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Case Report

Recent development of mixed matrix membrane as a membrane bioreactor for wastewater treatment: A review

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ABSTRACT

Wastewater treatment has emerged as the most effective method for addressing the scarcity of clean water, which is expected to cause a worldwide crisis in the near future. The membrane bioreactor (MBR) is a cutting-edge technology that combines membrane filtration with biological activity in the form of microorganisms. MBR has been considered the most efficient approach so far owing to its high effluent and relatively small space requirements. The membrane constituent material is an important aspect of producing MBR with maximum process performance. This study extensively evaluated the application of polymers, ceramics, and mixed matrix membranes (MMM) in wastewater treatment performance. MMM has better performance due to its hydrophilic nature, good chemical, mechanical, and thermal stability, and ease of synthesis. Various types of filler in MMM for MBR applications are also discussed, including metals, metal oxides, carbon, MOF, silica, and zeolite. The addition of fillers in the polymer matrix has been able to improve the characteristics of the membrane, including water flux, rejection of pollutants, and resistance to fouling. Subsequently, several important parameters of MMM that affect the performance of MBR, including hydrophilicity, surface charge, surface roughness, module, pore characteristics, and filler charge, have been reviewed. An investigation of the performance of the MBR, such as activated sludge characteristics, operating conditions, and fouling phenomena, is presented. Lastly, this review describes the challenges and perspectives of developing MMM-based MBR in the future.

1. Introduction

The depletion of clean water supply has become an urgent issue that challenges the world's population and ecosystem safety. It is estimated that the shortage of water could generate a huge crisis impacting 6 billion people in 2050 [1]. The achievement of wastewater treatment to supply clean water was confirmed by the reduction of global wastewater to 48%, where clean water production reached 359.4×10^9 $m^3.yr^{-1}$ annually (Fig. 1). However, there are still a number of countries that have very minimal efforts to treat wastewater such as South and Southeast Asia, especially densely populated countries such as India, Pakistan, Indonesia, China and Malaysia [2]. As a result, efforts must be made to address the problem of wastewater treatment to increase the availability of clean water worldwide to realize The Sustainable Development Goals (SDGs) related to clean water and sanitation (Number 6).

Several methods have been applied on wastewater treatment including MBR [3], conventional activated sludge method [4], membrane filtration [5], adsorption [6], coagulation [7], and flocculation [8]. Among these methods, MBR is considered as the advanced technique combining filtration and biodegradation technology [9,10]. The most advantage of MBR relies on practicality, facile operation condition, and high degradation rate [11,12]. In addition, MBR effectively reduces the organic pollutants indicated by the decline of COD and TSS level to 10–20 mg L^{-1} and 0 mg L^{-1} respectively [13]. Nevertheless, fouling phenomenon remains as the main issue to resolve on the employment of

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List of abbreviations:

AFM = Atomic Force Microscopy
AFMBR = Anaerobic Fluidized-bed Membrane
AMBR = Anaerobic Membrane Bioreactor
AG = Arabic Gum
AnMBR = Anaerobic Membrane Bioreactor
AnCMBR = Anaerobic Ceramic Membrane Bioreactor
BSA = Bovine Serum Albumin
BOD = Biological Oxygen Demand
CA = Cellulose Acetate
CAB = Cellulose Acetate Butyrate
CAS = Conventional Activated Sludge
CFV = Crossflow Velocity
CNT = Carbon Nanotubes
COD = Chemical Oxygen Demand
CTA = Cellulose Triacetate
DMAc = Dimethylacetamide
DMSO = Dimethyl Sulfoxide
DOC = Dissolved Organic Carbon
EEM = Excitation-Emission Matrix
EPS = Extracellular Polymeric Substances
F/M = Food to Microorganisms
FESEM = Field Emission Scanning Electron Microscopy
FO = Forward Osmosis
FRI = Biofouling Rate Index
FRR = Flux Recovery Ratio
FS = Flat Sheet
GO = Graphene Oxide
HA = Humic Acid
HDPE = High-density Polyethylene
HF = Hollow Fiber
HRT = Hydraulic Retention Time
IFR = Irreversible Fouling Ratio
MBR = Membrane Bioreactor
MF = Microfiltration
MGAC = Magnetic Granular Activated Carbon
MIL = Material Institute Lavoisier
MLSS = Mixed Liquor Suspended Solids
MMA = Methyl Methacrylic Acid
MMM = Mixed Matrix Membrane
MOF = Metal Organic Framework
MVB = Multivesicular Bodies
MWCO = Molecular Weight Cut-off
ND = Nanodiamond
NF = Nanofiltration
NIPS = Non-solvent Induced Phase Separation
NPs = Nanoparticles
OCMCS = O-Carboxymethyl Chitosan
OLR = Organic Loading Rate
OMWCNTs = Oxidized Multi-Walled Carbon Nanotubes
PAN = Polyacrylonitrile
PA = Polyamide
PDMS = Polydimethylsiloxane
PE = Polyethylene
PEG = Polyethylene Glycol
PES = Polyether Sulfone
PMMA-g-PEO = Poly(methylmethacrylate)-g-poly(ethyleneoxide)
PP = Polypropylene
PSf = Polysulfone
PVB = Polyvinyl Butyral
PVC = Polyvinyl Chloride
PVDF = Polyvinylidene fluoride
PWF = Pure Water Flux
RFR = Reversible Fouling Ratio
Rc = Cake Layer Resistance
Rm = Intrinsic Resistance
RO = Reverse Osmosis
ROS = Reactive Oxygen Species
Rp = Pore Blocking Resistance
Rr = Reversible Resistance
Rt = Total Membrane Resistance
SA = Serum Albumin
SCNT = Sulfonated Carbon Nanotubes
sCOD = Soluble Chemical Oxygen Demand
SEM = Scanning Electron Microscope
SMP = Soluble Microbial Products
SND = Silanized Nanodiamond
SRT = Solids Retention Time
TDS = Total Dissolve Solid
TEM = Transmission Electron Microscope
TIPS = Thermally Induced Phase Separation
TFR = Total Fouling Ratio
TMP = Transmembrane Pressure
TN = Total Nitrogen
TOC = Total Organic Compound
TP = Total Phosphorus
TSS = Total Suspended Solid
UF = Ultrafiltration
UV = Ultraviolet
VMR = Verified Market Research
WCA = Water Contact Angle
ZIF = Zeolitic Imidazolate Framework

MBR [14].

Fouling phenomenon occurred due to the accumulation of foulant particles (bio foulant and pollutant) on the surface of the membrane pores [15]. The clogged membrane hindered the feed to pass through the pores leading to the lower permeation, shorter durability and higher operation cost [16]. Membrane characteristics are considered as the main factor inducing fouling phenomenon, leading to many modifications attempts with to achieve the expected properties. Commonly, MBR is constructed by ceramic and polymer membrane [17,18]. However, polymer membrane is hydrophobic and susceptible to destruction during the operation [19]. Meanwhile, ceramic membrane is associated with complicated preparation and high cost [18]. Many studies have been developed to resolve aforementioned issues through the combination of several polymers [20], surface coating [21], and nanomaterial insertion into polymer matrix [22]. The large number of polymers that have hydrophobic properties makes polymer blending a method that is less desirable, as well as the surface coating method which has great potential for leaching. Therefore, the nanomaterial blending method is a very popular method, especially in overcoming the problem of fouling in MBR [23]. This is because most of the nanomaterials used as fillers in the polymer matrix have hydrophilic properties which minimize the interaction between the membrane and pollutant molecules which are generally hydrophobic. In addition, the addition of hydrophilic nanomaterials can also increase the air flux in the purification process. The latter method was commonly called as mixed matrix membrane. MMM comprises polymer membrane and nano material filler for instance ZnO_2 [24], SiO_2 [25], TiO_2 [26], Al_2O_3 [27], GO [28], Zeolite [29], etc. The filler performs as antifoulant through the properties enhancement such as mechanical strength, hydrophilicity, and thermal as well as chemical stability [30]. Many research claimed the excellent activity of MMM on permeation flux, pollutant rejection, and fouling prevention [23]. Those results infer the promising outcome of wastewater treatment over MBR. The latter method was commonly called as mixed matrix membrane. MMM comprises polymer membrane and nano material filler for instance ZnO_2 [24], SiO_2 [25], TiO_2 [26], Al_2O_3 [27], GO [28], Zeolite [29], etc. The filler performs as antifoulant through the properties enhancement such as mechanical strength, hydrophilicity, and thermal as well as chemical stability [30]. Many research claimed the excellent activity of MMM on permeation flux, pollutant rejection, and fouling prevention [23]. Those results infer the promising outcome of wastewater treatment over MBR.

Research related to MBR has been widely developed, especially in wastewater treatment. Fig. 2 illustrates the number of studies in the last thirteen years (2011–2023) on the topics of MBR and MMM as MBR. MMM grabbed the interest of the researcher to be utilized as an MBR to remediate wastewater. From 2011 to the present, it has been found that the growth of research on applications of MMM as MBR has been nearly four times larger, while the growth of MBR studies is more than three times larger. This suggests that the development of MMM plays an important role in promoting MBR. In Fig. 3, the bibliometric analysis was carried out to evaluate the research mapping for last five years of the topic on MMM as MBR using the co-occurrence map analysis by VOSviewer application [31]. These findings exhibited the potential of MMM for the MBR application in the future, as demonstrated by the investigation of MMM and these filler like ZIF was found in the recent year. To obtain satisfactory separation performances, several parameters have been studied on the condition, operation, process, and system of MBR. In addition, several review articles discussing MBR for wastewater treatment have been reported so far [32–45]. However, these articles generally only review the MBR operating system, especially anaerobic system [33,34,42,45–50], while modifications related to membrane building materials that function as MBR are still not reviewed, even though Al-Asheh et al. [51] and Vatanpour et al. [52] has reported that choosing the right membrane material can produce MBR with high water flux and pollutant rejection. Discussion about membrane constituent materials, especially MMM is urgently needed to be able to provide information to researchers related to future research directions to produce high-performance MBR in overcoming wastewater problems. The importance of using MMM as MBR is expected to be able to overcome the shortcomings of polymer and inorganic membranes. This article focuses on the discussion of MMM constituent materials as MBR, especially the types of polymers and fillers that can potentially improve MMM's characteristics and performance. This review also discusses the advantages of MMM compared to polymer and inorganic membranes by looking at its performance as an MBR in increasing air flux, rejecting pollutants, and resisting fouling in wastewater treatment. Measurement of MBR performance parameters using MMM is also presented in this article to provide information regarding optimal operating conditions for MBR. Significant challenges to overcoming the problem of fouling in MBR using MMM have also been discussed at the end of this article.

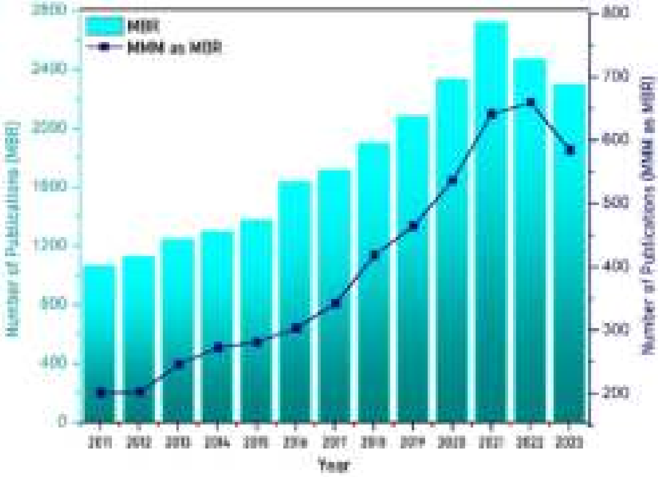


Fig. 2. Publication of MBR and MMM as MBR from 2011 to 2023 according to Scopus database accessed on 26 August 2023.

2. History and development of membrane bioreactors

The development of MBR is based on the use of activated sludge in the bioreactor during the processing. Fig. 4 illustrates the recent development of MBR. In 1913, Edward Arden and W.T. Lockett first conducted experiments on wastewater treatment in a reactor using activated sludge [53]. However, to continue to develop innovations in wastewater treatment, in 1969 Smith et al. [54] reported on wastewater treatment at the Sandy Hook factory, USA using an ultrafiltration membrane placed outside the bioreactor without a sedimentation tank. This has become a pioneer in the development of membranes with side stream configurations as shown in Fig. 5a. The experimental results produced a higher quality effluent than the CAS method, but due to the high cost and energy consumption, its distribution was still limited [55].

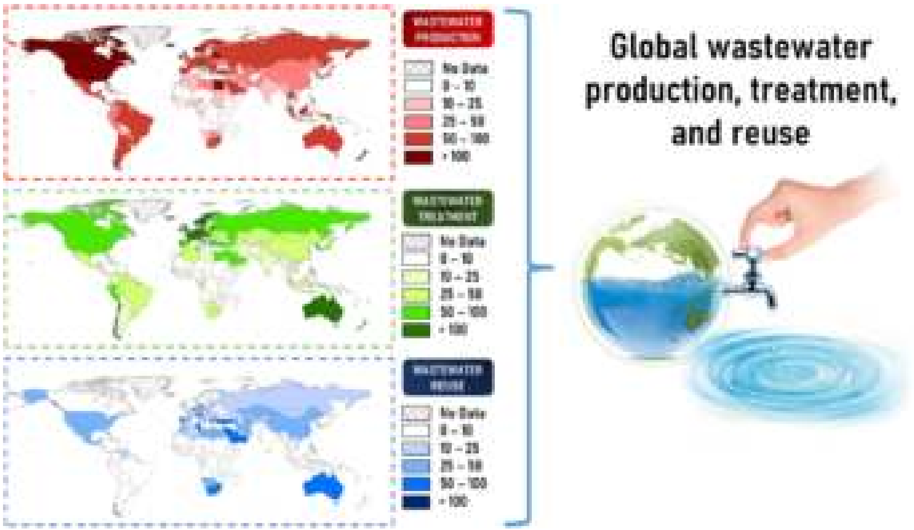


Fig. 1. Wastewater production, treatment and reuse at the Country scale [2].

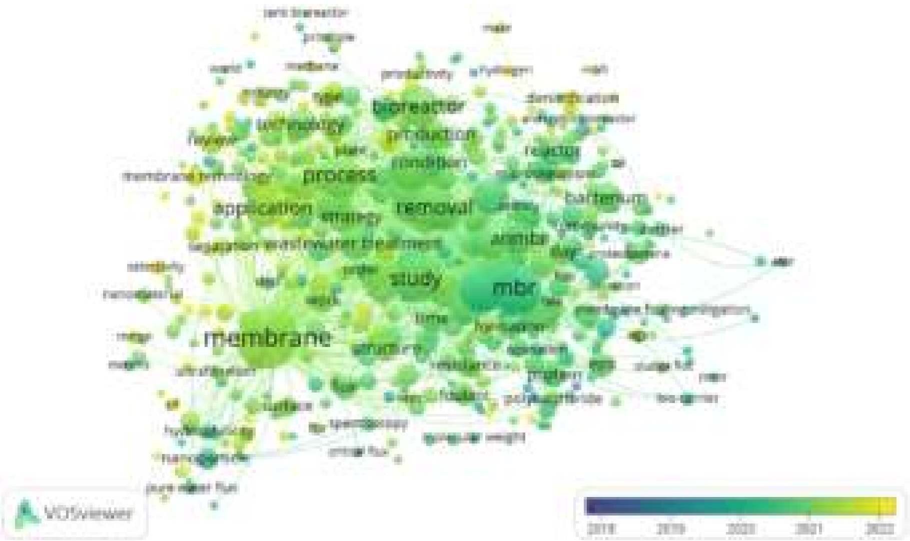
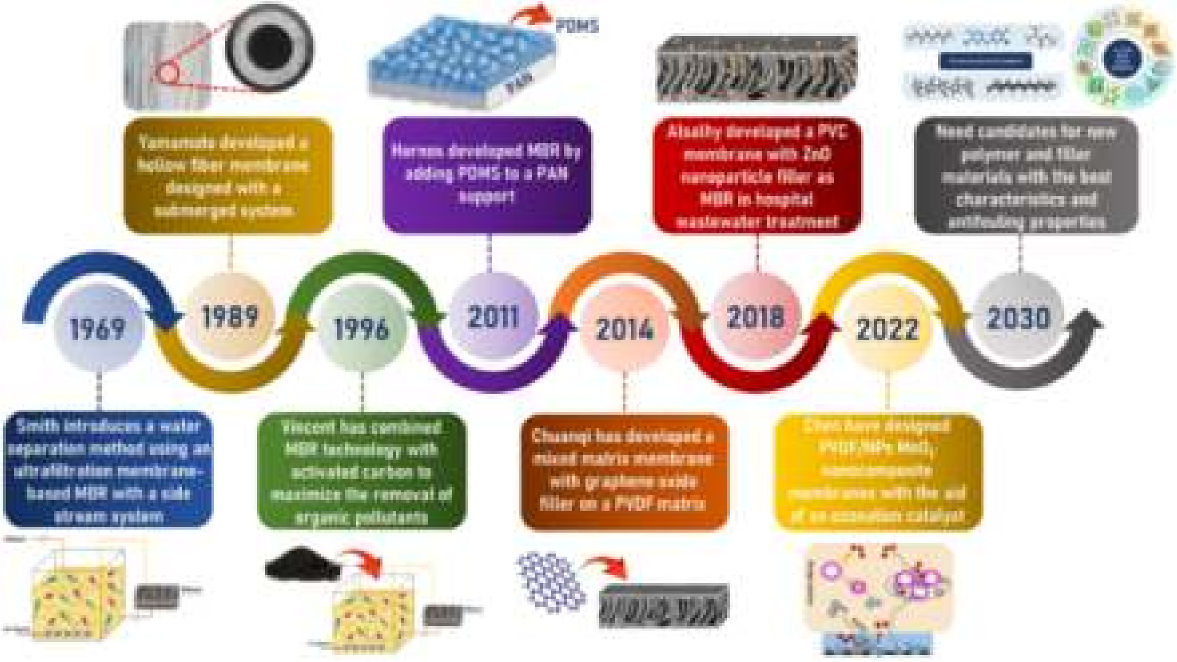


Fig. 3. The Results of the Analysis Using VOSviewer on the Keywords Publication of mixed matrix membrane as membrane bioreactor.



Yamamoto developed a hollow fiber membrane designed with a submerged system

Hornos developed MBR by adding PDMS to a PAN support

Alsalhy developed a PVC membrane with ZnO nanoparticle filler as MBR in hospital wastewater treatment

Need candidates for new polymer and filler materials with the best characteristics and antifouling properties

Smith introduces a water separation method using an ultrafiltration membrane-based MBR with a side stream system

Vincent has combined MBR technology with activated carbon to maximize the removal of organic pollutants

Chuanqi has developed a mixed matrix membrane with graphene oxide filler on a PVDF matrix

Chen have designed PVDF/NPs MnO_2 nanocomposite membranes with the aid of an ozonation catalyst

Fig. 4. Timeline of the development of Membrane bioreactors.

To resolve the aforementioned issue, in 1989 Yamamoto et al. [56] invented the submerged configuration where the hollow fiber membrane was placed inside the bioreactor. The next innovation was reported by Urbain et al. [57] in 1996, by combining membrane and adsorption technique. The activated carbon adsorbent was mixed with the sludge to enhance the adsorption of organic pollutant. Further modification was performed by Hornos et al. [58], by the addition of PDMS to PAN membrane and able to remove ethyl acetate from wastewater. Aside from polymer modification, the membrane technology was profoundly created by adding fillers to the polymer matrix. Zhao et al. [28] have modified the PVDF membrane by adding GO filler. In addition, Bilad et al. [59] have also used silica as a filler in the PVC matrix. The addition of filler to the membrane is done to improve the performance of the MBR, especially in overcoming the fouling phenomenon that has the potential to occur in the MBR. However, one of the challenges in MMM fabrication is that the filler material is easily agglomerated so that it is not evenly distributed throughout the membrane. To overcome this problem, nano-based filler materials have been developed to produce a better MBR process performance. In 2018, Alsalhy et al. [24] reported on PVC membrane with ZnO nanoparticle filler as MBR in hospital wastewater treatment. The addition of ZnO NPs was carried out to create MBR with good antifouling properties. In addition, Chen et al. [60] have designed PVDF/MnO_2 NPs nanocomposite membranes with the aid of an ozonation catalyst in overcoming biofouling that occurs on the membrane surface. The addition of MnO_2 NPs increase the hydrophilicity of the membrane and was effective in reducing the rate of biofouling formation on the membrane surface [60].

For the sustainability of science, innovation related to the development of MBR is very much needed in wastewater treatment. According to a survey by VMR, the projected market demand for MBR is anticipated to reach USD 3.1 billion in 2021. Furthermore, it is forecasted that by

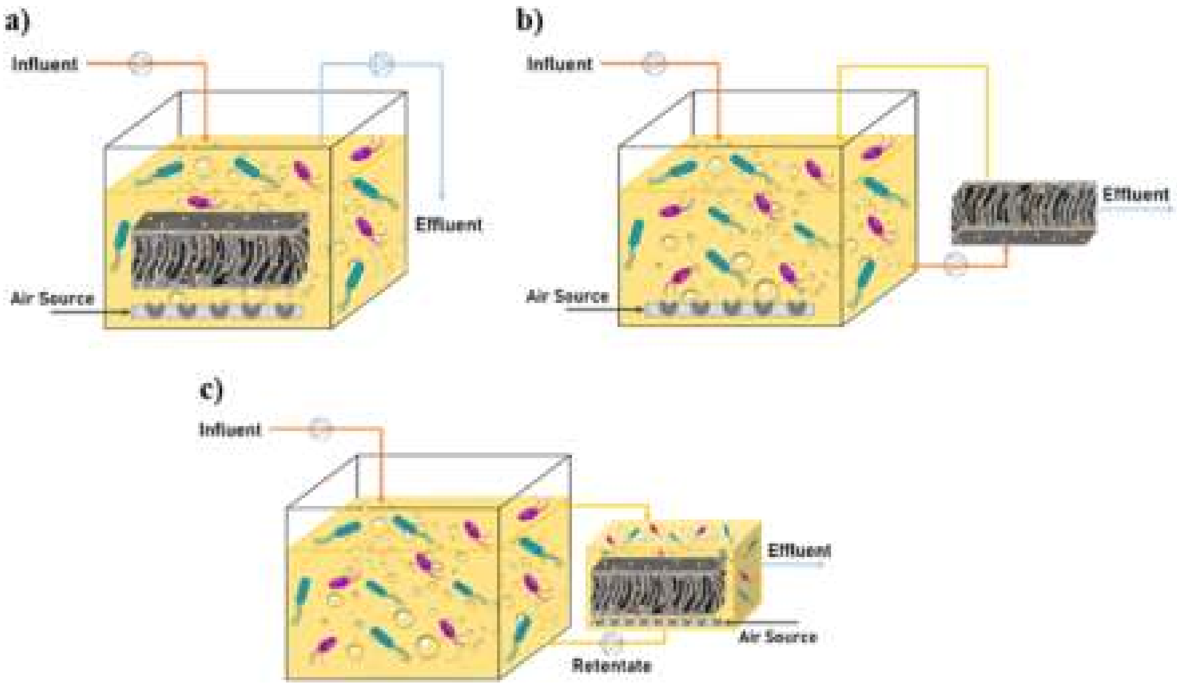


Fig. 5. MBR Configuration based on (a) Submerged, (b) Side stream and (c) External submerged.

2030 this demand might double, reaching a value of USD 6.5 billion. The request was based on environmental concerns caused by wastewater in various sectors. Therefore, to overcome the increasing threat, one of the efforts that can be made is to develop a more economical membrane material with optimal performance. Things that can be done to realize these expectations are by using polymer and filler materials that can be synthesized from various natural sources, for example, the development of cellulose acetate polymers obtained from natural lignocellulosic sources, Fe_3O_4 which can be obtained from iron sands and zeolite materials that can be obtained from fly ash and rice husk waste. In addition, new polymer and filler materials are needed to be used as candidate materials in the MBR fabrication process.

Another important aspect in the development of the MBR is its configuration. Based on the configuration, MBR can be divided into submerged, side stream and external submerged as shown in Fig. 5. All three have differences in the position and location of the membrane. In the immersion configuration, the membrane is immersed in activated sludge during the filtration process, while in the side stream the membrane is placed externally or outside the activated sludge. In addition, the submerged configuration has also been developed externally by placing the membrane module and smaller activated sludge separately from the main activated sludge. In general, submerged MBR is a configuration that is known to have a simple configuration, low production and maintenance costs and tends to be low in energy consumption [61,62]. In addition, the use of submerged MBR has been shown to result in a significant reduction in power usage, with potential energy savings ranging from 10 to 25 times when compared to the use of side stream MBR. In contrast, the lateral flow membrane MBR is recognized for its enhanced physical robustness and adaptability. Currently, submerged MBR is widely used on a large scale, while side stream and external submerged are more in demand in small-scale processing [55]. Table 1 presents the research that has been carried out using the three MBR configuration system.

Table 1
Comparison of MBR Configurations on their wastewater removal performances.

MBR Configurations	Module Type	Wastewater Type	Removal Percentage (%)	Reference
Side Stream	Tubular	Food Wastewater	94.6 (TSS), 93.7 (TDS), 97.6 (COD)	[63]
Side Stream	Hollow Fiber	Synthesis Wastewater	99.2 ± 2 (COD), 95 ± 2 (TOC)	[64]
Side Stream	Hollow Fiber	Slaughterhouse Wastewater	80.5 ± 8.7 (TN)	[65]
Side Stream	Tubular	Domestic Wastewater	91 (COD)	[66]
Submerged	Hollow Fiber	Municipal Wastewater	>90 (COD), >95 (BOD)	[67]
Submerged	Hollow Fiber	Municipal Wastewater	90 (COD), 92 (BOD)	[68]
Submerged	Hollow Fiber	Shale Gas Wastewater	77.8 (DOC)	[69]
Submerged	Flat Sheet	Medical Wastewater	94.77–97.45 (COD)	[70]
Submerged	Hollow Fiber	Domestic Wastewater	89 (COD)	[67]
External Submerged	Hollow Fiber	Municipal Wastewater	88 (COD), 93 (BOD)	[71]
External Submerged	Hollow Fiber	Palm Oil Wastewater	93–98 (COD)	[72]

3. Polymeric membrane

Polymer is a material that has been recognized as a promising and widely used material in the field of separation technology. Developments related to the synthesis of polymer materials and their applications have shown significant advances, especially in water treatment technology. This is expected to improve separation performance related to pollutant removal efficiency and optimal operating conditions [73]. The advantages of using polymers in the wastewater treatment process are flexibility, economics, low energy consumption, and easy fabrication and control processes [74,75]. These advantages make polymers an attractive material to be used as various types of membranes, one of which is MBR. Oberoi et al. [42] reported that one of the important factors that must be considered in the MBR design process is the membrane material. Many polymer materials have been used as MBR, such as CA [3], PVDF [69], PES [76], PSf [77], PE [78], and PA [79]. In the MBR fabrication process, each polymer has advantages and disadvantages as presented in Table 2.

The selection of polymeric materials as a constituent of MBR is an important parameter that must be considered. Some polymers, such as PES and PVDF, are preferred because they generally have high thermal stability with a decomposition temperature of 450–550 °C [80,81]. In addition, both of them also have high mechanical strength, up to 29 MPa [82]. However, their hydrophobic nature causes these two materials to easily experience fouling and only have a low water flux. In contrast, hydrophilic polymer membranes like cellulose acetate, polyvinyl alcohol, and polyacrylonitrile are known to be capable of producing higher water fluxes and minimizing the fouling phenomenon that occurs, but these polymeric materials have relatively low thermal and mechanical resistance [75]. Therefore, to overcome the shortcomings of polymer membranes, it is necessary to add material in the form of fillers to the polymer matrix to improve hydrophilicity, chemical stability, and mechanical strength and to reduce the phenomenon of fouling on the MBR. However, choosing a suitable polymer matrix is also one of the first steps to obtaining MMM with maximum characteristics and performance for use as MBR. Table 3 presents the types of polymers that have been used as MBR.

4. Ceramic membrane

Ceramic membrane, one of the inorganic membranes, is frequently used in separation technology for the treatment of wastewater (Table 4). In general, the oxide ceramic membranes used as membrane constituents are those made of aluminum, silicon, titanium, and zirconium oxide [92]. Due to their superior chemical stability and great temperature resistance, ceramic membranes are superior to polymer membranes in some circumstances. For this reason, ceramic membranes are considered suitable for use in industrial wastewater treatment processes, which generally operate at high temperatures [93]. However, ceramic membranes are usually more expensive than polymers. Despite the high production costs, ceramic membranes have lower operating and maintenance costs than polymers, so they still have great potential in wastewater treatment processes [94]. For this reason, it is considered important to develop ceramic membranes that have good thermal, mechanical, and chemical stability properties but have more economical fabrication costs. One solution that has been developed at this time is using inorganic materials used as fillers in polymer membrane matrices to produce inexpensive membranes with good characteristics such as hydrophilicity, high thermal and mechanical resistance, and maximum performance as MBR.

Table 2
Evaluation of different polymer materials used in MBR for wastewater treatment.

Polymer Material	Advantages	Disadvantages
PVDF	- High elongation - High mechanical strength - Pore size tends to be small. - Good chemical stability	- Formation of pore structures that tend to be difficult. - Hydrophobic
CA	- Hydrophilic - Easy fabrication process	- Low chemical stability - Low acid/base resistance
PSf	- Protected from leaking. - High mechanical strength - Simple to create structure	- Low chemical stability - Fragile
PES	- Good leaching control - Simple formation	- Low chemical stability - Fragile - Hydrophobic
PE	- Low cost - Elastic	- Pore size tends to be large

5. Mixed matrix membrane

The performance of polymer membranes as MBR in wastewater treatment can be seen from the relationship between water permeability and pollutant rejection during the filtration process as described in the previous subchapter. On the other hand, some inorganic membranes are known to have properties and perform well in the role of MBR, such as alumina [99], silicon carbide [103], zirconia [105], and titania materials [106]. The relatively high material costs, however, continue to place restrictions on the use of these materials [107]. In contrast, polymer membranes only require lower costs than inorganic materials in the fabrication process but have lower thermal resistance, mechanical strength, and chemical stability properties than inorganic membranes which is shown in Table 5.

To overcome the shortcomings of polymer membranes, in addition to polymer blending, another effort that can be made to maximize its performance as an MBR is to add inorganic fillers to the polymer matrix or known as MMM (Fig. 6). This relates to the development of the next generation of membrane fabrication technology to produce membranes that have superior performance in overcoming wastewater problems with higher water permeability and pollutant rejection, as well as the lack of fouling phenomena which are the main problems in MBR. Some inorganic materials that can be used as fillers in MMM are metal oxides, carbon and silica-based materials, zeolite and MOF as shown in Fig. 7.

Currently, there have been many membrane modification efforts carried out in the development of MMM as MBR, one of which is by exploring the right type of filler to be added to the polymer material. The following are several types of fillers that have been used in the fabrication of MMM as MBR in wastewater treatment as shown in Table 6.

5.1. *Metals and metal oxides based filler*

Metal/metal oxide is one of the materials that has received much attention in membrane fabrication technology. Adding metal/metal oxides in the polymer matrix aims to improve characteristics, including hydrophilicity, mechanical strength, stability, and resistance to fouling. Enhancements in membrane properties are expected to have a beneficial effect on the performance of the MBR, especially the water flux and rejection of pollutants. Several metal/metal oxides commonly used as fillers in MBR are Ag, Ag_3PO_4, Fe_3O_4, TiO_2, and MnO_2.

Ag or silver is a metallic element with atomic number 47, which is white and malleable. Ag has a good ability as an antibacterial because of its ability to destroy bacterial cells. Its form on the nanoscale provides better performance as an antibacterial agent. In MBR, biofouling, generally caused by bacteria, is a source of problems that can reduce membrane performance. Amouamouha et al. [110] experimented by adding Ag metal to the PVDF and PES matrices. Adding Ag to these polymer membranes can increase the water flux by more than 30%, compared to the unmodified membrane. In addition, the excellent anti-adhesion and antibacterial properties of the Ag-modified membrane have been reported to reduce the occurrence of biofouling. Ag as a filler for MBR can also be used in its oxide form, one of which is $AgPO_4$. Ghalamchi et al. [112] have made PES membranes with $AgPO_4$–NH_2/g-C_3N_4 composite fillers, which aim to overcome biofouling mitigation and increase the flux in MBR. The fillers were synthesized by coprecipitation and thermal pyrolysis methods. The results of the FESEM analysis showed that the size of the synthesized $AgPO_4$ had a spherical shape with a diameter of 20–70 nm. In manufacturing the membrane, the phase inversion method was used with two solvents, DMAc and DMSO. The entire synthesized membrane showed that adding $AgPO_4$–NH_2/g C_3N_4 produced a longer and broader fingerlike pore in the membrane. These characteristic changes have influenced membrane performance by increasing water flux, rejection,

Table 3
Polymeric membrane in MBR.

Membrane Material	Membrane Type	Membrane Characteristics	Wastewater Type	Operating Conditions			Flux (L. m^{-2}. h^{-1})	Influent Concentration (mg. L^{-1})	Rejection Percentage (%)	Ref.
				HRT (h)	Temp. (^{o}C)	pH				
PVDF	UF	HF membrane, surface area = 0.03 m^2	Cosmetic Wastewater	29	20	7	8	719–876	85.1 (COD)	[15]
PVDF	UF	HF membrane, surface area = 0.00052 m^2	Shale Gas Wastewater	48	20	5.23	12	36.94 (DOC)	77.8 (DOC)	[69]
PVDF	UF	HF membrane, pore size = 0.05 μm	Municipal Wastewater	20.64	–	7.85 ± 0.02	10.1 ± 0.04	9516 ± 147	91.4 ± 1.8 (COD)	[83]
PVDF	UF	Pore size = 0.02 μm, surface area = 0.012 m^2	Synthetic Wastewater	79.92	35	6.7	11	10,524 ± 380	97.3 ± 0.05 (COD)	[84]
PVDF	MF	FS membrane, pore size = 0.2 μm, surface area = 0.0036 m^2	Municipal Wastewater	8	25	–	8.675	500	90 (COD)	[85]
PVDF	UF	HF membrane, pore size = 0.04 μm, surface area = 0.93 m^2	Industrial Wastewater	168	–	–	12	3504 ± 311 (TSS)	–	[86]
PVDF	UF	HF membrane, pore size = 0.04 μm, surface area = 0.00322 m^2	Synthetic Wastewater	6	25	6.4	13	3680	81.7 (COD)	[87]
PVDF	UF	HF membrane, pore size = 0.04 μm, surface area = 0.9 m^2	Municipal Wastewater	33	19	–	16	1462 (COD)	91 (COD)	[88]
PVDF	MF	Pore size = 0.1 μm, surface area = 0.1 m^2	Phenol Wastewater	48–96	36	–	4.04	200	98.6 (COD)	[89]
PVDF	MF	HF membrane, surface area = 0.006 m^2, pore size = 0.22 μm	Synthetic Wastewater	12	20	–	5.3	330-370 (COD)	90.8 ± 1.4 (COD);	[90]
CTA	FO	Surface area = 0.00255 m^2	Municipal Wastewater	32–74	25	–	20	78.49 ± 4.73	96.47 ± 1.10 (TOC)	[3]
CTA	UF	Surface area = 0.025 m^2, membrane surface charge = −2.1 ± 0.3 mV	Municipal Wastewater	15–40	35	7	10	460 (sCOD)	>95 (sCOD)	[91]
PA	NF	HF membrane, pore size = 0.81 nm, contact angle = 40^{o}, MWCO = 1470 Da	Synthetic Wastewater	25	–	7.0–7.2	2	3500–3900	>95 (COD)	[79]
PES	NF	Contact angle = 80.3°	Food Wastewater	288	25	7.5	79	2180 (COD); 850 (TSS)	97.6(COD); 94.6 (TSS)	[76]
PE	MF	FS membrane, pore size = 0.2 μm, surface area = 0.015 m^2	Synthetic Wastewater	9	18–22	–	14	2500	98 (TOC)	[78]

Table 4
Ceramic membrane in MBR.

Membrane Material	Membrane Type	Membrane Characteristics	Wastewater Type	Operating Conditions			Flux (L. m^{-2}. h^{-1})	Influent Concentration (mg.L^{-1})	Rejection Percentage (%)	Ref.
				HRT (h)	Temp. (^{o}C)	pH				
Ceramic	MF	FS membrane, surface area = 0.12 m^2, pore size = 0.4 μm	Synthetic Wastewater	5.8	23–30.5	7.1–7.8	119.5	3000 - 5100 (COD)	78.6 (COD)	[95]
Ceramic	NF	FS membrane, pore size = 80 nm, surface area = 0.08 m^2	Municipal Wastewater	42–12	25	–	8	417 ± 61 (COD)	87 (COD)	[96]
Ceramic	MF	Tubular membrane, pore size = 0.02 μm	Municipal Wastewater	6	–	–	30	21 (COD)	99.7 (COD)	[97]
Alumina	UF	Pore size = 80 nm	Domestic Wastewater	18	25–30	–	6	330.4 ± 89.8 (COD)	88.6 ± 9 (COD)	[98]
Alumina	MF	Surface area = 0.035 m^2, pore size = 0.1 μm	Leachate Wastewater	7.5	35	6.9	52	3164 ± 84 (COD)	≥88 (COD)	[99]
Alumina	UF	FS membrane, average pore size = 0.1 μm, surface area = 0.0425 m^2	Synthetic Wastewater	11	23–25	6.5 & 7	15	200-220 (TOC)	97.8 ± 0.4 (TOC)	[100]
Alumina	–	FS membrane, pore size = 0,1 μm, surface area = 0,05 m^2	Domestic Wastewater	28	33	7	4.5 ± 0.5	878.6 (COD)	91.0 ± 13.8 (COD)	[101]
Pyrophyllite	MF	FS membrane, pore size = 0.15 μm, surface area = 0.0315 m^2	Municipal Wastewater	18	–	–	2.7 ± 0.12	600 - 800 (COD)	92.9 ± 5.5 (COD)	[102]
SiC	MF	FS membrane, surface area = 4.24 m^2, pore size = 0.2 μm	Municipal Wastewater	25	–	7.1	~10	127 (COD)	88.1 (COD)	[103]
Fly Ash	–	FS membrane, surface area = 0.05 m^2, pore size = 2–6 μm	Synthetic Wastewater	–	25–28	–	16.7	1600 (MLSS)	>90 (COD)	[104]

Table 5
Characteristics comparison of polymer, ceramic and MMM [51,108,109].

Characteristics	Polymer Membrane	Inorganic Membrane	Mixed Matrix Membrane
Chemical stability	Low	Moderate	High
Thermal stability	Low	High	High
Synthesis process	Easy	Hard	Easy
Production cost	Low	High	Moderate
Surface roughness	Low	High	Moderate
Ease in the cleaning process	Low	High	High
Mechanical strength	Low	High	High
Resistance to fouling	Low	Moderate	Moderate

and resistance to fouling.

Fe_3O_4 is an iron oxide material that has attracted much attention due to its excellent magnetic properties and biocompatibility [125]. Fe_3O_4, as a membrane filler, is favored in membrane technology because of its hydrophilic nature. This affects increasing the hydrophilicity of the membrane, which impacts improving water flux and reducing fouling. In addition, Fe_3O_4 has also been used as a material to produce membrane catalysts and photocatalysts in degrading pollutants in wastewater. Peng et al. [126] have made AFMBR with MGAC as filler for domestic wastewater treatment. Nano-Fe_3O_4 in the PVDF matrix aims to reduce membrane fouling by reducing the SMP products formed and increasing sludge dehydrogenase activity in the MBR. The experimental results showed that adding MGAC in the membrane reduced COD up to 89 ± 2.6% with a hydraulic retention time of 4 hours. In addition, it is also effective in overcoming fouling by decreasing the protein and polysaccharide content in EPS by 9.8 and 8.1%, respectively. The reduction of *Bacteroidetes* and *Proteobacteria* in the membrane cake layer with a percentage of 4.0 and 16.6%, respectively, indicates good anti-fouling ability on membranes modified with the addition of MGAC.

TiO_2 is a metal oxide material with a molecular weight of 79.87 g/mol and is widely used in various applications. Its non-toxicity, low cost, biocompatible, chemically stable, and large surface area are the main attractions of interest. In addition, TiO_2 is also a potent oxidizing agent with high photocatalytic activity. This makes TiO_2 a very suitable material to use as a filler for MBR to produce photocatalyst membranes with excellent pollutant degradation performance. Moghadam et al. [111] reported using TiO_2 as a filler for PVDF ultrafiltration membranes using UV light. The membrane was synthesized by the phase inversion method using DMAc with a TiO_2 loading percentage of 20%. The MBR performance testing process was carried out with submerged and HRT configurations for 10–14 hours with an influent COD concentration of 2300–2500 mg L^{-1}. The results of adding TiO_2 in the PVDF polymer

Fig. 6. MMM structure and filler in MBR

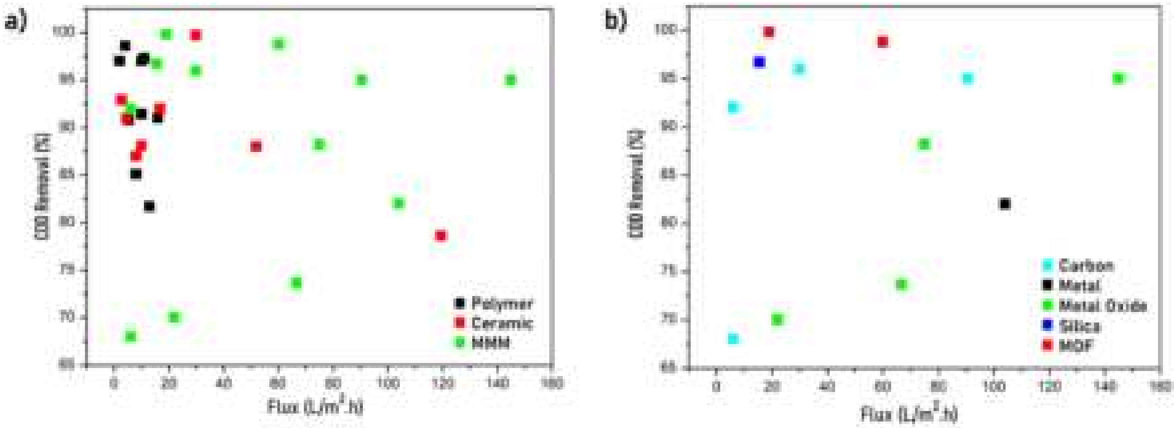


Fig. 7. Comparison of Performance (a) Polymer, Ceramic and MMM, (b) Filler incorporated MMM, the data obtained from Tables 3 and 4 dan 6.

Table 6
Mixed matrix membrane in MBR.

Filler	Polymer Matrix	Membrane Type	Membrane Characteristics	Wastewater Type	Operating Conditions			Flux (L. m^{-2}. h^{-1})	Influent Concentration (mg.L^{-1})	Rejection Percentage (%)	Ref.
					HRT (h)	Temp. (^oC)	pH				
Silver NPs	PVDF	MF	Pore size = 0.22 μm, filler size = 30 nm	Molasses Wastewater	30	35–37	–	104	100 (COD)	82 (COD)	[110]
TiO_2	PVDF	UF	Tensile strength = 3.13 MPa, elongation = 92.44%	Synthesis Wastewater	10–14	–	7.4	~75	2300 - 2500 (COD)	88.2	[111]
Fe_3O_4-OCMCS	PVDF	UF	Porosity = 86.2%, contact angle = 55.2°	Food Wastewater	44	25	–	145	2000 (COD)	92 - 99 (COD)	[10]
ZnO	PVC	UF	Contact Angle = 46.23^o, average pore size = 504.35 nm	Medical Wastewater	2	25	–	66.7	1000 (MLSS)	73.65 (COD)	[24]
Ag_3PO_4/g-C_3N_4	PES	MF	Contact angle = 53.2^o, tensile strength = 133 N/15mm	Food Wastewater	–	–	–	83	500	–	[112]
MnO_2 NPs	PVDF	–	Contact angle = 61.02^o, porosity = ~88.55%, pore size = ~32.5 nm	Industrial Wastewater	48	25	–	9.5	–	95 (TOC)	[60]
TiO_2 NPs	PVDF	UF	Contact angle = 72.21^o, porosity = 69.97%	Landfill Leachate Wastewater	5	28	7–8	288.3 (PWF)	1000	87.84 (COD)	[113]
TiO_2	PP	–	Contact angle = 106^o, porosity = 50.7%, tensile strenght = 4.7 MPa	Oil Wastewater	24	–	–	~22	176	70 (COD)	[114]
OMWCNTs/ZnO/AG	PES	UF	Contact angle = 48.6^o, porosity = 88.2%	Food Wastewater	2.16	25	7	~350	750 - 2000 (COD)	~95	[115]
PEG-CNTs	PSf	–	Contact angle = 55.41^o, porosity = 47.11%, average pore size = 17.68 nm	Feed Wastewater	–	Room temperature	7	9.45	200	–	[116]
ND	CA	UF	Contact angle = 58^o, porosity = 80.5%, tensile strength = 10.4 MPa, elongation = 12.7%	Medical Wastewater	24	Room temperature	7.2	85.75 (PWF)	1000	93.8	[117]
Ag-GO	PES	–	Contact angle = 39^o, pore size = 8.3 nm, surface zeta potential = −34.3 mV	Synthetic Wastewater	–	Room temperature	7	~90.5	2000	95 (COD)	[23]
CNTs	PSf	MF	Average pore size = 0.659 μm, contact angle = 72.158^o, surface roughness = 62.387 nm	Paper Industry Wastewater	12	25	7–10	6	1700 (COD)	92 (COD)	[118]
GO	PES	MF	Porosity = 61.6%, contact angle = 46.9°	Synthetic Wastewater	–	–	–	6.1	863 ± 183 (COD)	68 (COD)	[119]
SND	PSf	–	Contact angle = 76.44^o, surface area = 14.7 cm^2, mechanical strength = 5.59 MPa	Medical Wastewater	24	25	–	112 (PWF)	7500-8000 (MLSS)	–	[16]
NH_2-MWCNTs	PES	UF	Contact angle = 54°	Synthetic Wastewater	8	–	7–8	≥30	9000	96 (COD)	[120]
SiO_2	HDPE	MF	Contact angle = 97.2^o, mechanical strength = 2.5 MPa, Porosity = 69%, Elongation = 180%	Industrial Wastewater	24	Room temperature	–	15.5	3000 (COD)	96.7 (COD)	[25]
Ag–SiO_2	PVDF	–	Contact angle = ~90^o, mechanical strength = ~5.2 MPa	Medical Wastewater	12	–	–	–	1500 (COD)	94.5 (COD)	[22]
MOF	PES	UF	Pore size = 10 nm, MWCO = 1800 Da	Food Wastewater	–	24	–	19	10,500 (COD); 4200 (BOD); 1900 (TSS)	99.8 (COD); 99.7 (BOD); 99.8 (TSS)	[121]

(*continued on next page*)

Table 6 (*continued*)

Filler	Polymer Matrix	Membrane Type	Membrane Characteristics	Wastewater Type	Operating Conditions			Flux (L. m^{-2}. h^{-1})	Influent Concentration ($mg.L^{-1}$)	Rejection Percentage (%)	Ref.
					HRT (h)	Temp. (^oC)	pH				
MOF	PSf	UF	Porosity = 72%, contact angle = 53^o, surface area = 0.022 m^2	Food Wastewater	24	–	5.5	60	10,000 (COD)	98.8 (COD)	[122]
Fum-A NPs	PAN	MF	Porosity = 74.55%, pore size = 1.81 μm, fiber diameter = 223.16 nm	Industrial Wastewater	–	Room temperature	–	2125 (PWF)	500 (MLSS)	–	[123]
AgNPs/ Zeolite	PVDF	UF	Flat sheet Membrane, modulus young = 179.874 N/ m^2	Industrial Wastewater	–	–	–	202.62	–	99 (COD) 99 (BOD)	[124]

matrix increased the tensile strength by up to 3.13 ± 0.12 MPa compared to the PVDF membrane of 2.49 ± 0.12 MPa. Moreover, there was also a two-fold increase in membrane elongation, where the PVDF membrane without TiO_2 only had an extension of 46 ± 5.82%. In comparison, the membrane with the addition of TiO_2 produced an elongation increase of up to 92.44 ± 3.93%. The water flux obtained by adding TiO_2 reached ~75 L m^{-2} h^{-1} with a rejection of 85.6%, while MBR without TiO_2 addition only got water flux and rejection of ~30 L/m^2.h and 62.8%, respectively. TiO_2 as a filler for MBR has also been developed by Wang et al. [26], who synthesized TiO_2 nanoparticles using the sol-gel method. Introducing TiO_2 to the PVDF membrane matrix aims to increase water flux and its rejection of pollutants in leachate. The results showed that adding TiO_2 NPs produced membranes with better pore diameters, denser surfaces, and lower contact angles. The decrease in the contact angle affected the increase in the hydrophilicity of the PVDF/TiO_2 membrane, which also resulted in an increase in water flux from 61.5 to 288.3 L m^{-2} h^{-1}. Furthermore, the PVDF/TiO_2 membrane also succeeded in producing an average removal rate of COD, nitrogen, and ammonia 87.84, 89.95 and 92.97%, respectively, under the best operating conditions, namely MLSS = 3200 mg/L and HRT for 5 hours.

MnO_2 is a metal oxide with advantages such as a large surface area, good oxidizing and adsorption capabilities, low toxicity, low cost, and good acid resistance [127]. However, MnO_2 is rarely used as a membrane filler in MBR technology. Chen et al. [60] conducted experiments on adding MnO_2 nanoparticles to the PVDF membrane matrix as a new strategy to control biofouling in MBR based on in-situ ozonation. The results showed that adding MnO_2 nanoparticles caused a decrease in the membrane contact angle up to 61.02° ± 1.15. This is related to the increase in membrane hydrophilicity which can be seen from the excellent anti-biofouling performance with an FRI value of 0.67 kPa d^{-1}. The antifouling mechanism on the membrane and a summary of the experimental results are presented in Fig. 8. The community of bacterial genera that predominated in the experiment were *Nakamurella*, *Tahibacter*, and *Terrimonas*. The incorporation of MnO_2 nanoparticles facilitates the hydroxylation process, leading to the generation of hydroxyl groups on the modified membrane surface. Consequently, the presence of these hydroxyl groups induces the formation of a hydration layer on the membrane surface. This hydration layer effectively hinders the accumulation of hydrophobic pollutants and bacteria on the MBR.

5.2. Carbon based fillers

Carbon is a material widely used in various fields of application, such as membrane technology, catalyst support, and health. Carbon is one of the superior materials because it has good chemical stability, thermal resistance, mechanical strength, and a high surface area. In MBR applications, carbon can be used as a filler in MMM because of these advantages. Several types of carbon have been developed as fillers for MBR, such as carbon nanotubes, graphene oxide, nanodiamond, and activated carbon.

Iijima [128] discovered CNT in 1991 with an attempt to synthesize multi-walled carbon nanotubes and fabricated them by a simple arc vaporization method. CNT are arranged in hexagons and pentagons consisting of carbon atoms with a 3–15 nm diameter. CNT belongs to the fullerene subgroup, which is its carbon allotrope. CNT has been widely reported as an excellent antibacterial agent by releasing ions and reactive oxygen species to control bacterial populations by stimulating oxidative stress [129]. Asadi et al. [130] have carried out experiments by synthesizing MBR, which has antibacterial and antifouling properties with MWCNT fillers functionalized with silver ions and chlorophyll(a) (MWCNT-Chl(a)-Ag). The amount of MWCNT-Chl(a)-Ag added to the PVDF matrix varied in the synthesis process. The results showed that adding 0.7% MWCNT Chl(a) Ag reduced the WCA from 71.27 to 46.59° and increased the pure water flux from 21 to 42 kg m^{-2} h^{-1}.bar^{-1}. In addition, it is also suitable for antifouling properties with an FRR value of 97.24%. The overall results show better performance than pure PVDF membranes. This is also in line with the results of Mulopo's [118] research which reported testing the version of PSf/CNT membranes as AMBR in treating wastewater generated from the paper industry. The reduction in the percentage of pollutants with membranes added with CNT was better than that with GO, as reported by Lemos et al. [119]. Adding 0.04 wt% CNT to a 20% PSf polymer resulted in a pollutant reduction percentage of up to 92% (COD). The use of CNT in MBR has also been studied more deeply by Ayyaru et al. [129], who conducted an experiment by comparing PVDF ultrafiltration membranes added with CNT and SCNT fillers to see the antifouling performance of MBR. The characterization results showed that the addition of CNT and SCNT affected the porosity of the membrane by 81 and 84%, respectively, and the pore sizes were 50 and 60 nm, respectively. In addition to characteristics, adding the –SO_3H group to CNT affects the increase in water flux up to two times compared to CNT without sulfonation. This is due to a strong hydrogen layer on the PVDF-SCNT membrane originating from the –SO_3H group. The antibacterial performance of the membrane was evaluated with *E. coli*, *Staphylococcus aureus*, and *Candida tropicalis* bacteria. Fig. 9 shows the effect of using CNT and SCNT on reducing the size of the three bacteria. These results prove that the synthesized MBR has good antibacterial properties. This was also supported by the FRR values of the PVDF-CNT and PVDF-SCNT membranes, which were 72.74 and 83.52%, respectively. This value is higher than pure PVDF membrane with an FRR of 50.38%. The high antifouling properties of the PVDF-SCNT membrane are thought to be due to the sulfonic acid group, which is more negatively charged than the –OH group in the CNT. This triggers a stronger electrostatic repulsion between the membrane surface and the hydrophobic BSA molecule.

Graphene oxide is a monolayer of carbon atoms with significant sp2 and sp3 hybridization on other carbon atoms [131]. Currently, graphene is one of the nanomaterials that is widely used in various research fields.

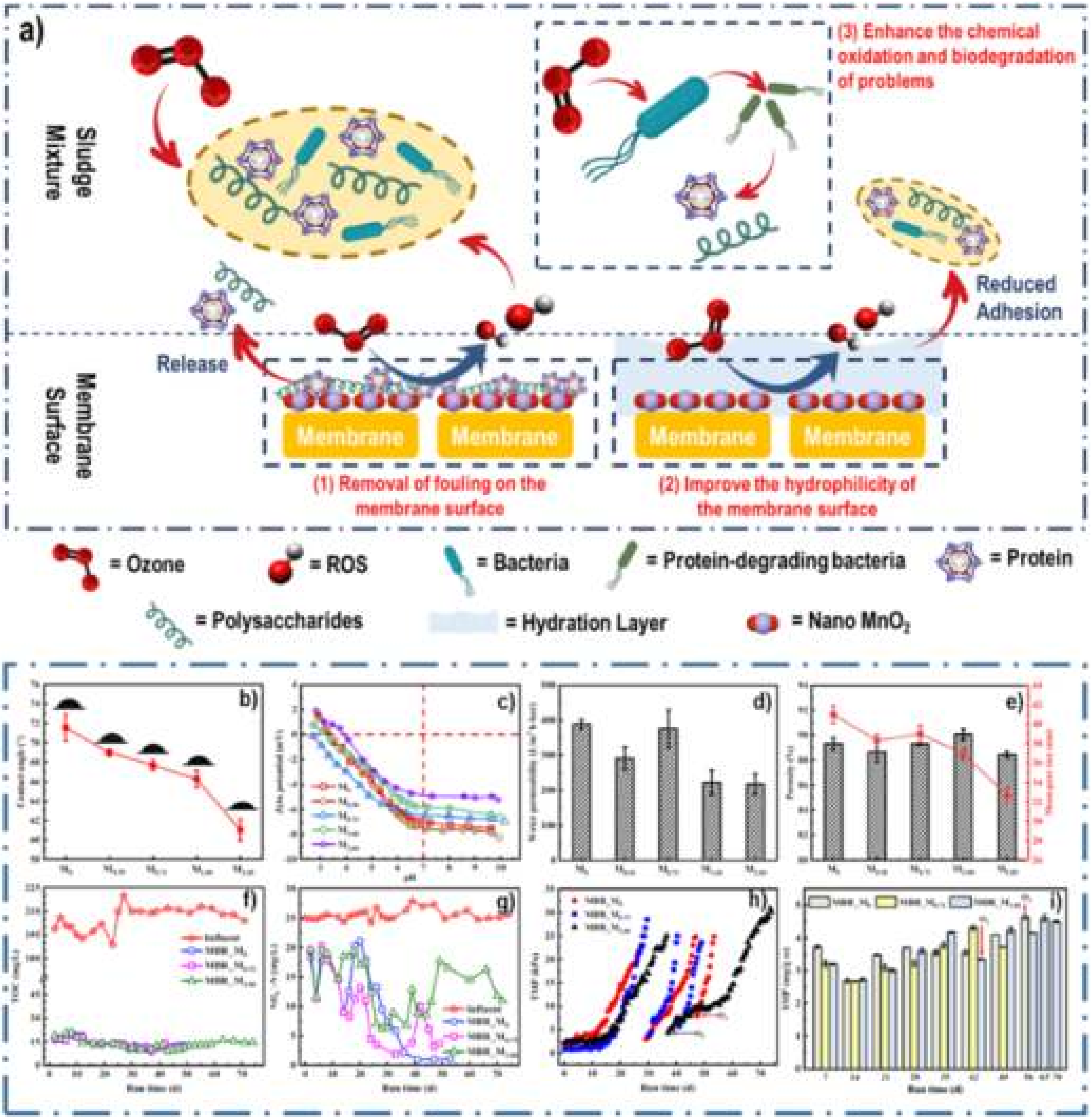


Fig. 8. a) Anti-fouling mechanism of nano-MnO_2 modified PVDF membrane coupled with *in-situ* ozonation in MBR, b) water contact angle, c) zeta potential at different pH, d) pure water permeability, e) porosity and mean pore size, f) TOC removal, g) NH_4^+-N removal, h) evaluation of TMP and h) the variations of concentrations of SMP and EPS in activated sludge [60], reproduced with permission from Elsevier.

This is due to its sound characteristics, including physical, thermal, chemical, and mechanical properties [132]. Lemos et al. [119] reported that the percentage of pollutant reduction in PES/GO membrane performance testing as an MBR was only 68% (COD) with an influent concentration of 863 ± 183 mg L^{-1}. In addition, the PES membrane has a permeability of 288 ± 19 L m^{-2} h^{-1}.bar^{-1}. The addition of GO also reduces the membrane's permeability, which decreases to 161 ± 11 L m^{-2} h^{-1}.bar^{-1}. However, the total PES/GO membrane fouling ratio for reversible and irreversible was 67% and 15%, respectively. These results are still better than pure PES membranes, which only have reversible and irreversible values of 52% and 42%, respectively. The reason is that GO added to the PES polymer makes MMM more hydrophilic, so hydrophobic pollutants prefer to stick to pure PES membranes than PES/GO. This is due to the hydrophobic nature of PES.

Nanodiamond is one of the most highlighted carbon nanomaterials because of its biocompatible nature, low toxicity, and easy functionalization. Another advantage of using ND as a filler in MBR is its hydrophilic nature, high mechanical and thermal properties, and its ability as an antibacterial. Seyfollahi et al. [117] reported using ND grafted with PEG and used as a filler for cellulose acetate membranes. CA/ND-PEG

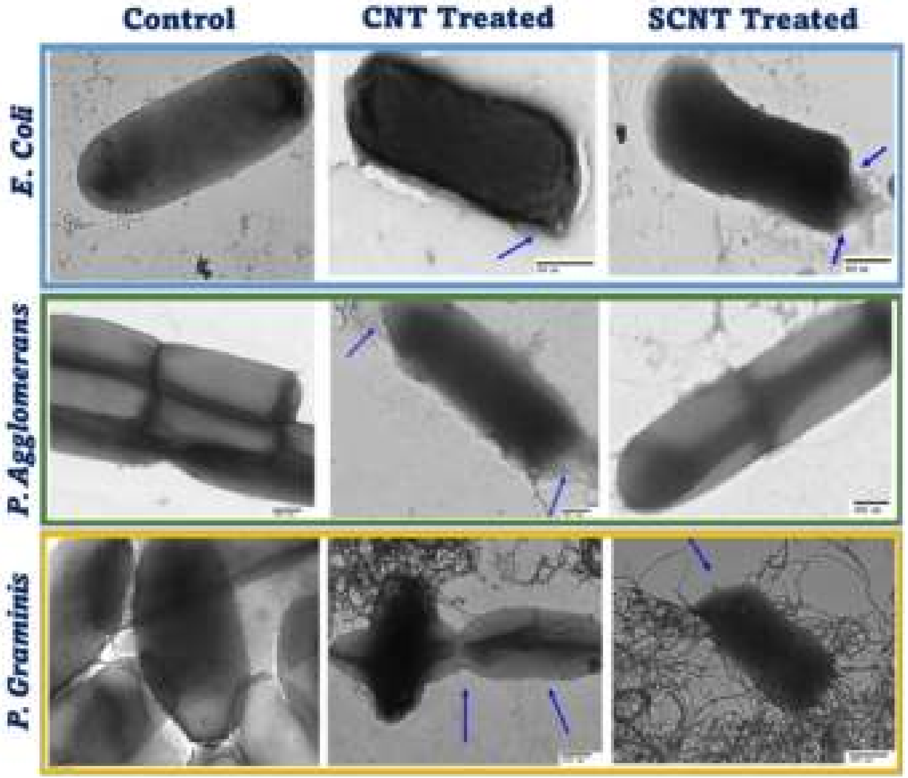


Fig. 9. Effect of adding CNT and SCNT to changes in bacterial size [129], reproduced with permission from Elsevier.

membranes were synthesized by the phase inversion method with a polymer concentration of 17.5% CA. The increase in porosity, hydrophilicity, and pore size of the CA/ND-PEG membrane caused an increase in water flux from 63.70 to 134.75 L m^{-2} h^{-1}. In addition, the addition of 0.5% ND-PEG also increased BSA rejection by 93.8%. This is because adding ND increases the surface hydrophilicity of the membrane, thereby reducing the interaction between the membrane and BSA. The addition of ND also affects lower TFR values and higher FR; because of that, the CA/ND-PEG membrane is said to have good antifouling properties.

Activated carbon is a porous carbon material with growing water and wastewater treatment applications. Activated carbon is a material with many advantages, such as porosity, mechanical strength, thermal strength, high surface area, and small pore diameter. Activated carbon contains as much as 90% carbon; the rest is oxygen, hydrogen, sulfur, and nitrogen. Experiments on using activated carbon as a filler for MBR have been carried out by Mohamadi et al. [133], who compared it to zeolite. The good antifouling properties of activated carbon make it the material of choice as a filler for PVDF membranes. The results showed that using activated carbon and zeolite on MBR both had the same effect on reducing EPS and SMP. However, in fouling mitigation, the membrane with activated carbon showed better antifouling properties than zeolite. This is evidenced by the lower cake mass formed on the surface of the PVDF/CA membrane compared to the PVDF/ZE.

5.3. Metal organic framework based fillers

Metal-Organic Framework (MOF) is a crystalline hydride compound formed due to coordination between metal clusters and organic ligands [134]. MOF generally has characteristics such as high surface area, pore size, and geometry that are easily modified and easy to synthesize [135]. In membranes, MOF is known to increase membrane permeability and porosity. Echaide et al. [136] showed that using the ZIF-11 membrane as a membrane filler increased the porosity and rejection of the membrane to pollutants. The use of MOF as an MBR filler has been reported by Lingfeng Ni et al. [137], who added CdS/MIL-101 to the PVDF matrix as a new strategy for controlling biofouling in MBR. Composite membranes produce smaller pore sizes and lower contact angles than pure PVDF membranes. This affects increasing the permeability of the composite membrane. In addition, the filler also functions as a photocatalyst by using radiation beams. The antimicrobial activity of *E. Coli* and *S. Aureus* showed excellent bacterial inactivation, reaching 93% and 89%, respectively. Compared to pure PVDF membranes, PVDF/CdS/MIL-101 membranes exhibit higher antifouling properties, lower flux reduction, and higher pollutant rejection rates (BSA, SA, and HA). The use of MIL101(Cr) has also been reported by Arbabi et al. [138], who used it as a filler in the PES polymer matrix in sodium acetate wastewater treatment. The characteristics of the composite membranes produced after the addition of MIL101(Cr) are increased membrane surface hydrophilicity, porosity, pore size, and resistance to fouling formation. Therefore, the MIL101(Cr)/PES composite membrane performed better than pure PES membranes, with an increased pure water flux of around 198.61% and COD removal of up to 99%. In addition, its effectiveness as an antifouling membrane is indicated by a lower irreversibility value of 10.43% and a higher FRR of 89.54%. This is due to the increase in hydrophilicity on the surface of the composite membrane resulting in a decrease in the interaction between pollutant molecules and the membrane.

The use of MOF as a filler for MBR has also been reported by Bazrafshan et al. [122], who used Cu-MOF to produce low-fouling MBR as a presented in Fig. 10. Adding MOF into the PSf polymer matrix increased the water flux to 350 LMH for the pure water flux test and 60 LMH for the cheese whey wastewater test. In addition, pollutant rejection increases with the increasing number of MOFs added to the membrane. Overall, the decrease in COD in the system is 98.8%. The PSf/Cu-MOF membrane antifouling test showed that the fouling resistance (FRR) results were two times higher than pure PSf membranes, which was ~85%. Better membrane characteristics influence the excellent

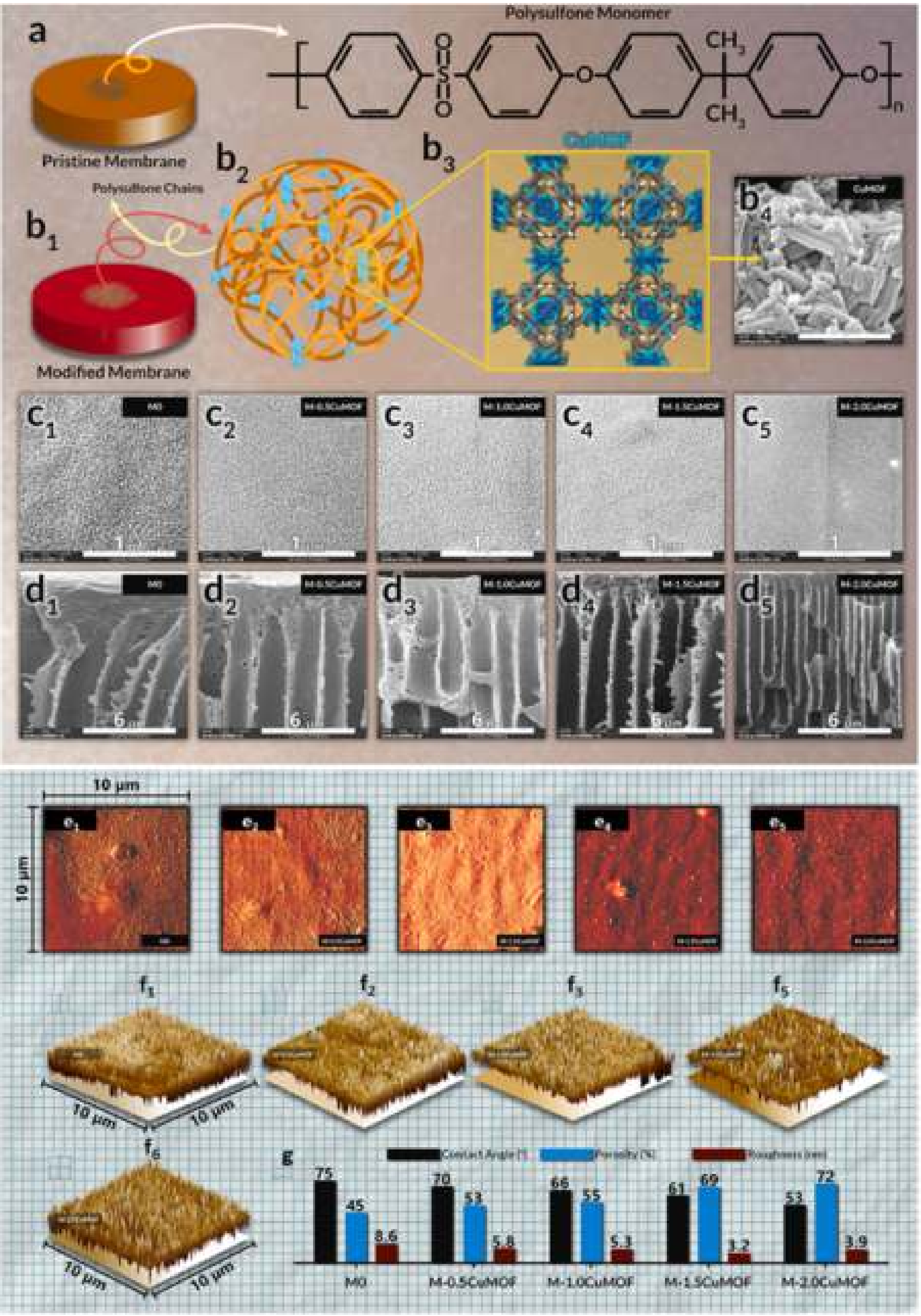


Fig. 10. a) Structure of PSf, b_1-b_3) Modification with Cu-MOF, b_4) Morphology of Cu-MOF, c_1-c_5) Morphology of surface of PSf/Cu-MOF membrane, d_1-d_5) Morphology of cross section of PSf/Cu-MOF membrane, e_1-f_5) Surface roughness of PSf/Cu-MOF membrane, and g) Value of contact angle, porosity and surface roughness of PSf/Cu-MOF membrane [122], reproduced with permission from Elsevier.

performance shown by composite membranes compared to polymer membranes. Where the PSf/MOF membrane with a percent loading of 2 wt% produces a contact angle, porosity, and surface roughness of the membrane, respectively 53°, 72%, and 3.9 nm.

5.4. *Silica based fillers*

Silica is the most abundant component in the earth's crust, which is most commonly found as quartz crystals and consists of SiO_4 tetrahedra arranged periodically with hexagonal rings via siloxane bonds [139]. The use of silica in MBR is due to its chemical resistance, high mechanical strength, and long service life. In addition, silica also has excellent biocompatibility. Amini et al. [25] added silica to the HDPE polymer matrix to form a bioreactor nanocomposite membrane. The more mass of SiO_2 added to the HDPE matrix, the lower the MBR contact angle and increase the hydrophilicity of the membrane. The increase in hydrophilicity can be seen from the large water flux in the filtration process using HDPE/SiO_2 membranes compared to pure HDPE. The fouling performance of the MBR is evaluated by measuring the TFR, RFR, and IFR. Adding SiO_2 lowers the TFR of the MBR by ~27%. This is because adding hydrophilic SiO_2 nanoparticles can increase the surface hydrophilicity of the membrane and reduce contamination by hydrophobic pollutants. The use of SiO_2 as an MBR filler has also been reported by Ahsani et al. [22], using PVDF polymer as the matrix for pharmaceutical wastewater treatment. The addition of Ag–SiO_2 to the membrane showed antibacterial properties against *E. Coli* and *S. Aureus* bacteria. In addition, it also affects the decrease in the membrane contact angle from 99° to 89°, which indicates an increase in membrane hydrophilicity. The membrane rejection of pure PVDF and PVDF/Ag–SiO_2 to pollutants was 90% and 95%, respectively. In addition, its resistance to fouling is shown by the FRR value of the PVDF/Ag–SiO_2 membrane, which is 76%. This is also supported by the results of EEM fluorescence spectroscopy, as presented in Fig. 11b–e. The B and C peaks loss in Fig. 11d and e indicates good performance on PVDF/SiO_2 and PVDF/Ag–SiO_2 membranes.

The use of silica in MMM as MBR was also reported by Zhang et al. [140], who added Ag@Silica fillers to the PVDF membrane. Silica nanopollen is used as a nanocarrier for Ag nanoparticles to increase the efficacy of silver delivery, avoid agglomeration and control the release of Ag^+ to bacteria. The results of the SEM analysis showed that Ag@silica, with a size of ~300 nm, was spread evenly over the membrane surface, which caused a decrease in the membrane contact angle and increased water permeability. Long-term MBR testing shows that the use of MMM can reduce the rate of TMP increase up to 0.88 ± 0.34 kPa/day. This result is lower than pure PVDF membrane 2.32 ± 0.86 kPa/day. Analysis of the bacterial community showed that the addition of Ag@Silica inhibited the colonization of Proteobacteria and Actinobacteria bacteria which are the cause of biofouling in MBR. In this case, silica nanopollens is important because it can potentially puncture the bacterial cell membrane that causes fouling with a needle-like topology. The Ag presence inside the nanopollen experienced dissolution, resulting in silver ions (Ag^+) being generated. These Ag^+ ions could subsequently penetrate biological cells. This ensures the effectiveness of PVDF/Ag@Silica as MBR, which has the potential to produce membranes with good anti-biofouling performance and a long period of use.

5.5. *Zeolite based fillers*

Zeolite is an inorganic crystal material belonging to the aluminosilicate compound, which is formed from tetrahedral alumina (AlO_4^{-5}) and silica (SiO_4^{4-}) [141]. Zeolite has apparent pore dimensions on the molecular scale, high adsorption properties, hydrophilic, and ability in

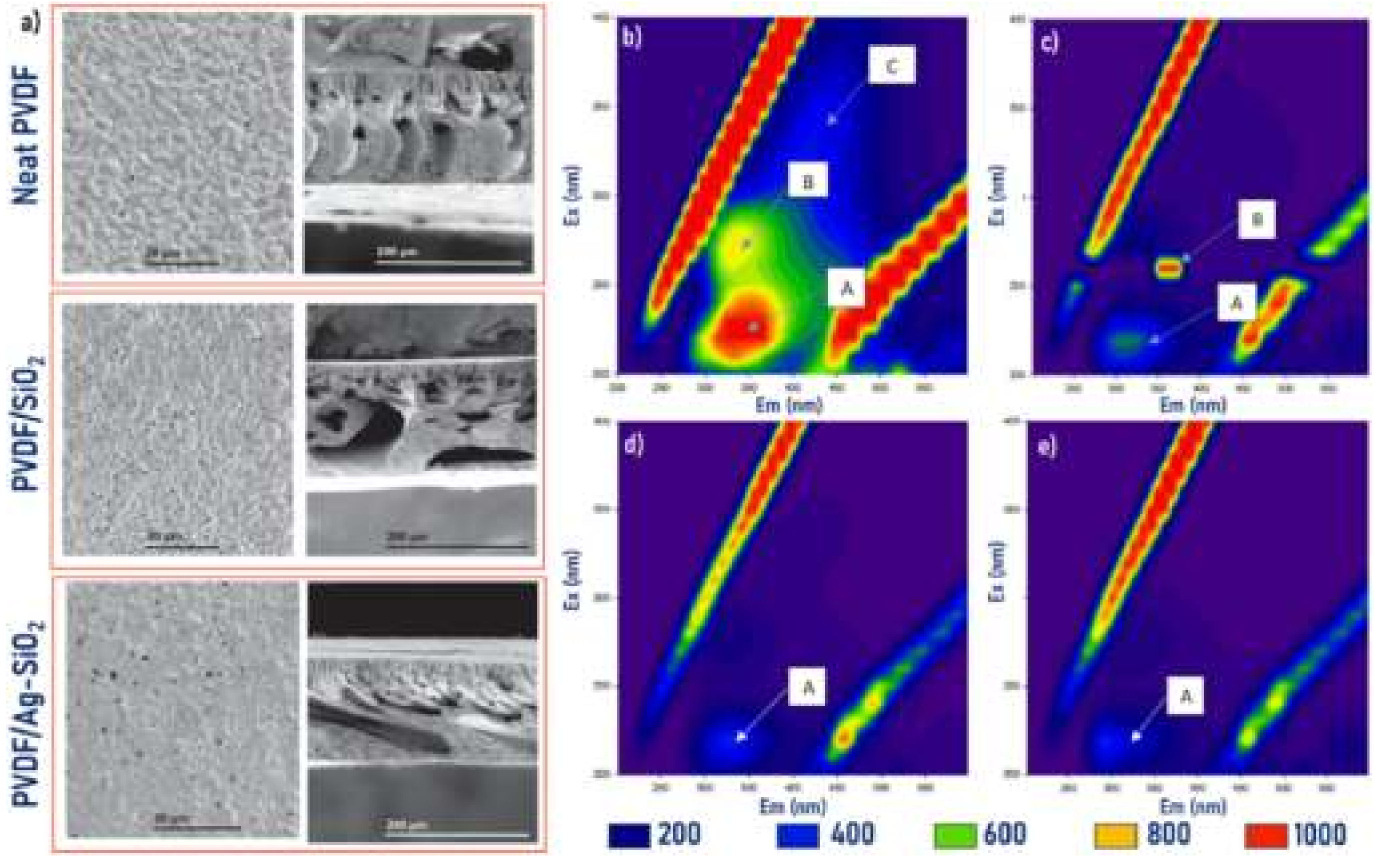


Fig. 11. a) Morphology of Neat PVDF, PVDF/SiO_2 and PVDF/Ag–SiO_2 and b-e) EEM fluorescence spectra of extracted EPS from sludge (b), neat PVDF (c), PVDF/SiO_2 (d) and (e) PVDF-Ag membranes/SiO_2 [22], reproduced with permission from Elsevier.

molecular filtration [142,143]. Its filtering ability makes zeolite a filler with very high diffusivity and selectivity. In addition, the size and shape of the pore distribution ensure excellent selectivity [144]. Its hydrophilic nature can also produce high flux when used as a filler in MMM. In MBR, zeolite filled MMM has good resistance to fouling due to its hydrophilic surface. Darmayanti et al. [124] have reported using AgNPs/zeolite as a filler in PVDF membranes. Using AgNPs/zeolite-Na-Y fillers aims to improve membrane performance, especially resistance to fouling in industrial wastewater treatment. The membrane was prepared using two methods, including the TIPS and dip coating methods, to see the effect of the preparation method on the performance of PVDF/AgNPs/zeolite-Na-Y as MBR. The experimental results showed that the optimum zeolite weight percent was 0.3 g for all membrane variations. Membranes prepared using the TIPS and dip coating methods have shown good performance results, including water flux (195.5 and 202.62 $L\ m^{-2}\ h^{-1}$), Rejection (COD: 98.5 and 99%; BOD: 98.5 and 99%; TSS: 99.8 and 99.9%; TDS: 65.6 and 66%). In addition, the membrane also showed good fouling resistance with FRR values (82.5 and 95%). This result is due to the hydrophilic nature of the zeolite; however, reports on using zeolite as MMM fillers still need to be completed. The relatively high cost of zeolite probably causes this. In order to exploit the potential of zeolite as a filler for MMM in the future, it is necessary to develop zeolite synthesized from natural materials to obtain cheaper zeolite materials to produce low-cost MBR.

Table 6 has summarized various materials developed as fillers in MBR which function as wastewater treatment membranes. Fillers in membrane membranes are one of the crucial components in the development of MBR. Due to membrane and inorganic polymers' limitations, they can list the presence of fillers in membranes. Each filler has different characteristics, so the match between the polymer and the type of pollutant is a crucial point that must be considered to obtain MMM with the best performance. In MBR technology, various fillers have been reported to be effective in improving membrane performance, especially water flux and its rejection of pollutants. Overall, fillers used in multiple polymer matrices generally have high hydrophilicity properties. Most organic pollutants have hydrophobic properties, so adding hydrophilic material to the membrane can reduce the interactions between the pollutant molecules and the membrane surface. In addition, the hydrophilicity of the membrane also affects the increase in the flux of filtered water. Hydrophilicity also affects the antifouling properties of the membrane. The antifouling ability of the membrane is one of the efforts that can overcome the significant challenges of MBR because fouling is a substantial factor in MBR problems. Using metal/metal oxide, carbon, MOF, Silica, and Zeolite based fillers has created good antifouling properties in MBR. In addition, thermal and mechanical resistance is also an advantage in using these materials. Metal/metal oxides and MOF can act as catalysts or photocatalysts in overcoming fouling problems to obtain superior membranes. However, the thing that must be considered is the possibility of leaching, which is feared to be the cause of new problems due to the generally toxic nature of metals. On the other hand, carbon and silica are non-toxic materials that are also suitable for use as filler materials in MBR. The high surface area is also an aspect of interest for these materials. Therefore, each of these materials uniquely produces MBR with high-quality performance.

6. Important characteristics of mixed matrix membrane for MBR

6.1. Hydrophilicity

Hydrophilicity is a membrane characteristic that tends for the surface to be wet or able to absorb water. The occurrence of hydrophilic properties on the surface of the membrane generally leads to the formation of bonds between the water molecules and the component molecules of the membrane [145]. The hydrophilicity of the membrane surface can be identified by measuring the contact angle of the membrane. The membrane is more hydrophilic the lower its contact angle. In MBR, membranes that have high hydrophilicity can produce high permeate fluxes with good quality, due to the low interaction between the membrane surface and activated sludge or pollutants in wastewater [55]. The biomass production in the form of hydrophobic activated sludge floc is attributed to the activity of microorganisms [51]. In addition, organic pollutants that are a source of problems in wastewater also generally have hydrophobic properties [146] so this triggers strong adhesion between the membrane surface and activated sludge and pollutants. Only a few polymers used as MBR materials have hydrophilic properties because most polymers are hydrophobic [51]. Efforts can be made to increase the hydrophilicity of the membrane surface area by modifying the membrane surface or its constituent materials. The development of MMM in MBR is one solution that can be done to produce hydrophilic membranes by adding inorganic fillers that have high hydrophilicity [147].

6.2. Membrane surface charge

The membrane surface charge is one of the important parameters in the MBR filtration process because it can evaluate the performance of the membrane by influencing the electrostatic repulsion between charged ions or molecules originating from pollutants in wastewater and the membrane surface [148]. Generally, membranes that have a negative surface charge are better for use as an MBR than a positively charged membrane [149]. This is because organic pollutants or activated sludge have a negative charge, making it easier for repulsion forces to occur between the membrane surface and pollutants [150]. As a result, fouling on the membrane surface is considerably reduced. The higher the zeta potential value of a negatively charged membrane, the better its performance to overcome the fouling phenomenon in MBR, due to the increased energy barrier and ability to maintain consistent repulsion interactions [151]. Mahmoudi et al. [23] have created MMM by adding Ag-GO filler to the PES matrix. The results of zeta potential measurements showed that the more filler Ag-GO was added to the membrane, the more negative the surface of the membrane was, where the addition of 2.5% Ag-GO caused an increase in charge up to −34.2 mV. This charge is higher than pure PES membranes which are only charged −3 mV. This difference in charge causes a difference in its performance as MBR, where MMM which is more negatively charged is able to produce higher pollutant rejection compared to pure membranes. This is also in line with its resistance to fouling.

6.3. Surface roughness

Surface roughness is a parameter that informs the size of the surface texture of a material. In membrane technology, membrane surface roughness is defined as a deviation or mismatch of the membrane surface from the supposed surface topography, which is an atomically smooth surface [152]. Surface roughness can be analyzed using AFM. The surface roughness of the MBR correlates with the fouling phenomenon that can occur during the filtration process. The risk of more foulants accumulating on the membrane surface rises as the roughness of the membrane surface increases [153]. The increase in the degree of membrane surface roughness is in line with the increase in the rate of membrane fouling [154]. In general, pure polymer membranes have a higher degree of roughness compared to MMM. Zinadini [155] reported a decrease in the degree of surface roughness of the membrane after the addition of ZnO/MWCNTs into the PES polymer matrix. This is evidenced by the FRR value of PES/ZnO/MWCNTs membranes which reached 90.5%, compared to pure PES membranes which only had an FRR of 51%.

6.4. Membrane module

Membrane modules are generally developed to obtain different characteristics under hydrodynamic conditions, energy consumption, filtration area, and others [156]. Several types of membrane modules that have been developed for use as MBR are tubular [157], hollow fiber [158], flat sheet [159], and spiral wound [160] as shown in Table 7. In general, the parameters that must be considered in tubular membranes and hollow fibers are the inner and outer diameters of the membrane and the length of the membrane, while in flat sheet membranes the length and width of the membrane, as well as its thickness. MMMs with hollow fiber modules have been prepared by adding WO_3 filler in the PVDF matrix. The performance results of the PVDF/WO_3 hollow fiber membrane as MBR showed that the maximum COD removal efficiency was achieved with a weight percent of 0.1% WO_3 and reinforced with braid. In addition, the addition of WO_3 also shows high fouling resistance with good antifouling properties with an FRR value of up to 67.1% (Koyuncu et al., 2023). Apart from hollow fibres, sheet sheets have also been prepared by adding TiO_2 particles to the PP polymer matrix. The test results showed that PP/TiO_2 membranes were able to produce MMM with better antifouling properties than pure PP membranes (Etemadi et al., 2020). In general, each MMM module as MBR has demonstrated high performance with good antifouling properties. Hashisho et al. (2016) conducted an experiment by comparing hollow fiber modules and flat sheets as MBR. The two membrane modules showed a small difference in COD reduction, wherein the hollow fiber membrane had a proportion of 71.4%, while the flat sheet had 68.5%.

6.5. *Pore size and pore distribution*

Pore size and distribution are very important parameters in the membrane fabrication process because they are considered characteristics that govern the course of the filtration process [161]. Membranes can be categorized into a number of different categories depending on the pore size, including MF, UF, NF, and RO. Currently, the use of SEM, TEM, and AFM instruments is widely used as microscopic methods to determine the pore size of membranes [162,163]. In general, the results of membrane pore size analysis using SEM and TEM produce smaller sizes than the results of AFM analysis. The observed phenomenon may be attributed to applying the conductor layer onto the sample. Additionally, it is hypothesized that structural alterations may occur due to the electron beam-induced damage during the analysis procedure [164]. The experimental results of Hashemi et al. [27] found that there was a relationship between the addition of alumina NPs and the pore structure of the membrane. The greater the concentration of alumina NPs in MMM, the more the MBR pore length increased. This is also in line with the report by Bazrafshan et al., which shows changes in the structure and pore size of the membrane when adding Cu-MOF fillers into the PSf polymer matrix, as shown in Fig. 10.

6.6. *Loading fillers*

To achieve the highest possible membrane performance, including a high-water flux, one of the membrane modification initiatives involves adding inorganic fillers to the polymer matrix, high pollutant, and bacterial rejection, and minimal fouling phenomena. In the MMM fabrication process, the selection of polymers, types of inorganic fillers, and loading fillers are important parameters that must be considered to produce membrane materials that have excellent characteristics and performance [165]. Some inorganic materials that have been used as fillers in MBR are metal nanoparticles [166], metal oxides [167], carbon [168], silica [169], MOF [137], and others. The use of these materials has been used as a filler in several polymer matrices such as PVDF, PES, PSF, PVC, CA, HDPE, and others. Alsalhy et al. [24] have reported the effect of different loadings of ZnO nanoparticle filler on the PVC matrix used as MBR. Fig. 12 shows the results addition of ZnO NPs with a load of 0.1, 0.2, 0.3, and 0.4 g gave a less significant effect on pollutant rejection, but based on the results of the water flux, the optimum ZnO loading was 0.1 g with a flux reaching 122.22 $L\,m^{-2}\,h^{-1}$. In addition, the effect of different ZnO load fillers is very visible in the formation of the cake layer on the membrane surface, the greater the load filler added to the polymer matrix, the smaller the thickness of the cake layer formed on the MBR surface, thereby reducing the possibility of fouling.

Table 7
Membrane module comparison.

Characteristics	Tubular	Hollow Fiber	Flat Sheet	Spiral Wound
Ease of cleaning	Easy	Hard	Moderate	Easy
Fabrication Cost	Low	High	Low	Moderate
Antifouling Properties	High	Low	Moderate	Low

7. Membrane bioreactor performance parameters

To obtain maximum results from the wastewater treatment process, several MBR performance parameters must be considered. In addition to the features of the filtering process's membrane, the characteristics of the activated sludge and the operating conditions of the MBR are also important aspects that must be prepared as shown in Fig. 13.

7.1. *Characteristics of activated sludge*

Activated sludge is a biological process due to aerobic biodegradation with unlimited growth rates of microorganisms and their respiration, as well as oxygen and nutrients. In activated sludge, a biological floc matrix is > 1 mm in diameter and contains billions of bacteria. The process of floc formation from microbes is an important parameter that shows the activated sludge is functioning correctly. The activated sludge aeration tank acts as a bioreactor by considering dissolved oxygen and specific concentrations of biomass to achieve a more effective and efficient reduction of COD [170,171]. Several characteristics of activated sludge that must be considered to obtain maximum performance are MLSS concentration, sludge viscosity, EPS, SMP, floc size, and surface charge. MLSS concentration and activated sludge viscosity have a relationship that affects the occurrence of biofouling on the membrane. Viscosity increases as the MLSS concentration rises. This increase has an impact on the phenomenon of fouling in the MBR. It is known that an increase in MLSS concentration correlates with an increase in the level of membrane fouling which causes a decrease in MMM performance [154,172]. Apart from MLSS, EPS is also one of the critical aspects that cause biofouling to occur in MBR, especially the formation of a cake layer on the surface of the membrane. EPS can also affect the properties of activated sludge, such as flocculation adhesion, hydrophobicity, and floc size, which decreases MBR performance [173].

Ostadi et al. [174] reported the effect of MLSS concentration on the MBR performance of MMM, namely CuO/PVDF. Experiments were carried out using optimum membranes with a constant aeration rate and F/M ratio. The variations in MLSS concentrations are 6000, 8000, 10, 000, and 12,000 mg L^{-1}. The test results showed that increasing the concentration of MLSS could reduce COD reduction by up to 3.6%. This is because the increase in MLSS concentration resulted in a high viscosity of the medium biomass. The minimum amount of dissolved oxygen and minimal air causes microorganisms to flake off, thereby reducing the percentage of COD reduction. The decrease in MMM performance was also seen from the results of the flux test. Overall, MLSS showed a flux that initially decreased and stabilized at all concentrations. This is related to fouling formation on the MMM surface due to concentration polarization processes, membrane pore blockage, and cake formation. The results of a decrease in flux were accompanied by an increase in MLSS concentration, as shown in Fig. 14a. The opposite was reported by Zinadini et al. [175], who reported using PVDF/GO membranes with MLSS variations of 6000, 10,000, and 14,000 mg L^{-1}. The test results show that an increase in MLSS causes an increase in the percentage reduction of COD, BOD, TN, TP, and water flux, as shown in Fig. 14b and c. This is associated with a decrease in SMP and EPS caused by a low F/M ratio. The difference in results reported earlier was due to

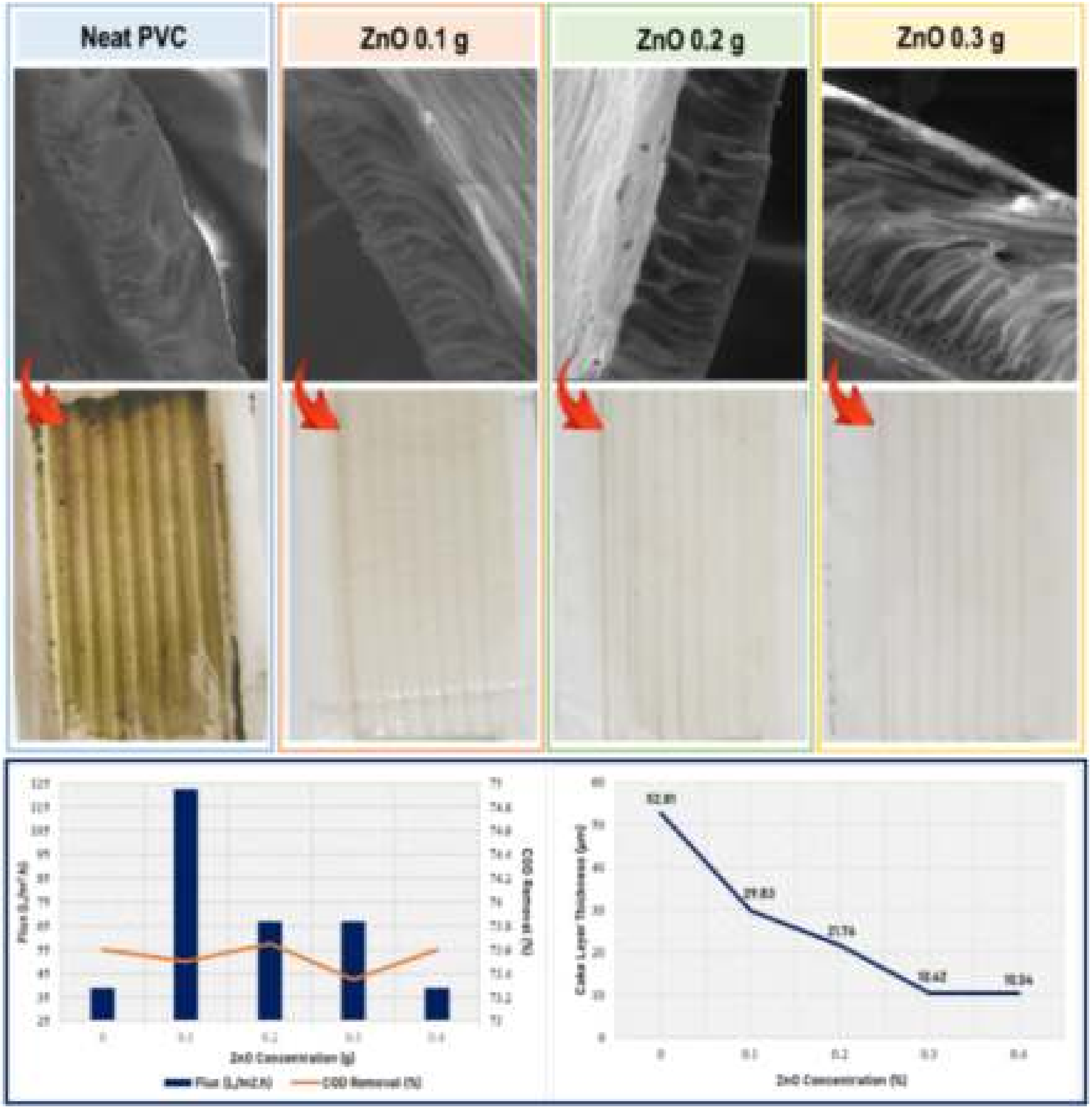


Fig. 12. The Difference in Loading Filler on MMM [24], reproduced with permission from Elsevier.

the difference in the F/M ratio in the two experiments. The low F/M ratio can cause a decrease in the amount of SMP and EPS to minimize the occurrence of fouling on the MMM surface. Therefore, determining the exact composition related to the characteristics of activated sludge is one way to obtain MBR with high-quality performance.

7.2. Operating conditions

Good MBR performance test results are inseparable from the operating conditions that are run correctly. In the operation of the MBR, several components must be considered during the performance testing process, such as temperature, SRT, HRT, aeration, and pH. Temperature is an important aspect that affects the biodegradation rate in activated sludge [154]. The lower the temperature conditions during the MBR testing process, the greater the tendency for fouling to occur on the membrane. This is because low temperatures can cause an increase in EPS production by microorganisms [176]. HRT and SRT are also essential aspects that affect the performance of the MBR process. Both are very influential on the fouling of the membrane. Many studies have reported that a decrease in HRT and SRT can stimulate the release of EPS by bacterial cells, causing an increase in EPS concentration which results in fouling formation. However, too high an increase in HRT and SRT also has a high probability of fouling.

Wang et al. [26] reported using PVDF/TiO_2 membranes as MBR by looking at the effect of HRT, pH, and the amount of dissolved oxygen on the reduction of COD, NH_4^+, and TN, as shown in Fig. 15. The results of experiments by varying the HRT for 4, 5, and 6 hours showed that the removal of COD, NH_4^+, and TN increased with increasing HRT. This is because an HRT that is too low can trigger an increase in EPS concentration which causes fouling on the MMM surface. In addition to HRT, pH varied in the range of 6–9, showing differences in COD, NH_4^+, and TN concentration. Optimum conditions were obtained at pH seven, caused by too high or too low a pH causing obstacles to the biodegradation process, affecting the results of pollutant removal. Differences in performance results were also obtained by varying the amount of dissolved oxygen from 0.5 to 3 mg L^{-1}, where the lowest removal of COD, NH_4^+, and TN was acquired at an additional dose of 0.5 mg L^{-1}. This is due to the low amount of oxygen dissolved in the system affecting the activity of bacteria in activated sludge. The analysis of aeration intensity is vital due to its potential to generate MBR process membranes that effectively

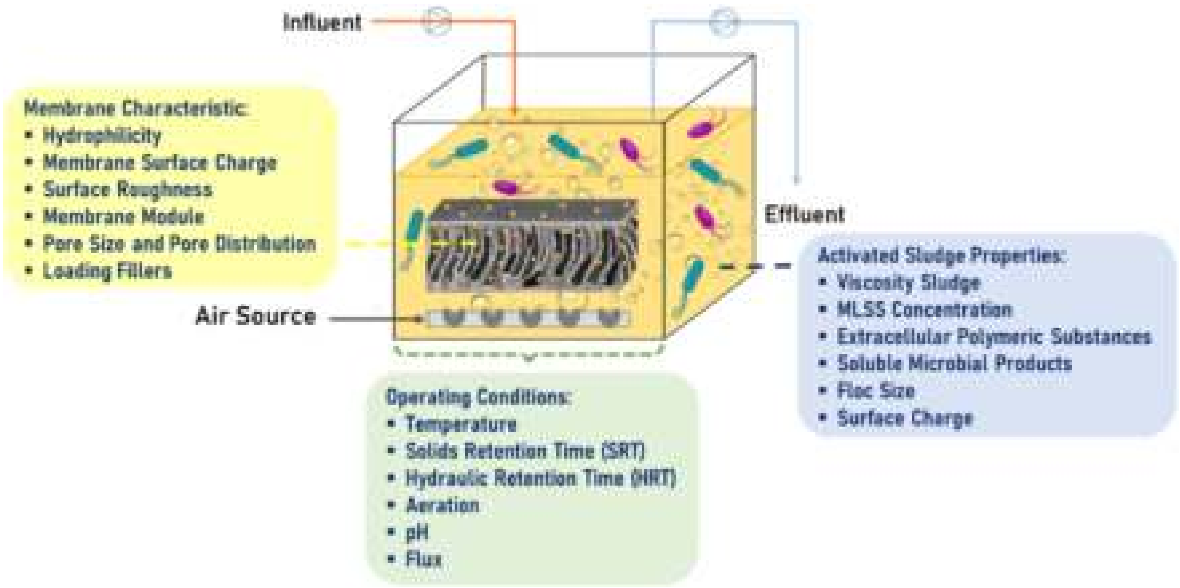


Fig. 13. MBR performance parameters.

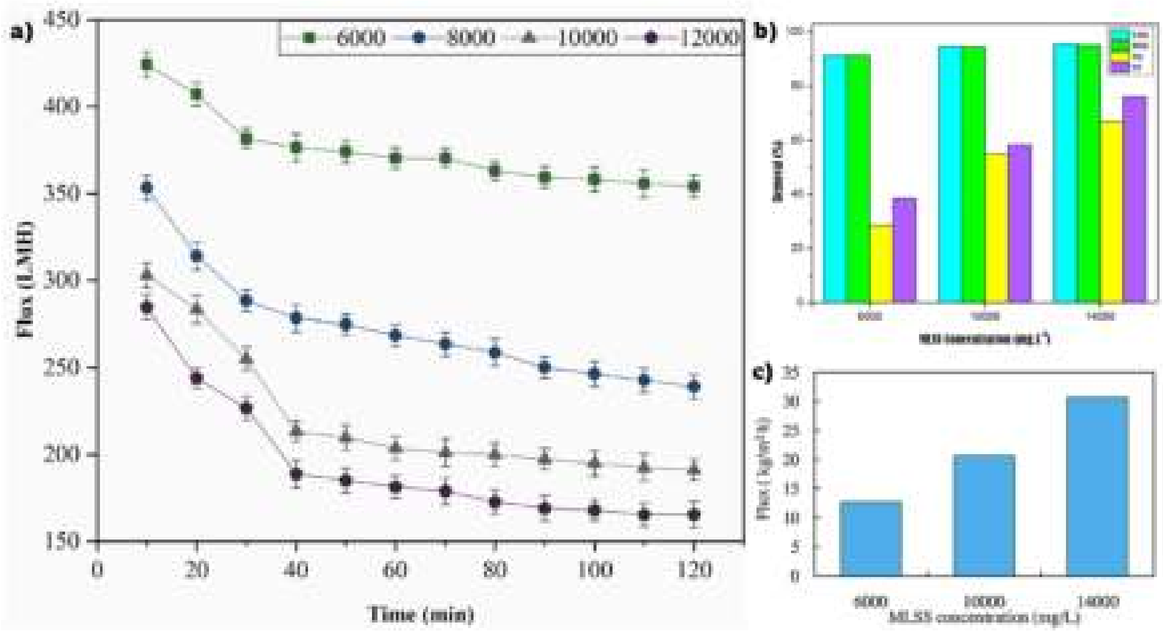


Fig. 14. a) Sludge Flux [174], b) Removal of COD, BOD, TN, TP and c) Flux at Different MLSS Concentrations [175], reproduced with permission from Elsevier.

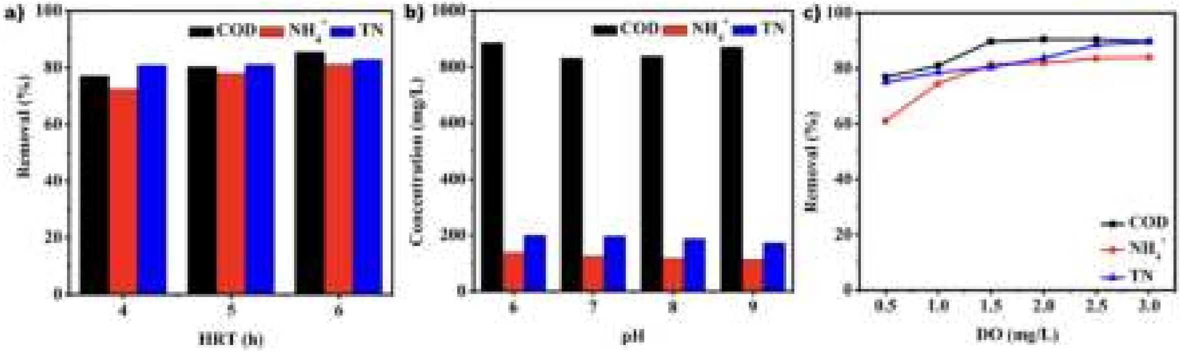


Fig. 15. The Effect of a) HRT, b) pH, and c) Dissolved Oxygen on COD, NH_4^+, and TN [26].

reduce fouling development on the MMM surface.

8. Fouling phenomenon on MBR

Fouling is a phenomenon of decreased membrane performance due to the inhibition of membrane pores by compound molecules contained in the mixed liquor as shown in Fig. 13. Fouling in the bioreactor membrane is caused by several foulants. Foulants can be divided into three types, namely inorganic foulants, organic foulants, and bio foulants. Inorganic foulants in the form of inorganic matter such as minerals that precipitate on the membrane surface cause blockage of the membrane pores. Organic foulants are organic compounds such as lipids, proteins, humic acids, polysaccharides, and other organic compounds that can accumulate on the membrane surface [40,177]. The secretions of bacteria, such as SMP and EPS, are examples of bio foulants, which are germs that build up on membrane surfaces. Bio foulant are the main causes of membrane fouling in MBR [178]. Membrane characteristics are also a factor that affects the fouling of the MBR. Membranes with smaller pore sizes have lower fouling rates. Membranes with large pores make it easier for foulants to enter the pores causing pore blockage [98].

Metal nanoparticles and metal oxides are an option to increase the hydrophilicity and antimicrobial membrane bioreactor to improve membrane anti-fouling ability. The addition of ZnO to the PVC membrane decreased the WCA from 64° to 46.23° indicating an increase in the hydrophilicity of the membrane. This causes a decrease in the thickness of the cake layer up to 80.27% and an increase in FRE reaching 80% compared to neat PVC, indicating the high anti-fouling ability of PVC/ZnO [24]. Due to its hydrophilicity, the membrane can form a very

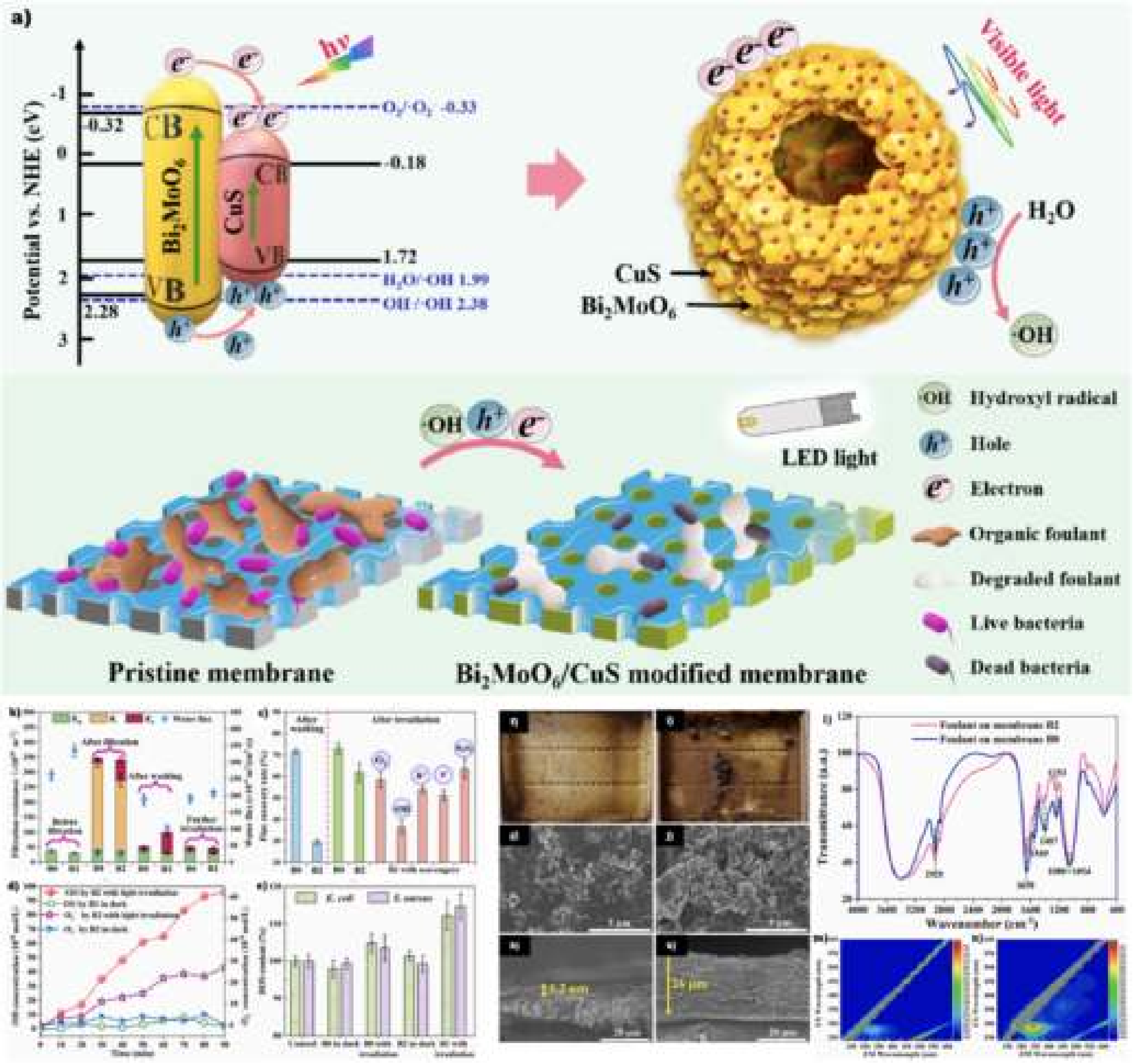


Fig. 16. a) The Mechanism of Membrane Photocatalytic Bi_2MoO_6/CuS Modified Membrane, b) Water Filtration Resistance and Flux of Membranes Before and After a Fouling Cycle, c) Water Flux Recovery, d) Generation of •OH and $•O_2^-$, e) Intracellular ROS content, f-k) Membrane B2 (Left) and B0 (Right), l) FTIR Spectra, 3D-EEM Spectra of Foulant on m) B2, and n) B0 [179], reproduced with permission from Elsevier.

thin water layer on the membrane surface and reduce the adsorption of hydrophobic foulants [25]. Another study modified the PES membrane with Ag_3PO_4–NH_2/g-C_3N_4 which showed antibacterial activity against *Staphylococcus aureus, salmonella,* and *Escherichia coli*. This antibacterial activity is caused by the release of Ag^+ ions which can encourage damage to cell membranes and proteins. In addition, the photocatalytic activity of Ag_3PO_4–NH_2/g-C_3N_4 may produce radical species that can damage cells. The presence of this antibacterial activity causes an increase in membrane anti-biofouling [112]. The same thing was also seen in other studies [110].

Ni et al. [179] tried controlling biofouling in MBR by adding Bi_2MoO_6/CuS to the PVDF polymer matrix, which can also function as a photocatalytic membrane, as shown in Fig. 16. The use of the Bi_2MoO_6/CuS heterojunction aims to increase the catalytic activity of the membrane in disinfecting bacteria and degrading microbes that cause fouling on the membrane surface. The effectiveness of using a catalytic membrane can be seen in the decrease in the Rir of membrane B2 (PVDF/Bi_2MoO_6/CuS), which decreased to 74.3% with an FRR value of 61.8%, while the B0 membrane (Neat PVDF) showed constant results as shown in Fig. 16b and c. This indicates that a catalytic degradation process can effectively overcome the foulant on the PVDF/Bi_2MoO_6/CuS membrane. This is also supported by the foulant morphology presented in Fig. 16f–k. The results of the SEM analysis showed differences in the thickness of the foulant on the B2 and B2 membranes, where the membrane without Bi_2MoO_6/CuS produced a thicker foulant than the membrane filled with Bi_2MoO_6/CuS. Likewise, the 3D-EEM fluorescence analysis results in Fig. 16m and n shows the absence of a red zone in the results of membrane B2 analysis. This causes the destruction of conjugated bonds and aromatic rings in pollutants. Some of these results have proven that using MMM has the potential to overcome the problem of fouling in MBR compared to polymer membranes.

9. Challenges and perspective

In order to meet SDGs, point 6 (related to clean water and sanitation) and to tackle the water crisis issues, research and development on wastewater treatment technologies play a vital role. Recently, MBR is an innovative wastewater treatment system that integrates membrane filtration operations with the biological activity of microorganisms. It has demonstrated significant progress over a period of three decades, with notable growth observed during the 2000s [180]. The use of MBR has been known to produce high-quality permeate. However, a major barrier that researchers are still facing in advancing MBR is the persistent occurrence of fouling phenomena inside the membranes. MMM is a prospective alternative to polymeric and inorganic membranes for the fabrication of high-performance membranes with superior antifouling properties [181]. Based on the existing literature, this review proposes relevant research considerations and suggestions for further investigations including:

1. The preceding section of this review discussed different types of fillers. Zeolite is a filler seldom used in MMMs, specifically in its application in membrane bioreactors (MBRs). Interestingly, zeolite, with hydrophilic characteristics, has promising potential for synthesizing MMMs that have favorable antifouling capabilities. In addition, by employing natural resources in the zeolite production process, the comparatively high cost of zeolite may be mitigated. In addition to zeolites, it is important to investigate further the utilization of metal/metal oxide types, carbon materials, MOF, and silica as fillers. This exploration includes incorporating filler materials in 2D and 3D structures to enhance the properties of MMMs, such as hydrophilicity, antifouling capabilities, chemical stability, thermal resistance, and mechanical strength. On the other hand, the determination of the optimal ratio between the polymer matrix and filler is crucial in order to consistently generate MMMs with excellent features and performance.
2. MMM, which functions as a catalytic or photocatalytic membrane, can potentially be used as an MBR in wastewater treatment. This encourages us to produce MBR with high antifouling properties in the future. Catalytic and photocatalytic membranes can be made by adding fillers that can degrade organic pollutants under certain conditions. Catalytic membranes generally require UV light to produce radical groups, which then function to lessen pollutants. The degradation process by radical groups can be a source of overcoming the problem of fouling in MBR. For this reason, it is necessary to explore the types of MMM fillers that can produce catalytic or photocatalytic membranes.
3. Currently, polymer membrane based MBRs are widely used on a large or industrial scale. The advanced development of MMM is significant due to its superior performance in comparison to polymer membranes. The excellent antifouling characteristics of MMM could result in the production of MBR systems that have extended service life and reduced maintenance costs, particularly when used on a large or industrial scale.
4. The fouling issue occurring in MBRs is also subject to the effect of the activated sludge's properties and the operational processes used. The careful evaluation of the appropriate formula pertaining to the properties of activated sludge, including MLSS concentration, viscosity, and microorganism type, is of utmost importance for ongoing advancements in achieving optimal conditions for wastewater treatment. This factor's significance also extends to determining the most favorable operating circumstances. For example, determining the suitable HRT and SRT can produce an MBR with minimal fouling. The lower the HRT and SRT, the more potential for membrane fouling. However, if both are increased, it can also expand the fouling on the membrane. Consequently, comprehensive study is recommended in order to acquire the most favorable HRT and SRT conditions.

10. Conclusion

MBR is an advanced and sophisticated technology in wastewater treatment that combines membrane filtration technology and biological activity. The use of MBR can provide benefits by producing quality effluent. Important parameters that must be considered in controlling the performance of the MBR include membrane characteristics, activated sludge characteristics, and operating conditions during the filtration process. To produce maximum process performance, the use of a mixed matrix membrane is the right solution because it has the potential to be used as MBR. The inclusion of fillers increases the chemical and thermal durability of the polymer matrix and gives additional benefits such as enzyme immobilization, mechanical strengthening, and antifouling qualities. Several fillers have been developed in MBR such as metal, metal oxide, carbon, silica, zeolite, MOF, and others. The big challenge in MBR is membrane fouling which is still prone to occur. Therefore, innovations are needed in the use of MMM as MBR with various polymer and filler modifications to produce MBR with single process performance and results.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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