Applied Chemical Engineering (2024) Volume 7 Issue 2
doi: 10.59429/ace.v7i2.1867

REVIEW ARTICLE

Cellulose and cellulose derivatives in sustainable membrane development for oil/water separation

Chel-Ken Chiam*, Zykamilia Kamin, Chi Huey Ng, Farhana Abd Lahin, Rosalam Sarbatly

Membrane and Nanofibre Research Group, Faculty of Engineering, Universiti Malaysia Sabah, Kota Kinabalu 88400, Malaysia

*** Corresponding author:** Chel-Ken Chiam, chiamchelken@ums.edu.my

ABSTRACT

Cellulose is a natural polymer and most abundant organic substance on Earth. Inexhaustible hydroxyl groups on the cellulose surface allow derivatives of cellulose produced. This article discusses the recent progress of cellulose and cellulose derivatives in membrane development for oil/water separation. Functional groups that are available on the cellulose and its derivatives provide modification features to improve membrane wettability. Membranes with super wetting properties possess remarkable self-cleaning abilities which in turn can enhance permeation fluxes and extend membrane lifespan. However, the role of cellulose-based membranes in oily wastewater treatments is still in its early stages. This review article emphasizes on the development and modification of cellulose-based membranes for improvement of wettability, flux and separation efficiency, and the future directions of research.

Keywords: membrane; cellulose; cellulose derivatives; wettability; oil/water separation

ARTICLE INFO

Received: 30 August 2023
Accepted: 1 December 2023
Available online: 13 March 2024

1. Introduction

In 2018, the United Nation Water remarked that 40% of people in the world are affected by water scarcity; 80% of wastewater is discharged into the environment without treatment; more than 2 billion people still lacked access to safe water; and more than 4.5 billion people lacked adequate sanitation services[1]. Continuous discharging large volumes of wastewater is inevitable due to the rapid growth of urbanization and industrialization. Oil slick as well as oil emulsion is one of the utmost elements of wastewater discharged by various industries such as oil and gas exploration and production, petroleum refineries, metallurgical processing, food and beverage, textile, cosmetic and pharmaceutical. The oily substances contained in the wastewaters are carcinogenic and mutagenic that highly threaten human health as well as flora and fauna.

Membrane technology has been recognized as one of the promising wastewater treatment techniques to produce high quality of water for reuse which directly supports the circular economy strategy and the Goal 6 of the Sustainable Development Goals (SDGs)[2]. In the process of oil removing from water, membrane separation demonstrates to be more viable than the traditional treatment techniques such as skimming, floatation, burning and chemical demulsification. The membrane techniques exhibit low energy consumption, low cost, light weight, mechanical flexibility, high separation efficiency, small footprint and compact design.

Separation of various types of oils from water can be accomplished by using the membranes with different wetting properties. In brief, as illustrated in **Figure 1a**, a hydrophilic and oleophobic membrane is used when oil is lighter than water. This membrane allows the water to pass through but retains the oil. On the other hand, a hydrophobic and oleophilic membrane rejects the water and permits the oil to transport through the membrane as described in **Figure 1b**. This type of membrane is suitable for denser oils. Many researchers have developed numerous techniques to enhance membrane wettability from hydrophilic/oleophobic to superhydrophilic/superoleophobic for lighter oils or from hydrophobic/oleophilic to superhydrophobic/superoleophilic for denser oils. The reference of contact angles for different wetting properties is given in **Table 1**. With these super-wetting properties, membrane fouling is minimized while maximizing the permeation flux and the membrane lifespan.

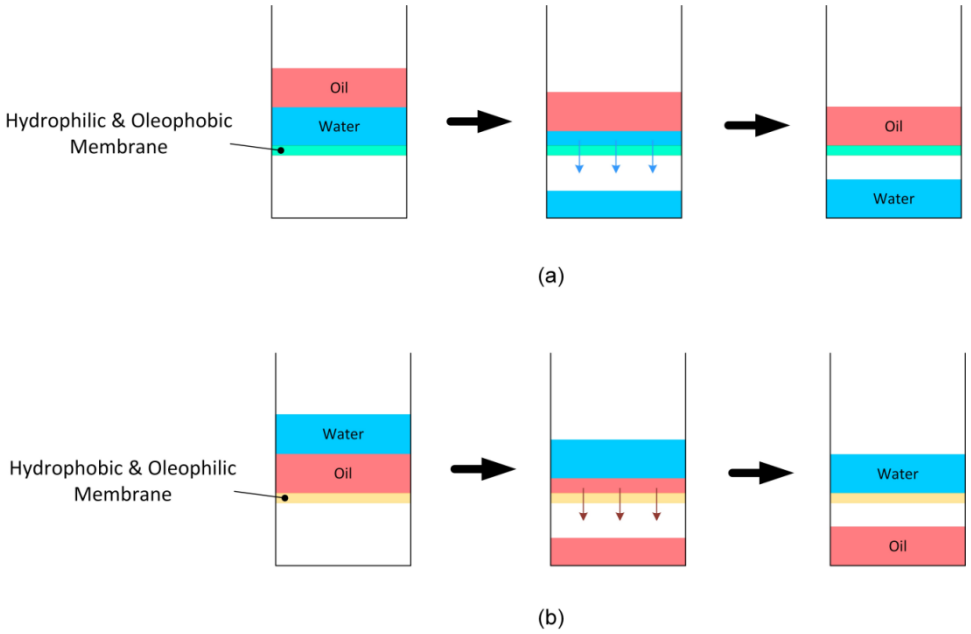

Figure 1. Separation of oil/water mixture using (a) hydrophilic and oleophobic (b) hydrophobic and oleophilic membrane.

Table 1. Wettability of membrane and contact angle.

Wettability	**Droplet**	**Contact angle**
Hydrophilic/Oleophilic	Water/Oil	<90°
Hydrophobic/Oleophobic	Water/Oil	90 < θ < 150°
Superhydrophilic/Superoleophilic	Water/Oil	<5° in a few seconds
Superhydrophobic/Superoleophobic	Water/Oil	>150°

Recently, super-wetting membranes have been tremendously designed and synthesized especially by modifying the traditional organic polymeric membranes such as polyvinylidene fluoride (PVDF)[3,4], polypropylene (PP)[5], polyethersulfone (PES)[6] and polysulfone (PSf)[7]. However, the organic polymers such as PSf, PP and PVDF can be easily damaged in harsh conditions[8] and they are poor in biodegradability. Sustainable materials as well as techniques to fabricate the membranes are in urgent need to reduce the hazards. Various types of biomaterials and biomaterial-derived solvents have been actively explored to prepare greener membranes due to their low toxicity, natural abundantly available, low cost and excellent biodegradability[9,10]. In the recent years, biopolymers derived from animal and vegetable sources have been recognized as more sustainable materials and potentially to replace fossil-based polymers in membrane development[11]. Number of publications relevant to biomaterials as well as biopolymers used in membrane separation for oily wastewater treatment has increased exponentially since about 10 years ago, as presented in **Figure 2**.

Nevertheless, membrane properties such as antifouling, stability in harsh environment and mechanical strength are crucial in oil/water separation when the membrane is fully as well as partially formulated from biopolymers. Biopolymers in generally can be categorized into natural and synthetic; both types of biopolymers can be biodegradable and non-biodegradable as illustrated in **Figure 3**.

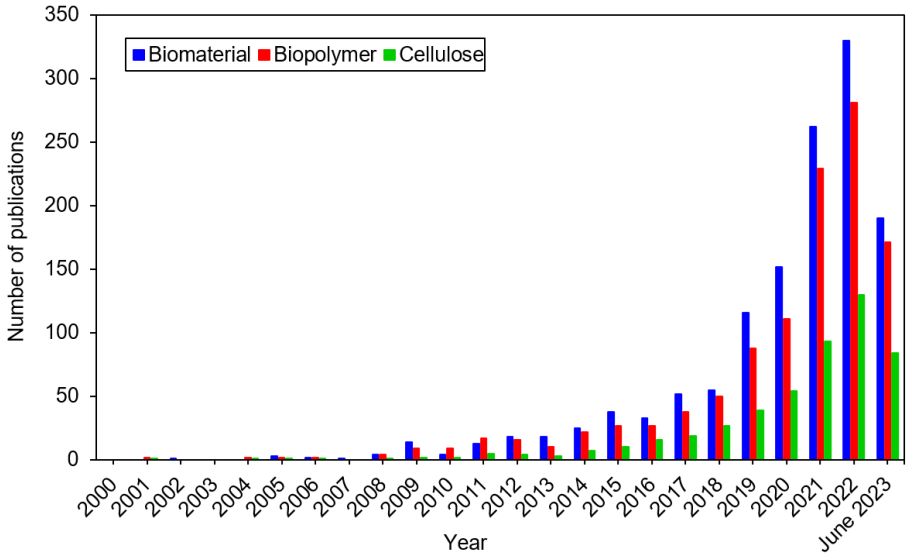

Figure 2. Publications related to biomaterial, biopolymer and cellulose-based membranes since 2000. (Data were analyzed from the SCOPUS database: 'All fields' for 'oily wastewater treatment', 'biomaterial' and 'biopolymer', and 'Keywords' for 'cellulose').

Cellulose has received a great attention as sustainable and low-cost material in membrane development because it is the most abundant biopolymer on Earth. Cellulose exists in different size and shape: (1) cellulose nanocrystals (CNC) which include nanocrystalline cellulose, nanocellulose whiskers and rod-like cellulose nanocrystals, (2) cellulose nanofibrils (CNF) which cover nanofibrillated cellulose, microfibrillated cellulose or cellulose nanofibers, and (3) bacterial nanocellulose. Cellulose derivatives such as carboxylmethyl cellulose (CMC), cellulose acetate (CA), hydroxypropyl methyl cellulose (HPMC) and methyl cellulose (MC) have been successfully used to modify and improve the properties of other membranes in water purifications[12–15]. The application of cellulose-based membranes in the oily wastewater treatment keeps increasing as depicted in **Figure 2**. This review highlights the recent techniques used to formulate membranes with various wetting properties from cellulose and its derivatives, and also to underline their performance in oil/water separation.

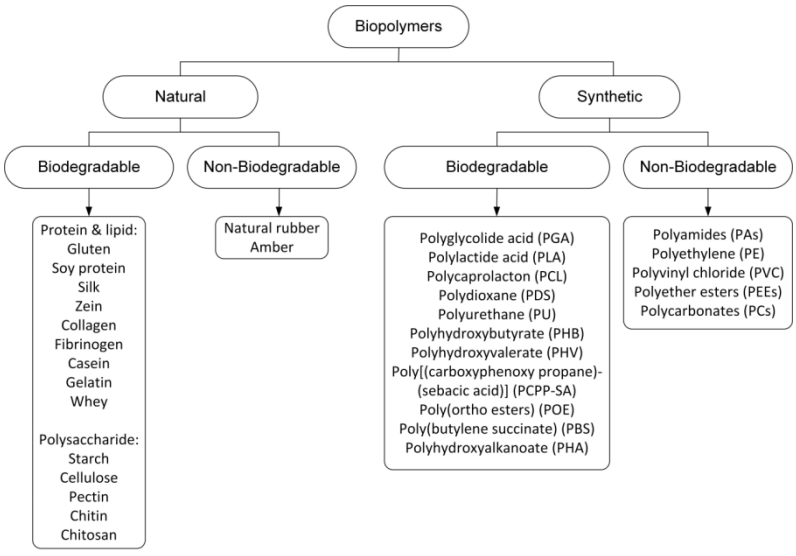

Figure 3. Categories of biopolymers.

2. Cellulose

Cellulose is a linear polymer composes of as many as ten thousand repeating D-glucose units covalently linked by β-1,4 glycosidic bonds stably. **Figure 4** shows the molecular structure of cellulose. Cellulose is an amphipathic macromolecule due to each glucose unit contains both equatorial hydroxyl groups that point radially away from the face of the pyranose ring and axial hydrogen atoms that are perpendicular to the face of the pyranose ring[16]. The existence of various strong intra- and inter-molecular hydrogen bonds between individual chains leads the cellulose becomes insoluble in water as well as conventional organic solvents[17] although it is characterized as hydrophilic with a mean water contact angle 34°[18].

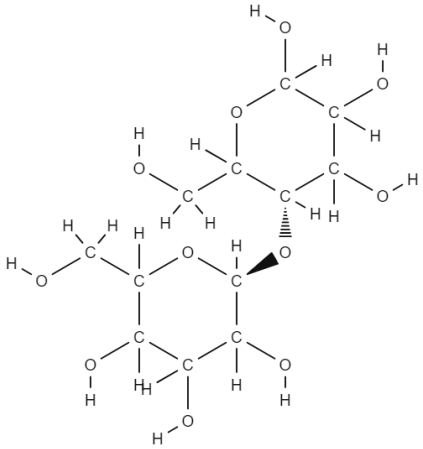

Figure 4. Molecular structure of cellulose.

In the case of oil/water separation by using membrane filtrations, numerous modification techniques have been explored to elevate wetting properties of cellulose membranes for improving self-cleaning capability and extending lifespan of the membranes. Xu et al.[19] oxidized some of the hydroxyl groups of cellulose filter paper with sodium periodate ($NaIO_4$) to become aldehyde groups, followed by a crosslinking process with hydrophilic polyvinyl alcohol (PVA) in a water solvent. The formation of covalent bonds from the crosslinking process revealed a stronger mechanical strength of the cellulose-PVA membrane. The cellulose-PVA membrane exhibited superamphilic in the air and underwater superoleophobic. Both water and oil droplets immediately spread and permeated through the membrane in air; while underwater contact angles (CAs) for different types of oils such as toluene, hexane, chloroform, cyclohexane, dichloromethane and kerosene exceeded 150°. Oil/water separation is achieved at the moment a milky white oil/water emulsion touched with the cellulose-PVA membrane surface, water is captured and passed through the membrane. The contact area between oil droplets and membrane surface decreased when water is permeated. The oil droplets coalesced, and they are repelled by the membrane surface.

Sodium alginate is a natural polymer derived from brown algae and it is comprised of a large number of polyanionic groups such as hydroxyl and carboxyl groups. Yang et al.[20] used cation Ca^{2+} to crosslink sodium alginate film grafted on the surface of cellulose filter paper. The cellulose filter paper was firstly coated with sodium alginate, followed by immersing into $CaCl_2$ aqueous solution. An ion-exchange process occurred between $COONa/Ca^{2+}$. The crosslinking reaction between sodium alginate chains took place which improved the stability. During submerging into Na_2CO_3 aqueous solution, the sodium alginate-Ca coated composite cellulose membrane captured the CO_3^{2-} ions and formed $CaCO_3$ through crystallization. The sodium alginate-Ca ionic bond adhered the generated $CaCO_3$ particles on the membrane surface. $CaCO_3$ is a hydrophilic inorganic compound. Compared with the underwater oil contact angle (OCA) of cellulose filter paper at 133.2°, the OCAs of cellulose-sodium alginate-$CaCO_3$ composite membranes increased from 148.2 to 150.1° when

the soaking in CaCl and Na_2CO_3 aqueous solutions increased from 3 to 9 cycles due to the growing of $CaCO_3$ particles on the membrane surface.

Abundant hydroxyl groups on the long chains enable cellulose fibers to form strong hydrogen bonding among themselves. As a result, cellulose membrane can be fabricated naturally through cellulose fibers self-crosslinking without complex post-crosslinking procedures and extra special crosslinkers. Li et al.[21] extracted the cellulose from cattail inflorescence by using NaOH, $NaClO_2$ and acetic acid aqueous solutions. The extracted cellulose hydrosols comprised of microfibers and nanofibers were washed to neutral pH. Next, the purified hydrosol was placed in a petri dish and dried at 40 ℃ to obtain pure self-crosslinking cellulose membrane. Water and oil droplets spread out completely and quickly on the membrane in the air. Conversely, an oil droplet sat steadily on the membrane surface without any penetration in water and thus made an OCA of approximately 151.3°. Additionally, the cellulose membrane possessed an excellent cleaning property as the oil droplets bounced back quickly without adhering to the membrane surface. Dissociation of hydrogen bonds between fibers might take place due to water adsorption, but the long microfibers still could form integral network structure and the short nanofibers filled in the network structure. On the other hand, cellulose nanocrystals that extracted from the mantle of tunicate have also been used to modify the underwater oleophobic cellulose filter paper into underwater superoleophobic through the physical formation of hydrogen bonding and epichlorohydrin crosslinking[22].

Nanofibers of cellulose that have nanoscale diameter possess more hydroxyl groups expose to the surface compare to the native cellulose. With these plentiful hydroxyl groups, cellulose membranes deposited by cellulose nanofibers reveal more oleophobicity in water. For instance, Halim et al.[23] fabricated cellulose membranes from two types of cellulose nanofibers, bamboo-based counter collision cellulose nanofiber (MECH-CNF) and wood-free fiber-based 2,2,6,6-tetramethylpiperidine-1-oxyl oxidized cellulose nanofiber (TEMP-CNF). Both MECH-CNF and TEMPO-CNF sheets displayed superoleophobic with underwater OCA exceeded 150° while the regenerated cellulose sheet showed oleophobic with OCA 140°.

Realistic oily wastewaters can contain dyes which comprise of cationic and anionic dyes. Separation of oil/water using superhydrophilic membranes becomes more cumbersome when dealing with water-miscible dyes because the dyes can foul the membranes. Ao et al.[24] *in situ* grew $La(OH)_3$ nanosheets on the cellulose nanofibrous membrane through one-pot electrospinning approach. The $LaCl_3$/cellulose spinning solution was electrospun and the resultant nanofibers were immersed into a coagulation bath contained 0.01 M NaOH aqueous solution. The $La(OH)_3$ transformed from nanoparticles to thin nanosheets when increasing the time of coagulant immersion due to reaction between La^{3+} and OH^- was extended. The solid particles were anchored on cellulose nanofibers mainly through hydrogen bonding and physical wrapping. In air, a water droplet required 160 ms to spread on the $La(OH)_3$/cellulose membrane surface while 400 ms on pristine cellulose nanofibrous membrane surface. Underwater OCA for the $La(OH)_3$/cellulose membrane recorded as exceeding 150° and even the oil droplet was forced against on the membrane surface with a visible deformed shape, the oil droplet detached easily which attributed to the synergy effect of enhanced hydroxyl groups in the membrane. Simultaneously, the $La(OH)_3$/cellulose membrane was able to separate the dye mixture of opposite as well as same charges.

Industrial oily wastewaters compose various types of organics, metallic dyes and ions as well as microorganism. Consequently, development of multifunctional membranes which not only can separate oil and water, but also reduce organic pollutants and microbial fouling is in urgent need. Corrosive substances in wastewaters and their precipitations can devastate the hydrophilicity of cellulose membranes. A superhydrophobic surface on cellulose membrane surface is possibly more resistant towards the erosion due to chemicals in wastewaters. Yin and co-researchers have created micro/nano structures on the cellulose-based membrane surface by depositing various types of photocatalysts such as Fe_2O_3[25], MnO_2[26], CuO[27], ZnO[28]

and CeO_2[29], and then coated with stearic acid (STA) to obtain superhydrophobic cellulose-based membranes. These membranes exhibited excellent self-cleaning ability with water contact angle (WCA) ranged from 162° to 167°, photocatalytic degradation of methylene blue organic dye exceeded 89%, underwater writable with WCA of 154.2°, reduced bio-adhesion of green algae *Chlorella* by more than 95%, separation efficiencies of oils greater than 88% whereby the oils included toluene, trichloromethane, n-hexane, chloroform and vegetable oil, and good fire-proof.

Nevertheless, poor affinity due to weak non-covalent interaction between inorganic nanoparticles and polymers lead to gradual detachment of nanoparticles which eventually reduces the multifunctional properties of modified membranes and create secondary pollution[30,31]. Polydopamine (PDA) is a powerful mussel-inspired adhesive material for various types of organic and inorganic materials. A combination of catechol and amine in PDA can physically interact with inorganic materials through metal coordination, π-π stacking, cation-π interaction and hydrogen bonding[32–35]. Li et al.[36] roughened cellulose paper surface by using PDA-induced in situ reduction of Ag ions to form Ag nanoparticles, followed by lowering the surface energy using n-dodecyl mercaptan grafting. Covalent immobilization of Ag nanoparticles prevents detachment of the nanoparticles from cellulosic substrate. The cellulose-PDA@Ag@n-DM membrane exhibited superhydrophobic which was excellent self-cleaning and anti-staining abilities. In addition, the membrane effectively reduced bacteria adhesion by approximately 97.2% for *E. coli* and 96.0% for *S. aureus*. In 30 minutes under visible light irradiation, photocatalytic bactericidal degradation achieved 100%.

A single piece of membrane owns both hydrophilic and hydrophobic properties can extend to more types of oil/water mixtures or emulsions. Such a switchable separation can be accomplished by a Janus membrane which possesses opposite wettability on both sides. Xie et al.[37] designed a Janus membrane by coating one surface of cellulose membrane with superhydrophilic PDA and another surface with superhydrophobic attapulgite (ATP). ATP itself is a hydrophilic nanomaterial with abundant active hydroxyl groups occupied on its surface. It is naturally available as MgAl-rich silicate clay mineral and comprises of a rod-shaped structure with 30 nm–80 nm diameters. ATP is hydrophobized by tetraethyl orthosilicate (TEOS) and hexadecyltrimethoxysilane (HDTMS) via the sol-gel method. On the PDA surface, OCAs under water, acid, alkaline and salty 3.5% NaCl exceeded 150°, while WCA in the air was 0° and water droplet that under oil penetrated the surface which characterized the PDA surface was superhydrophilicity/underwater superoleophobicity. On the hydrophobized ATP surface, WCAs in air, underoil, acid, alkaline and salty solution were greater than 150°, while OCA underwater was 0° which confirmed the surface was superhydrophobic/superoleophilic. Another fabrication method of Janus membrane is to use a superhydrophilic cellulose paper with a fibrous structure as the bottom layer and a superhydrophobic top layer formulated from polyurethane (PU), PVDF and SiO_2 nanoparticles is sequentially surface-loaded[38]. WCA in the air of this Janus membrane is 153° for the superhydrophilic surface and OCA underwater is 157° for the superhydrophobic surface.

Most of the membranes developed from cellulose materials show high separation efficiency, i.e., greater than 95% as listed in **Table 2**. However, the membrane flux varies differently which is significantly affected by configuration of raw cellulose materials and modification techniques[39,40]. Sophisticated and complex procedures with toxic and expensive reagents used to modify the cellulose membrane can hinder in large-scale application and commercialization. For instance, constructions of $Cu(OH)_2$ nanoribbons on cellulose membrane through adsorption and immersion process[41] and $Co(OH)_2$ macro/nano structure on nanocellulose membrane via chemical soaking method[42] peeling-off of the inorganic nanoparticles is possible when subject to long filtration process especially the nanostructured surfaces are in direct contact with challenging wastewaters. Both $Cu(OH)_2$ and $Co(OH)_2$ are very hazardous and toxic to aquatic life with long lasting effect. Although nanoparticle-free as well as fluorine-free superwetting cellulose composite membrane has been

successfully fabricated, the raw materials used such as furfurylamine, paraformaldehyde, etc. are toxic[43]. Tetraethyl orthosilicate (TEOS) that used to fabricate micro/nano hierarchical structures and superhydrophobic cellulose membrane surface by using one-step facile sol-gel strategy[44], is flammable and chronic hazardous to the aquatic environment. Handling and management of toxic chemicals during transportation, storage and disposal are cost ineffective which can burden in large-scale development.

3. Bacterial cellulose

Bacterial cellulose (BC), which is also known as microbial cellulose, is a pure cellulose synthesized through fermentation processes by various types of bacteria such as *Acetobacter*, *Pseudomonas*, *Achrobacter*, *Alcaligene*, *Aerobacter* and *Azotobacter*. The diameter of BC fibers ranges from 20 to 100 nm. Water retention of BC is high and exists as hydrogel when water content is as high as 99% which leads to being very hydrophilic. Nevertheless, the tightened fibers and small pore size of BC have limited its application as a permeable membrane filter.

Silica microparticles have successfully created irregular micropores in BC membrane with a high flux of about 10,660 L/m^2 h and a high separation efficiency of >99.9% in oil/water separation[45]. PDA has been used as a coating material to adhere the particles on the BC membrane through a one-pot approach technique. A water droplet made an angle of 26.2° on the pristine BC membrane and became zero after a few seconds while a water droplet spread immediately with zero angle on the silica/PDA modified BC membranes. The higher microporosity of the composite membranes and hydrophilic properties of silica and PDA have made the composite membranes become superhydrophilic.

Table 2. Performance of various configurations of cellulose membranes in oil/water separation process.

Configuration	Modification	Wettability	Oil/Water System	*J* (L/m^2 h)	*SE* (%)	Findings	Reference
Cellulose filter paper	Hydroxyl oxidation by $NaIO_4$ and crosslinking with PVA	Superhydrophilic/underwater superoleophobic	Hexane/water + Tween 80 Chloroform/water + Tween 80 Cyclohexane/water + Tween 80 Dichloromethane/water + Tween 80 Kerosene/water + Tween 80 Toluene/water + Tween 80	37 40 64 52 39 68	99.99 99.98 99.75 98.74 95.59 99.98	Complicated composition of commercial kerosene resulted in a relatively low *SE*; flux decreased with increasing the oil volume in emulsion because oil droplet became smaller; after 10 cycles toluene/water separation, *SE* still showed > 98%	[19]
Cellulose filter paper	Coating with SA, followed by grafting SA on filter paper surface using Ca^{2+}	Superhydrophilic/ underwater superoleophobic	Petroleum ether/water Hexane/water Toluene/water Soybean oil/water Dichloroethane/water	~790 ~780 ~800 ~550 ~420	> 99.2 > 99.2 > 99.2 > 99.2 > 99.2	Showed high flux for low viscosity oil; exhibited low flux for heavy oil (dichloroethane) and high viscosity oil (soybean oil); *SE* retained above 99% after 20 cycles and water flux decreased slightly; membrane weight loss after 20 cycles was negligible which proved that the stable film-forming property of SA and CaCO3 particles were adhered stably.	[20]
Cellulose hydrosols extracted from	Drying of purified uniform cellulose hydrosols at 40°C	Superhydrophilic/ underwater superoleophobic	Cyclohexane/water + Span	~170 ~180 ~160	~97.8 ~98.2 ~97	*SE* of cyclohexane/water emulsion increased	[21]

cattail inflorescence			n-Hexane/water + Span Trichloromethane/water + Span Dichloromethane/water + Span Soybean oil/water + Span	~165 ~145	~98.1 ~98	with increasing the membrane thickness while flux decreased; flux showed over 160 L/m^2 h during 10 cycles.	
Cellulose nanofibrous membrane	One-pot electrospinning; spinning solution contained cellulose, LiCl, DMA and $LaCl_3$	Superhydrophilic/ underwater superoleophobic	Hexane/water Cyclohexane/water Toluene/water Petroleum ether/water Pump oil/water Crude oil/water	5897.7 6318.9 ~6400 ~7600 ~6100 8586.1	98.8 98.9 99.7 99.3 98.9 99.1	Water flux by L-CNM was almost 2 times of CNM; *SE* still high and above 98.2% along with high flux over 5443 L/m^2 h after 60 cycles of hexane/water separation; able to separate tween 80-stablilized toluene/water emulsion with *SE* of 98.5% and water flux 436.4 L/m^2 h.	[24]
Cellulose fibers	Crosslinking with MA via esterification and plasma treatment	Superhydrophilic/ underwater superoleophobic	n-Hexane/water + Tween 80 Petroleum ether/water + Tween 80 Soybean oil/water + Tween 80	12070 10154 10035	99.0 99.6 98.1	Both micro-sized cellulose fibers and BC fibers improved the GFM structure and hydrophilic property; composite membrane reached a wet strength at 6.55 N.m/g after MA crosslinking which is same strength as commercial filter paper; high flux at 9000 L/m^2 h and high *SE* of 98.1% after 20 cycles of n-hexane/water emulsion separation;	[39]
Cellulose membrane	Sol-gel strategy with TEOS and HDTMS hydrolysis and polycondensation	Superhydrophobic/ superoleophilic	Diesel oil/water Toluene/water Hexane/water Petroleum ether/water Dichloroethane/water	-	~99.2 ~99.3 ~99.1 ~99.7 ~99.5	*SE* has no significant changes for 2 M of acid, alkali and salt/water separation; *SE* showed above 99% for petroleum ether after 10 cycles; micro/nano hierarchical structure remained unchanged after 10 cycles separation; great tape peeling resistance; great mechanical durability after scratch resistance test.	[44]
Microcrystalline cellulose	MCC and PVDF were mixed to form a membrane at 25°C and next lauric acid grafting	Superhydrophobic	n-Hexane/water Kerosene/water Xylene/water Petroleum ether/water Oleic acid/water	8800 3600 ~5100 ~7700 130	> 99 > 99 > 99 > 99 > 99	High viscosity of organic solvent resulted in low flux; stable performance after 20 cycles of kerosene/water separation; the membrane was stable under harsh acid (pH=1), base (pH=13) and salt environment with *SE*	[40]

							maintain above 99%; 91.01% and 94.92% of *SEs* for kerosene and xylene emulsions, respectively; membrane can degrade under natural conditions.	
Regenerated cellulose	PDA interface regulation and superhydrophobic SOATP spraying	Janus	1,2-dichloroethane/water + Tween 80 Petroleum ether/water + Tween 80 Toluene/water + Tween 80 Soybean oil/water + Tween 80 n-Hexane/water + Tween 80	~800 2567.7 ~1600 597.1 ~2300	> 99 > 99 > 99 > 99 > 99	*SEs* were > 97.5% and no obvious reduction of flux after 10 cycles of separation for different types of emulsions which indicated SOATP coating was strongly adhered to the membrane surface and exhibited good structural stability.	[37]

PVA: Polyviny alcohol; SA: Sodium alginate; MCC: Microcrystalline cellulose; MA: Maleic anhydride; BC: Bacterial cellulose; GFM: Glass fiber membrane; SOATP: superhydrophobic attapulgite.

The multifunctional BC membrane is developed by introducing photocatalysts such as titanium dioxide (TiO_2). TiO_2 has been tremendously investigated in many types of membrane separation applications due to its capabilities of self-cleaning, antifouling and pollutant degradation in addition to non-toxic and cost effective[46,47]. Cui et al.[48] used PDA adhered TiO_2 on BC fibers and micro-nano structure was created with large specific surface area. The porosity of the BC/PDA-TiO_2 membrane was further improved by adding sodium alginate (SA) crosslinked by $CaCl_2$ whereby a honeycomb porous morphology was successfully created. Although oil/water separation efficiencies were over 99% for six different types of oils i.e., dichloroethane, petroleum ether, toluene, soybean oil, diesel and hexane, the water fluxes obtained by the BC/PDA/SA-TiO_2 composite membrane varied distinctively. The water flux ranged from 7428 to 8774 L/m^2 h for heavy and viscous oils while the water fluxes were a bit higher when tested with light and less viscous oils i.e., between 9597 and 10,000 L/m^2 h. In the presence of low volatile oleic acid, the composite membrane exhibited hydrophilic and oleophilic. The composite membrane recovered its superhydrophilic and underwater superoleophobic properties after exposed to UV irradiation which indicated its self-cleaning ability.

Nonetheless, the photocatalytic function of TiO_2 is restricted under visible light due to its wide band-gap[49]. Zinc oxide (ZnO) is another cost-effective photocatalysts and similar band-gap energy with TiO_2. The combination of TiO_2 and ZnO can enhance the lifetime of charge carriers due to their conductive to the migration of photo-generated electron-hole pairs[50], and exhibited excellent hydrophilicity, permeability, photocatalysis and anti-fouling performances of modified membranes under visible light[51]. Wahid et al.[52] fabricated TiO_2/ZnO nanocomposite BC membranes and the membrane demonstrated a high efficiency of > 92% of photocatalytic activity under visible light. As a comparison, BC membrane modified with a single type of nanoparticles, either TiO_2 or ZnO, the photo-degradation was 44%–60%. The combination of TiO_2 and ZnO in BC membrane was also able to completely remove bacterial cells such as *S. aureus* and *E. coli*. In the air, water droplet spread immediately on the BC-TiO_2/ZnO composite membrane surface, while the underwater OCA was 151.4° with dichloromethane. The fluxes achieved by composite membrane were 8232.81 and 1498 L/m^2 h for separations of oil/water mixture and oil-in-water emulsion, respectively. Both separation efficiencies were greater than 99%.

Instead of superhydrophilic membrane, Wang et al.[53] fabricated a superhydrophobic BC membrane by loading $Cu(OH)_2$ nanoparticles and coated with stearic acid to form a petal-like micro-structure on the BC membrane surface. This rough surface structure gave a WCA of 162.3° due to air trapped in the interspaces.

Contrarily, kerosene oil droplets were absolutely immersed in the composite membrane. In this study, cheaper plant cellulose needle-leaf bleached kraft pulp was added to increase the pore size of BC membrane. The permeation flux of dichloromethane was 1667.63 L/m^2 h and separation efficiency was greater than 95%. After 10 cycles of oil/water separation, the composite membrane possessed a WCA of 152.6° and still maintained a high separation efficiency, which demonstrated excellent stability and durability.

4. Cellulose nanocrystals

Cellulose nanocrystals (CNC) is a product of acid hydrolysis of cellulose. Sulfuric acid is the typical hydrolyzing agent used to dissolve amorphous region and leaving behind is a crystalline portion. Esterification reaction occurs between sulfuric acid and hydroxyl groups of cellulose which allowing grafting of anion sulfate ester groups. The sulfate ester groups distributed on the surface of cellulosic nanoparticle and developed a negative electrostatic layer covering the surface which is able to prevent flocculation. The surface degree of substitution of sulfate ester groups could be as high as 26.32 when 65 wt% of sulfuric acid is used[54]. CNC is also known as nanowhiskers, nanorods and rod-like cellulose crystals which have typical diameter of 2 nm–25 nm and length of 100 nm–750 nm[55,56].

In the application of oil/water separation, CNC is mainly used as an enhancing filler and reinforcement phase to improve mechanical properties and structures of membranes. For instance, the addition of 1 wt% of the CNC can improve the Young's modulus of co-polyamide nanofiber membrane by 224% and the tensile strength by 110%[57]. Elongation at break of PVDF/CNC nanocomposite membrane increased essentially with increasing the content of CNC as a result of the membrane structure becomes more crystalline and more orderly in membrane matrix as well as stronger interfacial adhesion[58]. However, the tensile stress and Yong's modulus of membranes respectively reduced at 8 and 6 wt% of CNC. The CNC that blended with PVDF makes the network structure of PVDF membrane becomes more porous and permeable. Thus, the flux of oil/water separation is higher in PVDF/CNC membrane than that in the pristine PVDF membrane. In spite of that, CNC does not change much the values of WCA of the PVDF membranes[58,59].

Albeit nanofiber membranes possess a higher fouling resistance than casted phase inversion membranes[60], unstable structure of the nanofiber membrane due to poor adhesion of inter-fibers has restricted their durability especially in long-term oil/water separation. Wang et al.[61] strengthened the structural stability of PAN/CNC nanofiber membrane through NaOH hydrolysis by forming hydrogen bonding when hydroxyl groups in CNC are crosslinked with carbonyl groups in PAN. The addition of 10 wt% CNC has increased the tensile strength (4.2 MPa) and elongation at break (62.83%) respectively at 117.6% and 28.6% compared to the pristine PAN membrane. The hydrolyzed PAN/CNC membrane is superamphiphilic in the air and underwater oleophobic with UWOCA of 141°. Nevertheless, the swelling is possible when immersing the hydrolyzed nanofiber membrane in water because the nanofibers are superhydrophilic. The same researchers have further modified the hydrolyzed PAN/CNC with silica nanoparticles to produce a more structurally stable membrane[62]. The water absorption ratio, an indicator of swelling behavior, of silica modified PAN/CNC membrane was 6.7 which was greatly reduced from 25.4 of the unmodified PAN/CNC membrane. The tensile strength of silica modified PAN/CNC was higher than that of unmodified PAN/CNC but a bit lower than that of hydrolyzed PAN/CNC. The silica formed hierarchical assemblies on the fiber surface has made the membrane became more superhydrophilic and underwater superoleophobic.

Although CNC is a cheap biomaterial with good mechanical properties, good biocompatibility and easier in chemical modification due to the abundance of hydroxyl groups, the addition amount of CNC is still low because of different interfacial polarity of CNC/polymer blend and self-polymerization of CNC. Hence, Wang et al.[63] modified the physicochemical properties of CNC surface by using sulfhydryl functionalities. The optimum amount of sulfhydryl-functionalized CNC (SC) that could be blended with PAN was 48 wt%.

Additionally, the maximum tensile stress of SC(48)/PAN was 3.4 times higher than that of the pristine PAN. Spider-web like structure of SC(48)/PAN nanocomposite membrane with porosity of 91.7% and underwater superoleophobicity was produced.

Inspired by the phospholipid bilayer structure of cell membranes which is selective permeability, surface superhydrophilicity and high against pollution, Wu et al.[64] designed a biomimetic cellulose-nanocrystal-based composite membrane (CCM) from CNC and poly (2-vinylpyridine-b-2-(Dimethylamino)ethyl methacrylate) block polymers. Superhydrophilic and underwater superoleophobic of CCM was induced by the hydrophilic nature of CNC and emergence of micro-nano structure on the membrane surface. The membrane exhibited highly resistant to oily contaminants such as chloroform, kerosene and viscous silicone oils as the membrane remained clean after clean with water.

5. Cellulose acetate

Cellulose acetate (CA) is a product of acetylation of cellulose whereby the hydroxyl groups of cellulose are partially or completely acetylated. Partial acetylation of cellulose can result in the acetyl content varies between 29.0% and 44.8% which is corresponding to mono-, di- and triacetate[65]. Cellulose monoacetate is water-soluble, whereas cellulose triacetate is water-insoluble and hydrophobic[66]. Degree of substitution (DS) of cellulose triacetate is approximately 3 and may be subsequently acid-hydrolyzed to reduce the DS. **Figure 5** shows the molecular structure of cellulose triacetate.

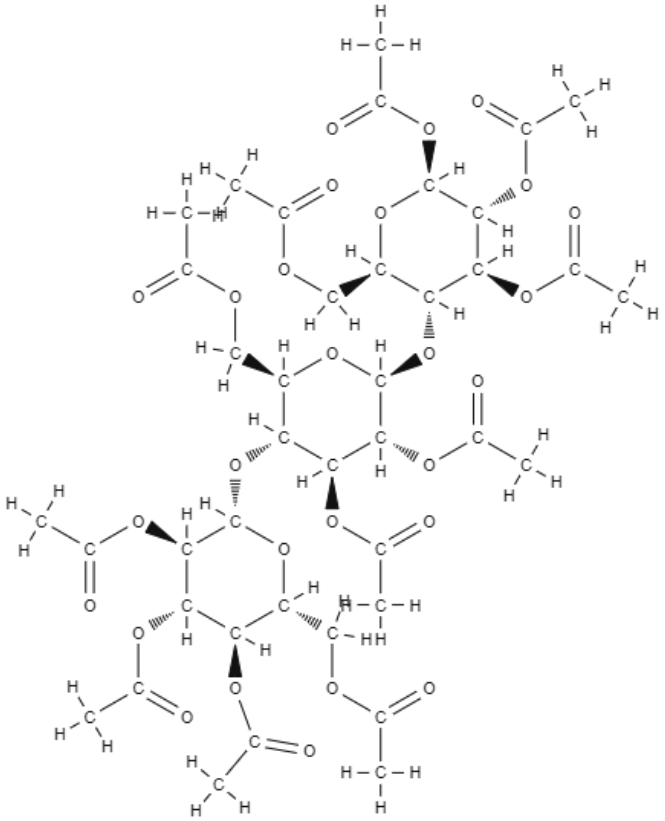

Figure 5. Molecular structure of cellulose triacetate.

Fouling in CA membranes can behave uniquely due to production process by different manufacturers will result in diverse membrane wettability. Thus, modification of CA membranes in various ways has been investigated by worldwide researchers to obtain superwetting properties of membranes when dealing with oily

wastewaters. Blending of hydrophilic components into a dope solution is the simplest technique to further improve the hydrophilicity of CA membrane. Anggraeni et al.[67] used a natural polar compound of methyl gallate to enhance the hydrophilicity of CA membrane. The methyl gallate at the content of 5 w/w% was able to reduce WCA from 68.01° of pristine membrane to 53.18° and boost the fouling recovery ratio to 98.73% for cooking oil emulsion. Nanoparticles such as amine-functionalized silicon carbide ($SiC-NH_2$) and PDA-sulfobetaine methacrylate (SBMA) respectively blended with CA membranes are able to lower the WCAs to 58.6° and approximately 54°[68,69]. P(PDA-SBMA) nanoparticle has slightly elevated the UWOCA from 121.97° of pristine CA membrane to 130.41°. Compare to flux recovery ratio of pristine CA membrane at around 60%–75%, both types of modified CA membranes achieved higher values at 84%–85%. However, the addition of nanoparticles did essentially reduce the tensile strength and elongation at break of CA membrane[68].

Wetting properties of most of the pristine as well as modified CA membranes are not sufficiently strong[67–69] which can shorten and discontinue the oil/water separation process due to fouling. To overcome this issue, the development of a hydration layer on the CA membrane surface is possible to drive away the oily foulants and prevent from fouling. Li et al.[70] constructed 3D hierarchical nanostructure on a superhydrophilic CA membrane surface to improve its underwater superoleophobicity by proposing a combination of 1D and 2D materials. Such hierarchical structure can trap the adsorbed water and develop a thin water layer on membrane surface which can significantly hamper the interaction between membrane surface and oil. The pristine CA membrane exhibited severe fouling and nearly no possibility for reuse after decane-in water emulsion filtration even the membrane was superhydrophilic in the air. The 3D hierarchical nanostructure designed from graphene oxide (2D material) and sepiolite (1D materials) recorded >90% of permeability recovery after the third cycle of filtration. On the other hand, Wang et al.[71] deacetylated a cellulose diacetate (39.8 wt% acetyl and 3.5 wt% hydroxyl) nanofiber membrane which initially was hydrophobic, superoleophilic and amphiphobic under water and oil. During deacetylation with a weak alkali, the ester groups of CA membrane were converted into hydroxyl. The hydroxyl groups that are available on deacetylated CA (d-CA) membrane surface formed hydrogen bonds with water molecules and hence developed a thin water film. The d-CA membrane exhibited multifunctional properties such as superhydrophilic and superoleophilic in the air, superhydrophilic underoil and oleophobic underwater. The separation flux was several times higher than that of commercial CA membranes.

Nevertheless, poor mechanical properties of modified membranes especially nanofiber membranes are crucial in industrial applications. Several researchers have introduced a few polymers which considerably good mechanical properties to modify the CA nanofiber membranes such as polyacrylonitrile (PAN)[72], thermoplastic polyurethane (TPU)[73] and polyamide acid (PAA)[74,75]. Karki et al.[72] staked by alternate electrospinning between hydrophobic CA and hydrophobic polyacrylonitrile (PAN) fibrous layers to form a nanofiber composite membrane. The stacking layers of CA/PAN composite fibers were pressed by using a hot roller at 80 ℃ to enhance the entanglements and attachment of fibers. The WCA of CA/PAN fiber composite membrane was 126.2° which was hydrophobic. The CA/PAN composite fiber layers were subjected to deacetylation to produce cellulose/PAN with WCA reduced to 25°. The cellulose/PAN composite membrane exhibited a high resistance to deformation with stress 1.64 MPa and strain 109.81% which were greater than individual cellulose and PAN. Wang et al.[73] documented that the elongation at break of dCA/TPU composite membranes increased from approximately 8.98 to 126.39% when the TPU content increased which was due to the prominent elasticity of the TPU material. The maximum ultimate tensile strength was 20.95 MPa for a mass ratio CA:TPU at 3:7 and the ultimate tensile strength at this mass ratio was greater than individual d-CA (2.36 MPa) and d-TPU (11.2 MPa). These dCA/TPU composite membranes exhibited hydrophobic and superoleophilic in the air, oleophobic underwater and hydrophobic underoil. Co-axial electrospinning of CA and PAA, and subsequently imidizated have been successfully to form a high-strength core-sheath CA/PI nanofiber membrane[74]. The tensile strength of CA/PI membrane was 230 MPa which was about 20 times

higher than that of CA membrane whereas the tensile strain was around 11%. The tensile strain of CA/PI was extended to 52% when ether linkages in the backbone were introduced to PAA[75]. However, the tensile strength was reduced to 130 MPa. The CA/PI fibers were further modified with fluorinated polybenzoxazine and silica nanoparticles to obtain superhydrophobic and superoleophilic surfaces.

CA has also been applied in the development of multifunctional Janus membranes. Thermoplastic polymers with excellent in mechanical strength, chemical stability, corrosion resistance, flexibility, ability to withstand harsh environment and low surface energy such as PVDF-HFP, PVDF and PU have been used to fabricate the Janus membrane with CA[76–78]. Deacetylation of CA membrane not only can produce outstanding wetting properties i.e., superamphiphilic in the air, superhydrophilic underoil and oleophobic underwater[77], but also enhanced the interface bonding hydrophilic-hydrophobic bilayer membranes[76]. On the other hand, Zhang et al.[78] enhanced the interface bonding of CA/PU by considering the polymer molecular chain interaction through the formation of hydrogen bonds between hydroxyl, carbonyl and amide groups.

6. Carboxymethyl cellulose

Carboxymethyl cellulose (CMC) is generated from a reaction of cellulose with chloroacetate in an alkali condition. In CMC, substitution of carboxymethyl groups with hydroxyl groups on C2, C3 or C6 positions of glucopyranose monomers which are the backbone of cellulose[79,80]. **Figure 6** shows the molecular structure of CMC. CMC is anionic and water soluble. Solubility of CMC relies on a degree of polymerization (DP) and degree of substitution (DS). The solubility of CMC in water increases when DP decreases and DS increases[81].

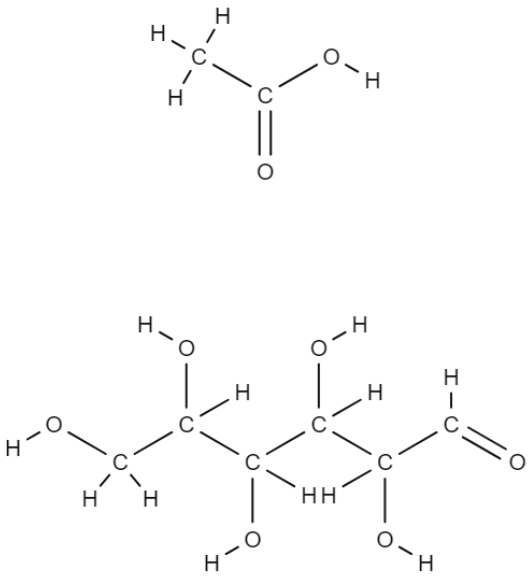

Figure 6. Molecular structure of carboxymethyl cellulose.

Natural sodium CMC has been used as an organic ligand because it is plentiful of COO- groups which can crosslink with metal ions such as Fe(III) to form Fe(III)-CMC chelate hydrogel[82]. The Fe(III)-CMC chelate hydrogel that coated on the needlelike structure of copper oxide has created superhydrophilic and underwater oleophobic surface. The hydrogel was excellent in water stability and seawater. However, WCA increased i.e., the hydrogel became unstable when acidity increased to below pH 4. Other researchers created a spider-web like structure using CMC to fabricate superhydrophilic and underwater superoleophobic surface on a PVDF membrane[83]. CMC was mixed with polyvinylpyrrolidone (PVP) to form a gel solution. The PVDF membrane was dip coated with the gel and binding occurred through diffusion, van der Waals forces and electrostatic interactions during heat treatment. Further chemical crosslinking by epichlorohydrin to promote an ultra-thin gel layer formed inside the spider web. The oil/water separation flux of the 0.5 wt% CMC spider-

web on the PVDF membrane exhibited 4.2-fold higher than that of the pristine PVDF membrane. Additionally, the elastic modulus and fracture strength of CMC/PVDF membranes increased with increasing the CMC content while the elongation achieved maximum at 0.5 wt% CMC.

Organic solvents such as N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), dimethylacetamide (DMA) and dimethyl sulfoxide (DMSO) are commonly used to fabricate membranes via nonsolvent-induce phase separation (NIPS). A polymer is dissolved in the organic solvent and a polymeric membrane is formed through a phase separation when coagulated in a nonsolvent bath. However, these organic solvents are toxic, flammable and hazardous to the environment and human. For instance, NMP has been banned since 2020 by the European Union due to the toxic concern[84]. Li et al.[85] proposed to fabricate sodium CMC membrane using aqueous phase separation (APS) which used water as both solvent and nonsolvent. CMC and chitosan (CS) were mixed at low pH i.e., pH 1, whereby CMC was uncharged. The casting film of CMC/CS was then immersed in a high pH i.e., pH 5; hence CMC was negatively charged and form a water insoluble polyelectrolyte complex with the positively charged CS. The CMC/CS membrane can withstand water pressure up to 4 bars in microfiltration. However, the mechanical strength of the membrane is relatively low; for example, Young modulus was 4.29 MPa, elongation at break was 6.84% and tensile stress was 0.22 MPa. Furthermore, the membrane permeability was low because the membrane structure was greatly controlled by the pH. The membrane was swollen at low and high pHs because the formation of polyelectrolyte complex was unstable.

Although CMC has been much developed and investigated in other applications such as food and beverage[86], packaging[87], drug delivery[88], tissue engineering[89] and advanced battery applications[90] as well as wastewater treatment[91–93], its application in oil/water separation is still very limited.

7. Conclusions and remarks for future directions

The combination of biomaterials and bio-inspired concepts in membrane development is a more sustainable solution to oily wastewater treatment. The oil/water separation performance as well as mechanical properties of bio-membranes formulated from cellulose and its derivatives is competitive with that of traditional membranes designed from fuel-based polymers. Nonetheless, the application of cellulose especially its derivatives in membrane development for oil/water separation is still in infancy with countable publications. A few remarks of future research directions are summarized as follows.

- As documented in current literatures, almost all membrane formulations employ cellulose or cellulose derivatives partially in fabricating the membranes for oil/water separation. Investigation of new simple techniques that fully utilize either cellulosic materials alone or blending with other biomaterials in membrane preparation is recommended for future research. In addition, it is desirable to substitute the traditional organic solvents with greener solvents. Nanoparticles, crosslinkers and substrates that are derived from agricultural wastes are highly needed to fabricate a sustainable and smart membrane in the oily wastewater treatment.
- Innovative techniques of fabrication and modification on cellulose based membranes are essential to optimize the membrane structure and thus improve the separation performance. Because of the nature of cellulose, the hydroxyls interact and form hydrogen bonds within the structure and make the membrane structure denser. Porous structure is preferable to attain high water fluxes.
- Extension and comprehensive studies on cellulosic membrane stability in harsh and corrosive oily wastewaters are indispensable. These include the effects of cellulosic materials on mechanical properties, swelling, disintegration of membrane structure, detachment of bio-modifiers and long-term operation due to biodegradability.

- Investigation of multifunctional cellulosic membranes in large-scale applications with real oily wastewaters will be an interesting and attractive topic in future. Modelling studies are less reported in the current literatures. Rigorous models of membrane development and oil/water separation performance as well as cost analysis are required.

Acknowledgments

The authors would like to thank Universiti Malaysia Sabah for providing the resources to complete this article.

Conflict of interest

The authors declare no conflict of interest.

References

1. United Nations, Secretary General Assembly—Remarks at Launch of International Decade for Action "Water for Sustainable Development" 2018–2028. Available online: https://www.un.org/sg/en/content/sg/speeches/2018-03-22/decade-action-water-sustainable-development-remarks (accessed on 10AM, 30 June 2023 XX).
2. UNESCO and UNESCO i-WSSM. Water Reuse within a Circular Economy Context (Series II). Global Water Security Issues (GWSI) Series–No. 2. UNESCO Publishing; 2020.
3. Cui J, Zhou Z, Xie A, et al. Bio-inspired fabrication of superhydrophilic nanocomposite membrane based on surface modification of SiO2 anchored by polydopamine towards effective oil-water emulsions separation. Separation and Purification Technology. 2019, 209: 434-442. doi: 10.1016/j.seppur.2018.03.054
4. Xu Z, Li L, Liu J, et al. Mussel-inspired superhydrophilic membrane constructed on a hydrophilic polymer network for highly efficient oil/water separation. Journal of Colloid and Interface Science. 2022, 608: 702-710. doi: 10.1016/j.jcis.2021.09.123
5. Sun F, Li TT, Zhang X, et al. In situ growth polydopamine decorated polypropylen melt-blown membrane for highly efficient oil/water separation. Chemosphere. 2020, 254: 126873. doi: 10.1016/j.chemosphere.2020.126873
6. Abdel-Aty AAR, Aziz YSA, Ahmed RMG, et al. High performance isotropic polyethersulfone membranes for heavy oil-in-water emulsion separation. Separation and Purification Technology. 2020, 253: 117467. doi: 10.1016/j.seppur.2020.117467
7. Kumar A, Nayak K, Münch AS, et al. Mussel primed grafted zwitterionic phosphorylcholine based superhydrophilic/underwater superoleophobic antifouling membranes for oil-water separation. Separation and Purification Technology. 2022, 290: 120887. doi: 10.1016/j.seppur.2022.120887
8. Fan T, Miao J, Li Z, et al. Bio-inspired robust superhydrophobic-superoleophilic polyphenylene sulfide membrane for efficient oil/water separation under highly acidic or alkaline conditions. Journal of Hazardous Materials. 2019, 373: 11-22. doi: 10.1016/j.jhazmat.2019.03.008
9. Lustenberger S, Castro-Muñoz R. Advanced biomaterials and alternatives tailored as membranes for water treatment and the latest innovative European water remediation projects: A review. Case Studies in Chemical and Environmental Engineering. 2022, 5: 100205. doi: 10.1016/j.cscee.2022.100205
10. Naziri Mehrabani SA, Vatanpour V, Koyuncu I. Green solvents in polymeric membrane fabrication: A review. Separation and Purification Technology. 2022, 298: 121691. doi: 10.1016/j.seppur.2022.121691
11. Galiano F, Briceño K, Marino T, et al. Advances in biopolymer-based membrane preparation and applications. Journal of Membrane Science. 2018, 564: 562-586. doi: 10.1016/j.memsci.2018.07.059
12. Guo P, Wang F, Duo T, et al. Facile Fabrication of Methylcellulose/PLA Membrane with Improved Properties. Coatings. 2020, 10(5): 499. doi: 10.3390/coatings10050499
13. Liu M, He Q, Guo Z, et al. Composite reverse osmosis membrane with a selective separation layer of double-layer structure for enhanced desalination, anti-fouling and durability properties. Desalination. 2021, 499: 114838. doi: 10.1016/j.desal.2020.114838
14. Jabbarvand Behrouz S, Khataee A, Safarpour M, et al. Carboxymethyl cellulose/polyethersulfone thin-film composite membranes for low-pressure desalination. Separation and Purification Technology. 2021, 269: 118720. doi: 10.1016/j.seppur.2021.118720
15. Mansor ES, Abdallah H, Shaban AM. Development of TiO_2/polyvinyl alcohol-cellulose acetate nanocomposite reverse osmosis membrane for groundwater-surface water interfaces purification. Materials Science and Engineering: B. 2023, 289: 116222. doi: 10.1016/j.mseb.2022.116222
16. McNamara JT, Morgan JLW, Zimmer J. A Molecular Description of Cellulose Biosynthesis. Annual Review of Biochemistry. 2015, 84(1): 895-921. doi: 10.1146/annurev-biochem-060614-033930

17. Zuppolini S, Salama A, Cruz-Maya I, et al. Cellulose Amphiphilic Materials: Chemistry, Process and Applications. Pharmaceutics. 2022, 14(2): 386. doi: 10.3390/pharmaceutics14020386
18. Grundke K, Pöschel K, Synytska A, et al. Experimental studies of contact angle hysteresis phenomena on polymer surfaces—Toward the understanding and control of wettability for different applications. Advances in Colloid and Interface Science. 2015, 222: 350-376. doi: 10.1016/j.cis.2014.10.012
19. Xu X, Long Y, Li Q, et al. Modified cellulose membrane with good durability for effective oil-in-water emulsion treatment. Journal of Cleaner Production. 2019, 211: 1463-1470. doi: 10.1016/j.jclepro.2018.11.284
20. Yang J, Cui J, Xie A, et al. Facile preparation of superhydrophilic/underwater superoleophobic cellulose membrane with $CaCO_3$ particles for oil/water separation. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2021, 608: 125583. doi: 10.1016/j.colsurfa.2020.125583
21. Li Z, Qiu F, Yue X, et al. Eco-friendly self-crosslinking cellulose membrane with high mechanical properties from renewable resources for oil/water emulsion separation. Journal of Environmental Chemical Engineering. 2021, 9(5): 105857. doi: 10.1016/j.jece.2021.105857
22. Huang Y, Zhan H, Li D, et al. Tunicate cellulose nanocrystals modified commercial filter paper for efficient oil/water separation. Journal of Membrane Science. 2019, 591: 117362. doi: 10.1016/j.memsci.2019.117362
23. Halim A, Xu Y, Lin KH, et al. Fabrication of cellulose nanofiber-deposited cellulose sponge as an oil-water separation membrane. Separation and Purification Technology. 2019, 224: 322-331. doi: 10.1016/j.seppur.2019.05.005
24. Ao C, Zhao J, Xia T, et al. Multifunctional $La(OH)_3$@cellulose nanofibrous membranes for efficient oil/water separation and selective removal of dyes. Separation and Purification Technology. 2021, 254: 117603. doi: 10.1016/j.seppur.2020.117603
25. Yin Z, Yuan F, Li M, et al. Self-cleaning, underwater writable, heat-insulated and photocatalytic cellulose membrane for high-efficient oil/water separation and removal of hazardous organic pollutants. Progress in Organic Coatings. 2021, 157: 106311. doi: 10.1016/j.porgcoat.2021.106311
26. Yin Z, Chen X, Zhou T, et al. Mussel-inspired fabrication of superior superhydrophobic cellulose-based composite membrane for efficient oil emulsions separation, excellent anti-microbial property and simultaneous photocatalytic dye degradation. Separation and Purification Technology. 2022, 286: 120504. doi: 10.1016/j.seppur.2022.120504
27. Yin Z, Yuan F, Xue M, et al. A multifunctional and environmentally safe superhydrophobic membrane with superior oil/water separation, photocatalytic degradation and anti-biofouling performance. Journal of Colloid and Interface Science. 2022, 611: 93-104. doi: 10.1016/j.jcis.2021.12.070
28. Yin Z, Li M, Chen Z, et al. A superhydrophobic pulp/cellulose nanofiber (CNF) membrane via coating ZnO suspensions for multifunctional applications. Industrial Crops and Products. 2022, 187: 115526. doi: 10.1016/j.indcrop.2022.115526
29. Yin Z, Li Z, Deng Y, et al. Multifunctional CeO_2-coated pulp/cellulose nanofibers (CNFs) membrane for wastewater treatment: Effective oil/water separation, organic contaminants photodegradation, and anti-bioadhesion activity. Industrial Crops and Products. 2023, 197: 116672. doi: 10.1016/j.indcrop.2023.116672
30. Orooji Y, Liang F, Razmjou A, et al. Preparation of anti-adhesion and bacterial destructive polymeric ultrafiltration membranes using modified mesoporous carbon. Separation and Purification Technology. 2018, 205: 273-283. doi: 10.1016/j.seppur.2018.05.006
31. Toh MJ, Oh PC, Ahmad AL, et al. Enhancing membrane wetting resistance through superhydrophobic modification by polydimethylsilane-grafted-SiO_2 nanoparticles. Korean Journal of Chemical Engineering. 2019, 36(11): 1854-1858. doi: 10.1007/s11814-019-0362-3
32. Ryu JH, Messersmith PB, Lee H. Polydopamine Surface Chemistry: A Decade of Discovery. ACS Applied Materials & Interfaces. 2018, 10(9): 7523-7540. doi: 10.1021/acsami.7b19865
33. Farzad E, Veisi H. Fe_3O_4/SiO_2 nanoparticles coated with polydopamine as a novel magnetite reductant and stabilizer sorbent for palladium ions: Synthetic application of Fe_3O_4/SiO_2 @PDA/Pd for reduction of 4-nitrophenol and Suzuki reactions. Journal of Industrial and Engineering Chemistry. 2018, 60: 114-124. doi: 10.1016/j.jiec.2017.10.017
34. Hong SH, Ryu JH, Lee H. Effect of charge on in vivo adhesion stability of catechol-conjugated polysaccharides. Journal of Industrial and Engineering Chemistry. 2019, 79: 425-430. doi: 10.1016/j.jiec.2019.07.017
35. Chen T, Yang M, Yang H, et al. Construction of DOPA-SAM multilayers with corrosion resistance via controlled molecular self-assembly. Journal of Industrial and Engineering Chemistry. 2019, 69: 179-186. doi: 10.1016/j.jiec.2018.09.018
36. Li H, Wu L, Zhang H, et al. Mussel-inspired fabrication of superhydrophobic cellulose-based paper for the integration of excellent antibacterial activity, effective oil/water separation and photocatalytic degradation. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2022, 640: 128490. doi: 10.1016/j.colsurfa.2022.128490
37. Xie A, Cui J, Liu Y, et al. Preparation of Janus membrane based on biomimetic polydopamine interface regulation and superhydrophobic attapulgite spraying for on-demand oil-water emulsion separation. Journal of Membrane Science. 2021, 627: 119242. doi: 10.1016/j.memsci.2021.119242

38. Zhang M, Yang Q, Gao M, et al. Fabrication of Janus cellulose nanocomposite membrane for various water/oil separation and selective one-way transmission. Journal of Environmental Chemical Engineering. 2021, 9(5): 106016. doi: 10.1016/j.jece.2021.106016
39. Xi J, Lou Y, Jiang S, et al. High flux composite membranes based on glass/cellulose fibers for efficient oil-water emulsion separation. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2022, 647: 129016. doi: 10.1016/j.colsurfa.2022.129016
40. Huang F, Li Q, Ji G, et al. Oil/water separation using a lauric acid-modified, superhydrophobic cellulose composite membrane. Materials Chemistry and Physics. 2021, 266: 124493. doi: 10.1016/j.matchemphys.2021.124493
41. Cao C, Cheng J. A novel Cu(OH)2 coated filter paper with superhydrophobicity for the efficient separation of water-in-oil emulsions. Materials Letters. 2018, 217: 5-8. doi: 10.1016/j.matlet.2018.01.026
42. Yin Z, Li M, Li Z, et al. A harsh environment resistant robust $Co(OH)_2$@stearic acid nanocellulose-based membrane for oil-water separation and wastewater purification. Journal of Environmental Management. 2023, 342: 118127. doi: 10.1016/j.jenvman.2023.118127
43. Ejeta DD, Tan FH, Mathivathanan A, et al. Preparation of fluorine- and nanoparticle-free superwetting polybenzoxazine/cellulose composites for efficient oil/water separations. Separation and Purification Technology. 2022, 288: 120675. doi: 10.1016/j.seppur.2022.120675
44. Xie A, Cui J, Chen Y, et al. One-step facile fabrication of sustainable cellulose membrane with superhydrophobicity via a sol-gel strategy for efficient oil/water separation. Surface and Coatings Technology. 2019, 361: 19-26. doi: 10.1016/j.surfcoat.2019.01.040
45. Wahid F, Zhao XJ, Duan YX, et al. Designing of bacterial cellulose-based superhydrophilic/underwater superoleophobic membrane for oil/water separation. Carbohydrate Polymers. 2021, 257: 117611. doi: 10.1016/j.carbpol.2020.117611
46. Shi Y, Chen X, Wu Q, et al. Enhance organic pollutants removal of wastewater by a PVDF/PDA-TiO_2 composite membrane with photocatalytic property. Journal of Environmental Chemical Engineering. 2023, 11(5): 110389. doi: 10.1016/j.jece.2023.110389
47. Han L, Shen L, Lin H, et al. 3D printing titanium dioxide-acrylonitrile-butadiene-styrene (TiO_2-ABS) composite membrane for efficient oil/water separation. Chemosphere. 2023, 315: 137791. doi: 10.1016/j.chemosphere.2023.137791
48. Cui Y, Zheng X, Xu T, et al. A Self-Cleaning TiO_2 Bacterial Cellulose Super-Hydrophilic Underwater Super-Oleophobic Composite Membrane for Efficient Oil–Water Separation. Molecules. 2023, 28(8): 3396. doi: 10.3390/molecules28083396
49. Etacheri V, Di Valentin C, Schneider J, et al. Visible-light activation of TiO_2 photocatalysts: Advances in theory and experiments. Journal of Photochemistry and Photobiology C: Photochemistry Reviews. 2015, 25: 1-29. doi: 10.1016/j.jphotochemrev.2015.08.003
50. Tian J, Chen L, Yin Y, et al. Photocatalyst of TiO2/ZnO nano composite film: Preparation, characterization, and photodegradation activity of methyl orange. Surface and Coatings Technology. 2009, 204(1-2): 205-214. doi: 10.1016/j.surfcoat.2009.07.008
51. Li N, Tian Y, Zhang J, et al. Precisely-controlled modification of PVDF membranes with 3D TiO2/ZnO nanolayer: enhanced anti-fouling performance by changing hydrophilicity and photocatalysis under visible light irradiation. Journal of Membrane Science. 2017, 528: 359-368. doi: 10.1016/j.memsci.2017.01.048
52. Wahid F, Zhao XQ, Cui JX, et al. Fabrication of bacterial cellulose with TiO2-ZnO nanocomposites as a multifunctional membrane for water remediation. Journal of Colloid and Interface Science. 2022, 620: 1-13. doi: 10.1016/j.jcis.2022.03.108
53. Wang F ping, Zhao X jun, Wahid F, et al. Sustainable, superhydrophobic membranes based on bacterial cellulose for gravity-driven oil/water separation. Carbohydrate Polymers. 2021, 253: 117220. doi: 10.1016/j.carbpol.2020.117220
54. Lin N, Dufresne A. Surface chemistry, morphological analysis and properties of cellulose nanocrystals with gradiented sulfation degrees. Nanoscale. 2014, 6(10): 5384-5393. doi: 10.1039/c3nr06761k
55. Islam MN, Rahman F. Production and modification of nanofibrillated cellulose composites and potential applications. Green Composites for Automotive Applications. Published online 2019: 115-141. doi: 10.1016/b978-0-08-102177-4.00006-9
56. Ratna AS, Ghosh A, Mukhopadhyay S. Advances and prospects of corn husk as a sustainable material in composites and other technical applications. Journal of Cleaner Production. 2022, 371: 133563. doi: 10.1016/j.jclepro.2022.133563
57. Sobolčiak P, Tanvir A, Popelka A, et al. The preparation, properties and applications of electrospun co-polyamide 6,12 membranes modified by cellulose nanocrystals. Materials & Design. 2017, 132: 314-323. doi: 10.1016/j.matdes.2017.06.056
58. Wang X, Cheng W, Wang D, et al. Electrospun polyvinylidene fluoride-based fibrous nanocomposite membranes reinforced by cellulose nanocrystals for efficient separation of water-in-oil emulsions. Journal of Membrane Science. 2019, 575: 71-79. doi: 10.1016/j.memsci.2018.12.057

59. Mousa HM, Fahmy HS, Abouzeid R, et al. Polyvinylidene fluoride-cellulose nanocrystals hybrid nanofiber membrane for energy harvesting and oil-water separation applications. Materials Letters. 2022, 306: 130965. doi: 10.1016/j.matlet.2021.130965
60. Sarbatly R, Chiam CK. An Overview of Recent Progress in Nanofiber Membranes for Oily Wastewater Treatment. Nanomaterials. 2022, 12(17): 2919. doi: 10.3390/nano12172919
61. Wang D, Yang H, Wang Q, et al. Composite membranes of polyacrylonitrile cross-linked with cellulose nanocrystals for emulsion separation and regeneration. Composites Part A: Applied Science and Manufacturing. 2023, 164: 107300. doi: 10.1016/j.compositesa.2022.107300
62. Wang D, Mhatre S, Chen J, et al. Composites based on electrospun fibers modified with cellulose nanocrystals and SiO2 for selective oil/water separation. Carbohydrate Polymers. 2023, 299: 120119. doi: 10.1016/j.carbpol.2022.120119
63. Wang Q, Wang D, Cheng W, et al. Spider-web-inspired membrane reinforced with sulfhydryl-functionalized cellulose nanocrystals for oil/water separation. Carbohydrate Polymers. 2022, 282: 119049. doi: 10.1016/j.carbpol.2021.119049
64. Wu J, Cui Z, Su Y, et al. Biomimetic cellulose-nanocrystalline-based composite membrane with high flux for efficient purification of oil-in-water emulsions. Journal of Hazardous Materials. 2023, 446: 130729. doi: 10.1016/j.jhazmat.2023.130729
65. Kaur G, Grewal J, Jyoti K, et al. Oral controlled and sustained drug delivery systems. Drug Targeting and Stimuli Sensitive Drug Delivery Systems. Published online 2018: 567-626. doi: 10.1016/b978-0-12-813689-8.00015-x
66. Holtzapple MT. CELLULOSE. Encyclopedia of Food Sciences and Nutrition. Published online 2003: 998-1007. doi: 10.1016/b0-12-227055-x/00185-1
67. Anggraeni VS, Sutrisna PD, Goh PS, et al. Development of antifouling membrane film for treatment of oil-rich industrial waste. Materials Today: Proceedings. Published online March 2023. doi: 10.1016/j.matpr.2023.02.151
68. Bose J, Dasgupta J, Adhikari U, et al. Tuning permeation characteristics of cellulose acetate membrane embedded with raw and amine-functionalized silicon carbide nanoparticle for oil-water separation. Journal of Water Process Engineering. 2021, 41: 102019. doi: 10.1016/j.jwpe.2021.102019
69. De Guzman MR, Andra CKA, Ang MBMY, et al. Increased performance and antifouling of mixed-matrix membranes of cellulose acetate with hydrophilic nanoparticles of polydopamine-sulfobetaine methacrylate for oil-water separation. Journal of Membrane Science. 2021, 620: 118881. doi: 10.1016/j.memsci.2020.118881
70. Li F, Gao R, Wu T, et al. Role of layered materials in emulsified oil/water separation and anti-fouling performance of modified cellulose acetate membranes with hierarchical structure. Journal of Membrane Science. 2017, 543: 163-171. doi: 10.1016/j.memsci.2017.08.053
71. Wang W, Lin J, Cheng J, et al. Dual super-amphiphilic modified cellulose acetate nanofiber membranes with highly efficient oil/water separation and excellent antifouling properties. Journal of Hazardous Materials. 2020, 385: 121582. doi: 10.1016/j.jhazmat.2019.121582
72. Karki HP, Kafle L, Ojha DP, et al. Cellulose/polyacrylonitrile electrospun composite fiber for effective separation of the surfactant-free oil-in-water mixture under a versatile condition. Separation and Purification Technology. 2019, 210: 913-919. doi: 10.1016/j.seppur.2018.08.053
73. Wang W, Ma X, Si J, et al. Deacetylated Cellulose Acetate/Polyurethane Composite Nanofiber Membranes with Highly Efficient Oil/Water Separation and Excellent Mechanical Properties. Macromolecular Materials and Engineering. 2021, 306(10). doi: 10.1002/mame.202100270
74. Ma W, Zhang Q, Samal SK, et al. Core–sheath structured electrospun nanofibrous membranes for oil–water separation. RSC Advances. 2016, 6(48): 41861-41870. doi: 10.1039/c6ra06224e
75. Ma W, Guo Z, Zhao J, et al. Polyimide/cellulose acetate core/shell electrospun fibrous membranes for oil-water separation. Separation and Purification Technology. 2017, 177: 71-85. doi: 10.1016/j.seppur.2016.12.032
76. Guo Z, Guo F, Gao L, et al. A Janus Mesh with Robust Interface and Controllable Wettability for Water Transport. Parvinzadeh Gashti M, ed. Journal of Nanomaterials. 2022, 2022: 1-10. doi: 10.1155/2022/8020914
77. Si J, Zhao M, Marcelle S seukep alix, et al. Design and Modification of Janus Polyvinylidene Fluoride/Deacetylated Cellulose Acetate Nanofiber Membrane and its Multifunctionality. Advanced Materials Interfaces. 2023, 10(11). doi: 10.1002/admi.202201550
78. Zhang Y, Yang M, Zhou Y, et al. Transition sandwich Janus membrane of cellulose acetate and polyurethane nanofibers for oil–water separation. Cellulose. 2022, 29(3): 1841-1853. doi: 10.1007/s10570-021-04402-8
79. McDonald JE, Rooks DJ, McCarthy AJ. Methods for the Isolation of Cellulose-Degrading Microorganisms. Methods in Enzymology. Published online 2012: 349-374. doi: 10.1016/b978-0-12-415931-0.00019-7
80. Janmohammadi M, Nazemi Z, Salehi AOM, et al. Cellulose-based composite scaffolds for bone tissue engineering and localized drug delivery. Bioactive Materials. 2023, 20: 137-163. doi: 10.1016/j.bioactmat.2022.05.018
81. Ergun R, Guo J, Huebner-Keese B. Cellulose. Encyclopedia of Food and Health. Published online 2016: 694-702. doi: 10.1016/b978-0-12-384947-2.00127-6
82. Dai J, Chang Z, Xie A, et al. One-step assembly of Fe(III)-CMC chelate hydrogel onto nanoneedle-like CuO@Cu membrane with superhydrophilicity for oil-water separation. Applied Surface Science. 2018, 440: 560-569. doi: 10.1016/j.apsusc.2018.01.213

83. Yang J, Lin L, Wang Q, et al. Engineering a superwetting membrane with spider-web structured carboxymethyl cellulose gel layer for efficient oil-water separation based on biomimetic concept. International Journal of Biological Macromolecules. 2022, 222: 2603-2614. doi: 10.1016/j.ijbiomac.2022.10.043
84. Zou D, Nunes SP, Vankelecom IFJ, et al. Recent advances in polymer membranes employing non-toxic solvents and materials. Green Chemistry. 2021, 23(24): 9815-9843. doi: 10.1039/d1gc03318b
85. Li L, Baig MI, de Vos WM, et al. Preparation of Sodium Carboxymethyl Cellulose–Chitosan Complex Membranes through Sustainable Aqueous Phase Separation. ACS Applied Polymer Materials. 2023, 5(3): 1810-1818. doi: 10.1021/acsapm.2c01901
86. Zhou L, Jiang J, Feng F, et al. Effects of carboxymethyl cellulose on the emulsifying, gel and digestive properties of myofibrillar protein-soybean oil emulsion. Carbohydrate Polymers. 2023, 309: 120679. doi: 10.1016/j.carbpol.2023.120679
87. Ramakrishnan R, Kulandhaivelu SV, Roy S, et al. Characterisation of ternary blend film of alginate/carboxymethyl cellulose/starch for packaging applications. Industrial Crops and Products. 2023, 193: 116114. doi: 10.1016/j.indcrop.2022.116114
88. Karimi T, Mottaghitalab F, Keshvari H, et al. Carboxymethyl chitosan/sodium carboxymethyl cellulose/agarose hydrogel dressings containing silk fibroin/polydopamine nanoparticles for antibiotic delivery. Journal of Drug Delivery Science and Technology. 2023, 80: 104134. doi: 10.1016/j.jddst.2022.104134
89. Shah SA, Sohail M, Karperien M, et al. Chitosan and carboxymethyl cellulose-based 3D multifunctional bioactive hydrogels loaded with nano-curcumin for synergistic diabetic wound repair. International Journal of Biological Macromolecules. 2023, 227: 1203-1220. doi: 10.1016/j.ijbiomac.2022.11.307
90. Tangthuam P, Kao-ian W, Sangsawang J, et al. Carboxymethyl cellulose as an artificial solid electrolyte interphase for stable zinc-based anodes in aqueous electrolytes. Materials Science for Energy Technologies. 2023, 6: 417-428. doi: 10.1016/j.mset.2023.04.003
91. Zhao M, Fang G, Zhang S, et al. Template-directed growth of sustainable carboxymethyl cellulose-based aerogels decorated with ZIF-67 for activation peroxymonosulfate degradation of organic dyes. International Journal of Biological Macromolecules. 2023, 230: 123276. doi: 10.1016/j.ijbiomac.2023.123276
92. Zhu H, Chen S, Duan H, et al. Removal of anionic and cationic dyes using porous chitosan/carboxymethyl cellulose-PEG hydrogels: Optimization, adsorption kinetics, isotherm and thermodynamics studies. International Journal of Biological Macromolecules. 2023, 231: 123213. doi: 10.1016/j.ijbiomac.2023.123213
93. Zhang H, Yang H, Shao J, et al. Multifunctional carboxymethyl cellulose sodium encapsulated phosphorus-enriched biochar composites: Multistage adsorption of heavy metals and controllable release of soil fertilization. Chemical Engineering Journal. 2023, 453: 139809. doi: 10.1016/j.cej.2022.139809