

Chapter 2

Natural Composite Membranes for Water Remediation: Toward a Sustainable Tomorrow

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Abstract Natural composites as green membranes have shown great potential in water remediation. These membranes combine merits from both natural polymer and inorganic or organic additives. Natural polymers are biodegradable, non-toxic and offer flexibility for design purposes. Incorporation of additives can enhance the mechanical and thermal properties or impart antibacterial and catalytic properties to the composite. This chapter provides an overview of the different types of natural polymer composite membranes and their functions. It also highlights the recent development of cellulose, chitosan, and natural rubber composite-based membranes in water treatment technologies between 2010 and 2015.

Keywords Natural polymer • Membrane • Composite • Additive • Water treatment

2.1 Introduction

The global population has increased from 5.3 billion in 1990 to 7.3 billion in 2015 [1]. With this increase, there has been a race toward rapid industrialization to provide a so-called better quality of living. Sadly, this has caused a rise in both air and water pollution. Numerous measures have been taken to curb the extent of toxic waste especially in water resources, as water is one of the fundamental essentials in our everyday life. Although the numbers have decreased over the years, 663 million people worldwide still lack improved drinking water resources, while 159 million people still use surface water [1].

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In recent years, the development of membrane technology has geared up as a means to overcome water pollution effectively. Statistics show that membrane technologies contribute up to 53 % of the total world processes for clean water production [2]. The increasing demand in membrane technology is mainly due to their features itself as well as the ability to apply them in sustainable industrial designs. Ideally, membranes should have characteristics such as increased life span, good mechanical, thermal, and chemical stability, low cost, and minimum maintenance. The use of membranes also enables the improvement of industrial design whereby less land space is required for the setting up of various processes, energy consumption is low, and no additional chemical is needed when compared to conventional technologies. This renders membranes as an economical technology with potential in various fields such as separation, filtration, and catalysis for water treatment.

Membranes have been used for water treatment for more than 45 years. A wide range of materials are available for the fabrication of membranes. These materials can generally be grouped into ceramic-based and polymeric-based membranes. Ceramic-based membranes are popular as they are thermally and chemically more stable, have high porosity, and have a longer life span. Even so, they are also more expensive and brittle. Polymer-based membranes on the other hand offer flexibility in design, are cheaper, and can remove dissolved ions and organics more efficiently [3]. Nevertheless, they also have some disadvantages including high hydrophobicity, exposure to biofouling, low fluxes, and low mechanical strength. We realize that there is an abundance of literatures on both ceramic- and polymeric-based membranes [4–8]. Particularly, recent reviews on polymer nanocomposites for membrane applications have emerged [9, 10]. The majority of these reviews are focused on synthetic polymers. Hardly any reviews related to natural polymer composite membranes can be found in the literature [11]. As such, this chapter has been organized to give the readers an overview of the different types of natural polymer composite membranes and their functions. This chapter highlights the application of interesting cellulose-, chitosan-, and natural rubber-based composite membranes in sustainable technologies between 2010 and 2015.

2.2 Natural Composite Membranes

The interest in natural polymers has escalated in recent years as these materials are biodegradable and non-toxic. It is an alternative to petroleum-based polymers which, although has widespread application, has depleted drastically while causing severe environmental and health problems. According to John and Thomas [12], natural polymers can be categorized into two main classes. These are polymers which are readily available in living organisms as well as those which originate from renewable resources but have to be polymerized. The earlier type includes cellulose and protein, while examples of the later are lactic acids and triglycerides. As membranes, polymers such as cellulose, chitin, and chitosan are commonly

used. However, other polymers such as gum and alginate have also attracted interest. Mostly, these polymers are rarely used solely. The main reason being that by itself, these polymers are unable to meet the specific requirements required to fabricate effective membranes. For instance, pure chitin is brittle, has low porosity, and low chemical affinity [13]. Cellulose is more widely used as membranes. The suitability of this natural polymer for membrane applications lies in the fact that they are cost-effective, hydrophilic, semipermeable, porous, offer good transport characteristics, and has film-forming ability. Even so, cellulose membranes also suffer from poor chemical and thermal resistances and lack an abundance of reactive functional groups, inferior mechanical strength, lower fluxes, and fouling issues. Throughout the years, there have been continued efforts to improve natural-based membranes' performance from different aspects—material modifications, material processing, and module's design. In terms of material modifications, the various shortcomings of these renewable polymers can be addressed by (1) combining a polymer or inorganic layer with a natural polymer or (2) incorporating an inorganic/organic additive into the natural polymer. Such modifications of the polymers for membrane technology are critical in order to develop high-performance membranes. Considering the nature of natural composite membranes, we define natural composite membrane as a physical barrier primarily made from green materials that create an interface for mass transfer and/or reactions between two phases. It can be inert or catalytically active depending on its composition.

Modification of natural polymers by combination with another polymer is one of the most popular methods for the preparation of natural membranes. Polymer blending between a synthetic polymer and a natural polymer has frequently been investigated. Prakash et al. [14] highlighted the use of chitosan and nylon 6 blends as membranes for the removal of copper and cadmium ions from synthetic wastewater. In contrast, El-Gendi et al. [15] used blends of these polymers for water desalting purposes. However, as a route toward sustainable technologies, the development of membranes composed of only blended natural polymers, such as natural rubber and chitosan [16], chitin and cellulose [13] or N, O-carboxymethyl chitosan and cellulose [17], has been reported. Blending chitin with cellulose is advantageous for adsorption of heavy metals as it combines the porosity and chemical affinity of cellulose with the excellent binding forces of chitin toward heavy metals. The polymers complement each other resulting in a porous membrane with better uptake capacity of heavy metals due to the availability of acetyl groups from chitin [13].

Grafting is another alternative to alter the properties of a polymer with another. This method allows the introduction of new functional groups which among other purposes can inhibit dissolution of a hydrophilic polymer during the treatment process and additionally increase the number of adsorption sites [18]. An interesting method to graft chitosan to another polymer was presented by Mansourpanah and coworkers. In their work, polyethersulfone (PES) membranes coated with

chitosan-grafted acrylamide were developed using a microwave as the grafting agent [19]. The microwave generates radicals at O and N atoms by breaking the bonds of O–H and N–H of chitosan. This then leads to grafting or graft polymerization.

Addition of inorganic/organic additives into natural polymers has received less attention when compared to modification via polymer–polymer blending or grafting. Generally, natural polymer composites are a material formed through a combination of polymer as the continuous phase (called the matrix) and additive which makes the dispersed phase. It can also be defined as a multilayer or combination of organic and inorganic phases. The combination of polymer and additive affords a multifunctional material which adopts properties of the respective constituents. When discussing natural polymer composites, the natural polymer can act as either or both the matrix or dispersed phase. An example is the incorporation of nanochitin whiskers (NCW) in poly(vinylidene fluoride) (PVDF) membranes. The NCW improve not only the mechanical strength of the membrane but also the water permeability and antifouling properties [20]. Addition of the NCW enhances the hydrophilicity properties of PVDF which is originally hydrophobic. Another work which discusses the function of natural polymer as dispersed phase is found elsewhere [21]. Further discussions highlighting the use of natural polymers as the matrix for the formation of membranes are presented in the following sections. A summary of various inorganic–organic membranes reported between 2010 and 2015 is presented in Table 2.1.

2.3 Types and Shapes of Natural Composite Membranes

Natural composite membranes can be divided into two major groups, which are organic–organic and inorganic–organic membranes, as in Fig. 2.1. Various types of membranes can be obtained depending on the fabrication techniques employed. As such, organic–organic membranes can further be segmented according to thin-film composites and blends. This is shown in Fig. 2.2a, b, respectively. Thin-film composites refer to membranes that have a bi- or multilayer structure. In contrast, membranes formed from polymer blends have monolayer structures. Both the thin-film and blend composites can be achieved by chemical or physical means. Blend membranes were formed by Almaria and coworkers from poly(vinyl alcohol) (PVA) and sago starch. The blend was cast in a monolayer form and used for the recovery of ethyl acetate from water [90]. Thin-film composites may be composed of several layers, formed from a combination of separate polymers, grafted polymers and/or polymer blends. The blends include reactive and non-reactive polymers. Chen et al. [91] described the fabrication of a thin-film polymer composite via grafting whereby polyacrylonitrile (PAN) was grafted to cellulose acetate to form the so-called layers. In contrast, the thin-film composites can be accomplished

Table 2.1 Summary of natural polymer composite membranes

Natural polymer matrix	Additives	Type	Function	Application	Refs.
Chitosan	Clay	TFC	Filtration	Removal of Hg(II) and As(III)	[22]
	TiO ₂ /glass plates	TFC	Adsorption/catalysis	Removal of Reactive Red 4 dye	[23]
	Mesoporous carbon particles	MM	Adsorption	Adsorption of fuchsin dye	[24]
	Fe ₃ O ₄ NPs	MM	Catalysis	Degradation of RB 19 dye	[25]
	Cobalt phthalocyanine	TFC	Catalysis	Degradation of rhodamine B	[26]
	MMT	MM	Adsorption/filtration	Removal of Bezaktiv Orange V-3R dye	[27]
Chitosan/PVA	Laccase-MWCNT	MM	Catalysis	Degradation of diclofenac	[28]
	Laccase	MM	Catalysis	Removal of 2, 4-dichlorophenol	[29]
	NH ₂ -functionalized MWCNT	MM	Adsorption	Removal of Cu(II)	[30]
	CNT	MM	Adsorption	Removal of total dissolved solids	[31]
Chitosan/cellulose	Ag NPs	MM	Antimicrobial	Anti-biofouling	[32]
	Polyacrylic acid-Ag NPs	MM	Antimicrobial	Anti-biofouling	[33]
	Dithizone	TFC	Adsorption	Adsorption of lead	[34]
	5,10,15,20-Tetrakis (1-methyl-4-pyridinio) porphyrin tetra (p-toluenesulfonate)	TFC	Adsorption	Removal of cadmium	[35]

(continued)

Table 2.1 (continued)

Natural polymer matrix	Additives	Type	Function	Application	Refs.
Chitosan/polyacrylonitrile	Amine-Fe ₃ O ₄	MM	Adsorption	Removal of humic acid	[36]
Chitosan/polyethersulfone	Fe ₃ O ₄	MM	Filtration/antimicrobial	Removal of Direct Red 16 dye	[37]
Chitosan/polyamide	Graphene oxide	TFC	Antimicrobial	Antifouling	[38]
Cellulose	CuO NPs	MM	Antimicrobial	Disinfection of water	[39]
	TiO ₂ nanothorn	TFC	Filtration/catalysis	Removal of MB and humic acid	[40]
	Dendrimer-Ag	MM	Catalysis/antimicrobial	Removal of rhodamine B/disinfection of water	[41]
Oxidized cellulose	Cu NPs	MM	Catalysis	Degradation of p-nitrophenol	[42]
Regenerated cellulose	TiO ₂	MM	Catalysis	Degradation of phenol	[43]
	Quaternary ammonium salt, amino alkyl		Antimicrobial/filtration	Anti-biofouling	[44]
Regenerated cellulose/polydopamine	SiO ₂	MI	Adsorption/filtration	Removal of artemisinin	[45]
Cellulose/PVC	Fe ₃ O ₄ NPs	MM	Adsorption/filtration	Removal of lead	[46]
Cellulose acetate	SDS	TFC	Filtration	Rejection of pesticides	[47]
	L-dopa	TFC	Filtration	Antifouling	[48]
	POSS NPs	MM	Filtration	Salt rejection	[49]
	Alkyl derivative of resorcinarene	PI	Adsorption/filtration	Removal of Pb(II), Cd (II), and Zn(II)	[50]
	Iron NPs	MM	Filtration	Rejection of phosphates and organic pollutants	[51]

(continued)

Table 2.1 (continued)

Natural polymer matrix	Additives	Type	Function	Application	Refs.
	TiO ₂	TFC	Filtration	Separation of chlorine and turbidity	[52]
	MWCNTs	MM	Filtration	Salt rejection	[53]
	Resorcinarene derivatives	PI	Filtration	Separation of Zn(II) and Cd(II)	[54]
	Ag NPs	MM	Filtration	Anti-biofouling	[55]
	MSG	MM	Filtration	Rejection of solute	[56]
	ZnO	TFC	Antimicrobial/adsorption	Salt rejection, anti-biofouling	[57]
	SPEEK-bentonite	TFC	Filtration	Daily wastewater treatment	[58]
	Modified coal	MM	Filtration	Separation of solute	[59]
	(BMIM)Cl	MI	Filtration/adsorption	Removal of salicylic acid	[60]
	CNT	MM	Filtration	Salt rejection	[61]
	Organo-MMT	MM	Filtration	Removal of humic acid	[62]
	TiO ₂ /ZnO	TFC	Filtration/catalysis/antimicrobial	Removal of humic acid/antifouling	[63]
	ZnO	MM	Catalysis	Degradation of rhodamine B	[64]
	Ag/TiO ₂ , Au/TiO ₂	MM	Catalysis	Degradation of MB	[65]
	TiO ₂ /carbon	MM	Catalysis	Degradation of MO	[66]
	SrTiO ₃ /TiO ₂	TFC	Filtration/catalysis	Removal of acid orange 7	[67]

(continued)

Table 2.1 (continued)

Natural polymer matrix	Additives	Type	Function	Application	Refs.
	TiO ₂ /ZnO	MM	Catalysis	Degradation of rhodamine B	[68]
NH ₂ -functionalized cellulose acetate	SiO ₂ NPs	MM	Adsorption	Removal of Cr(VI) ions	[69]
Cellulose acetate/PEG-600	Ag	MM	Antimicrobial	Salt rejection/anti-biofouling	[70]
Cellulose acetate/PANI	Ag NPs	TFC	Filtration/antimicrobial	Salt rejection/anti-biofouling	[71]
Cellulose acetate/PANI	Phytic acid	MM	Adsorbent	Removal of Hg(II) and Cr(VI)	[72]
Cellulose acetate/PEG	SiO ₂	MM	Filtration	Salt rejection	[73]
Cellulose acetate/polyethersulfone	Bentonite	MM	Filtration	Car wash effluent treatment	[74]
Cellulose acetate/cellulose triacetate	Boehmite	MM	Filtration	Salt rejection	[75]
Cellulose triacetate	Modified ZnO	MM	Filtration	Separation of rhodamine B	[76]
	Aliquat 336	PI	Adsorption	Separation of acid violet 90 and acid yellow 127	[77]
	Cyphos	PI	Filtration/adsorption	Separation of Zn(II)	[78]
	Activated carbon (AC)	MM	Adsorption/filtration	Removal of uranium	[79]
	2-(10-carboxydecylsulfanyl) benzoic acid methyl monoester	PI	Filtration	Separation of Pb(II)	[80]
	Cyanex 923	PI	Adsorption/filtration	Removal of phenol	[81]

(continued)

Table 2.1 (continued)

Natural polymer matrix	Additives	Type	Function	Application	Refs.
	AC	MM	Filtration/adsorption	Removal of arsenic	[82]
	Iron-doped AC	MM	Filtration/adsorption	Removal of uranium	[83]
Carboxymethyl cellulase/polyelectrolyte complex	SiO ₂	MM	Adsorption	Separation of isopropanol	[84]
Hydroxyl ethyl cellulose/sodium alginate	Humic acid	MM	Adsorption	Adsorption of Cd(II)	[85]
	Humic acid	MM	Adsorption	Removal of MB and rhodamine B	[86]
Nitrocellulose	Polyvinyl-N-carbazole-CNTs	TFC	Antimicrobial	Anti-biofouling	[87]
ENR	Fe ₃ O ₄	MM	Adsorption	Removal of oil	[88]
ENR/PVC	TiO ₂	TFC	Catalysis	Degradation of MB	[89]

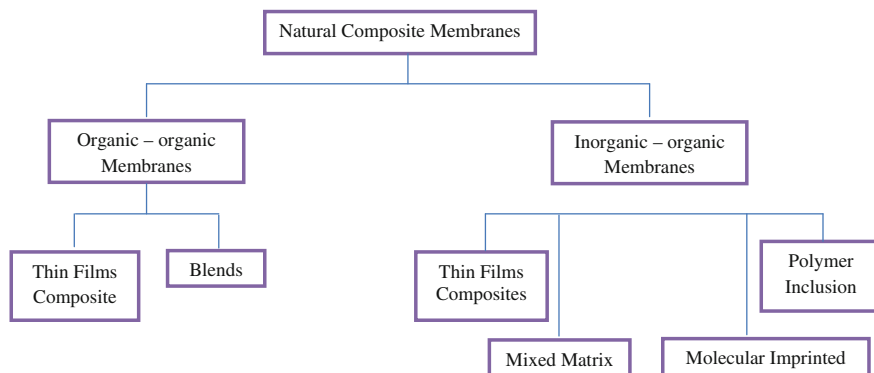


Fig. 2.1 The types of natural composite membranes

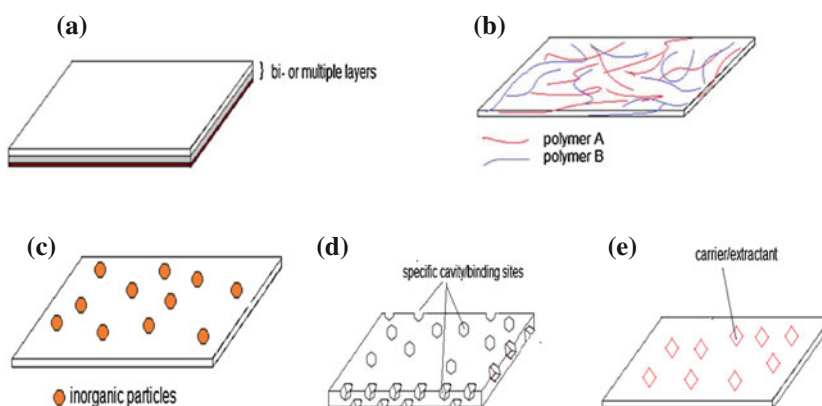


Fig. 2.2 Structures of various natural composite membranes: **a** thin-film composites, **b** blends, **c** mixed matrix, **d** molecular imprinted, and **e** polymer inclusion

physically by simple casting or spin coating techniques. An example of these kinds of membranes is the combination of a PAN layer which acts as a support with a cross-linked cellulose layer on top [92].

In contrast to organic–organic membranes, there exist four types of inorganic–organic membranes. In this case, the bi- or multilayer thin-film composites can be composed of layers of inorganic and organic materials. These arrangements can be fabricated by simple casting, spin coating, or impregnation/dip-coating technique. Thin-film composite membranes of ceramic and cellulose acetate layers were prepared using dip-coating technique [93]. Another example is the fabrication of a layer of PAN followed by a film of cellulose acetate with silver nanoparticles on top. The layer of silver nanoparticles functions as an antibacterial agent for

antifouling purposes, while CA plays the role of a stabilizer to control the dispersion and growth of the Ag particles. The PAN on the other hand acts as a filter for water. This shows that in this type of membrane, each layer has a specific role [71].

The mixed matrix membrane differs from thin-film composite in terms of, only one layer exists and it is usually composed of inorganic particles dispersed throughout a natural polymer matrix. Inorganic particles generally carry the role of improving certain properties of the polymer matrix. For instance, the water permeation and thermal stability of the cellulose acetate membrane can be greatly enhanced by incorporating TiO_2 nanoparticles [94].

Polymer inclusion membrane is also known as a liquid membrane. Generally, it consists of a polymer, plasticizer, and carrier. The most frequently used natural polymer for the formation of these membranes is cellulose triacetate. This is attributed to their characteristic which demonstrates good stability [95]. The carrier plays the most significant role in these types of membranes, as it facilitates the transport of matter for separation. Mainly, when natural polymers are employed, it has been applied for the separation of heavy metal ions [54, 78, 80]. However, some works have reported the use of this kind of natural membrane for the extraction or organic molecules such as phenol [81] and acid dyes [77].

Molecular imprinted membranes are natural polymers with additives (inorganic fillers, functional monomers, and ionic liquids [60]) designed to target specific substances. In other words, this type of membrane is tailor-made for the treatment of particular molecules in wastewater. Basically, the membranes are formed by polymerizing the polymer in the presence of a template. Upon formation, the templates are removed. These molecular imprinted membranes can stand-alone; however, inorganic fillers can add value to the membranes. For example, in the absence of inorganic filler such as TiO_2 , a calcium alginate-based molecular imprinted membrane is capable of removing methyl orange dye physically [96]. Even so, addition of TiO_2 improves the functionality of this membrane by allowing adsorption followed by the degradation of the methyl orange dye [97]. Other works have been conducted using SiO_2 as filler in cellulose-based molecular imprinted membranes. In this case, the SiO_2 imparts better mechanical strength to the membrane [45].

Natural polymer composite membranes are generally fabricated into three shapes: flat sheet, hollow fiber, and nanofibrous. These are shown in Fig. 2.3a–c. Flat sheet membranes are easily prepared, and the permeating substances can be extracted by using gravity flow without the aid of high-pressure technologies [98]. As compared to flat sheet membranes, both hollow fiber and nanofibrous membranes exert higher surface area per volume, making them more efficient adsorbents, filters, or catalysts. Hollow fiber membranes also enable very compact and high-packing-density systems which consume a small floor place. On the other hand, nanofibrous membranes have advantages of high porosity and charge density, good mechanical strength, and high flux permeability [99, 100].

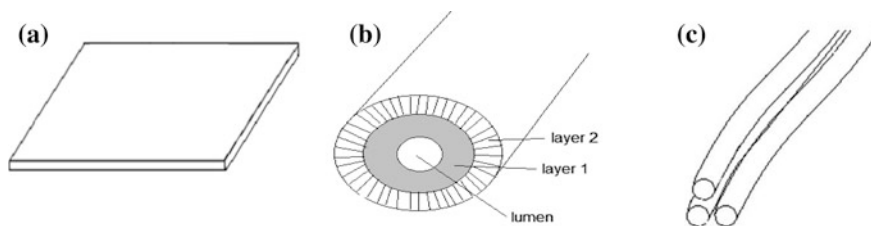


Fig. 2.3 Various shapes of natural composite membranes: **a** flat sheet, **b** hollow fiber, and **c** nanofibrous

2.4 Main Functions and Characteristics of Natural Composite Membranes

As natural polymer composite membranes can be either inert or catalytically active, the role of these membranes can be categorized based on the following areas:

(i) Filtration

This process can be further classified according to the pore size of the filter. This includes microfiltration, ultrafiltration, nanofiltration, and reverse and forward osmosis. A detailed summary on the various classes, their respective pore sizes, and the materials these filters are capable of removing has been given elsewhere [101].

(ii) Adsorption

This process involves the capture of substances by physical or chemical means. Physisorption is a reversible reaction that allows substance recovery possible, while the latter is not. Adsorption has been extensively applied for the removal of multivalent heavy metal ions, for example, Pb (II), Cd (II), and Cr (IV) [34, 35, 69]. Organic substances such as phenol, dyes, and artemisinin can also be removed and recovered by using molecular imprinted membranes with high selectivity.

(iv) Catalysis

In these membranes, metal or semiconductor nanoparticles are normally incorporated to serve as the active component (catalyst) for a certain catalytic reaction [44, 63, 65, 66]. When semiconductors such as TiO₂ or ZnO are employed, a light source (e.g., UV, sunlight) is needed to initiate the reaction. Thus far, the application of catalytic membranes is limited to the degradation of synthetic dyes and nitro aromatic compounds and photocatalytic antimicrobial purposes.

(iv) Antimicrobial/fouling

One of the biggest challenges of membranes in water treatment application is fouling or particularly biofouling. Fouling is the buildup of unwanted particulates onto a wetted surface. This layer of particulate tends to cause severe

loss in performance and reduces the life span of membranes. Furthermore, it results in high cleaning maintenance. Generally, there are three approaches to reduce the biofouling problems in a membrane:

1. Suppress the adhesion of biologic particulates onto the membrane;
2. Biocide leaching or toxic release;
3. Contact killing.

The first strategy involves the alteration of the surface hydrophilicity, roughness, or charges of the membranes. In contrast, the latter two strategies address the biofouling problems by incorporating inorganic species as the antimicrobial agent in the membranes. Silver nanoparticles, carbon nanotubes, oxide nanoparticles, and ammonium salts are some of the examples. Organic antimicrobial agents can also be employed. However, this is less favorable due to their poorer ability to withstand adverse processing conditions as compared to inorganic antimicrobial agents.

2.5 Cellulose-Based Composite Membranes

Cellulose is one of the most prevalent polysaccharides that is composed of repeating glucose units joined in a β -1,4-glycosidic linkage. It is abundant, naturally occurs, biodegradable, and biocompatible. Cellulose can be found in the cell walls of most plants as it gives rigidity and support to the stems. It can also be produced by some bacteria, especially from *Acetobacter*, *Agrobacterium*, and *Sarcina ventriculi* for various biologic purposes such as maintaining an aerobic environment and for flocculation [102]. Recently, scientists have also found that a sea animal—tunicate—can also produce cellulose to construct their body mantle. However, natural cellulose, especially plant cellulose, is insoluble in water and most organic solvents due to its closely packed structure caused by intrahydrogen bonding. This structure hampers it from further development. Hence, regenerated cellulose or cellulose derivatives are produced to overcome its processing handicap. Figure 2.4 depicts some common cellulose derivative structures that have been applied in membrane technology.

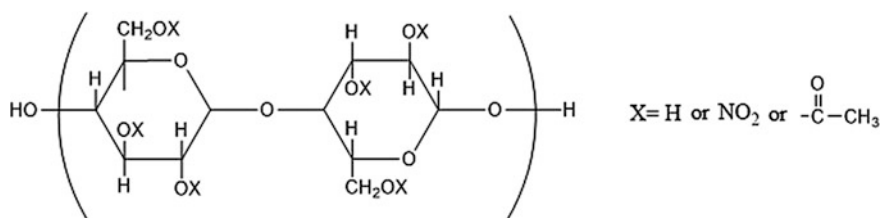


Fig. 2.4 Commonly used cellulose structures in membrane technology

The application of cellulose-based membranes in water filtration has been greatly explored since the 1960s. In fact, cellulose acetate membranes were the first membranes used in commercial reverse osmosis plants in 1965 [103]. To date, cellulose filter membranes with various pore sizes can be found commercially to remove different sizes of substances. Cellulose membranes have been used in a broad range of filtration spectra that cover from microfiltration to osmosis processes. They are capable of removing bacteria, viruses, antibiotics, pesticides, synthetic dyes, oil and grease, heavy metals, and even dissolved salts. The features of cellulose filter membranes can be improved by adding additives. Bentonite [58, 74], boehmite [75], modified coal [59], and sodium dodecyl sulfate (SDS) [47] are incorporated into cellulose to increase the water permeability of the filter membranes (higher flux) by modifying the membranes' surface porosity and hydrophilicity. Other additives such as silica [73], iron nanoparticles [51], and CNTs [61] also improve the cellulose membrane in terms of their durability and thermal and mechanical properties. Nonetheless, a decrement in salt rejection and mechanical strength has been observed when polyoctahedral silsesquioxane (POSS) nanoparticles are applied as the additives [49].

In most cases, adsorption occurs besides filtration. Positively charged heavy metal ions are favorably adsorbed onto the negatively charged cellulose membrane, while water permeates through the interconnected pores of the membrane. However, due to the low surface area of cellulose, the absorptive sites are occupied quickly by metal ions and cause a drastic drop in metal ion rejection. Complexing agents (e.g., humic acid, phytic acid), adsorbent particles (e.g., iron oxide, graphite, silica) or carriers (e.g., Calix resorcinarens) are integrated into the cellulose membranes to increase the metal removal efficiency from water. A common feature between these additives is their capability to form interaction with metal ions. For example, activated carbon and iron oxides offer negatively charged surfaces to adsorbed U(VI) and Pb(II), respectively, through complexation [46, 79]. Nevertheless, the metal removal efficiency of cellulose composite membranes is also dependent on other parameters such as pH, dopant, concentration of metal ions, and temperature [86].

The fabrication of silver-cellulose membranes and their biofouling resistance properties have been reported in many studies. Silver nanoparticles not only increase the surface hydrophilicity of the membrane, but also release the silver ions (biocides) that will eventually kill bacteria. Nevertheless, the strength of the biofouling resistance of silver-cellulose membranes is dependent on the amount, size, and the location of silver nanoparticles in the membrane. Sile-Yuksel et al. [55] conducted SEM-EDS mapping studies on a series of Ag polymer membranes and correlated them with their antimicrobial properties. They demonstrated that the silver nanoparticles located on the top layer of the membrane are easier to leach out and hence exert higher antibacterial properties. Copper oxide particles in the cellulose membranes also show superior antibacterial properties [39]. Similar to silver, its origin of toxicity comes from the leaching of metal ions.

Photocatalytic antibacterial properties of semiconductor oxides especially TiO_2 and ZnO in cellulose membranes have also been explored. Under the irradiation of

light, reactive oxygen species such as OH^- , H_2O_2 , and O^{2-} are generated. These oxygen species can penetrate through bacteria's cell wall and inhibit their growth [57, 63]. Besides imparting antimicrobial properties, the photocatalytic properties of these membranes can also be used for the degradation of pollutants in water. Furthermore, the presence of semiconductor oxides can lead to simultaneous improvement in membrane stability, flux permeability, and porosity [94]. Bai et al. [43, 63] have prepared multifunctional TiO_2 and TiO_2/ZnO -cellulose membranes for water purification. These membranes were used for concurrent filtration and photodegradation to remove methylene blue and humic acid with high flux and antifouling properties.

Carbon nanotubes (CNTs) and ammonium salts have been composited into cellulose to form the contact-active/contact-kill antibacterial membranes. Unlike metals or metal oxides, the application of contact-kill materials does not cause secondary contamination in the environment. The bacteria are killed once they come in contact with active sites such as CNT which are anchored to the cellulose membranes. Even though CNTs have shown promising antibacterial properties, the high cost, toxicity, and poor dispersion of CNTs in the cellulose membranes are obstacles. As such, polyvinyl-N-carbazole (PVK) has been used as a stabilizer to improve the dispersity of CNTs in cellulose and reduce the cost of membrane preparation [87]. Meng et al. [44] have modified cellulose membranes with ammonium or amino groups via alkoxysilane polycondensation reactions and assessed their antimicrobial performance. The study suggested that the bactericidal performance of the membranes is dependent on the overall molecular structure as well as the length of the alkyl group. Longer alkyl groups and higher charge density of the cationic groups enhance the interactions with the cytoplasmic membrane of the bacteria which in turn results in higher antimicrobial activity.

Cellulose composite membranes for catalytic applications are relatively less studied. Bendi and Imae [42] were the first to prepare metal-loaded cellulose membranes for catalytic reduction of p-nitrophenol in the presence of NaBH_4 . 2,2,6,6-tetramethylpiperidine-1-oxyl radicals (TEMPO) were applied to selectively oxidize the hydroxyl group of cellulose at the C6 position to form the carboxylate groups. The carboxylate groups are responsible for the well dispersion and stabilization of Cu nanoparticles in the membrane. The resultant Cu-cellulose membranes were stable, tough, and effective even after 10 cycles. The same group of researchers [41] has also demonstrated the preparation of dendrimer-stabilized Ag-cellulose membranes and their application in the chemical degradation of rhodamine B. In this case, poly(amido amine) (PAMAM) was used as the dendrimer to protect the growth of Ag and serve as an adsorbent for rhodamine dyes. The catalytic activity of the PAMAM-stabilized Ag-cellulose membranes increases with the increase of Ag content and the surface area of the membrane by pricking it with a needle.

Semiconductor oxides such as TiO_2 or ZnO are known photocatalyst that have been used to degrade various organic pollutants. For the ease of separation, semiconductor nanoparticles are immobilized on various supports. Regenerated cellulose provides porous structures and hydroxyl groups which can effectively

immobilize semiconductor oxide particles to form the composite membranes for photocatalytic purposes. The effectiveness of TiO_2/ZnO -cellulose composites as photocatalytic membranes in the degradation of phenol [43], methylene blue (MB), humic acid [40], rhodamine B (RhB) [64, 68], and methyl orange (MO) [66] was studied. Likewise, pristine $\text{TiO}_2/\text{TiO}_2$ -cellulose catalytic membranes work well in the UV range, but less effective in the visible region. In order to widen its spectrum window, the membrane was doped with noble metals (Au and Ag) [65]. The Au- or Ag-doped TiO_2 -cellulose membranes resulted in $\sim 75\%$ of MB degradation as compared to undoped membranes that only gave 60 % of MB degradation.

While most of the studies on semiconductor oxide-cellulose membranes are focused on their role as solely photocatalytic membranes, Bai et al. [40, 63] have looked at the possibility of creating multifunctional membranes which can be cocurrently used for filtration, catalytic degradation, and antifouling purposes. They functionalized the surface of cellulose acetate membrane with the hierarchical $\text{SrTiO}_3/\text{TiO}_2$ [67] and TiO_2/ZnO [63] using hydrothermal method. These membranes showed excellent water purification performances with high water flux and high photocatalytic and high antimicrobial activities.

2.6 Chitosan-Based Composite Membranes

Chitosan is a polysaccharide derived from the deacetylation of chitin. It is abundantly applied in a wide range of applications, as a stabilizer and an adsorbent, mainly due to its unique structure that consists of functional groups such as amino and hydroxyl groups [104]. This environmentally friendly material can be shaped into various forms. As an example, beads, powder, sponge, membranes, and hollow fibers are among the numerous structures of chitosan which have been developed. The intention of chitosan in the form of hollow fibers, beads, and sponge is mainly to enable the increase in its surface area and porosity. Increase in surface area and porosity is commonly related to enhanced adsorption, filtration, etc. However, this is not always advantageous, especially for chitosan-based membranes mainly because of its brittleness and due to the fact that it can agglomerate easily in an aqueous medium [30, 105].

As an adsorbent or filter, chitosan-based membranes have been used for the removal of transition metals as well as organic molecules. For added value, researchers have been challenged to find additives which are economical while maintaining its environmentally friendly characteristics. Metal ions such as Cu ions have been removed using thin composite membranes of chitosan/polyvinyl alcohol with MWCNT- NH_2 [30]. Apart from metal ions, the adsorption of humic acid using polyacrylonitrile-coated chitosan impregnated with amine-stabilized magnetite nanoparticles has also been reported [36]. Other works reported are on montmorillonite (MMT)/chitosan for the adsorption of Bezaktiv Orange V-3R dye [27], mesoporous carbon/chitosan for the adsorption of fuchsin [24], chitosan/PEG/CNT for the adsorption of methyl orange [106], and thin composite membranes of $\text{TiO}_2/$

chitosan/glass plate for the adsorption of Reactive Red 4 [23]. In the later work, the thin composite membrane offers several advantages. Apart from a bifunctional photocatalysis—adsorption system, the TiO_2 shields the chitosan from direct exposure to the irradiation source which can ultimately change the structure of chitosan and its adsorption capacity.

Other bifunctional systems that have been put forward are for filtration and antifouling purposes. Zinadini and coworkers described the use of PES membranes incorporated with O-carboxymethyl chitosan-bound magnetite nanoparticles for filtration of Direct Red 16 dye. Here, the magnetite was employed as a support for chitosan [37]. The membranes exhibited superior pure water flux, higher rejection of dyes, and good antifouling properties as compared to unmodified PES membranes. Fouling generally deteriorates a membrane and causes hikes in operational costs. Current membranes are composed of a reinforcing fabric polymer, followed by a layer of polysulfonic and polyamide. Modification of the upper polyamide layer with graphene oxide and chitosan improves the fouling resistance characteristics of the membrane by two modes: first by increasing the hydrophilic nature of the membrane and reducing its surface roughness and second by enhancing the electrostatic repulsion between membrane surface and protein molecules [38].

Various studies on the use of chitosan as a membrane for catalytic application have also been reported. In these studies, it is interesting to note that most researches have favored to shape the membranes in the form of hollow fibers or nanofibrous [25, 28, 29]. This gives the advantage of increasing the surface area in which the catalytic membrane can be exposed to the substrate. The chitosan in these catalytic membranes mainly functions as a support or stabilizer for the active phase for a particular catalytic reaction. As an example, Seyed Dorraji and coworkers [25] prepared chitosan-supported Fe_3O_4 membranes. They compared the use of pure cross-linked chitosan and chitosan/ Fe_3O_4 for the degradation of the dye, Reactive Blue 19. They reported that chitosan/ Fe_3O_4 was only slightly effective as a catalytic membrane when compared to its corresponding pure chitosan hollow fiber. In the presence of chitosan/ Fe_3O_4 , adsorption of the dye occurred. In contrast, in the presence of hydrogen peroxide, H_2O_2 , the Fenton-like reaction occurs, resulting in the generation of OH radicals. This improves the performance of the catalytic membranes drastically whereby degradation of the dye occurs simultaneously with its adsorption. Another work in which chitosan/Co phthalocyanine membranes were prepared for the degradation of rhodamine B has also been reported [26]. The authors did not typically form catalytic membranes via electrospinning technique. However, to optimize the available surface area, double-layer membranes were prepared. The membranes showed excellent degradation efficiency of up to 99 % within 60 min. Even so, the authors noted that this was achievable at pH values of 6 and below. Higher pH values resulted in a significant decrease in the extent of rhodamine B degradation. From a realistic perspective, this may pose a problem in terms of the reusability of the membranes, as chitosan dissolves at pH values of <4.

Enzymes, specifically laccase, have also been immobilized on nanofibrous membranes composed of chitosan and poly(vinylalcohol) [29] as well as chitosan/poly(vinylalcohol)/multiwalled carbon nanotubes (MWCNT). In these

works, chitosan/poly(vinylalcohol) gels were prepared to improve the mechanical strength of chitosan. This improves spinnability during electrospinning to form the nanofibrous membranes [29]. Laccase which is a multicopper oxidase is immobilized to the chitosan covalently via the formyl groups of glutaraldehyde that have shown to be effective for the degradation of 2, 4-dichlorophenol [29]. To improve the catalytic effect of laccase, an electron transfer agent like multiwalled carbon nanotubes can be introduced into the chitosan/poly(vinylalcohol) [28]. This novel approach has proven to eliminate diclofenac successfully as compared to nanofibrous based on chitosan/poly(vinylalcohol) [28].

2.7 Natural Rubber-Based Composite Membranes

Natural rubber (NR) is obtained from the tree *Hevea brasiliensis*. Its latex consists of three phases, namely the rubber, aqueous, and luteoid phase [107]. The rubber phase comprises of spherical to oval particles which consist of repeating *cis*-1,4-polyisoprene units. These particles are surrounded by a layer of proteins such as α -globulin. The aqueous phase on the other hand contains carbohydrates, proteins, and amino acids, while the main component of the luteoid phase is water, protein, and phospholipids [107]. In general, the protein in natural rubber plays an important role. It prevents coagulation of the rubber particles and provides binding sites for additives such as metal nanoparticles [108]. This is mainly attributed to the availability of $-\text{COOH}$ and $-\text{NH}_2$ functional groups in the proteins.

To date, the use of natural rubber-based composite membranes in wastewater treatment is limited. Several works have appeared for adsorption and catalytic purposes. However, none have reported on its use for filtration and antibacterial/fouling. The main reasons for the lack of research in these areas may be due to the nature of natural rubber which lacks porosity and hydrophobicity. For adsorption, epoxidized natural rubber (ENR)-incorporated magnetite-mixed matrix membranes has been used for oil recovery [88]. Adsorption of the oil was promoted by the hydrophobicity and porosity of the membrane itself. The porous structure of ENR was formed via dissolution of SiO_2 (incorporated during synthesis) with HF. The addition of magnetite into the natural composite membranes allows magnetic recovery.

In another work, thin-film composites composed of layers of NR, SiO_2 , and TiO_2 have been used for the photocatalytic degradation of methylene blue [109]. The authors reported that TiO_2 not only aided in the degradation of the dye but also improved the life span of the NR. Sriwong et al. [110] also conducted a detailed study comparing the performances of powder TiO_2 with TiO_2 -supported NR membranes for the degradation of methylene blue. In this work, both systems demonstrated comparable efficiencies; however, powder TiO_2 exhibited a faster degradation time. Although these works are interesting, both were carried out before the year 2010. Since then, only Nawi et al. [89] have reported a study on thin-film composite membranes comprising of TiO_2 , ENR, and PVC for the

degradation of dyes. Our group has also actively investigated NR-based composite membranes for the degradation of methylene blue in the presence of borohydride [111] and methyl orange using a UV light [112]. In these works, NR-Ag films were prepared via soft thermal treatments. Results show that the NR-Ag membranes were effective for the degradation of both dyes.

2.8 Future of Natural Composite Membranes

To what extent is it ‘green’? This is one of the questions which frequently pop up when the topic of discussion circulates around renewable materials. When discussing natural composite membranes, the extent to which it is ‘green’ can be reflected from several aspects, that is, the preparation, materials, and function of the membrane.

Basically, the technique with which natural composite membranes are prepared should be environmentally friendly. This means that the overall process should not create secondary pollutants and consumes less energy. For this matter, considerations such as the method to cross-link or graft polymers should be scrutinized. The use of microwaves or UV irradiation as an alternative to solvents may be a more viable option in this sense. In terms of materials for natural composite membranes, ‘green’ can be accomplished by minimizing the use of any toxic materials during or in its fabrication. Avenues which have yet to be explored in depth are the use of ionic liquids as solvents or solely renewable materials such as natural polymers reinforced with agricultural waste for the fabrication of membranes. It is undeniable that work has been done on such composites for instance natural rubber reinforced with peanut shell powder [113]. Unfortunately, there has been a lack in the use of these composites for wastewater treatment. Another aspect that should be looked at is the persistency of these natural composite membranes in the environment. Additives in the natural polymer membranes can change the degradability of the composite membranes. As such, an active role should be taken to ensure that the membranes can easily be degraded after its life span. From a functionality point of view, the current situation with natural composite membranes is that most of these membranes are constricted to monofunctions. The development of multifunctional or hybrid natural membranes is still at its infant stage and should be given more focus in future as compact industrial designs save space and energy, which is more economical. Furthermore, these multifunctional membranes allow the possibility of creating membranes with superior removal efficiency and selectivity.

Although these ideas can pave a way toward a sustainable tomorrow, in reality detailed technical study is required to bridge the gap between laboratory-scale and industrial applications. In the past years, there has been significant achievement in the fabrication of numerous natural composite membranes. Generally, most of these membranes have showed promising performances. However, it has to be pointed out that the achievements accomplished are only at laboratory scale.

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