended with natural and synthetic polymers such as chitosan [59], carboxymethyl cellulose [60], polyethersulfone [61], polyvinyl alcohol [62], polyethylene glycol [63] or polyurethane [64], in all cases a positive influence in membrane antifouling performances being observed.

Fouling occurs as a result of the accumulation of chemical species on the membrane surface and translates mainly into a decrease in the flow and filtration capacity [58,65]. Since CA membranes are used in all types of membrane processes, the fouling nature varies from organic and inorganic substances to biological or colloidal aggregate species. The main methods of avoiding these inconveniences consist of membrane modification, either by blending various particles or nano species in the polymer solution, thus resulting in composite membranes, or by the functionalization of the membrane surface. Metal oxides [66] or carbon nanotubes [67] have been proven to be effective in fouling prevention due to their ability to electrostatically charge the membrane surface. Moreover, increasing membrane hydrophilicity by functionalization with silane derivatives effectively prevents especially the biofouling phenomenon, this translating into multiple advantages in the water filtration processes [68].

One of the easiest methods of manipulating the separation properties of polymeric membranes is the use of surfactants as additives in the polymer solution [69]. Studies showed that the use of dimethyl-dioctodecil ammonium bromide, alkyl-benzyl-dimethyl ammonium chloride or N-dodecyl–pyridinium chloride as additives for cellulose acetate solutions led to increased porosity of the membranes active layer and significant increases in the retention of amino acids and proteins [70]. Halleb et al. [71] studied the effect of using non-ionic, cationic and anionic surfactants on the separation properties of cellulose acetate membranes used for reverse osmosis. The surfactants were added separately in the polymeric solution, thus studying the interactions between surfactant molecules and membrane surface. Although the flux values varied slightly, the membrane rejection capacity had a variation of up to 20% depending on the type of surfactant, the best result is obtained when using the non-ionic surfactant at a concentration of 100 mg/L. Furthermore, the use of surfactants to manipulate the morphology and separation properties of cellulose acetate membranes, other organic substances have proven similar effects. An example is represented by glycerol, which added to the polymer solution increases the porosity of the membrane support layer, thus improving the mechanical and separation properties of the active layer [72].

Apart from their filtering capacity, membranes can also be used as support for various water-purifying particles such as silver [73]. It was shown that silver nanoparticles provide the best antibacterial membrane performance but they are difficult to immobilize in the membrane structure [74]. A solution for this issue was provided by Rusen et al. which reported the synthesis of membranes based on cellulose acetate and silver nanoparticles-functionalized carbon nanotubes with strong antibacterial effects [75]. The membrane preparation process consisted in filtering a suspension of silver nanoparticles-functionalized carbon nanotubes through a commercial CA membrane, followed by the covering of both membrane surfaces with poly (methyl methacrylate) to ensure its stability. In this way, the loss of the nanostructured modification agents is avoided, regardless of the future filtering processes for which the membrane might be used.

The applications of CA membranes for reverse osmosis processes are relatively few, these being limited by the mechanical properties of this polymer. Moreover, for an effective reverse osmosis process, the use of polymers molecular with large molecular weight is required but the disadvantage is that these types of polymers are difficult to process in order to manufacture membranes [76]. A solution is represented by the preparation of composite membranes to stiffen the polymer matrix and at the same time to improve the separation properties. For desalination processes, cellulose acetate membranes are usually composited with fillers that have a high salts absorption capacity, the most frequently used being carbon nanotubes and graphene [77–80]. A more accessible type of fillers for this application is represented by zeolites. For example, the use of zeolitic imidazolate framework (ZIF-8) particles in cellulose acetate membranes led to reverse flow yields of up to 2.84 g/m^2 h [81]. The mechanical and structural properties necessary for use in desalination processes can also be induced by the preparation of polymer–polymer composite membranes. Cellulose acetate/polyether sulfone mixed matrix membranes enriched with TiO_2 nanoparticles showed salt rejection properties of up to 76.8%, the presence of TiO_2 particles significantly improving the flow value through the composite membrane [82]. Other wastewater remediation processes using cellulose acetate membranes aimed at separating oil–water emulsions especially in the oil industry [83–85] or at combining the separation properties of these systems with an antibacterial action [86] for membranes obtained by electrospinning.

3. Cellulose Acetate Membranes and Materials for Removal of Heavy Metals, Pharmaceutics and Dyes from Water

3.1. Removal of Heavy Metals from Water Using Cellulose Acetate Membranes

Heavy metals are present in the environment due to the residues generated by the electronic industry and also from products such as batteries or fuels. They have the ability to bioaccumulation and are toxic even in small quantities [87]. One of the most harmful heavy metals are hexavalent chromium (Cr(VI)) because it can easily bio accumulate in drinking water due to improper discharge of chrome-based dyes, paints and alloys used in the textile, metallurgical or chemical industries [88]. In this context, Wen et al. designed electrospun membranes based on cellulose acetate and TiO_2 nanoparticles (Figure 3). The composite membranes were further surface modified with polydopamine and grafted with polyethyleneimine to improve the compatibility between the polymeric fibers and the TiO_2 nanoparticles. Adsorption tests performed at 25 °C, using a pH 2 Cr(VI) solution showed that the membranes not only retain hexavalent chromium with a yield of 72% but also have the ability to reduce it to non-toxic trivalent chromium (Cr(III)) [89].

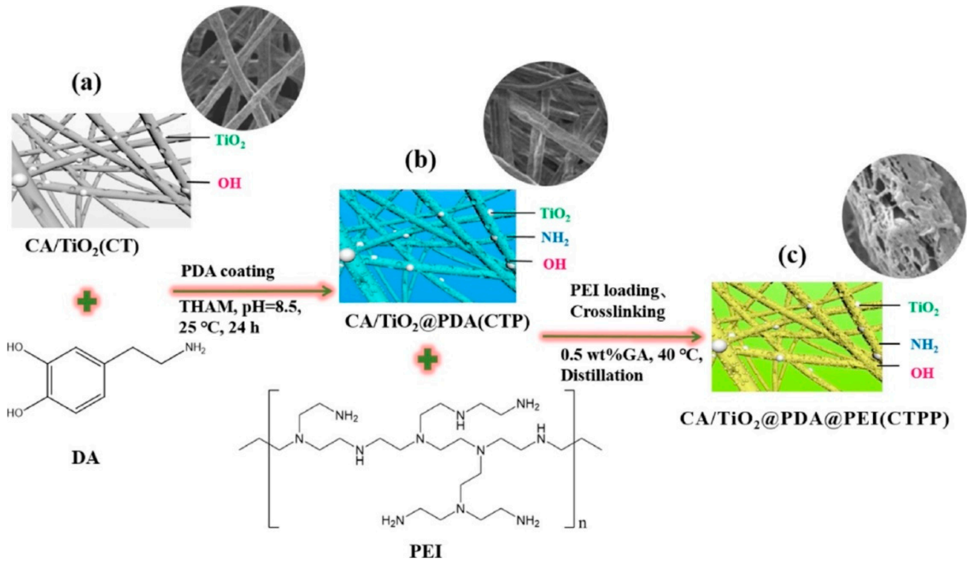

Figure 3. Schematic representations showing the fabrication procedures of the CA/TiO_2-PDA-PEI (CTPP) fibrous membranes [89]. The acronyms are CA—cellulose acetate, DA—dopamine, PDA—polydopamine, PEI—polyethylene imine, and the authors of original work notated with CT the prepared CA/TiO_2 fibrous membranes (**a**), with CTP the prepared CA/TiO_2@PDA fibrous membranes with in situ polymerized dopamine (**b**) and with CTPP the final obtained membrane with grafted PEI onto CA/TiO_2@PDA (**c**).

Gadolinium is another frequently encountered heavy metal. It is employed in the form of salts (e.g., gadolinium nitrate) as a contrast agent in medical imaging or as neutron poison for nuclear reactions, being currently the main moderator used to control processes in nuclear reactors [90,91]. Although the use of gadolinium derivatives is strictly regulated and controlled, accidental leakage may occur and, in this case, it must be quickly removed in order to avoid its spread. The most used gadolinium removal methods are the ones that imply ion exchangers [92]. Nevertheless, ion exchangers are very expensive and their use in environmental decontamination raises technology and logistics issues. A competitive alternative to ion exchangers is represented by cellulose acetate membranes functionalized with crown ethers have the ability to retain Gd(III) ions from aqueous solutions. The preparation of these membranes involved partial hydrolysis in the presence of NaOH to increase the number of available reactive -OH groups, and functionalization with aminopropyl-triethoxysilane (APTES) to obtain free amino groups for further binding of glutaraldehyde (GA). Next, 4′-aminobenzo-15-crown-5-ether (AB15C5) was immobilized on the glutaraldehyde ends, thus resulting functionalized membranes that showed an ability to complex Gd(III) ions with a retention efficiency of up to 86% [93]. AB15C5-functionalized membranes were also proven to be adequate for the retention of Ca^{2+} ions from aqueous solutions, thus opening multiple potential applications in the biomedical field, particularly for osseointegration [94–96].

The same research team developed functionalized cellulose acetate membranes that provide an evaluation of the Gd(III) separation process by changing their color from blue to pink as the retention of the metallic ions occurs. The membrane synthesis steps were similar to the previous studies—partial hydrolysis and successive functionalization with APTES and GA followed by the immobilization of calmagite, a complexometric indicator used to identify the presence of metallic cations aqueous solutions [97]. Calmagite-functionalized membranes open up new horizons in the field of polymer membranes-based environmental decontamination, this new generation of materials removing the necessity of time-consuming analysis to see if the membranes successfully separated the species of interest. Another category of highly effective heavy metals retentive agents are nanostructured carbon-based molecules such as carbon nanotubes or graphenes [98].

Their retention mechanism is based on the physical adsorption of the metal cations via electrostatic interactions with the delocalized electrons at the surface of the carbonaceous nanostructures [99,100].

The efficiency of the heavy metals separation process also depends on the morphological characteristics and homogeneity of the membrane material. These, in turn, are influenced by the parameters of the coagulation process such as type of solvent and non-solvent, coagulation bath temperature, or polymer concentration, and especially by the ultrasonication step used to disperse the nanostructured fillers in the polymer solution. If the ultrasonication time is too long, it leads to chemical modification of the nanostructures, affecting both the mechanical and thermal properties of the composite membranes, as well as the homogeneity of the final material. A too short ultrasonication time leads to the formation of membranes with areas of agglomerated fillers and low efficiency of the filtration process, respectively [101]. Therefore, an optimal ultrasonication time must be calculated, either by molecular modeling according to the characteristics of the filler used, or by experiments at different ultrasonication times and subsequent characterization of the obtained membranes.

Other effective absorbents that can be used in the preparation of cellulose acetate-based composite membranes are hydroxyapatite (HA) and its derivatives [12]. Due to its high porosity, as well as the reduced costs compared to other filler materials, hydroxyapatite can be used for the retention of different contaminants including organic molecules and heavy metals. Moreover, hydroxyapatite is a sustainable resource with a natural origin and can be easily obtained from the bone tissue of animals [38,102]. Another cost-effective adsorbent is represented by silica clay derivatives, used either as such or in the form of nanowires, the latter significantly improving the mechanical and thermal properties of the composite membranes [103]. Cellulose acetate/montmorillonite composite membranes were studied for the retention of copper ions. The adsorption tests were performed by placing 100 mg of the composite membrane in an aqueous Cu^{2+} solution with a concentration of 100 mg/L for 24 h at room temperature. Results showed that the composite membrane retained up to 60,272 mg of Cu^{2+} per membrane when a concentration of 5% wt montmorillonite relative to the polymer content was used [104]. For increased compatibility with CA, the montmorillonite particles were initially modified with chitosan, acetic acid or sodium dodecyl sulfonates. The best compatibility was obtained in the case of chitosan-modified particles, for which the highest value of static absorption was obtained at 10 h. Moreover, the membrane could be regenerated in the presence of tetra acetic acid/diamino ethylene, thus ensuring the scalability of the entire process due to the use of three regenerable components. ZnO particles obtained by precipitation and embedded in cellulose acetate membranes (dispersion in the polymer solution, followed by membrane formation through immersion precipitation in distilled water) were also proven to be effective in retaining lead (97% retention efficiency) from simulated wastewater of the battery industry [105]. Ideal in such a use is that the oxide particles be situated in the micrometer dimension area so that they are not lost during the membrane coagulation process or in the filtering process [106].

3.2. Removal of Pharmaceutics from Water Using Cellulose Acetate Membranes

Until 3–4 decades ago, the concentration of organic micropollutants in the environment was not significant enough to raise problems. However, nowadays they represent a challenge, especially in terms of wastewater treatment. Pharmaceutical active compounds or endocrine disruptive chemicals come mainly as a result of activities in the biomedical (e.g., hospitals and pharmaceuticals production facilities) and agricultural (e.g., poultry farms) fields, the waste discharge regulations being established much later compared to other environmental pollutants [107]. A solution to this issue was proposed by Pandele et al. that developed an innovative method of reactive tetracycline retention using functionalized cellulose acetate membranes [108]. In this study, commercial CA membranes were partially hydrolyzed in the presence of NaOH to increase the number of available reactive -OH groups and functionalized with aminopropyl triethoxysilane (APTES) to obtain free amino groups for the subsequent binding of cyanuric chloride (Figure 4). The reactive separation tests were performed by passing a synthetic tetracycline solution through the membrane using a dead-end filtration setup. The antibiotic solution was previously heated at 60 °C to facilitate the reaction between a chlorine atom in cyanuric chloride and the amino group from tetracycline. Studies showed that the adsorption capacity increased from 16% to 88% for the cyanuric chloride-functionalized CA membranes compared to the neat ones.

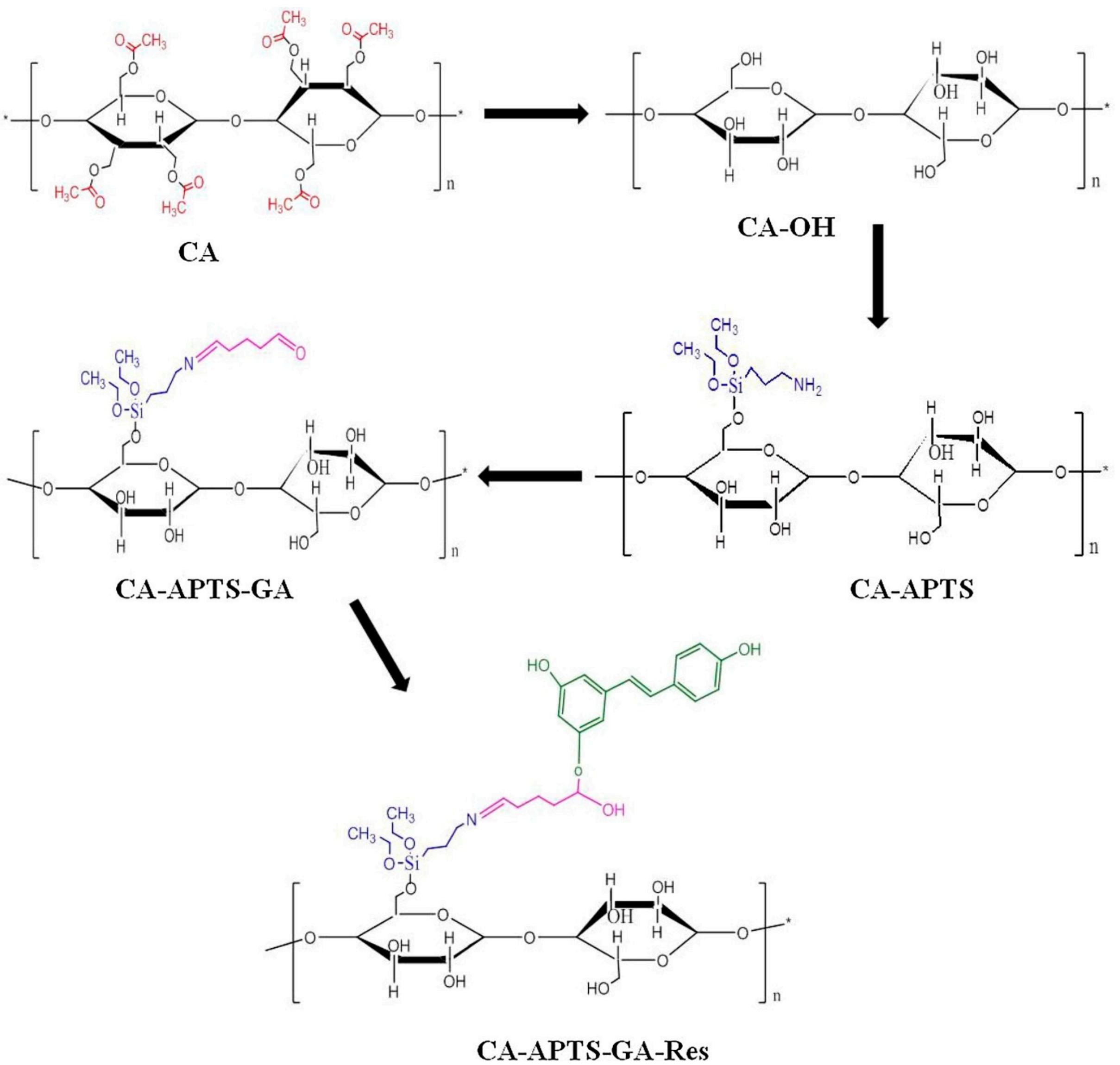

Figure 4. The modification protocol of CA membrane surface with cyanuric chloride and TYC bonding. The scheme is simplified and illustrates only the mechanism of the CA functionalization [108].

State-of-the-art solutions for the removal of organic micropollutants involve enzymatic degradation techniques. For example, the immobilization of laccase in the structure of a cellulose acetate membrane resulted in high removal efficiency (58%) of diclofenac and also the total degradation of the retained drug retained [109]. These materials are, however, limited by the very presence of the enzyme in the membrane structure. The modified membrane must be preserved at temperatures that do not exceed 4 °C, for a period of maximum two weeks, after this period the enzymatic activity decreasing to a value that no longer allows the drug degradation process to take place. Composite cellulose acetate/layered double hydroxide (LDH) membranes were also successfully used for the removal of diclofenac sodium and tetracycline from water. The membranes showed a drug retention efficiency of 20 and 23%, respectively, after four cycles of recirculation. Moreover, the water flow through these membranes was 529 $L/m^2\ h^{-1}$, allowing an improvement of the filter caps by multiple recirculation [110].

Another effective procedure for the purification of water contaminated with organic micropollutants such as dyes, pharmaceuticals or pesticides is based on Fenton degradation. The process is conditioned by the presence of catalysts in the membranes structure, the most common one being titanium dioxide. However, TiO_2 immobilization in composite membranes is difficult because of its small size and there is a great risk of losses especially during the membrane coagulation process. It was shown that the decoration of nanostructures such as carbon nanotubes with TiO_2 nanoparticles, followed by the synthesis of composite membranes, brings stability to the overall system [111] and the resulting materials have good results when they are used for the degradation of ampicillin and erythromycin. Complex catalysts are more expensive but offer better results both in terms of synthesized membranes quality and pollutants degradation process performance. A recent study performed by Wang et al. described the synthesis of a complex catalyst based on Fe(III) starting from a Schiff base (N,N′-bis-(2-hydroxy-1-naphthalidehydene)-(1R,2R)-cyclohexane-1,2-diamines(L)) mixed with $Fe(NO_3)_3{\cdot}9H_2O$ and NaN_3 in dimethylformamide and filtered to obtain crystals of Fe-complex (Fe(L)(N_3)(DMF), which were later incorporated into microfiltration cellulose acetate membrane membranes (Figure 5) [112]. In the presence of low concentrations of H_2O_2, the CA-Fe complex system degraded basic fuchsin, methylene blue and sulfadiazine with an efficiency of 100%, 93.4% and 95.7% after irradiation for 60 min. Moreover, the membranes kept their catalytic performance after four successive degradation cycles.

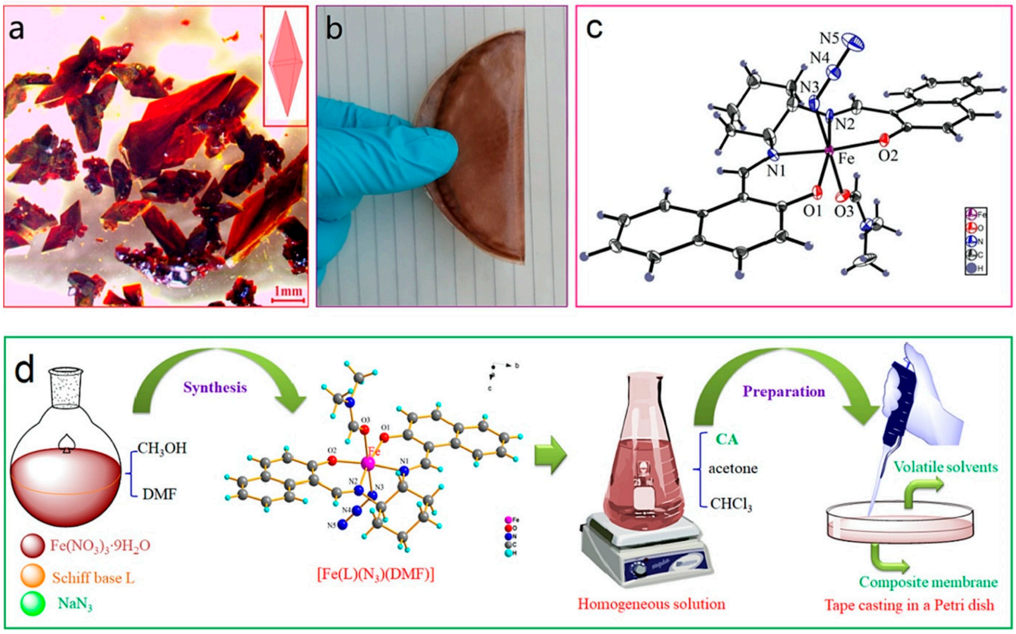

Figure 5. (**a**) Single-crystal photomicrograph of [Fe(L)(N_3)(DMF)], (**b**) photograph of the prepared Fe-complex/CA composite membrane, (**c**) crystal structure of [Fe(L)(N_3)(DMF)], and (**d**) the preparation process of the Fe-complex/CA composite membrane [112].

Complex catalytic systems can also be obtained by the combination of two basic catalysts. Furthermore, by being cost-effective, this technique offers superior efficiency of the photocatalytic degradation process and at the same decreases the energy requirements. In this context, Mofokeng et al. designed hybrid catalysts based on CuO/TiO_2 immobilized on graphitic carbon nitride and incorporated them into ultrafiltration cellulose acetate membranes. The presence of graphitic carbon nitride has a fixating role for the two oxides with catalytic activity, thus providing stability to the entire system, as well as a separative role, due to the porosity it possesses having the ability to retain other polluting species from water. The materials were used for the degradation of ketoprofen and showed a process efficiency of up to 78% [113].

3.3. Removal of Dyes from Water Using Cellulose Acetate Membranes

One of the major classes of water pollutants is represented by dyes which are responsible for almost 20% of the entire number of wastewaters globally [114]. Coming both from household activities (e.g., washing of clothes), as well as from the textile or cleaning industry, they are molecules with stable organic structures, which usually do not degrade in the environment. It is estimated that annually over 700,000 tons of dyes-related residues are generated [115]. More than that, dye retention on filtration membranes is difficult because of their small molecular, the most effective membrane separation processes for their removal being ultrafiltration or even nanofiltration. Cellulose acetate membranes showed good results in dye retention processes, either as composite membranes [116] or as functionalized membranes [117]. An innovative technique for surface modification of cellulose acetate membranes in order to improve their dye retention ability was proposed by Ong et al. [118]. The surface modification was achieved via filtration of aqueous graphene oxide (GO) dispersion through commercial cellulose acetate membranes, followed by the filtration of a polyethylene imine solution to obtain an active surface bilayer which due to the dual electrostatic charging—negative from graphene oxide and positive from polyethylene imine—has the capacity to retain a wide range of dyes. Methylene Blue and Eryochrome Black T were retained with an effectiveness of 80% and 90%, respectively. The results obtained were clearly superior compared to standard CA membranes or even to CA-GO composite membranes where the retention efficiency is influenced by the porosity of the active layer, hydrodynamic limitations or the access of dye molecules to the GO particles in the membrane structure [117]. Activated carbon is also a proper filler for the preparation of composite membranes for dye retention as it can significantly improve their separation capacity due to its highly absorbent properties [119,120]. Nano-activated carbon embedded in cellulose acetate membranes led to a significant increase in the retention ability of methylene blue (70%) compared to neat CA membrane that presented only a 30% retention ability [121].

Functionalization is an important tool in the development of membranes for the separation of organic compounds or even mixtures of such compounds with other natural species. In a recent study, Vatanpour et al. prepared cellulose acetate-based nanofiltration (NF) membranes modified by sulfonic acid-functionalized dendrimer-grafted cellulose (Cel-dend-SO_3H) to improve the separation and filtration properties (Figure 6). The functionalized membranes were tested for the retention of organic (Rose Bengal, Reactive Blue 50, Azithromycin) and inorganic (Pb(II), As(V), Na_2SO_4 and NaCl) contaminants [122]. After the modification, the membranes presented superior properties—the water flux reached a value of 82.7 $L/m^2\ h^{-1}$ compared to 30.8 $L/m^2\ h^{-1}$ for the neat membrane and the separation yield was increased by 2.1%, 8.2% and 5.3% for Rose Bengal, Reactive Blue 50 and Azithromycin, respectively. Moreover, heavy metals and salt retention ranged from 80% in the bare cellulose acetate membranes to 95% in the functionalized ones.

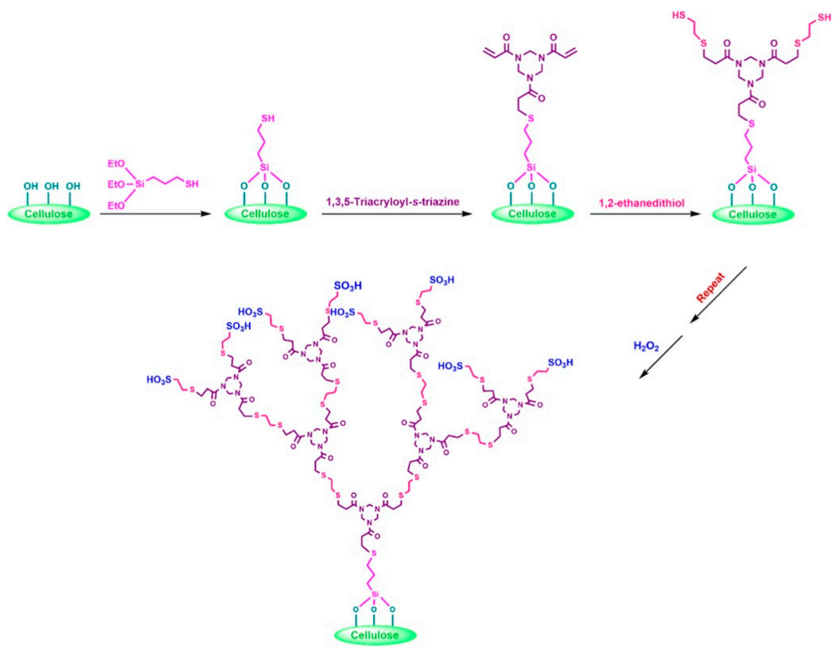

Figure 6. Schematic of synthesis steps of sulfonic acid—functionalized dendrimer-grafted cellulose [122].

Composite membranes also showed good results for dye removal from wastewaters, ZnO is one of the most effective fillers used for photocatalytic degradation of dye molecules [123,124]. ZnO nanorods obtained by solvothermal synthesis, starting from hexamethylenetetramine and $Zn(NO_3)_2$, were dispersed in a cellulose acetate solution and the membrane synthesis was realized by phase inversion [125]. The resulting membranes were used for the photocatalytic degradation of methylene blue with an efficiency of up to 30% for only 1% ZnO content, relative to the polymer mass. ZnO also increased the hydrophobicity of the CA membrane, thus decreasing the fouling effect and increasing the porosity of the active layer [66]. Although the water flux of ZnO composites tends to decrease compared to the control membrane, the efficiency of the filtration process is still higher [126]. Abu-Dalo et al. conducted a complex study on CA-ZnO composite membranes for methylene blue degradation. The fillers were either in the shape of nanoparticles or nanowires to investigate the influence of the shape and size of the nanostructures on the membrane performances. Compared to the neat membrane, both types of composites exhibited enhanced photocatalytic activity and degradation of methylene blue under UV-light and sunlight irradiation and inhibited the development of bacteria on the materials surface [123]. Other studies proposed hematite (α- Fe_2O_3) particles as effective fillers for the increase of the dye retention capacity of cellulose acetate membranes. The CA/α- Fe_2O_3 were tested for adsorption of hydrolyzed Reactive Black 5 from simulated wastewaters and showed an excellent absorption capacity of 105.26 mg/g^{-1} [127].

4. Conclusions

Cellulose acetate-based membranes or materials provide an excellent sustainable source for applications in the field of water treatment due to their natural source and chemical properties. Functionalized cellulose acetate-based membranes or materials can be successfully used for the retention of antibiotics, heavy metals or dyes, depending on the functional molecules used and their chemical behavior. Molecules with the ability to complex cations increase the capacity of these materials to retain heavy metals. Composite materials metal oxides can be used for the photodegradation of organic compounds, while composite materials with graphene or carbon nanotubes present high adsorption capacity at the surface of these nanofillers.

5. Future Perspectives

The use on an industrial scale of cellulose acetate for the preparation of membranes for filtration processes is limited primarily by its mechanical resistance and secondly by its chemical properties. Both inconveniences can be solved either by designing composite membranes or by functionalization of the membranes' surface.

From the composite membranes' point of view, it is very unlikely that the chemical species that provide the best properties (e.g., graphene or carbon nanotubes) will become sufficiently cheap and accessible so that large quantities of fillers can be produced and used in desalination processes. However, if water scarcity will continue to grow, it is possible that in the future such composite membranes will be produced for particular situations, such as solving a major environmental problem or ensuring a critical mass of water that can be recirculated and reused in a closed system. Therefore, a great challenge will be finding fillers that are sufficiently accessible and also considerably improve the separation process efficiency and the physical properties of the membrane. Such fillers should have the ability to form chemical bonds with the polymer matrix to ensure system stability. Another important aspect is their provenience source which should be renewable or recyclable in order to reach the current goals of raw material reuse and to minimize the impact on the environment. Zeolites or modified silica clay could constitute a viable alternative from these points of view because even by applying successive steps of chemical modification to increase their compatibility with the polymer matrix their environmental impact is still minimum. Moreover, from the point of view of retention performance, even in the case of organic molecules with low or medium molecular weight, these fillers would be ideal candidates.

Surface functionalization still represents a challenge owing to technological issues. For example, a functionalization reaction with silanes that can proceed very easily in a research laboratory raises problems in an industrial context because, currently, there are no equipment or workflows that ensure adequate conditions for the functionalization of membranes with large surfaces. Even if such technologies were developed, the manufacturing cost of such membranes would be very high, thus making the approach unfeasible.

Despite its limitations, cellulose acetate remains a much more accessible and environmentally friendly alternative for many of the technical polymers used to obtain membranes, but as more complex types of separations will be required, the use of CA membranes could become progressively restrictive. In the current context, it can be stated that it is easier to maintain the clean water that is still available than to develop complex materials and processes for water purification. If the natural water resources will continue to be damaged at the same pace, it is estimated that drinking water will become a very expensive product in 20–30 years, and the costs of water for agriculture or domestic activities will be a lot higher than the ones of energetic resources.

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