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Membrane design for extractive membrane bioreactor (EMBR):

mass transport, developments, and deployment

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Abstract

Economic development throughout the world is generating harmful contaminants which are progressively damaging water reservoirs, groundwater, soil, ecosystems, and organisms. Thus, there is an urgent need to remove these pollutants economically and in an eco-friendly way before their discharge to the environment. The novel extractive membrane bioreactor (EMBR) system requires less energy, produces high-quality water, and presents higher removal efficiency with zero by-products and thus has attracted attention as a somewhat niche but potentially viable alternative to traditional technologies. The EMBR has been progressed in recent years with new design of membranes and configurations for removing a variety of emerging pollutants. However, the practical use of EMBR technology remains a challenge due to two factors: (i) the availability of appropriate membranes and (ii) membrane fouling issue. In this review, the principles of the EMBR process are explained. Then, the performance of membranes for pollutant extraction is discussed based on various experimental results and theoretical considerations. State-of-the art membrane manufacturing techniques are also reviewed to assist with an assessment of the long-term sustainable development of the EMBR process. To achieve an economical process, there will need to be not only technological progress but also an appropriate evaluation of the environmental benefits.

1 Introduction

The rapid increase in the amount of industrial wastewater and direct discharge adversely impacts the ecosystem (quality of rivers, lakes, and oceans) and has the potential to endanger human beings [1, 2]. At present, emerging contaminants (ECs) have gained prominent attention due to their expanding capabilities and the vast array of anthropogenic and natural substances [3-5]. The ubiquity of these ECs in the paper, pharmaceutical, chemical, and fertilizer industrial wastewater is an alarming situation as they are untreatable or hard-to-treat even at lower concentrations [6, 7]. Consequentially ECs are increasingly highly regulated by the national legislation on the environment because the treatment of wastewater is a basic rquirement for a sustainable environment [8]. One such group of substances of concern are the phenolics: phenol, toluene, benzene, xylene, etc. [9].

Studies related to the treatment of ECs have shown that the removal and transformation depend on wastewater composition, chemical characteristics, and treatment technology [10, 11]. The traditional technologies adopted for the removal of ECs are categorized as biological, chemical, and physical techniques [11, 12]. By altering various operating conditions and designs, the experimental approaches accomplished a higher removal rate of these ECs. However, such conventional treatment technologies are still facing many severe economic and technical limitations due to higher energy cost, poor effluent quality, large and complex footprints. These can be grouped into three areas as tabulated in Table 1.

Table 1. Traditional technologies for treating wastewater.

	Physical treatment	Chemical treatment	Biological treatment
Treatment methods	Adsorption Filtration Extraction Coagulation and flocculation Photolysis	Chemical oxidation Thermal oxidation Chemical precipitation Ion exchange	Aerobic Anaerobic
Benefits	Economical capital cost Easy to operate Better safety	Higher degree of treatment Elimination of dissolved contaminants	Intrinsic safety is superior Elimination of dissolved contaminants Volatile emissions
Limitations	Volatile emissions Complex maintenance Higher energic cost	High operational and capital cost Difficult operation	Prone to operational upsets caused by antibiotics May not remove EC whilst treating more abundant easier-to-treat organics Required sludge removal

Generally, the treatment technique selection is based on its economic feasibility, removal efficiency and by-product generation. However, the conventional techniques are not fully accepted nowadays due to their higher cost, operational difficulties, and higher production rate of by-products [13, 14]. Thus, an updated and most feasible treatment technique is required to cover these drawbacks. For ECs such as phenolics, the membrane bioreactor (MBRs) has the potential to overcome these issues by combining the activated sludge biological treatment and membrane filtration [15]. Over conventional technologies, the MBR possess several advantages, including smaller footprints, higher effluent quality, better microbial separation, controlled solids retention time (SRT) and hydraulic retention time (HRT), lesser sludge bulking and higher biomass contents,

lower sludge production [16, 17]. In particular, the extractive membrane bioreactor (EMBR) is regarded as a competitive technology as it requires less energy, produces high-quality water, has higher removal efficiency with zero byproducts [18-20]. In this process, a dense membrane controls the migration of pollutant from the feed side (potentially hostile wastewater) into bio-medium (receiving side) to enable biodegradation to occur, based on a solution-diffusion mechanism.

In 1994, the first utilization of EMBR was reported to extract and detoxify the toxic organics present in chemical wastewater [21]. Unlike the pervaporation systems in development at the same time [22-24], its application to the recovery of phenolics reached pilot scale. Since then, the development and application of various membranes, modules and setup configurations begin to accelerate in this era. A recently published review article highlighted the prominence of EMBRs application for denitrification process and treatment of wastewater and waste gas [25]. However, it is noteworthy that the EMBR operation is still facing hurdles such as: (1) membrane fouling and thicker biofilm growth due to biological and filtration activity; and (2) limited configurations. These issues hinder the beneficiary of EMBR by increasing the maintenance cost and reducing the extraction efficiency [26-28]. As in EMBR process, the extraction efficiency highly depends on the selectivity and placement of the membrane. The earliest data with silicon rubber tubes and the newest with polymeric (tubular and composite) membranes have been analyzed to determine some of the research issues [29]. Nevertheless, despite progress with these studies, the EMBR system has not been commercialized at full-scale. Thus, a better understanding to highlight the advantages of this technology in terms of operational flux, recent developments, and strategies to diminish the fouling and control the biofilm via membrane material and design specially for EMBRs is still needed.

In this review, the EMBR process is briefly discussed, and then the main focus is on the working mechanism and the associated membrane technology. Following a section on the calculation of pollutant mass transport, manufacturing techniques for hydrophobic and hydrophilic layers are discussed. A critical pathway to commercialization of EMBR probably lies, in part, with membrane development and the enhancement of selective solution-diffusion capability. The selection and deposition of nanoparticles (Nps) into hydrophobic layer to enhance performance in term of operational flux is discussed. The paper concludes with a consideration of the challenges and application of EMBR for the treatment of ECs.

2 Fundamentals of EMBR process

2.1 Working Mechanism

The EMBR setup consists of a feed side and receiving side, which are wastewater and bio-medium, respectively. The installed beneficial organophilic membrane preferentially extracts the organic pollutants from the hazardous wastewater feed (prior to the pre-treatment e.g., higher salinity or extreme pHs). The transport of targeted pollutants is via a solution-diffusion mechanism driven by a concentration gradient existing across the membrane surfaces [28]. Conversely, the water molecules, metals, salts, and hazardous components are retained in the feed side as illustrated in Figure 1. On the receiving side, the extracted pollutants are subsequently biodegraded by a specific microorganism layer present as a biofilm. The biofilm maintains the concentration of pollutant close to zero in the bio-medium and by consuming the pollutant enhances the concentration gradient across the membrane [30]. To some extent, the developed biofilm promotes positive consequences in the treatment of volatile organic carbons and heavy organic matters.

1 　However, continuous EMBR operation can lead to the development of excessive biofilm on the

2 　membrane surface, which significantly decreases the transfer rate of organics [31, 32].

3 　　In comparison with other conventional treatment methods, the EMBR process poses several

4 　benefits such as (1) a point source process without pretreatments; (2) operating at room

5 　temperature and atmospheric pressure; (3) steep concentration gradient across the membrane due

6 　to continuous biodegradation; (4) separated and controlled optimization of microbial activity; and

7 　(5) the byproduct (waste stream) is even less than 1% of fed wastewater.
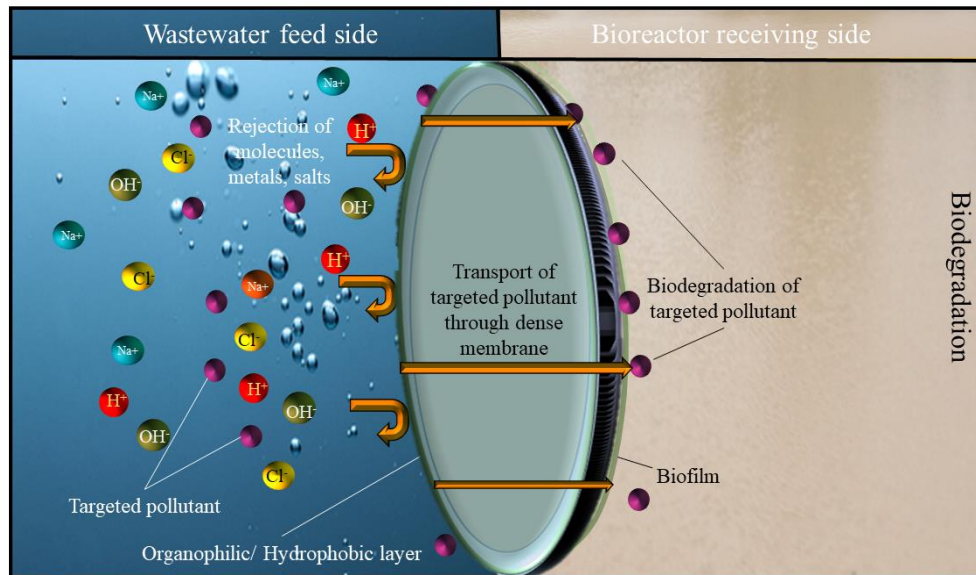
8

9 　　Figure 1. Basic mechanism of organophilic/hydrophobic membrane in EMBR.

10

11 　**2.2 Mass transport theory**

12 　The EMBR performance depends on the partition coefficient of targeted organic between the

13 　different phases (feed, receiving and membrane), microbial activity, hydrodynamic boundary

14 　layers on both sides and physio-chemical properties of the membrane. This section introduces the

15 　mathematical models to calculate the overall mass transfer coefficient, overall resistance, biofilm

1   resistance on the membrane and normalized overall mass transfer coefficient, together with other

2   relevant expressions for pollutant removal.

3

4   **Overall mass transfer coefficient**

5   To understand the efficiency of organic pollutant transfer across the membrane, an overall

6   mass transfer is needed which is independent of concentration driving force. The following mass

7   balance equation is utilized to calculate the overall mass transfer coefficient:

8

9
$$V_r \frac{dCr}{dt} = K_0 A (C_f - C_r) - Q C_r \qquad (1)$$

10

11   Here, V_r represents the volume of receiving solution; K_o is overall mass transfer coefficient;

12   A is the membrane area; C_f and C_r are the concentration of feed and receiving solution; Q is

13   overflow rate; dC_r/d_t is the concentration change of pollutant in receiving solution. Since the

14   concentration of pollutant in receiving side would reach zero due to continuous degradation [28],

15   the equation can be modified according to required condition:

16

17
$$V_r \frac{dCr}{dt} = K_0 A (C_f - C_r) \qquad (2)$$

18

19   By rearranging Eq. 2,

20
$$K_o = (V_r \frac{dCr}{dt}) / \{A(C_f - C_r)\} \qquad (3)$$

21

1   The K_o can also be calculated based on changed concentration of targeted organic in feed.

2   Where $\frac{dCf}{dt}$ is the change in concentration of pollutant in feed; V_f is the volume.

3

$$K_o = (V_f \frac{dCf}{dt})/\{A(C_f - C_r)\} \qquad (4)$$

5

6   To examine the rejection of inorganic salt and water, the salt flux (Js, mg/m2h) is measured.

$$J_S = \triangle c.V (\triangle t.A) \qquad (5)$$

8   Where $\triangle$c is presenting the change in NaCl concentration at receiving side; V (L) is volume,

9   and $\triangle$t (h) is the time interval.

10

11 **Overall resistance**

12 In this case, assuming the resistances-in-series model for the targeted pollutant, the overall

13 resistance can be calculated as follo)wing:

14

$$R_o = \frac{1}{K_o} + \frac{1}{K_f} + \frac{1}{K_{rs}} + \frac{1}{K_m} \qquad (6)$$

16

17 Here, R_o is the overall resistance, K_f mass transfer coefficient at feed side; K_{rs} is mass transfer

18 coefficient at receiving side; K_m is the mass transfer coefficient of the membrane.

19

20 **Biofilm resistance on membrane**

21 As the growth of biofilm on the surface of membrane, initiate more resistance [30]. The

22 overall resistance of biofilm can be determined as:

1

$$R_o = \frac{1}{K_o} = \frac{1}{K_f} + \frac{1}{K_{rs}} + \frac{1}{K_m} + R_{biofilm} \qquad (7)$$

Here, $R_{biofilm}$ is presenting the biofilm resistance.

The biofilm growth and cake layer attachment on the surface of membrane likewise decreases the K_o value, which is ascribed as normalized K_o:

$$Normalized\ K_o = \frac{Final\ K_o}{Initial\ K_o} \times 100\% \qquad (8)$$

Here, the value of normalized K_o is the observed value on any specific day and initial K_o is the K_o value on the first day.

Estimation of the removed pollutant

During long-term EMBR operation, the amount of removed pollutant from feed side is also essential to calculate to top-up. The amount of pollutant removed daily can be calculated as described following:

$$\text{Daily removal of pollutant (mg/day)} = (V_f C_{f\ t=0\ hr}) - (V_f C_{f\ t=24\ hr}) - (V_r C_{r\ t=24\ hr}) \qquad (9)$$

Here, $C_{f\ t=0}$ is the initial concentration of pollutant in feed; $C_{f\ t=24\ hr}$ is the final concentration of the pollutant after 24 hr; and $C_{r\ t=24\ hr}$ is concentration of pollutant in receiving side after 24 hr, which is assumed to be zero.

Moreover, the elimination capacity of pollutant per membrane area can be calculated as mentioned below:

$$\text{Pollutant elimination capability} = \frac{\frac{\text{Daily removal}}{24000}}{\text{membrane effective area}} \qquad (10)$$

In the end, the overall removal of pollutant can be calculated by following equation:

$$\textit{O}\text{verall removal of pollutant (\%)} = (1 - (\frac{V_f C_{f\ t=24\ hr}}{V_f C_{f\ t=0\ hr}})) \times 100\% \qquad (11)$$

2.3 EMBR configurations

As a combined process, the compatibility of the membrane filtration unit and the bioreactor is a key part of EMBR operation and maintenance. The reactor design is based on higher mass transfer, energy sufficiency and biofilm growth control [25, 32]. To date, two types of configurations have been utilized, the crossflow EMBR and the submerged EMBR. As presented in Figure 2, the main difference between the two configurations is that the membrane is directly exposed to bio-medium in submerged EMBR, while it is separated in the case of crossflow EMBR. In submerged EMBR, the upflow bubble flow enables the formation of a bubble-induced hydrodynamic shear adjacent to the surface of membrane, which scours biofilm deposits from the surface [31]. In summary, design of novel configurations with higher mass transfer capability to reduce the membrane fouling and overall operation cost will be beneficial and of significance for EMBR.
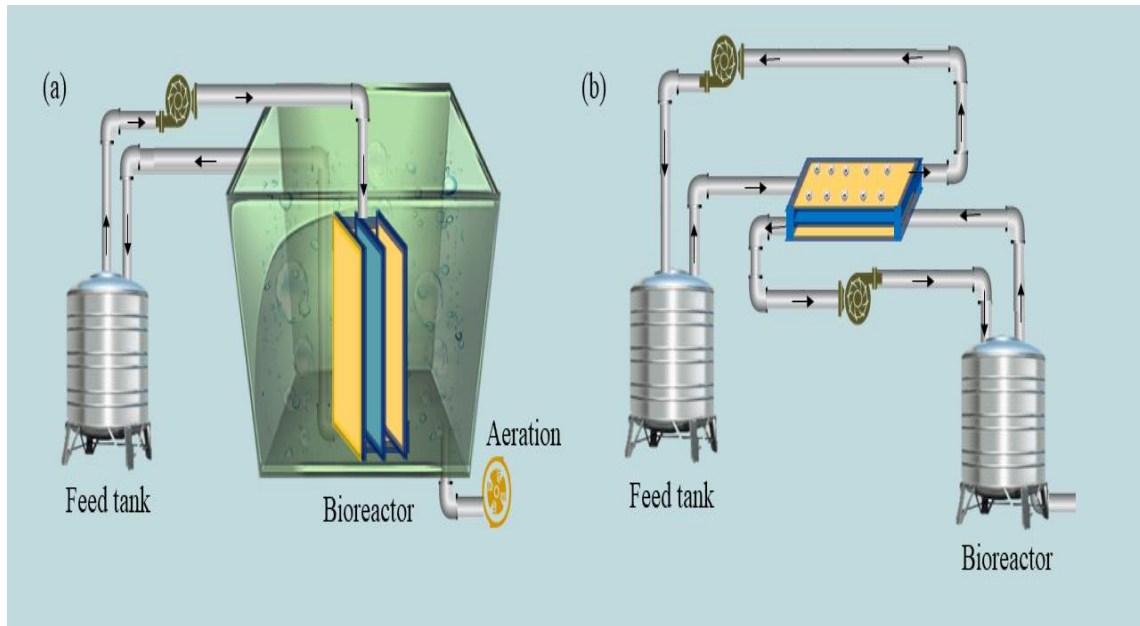
Figure 2. Schematic illustration of (a) Submerged EMBR (b) Crossflow EMBR.

3 Membrane technology

According to the literature, the membrane performance highly depends on the manufacturing technique, material, and thickness of membrane [33, 34]. In early stage, the commercial silicon rubber tubes were incorporated in EMBR for fundamental studies but are unable to attain higher overall mass transfer of targeted pollutant due to their thickness (at least 0.2 mm) [27, 35]. Subsequently hollow fiber membranes were utiised for EMBRs and a 7.5 times higher K_o was obtained compared with commercial silicon rubber tubes [29, 36]. As a higher thickness of membrane results in greater resistance, resulting into lower mass transfer flux, consideration has been given to thin-film composite (TFC) membranes which are composed of a top thin selective layer and a porous substrate for mechanical support (Figure 3a). The TFC membranes show higher overall mass transfer than all other commercial membranes [28]. The efficiency of TFC membranes in EMBR depends on intrinsic properties of membranes, targeted ECs, and operating

12

conditions (with specific factors illustrated in Figure 3b). Firstly, the desired key properties of membranes include: (1) high organophilicity to organics and superhydrophobicity to inorganic salts, water, caustic acid, and (2) stability under harsh conditions for long-term usage. Secondly, the properties of targeted ECs and the compatibility with membrane material is also essential to achieve higher flux. Thirdly, the operating conditions of EMBR, such as the temperature, feed quality, flux and rejection/recovery also influence the operating flux of membrane [37, 38].

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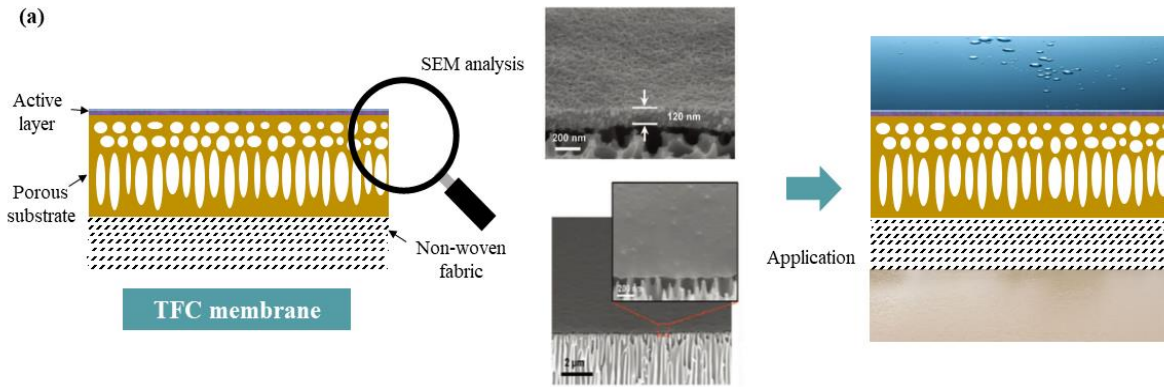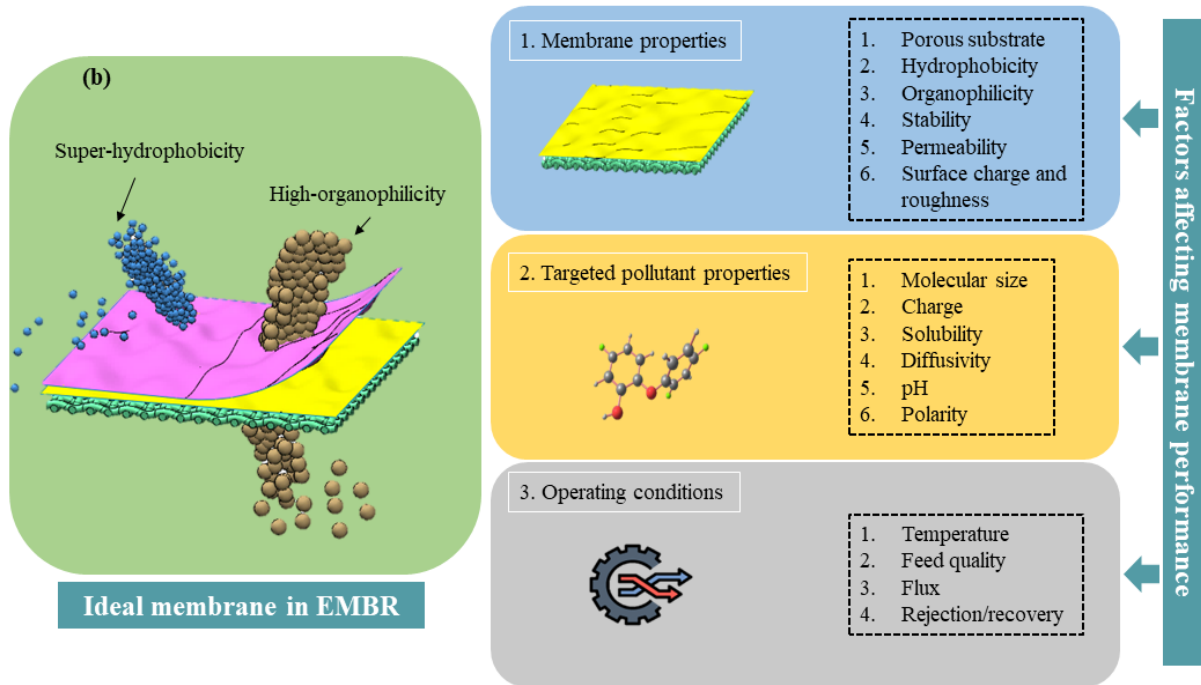
Figure 3. Illustration of EMBR incorporated membranes. (a) Diagram of multi-layer TFC

membrane (Reproduced and modified [39]). (b) Factors affecting the membrane performance.

Having shown that the membrane is of great significance in EMBRs the sections below

provide an overview of various TFC membrane manufacturing techniques for the development of

the support layer, the selective layer, as well as the incorporation of nanoparticles into selective

layer for surface modification which can be used to enhance selective permeability of ECs.

3.1 Support layer/Substrate

The chemistry and performance of both top-layer and substrate can independently be

manipulated to optimize the overall efficiency to attain desired permeability and selectivity while

offering compressive resistance and mechanical strength [28]. Whilst most of researchers consider

the top selective layer to be the key factor in the performance of membrane in EMBR, and most

available information concerns the physical and chemical properties of the top selective layer, the support layer properties are also important. The substrate needs to have adequate porosity, roughness, an appropriate pore size, hydrophilicity and mechanical strength [40]. The morphology of pores and physical-chemical properties of substrate control the residual volume in pores and surface [41]. Most importantly, the optimum pore size of substrate is required to avoid intrusion of the top selective layer, as illustrated in Figure 4.
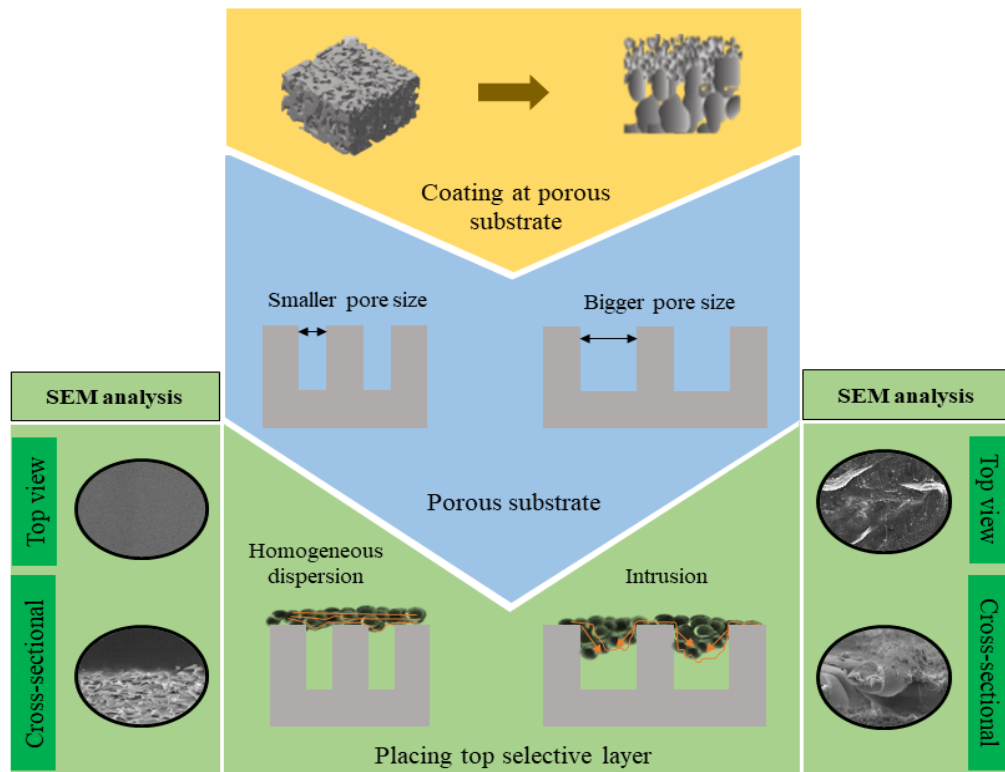
Figure 4. The impact of substrate pore size on formation of TFC membrane (Reproduced and modified [41]).
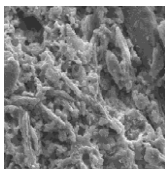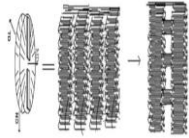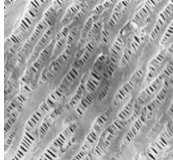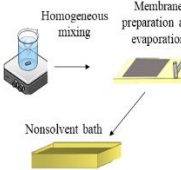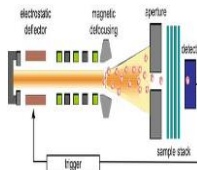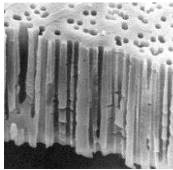
Various substrate manufacturing techniques have been assessed to achieve the desired pore size and suitable architecture. A number of manufacturing techniques including phase inversion [42], stretching [43], sintering [44], and track-etching [45] are available to fabricate the substrate.

1   These methods provide various unique architectural characteristics including porosity, surface area,

2   and alignment/orientation. The aforementioned manufacturing techniques have been summarized

3   by Liao Yuan et al. (2018). A comparative analysis is presented in Table 2.

4

5   Table 2: Substrate manufacturing techniques [46].

Manufacturing technique	Schematic process	Porous structure	Mean pore size	Porosity	Material	SEM analysis	Disadvantages
Sintering		Cloudy	0.1-10 μm	10-20%	1. Metals 2. Ceramics		1. Higher temperature requirement 2. Hard to achieve pore size lower than 100nm 3. Narrow size particle distribution is required
Stretching		Ladder like slits	0.2-20 μm	60-80%	1. PTFE 2. PE, 3. PP		1. Higher temperature requirement
Phase inversion		Form small surface pores and large bulk pores	Adjustable	80%	1. PTFE 2. PAN 3. PVDF		1. The polymer must be soluble in a solvent or solvent mixtures
Track-etching		Cylindrical pores	0.02 - 10 μm	10%	Limited to suitable polymers		1. High cost

Electro-spinning		core-sheath, Janus, tri-layer nanofibers	-	90%	Polymers		1. Hard to obtain nanofibers with diameters below 100 nanometers 2. Hard to obtain ENMs with maximum pore sizes smaller than 100 nanometers
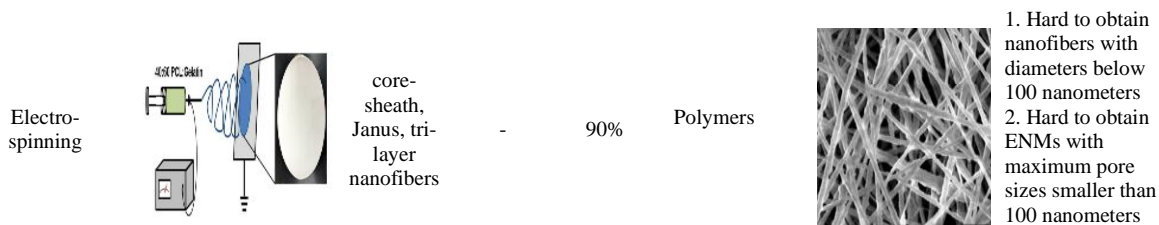
Ultrafiltration (UF) membranes are suitable as the substrate for EMBR membranes to diminish the top layer intrusion; they come in a range of smaller pore sizes and possess high porosity [25]. Nanofibrous substrate with large surface opening have also shown a good performance for EMBR membranes if the substrates were pre-wetted with viscous glycerol solution to prevent the intrusion of the selective layer [47, 48]. Polymeric material has been intensively investigated due to their higher selectivity, corrosive resistance, chemical resistance, and relatively low cost. Till now, the polymeric materials such as polyacrylonitrile (PAN), polytetra-fluoroethylene (PTFE), and polyvinylidene fluoride (PVDF) have been used to fabricate the substrate for EMBR. The PAN polymer has been widely used in the manufacture of MF or UF membranes via electro-static spinning or conventional casting technique and they possess good chemical resistance and good hydrophilicity [49]. PTFE has been extensively utilized due to its thermal stability, toughness, chemical stability, corrosion resistance and good mechanical strength [32, 50]. The PTFE membranes are mostly produced via the post-stretching method and extrusion or solvent-free melt spinning, which limits their usage as it results a membrane of comparatively low porosity albeit one with relatively uniform pore size distribution. A more balanced polymer, PVDF, can be easily fabricated either via non-solvent induced phase separation (NIPS), thermal induced phase separation (TIPS), or electrospun spinning techniques. Jin et al. designed dual-layer PVDF substrates to provide defect-free thin top selective layer and sufficient mechanical strength.

1 The average diameter of nanofibrous substrate decreased from bottom to top ranging from 148±16

2 - 72±14 nm [48]. The same trend was observed in another study [51]. To date, the substrates for

3 EMBR membranes only covers the polymeric UF membrane or nanofibrous membranes[32, 52].

4 The other types of membranes such as ceramic, metallic and carbon materials which have been

5 extensively studied in other membrane processes has never been utilized as substrates for EMBR

6 and this is likely to remain the case.

7

8 **3.2 Top selective layer**

9 The main objective when selecting a TFC membrane is to achieve thin top selective layer

10 having less resistance and higher partition coefficient. At present, a large number of hydrophobic

11 and organophilic polymers are available. Owing to its hydrophobicity and organophilicity that

12 allows preferential transfer of ECs while rejecting water and inorganics, polydimethylsiloxane

13 (PDMS) has been employed as most popular material for selective layer [53] and

14 organofunctionalized PDMS has also been researched [23, 24]. The PDMS contains the siloxane

15 (Si-O) bond with a substituted methyl group on Si atoms [54]. In EMBR, this property enlists the

16 PDMS as a strong repellent to water, harsh compounds, and inorganic salts, and is proficient to

17 transfer/extract the organic compound from feed side to bio-medium. The PDMS adopts a three-

18 dimensional structure with four-armed quaternary-siloxy groups as the junction points connecting

19 the dimethylsiloxane backbones [55]. In general, the partition coefficient of the desired ECs in

20 polymer matrix depends on free volume within the polymer, segmental mobility of polymer chain

21 and interaction between targeted compound and polymer matrix [56]. The aforementioned

22 influenced parameters are controlled by selecting the nature of polymer material, cross-linking

23 degree, crystallinity and existence of substituent [57, 58]. Accordingly, the improvement in

partition coefficient could be explained by considering the architecture and polymer backbones of PDMS dense membrane. Moreover, the density of siloxy group (Si-O) and their nitration intensity (van der Waals forces and hydrogen bonding) with targeted molecules in unit volume could also improve the partition coefficient. Moreover, the siloxy units offer increased contact between PDMS and targeted molecules via van der Waals forces and hydrogen bonding. Jin et al. provided the schematic route of phenol molecules transport through PDMS in order to understand the interaction between PDMS and phenol molecule (Figure 5) [48]. Organofunctionalisation of PDMS has its advantages and disadvantages as discussed elsewhere [23, 24].
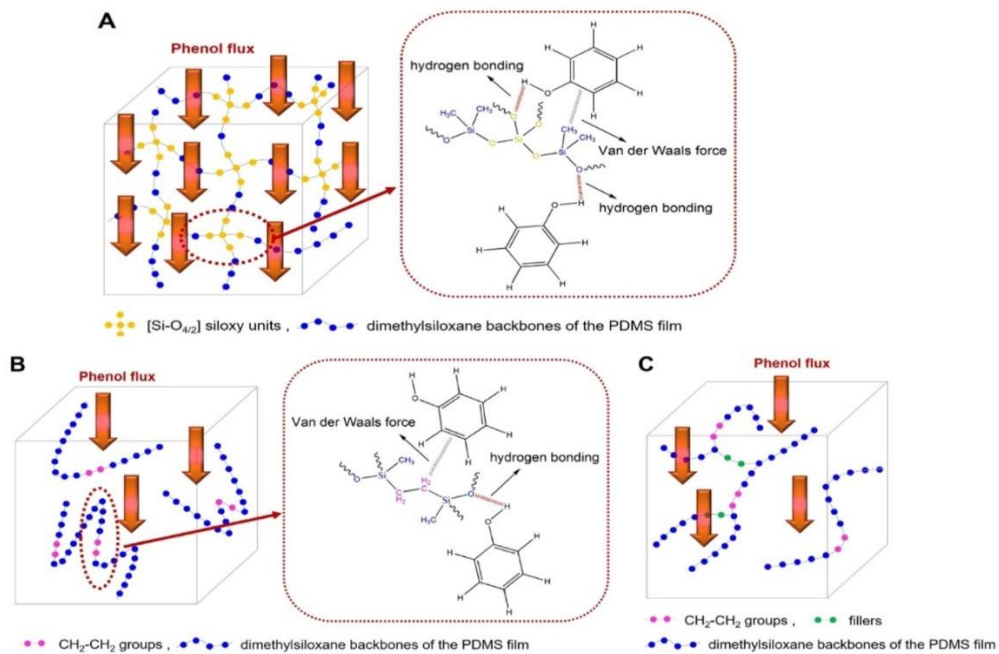
Figure 5. Schematic diagrams showing phenol transport through PDMS unit volume and the primary interactions between phenol molecules and PDMS: (A) PDMS with network architecture, (B) PDMS with a linear architecture and (C) With a combination of linear and branch architectures (Copied with permission [48]).

Membrane performance greatly depends on the thickness of selective layer [39]. Various techniques have been adopted to fabricate a thin and defect-free PDMS layer as far as possible on a porous substrate to maximize their capacity. Stable and reproducible methods are required to ensure the formation of unique architectural defect-free thin layer. At present, dip coating, electrospinning, knife casting and spray coating have been adopted to fabricate thin PDMS layer with different architecture in the EMBR system (Figure 6). Dip coating is an abundantly adopted technique to place the hydrophobic coating since its waste-free, low-cost, easy to scale up, and proposes controlled thickness. In this technique, the substrate is completely immersed in PDMS solution for a certain time. Subsequently, a desired hydrophobic coating is obtained after lifting out the membrane followed by air-drying or thermal treatment. Moreover, the dip-coating technique is appropriate for the modification of 3D structural materials. Naik et al. proposed a composite membrane by surface dip coating PVDF nanofibrous substrate with of PDMS [59]. The electrospinning technique contributes to allowing the controlled PDMS formation on substrate. This technology advance to fabricate an ultrathin top layer by unique architecture of nanofibrous scaffolds and presenting the lowest obtained thickness (6.2 ± 0.4 µm) [46, 60]. However, the scalability, stability and safety of this technique needs to be further verified, because a high flammable solvent n-hexane was used in the electrospinning of PDMS which is not safe under the high-voltage over 15 kilovolts [46]. Classically, knife-casting is a facile and economical method for depositing a PDMS layer; gap setting of the casting knife controls the thickness. Long-fei et al. and others have deposited PDMS layers by the casting method and successfully obtained a non-porous and smooth surface [32]. As an alternative that is straightforward and gives a relatively this film there is spray coating. This method generates a thin, uniform coating layer in a fast, simple, reproducible mode, and is capable of large-scale promotion. Jin et al. prepared condensation-cured

a PDMS membrane with network architecture by spray coating onto an electrospun PVDF substrate. The overall mass transfer coefficient was evaluated as being relatively high for an extractive process [48]. Liao et al. prepared a 12 ± 1 µm PDMS top layer by spray coating and obtained smooth and defect-free morphology [28].
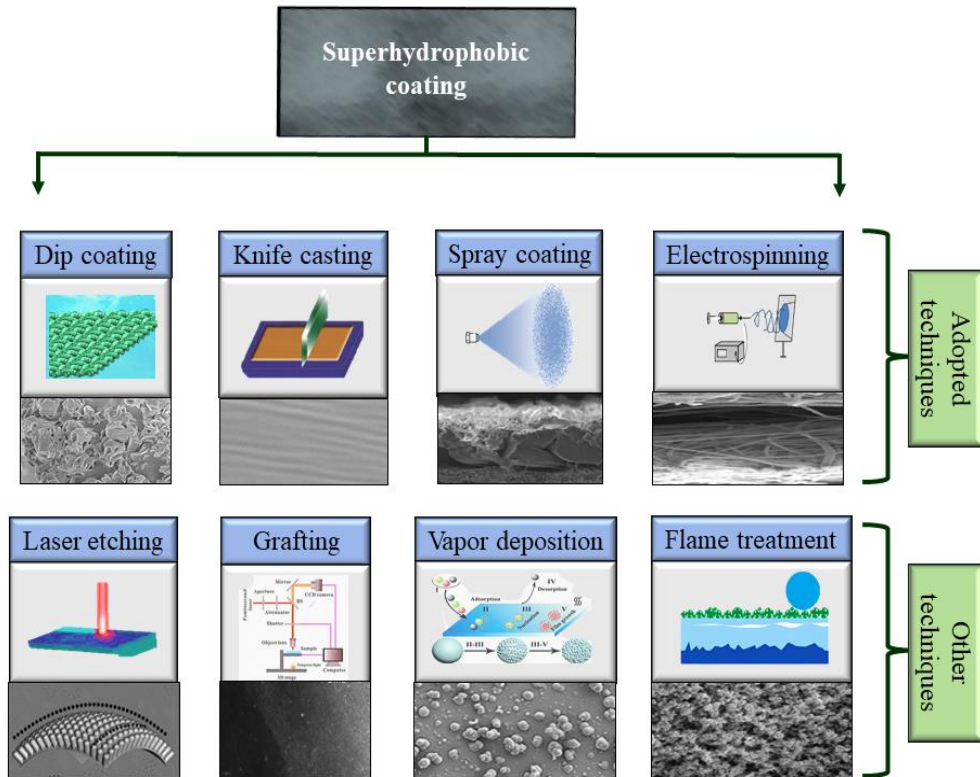
Figure 6. Methods (current adopted techniques and other techniques) for the preparation of superhydrophobic PDMS.

Given that the resistance of the PDMS layer is just one of the resistances (see Eq. 5) further reduction in its thickness will bring little overall benefit. However as the mechanism of transport across this selective layer is one of solution-diffusion mechanism improvements in the selectively of this layer will be beneficial [61]. In summary, manufacturing techniques impact the performance of membranes by influencing the control of thickness and architecture. Overall the

spray coating technique is a more environment-friendly and more efficient way to fabricate a

PDMS layer due to easy control of thickness, less amount of solvent, and safe working condition.

Table 3. Comparative analysis of various PDMS application techniques.

Technique	Instrumental type	Support layer	Handling	Advantages	Limitations
Dip coating	Oven, Container	Easy	Glass, porous material, Fabric, wooden	1. Time saving (Fast) 2. Uniform coating 3. Continuous production 4. Suitable for various substrate 5. Economic	1. Requirement of organic solvents 2. Difficulty in controlling morphology
Electrospinning	Electrospinning equipment	Tough	-	1. Uniform coating 2. Porous hydrophobic membrane 3. Continuous production	1. Time consumming 2. Higher cost of instrument 3. Finely tuned processing parameters
Knife casting	Instrument	Easy	-	1. Economical 2. Uniform coating 3. Continuous production	1. Lower fatigue strength of layer 2. Casting defects
Spray coating	Spray gun	Easy	Metallic surface, glass, porous substrate	1. Uniform coating 2. Continuous production 3. Larger scale 4. Time saving (Fast)	1. Harder in controlling surface morphology 2. Only for outer surface 3. Requirement of organic solvents

**3.3 Incorporation of porous nanoparticle (Np) into selective layer**

Recent developments in PDMS polymeric material has suggested that it has a limit. For

example, it has been reported that the overall transport coefficient of phenol through PDMS ranges

from 4 to 7×10^{-7} m/s in EMBR [36, 51]. Hence, the separation capability of PDMS coated

membranes is not good enough to meet the requirements of full-scale application. To address this issue, doping PDMS polymer with various porous Nps has proven to be an effective strategy. The deposition of Nps into PDMS provides different interface morphology and enhances the mechanical and thermal properties of top selective layer [62]. Recently, major areas of investigation have been directed towards finding suitable combinations of PDMS and Nps, the PDMS/Nps interface morphology and physical properties of porous Nps (e.g., particle size, structure, and particle agglomerations) [18, 63].

To date, wide range of porous Nps have been introduced based on their larger porosity, higher surface area, facile functionalization, pore volume, tunable pore size and shape, chemical and thermal stability, and excellent compatibility with PDMS polymer [64, 65]. Smaller particles (less than 50 nm) will provide more PDMS/Nps interfacial area, opportunity to disrupt polymer chain packing and potentially enhance the separation capability [46, 66]. The incorporation of Nps into PDMS provides transport through the channel of inner cages, serving as expressways with lower mass transfer resistance [67]. It has been found that the trend of organophilicity increases due to the addition of the pore-flow mode of Nps alongside the solution-diffusion mode [32, 62, 64]. The schematic illustration of transport mechanism through PDMS (solution-diffusion mechanism) and pores (pore-flow mode) is shown in Figure 7a. The attachment of available functional groups on Nps and PDMS enhance the dispersion of Nps into selective layer [68]. However, no general strategy is available to deposit the Nps evenly into PDMS polymer (Figure 7b represents the ideal morphology of Np dispersed into PDMS). Phase separation between Np and PDMS polymer leads to detachment of Nps from the host polymer and can result in the creation of interface voids (As illustrated in Figure 7c). The interface voids are presumed to be the major cause of a deterioration in performance due to by-passing of the particles [69]. Other possible causes for interface voids

1　include repulsive forces between PDMS and Nps and different coefficients of expansion [70]. To

2　overcome these problems, the hydrophobic modification of the pores surface of Np is beneficial

3　as it can enable homogenous dispersion within PDMS [71-73].
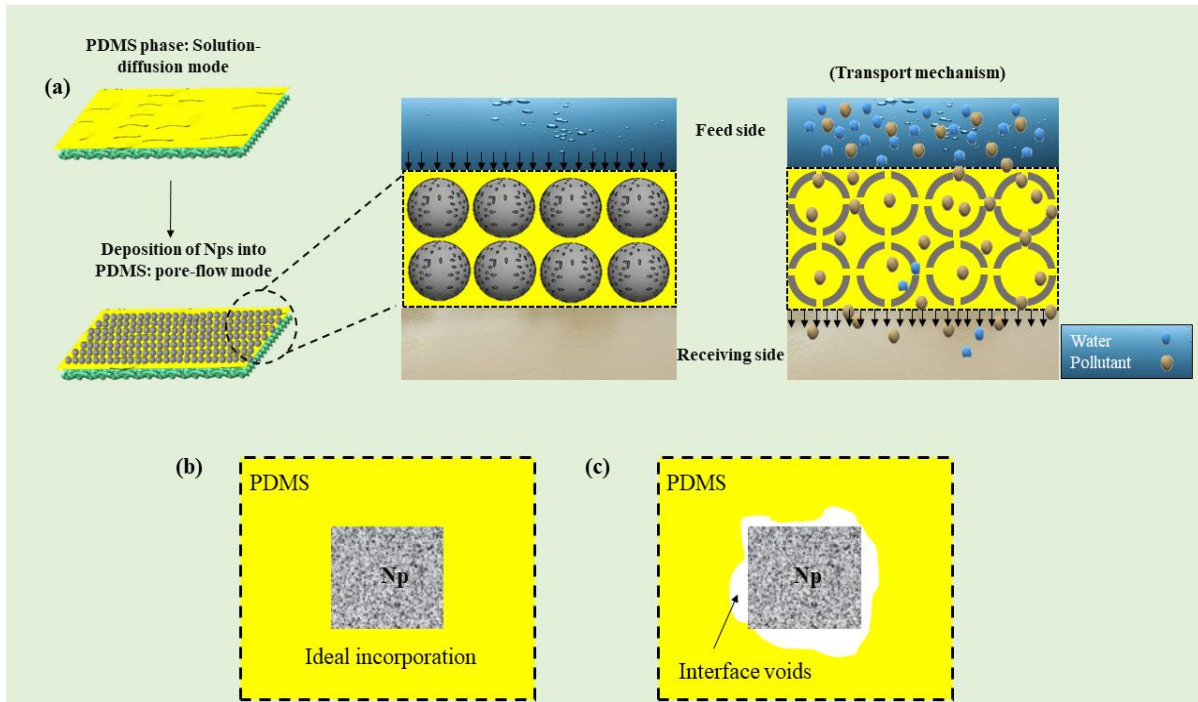
5　Figure 7. Schematic transport mechanism. (a) Transport via pore-flow mode (Reproduced and

6　modified [48]). (b, c) Morphology of Nps (Reproduced and modified [69]).

7

8　　　Emerging as a comparatively new group of porous materials, covalent organic frameworks

9　(COFs), metal organic frameworks (MOFs) and carbon nanotubes (CNT) have captured wide

10　attention recently due to their tailorable structure, crystalline nature, and most importantly

11　functional applications in various fields. COFs are porous crystalline materials containing covalent

12　bonded blocks, and they have gained great attention since first being reported in 2005 [74]. The

13　availability of unreacted amino and aldehyde groups in pore channels of imine-based COFs are

14　expected to form hydrogen bonds with water molecule and hinder water transport. The pore size

of COFs can be tuned via building blocks and various pore size distributions can be achieved. The theoretical pore width (0.78 nm) of COF-300 provides sufficiently large channels for ECs [75]. Moreover, the incorporation of COFs in PDMS have been achieved in many studies [76-78], which suggests that they should be evaluated for the EMBR process.

In the case of MOFs, inorganic units bridged by organic ligands suggests that it could be a candidate for enhancing the EMBR process. Various water stable structure of MOFs such as ZIF-8, MIL-53(Al) and NH_2-UiO-66 provides different window sizes which are 0.34, 0.86 and 0.6 nm respectively [79]. Liao et al. successfully coated Ag-MOFs on PDMS surface and achieved 33.0×10^{-7} m/s mass transfer coefficient for phenol in an EMBR process. Thus, it can be anticipated that the incorporation of other structures would provide higher mass transfer for other ECs and that there can be a suitable tailoring of the size of the channels of the porous cages. In the case of CNTs, nanotubes as porous materials presents nanochannels (one-dimensional and two-dimensional) and high throughput. In CNTs, inherent atomic-scale smoothness of interior channels enables rapid transport of targeted molecules. In addition, CNTs induce excellent selectivity for targeted pollutants. However, it is difficult to achieve the homogeneous dispersion of CNTs in polymeric solutions, due to their flexibility and the availability of van der Waal forces which leads to the creation of entangled bundles. The recommended methods for homogenous dispersion are chemical vapor deposition (CVD) treatment, ozone mediated and acid treatment [80-82].

4 Applications of EMBR

The advantages of EMBR technology enable its application in many fields, including denitrification of nitrate and waste gas treatment as explained elsewhere [25]. For wastewater treatment, EMBR has been applied for the removal of ECs such as monochlorobanzene [83], 1, 3-dichloropropene [84], nitrobenzene [21], phenol [36], 1, 2-dichloroethane [85], 3-chloro-4-

methylaniline [86] and 3-chloronitrobenzene [87]. In this case, the EMBR technology presents higher removal of organic compounds and highest mixed liquor suspended solids (MLSS) concentration [88]. The higher MLSS concentration results in smaller footprints and higher quality treated water, advantaging this technology over traditional activated sludge and MBRs [25]. According to literature, the EMBR has been operated widely at laboratory scale for months without pre-treatments or diluting the feed wastewater [27]. The detailed extraction of other ECs, membrane properties and operating conditions of EMBR are summarised in Table 4.

Phenol as an EC has been widely gained attention and treated with various tradition technologies, as mentioned above. The biodegradation of Phenol by EMBR is significant due to higher removal rate. Livingston et al. reported a study to biodegrade the phenolic compounds in salty and acidic concocted wastewater using silicon rubber tubes. The results showed 65% removal of phenol at constant temperature (30 °C) and pH (6.7). Moreover, the biofilm growth was observed on the membrane surface caused decrease in mass transfer [89]. In another study [32], electrospinning-phase inversion composite PDMS membrane was optimized for phenol removal and achieved higher mass transfer coefficient (8.8×10^{-7}). However, the influence of biofilm growth was observed in every applied study. The scientists placed different EMBR setups, including, submerged and cross-flow mode for long-term operation to observe the effect of biofilm. The biofilm growth on membrane surface decreased the value of k_o up to 65% [28]. Based on these studies, it can be stated that the biofilm growth can be effectively controlled by fine tuning the organic loading rate [37]. However, the incorporated membranes are still facing lower structural integrity and salt leakage issues, need to be resolved. Various applied conditions and membrane modifications have been discussed in biofilm section to control the growth of biofilm.

1   Toluene, as second EC has been extensively treated using EMBR. Emanuelsson et al. studied

2   the removal of nitrate by using PDMS and nitrate in EMBR [90]. In this study, the nitrate was used

3   instead of oxygen due to lower solubility of oxygen in water, to control the growth of biofilm in

4   EMBR. The less solubility of oxygen influences the relationship between biofilm growth and

5   organic flux. Therefore, nitrate was incorporated to deal with this problem. The nitrate

6   incorporation was studies under three different conditions. In first condition, low nitrate

7   concentration resulted in lower flux and biofilm growth. In second condition, excessive nitrate

8   concentration resulted into no biofilm formation and constant flux over time. In third condition,

9   excess nitrate concentration with ferric nitrate flocculent resulted in biofilm formation but toluene

10   flux decreased concomitantly with the growth of biofilm. Thus, it enlightens that electron acceptor

11   solubility is not essential to control biofilm growth in EMBR. In summery for wastewater

12   treatment with EMBR, the EMBR showed higher removal rate of targeted pollutants based on

13   concentration driven mechanism.

Table 4. EMBR for the treatment of emerging contaminants.

Targeted component	EMBR configuration	Membrane properties	Operating conditions	Mass transfer Coefficient (k_0 m/s)	Reference
	Flat sheet	Top layer: PDMS	Concentration: 1000 ppm	Aq-aq ext: 9.3E-7	[51]
		Substrate: PVDF/LiCl/DMF	Operating time: 14 days	EMBR: 4.1E-7	
	Flat sheet	Top layer: PDMS	Concentration: 1000 ppm	Aq-aq ext: 18.3E-7	[48]
	Effective area= 36 cm^2	Substrate: PVDF	Operating time: 14 days		
	Flat sheet	Top layer: PDMS	Concentration: 1000 ppm	Aq-aq ext: 12E-7	[31]
	Effective area= 238 cm^2	Substrate: PVDF	Operating time: 14 days	EMBR: 7.0E-7	
	Silicon rubber tubular membrane	(0.4m×2.07mm ID×4.08mm OD)	Concentration: 2000 ppm Operating time: 14 days	EMBR: 0.8E-7	[30]
Phenol	Flat sheet	Top layer: PDMS	Concentration: 1000 ppm	Aq-aq ext: 12E-7	[28]
	Effective area =36 cm^2	Substrate: ultrafine nanofibrous layer, a coarse nanofibrous layer, a non-woven mechanical support, and a micro/nano-beaded layer	Operating time: 14 days	EMBR: 5.7E-7	
	Hollow fiber membrane	Top layer: PDMS	Concentration: 2000 ppm	Aq-aq ext: 30E-7	[36]
		Substrate: Polyetherimide	Operating time: 14 days	EMBR: 7.5E-7	
	Flat sheet	Top layer: PDMS	Concentration: 1000 ppm	Aq-aq ext: 18E-7	[48]
	Effective area =36 cm^2	Substrate: PVDF	Operating time: 14 days		

	Flat sheet	Top layer: PDMS	Concentration: 1000 ppm	Aq-aq ext: 37.9E-7	[60]
	Effective area =22 cm^2	Substrate: PVDF/non-woven fabric nanofibrous	Operating time: 4.3 days		
	Flat sheet	Top layer: PDMS	Concentration: 2500 ppm	EMBR: 8E-7	[32]
	Effective area =48 cm^2	Substrate: PPMA	Operating time: 18 days		
	Flat sheet	Top layer: (TiO$_2$@ZIF-8) PDMS	Concentration: 1000 ppm	Aq-aq ext: 25.28E-7	[61]
	Effective area =24 cm2	Substrate: PVDF	Operating time: 14 days		
	Flat sheer	PDMS/PPMA	Concentration: 14-290 ppm	EMBR: 9E-7	[52]
	Effective area =48 cm^2		Operating time: 32 days		
	Flat sheer	PDMS/PMMA/MWCNTs	Concentration: 14-290 ppm	EMBR: 7E-7	[19]
	Effective area =20 cm^2		Operating time: 1.2 days		
	Flat sheet	Top layer: (Ag-MOFs). PDMS	Concentration: 1000 ppm	EMBR: 33E-7	[18]
	Effective area =36 cm^2	Substrate: PVDF	Operating time: 1.2 days		
Toluene	Silicon tubular membrane	(6.2m×3.0mm ID×3.7mm OD)	Concentration: - Operating time: 38days	-	[91]
3-chloronitrobenzene	Silicon tubular membrane	(15m×3.0mm ID×4.0mm OD)	Concentration: 158 ppm Operating time: 16 days	EMBR: 2.9E-6	[92]
2,3-dichloroaniline	Silicon tubular membrane	(15m×3.0mm ID×4.0mm OD)	Concentration: 194 ppm Operating time: 16 days	EMBR: 1.81E-6	[87]
Chlorobenzene	Silicon tubular membrane	(350×3m×3.0mm ID×3.6mm OD)	Concentration: 10-250 ppm Operating time: 62.5 days	EMBR: 0.5-1.5E-6	[83]

| Trichloroethylene | Polypropylene hollow fiber | (5600×23.9cm×240µm ID×300µm OD) | Concentration: 10-250 ppm Operating time: 62.5 days | EMBR: 0.18-0.95E-6 | [93] |
| Methyl tert-butyl ether | Tubular semipermeable silicon membranes | (25m×3.8mm ID×0.4mm OD) | Concentration: 150 mg/L Operating time: 28 days | EMBR: 4.25E-7 | [94] |

* Polydimethylsiloxane (PDMS); N,N-Dimethylformamide (DMF); Polyvinylidene fluoride (PVDF); PPMA: poly (methyl methacrylate); Aquous-aquous extraction (Aq-aq ext)

5 Limitations in EMBR development

Despite the benefits of EMBRs, the main obstacles impending this technology includes: (1) membrane fouling and significant flux decline and (2) lack of biofilm control strategies which are addressed in the next sections.

5.1 Membrane fouling

After diffusing through the selective layer of a thin-film composite membrane, the pollutants need to pass through a non-porous selective layer. Potential problems are the microbial growth promoted by the disused pollutant and their binding onto the porous substrate. Biofilm growth within the porous support will significant reduction of mass transfer by increased membrane resistance, and therefore enhancing operational and maintenance cost. Typically, membrane fouling is ameliorated by: (1) appropriate membrane selection; and (2) careful control of membrane operating and cleaning regimes.

In EMBR, simultaneous biological and filtration activities on membrane surface cause membrane fouling. During the biological activity, the production of soluble microbial products (SMP) and extra-cellular polymeric substances (EPS) is identified as crucial source of pollutants [25, 95]. Moreover, the EPS/SMP chemically develops as an insoluble gel-like on membrane surface owing to inter-/intra-molecular ionic cross-linking chemical reaction due to polyvalent cations of metals (Ca, Mg, Al, Fe, Si) and hexoses/methylpentose/uronic acids (alginic/pectin acids) units in EPS/SMP molecules [96, 97]. To avoid pore blockage the biofilm should be a retained layer on the surface [52]. Various strategies such as: (1) appropriate operation conditions, including membrane relaxation; (2) appropriate aeration; (3) backwash; (4) coagulation/flocculation [98]. These physical or chemicals methods can be used alone or integrated. According to the research literature, UV irradiation treatment has been proposed to

control biologically membrane fouling [99] but practical issues have yet to be addressed. Future research can focus on controlling biofilms in a more environmentally friendly and economical way, or by modulating the chemical properties of the membrane surface, to achieve micro-interface regulation by releasing antifouling substances.

In addition to biofouling on the receiving side there is the issue of fouling on the feedside. The membrane characteristics such as reduced surface roughness, optimized hydrodynamic conditions, lower surface energy, and antibacterial capability can also help to reduce the membrane fouling. The hydrophobic PDMS as selective layer possess smooth and slippery surface. The flexible backbone of Si-O and lower surface energy hinders the deposition of foulants and can be removed conveniently by up-flowing air bubbles. Given the success of traditional flat-sheet MBRs we are optimistic that the main fouling issue will be on the receiving side, and not the feedside, but this can only be determined by longterm trials.

Regarding the receiving side a hydrophilic porous substrate or one with a highly hydrophilic coating can inhibit the attachment of bacteria and proteins. The unique characteristics of poly-ethylene glycol (PEG) has gained attention to enable superhydrophilicity. The chemical coating of PEG on PVDF and PTFE polymeric substrates can enhance the hydrophilicity of membrane with reduced membrane fouling. The enhanced hydrophobicity is attributed to segregation of PEG groups and swelling of the PEG domain [100].

5.2 Biofilm formation

The biofilm attached to the membrane surface on receiving side is composed of microorganism's micro-colonies and trapped in a gel-like EPS matrix. The biological activity of these microorganisms causes the formation of biofilm on receiving side. The availability of

microorganisms in wastewater might occur the possibility to grow biofilm at the feed side after the long-term application in EMBR, however, our current study is mainly considering the biofilm at receiving side. To some extent, biofilm thickness (>0.5mm) is adventurous [30]. The uncontrolled growth of biofilm affects the stability of EMBR. The biofilm thickness likewise influences the permeate flux of pollutant through membrane as thicker biofilm results into higher transfer resistance [27]. Despite the drawbacks of enhancing the mass transfer resistance and declining the permeate flux, the biofilm enhances the membrane's capability to inhibit the small objects like inorganic ions and viruses. Some researchers have employed membrane biofilm reactors to remove organic carbon and nitrogen simultaneously from one reactor [101]. Moreover, it has been found that the formation of a biofilm on a microfiltration membrane improved the quality of treated water [102].

The presence of biofilm is critical for EMBRs but attaining the optimal thickness on the surface of membrane is challenging. Figure 8 indicates that a thinner biofilm thickness (earlier times) results in higher permeate fluxes. Thus the incorporation of various techniques or good choice of EMBR configuration should enable the attainment of an optimal biofilm thickness. Various membrane properties such as membrane roughness and hydrodynamic conditions were revealed as the factors affecting the biofilm growth [31]. Also specific conditions such as the addition of sodium chloride have been employed. Its addition into an EMBR has been found to lessen the growth of chlorobenzene-degrading *Pseudomonas* species. Salt addition influences the maintenance energy of the microorganisms because it enhances the pumping energy requirements for salt [37]. Secondly UV inactivation and membrane relaxation have been used and membrane fouling decreased by up to 24%. Also thirdly there has use of nitrate and ferric nitrate flocculent [25]. Excessive amount of nitrate and ferric nitrate flocculent are used to force the biofilm

1 formation with toluene as the pollutant. However the flux across the membrane decreases

2 concomitantly with the growth of biofilm. Fourthly mention is made of a Liquid carrier. By

3 keeping the membrane and bio-medium separately, a suitable liquid carrier delivers the permeate

4 from surface to bio-medium for biodegradation [103]. Although this yields a higher permeate flux,

5 the system has a complex configuration.

6

(a) *Table: Membranes and operating conditions of EMBRs*

Serial number	Membrane type	Feed side	Receiving side	Operation time (hr)	Ref.
A	Nanofiber composite membrane NC	1000ppm Phenol, 5 g/L NaCl		288	[28]
B	PDMS/polyetherimide (PEI)	1000ppm Phenol, 50 g/L NaCl		280	[36]
C	PDMS/PVDF	1000ppm Phenol, 5 g/L NaCl	Biomedium	336	[51]
D	PDMS tube	2000ppm Phenol		336	[30]
E	PDMS/PVDF	1000ppm Phenol, 5 g/L NaCl		336	[31]

(b)
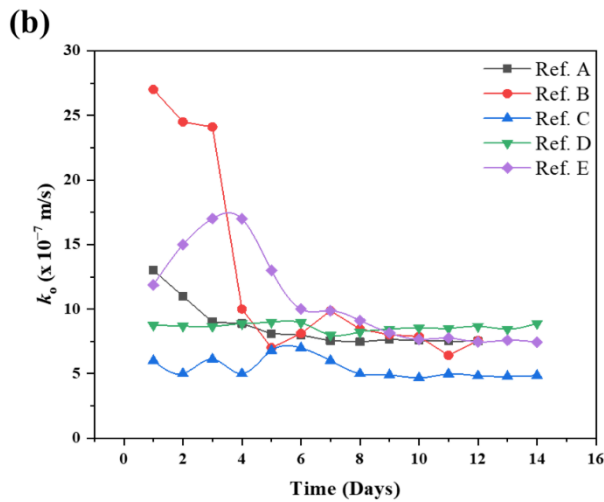
*Mass transfer coefficient variations in EMBRs*

(c)
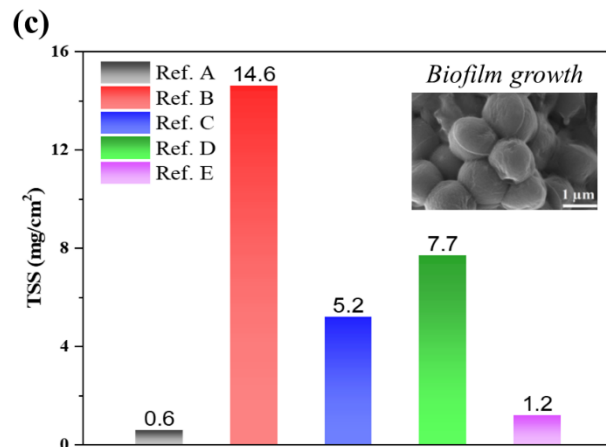
Membranes autopsies after operation

7

34

Figure 8. Biofilm growth and permeating influence in EMBR (Presented data reproduced from [28], [30], [31], [36] and [51]). (a) Membranes and operating conditions. (b) Mass transfer coefficient variations. (c) Membrane autopsies after operation.

Lastly hybrid processes in which there is addition of modified and water stable bio-carriers (sponges) to the effluent tank might be useful to increase efficiency. Aeration and sponges may well beneficially limit biofilm growth on the membrane surface. A possible concept is illustrated in Figure 9. As a concluding observation it is noted that successful pervaporation applications generally involve hybrid processes [22, 104]. Thus the success of EMBRs might be dependent upon the development of hybrid processes. Whatever form the processes take, as with all MBR processes trials over extended periods are essential because these biofilms need weeks to establish a pseudo steady-state.
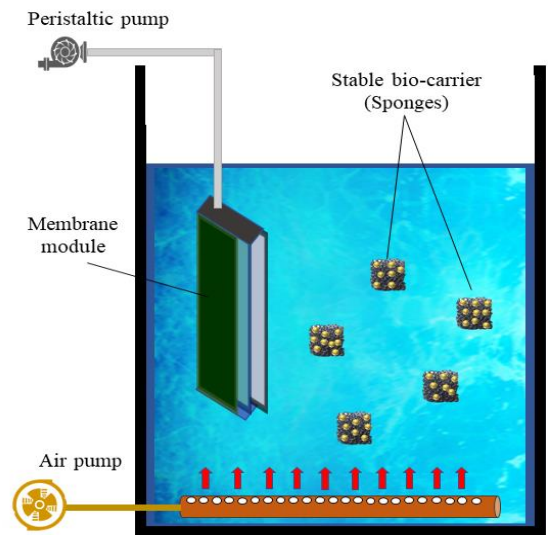
Figure 9. Enhanced EMBR configuration with aeration and bio-carrier.

6 Conclusion and future prospective

EMBR is, in principle, an attractive technology for the biodegradation of toxic compounds in wastewater such as contaminents of emerging concern. This is particularly so where the wastewater has harsh conditions making conventional treatment difficult. Despite their potential to deal with hard conditions, EMBRs have yet to progress significantly beyond conceptualization and laboratory evaluation. Increasing need for water recycle may encourage a company to invest in long-term trials in order to achieve a deep clean of its wastewater in order to remove recalcitrant compounds that are only slowly biodegradable. Current results are essentially preliminary because of the time constants in biologically based systems.

Membrane technology, the key component of EMBR, has been reviewed in this study in order to guide future research. It was concluded that an appropriate choice of polymer and a design involving TFC membranes would enable EMBR technology to achieve higher mass transfer fluxes. Furthermore manufacture of the substrate (PVDF and PTFE) via electrospinning technique has a great potential to minimize the intrusion of top selective layer and control the residual volume in pores and surface. As far as coating for antifouling properties are concerned, coating the surface with polymer (PEG), which presents an optimized and lower energy surface architecture, has shown promising results.

Moreover with regard to the selective layer, the efficacy and application of PDMS was highlighted as being the most common and appropriate polymer for the selective layer of a TFC membrane. Among the major advances achieved in past decades there is the development of novel approaches to apply selective layer such as spray coating which minimises thickness. However, PDMS has certain drawbacks including lower organophilicity and less mechanical strength.

Tailoring through the incorporation of nanomaterials such as MOF, COF and CNTs facilitates a pore-flow mode for pollutant transport along side the solution-diffusion mechanism.

Hybrid processes such as the addition of stable bio-carriers to the effluent tank might be important to the commercialization of EMBRs because the blend of two processes offers advantages that the component processes do not possess. Also an appropriate evaluation of the environmental benefits with explicit weighting of environmental impacts should facilitate technological progress in this area.

7 Conflict of interest

There are not conflicts to declare.

8 Acknowledgement

Reference

[1] S.S. Hassan, G.A. Williams, A.K.J.R. Jaiswal, S.E. Reviews, Moving towards the second generation of lignocellulosic biorefineries in the EU: Drivers, challenges, and opportunities, Renewable & sustainable Energy Reviews 101 (2019) 590-599.

[2] R.J. Newton, J.S. McClary, The flux and impact of wastewater infrastructure microorganisms on human and ecosystem health, Current opinion in biotechnology 57 (2019) 145-150.

[3] D. Mooney, K.G. Richards, M. Danaher, J. Grant, L. Gill, P.-E. Mellander, C. Coxon, An investigation of anticoccidial veterinary drugs as emerging organic contaminants in groundwater, Science of the Total Environment 746 (2020) 141116.

[4] M.B. Asif, J. Hou, W.E. Price, V. Chen, F.I. Hai, Removal of trace organic contaminants by enzymatic membrane bioreactors: Role of membrane retention and biodegradation, Journal of Membrane Science 611 (2020) 118345.

[5] M.B. Asif, Z. Zhang, Ceramic membrane technology for water and wastewater treatment: a critical review of performance, full-scale applications, membrane fouling and prospects, Chemical Engineering Journal (2021) 129481.

[6] M. Bilal, M. Adeel, T. Rasheed, Y. Zhao, H.M. Iqbal, Emerging contaminants of high concern and their enzyme-assisted biodegradation–a review, Environment international 124 (2019) 336-353.

[7] Y.P. Tang, L. Luo, Z. Thong, T.S. Chung, Recent advances in membrane materials and technologies for boron removal, Journal of Membrane Science 541 (2017) 434-446.

[8] N.K. Khanzada, M.U. Farid, J.A. Kharraz, J. Choi, C.Y. Tang, L.D. Nghiem, A. Jang, A.K. An, Removal of organic micropollutants using advanced membrane-based water and wastewater treatment: A review, Journal of Membrane Science 598 (2020) 117672.

[9] W. Song, S. Zhou, S. Hu, W. Lai, Y. Lian, J. Wang, W. Yang, M. Wang, P. Wang, X. Jiang, Surface engineering of CoMoS nanosulfide for hydrodeoxygenation of lignin-derived phenols to arenes, ACS Catalysis 9(1) (2018) 259-268.

[10] N.H. Tran, M. Reinhard, K.Y.-H. Gin, Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions-a review, Water research 133 (2018) 182-207.

[11] M.B. Ahmed, J.L. Zhou, H.H. Ngo, W. Guo, N.S. Thomaidis, J. Xu, Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: a critical review, Journal of Hazardous Materials 323 (2017) 274-298.

[12] F.J. Álvarez-Hornos, V. Martínez-Soria, P. Marzal, M. Izquierdo, C. Gabaldón, Performance and feasibility of biotrickling filtration in the control of styrene industrial air emissions, International Biodeterioration Biodegradation 119 (2017) 329-335.

[13] W.S. Chai, J.Y. Cheun, P.S. Kumar, M. Mubashir, Z. Majeed, F. Banat, S.-H. Ho, P.L. Show, A review on conventional and novel materials towards heavy metal adsorption in wastewater treatment application, Journal of Cleaner Production 296 (2021) 126589.

[14] S. Bairagi, S.W. Ali, Conventional and advanced technologies for wastewater treatment, Environmental Nanotechnology for Water Purification (2020) 33-56.

[15] S.A. Deowan, F. Galiano, J. Hoinkis, D. Johnson, S.A. Altinkaya, B. Gabriele, N. Hilal, E. Drioli, A. Figoli, Novel low-fouling membrane bioreactor (MBR) for industrial wastewater treatment, Journal of membrane science 510 (2016) 524-532.

[16] S. Judd, C. Judd, The MBR Book: Principles and Applications of Membrane Bioreactors for Water and Wastewater Treatment 2nd ed., Publ, Elsevier, UK, 2011.

[17] X. Zhang, Selective separation membranes for fractionating organics and salts for industrial wastewater treatment: Design strategies and process assessment, Journal of Membrane Science 643 (2022) 120052.

[18] G. Yuan, Y. Tian, B. Wang, X. You, Y. Liao, Mitigation of membrane biofouling via immobilizing Ag-MOFs on composite membrane surface for extractive membrane bioreactor, Water Research (2021) 117940.

[19] M. Adeel, Y. Xu, L.-F. Ren, J. Shao, Y. He, Improvement of phenol separation and biodegradation from saline wastewater in extractive membrane bioreactor (EMBR), Bioresource Technology Reports 17 (2022) 100897.

[20] N.R. Mullins, A.J. Daugulis, The biological treatment of synthetic fracking fluid in an extractive membrane bioreactor: selective transport and biodegradation of hydrophobic and hydrophilic contaminants, Journal of Hazardous Materials 371 (2019) 734-742.

[21] A.G. Livingston, Extractive membrane bioreactors: a new process technology for detoxifying chemical industry wastewaters, Journal of Chemical Technology Biotechnology: International Research in Process, Environmental Clean Technology 60(2) (1994) 117-124.

[22] F. Lipnizki, R. Field, Pervaporation-based hybrid processes in treating phenolic wastewater: technical aspects and cost engineering, Separation Science & Technology 36(15) (2001) 3311-3335.

[23] P. Wu, R. Field, R. England, B. Brisdon, A fundamental study of organofunctionalised PDMS membranes for the pervaporative recovery of phenolic compounds from aqueous streams, Journal of Membrane Science 190(2) (2001) 147-157.

[24] P. Wu, R. Field, B. Brisdon, R. England, S. Barkley, Optimisation of organofunction PDMS membranes for the pervaporative recovery of phenolic compounds from aqueous streams, Separation & Purification Technology 22 (2001) 339-345.

[25] I.G. Wenten, D.L. Friatnasary, K. Khoiruddin, T. Setiadi, R. Boopathy, Extractive membrane bioreactor (embr): recent advances and applications, Bioresource Technology 297 (2020) 122424.

[26] N.R. Mullins, A.J.J.J.o.h.m. Daugulis, The biological treatment of synthetic fracking fluid in an extractive membrane bioreactor: selective transport and biodegradation of hydrophobic and hydrophilic contaminants, 371 (2019) 734-742.

[27] L.-F. Ren, R. Chen, X. Zhang, J. Shao, Y. He, Phenol biodegradation and microbial community dynamics in extractive membrane bioreactor (EMBR) for phenol-laden saline wastewater, Bioresource Technology 244 (2017) 1121-1128.

[28] Y. Liao, S. Goh, M. Tian, R. Wang, A.G. Fane, Design, development and evaluation of nanofibrous composite membranes with opposing membrane wetting properties for extractive membrane bioreactors, Journal of Membrane Science 551 (2018) 55-65.

[29] M. Manetti, M.C. Tomei, Extractive polymeric membrane bioreactors for industrial wastewater treatment: Theory and practice, Process Safety and Environmental Protection 162 (2022) 169-186.

[30] B.J. Yeo, S. Goh, A.G. Livingston, A.G. Fane, Controlling biofilm development in the extractive membrane bioreactor, Separation Sciecne and Technology 52(1) (2017) 113-121.

[31] Y. Liao, M. Tian, S. Goh, R. Wang, A.G. Fane, Effects of internal concentration polarization and membrane roughness on phenol removal in extractive membrane bioreactor, Journal of Membrane Science 563 (2018) 309-319.

[32] L.-F. Ren, C. Liu, Y. Xu, X. Zhang, J. Shao, Y. He, High-performance electrospinning-phase inversion composite PDMS membrane for extractive membrane bioreactor: Fabrication, characterization, optimization and application, Journal of Membrane Science 597 (2020) 117624.

[33] X. Qian, M. Ostwal, A. Asatekin, G.M. Geise, Z.P. Smith, W.A. Phillip, R.P. Lively, J.R. McCutcheon, A critical review and commentary on recent progress of additive manufacturing and its impact on membrane technology, Journal of Membrane Science (2021) 120041.

[34] S. Huang, J. Mansouri, P. Le-Clech, G. Leslie, C.Y. Tang, A.G. Fane, A comprehensive review of electrospray technique for membrane development: Current status, challenges, and opportunities, Journal of Membrane Science (2022) 120248.

[35] J. Buenrostro-Zagal, A. Ramirez-Oliva, S. Caffarel-Mendez, B. Schettino-Bermudez, H. Poggi-Varaldo, Treatment of a 2, 4-dichlorophenoxyacetic acid (2, 4-D) contamined wastewater in a membrane bioreactor, Water Science Technology 42(5-6) (2000) 185-192.

[36] C.H. Loh, Y. Zhang, S. Goh, R. Wang, A.G. Fane, Composite hollow fiber membranes with different poly (dimethylsiloxane) intrusions into substrate for phenol removal via extractive membrane bioreactor, Journal of Membrane Science 500 (2016) 236-244.

[37] L. Strachan, L.F. Dos Santos, D. Leak, A. Livingston, Minimisation of biomass in an extractive membrane bioreactor, Water Science and Technology 34(5-6) (1996) 273-280.

[38] C.H. Koo, A.W. Mohammad, M.Z.M. Talib, Review of the effect of selected physicochemical factors on membrane fouling propensity based on fouling indices, Desalination 287 (2012) 167-177.

[39] Z. Alihemati, S. Hashemifard, T. Matsuura, A. Ismail, N. Hilal, Current status and challenges of fabricating thin film composite forward osmosis membrane: A comprehensive roadmap, Desalination 491 (2020) 114557.

[40] L.E. Peng, Z. Yang, L. Long, S. Zhou, H. Guo, C.Y. Tang, A critical review on porous substrates of TFC polyamide membranes: Mechanisms, membrane performances, and future perspectives, Journal of Membrane Science 641 (2022) 119871.

[41] F. Liu, L. Wang, D. Li, Q. Liu, B. Deng, A review: the effect of the microporous support during interfacial polymerization on the morphology and performances of a thin film composite membrane for liquid purification, RSC advances 9(61) (2019) 35417-35428.

42

[42] K. Yoon, B.S. Hsiao, B. Chu, High flux nanofiltration membranes based on interfacially polymerized polyamide barrier layer on polyacrylonitrile nanofibrous scaffolds, Journal of Membrane Science 326(2) (2009) 484-492.

[43] H. Tang, J. He, L. Hao, F. Wang, H. Zhang, Y. Guo, Developing nanofiltration membrane based on microporous poly (tetrafluoroethylene) substrates by bi-stretching process, Journal of Membrane Science 524 (2017) 612-622.

[44] M. Wang, M.-L. Huang, Y. Cao, X.-H. Ma, Z.-L. Xu, Fabrication, characterization and separation properties of three-channel stainless steel hollow fiber membrane, Journal of Membrane Science 515 (2016) 144-153.

[45] B. Sartowska, W. Starosta, P. Apel, O. Orelovitch, I. Blonskaya, Polymeric track etched membranes-application for advanced porous structures formation, Acta Physica Polonica A 123(5) (2013) 819-821.

[46] Y. Liao, C.-H. Loh, M. Tian, R. Wang, A.G. Fane, Progress in electrospun polymeric nanofibrous membranes for water treatment: Fabrication, modification and applications, Progress in Polymer Science 77 (2018) 69-94.

[47] P. Cay-Durgun, S.C. Herrera, M.L. Lind, Filler materials to prevent polymer intrusion into mesoporous substrates during thin film formation, Microporous and Mesoporous Materials 296 (2020) 109956.

[48] M.-Y. Jin, Y. Liao, C.-H. Tan, R. Wang, Development of high performance nanofibrous composite membranes by optimizing polydimethylsiloxane architectures for phenol transport, Journal of Membrane Science 549 (2018) 638-648.

[49] Y.-N. Wang, K. Goh, X. Li, L. Setiawan, R. Wang, Membranes and processes for forward osmosis-based desalination: Recent advances and future prospects, Desalination 434 (2018) 81-99.

[50] Y. Huang, Q.-L. Huang, H. Liu, C.-X. Zhang, Y.-W. You, N.-N. Li, C.-F. Xiao, Preparation, characterization, and applications of electrospun ultrafine fibrous PTFE porous membranes, Journal of Membrane Science 523 (2017) 317-326.

[51] M.-Y. Jin, Y. Liao, C.H. Loh, C.-H. Tan, R. Wang, Preparation of polydimethylsiloxane–polyvinylidene fluoride composite membranes for phenol removal in extractive membrane bioreactor, Industrial Engineering Chemistry Research 56(12) (2017) 3436-3445.

[52] L.-F. Ren, H.H. Ngo, C. Bu, C. Ge, S.-Q. Ni, J. Shao, Y. He, Novel external extractive membrane bioreactor (EMBR) using electrospun polydimethylsiloxane/polymethyl methacrylate membrane for phenol-laden saline wastewater, Chemical Engineering Journal 383 (2020) 123179.

[53] M.J. Gómez, S. Herrera, D. Solé, E. García-Calvo, A.R. Fernández-Alba, Automatic searching and evaluation of priority and emerging contaminants in wastewater and river water by stir bar sorptive extraction followed by comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry, Analytical Chemistry 83(7) (2011) 2638-2647.

[54] J. Li, Y. Pan, W. Ji, H. Zhu, G. Liu, G. Zhang, W. Jin, High-flux corrugated PDMS composite membrane fabricated by using nanofiber substrate, Journal of Membrane Science 647 (2022) 120336.

[55] H.-Y. Mi, X. Jing, H.-X. Huang, L.-S. Turng, Novel polydimethylsiloxane (PDMS) composites reinforced with three-dimensional continuous silica fibers, Materials Letters 210 (2018) 173-176.

[56] C. Nagel, K. Günther-Schade, D. Fritsch, T. Strunskus, F. Faupel, Free volume and transport properties in highly selective polymer membranes, Macromolecules 35(6) (2002) 2071-2077.

[57] J. Chen, J. Li, R. Qi, H. Ye, C. Chen, Pervaporation performance of crosslinked polydimethylsiloxane membranes for deep desulfurization of FCC gasoline: I. Effect of different sulfur species, Journal of Membrane Science 322(1) (2008) 113-121.

[58] S.C. George, S. Thomas, Transport phenomena through polymeric systems, Progress in Polymer science 26(6) (2001) 985-1017.

[59] P.V. Naik, R. Bernstein, I.F.J. Vankelecom, Influence of support layer and PDMS coating conditions on composite membrane performance for ethanol/water separation by pervaporation, Journal of Applied Polymer Science 133(28) (2016).

[60] J.J. Huang, Y. Tian, L. Chen, Y. Liao, M. Tian, X. You, R. Wang, Electrospray-Printed Three-Tiered Composite Membranes with Enhanced Mass Transfer Coefficients for Phenol Removal in an Aqueous–Aqueous Membrane Extractive Process, Environmental Science & Technology 54(12) (2020) 7611-7618.

[61] M. Zarak, S. Atif, X. Meng, M. Tian, Enhancing interfacial interaction of PDMS matrix with ZIF-8 via embedding TiO2@ ZIF-8 composites for phenol extraction in aqueous-aqueous membrane extractive process, Chemical Engineering & Research Design (2022).

[62] Y. Pan, Y. Guo, J. Liu, H. Zhu, G. Chen, Q. Liu, G. Liu, W. Jin, PDMS with Tunable Side Group Mobility and its Highly Permeable Membrane for Removal of Aromatic Compounds, Angewandte Chemie International Edition (2021).

[63] M.-Y. Jin, Y. Lin, Y. Liao, C.-H. Tan, R. Wang, Development of highly-efficient ZIF-8@ PDMS/PVDF nanofibrous composite membrane for phenol removal in aqueous-aqueous membrane extractive process, Journal of Membrane Science 568 (2018) 121-133.

[64] A.-S. Zhang, S.-H. Li, H. Mao, L.-H. Xu, M.-Y. Lv, Z.-P. Zhao, Significantly improved pervaporation performance by relatively continuous and defect-free distribution of IL-modified ZIF-8 in PDMS membrane, Advanced Membranes 1 (2021) 100006.

[65] J. Kao, K. Thorkelsson, P. Bai, B.J. Rancatore, T. Xu, Toward functional nanocomposites: taking the best of nanoparticles, polymers, and small molecules, Chemical Society Reviews 42(7) (2013) 2654-2678.

[66] W. Tu, K. Ngai, M. Paluch, K. Adrjanowicz, Dielectric Study on the Well-Resolved Sub-Rouse and JG β-Relaxations of Poly (methylphenylsiloxane) at Ambient and Elevated Pressures, Macromolecules 53(5) (2020) 1706-1715.

[67] M.-Y. Jin, Y. Lin, Y. Liao, C.-H. Tan, R. Wang, Development of highly-efficient ZIF-8@ PDMS/PVDF nanofibrous composite membrane for phenol removal in aqueous-aqueous membrane extractive process, Journal of Membrane Science 568 (2018) 121-133.

[68] H. Mao, H.-G. Zhen, A. Ahmad, S.-H. Li, Y. Liang, J.-F. Ding, Y. Wu, L.-Z. Li, Z.-P. Zhao, Highly selective and robust PDMS mixed matrix membranes by embedding two-dimensional ZIF-L for alcohol permselective pervaporation, Journal of Membrane Science 582 (2019) 307-321.

[69] T.-S. Chung, L.Y. Jiang, Y. Li, S. Kulprathipanja, Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation, Progress in polymer science 32(4) (2007) 483-507.

[70] Y. Li, T.-S. Chung, C. Cao, S. Kulprathipanja, The effects of polymer chain rigidification, zeolite pore size and pore blockage on polyethersulfone (PES)-zeolite A mixed matrix membranes, Journal of Membrane Science 260(1-2) (2005) 45-55.

[71] Y. Ji, M. Zhang, K. Guan, J. Zhao, G. Liu, W. Jin, High-performance CO_2 capture through polymer-based ultrathin membranes, Advanced Functional Materials 29(33) (2019) 1900735.

[72] H. Kim, H.-G. Kim, S. Kim, S.S. Kim, PDMS–silica composite membranes with silane coupling for propylene separation, Journal of Membrane Science 344(1-2) (2009) 211-218.

[73] Z.-Y. Wu, C. Li, H.-W. Liang, Y.-N. Zhang, X. Wang, J.-F. Chen, S.-H. Yu, Carbon nanofiber aerogels for emergent cleanup of oil spillage and chemical leakage under harsh conditions, Scientific Reports 4(1) (2014) 1-6.

[74] A.P. Cote, A.I. Benin, N.W. Ockwig, M. O'Keeffe, A.J. Matzger, O.M. Yaghi, Porous, crystalline, covalent organic frameworks, Science 310(5751) (2005) 1166-1170.

[75] F.J. Uribe-Romo, J.R. Hunt, H. Furukawa, C. Klock, M. O'Keeffe, O.M. Yaghi, A crystalline imine-linked 3-D porous covalent organic framework, Journal of the American Chemical Society 131(13) (2009) 4570-4571.

[76] S. Li, P. Li, D. Cai, H. Shan, J. Zhao, Z. Wang, P. Qin, T. Tan, Boosting pervaporation performance by promoting organic permeability and simultaneously inhibiting water transport via blending PDMS with COF-300, Journal of Membrane Science 579 (2019) 141-150.

[77] C. Zhong, M. He, H. Liao, B. Chen, C. Wang, B. Hu, Polydimethylsiloxane/covalent triazine frameworks coated stir bar sorptive extraction coupled with high performance liquid chromatography-ultraviolet detection for the determination of phenols in environmental water samples, Journal of Chromatography A 1441 (2016) 8-15.

[78] Y. Meng, J.L. Anderson, Tuning the selectivity of polymeric ionic liquid sorbent coatings for the extraction of polycyclic aromatic hydrocarbons using solid-phase microextraction, Journal of Chromatography A 1217(40) (2010) 6143-6152.

[79] J. Li, H. Wang, X. Yuan, J. Zhang, J.W. Chew, Metal-organic framework membranes for wastewater treatment and water regeneration, Coordination Chemistry Reviews 404 (2020) 213116.

[80] H.T. Ng, M.L. Foo, A. Fang, J. Li, G. Xu, S. Jaenicke, L. Chan, S.F.Y. Li, Soft-lithography-mediated chemical vapor deposition of architectured carbon nanotube networks on elastomeric polymer, Langmuir 18(1) (2002) 1-5.

[81] L. Miao, J. Wan, Y. Song, H. Guo, H. Chen, X. Cheng, H. Zhang, Skin-inspired humidity and pressure sensor with a wrinkle-on-sponge structure, ACS applied materials & interfaces 11(42) (2019) 39219-39227.

[82] D. Wu, M. Wei, R. Li, T. Xiao, S. Gong, Z. Xiao, Z. Zhu, Z. Li, A percolation network model to predict the electrical property of flexible CNT/PDMS composite films fabricated by spin coating technique, Composites Part B: Engineering 174 (2019) 107034.

[83] A.G. Livingston, J.-P. Arcangeli, A.T. Boam, S. Zhang, M. Marangon, L.M.F. dos Santos, Extractive membrane bioreactors for detoxification of chemical industry wastes: process development, Journal of Membrane Science 151(1) (1998) 29-44.

[84] E. Katsivela, D. Bonse, A. Krüger, C. Strömpl, A. Livingston, R.-M. Wittich, An extractive membrane biofilm reactor for degradation of 1, 3-dichloropropene in industrial waste water, Applied Microbiology & Biotechnology 52(6) (1999) 853-862.

[85] L.F. dos Santos, A. Livingston, Extraction and biodegradation of a toxic volatile organic compound (1, 2-dichloroethane) from waste-water in a membrane bioreactor, Applied Microbiology & Biotechnology 42(2) (1994) 421-431.

[86] A. Splendiani, J.A. Moreira de Sa, R. Jorge, C. Nicolella, A.G. Livingston, K. Hughes, S. Cook, Development of an extractive membrane bioreactor for degradation of 3 chloro-4-methylaniline: From lab bench to pilot scale, Environmental Progress 19(1) (2000) 18-27.

[87] P. Brookes, A. Livingston, Biological detoxification of a 3-chloronitrobenzene manufacture wastewater in an extractive membrane bioreactor, Water Research 28(6) (1994) 1347-1354.

[88] A.M. Abdelrahman, H. Ozgun, R.K. Dereli, O. Isik, O.Y. Ozcan, J.B. van Lier, I. Ozturk, M.E. Ersahin, Anaerobic membrane bioreactors for sludge digestion: Current status and future perspectives, Critical Reviews in Environmental Science and Technology (2020) 1-39.

[89] A.G. Livingston, A novel membrane bioreactor for detoxifying industrial wastewater: I. Biodegradation of phenol in a synthetically concocted wastewater, Biotechnology & bioengineering 41(10) (1993) 915-926.

[90] E.A.C. Emanuelsson, A.G. Livingston, Study of membrane attached biofilm performance with nitrate as electron acceptor, Desalination 149(1-3) (2002) 211-215.

[91] E.A. Emanuelsson, J.-P. Arcangeli, A. Livingston, The anoxic extractive membrane bioreactor, Water research 37(6) (2003) 1231-1238.

[92] A.G.J.B. Livingston, bioengineering, A novel membrane bioreactor for detoxifying industrial wastewater: II. Biodegradation of 3-chloronitrobenzene in an industrially produced wastewater, 41(10) (1993) 927-936.

[93] C.E. Aziz, M.W. Fitch, L.K. Linquist, J.G. Pressman, G. Georgiou, G.E. Speitel, Methanotrophic biodegradation of trichloroethylene in a hollow fiber membrane bioreactor, Environmental Science Technology 29(10) (1995) 2574-2583.

[94] I. Guisado, J. Purswani, J. González-López, C. Pozo, An extractive membrane biofilm reactor as alternative technology for the treatment of methyl tert-butyl ether contaminated water, Biotechnology progress 32(5) (2016) 1238-1245.

[95] A. Mahboubi, P. Ylitervo, W. Doyen, H. De Wever, M.J. Taherzadeh, Reverse membrane bioreactor: Introduction to a new technology for biofuel production, Biotechnology Advances 34(5) (2016) 954-975.

[96] B. Jiang, Q. Zeng, Y. Hou, H. Li, J. Liu, J. Xu, S. Shi, F. Ma, Impacts of long-term electric field applied on the membrane fouling mitigation and shifts of microbial communities in EMBR for treating phenol wastewater, Science of the Total Environment 716 (2020) 137139.

[97] S. Meng, R. Wang, X. Meng, Y. Wang, W. Fan, D. Liang, M. Zhang, Y. Liao, C. Tang, Reaction heterogeneity in the bridging effect of divalent cations on polysaccharide fouling, Journal of Membrane Science 641 (2022) 119933.

[98] B. Ensano, L. Borea, V. Naddeo, V. Belgiorno, M.D. de Luna, F.C. Ballesteros Jr, Combination of electrochemical processes with membrane bioreactors for wastewater treatment and fouling control: a review, Frontiers in Environmental Science 4 (2016) 57.

[99] W. Yu, L.C. Campos, N. Graham, Application of pulsed UV-irradiation and pre-coagulation to control ultrafiltration membrane fouling in the treatment of micro-polluted surface water, Water research 107 (2016) 83-92.

[100] I. Banerjee, R.C. Pangule, R.S. Kane, Antifouling coatings: recent developments in the design of surfaces that prevent fouling by proteins, bacteria, and marine organisms, Advanced materials 23(6) (2011) 690-718.

[101] H. Shaowei, Y. Fenglin, S. Cui, J. Zhang, W. Tonghua, Simultaneous removal of COD and nitrogen using a novel carbon-membrane aerated biofilm reactor, Journal of Environmental Sciences 20(2) (2008) 142-148.

[102] S.L. Khor, D.D. Sun, Y. Liu, J.O. Leckie, Biofouling development and rejection enhancement in long SRT MF membrane bioreactor, Process Biochemistry 42(12) (2007) 1641-1648.

[103] S.H. Yeom, A.J. Daugulis, Development of a novel bioreactor system for treatment of gaseous benzene, Biotechnology & bioengineering 72(2) (2001) 156-165.

[104] F. Lipnizki, R.W. Field, P.-K. Ten, Pervaporation-based hybrid process: a review of process design, applications and economics, Journal of Membrane Science 153(2) (1999) 183-210.