Chapter

Organic-Inorganic Hybrid Membranes for Agricultural Wastewater Treatment

Katrina Jose, Fadi Layyous Gedeon and Chil-Hung Cheng

Abstract

The global agricultural sector consumes a large amount of fresh water for irrigation. Less than half of agricultural wastewater is properly treated before discharging to environment or recycling. Treatment of agricultural wastewater for reuse in irrigation can alleviate burden on water resources as well as protect the environment from detrimental effects caused by various organics, pesticides, and soluble ions in the wastewater stream. This work reviews several current membrane technologies that are applied at removing the pollutants in agricultural wastewater. Subsequently, several strategies to further improve membranes' performance are highlighted. The advancement of materials science at the nanometer scale can assist the fabrication of membranes with higher selectivity of pollutant removal, higher permeate flux, and lower membrane fouling.

Keywords: agricultural wastewater, mixed-matrix membranes, membrane filtration, osmosis, membrane distillation, metal-organic frameworks, zeolites, nanofillers

1. Introduction

The agricultural sector is the biggest freshwater user, which accounts for over 70% of world's total freshwater consumption. This specific usage varies depending on geographical locations, as shown in **Figure 1** [1]. For example, Asia and Africa both show about 81% of total withdrawal water is used by the agricultural sector, with the volumes of 2069 × 10^9 and 184 × 10^9 m^3/year, respectively. In North America, as of 2010, about 34% of total freshwater withdrawal is used by the agricultural sector [2]. For instance, estimated 4.75 × 10^9 m^3/year freshwater was withdrawn by the agricultural sector in Canada during the period of 2008–2012. The demand of freshwater generates a heavy burden on water resources management globally. In addition, surface run off which is one of hydrological cycle mechanisms, brings rotting plants, pesticides, fertilizers, and contaminations into watersheds. These contaminants, nitrates, phosphates, and others cause algae blooms in waters. The growth of algae results in hypoxic conditions with low biochemical oxygen demand (BOD). This significantly impacts the livestock and aesthetics of aqua systems. Moreover, some of the aforementioned contaminants with biological activity would alter the endocrine system of aquatic organisms (endocrine disrupters, EDs), when presenting excessively in aqua systems. Some EDs might trigger hormonal changes in some aquatic species. Thus, if EDs enter water sources for human consumption, it poses huge adverse impacts on human health [3]. Hence, reuse of wastewater for the agricultural sector is an alternative resolution to alleviate the demand on freshwater.

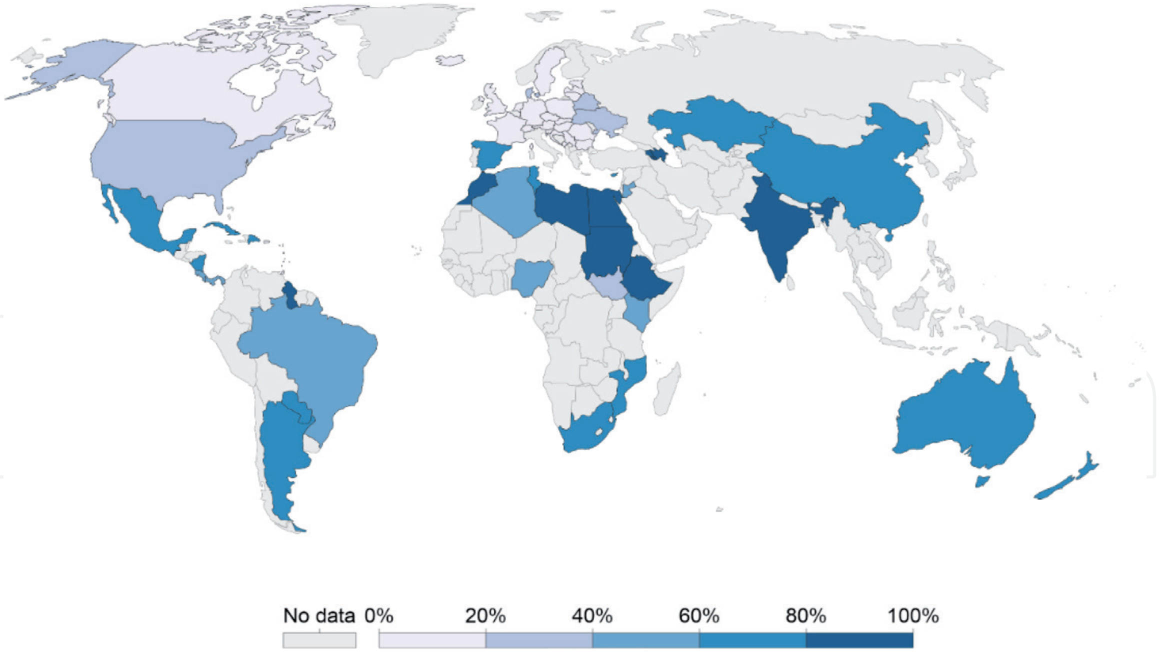

Figure 1.
In 2015, the percentage of agricultural water in the total water withdrawals which is the total water used for agriculture, industry, and domestic purposes [1]. Agricultural water is defined as the annual quantity of self-supplied water withdrawn for irrigation, livestock, and aquaculture usage.

Geographical location	North America[1]	Latin America[2]	Europe[3]	The Russian Federation[4]	Middle East and North Africa[5]	Sub-Saharan Africa[6]	Oceania[7]	Asia[8]
Estimated yearly volume of generated wastewater (km^3)	85	29.8	52.4	27.48	22.3	3.7	2.1	133.3
Percentage of generated wastewater that was treated	71%	20%	71%	51%	51%	n/a	84%	32%
Percentage of treated wastewater for agriculture	45%	n/a	n/a	n/a	51%	n/a	n/a	1%

Time period of collected data in Ref. [7].
[1]2004 and 2010.
[2]1996–2002.
[3]2003–2013.
[4]2003–2012.
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[6]2000–2003.
[7]2010 and 2012.
[8]2001–2012.

Table 1.
Statistics of generated wastewater and wastewater treated [7].

Reuse of wastewater for agricultural usages not only alleviate the demand of fresh water, but also have several benefits through the ripple effect of water conservation: energy saving on the cost of re-surfacing ground water [3], improvement of crop yield [4], increase of soil quality, expansion of agricultural border, as well as reduction of fertilizers usage and expenses [5, 6]. As summarized in **Table 1**, the volume of yearly-generated wastewater and the percentage of treated wastewater vary dramatically depending on geography, possibly due to the economy level and industrialization. In general, the percentage of generated wastewater that receive appropriate treatment before reuse or discharge is about 50%. However, it is noteworthy that less than half of the appropriately-treated wastewater is reused in agriculture sectors in most of continents. This low usage of treated wastewater implies that there exist a great opportunity to maximize the portion of treated wastewater, such that it can alleviate the loads on fresh water resources.

2. Status quo of agricultural wastewater treatment

In nature, one of wastewater treatment processes that occur spontaneously is where bacteria or other micro-organisms in the wastewater stream digest the sewage and other organic matters, yielding new micro-organisms, carbon dioxide and others [8]. In community, wastewater treatment plant is to speed up the natural processes from which the water is purified. Firstly, the wastewater from communities flows through screens, and grit chambers to remove large particulate pollutants, such as sand, debris, and floating objects. The stream subsequently passes through a sedimentation tank to remove suspended solids. This is categorized as the primary treatment. In order to meet more stringent environment regulations, the effluent from the primary treatment flows through a trickling filter and/or an activated sludge process, with the main purpose to remove organic matters. The effluent from the process is sent to another sedimentation tank to remove excess bacteria. At the end, the exit stream from the sedimentation tank is disinfected with chlorine before being discharged into environment. This is the secondary treatment. More advanced waste treatment techniques are applied after the secondary treatment, in order to produce more usable treated water for discharging or for reuse. These techniques include filtration, distillation, and reverse osmosis. The following lists techniques that are used for agricultural wastewater treatment:

2.1 Constructed wetland (CW)

Wetlands are midway areas between land and lakes or oceans, such as swamps or tidal wetlands. Commonly, wetlands are featured with the flow of surface or near-surface shallow water, and saturated substrates. The saturated substrates are usually under oxygen-poor conditions that support the growth of anaerobic microorganisms community. The near-surface shallow water flow can maximum the mass transfer rate and interfacial area between gas and water. The synergic effect from complex mechanisms in wetlands can breakdown or transform various organic and inorganic substances or compounds. A constructed wetland (CW) consists of a properly-designed basin that contains water, a substrate and vascular plants [9]. A schematic diagram is shown in **Figure 2** [10, 11]. Generally, CWs can improve water quality, can serve as a buffer zone to desynchronize storm rainfall and surface runoff, as well as to recycle nutrients from wastewater stream. A recent survey on performances of 25 full-scale CWs across Eastern Canada and Northeastern USA, indicated that CWs effectively reduce various agricultural wastewaters, based on indices of five-day biochemical oxygen demand (BOD_5, 81%), total suspended solids (TSS, 83%), *E. coli* (log reduction, 1.63), fecal coliforms (log reduction, 1.93), total Kjeldahl nitrogen (TKN, 75%), ammonia-ammonium-N ($NH_3^+NH_4^+$-N, 76%), nitrate-nitrogen (NO_3^-N, 42%), and total phosphorous (TP, 64%) [12]. It is noteworthy

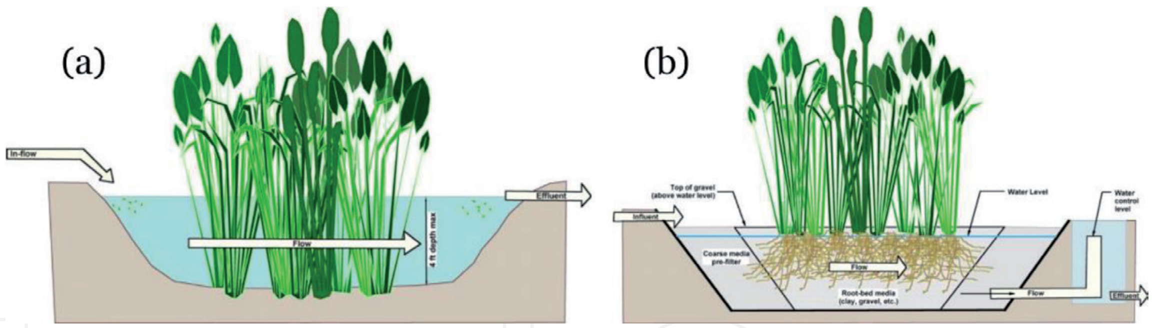

Figure 2.
A schematic diagram of (a) surface flow wetland and (b) subsurface flow wetland designed for treatment of agricultural wastewater [10].

that subsurface flow CWs exhibit higher performance than surface flow CWs. This is possibly because the subsurface flow CWs are capable of insulating micro-organisms from cold winter air temperatures during winter of surveyed regions.

CWs are a comparably economical, low-maintenance, and low operational cost option for treating large variety of wastewater types of wastewaters that include farmyard runoff, dairy spillover, aquaculture wastewater, and abattoir wastewater among others [4]. In addition, CWs can buffer fluctuations of surface water or subsurface water flowrate, as well as to enhance the water reuse/recycling. On the other hand, CWs also inherit naturally some limitations, such as the requirement of large land that makes CWs more practical in rural areas, the seasonally-dependent performance that effluent quality may not meet the environment standards all the times, the environmentally-sensitive micro-organisms that may not survive under toxic conditions.

The effluent from the secondary treatment still contains suspended particles, organic pathogens, and nutrients that can pose potential adverse effects on downstream water distribution systems, and elevate health and environment risks, for example, pipe clogging, and cancer [13, 14]. Thus, the effluent from the secondary treatment is not suitable for agricultural reuse in irrigation application, and requires a tertiary treatment in order to achieve the quality standards for agricultural water. The standards are assessed using salinity level or sodium adsorption ratio (SAR), which is defined as follows [15]:

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \tag{1}$$

According to standards of Food and Agriculture Organization (FAO), reclaimed water after tertiary treatment that can be reused in agricultural irrigation, should contain 0–400 and 0–61 mg/L for calcium and magnesium, respectively.

2.2 Membrane filtration

The tertiary treatments involve salt removals using membranes in nanofiltration (NF), microfiltration (MF)/ultrafiltration (UF), reverse osmosis (RO), forward osmosis (FO), and membrane distillation (MD) [16, 17]. The classification of these treatments depends on the sieving effect posed by the pore diameter within their membranes through which eluents are pressurized to flow, i.e., the pore diameter of NF membranes ranges from 1 to 10μm. NF and RO demonstrate the capability of removing diverse monovalent ions from wastewater streams. However, the low-sodium treated water is not appropriate for reuse in agricultural irrigation, as some divalent ions (Ca^{2+} or Mg^{2+}) are essential nutrients for crops growth. Furthermore, most organic matters, like pesticides, in the effluents from the secondary treatment cause severe fouling to NF and RO membranes, which shortens the membrane lifetime, and increases the operation costs [15, 18]. MF is suitable for removal of suspended solids and micro-organisms. UF is mainly applied to remove viruses and organics whose size down to 20 nm [19]. Thus, MF/UF are strategically applied as the pretreatment step prior to NF-RO process. The energy cost of wastewater reuse using the MF/UF-NF/RO scheme was estimated 0.8–1.2 kWh/m^3, which is slightly higher than that of the conventional surface water treatment of 0.15–0.3 kWh/m^3. However, the MF/UF-NF/RO scheme demonstrated a much better energy cost than desalination of brackish water or seawater [18]. Furthermore, the salt rejection rate of MF/UF-NF/RO scheme increased to 98.2–98.8%, compared to that of RO-alone scheme (94.3–97%) [20].

FO is a naturally-occurring separation process that can draw water from a low concentration environment (feed solution) to a high concentration one (draw solution), due to the inequality of chemical potentials across the FO membranes [15]. FO can be utilized in combination with RO (FO-RO) or as a standalone process (FO-only) to retain some nutrients in agricultural wastewater, such that the quality of treated water from FO-RO process can meet irrigation water regulations, compared to the single RO system. A schematic diagram of FO-RO integrated system is shown in **Figure 3**. For a total system operated at a recovery of 70%, the FO-RO process demonstrated about 30% of energy consumption (kWh/m^3), compared to the RO-alone system [21]. It is also noteworthy that the rejections of ammonium and phosphate of FO-RO integrated system were >92.1 and >99.8%, respectively; whilst, the rejections of ammonium and phosphate of FO-along system were 50–80 and >90%, individually [22, 23].

The aforementioned wastewater treatment technologies are based on pressure-driven membrane processes. On contrary, there are thermally-driven membrane processes that are suitable to treat wastewater with high salinity and toxic contaminants. Membrane distillation (MD) is one of promising technologies in this category. MD utilizes low-grade or waste heat as the driving force at creating the vapor pressure difference across a microporous hydrophobic membrane which is permeable for volatile compounds from the feed side. In principle, the volatile compounds of wastewater at the feed side can be fully collected at the permeate side of the membrane, separated from the nonvolatile compounds, and solids in the

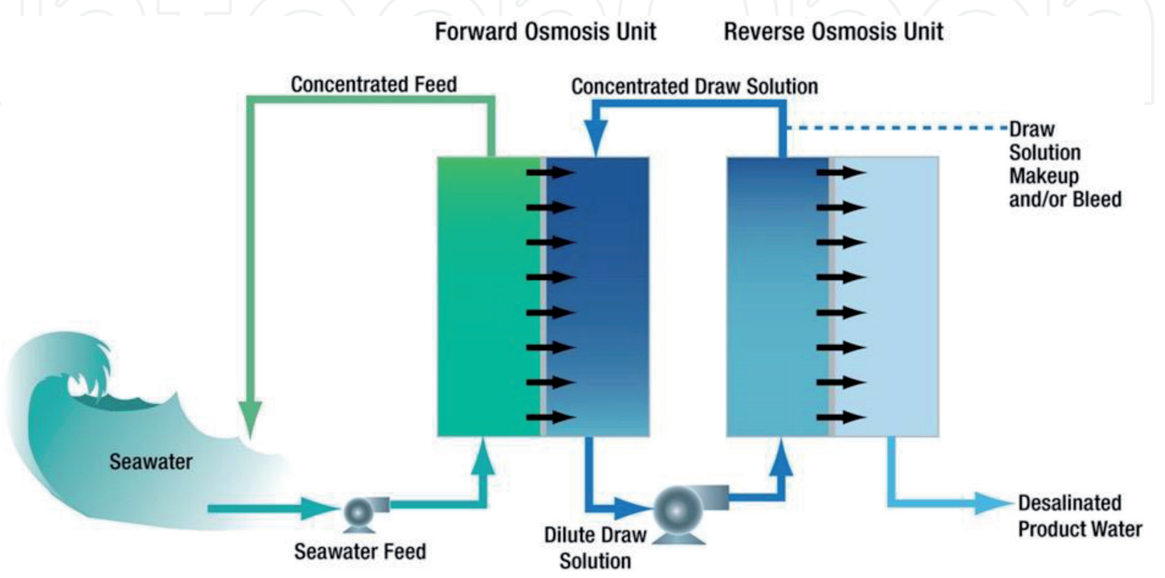

Figure 3.
Schematic diagram of FO-RO integrated system for seawater treatment for agricultural uses [21].

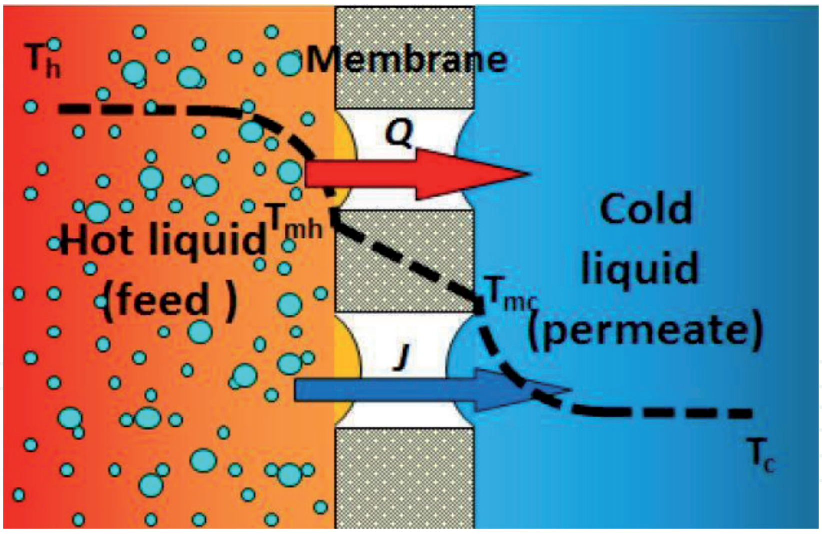

Figure 4.
Schematic diagram of MD for wastewater treatment for agricultural uses [25]. Q is the heat flux across the membrane due to the temperature gradient between the feed and permeate. J is the mass flux of permeable vapor across the membrane due to the pressure gradient between the feed and permeate, created by the temperature gradient.

wastewater [15, 24]. A MD schematic diagram is illustrated in **Figure 4**. A functionable MD membrane should demonstrate the following features simultaneously: (1) hydrophobic micropores for high liquid entry pressure (LEP); (2) thin membrane thickness for high mass transfer rate of volatile compounds; (3) low thermal conductivity for maintaining high vapor pressure graduate across the membrane; (4) high chemical resistance for maintaining the sieving effect of the membrane.

Compared with those pressure-driven membrane technologies, MD exhibits several advantage edges, such as lower operation pressure at the feed side, cost-effective, less propensity of membrane fouling, as well as generating high purity of treated permeate. However, the last advantage can be a potential MD shortfall in its application in agricultural irrigation due to the low or zero ion concentration. In addition, not many membrane materials can meet those criteria of successful MD membrane. This becomes a big hurdle at commercializing MD process in industry. Thus, it is projected that MD processes might be more suitable as the pre-treatment step for RO, in order to improve water recovery and minimize the permeate disposal.

3. General aspects of membrane technologies

As mentioned in previous section, MF and UF technologies are adopted to remove suspended particulates and organic matters in wastewater stream. Given that the pore size of semipermeable membranes in MF and UF are in the range of 0.1–10 and 0.01–0.1 μm, respectively [19, 26]. MF membranes are commonly made from polymer materials, such as polysulfone (PS), polyether sulfone (PES), polyvinylidene fluoride (PVDF), polypropylene (PP), polyethylene (PE), polytetrafluoroethylene (PTFE), cellulose acetate (CA), ceramic metal or metal oxides [27]. The organic membranes are usually prepared via phase inversion technique, and the ceramic metal oxides membranes are most prepared via sol-gel technique. Organic MF/UF membranes are prepared by controlling several operational and compositional synthesis variables in the phase inversion reaction, such as the volatility of solvent [28]; while inorganic MF/UF membranes are tailored by controlling heat treatment conditions, pore forming additives, and sol-gel precursors [29].

Index	Unit	MF	UF	MF-UF
TOC	mg/L	71.9 (94.1%)	25.9 (97.9%)	trace (100%)
TDS	mg/L	1154 (27.7%)	424 (27.7%)	8.4 (99.4%)
TSS	mg/L	9 (97.4%)	5 (98.5%)	trace (100%)
Oil and grease	mg/L	21.5 (99.4)	1.5 (99.4)	trace (100%)

The percentages in the parenthesis are the extent of reduction in each assessment index [30].

Table 2.
Several indices for evaluation of MF, UF, and MF-UF membrane's performance.

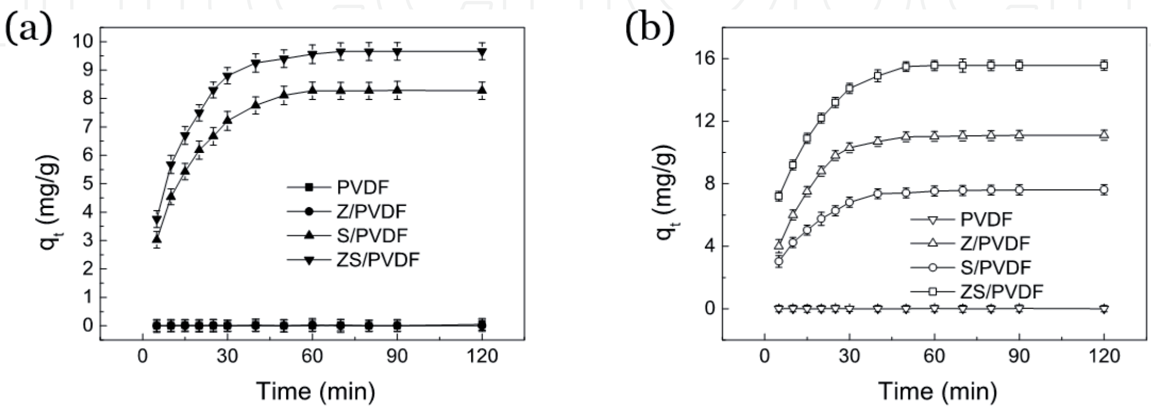

Figure 5.
(a) Nitrate adsorption with an initial concentration of 20 mg-N/L; (b) phosphate adsorption with an initial concentration of 20 mg-P/L. Z: Functional layer of PVDF membrane made of zirconium hydroxide. S: Functional layer of PVDF membrane made of SDMOAC. It is clearly elucidated that pristine PVDF (UF) membrane has no adsorption selectivity and capacity towards nitrate and phosphate [31].

A recent study on the performance of MF, UF, and MF-UF membrane processes, respectively, in oily wastewater treatment was carried out on PES, and PVDF membranes [30]. Total organic carbon (TOC), total dissolved solids (TDS), total suspended solids (TSS), and oil-and-grease content, are applied as indexes to access the membranes' performance which follows the order of MF-UF > UF > MF, as shown in **Table 2** [30]. The results clearly indicated that the combined MF-UF technique was better than individual MF, and UF techniques, in terms of the solid removal rate. It is also noted that the operation conditions of membrane techniques, such as transmembrane pressure (TMP), cross-flow velocity and oil concentration at the feed side, affect each membrane technique greatly. Other studies also indicate that the rejection of phosphate, nitrate, and ammonium ions using MF or UF processes is too low, such that the effluent from these treatment cannot meet the environment standards prior to discharging to the aquatic environment [31] (**Figure 5**).

Nanofiltration (NF) processes are an advanced separation technology applied to remove pesticides, ammonium ions from wastewater stream [32]. The pore size of NF membranes is in the range of 1–10 nm [19, 26]. NF membranes are commonly made from polymer materials, such as polysulfone (PS), polyether sulfone (PES), polyaniline (PAN), polyether ether ketone (PEEK), polyimide (PI), and polyamide (PA) via phase inversion technique [33, 34]. Alternatively, inorganic ceramic membranes are adopted in NF, such as zeolites, carbon nanotubes, graphene, metal oxides, and metal-organic frameworks among others [20, 34]. Given the pore size range falls in between atomic and molecular levels, the separation mechanism of constituents in the feed solution is based on the diffusivity of pollutants across the membrane (Knudsen diffusion). In addition, NF membranes usually carry positive or negative surface charges, due to the dissociation of surface sulfonated or carboxyl groups. The electrical field of surface charges alter the permeability of ions in the wastewater stream accordingly. Thus, NF membranes exhibits higher selectivity of salt rejection towards most divalent cations and some monovalent cations than MF and UF, while the operation pressure and energy consumption are lower than those of RO. Polymeric NF membranes are most fabricated via the phase inversion technique during the interfacial polymerization reaction [33].

A study using a commercial NF membrane (polypiperazine-amide thin-film composite) was conducted to investigate the nitrate removal efficiency from a real groundwater. The nitrate rejection was about 55.1–62.2%, due to the adsorption competition of sulfate with nitrate [35]. However, the membrane demonstrated a complete removal of phosphate [36]. The treated water would require another post-treatment process, such as RO, in order to meet the environment standards [35].

RO processes are a tertiary wastewater treatment technology applied to remove monovalent ions from wastewater stream [32]. The pore size of RO membranes is in the range of 0.1–1 nm [19, 26]. RO membranes are mainly made from polyamide thin film composite (TFC) via interfacial polymerization from two monomers, an amine, and an acid chloride [37]. The thin polyamide layer deposits on a microporous hydrophilic polysulfone membrane as a mechanical support to polyamide. The polysulfone layer is sandwiched between polyamide and mesoporous polyester. Given these small pore diameters, the separation of different components from the feed solution side is based on the solubility and diffusivity of each component into the polymer membrane matrix.

As shown in **Figure 6**, RO membrane displayed high removal of divalent ions (>99%), and had comparable monovalent ions rejection as published results. Overall, the RO process had better total dissolved solute (TDS) rejection than the NF process. Furthermore, the performance of both NF and RO processes declined after 3 years operation. It is noteworthy that the Cl^- rejection of RO process (94.4%) declined to 43.9% after 3 years operation. The declination rate is more significant than that of NF process. In addition, the SO_4^{2-} and Ca^{2+} rejections of NF process decreased more than those of RO process. The former declined performance was suspected to the vulnerability of RO membranes to chloride ions. The latter declined rejection was possibly due to the membrane fouling [38].

Although most of RO membranes demonstrate very high salt rejection (>99%), it is also widely recognized that RO membranes suffer two major drawbacks: (i) membrane fouling to all matters in the feed stream, (ii) sensitive to the presence of chlorine or chloride ions, due to the electrophilic nature of amide nitrogen and aromatic rings of polyamide in RO membranes [39]. To overcome these drawbacks, several strategies can be adopted (i) pretreatment of feed stream prior to RO processes, (ii) surface modification using physical adsorption of hydrophilic polymers or chemical grafting of hydrophilic functional groups [39].

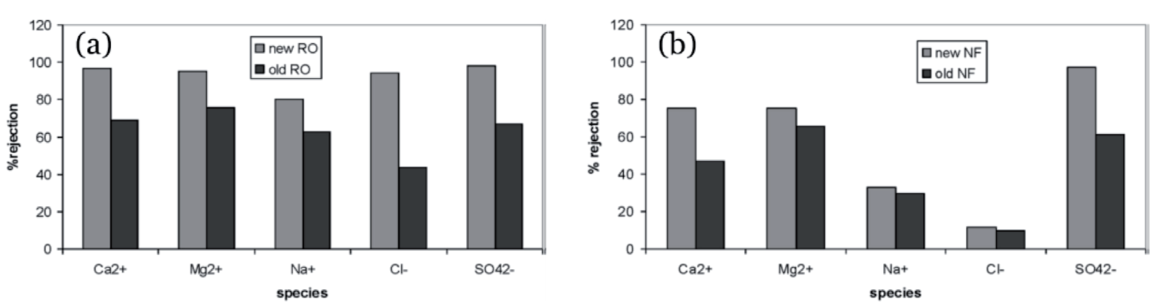

Figure 6.
Performance comparisons of (a) RO process and (b) NF process. New means the beginning of the operation using new membranes. Old means the membranes after 3 years of operation [38].

4. Promising technologies of membranes for agricultural wastewater treatment

It is widely recognized that membrane-based processes are the most energy-efficient, compact, and high throughput technology for agricultural wastewater treatment. There are several strategies to further improve the performance of membranes in each type of processes, such that the most cost-effective system can be applied at industrial scale:

4.1 Combination of various membrane filtration processes

Wastewater nutrient recovery is a promising strategy to recycle nutrients and pesticides while minimizing or avoiding the energy penalty for removing those nutrients in wastewater treatment facilities. It was estimated that 30% of nitrogen and 16% of phosphorus from fertilizers exist in wastewater. Thus, wastewater nutrient recovery can minimize the usage of fertilizer for crop production [17, 40]. For example, combining NF-RO processes together can generate water for agricultural irrigation application [41]. The NF step in this integrated process is to concentrate divalent ions at the retentate side, while the RO step is to produce high purity recycled water with low SAR at the permeate side. Combining the concentrated divalent ions stream from NF, with the purified recycled water stream from RO can prepare the quality of treated water to meet the standards for agricultural irrigation. As shown in **Table 3**, UF is perfect for the removal of suspended solids (TSS) as well as pathogens (BOD, COD, and TOC). However, RO is an ultimate treatment processes to remove most of soluble ions [13]. It is expected that membrane fouling would be severe at the UF process.

When searching for a low fouling technology, FO processes stand up by its nature of separation mechanism. An interesting study was conducted using a pilot scale FO-RO hybrid process to treat a synthetic wastewater. The salt rejection (NaCl) is about 95–97% which is lower than that of RO process only [42]. However, the nutrients rejection performance of the hybrid system was superior than each individual process, shown in **Table 4**. The treated water quality was better than EPA primary drinking water standards. It is also noticeable that the membrane fouling was observed in the spiral wound FO membrane, although the fouling was mostly reversible. This contributed to the restored water flux after membrane cleaning.

Performance index	UF rejection (%)	UF + RO rejection (%)
BOD	94.5	96.0
COD	92.0	98.0
TOC	41.0	95.6
TSS	99.3	100.0
Cl	2.3	81.1
Na	10.7	85.0
K	3.7	51.4
Ca	12.2	88.3
Mg	2.4	88.1
$N\text{-}NH_4$	20.6	80.5
PO_4	12.0	93.4

Table 3.
Performance of UF-RO integrated systems at agricultural wastewater treatment [13].

Performance index	FO-only	RO-only	FO-RO
Phosphate rejection (%)	99.6	99.6	>99.99
Nitrate rejection (%)	76.7	83.2	95.8
Dissolved organic carbon (DOC, %)	98.6	99.8	>99.99

Table 4.
Comparison of nutrients rejection of FO-only, RO-only, and FO-RO [42].

Similarly, a FO-NF hybrid process was applied to treat real wastewater with a salinity of 3–5 mS cm^{-1} for 480 days [43]. It was found that when magnesium chloride solution was used the draw solutions of FO, the membrane fouling became reversible and less extent. The permeate of the FO-NF hybrid process can meet the agricultural irrigation standards without further adjustment. The only disadvantage of FO-NF process is its cost of treated water higher than that of FO-RO technology, owing to higher energy consumption (40%) and the chemical loss of draw solution.

4.2 Modification of membrane surface properties via grafting or blending

FO processes are the best candidate to remove ammonium ions in wastewater, among the pressure-driven and temperature-driven membrane separation techniques. However, the ammonium rejection rate is low, around 48% [44]. The poor performance can be attributed to the small molecular weight and diffusivity of ammonium ions, which are comparable to the solvent molecules [45]. One of strategies to enhance the ammonium rejection rate is to change the membrane surface to become more positively-charged and hydrophilic, such that the FO membranes can retard the permeability of ammonium ions via Donnan exclusion effect. For example, a latest development is to modify a polyamide (PA) membrane surface to form amine-functionalized membranes, via a cross-linking agent (N,N′-dicyclohexylcarbodiimide) followed by a nucleophilic attack from polyethylenimine (PEI), shown in **Figure 7**. The zeta potential of amine-functionalized PA membrane is largely increased compared with the pristine PA membrane, indicating the presence of positive surface charges on the modified membranes. The ammonium rejection of amine-functionalized PA membrane exhibited higher performance then the pristine PA membrane (100 vs. 97% for synthetic ammonium solution, and 89.3 vs. 75.5% for a real wastewater correspondingly) [45].

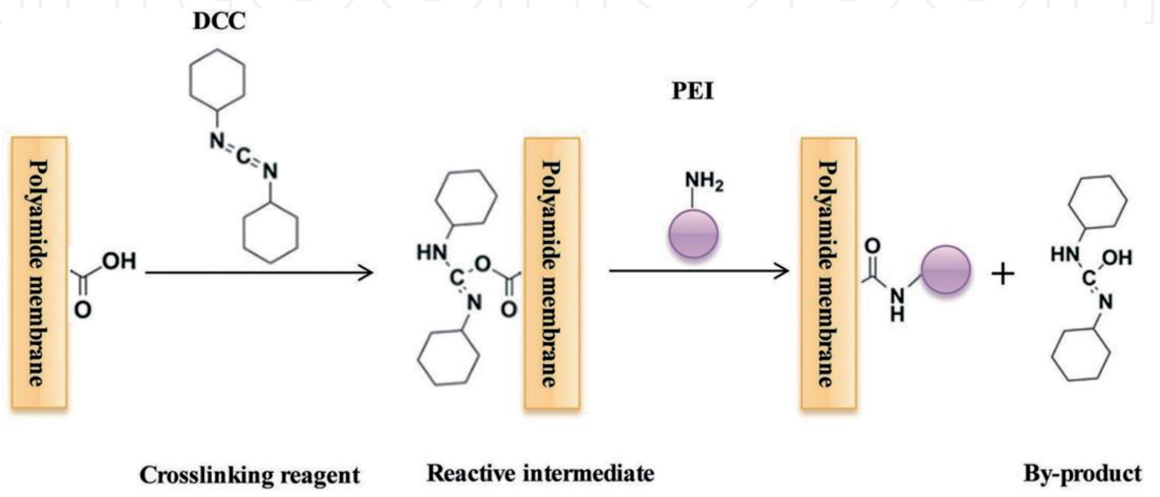

Figure 7.
Schematic diagram of surface modification of RO membrane via grafting [45].

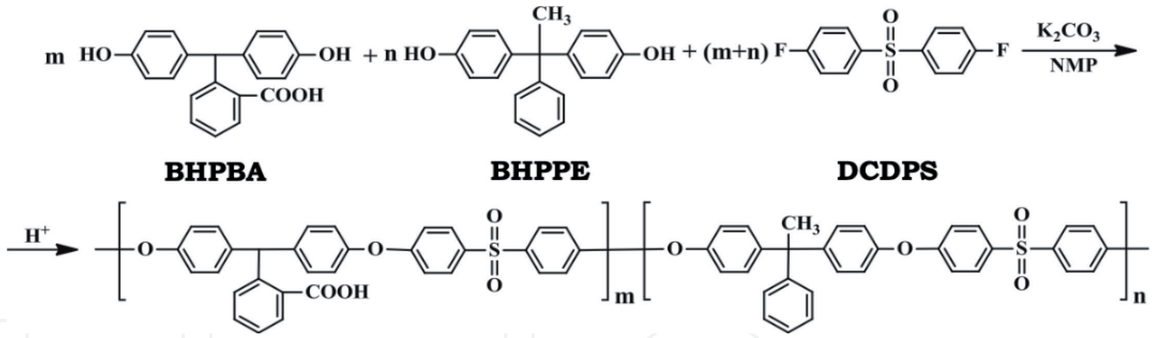

Figure 8.
Synthesis of hydrophilic NF membranes via copolymerization [46].

The modification of membrane surface properties via grafting is not applicable to a few commercial polymers. In addition, the introduction of functional group via grafting yields functionalized membranes with lower thermal resistance and mechanical strength. An alternative approach to functionalize membrane surface or matrix is to introduce the hydrophilic groups (carboxylic or sulfonic acids) via co-polymerization reaction of strategically selected monomer containing designated functional groups, with polymer membranes. For instance, Zhang' group fabricated hydrophilic NF membranes by copolymerization of 2-(bis(4-hydroxyphenyl)methyl) benzoic acid (BHPBA), 1,1-bis(4-hydroxylphenyl)-1-phenylethane (BHPPE) and 4,4′-dichlorodiphenyl sulfone (DCDPS). The schematic diagram is shown in **Figure 8** [46]. The resulted NF membranes with adjusted COOH contents exhibit high glass transition temperatures (T_g), ranging from 184 to 246°C, that are comparable or superior than pristine PES membrane. This is due to the high benzene ring content in each monomer. In addition, the carboxyl groups introduced into the NF membranes are located on the pendent benzene ring of PHPBA, instead of being located on the backbone of the polymer. This will enhance the thermal stability of copolymer.

The dye rejection of the fabricated NF membranes via copolymerization increased along with the content of carboxylic groups (>90% for RB2 dye, and >74% for RO16 dye), due to the smaller membrane pore size by incorporating the functional groups. The salt rejection of the investigated NF membranes showed the following order: Na_2SO_4 (84%) > NaCl (19%) > $MgSO_4$ (11%) > $MgCl_2$ (6.6%). Furthermore, the fouling resistance ratios of the investigated NF membranes increased along with the content of carboxylic groups. This is due the electrostatic force interaction between the soluble microbial products (BSA and humic acid) and the functional groups of membranes [46].

4.3 Incorporation of nanofillers in polymeric membranes

Membrane bioreactor (MBR) processes are a hybrid wastewater treatment technology, combining biological wastewater treatment and MF-UF processes simultaneously. MBR processes are usually considered as a pre-treatment step for NF and RO processes, because they exhibit high tolerance at total suspended solids of influent composition variation, and production of high effluent quality (**Table 3** in Refs. [47, 48]) However, the membrane fouling is a major hurdle on applying MBR processes at larger scale. An approach to circumvent this hurdle is to increase the membranes' hydrophilicity via incorporating inorganic nanocrystals (nanofillers) in polymeric membranes, also named organic-inorganic mix-matrixed membranes (MMM) [49]. The benefits of applying MMMs in MBR processes include: (i) energy saving due to lower transmembrane pressure (TMPs), which are reduced 31.38 (Z4-MBR) to 40.45% (Z8-MBR) upon the incorporation of zeolite nanofillers in MMMs compared with the bare polymer membrane; (ii) higher throughput due to

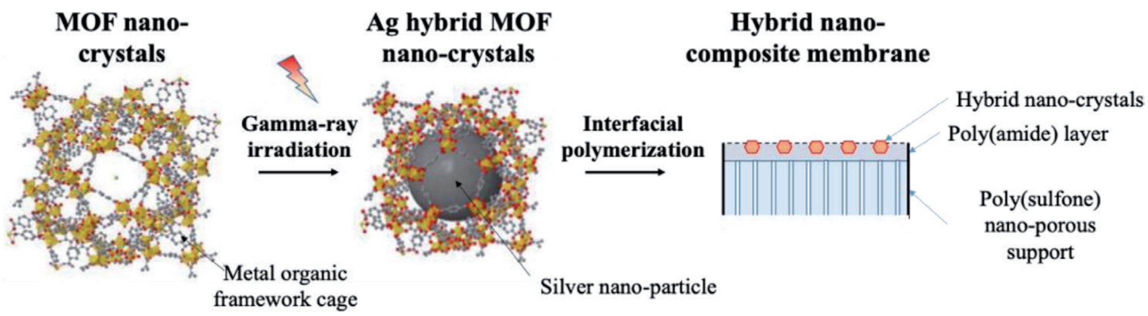

Figure 9.
Schematic diagram of hierarchically-nanostructured mix-matrixed membranes in RO processes [52].

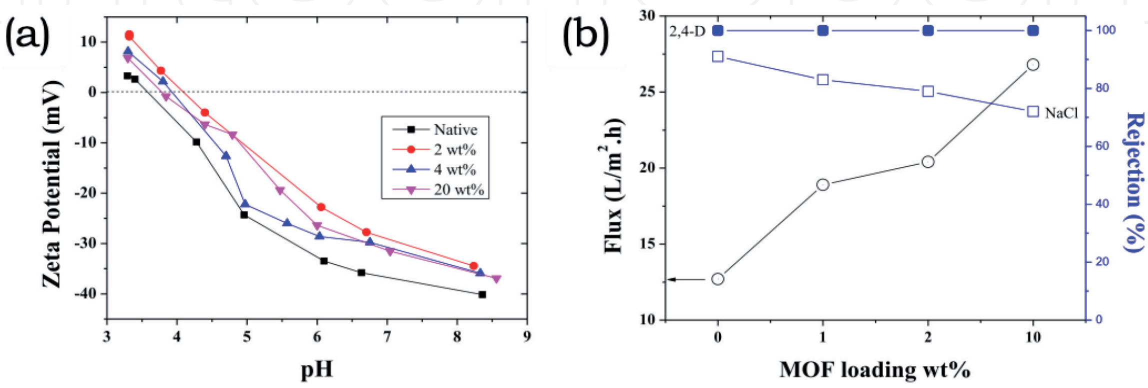

Figure 10.
(a) Zeta potentials of hierarchically-nanostructured Ag-MOF nanocrystals in PA; (b) the membrane performance of Ag-MOF nanocrystals in PA using 2,4-dicholorophenoxyacetic acid as the model compound in a simulated wastewater. The numbers in the legend of part (a) indicate the content of MOF nanocrystals in membranes [52].

lower membrane fouling. The zeta potentials of MMMs were enhanced to −7.7 mV (Z4-MBR) to −5.35 mV (Z8-MBR) compared to that of bare polymer membrane (−14.3 mV). The more hydrophilic MMMs reduce the soluble microbial products (SMPs) by 18.94 (Z4-MBR) and 42.11% (Z8-MBR) respectively, via the direct adsorption of SMPs on zeolite nanofillers in MMMs. This yields a lower propensity of membrane fouling.

In parallel with MBR processes that use the physical adsorption/molecular sieving mechanism at wastewater treatment, catalytic membrane reactors (CMR) has shown their potentials in degradation and destruction of pesticides and pathogens (catalytic reaction), and purification of the degraded wastewater through pores within membranes (physical adsorption/molecular sieving) simultaneously [50]. To CMR processes, mixed-matrixed membranes are fabricated to have both functionalities, by incorporating catalytic nanoparticles in microporous polymeric membranes. Long-term stability of MMMs in CMR, and homogeneous dispersion of catalytic nanoparticles in polymer matrix are vital factors at their applications at large scale [51]. A recent design of hierarchical nanostructure MMMs was achieved to address the aforementioned issues, by incorporating catalytic metal nanoparticles inside the cavities of metal organic frameworks (MOFs) nanocrystals. The metal-incorporated MOFs nanocrystals were subsequently imbedded into polyamide (PA) RO membranes via interfacial polymerization. The schematic diagram is illustrated in **Figure 9** [52].

The zeta potentials of hierarchically-nanostructured mix-matrixed membranes increased with the content of MOF nanocrystals, exhibiting more hydrophilic feature upon incorporating nanocrystals compared with the pristine PA membrane. This contributed to higher permeate flux from 12.5 kg m^{-2} h^{-1} of pristine PA membrane to 27 kg m^{-2} h^{-1} of 20 wt% MOF incorporated membrane. However, the salt rejection capability decreased by 20%, due to the presence of interfacial spaces between MOF nanocrystals and PA matrix. It is noteworthy that the organic compound rejection of 100% was exhibited, no matter if nondegraded or degraded organic compounds presented, shown in **Figure 10**.

5. Outlook

Membrane technologies are considered as the feasible solution to address the water reuse and nutrients recovery in agricultural sectors [15]. The efficiency of pollutant rejection and permeate productivity are the major factors to maximize membrane processes at a larger scale. This depends on the membranes' ability to maintain its selectivity towards retaining pollutants as well as their ability to minimize the membrane fouling, while keeping its fabrication cost-effective. Several approaches are developing to address these issues. For example, the concept of nutrients recovery from wastewater stream leads to develop hybrid membrane processes such as NF-RO [41], FO-RO [21], and FO-MD [53]. FO is a low membrane fouling technology and relative low pressure compared with RO. MD is also a low membrane fouling technology to concentrate volatile organic matters in wastewater stream.

Alternative approach is to modify the membrane surface hydrophilicity via grafting hydrophilic monomers on membrane matrix and/or incorporating inorganic nanoparticles in polymeric membranes. The modified membranes can exhibit less propensity of membrane fouling. For instance, a nanofiltration PVDF membrane was modified with tannic acid (TA), polyethylenimine (PEI), and halloysite nanotubes (HNTs). The modified membrane exhibited higher dye removal (92.5%), heavy metal rejections (54.6% for Cu^{2+}, 47.9% for Cd^{2+}, 61.6% for Fe^{3+}), and permeate flux (42 L m^{-2} h^{-1}), compared with pristine PVDF membrane, shown in **Figure 11** [54]. Similarly, ultrafiltration membrane PS can have a higher nitrate removal (41.4%), higher permeate flux (43.3 L m^{-2} h^{-1}), and less membrane fouling (flux recovery ratio, 81.2%) when graphene oxide (GO) nanocrystals were blended in the polymeric matrix, compared with those of pristine PS membrane (15.50%, 17.84 L m^{-2} h^{-1}, and 30.56% respectively) [55].

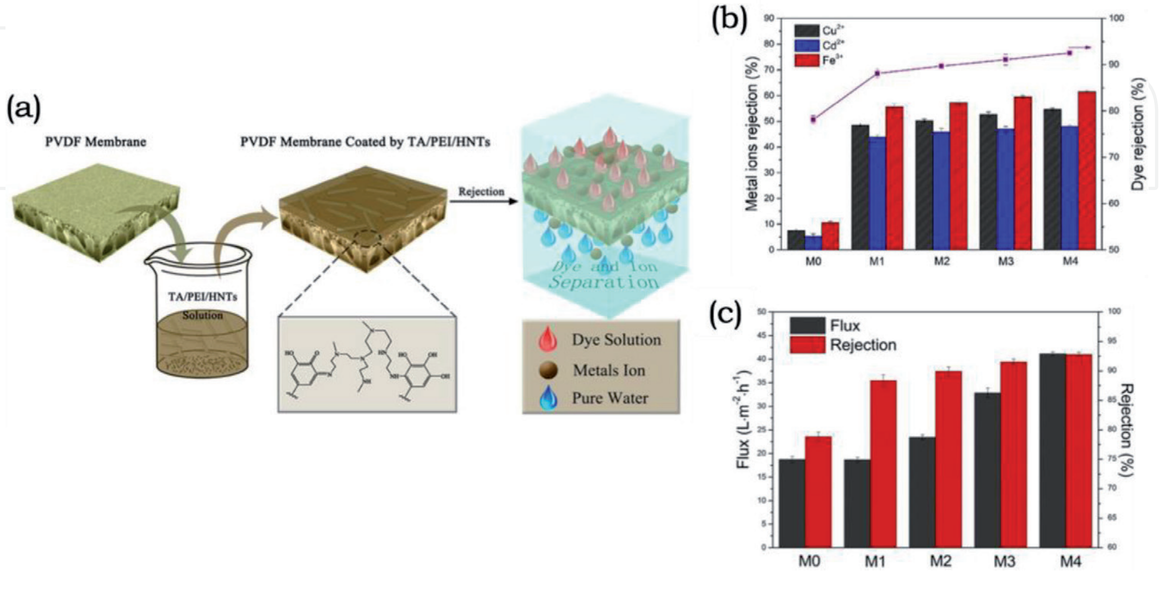

Figure 11.
Modification of nanofiltration membrane towards antifouling. (a) Schematic diagram of modified membrane preparation, (b) performance of heavy metal rejection, (c) performance of dye rejection (direct red).M0: Pristine PVDF membrane. M1: PVDF + TA + PEI. M2: PVDF + TA + PEI + HNTs (1 mg/mL). M3: PVDF + TA + PEI + HNTs (2 mg/mL). M4: PVDF + TA + PEI + HNTs (3 mg/mL) [54].

6. DDD

When we consider the irrigation water quality published by Food and Agriculture Organization, and the recycling the nutrients (pesticides, and some divalent ions) in agricultural wastewater, membrane technologies such as NF, RO, FO, or MD would emerge themselves from others, in terms of selectivity of pollutant removal and productivity of water reclamation for agricultural reuse. The energy cost of operating membrane processes replies on membranes' performance in the wastewater treatment processes, such as high salt rejection, low membrane fouling, high permeate flux, high mechanical strength and high long-term stability. While current membranes exhibit most of the aforementioned features, the membrane fouling is inexorable in most of the pressure-driven membrane separation processes. Membrane surface modifications can tailor the membrane surface hydrophilicity to alleviate the fouling extent. The strategies include copolymerization of hydrophilic monomers in polymer membranes, grafting hydrophilic functional groups on membranes, incorporating novel nanofillers (GO, MOFs, zeolites, metal oxides) in polymer membranes, and depositing hydrophilic thin film on membranes. These strategies usually create some challenges towards how to balance the membranes performance with permeate flux declination, as well as how stable these modified membranes are at the operation conditions. Being able to address both concerns can broaden membrane technology applications.

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Author details

Katrina Jose, Fadi Layyous Gedeon and Chil-Hung Cheng*
Department of Chemical Engineering, Ryerson University, Toronto, ON, Canada

*Address all correspondence to: chilhung.cheng@ryerson.ca

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