A critical review on nanomaterials membrane bioreactor (NMs-MBR) for wastewater treatment

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The concept of nanomaterials membranes (NMs) promises to be a sustainable route to improve the membrane characteristics and enhance the performance of membrane bioreactors (MBRs) treating wastewater. This paper provided a critical review of recent studies on the use of membranes incorporating nanomaterials in membrane bioreactor (NMs-MBR) applications for wastewater treatment. Novel types of nanomaterials membranes were identified and discussed based on their structural morphologies. For each type, their design and fabrication, advances and potentialities were presented. The performance of NMs-MBR system has been summarized in terms of removal efficiencies of common pollutants and membrane fouling. The review also highlighted the sustainability and cost viability aspects of NMs-MBR technology that can enhance their widespread use in wastewater treatment applications.

npj Clean Water (2020) 3:43; https://doi.org/10.1038/s41545-020-00090-2

INTRODUCTION

Membrane bioreactors (MBRs) have proven to be one of the most effective technologies globally for treating wastewater from different sources. In MBRs operation, wastewater treatment is carried out via a combination of biological unit (for the biodegradation of waste streams) and membrane filtration unit (for the separation of treated water from biosolids using membrane module). The two major categories of MBRs, based on their configuration and hydrodynamic control of membrane fouling, are submerged (SMBRs) and side stream MBRs. This technology was introduced >30 years ago and offers the advantages of a smaller footprint, high-quality treated water, less sludge production, low energy demand, and a higher removal rate for pollutants. Therefore, for obtaining high-quality treated wastewater, MBRs are recommended over other techniques, such as activated carbon adsorption, filtration, coagulation etc.; they can also be integrated with oxidation processes, such as photolysis, sonolysis and chemical/electrochemical oxidation for removal of micropollutants. Thus, MBRs are well suited for on-site reuse of treated wastewater. As a consequence, driven by growing water scarcity, ageing infrastructure and increasingly stringent discharge norms, the MBR market is growing rapidly and has successfully contributed to the broader wastewater treatment market; furthermore, MBRs represent a significant market source for other membrane systems, especially microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and forward osmosis (FO).

Based on the literature, it is evident that in recent years, remarkable progress has been made in wastewater treatment via MBR technology. Wastewater reuse has been targeted and a range of industrial wastewaters have been tested. Of particular interest are highly polluting effluents from sectors, such as tanneries and textiles, as well as wastewaters with high salinity. For example, textile wastewater containing azo dyes has been treated in a bioaugmented MBR coupled with a granular activated carbon (GAC) packed anaerobic zone resulting in over 95% dye removal in a short time. Removal of micropollutants is also a focus area. For example, Trinh et al. investigated a full-scale MBR treating municipal wastewater for the removal of 48 trace organic chemical contaminants and found that removal percentage was over 90%. Katsou et al. illustrated removal of heavy metals from wastewater with removal efficiencies of Cu (II), Pb (II), Ni (II), and Zn (II) of 80%, 98%, 50%, and 77%, respectively. Mannina et al. reported an MBR pilot plant experimental study designed to treat saline wastewater contaminated with hydrocarbons, which resulted in a high total chemical oxygen demand (COD) removal of ~90%.

A plethora of studies have been done to enhance the performance of MBRs by integrating them with other systems. In general, objectives of the integrated MBR systems are to improve permeate rates, decrease membrane fouling, increase process stability and to obtain treated wastewater of requisite quality. Laera et al. integrated an MBR with oxidation (either ozonation or a UV/H2O2 process) for the removal of organics and degradation of components in pharmaceutical wastewater. This integrated system was able to remove COD in the range of 85 – 95% with complete removal of degraded products. De Jager et al. investigated color removal from textile wastewater using a pilot-scale, dual-stage MBR-Reverse osmosis (RO) system. The performance analysis revealed that total organic carbon (TOC) removal exceeded 80%, and in excess of 90% color removal efficiencies were recorded, potentially meeting the required discharge and reuse standards for wastewater. Phattaranawik et al. reported on a novel wastewater treatment process using membrane distillation bioreactor (MDBR) technology. This

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system has the potential to produce high-quality treated wastewater in one-step with capital and operation cost comparable to MBR coupled with RO.

In all MBR studies, membrane fouling is recognized as a major obstacle to the smooth operation and widespread application of this technology18–31. Fouling, in turn, requires membrane cleaning leading to higher operating costs due to additional energy, chemicals and system downtime. A variety of measures has been investigated for fouling control. To enhance performance, additives such as activated carbon have been used32. Deng et al.33 reported membrane fouling reduction using a sponge-coupled nanotechnology with improves land membrane bioreactor (NTs-MBR)59,60, (4) nanocrystals membrane fouling reduction41 and this approach has been used successfully in MBR technology. Many efforts have been made to embed various types of nanomaterials into (NMs-MBR) wastewater treatment technology. Many efforts have been made to embed various types of nanomaterials into membrane bioreactors can be classified as follows: (1) nanofibers membrane bioreactor (NFS-MBR)52,55, (2) nanoparticles membrane bioreactor (NPs-MBR)57,58, (3) nanotubes membrane bioreactor (NTs-MBR)59,60, (4) nanocrystals membrane bioreactor (NCS-MBR)61,62, (5) nanowires membrane bioreactor (NWs-MBR)63 and (6) nanosheets membrane bioreactor (NSs-MBR)64,65 (Fig. 1a). Growing recent publications related to the application of novel nanomaterial-based membranes in MBRs is evidence of increasing interest in this field (Fig. 1b) and historical development of nanomaterials membrane bioreactor technology has been depicted in Fig. 1c. The sustainability and cost-benefit analysis of NMs-MBR technology are also discussed in this work for broader application. Finally, the challenges and future perspectives of this new technology are provided.

FUNDAMENTALS OF NMS-MBR TECHNOLOGY

Despite the advantages of MBRs with respect to a smaller footprint and better treated water quality, the technology is limited by membrane fouling, which results in flux deterioration and downtime for membrane cleaning. The conventional MBR market is dominated by polymeric membranes such as polyvinylidene difluoride (PVDF) and polyethersulfone (PES)56–68. Among the various strategies investigated to reduce membrane fouling, improvement in membrane properties is one method. Examples include the implementation of NMS-MBR technology and other NM-based membranes69. The design and development of NMs-MBR systems represent a breakthrough technology as NMs-MBR are expected to comprehensively address the fouling issue while maintaining high flux and treated effluent quality. The set-up would be similar to conventional MBRs coupling aerobic or anaerobic biological treatment and membrane filtration, as shown in a typical schematic representation of submerged (a) aerobic NMs-MBR (ANMs-MBR)59 and (b) anaerobic NMs-MBR (ANMs-MBR)71 are shown in Fig. 2. NMs-based membranes are more effective than conventional membranes with respect to hydrophilicity, surface roughness, thermal stability, hydraulic stability, fouling control, higher water permeability, and higher selectivity due to their small surface pore size72,73. Because of the improved properties of NMs-based membranes, the system footprint can be further reduced and overall performance enhanced. The fabrication methods used for NM membranes focus mainly on the addition of NMs into the polymer support, but deposition of NMs on the surface of the membrane is also increasingly used74. To date, a variety of NM-based membranes, including nanofibres75, nanoparticles76, nanotubes77, nanocrystals78, nanowires79 and nanosheets80 have been used for water treatment applications.

NMS-MBR TECHNOLOGY: PERFORMANCES AND PROGRESS

The unprecedented success of NMs membrane is recognized as an alternative route to enhance the performance, including mitigation of fouling issues. Here, we summarize briefly the common types of NMs-MBR that have been used in wastewater treatment.

Nanoﬁbers membrane bioreactor (NFs-MBR)

Generally, nanofibers (NFs) membranes contain ﬁbers with diameters that are typically less than 100 nm80,81. NFs-based membranes offer a suitable platform for a variety of applications due to their extremely high aspect ratio, which helps them to interlock with each other in a subtle form. Of all the methods available for the fabrication of NFs membranes, electrospinning is the most common approach and is followed by several researchers and industries worldwide82,83. Electrospinning offers several advantages such as ease of operation, material selectivity, and low cost. Additionally, the fiber characteristics in terms of high porosity, surface-to-volume ratio and variable arrangements can be controlled84. The physical and chemical properties of electrospun NFs membranes can be easily adjusted for multi-purpose applications. In particular, several studies presented in the literature have shown that NFs membranes are highly effective adsorbents and catalysts85,86. For example, Sundaran et al. synthesized a novel polyurethane (PU)/graphene oxide (GO)-based electrospun NFs membrane for dye adsorption that could remove 95% methylene blue and 92% rhodamine B, respectively. Hosseini et al.88 prepared a novel montmorillonite (MMT) clay-chitosan/poly(vinyl alcohol) (PVA)-based electrospun NFs affinity membrane that removed 95% Basic Blue 41 (BB41) and was characterized by high flux and antifouling properties.

Motivated by the above mentioned potential of NFs membranes, researchers have coupled them with MBRs to create NFs-MBRs (Fig. 3). The use of electrospun NFs in MBRs was initiated by Bjorge et al.89 and different applications examined. First, the
membrane was functionalized using silver nanoparticles for pathogen removal; the functionalized membrane showed significantly higher pathogen removal (63%) than the non-functionalized membrane (10%). Second, the flat-sheet electrospun NFs membrane was used for wastewater treatment in a lab-scale submerged MBR. The results showed high removal of turbidity (99%), total suspended solids (TSS) (99%), COD (94%) and ammonium (NH$_4^+$) (93%). Last, wastewater generated in a music festival was treated in the NFs-MBR and the removal of suspended solids (SS), COD, total nitrogen (TN), and total phosphorus (TP) were within discharge limits.

Daeils et al.\cite{96} reported a comparative study of electrospun NFs membranes in three MBR set-ups viz., an activated sludge MBR, an activated sludge MBR with a cationic polymer (MPE50) flux...
enhancer, and a trickling filter (TF)-MBR. In the presence of the trickling filter, the NFs-MBR possessed better performance in terms of reduced irreversible fouling due to simultaneous turbidity removal of 75% by the membrane and trickling filter. Bilad et al.55 prepared electrospun NFs membrane and compared them with conventional commercial membranes in a lab-scale MBR. Heat treatment of the NFs membranes prevented layered fouling on the membrane surface and the overall performance was comparable to commercial membranes. Kim et al.91 fabricated and explored the performance of flat-sheet electrospun NFs membrane using PVDF blended with polymethyl methacrylate (PMMA) for wastewater treatment in the laboratory and pilot-scale MBR systems. The prepared membrane surface was much smoother and had higher levels of porosity and permeability than a conventional cast membrane, indicating lower fouling. In pilot tests with secondary effluent from the wastewater treatment plant of the local zoo, COD removal (48%) was low but suspended solids removal was complete.

Nanoparticles (NPs) addition in NFs membranes has also been reported. Zhao et al.92 fabricated three-dimensional (3D) woven fabric filters decorated with silver nanoparticles doped polyacrylonitrile (PAN) NFs for wastewater treatment in an MBR. Microscopy of the used membrane showed that NPs-embedded fabric filter surface had few clusters of proteins, bacteria cells and polysaccharides. The silver nanoparticles doped NFs membranes showed 40–50% higher flux and substantially greater flux recovery than the undoped membranes. The results were attributed to the excellent antimicrobial property of the silver nanoparticles. Moradi et al.56 investigated the performance of PAN electrospun NFs membrane deposited with fumarate-alumoxane (FumA) nanoparticles for use in an MBR application. Incorporating low amounts of FumA nanoparticles improved surface hydrophilicity and reduced the irreversible fouling in terms of the highest flux recovery ratio of 96% and the lowest irreversible fouling rate of 4% for 2 wt% Fum-A addition.

Fig. 2 A typical schematic representation of submerged nanomaterials membrane bioreactor (NMs-MBR). A typical schematic representation of submerged (a) aerobic nanomaterials membrane bioreactor (ANMs-MBR). The feed tank was loaded with wastewater influent and the mixture was ensured for continuous flow. Then feed tank was connected into the bioreactor tank through a pump and a membrane module (where different types of nanomaterials membrane can be used) was placed in the bioreactor tank and aeration medium was created by an air compressor in order to obtained simultaneous aeration/filtration system. In addition, a pressure gauge was activated to close the suction pump flow and open the backup channel when the range of transmembrane pressure out of standard and consequently fouling on the membrane surface appeared. Finally, the effluent tank collected clean water for further application. b Anaerobic nanomaterials membrane bioreactor (ANMs-MBR). The feed tank loaded wastewater influent was pumped into the bioreactor with a membrane module (where different types of nanomaterials membrane can be used). In this case, the reactor was fully air locked, and the production of biogas amount was detected by a portable gas meter. Subsequently, clean water was storage at the effluent tank for further use.
Nanoscale fibers-based membranes have also been used in extractive MBRs (EMBR), which is based on combining an aqueous-aqueous extractive membrane process and biodegradation. For example, Wang’s group first applied polydimethylsiloxane (PDMS)-coated PVDF nanofibrous composite membrane for phenol removal in EMBR. Results showed that after two weeks of operation, the mass transfer coefficient of phenol removal was stable at 4.1 ± 0.3 × 10⁻⁷ m s⁻¹; this was four times higher than with commercial silicone rubber. Subsequently, they developed a novel PDMS-coated NFs composite membrane with superhydrophobic or superhydrophilic surfaces with better performance. Among them, a nanofibrous membrane with superhydrophobic surface exhibited higher stability over 14 days for industrial wastewater treatment and demonstrated 10-times higher phenol extraction efficiency than that of the conventional PDMS membrane. On the other hand, superhydrophilic surface was covered by more polysaccharides and led to lower stability.

In another work, Shaot's group prepared PDMS/PMMA-based electrospun nanofiber membrane and used it in an EMBR system for phenol saline wastewater treatment. High mass transfer coefficient of phenol (8.8 × 10⁻⁷ m s⁻¹) and high salt rejection (>99.96%) indicated high selectivity of salt/phenol. The same membrane was used in treating phenol-laden saline wastewaters in a novel external EMBR system. High simultaneous removal of phenol (14.1–290.7 mg L⁻¹) and ammonium (0.5–43.5 mg L⁻¹) were achieved with a decrease in toxicity (6.3–70.5%).

The role of electrospun nanofiber membranes in anaerobic membrane bioreactors has been examined recently. Results showed that during short-term filtration test, the as-prepared PVDF nanofiber membrane performed better than the commercial membrane in terms of low transmembrane pressure (TMP) with excellent flux retention. Additionally, suspended solids removal was over 99%, which was comparable to the commercial membrane. The membrane is currently being investigated on a full-scale anaerobic membrane bioreactor system. Table 1 summarizes NFs-MBR technology used in wastewater treatment.

Nanoparticles membrane bioreactor (NPs-MBR) technology
The use of NPs represents a promising direction for enhancing the performance of NMS-based media in wastewater treatment due to their large surface area and size- and shape-dependent properties. Additionally, they are suitable for functionalization with several chemical groups to augment their catalytic properties. However, there are still some limitations to the widespread use of NPs in wastewater treatment applications. These include the separation of exhausted NPs from the treated water for reusability, their tendencies to aggregate in the system and the need for an in-depth understanding of the behavior and fate of NPs in the wastewater treatment systems. Hence, it is necessary to develop supporting material that could help to maintain their performance. Membrane-based materials are playing a key role in the development of novel NPs-based membranes for effective wastewater treatment.

Recent attempts have shown that NPs-embedded membrane can be used to improve the performance of MBR systems. Bae and Tak published a pioneering work on self-assembled titanium dioxide (TiO₂) nanocomposite membrane that reduced fouling significantly in MBR wastewater treatment system. This work inspired many researchers to investigate NPs-MBR systems for wastewater treatment. For instance, Su et al. explored a similar approach using a TiO₂ composite membrane in the MBR system. The presence of TiO₂ NPs coated on the membranes improved the surface hydrophilicity and reduced membrane fouling than the virgin membrane. Liu et al. developed nano-TiO₂/PVA polyester composite membrane with 10 μm pore size and tested in anoxic/oxic MBR systems. Incorporation of nano-TiO₂ played a significant role in improving membrane performance in terms of lower fouling rate with higher pure water flux, as well as higher removal of contaminants compared to commercial PVDF membrane. Hu et al. applied nano-TiO₂ on the PVDF membrane surface and tested in algal MBRs for wastewater treatment. The modified membrane showed the best removal efficiencies of P (78%) and N (34%); it had enhanced hydrophilicity and only 50% of the total resistance of the pristine membrane. Tavakolimoghadam et al. modified PVDF membrane surface by sputtered nano-TiO₂ and applied in MBRs. The modified membrane had higher hydrophilicity and two-fold improvement in the filtration index compared to the pristine membrane. In addition, minimal leaching of nano-TiO₂ particles occurred after washing, as confirmed by EDX analysis. Compared to pristine polypropylene membranes, polypropylene/TiO₂ nanocomposite membranes used in MBR for treatment of oil refinery wastewater showed better antifouling characteristics. The results demonstrated...
Table 1. Applications of nanofibers membrane bioreactor (NFs-MBR) system.

| Membrane materials | Membrane characteristics | Wastewater type/characteristics | Configuration | Operational conditions | Performance | Ref. |
|---------------------|--------------------------|-------------------------------|---------------|------------------------|------------|------|
| Polyamide (PA) 6, Polyamide 66, Polyamide 69 | Mean pore size = 0.21 µm, Fiber diameter = 250 nm, Area-weight = 20 g m⁻² | Synthetic wastewater | HT-MBR | V = 50 L, HRT = 0.5 d, R = 3/1, A = 0.0073 | Flux decreased | 55 |
| Polyacrylonitrile (PAN)/fumarate-alumoxane (Fum-A) nanoparticles | Fiber diameter = 223.16 nm, Porosity = 74.55%, Membrane area = 12.56 cm² | Industrial wastewater | Filtration + MBR | 400 rpm for 20 min, operating pressure of 1 atm and 25 °C | Flux recovery ratio, FRR (96%); lowest irreversible fouling (4%) for 2 wt% Fum-A addition | 56 |
| Polyacrylic acid (PAA), polysulfone (PSf) and polyethylenimine (PEI), polyamide (PA) | Mean pore size = 0.4 µm, Fiber diameter = 50–100 nm, Thickness = 120 µm | Municipal wastewater | Submerged MBR | V = 50 L, HRT = 0.5 d, R = 3/1, V/V = 2/1, A = 0.0073 m², T = 20 °C | Flux decreased | 57 |
| Polyvinylidene difluoride (PVDF), polymethyl methacrylate (PMMA) | Mean pore size = 0.45 µm, Porosity = 82.8 % | Synthetic wastewater | MBR | V = 12 L, Flux = 10 L m⁻² h⁻¹, HRT = 6 h, SRT = 10d, MLSS = 11,017 ± 980 mg L⁻¹, MLVSS = 10,858 ± 970 mg L⁻¹, DO = 7.0 ± 0.1 mg O₂ L⁻¹ | Short-term fouling | 58 |
| PAN/silver nanoparticles | Membrane area = 19.6 cm² | Municipal wastewater | Submerged MBR | V = 5 L, HRT = 20 h, MLSS = 4500–5200 mg L⁻¹, turbidity = 17.6 NTU, pH = 7.0–7.5, T = 12–20 °C | Flux recovery ratio (85%–93%) | 59 |
| PVDF | Nanofiber diameter = 129 ± 13 nm, Thickness = 56 ± 1 µm | Phenol solution | Extractive membrane bioreactor (EMBR) | V = 1 L, pH = 6.9 ± 0.4, flow rate = 15 mL min⁻¹, T = 20 °C | 4 times higher phenol extraction efficiency than that of the commercial silicone rubber | 60 |
| PVDF | Membrane area = 238 cm² | Industrial wastewater | Submerged EMBR | V = 1 L, pH = 6.9 ± 0.4, conductivity = 4.7 ± 0.4 mS cm⁻¹ | 10 times higher phenol extraction efficiency compared to the commercial membrane | 61 |
| PDMS/PMMA | Porosity = 64.9 ± 8.2%, Thickness = ~56.5 µm | Synthetic phenol saline wastewater | EMBR | V = 2 L, HRT = 24 h, flow rate = 0.083 L h⁻¹ | Phenol removal rate 5089 mg L⁻¹ d⁻¹, mass transfer coefficient 8.8 × 10⁻³ m s⁻¹ | 62 |
| PDMS/PMMA | Effective area = 0.0048 m² | Phenol-laden saline wastewater | External EMBR | V = 4.5 L, HRT = 20 h, DO = 5.5–1.5 mg L⁻¹, pH = 7.1–7.5, T = 24–26 °C | Phenol removal efficiency (99.2–100.0%) | 63 |
| PVDF | Effective area = 0.042 m² | Synthetic wastewater | Anaerobic membrane bioreactor | V = 5 L, HRT = 8 h, MLVSS = 3000 mg L⁻¹, COD = 450 mg L⁻¹, T = 25 °C | Suspended solids removal >99% | 64 |

V working volume, HRT hydraulic retention time, SRT sludge retention time, T temperature, COD chemical oxygen demand, TN total nitrogen, TP total phosphorous, N (NH₄-N) ammonium, DO dissolved oxygen, TSS total suspended solids, TOC total organic carbon, MLVSS mixed liquor volatile suspended solids, HT-MBR high-throughput membrane bioreactor, TF-MBR trickling filter membrane bioreactor.
that presence of small amount of nano-TiO$_2$ (0.75 wt%) enhanced the thermal and mechanical properties of the modified membrane besides increasing the critical flux (64 L m$^{-2}$ h$^{-1}$ for the modified membrane compared to 34.5 L m$^{-2}$ h$^{-1}$ for the pristine membrane).

Homayoonfal et al.\textsuperscript{109} examined polysulphone (PSf)/alumina nanocomposite membranes with the principal aim of reducing biofouling in the MBR system. Their filtration experiments demonstrated that the addition of alumina NPs increased the membrane hydrophilicity and resulted in 83% reduction in membrane fouling. In addition, 91% of dye rejection (DR) could be achieved, indicating that nanoparticles blended membranes enhanced MBR performance. A magnetic nanocomposite membrane influences MBR treatment performance, as reported by Mehrnia et al.\textsuperscript{13} They prepared a magnetic membrane by blending Fe$_3$O$_4$ NPs of size 60–70 nm into a PSf ultrafiltration membrane. The results demonstrate that nanocomposite membranes have 27% lower filtration resistance (Rf), 30% higher flux and led to 41% higher COD removal than a commercial membrane. Amini et al.\textsuperscript{110} introduced silica (SiO$_2$) NPs-based high-density polyethylene (HDPE) membranes for the MBR system. They produced a flat-sheet type of membrane via a thermally induced phase separation (TIPS) approach. An increased amount of SiO$_2$ NPs (0.5 wt.% and above) could enhance the membrane porosity, NPs addition controlled fouling with 70% reduction in irreversible fouling ratio. Liang et al.\textsuperscript{111} tethered superhydrophilic silica NPs to poly(methacrylic acid) grafted PVDF membrane for fouling control in an MBR system. While the bare membrane showed rapid flux decline to ~40% of the initial flux, the functionalized membrane maintained ~56% of the initial flux and flux recovery upon cleaning was ~100%.

NPs incorporated membranes have also been investigated in the electric field attached MBRs. Li et al.\textsuperscript{112} synthesized and tested graphene (Gr)/PANI-phytic acid membrane in such a system. Even with a small amount of graphene (0.02 mg L$^{-1}$), the membrane displayed good conductivity, antifouling and filtration properties. Liu et al.\textsuperscript{113} modified polyester filter cloth with Gr/polypyrrole (PPy) or GO/PPy and successfully investigated the antifouling property with yeast suspension. Application of electric field enhanced flux in the Gr/PPy modified membrane by 20% compared to 10% with the membrane modified by PPy alone.

Alsalhy et al.\textsuperscript{114} studied the effect of zinc oxide (ZnO) NPs on polyvinyl chloride (PVC) membrane performance for the treatment of hospital wastewater through MBR technology. The benefit of using ZnO NPs was that they acted as an antibiofouling material, thus overcoming the formation of a cake layer on the membrane surface. Addition of 0.1 g of ZnO NPs improved pure water permeability by 315% and a maximum flux recovery efficiency of 87% was obtained with the incorporation of 0.3 g of ZnO NPs. Functionalized NPs have also been incorporated in MBR membranes. Etemadi et al.\textsuperscript{115} prepared a dual functionalized nanodiamond (ND) using an amino group as well as polyethylene glycol (PEG) grafted onto a cellulose acetate (CA) nanocomposite membrane to improve its surface hydrophilicity and efficiency within the MBR system. Fouling recovery ratio of 95% was obtained. Tizchang et al.\textsuperscript{116} prepared silanized nanodiamond (SND) NPs intercalated PSf membrane that was tested in an MBR system for wastewater treatment. The neat PSf membrane exhibited a higher contact angle (83.10$^\circ$) and lower flux recovery ratio (FRR) (28.89%), while the functionalized membrane revealed higher FRR (58.93%) and improved hydrophilicity (contact angle 76.44$^\circ$). In sequence, they reported improved FRR in their other study carried out by Kivi et al.\textsuperscript{117} wherein nanodiamond nanoparticles were modified using two approaches viz. thermal carboxylation (ND-COOH) and grafting with polyethylene glycol (ND-PEG) and then used in preparing HDPE composite membrane for enhanced MBR system performance. Membranes with 0.75 wt % ND-PEG were the best in terms of high flux and anti-fouling properties exhibiting FRR of 77.9% compared to 61.7% for the bare membrane.

Pirsaheb et al.\textsuperscript{118} fabricated a novel nanocomposite PES membrane using hydrophilic polycitrate-Alumoxane (PC-A) NPs and achieved better MBR performance. The addition of these hydrophilic PC-A NPs increased the surface hydrophilicity of the membrane resulting in a high antifouling ability; complete turbidity removal was also obtained. Mahmoudi et al.\textsuperscript{119} prepared silver-decorated GO (Ag-GO)/PES membrane for MBR application. For the modified membrane, hydrophilicity was significantly improved (39 ± 2.9$^\circ$) compared to the bare membrane (67 ± 3.59$^\circ$). Moreover, the pristine membrane operation stability was limited to 20 h during MBR run, while the modified membrane continued to operate for a longer period with effective resistance against fouling. Ahsani et al.\textsuperscript{120} fabricated PVDF nanocomposite membrane with immobilized Ag-SiO$_2$ nanoparticles and tested it in a submerged MBR system treating real pharmaceutical wastewater. The nanocomposite membrane showed improved hydrophilicity and considerable antibiofouling ability with FRR of 76%, while the neat membrane surface exhibited more extracellular polymeric substance with a lower FRR of 58%. Behboudi et al.\textsuperscript{57} developed PVCmodified Ag NPs membrane; studies in an MBR system showed higher COD removal of 94% compared to 66% with the pristine membrane. Subsequently, they prepared and tested polyvinyl chloride/poly carbonate/modified silver NPs-based nanocomposite membrane.\textsuperscript{120} The presence of nanoparticles enhanced the membrane performance in MBR system in terms of higher removal percentage of COD (98.1%) and increased flux.
Nanotubes membrane bioreactor (NTs-MBR)

Nanotubes (NTs), which are primarily carbon-based materials, have received significant attention for removal of contaminants from wastewater. Their tunable properties, namely, high aspect ratios, large surface areas, easy functionalization and water transport, make them particularly attractive. Compared to activated carbon, carbon NTs offer the advantages of excellent self-assembly on supporting materials via chemical vapor deposition and can be immobilized in membrane filters. NTs-based membranes have been employed in MBR systems (NTs-MBR) to enhance the system performance (Fig. 5).

Rahimi and co-workers designed a novel membrane using multi-walled carbon nanotubes (MWCNTs) blended PES for an MBR system. The carbon NTs were initially functionalized with amino groups before embedding in the PES substrate using the phase inversion method. Different concentrations of MWCNTs (0.05, 0.1 and 1 wt.%) were used and the modified MWCNTs exhibited excellent stability (up to 5 h). Among the different membranes, 0.1 wt.% loaded sample showed high porosity (89.9%) and low contact angle (52°), leading to the most permeable membrane with pure water flux of 106.75 kg/m² h⁻¹. This membrane showed higher bovine serum albumin (BSA) rejection (~60%) compared to the control (bare) membrane (~25%). The anti fouling property was also improved with a FRR of 89.7% against 70% for the control; this was attributed to ionized amine groups on the modified MWCNTs surface bonding with a water layer thereby averting protein adsorption and consequent fouling.

In another study, Ayyaru et al. fabricated a novel PVDF membrane blended with CNTs, with and without sulfonation; these membranes were studied for sludge retention in a wastewater treatment plant via an MBR system. Though incorporation of CNTs improved the membrane properties compared to the pristine PVDF membrane, sulphonated CNTs were more effective compared to CNTs without functionalization. Incorporation of sulphonated CNTs increased membrane porosity (84%), enhanced hydrophilicity (contact angle of 51°) and improved protein (BSA) rejection (90%). The FRR (83.52%) was considerably higher than for the pristine PVDF membrane (50% FRR). Finally, the authors demonstrated that unlike the CNTs, the prepared modified membranes were non-toxic to bacteria.

Carbon nanotubes hollow fiber membranes (CNTs-HFMs) have also been developed and used in anaerobic electro-assisted membrane bioreactor. The performance of this novel system was quantified at low temperature (15 – 20°C) over an operation period of around 100-days. Good TMP recovery with a COD removal of over 95% was reported with the application of the electric field. Their next studies in anaerobic MBR with CNTs membrane in the presence of electric field showed a similar trend. It was noticed that after 120 min filtration, a relatively high membrane flux rate (412.2 L m⁻² h⁻¹) was achieved for electric-assisted MBR while flux rate was halved (200.6 L m⁻² h⁻¹) in the absence of electric field. The quality of treated effluent was good (COD < 50 mg L⁻¹, NH₄⁺-N < 2 mg L⁻¹). Overall, the results strongly demonstrated that the presence of electric field could significantly alleviate the fouling plus enhance pollutants removal during MBR operation.

Mulopo prepared CNTs-PSf nanocomposite membranes for use in an anaerobic MBR designed to treat the bleach effluent from pulp and paper industries. Permeability of the CNTs nanocomposite membrane was higher (0.6–0.7 L m⁻² h⁻¹) compared to the neat PSf membrane (0.15–0.25 L m⁻² h⁻¹); this is due to the O–H bonds that modifies membrane properties such as contact angle and roughness. However, COD and SS removal were similar with both membranes.

In another study by Khalid et al., CNTs were functionalized with PEG and used as nanofilms in the preparation of PSf nanocomposite membrane for wastewater treatment in MBR. They followed a non-solvent induced phase separation (NIPS) method. The prepared CNTs-PEG showed excellent dispersion stability even after 30 days without any agglomeration while the pure CNTs had poor dispersion stability of 1 day. The addition of varying amounts of CNTs-PEG (0.1–1.0 wt%) improved membrane hydrophilicity and water permeability. Best results were obtained with 0.25 wt% CNTs-PEG addition with increased hydrophilicity evinced by lower contact angle (57°) compared to 65° for pristine PSf membrane. The membrane porosity was higher—54% for CNTs-PEG PSf compared to 44% for pristine PSf. The permeability increased four-fold (from 4.41 L m⁻² h⁻¹ bar⁻¹ for pristine PSf to 16.84 L m⁻² h⁻¹ bar⁻¹ for CNTs-PEG PSf) and the FRR was enhanced as well (57% for pristine PSF against 80% for CNTs-PEG PSF). Table 3 presents the data of NTs-MBR technology used for wastewater treatment.

Carbon nanotubes hollow fiber membranes (CNTs-HFMs) have also been developed and used in anaerobic electro-assisted membrane bioreactor. The performance of this novel system was quantified at low temperature (15 – 20°C) over an operation period of around 100-days. Good TMP recovery with a COD removal of over 95% was reported with the application of the electric field. Their next studies in anaerobic MBR with CNTs membrane in the presence of electric field showed a similar trend. It was noticed that after 120 min filtration, a relatively high membrane flux rate (412.2 L m⁻² h⁻¹) was achieved for electric-assisted MBR while flux rate was halved (200.6 L m⁻² h⁻¹) in the absence of electric field. The quality of treated effluent was good (COD < 50 mg L⁻¹, NH₄⁺-N < 2 mg L⁻¹). Overall, the results strongly demonstrated that the presence of electric field could significantly alleviate the fouling plus enhance pollutants removal during MBR operation. Mulopo prepared CNTs-PSf nanocomposite membranes for use in an anaerobic MBR designed to treat the bleach effluent from pulp and paper industries. Permeability of the CNTs nanocomposite membrane was higher (0.6–0.7 L m⁻² h⁻¹) compared to the neat PSf membrane (0.15–0.25 L m⁻² h⁻¹); this is due to the O–H bonds that modifies membrane properties such as contact angle and roughness. However, COD and SS removal were similar with both membranes.
## Table 2. Applications of nanoparticles membrane bioreactor (NPs-MBR) system.

| Membrane materials                | Membrane characteristics | Wastewater type/characteristics | Configuration | Operational conditions | Performance | Ref. |
|-----------------------------------|--------------------------|---------------------------------|---------------|------------------------|-------------|------|
| Polyethersulfone (PES)/TiO$_2$ NPs | Membrane pore size = 0.2 µm | Synthetic wastewater            | Submerged MBR | SRT = 50 d, MLSS = 6900 mg L$^{-1}$, MLVSS = 4400 mg L$^{-1}$, T = 24 ± 2°C | Lower rate of membrane fouling | 51   |
| Polyethylene (PE)/Fe$_3$O$_4$ NPs | Membrane surface area = 23.75 cm$^2$ | Industrial wastewater          | MBR           | V = 7.5 L, pH = 8 ± 1, T = 25–27°C, SRT = infinite days | COD (98%), 30% higher flux, 27% lower filtration resistance | 53   |
| Polyvinyl chloride (PVC)/zinc oxide NPs | Membrane mean pore size = 504.35 nm, Mean roughness = 13.6 nm | Hospital wastewater            | UCT-MBR       | V = 8.0 L, HRT = 2 h, SRT = 25 d, T = 25 ± 2°C | COD (73.5%), FRE (87%) | 114  |
| High-density polyethylene (HDPE)/SiO$_2$ NPs | Membrane surface area = 14 × 10$^{-4}$ m$^2$ | Milk processing wastewater     | MBR           | V = 1.2 L, HRT = 24 h, SRT = 20 d, aeration rate 0.5 L min$^{-1}$, MLSS = 8000 mg L$^{-1}$ | COD (96.7%), FRR (89.9%) | 110  |
| Cellulose acetate (CA)/cellulose ester/TiO$_2$ NPs | Membrane surface area = 26.42 cm$^2$ | Yeast suspension solution      | Electric field MBR | V = 2.7 L, aeration rate = 0.2 m$^3$ h$^{-1}$, MLSS = 2000 mg L$^{-1}$ | ~11% higher filtration efficiency | 112  |
| PES/polyelectrolyte-alumoxane NPs | Membrane surface area = 12.56 cm$^2$ | Yeast suspension solution      | Electric field MBR | V = 4 L, aeration rate = 0.2 m$^3$ h$^{-1}$, MLSS = 5000 mg L$^{-1}$ | Better antifouling performance | 113  |
| Polyvinyl alcohol (PVA)/TiO$_2$ NPs | Membrane surface area = 40 cm$^2$ | Synthetic wastewater          | Submerged anoxic/oxic MBR (A/O-MBR) | V = 8 L, HRT = 6 h, SRT = 24 d, aeration = 2–3 m$^3$ m$^{-2}$ h$^{-1}$, MLSS = 6000–7000 mg L$^{-1}$, T = 15–20°C | Less fouling (87%), NH$_4$-N (97%), TN (80%) | 104  |
| PVDF/TiO$_2$NPs                  | Membrane surface area = 50 cm$^2$ | Synthetic wastewater          | Algal membrane bioreactor (A-MBR) | V = 4 L, HRT = 0.5 d, SRT = 25 d, T = 23 ± 2°C | Better antifouling property (78%), N (34%) | 105  |
| PVDF/TiO$_2$NPs                  | Membrane surface area = 15.89 cm$^2$ | Oil wastewater                 | Submerged MBR | V = 1.0 L, HRT = 25–28 h, SRT = 70–100 d, MLSS = 6000–7000 mg L$^{-1}$ | Higher pure water flux (95%), Lower fouling resistance | 106  |
| PES/Ag-GO                       | Membrane surface area = 38 cm$^2$ | Synthetic wastewater and sludge | Submerged MBR | V = 50 L, pressure = 0.6 bar, aeration = 8 L min$^{-1}$, MLSS = 8500 ± 750 mg L$^{-1}$, pH = 7 ± 0.5 | COD (>95%) | 119  |
| Polypropylene (PP)/TiO$_2$ NPs   | Membrane surface area = 14.7 cm$^2$ | Real wastewater                | Submerged MBR | V = 1.2 L, HRT = 24 h, SRT = 20 d, pressure = 0.1 bar, aeration = 0.5–1.5 m$^3$ m$^{-2}$ h$^{-1}$, MLSS = 7000 mg L$^{-1}$ | COD (70%) | 108  |
| PP/TiO$_2$ NPs                  | Membrane surface area = 14 cm$^2$ | Real wastewater                | Aerobic MBR   | V = 2.0 L, HRT = 24 h, SRT = 20 d, pressure = 0.1 bar, aeration = 0.5 L min$^{-1}$, MLSS = 7000 mg L$^{-1}$, T = room temp, pH = 6.8–7.6 | COD (65.16%) | 107  |
| PVDF/Ag-SiO$_2$ NPs             | Membrane surface area = 56.52 cm$^2$ | Pharmaceutical wastewater     | Submerged MBR | V = 20 L, HRT = 12 h, SRT = 20 d, pressure = 0.2 bar, MLSS = 7000–8000 mg L$^{-1}$ | COD (>90 %), NH$_4$-N (>95 %), FRR (58.93 %) | 116  |
| PS/ND                          | Membrane surface area = 11.07 cm$^2$ | Pharmaceutical wastewater     | Submerged MBR | V = 20 L, HRT = 12 h, SRT = 20 d, pressure = 0.2 bar, MLSS = 7000–8000 mg L$^{-1}$ | COD (>90 %), NH$_4$-N (>95 %), FRR (58.93 %) | 116  |
In another study, Li et al. developed Pd- reduced graphene oxide (rGO)/PVDF-carbon fiber cloth membrane and tested it for wastewater treatment in an MBR/MFC-coupled system. Here, Pd nanocrystal-rGO composite was synthesized and deposited on the surface of PVDF/carbon fiber through the electrodeposition process. The anti-fouling flux of the membranes was measured under two conditions viz. with and without application of electric field; the developed membrane functioned as a cathode. The presence of electric field enhanced the flux rate nearly two-fold 128–130 L m⁻² h⁻¹ compared to 66 L m⁻² h⁻¹ in the absence of electric field, indicating that membrane fouling could be controlled through the application of electric field during MBR operation. Removal of contaminants after 30 days of operation was stable with a high removal efficiency of COD (90%) and NH₄⁺–N (81%) being achieved. The details are presented in Table 4.

Nanowires membrane bioreactor (NWs-MBR)
Within the family of NMs membranes, nanowire (NW) membranes have also emerged as materials with excellent mechanical, chemical, and thermal stabilities for use in wastewater treatment. Nanowires offer higher aspect ratio (length to diameter/width ratio) of over 1000 compared to other one-dimensional nanomaterials such as nanofibers with an aspect ratio of 3–5; this makes nanowires useful in environmental applications. The presence of NWs on a membrane surface enhanced pollutant removal and compared to conventional membranes, NW membranes exhibit flexible, uniform and multifunctional activity and could be used to remove other foulants such as microorganisms and trace organics.

NWs-based membranes can be used in MBRs (NWs-MBR) to control membrane fouling and to achieve high treatment efficiency (Fig. 7). The only scientific article on NWs-MBR was published recently by Yin et al. where they prepared an innovative Cu-NW conductive microfiltration membrane and used it successfully in MBR application. Long-term operation was conducted at the presence of spontaneous electric field (SEF-MBR) to enhance the reduction in membrane fouling. In the initial 40 days, the membrane flux decreased and then became stable for both the Cu-NW membrane and commercial PVDF membrane. The SEF-MBR flux was 2.1 times higher than the control MBR with the commercial PVDF membrane; the fouling layer of around 80 μm on the Cu-NW membrane surface was thinner than on the PVDF membrane (179 μm). Monitoring the extracellular polymeric substances (EPS) on the membrane surface as an indicator of the extent of fouling showed that the total EPS amount was 62.0 mg/g VSS for the commercial PVDF membrane, while Cu-NW membrane surface had a lower total EPS content of 42.4 mg/g VSS. COD, total nitrogen and total phosphorous removal (94.5%, 78.5%, and 86.6%, respectively) were marginally better in the SEF-MBR when compared to the conventional MBR (92.7% COD, 70.5% total nitrogen and 80.4% total phosphorous removal). Overall, these results suggested that novel NMs-based membranes combined with an electric field could considerably enhance MBR performance. The details are presented in Table 4.

Nanosheets membrane bioreactor (NSs-MBR)
Nanosheets, two-dimensional (2D) NMs with atomic or molecular ratios, have received significant consideration as next-generation membrane materials for wastewater treatment. Various kinds of nanosheet membranes, such as boron nitride (BN) nanosheet membranes, GO nanosheet membranes, titania nanosheet membranes, molybdenum disulfide (MoS₂) nanosheet membranes and graphitic carbon nitride (g-C₃N₄) nanosheet membranes have been used in water purification. Among these, the GO-based nanosheet membranes have demonstrated high efficiency due to their high charge density, different oxidation states and high mechanical strength.

Table 2 continued

| Membrane materials | Membrane surface area | Membrane characteristics | Operational conditions | Performance | Ref. |
|--------------------|-----------------------|--------------------------|------------------------|-------------|------|
| HDPE/ND-PEG         | 147 cm²               | Submerged MBR            | V = 50 mL, HRT = 24 h, SRT = 25 d, pressure = 3 m³−2 h−1, MLSS = 7500 mg L⁻¹, T = 25 °C  | Flux recovery efficiency = 71.9% | 31   |
| PVC/polycarbonate/AgNPs | 147 cm²               | Submerged MBR            | V = 25 mL, HRT = 4 h, SRT = 25 d, pressure = 0.1 bar, aeration = 1 L min⁻¹, MLSS = 7500 mg L⁻¹, T = 25 °C | Flux recovery efficiency = 99.8% | 31   |
| PC/Ag NPs           | 147 cm²               | Submerged MBR            | V = 25 mL, HRT = 24 h, SRT = 25 d, pressure = 0.1 bar, aeration = 1 L min⁻¹, MLSS = 7500 mg L⁻¹, T = 25 °C | Flux recovery efficiency = 99.8% | 31   |

The developed membrane functioned as a cathode. The presence of electric field enhanced the flux rate nearly two-fold 128–130 L m⁻² h⁻¹ compared to 66 L m⁻² h⁻¹ in the absence of electric field, indicating that membrane fouling could be controlled through the application of electric field during MBR operation. Removal of contaminants after 30 days of operation was stable with a high removal efficiency of COD (90%) and NH₄⁺–N (81%) being achieved. The details are presented in Table 4.

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NWs-based membranes can be used in MBRs (NWs-MBR) to control membrane fouling and to achieve high treatment efficiency (Fig. 7). The only scientific article on NWs-MBR was published recently by Yin et al. where they prepared an innovative Cu-NW conductive microfiltration membrane and used it successfully in MBR application. Long-term operation was conducted at the presence of spontaneous electric field (SEF-MBR) to enhance the reduction in membrane fouling. In the initial 40 days, the membrane flux decreased and then became stable for both the Cu-NW membrane and commercial PVDF membrane. The SEF-MBR flux was 2.1 times higher than the control MBR with the commercial PVDF membrane; the fouling layer of around 80 μm on the Cu-NW membrane surface was thinner than on the PVDF membrane (179 μm). Monitoring the extracellular polymeric substances (EPS) on the membrane surface as an indicator of the extent of fouling showed that the total EPS amount was 62.0 mg/g VSS for the commercial PVDF membrane, while Cu-NW membrane surface had a lower total EPS content of 42.4 mg/g VSS. COD, total nitrogen and total phosphorous removal (94.5%, 78.5%, and 86.6%, respectively) were marginally better in the SEF-MBR when compared to the conventional MBR (92.7% COD, 70.5% total nitrogen and 80.4% total phosphorous removal). Overall, these results suggested that novel NMs-based membranes combined with an electric field could considerably enhance MBR performance. The details are presented in Table 4.
The critical flux was obtained compared to the pristine PVDF membrane. A small amount of SLGO coating (6.2 mg m\(^{-2}\)) was adequate to obtain 99% TOC removal in long-term MBR operation. The reason could be explained that the GO flates were grafted by extra functional groups such as carboxyl or hydroxyl groups during UV-irradiation, which promoted the performances.

In 2014, Zhao et al.\(^{65}\) developed a novel composite microfiltration membrane by blending PVDF and GO nanosheets for MBR system. The GO-modified membrane showed higher hydrophilicity (contact angle of 60.50 ± 1.80°) than pristine PVDF membrane (contact angle of 78.30 ± 2.40°) because of the hydrophilic nature of GO, which actively increased the surface charge ratio of oxygen-containing groups on the membrane surface. Larger pore size (0.089 μm) and higher water permeability (552 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)) was obtained compared to the pristine PVDF membrane (0.041 μm pore size and 171 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) water permeability). The critical flux (the flux above which deposition of particles or colloids occurs rapidly on the membrane surface forming cake or gel layer) was higher for the modified membrane (48–50 L m\(^{-2}\) h\(^{-1}\)) compared to the pristine PVDF (30–33 L m\(^{-2}\) h\(^{-1}\)). Concentration of EPS (17.87 g/m\(^2\)) deposited on the pristine PVDF membrane was over three-time higher than with the modified membrane (5.97 g/m\(^2\)). As a consequence of this lower fouling, cleaning frequency was reduced with the modified membrane exhibiting three-times longer filtration time than the PVDF membrane.

Ghalamchi et al.\(^{150}\) prepared a novel PES microfiltration membrane containing g-C\(_3\)N\(_4\) nanosheets/Ag\(_3\)PO\(_4\) NPs through a phase inversion process for use in an MBR system. The addition of nanosheets improved the hydrophilicity of the prepared membrane compared to the bare PES membrane. Water flux was enhanced from 262 L m\(^{-2}\) h\(^{-1}\) to 360 L m\(^{-2}\) h\(^{-1}\) with a loading of 0.5 wt% nanosheet on the membrane surface. Moreover, the antifouling ability (determined with BSA filtration) was improved with an FRR of 57.5% for the nanosheet membrane; this was higher than the FRR of the bare PES membrane (39.1%).

Zinadini et al.\(^{151}\) synthesized GO nanosheet intercalated PES membranes with varying amounts of PES and GO for the treatment of milk process wastewater in an MBR system. Addition of GO decreased the contact angle and increased the water flux. A combination of 15 wt% PES loaded with 0.5 wt% GO was the most optimal in terms of high water flux and anti-fouling ability (FRR of 92.8%). The MBR performance improved at high mixed liquor suspended solids (MLSS) concentration of 14,000 mg/L with high flux (~30 kg m\(^{-2}\) h\(^{-1}\)) and high removal of COD (95.4%), TN (66.8%) and TP (76.1%).

Fig. 8 displays the schematic for NSs-MBR system for wastewater treatment. In a recent study, Fathizadeh et al.\(^{64}\) prepared novel PES hollow fiber (HF) membranes coated with single-layer GO nanosheet (SLGO) and UV-treated SLGO and successfully tested these in MBR applications. The pure PES membrane surface roughness was 44 nm and after loading of SLGO, it decreased to 33 nm due to the UV-irradiation process. Also, the modified membrane exhibited excellent permeability (65 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)) and the low fouling (<15% permeance reduction) compared to the pure PES membrane. A small amount of SLGO coating (6.2 mg m\(^{-2}\)) was adequate to obtain 99% TOC removal in long-term MBR operation. The reason could be explained that the GO flates were grafted by extra functional groups such as carboxyl or hydroxyl groups during UV-irradiation, which promoted the performances.

In another work, Wu et al.\(^{154}\) prepared PVP-GO/PVDF membrane through the chemical grafting approach and applied the membranes in algae-membrane photo-bioreactor (MPBR) systems for treating organic-rich wastewater. The PVP-GO/PVDF membrane demonstrated higher hydrophilicity (contact angle 62°) compared to the pristine PVDF membrane (contact angle 97°) and a remarkable improvement in pure water flux from 380 L m\(^{-2}\) h\(^{-1}\) (pristine membrane) to 614 L m\(^{-2}\) h\(^{-1}\) (PVP-GO/PVDF membrane). Moreover, contaminants removal efficiency in PVP-GO/PVDF–MBR (COD 97.8%, NH\(_4\)-N 96.8%, NO\(_3\)-N 76.9%) was higher than that in conventional PVDF-MBR (COD 93%, NH\(_4\)-N 93.1%, NO\(_3\)-N 70.6%). The details are presented in Table 4.

### MEMBRANE FOULING

It is well recognized that membrane fouling in MBRs continues to be a major challenge\(^{136}\). Fouling in MBRs resulting from an interaction between the sludge components and the membrane material, can be either reversible or irreversible. While reversible fouling can be removed by applying physical treatments like air sparging and backflushing, chemical cleaning is needed to eradicate irreversible fouling. Reversible fouling always has a higher fouling rate than irreversible fouling\(^{153}\). From the foulant materials perspective, fouling can be classified under biological,
Applications of nanotubes membrane bioreactor (NTs-MBR) system.

| Membrane materials | Wastewater type | Membrane area | Working volume | HRT | COD | Mixed liquor suspended solids | Sludge retention time | MF recovery ratio | Cost savings |
|--------------------|-----------------|---------------|----------------|-----|-----|-------------------------------|----------------------|------------------|-------------|
| Polyvinylidene diﬂuoride (PVDF)/CNTs | Industrial wastewater | 1.256 m² | 0.18 m³ | 7 | 25 °C | 5500 mg L⁻¹ | 10 days | 92% | 60% |
| Polyvinyl butyral (PVB)/CNTs/MWCNTs | Paper industry wastewater | 0.18 m³ | 0.18 m³ | 8 | 20 °C | 14000 mg L⁻¹ | 15 days | 96% | 80% |
| Polysulfone (PSf)/CNTs | Protein solution | 2.98 x 10⁻³ m² | 0.18 m³ | 25 | 20 °C | 1700 mg L⁻¹ | 15 days | 92% | 80% |

SUSTAINABILITY AND COST VIABILITY

The concept of sustainability in wastewater treatment has been of concern in the scientific community for many years. In the literature, there are many studies available on the development of membranes incorporating NMs using green chemistry principles, but the application of such membranes in MBRs for wastewater treatment are not yet reported on a lab-scale/commercial scale. For example, Lv et al.159 fabricated electrospun nanofibrous PVA and konjacglucomannan (KGM)-based membranes loaded with ZnO nanoparticles with ecofriendly thermal cross-linking. These membranes were tested for environmental applications such as air filtration, photocatalytic degradation of dyes and bacteria. In another study, Ren et al.160 reported poly(lactic acid) (PLA)
Fig. 6 Conceptual illustration of nanocrystals membrane bioreactor (NCS-MBR) technology. The synthesis of nanocrystals was possibly hydrolysis step was followed. Then, it was added to the glass plate nanocrystal membrane. Accordingly, the as-prepared membrane was fixed in the MBR membrane module in order to have a better quality of effluent.

stereocomplex crystallite (SC)-based electrospun nanofibers loaded with an adsorbent obtained by the polymerization of tannic acid and hexamethylenediamine for Cr(VI) removal. Environment-friendly plant-based components have also been examined. Copper oxide nanoparticles, produced by plant mediated green synthesis, have been incorporated in PES-CA nanocomposite membranes and plant extracts like curcumin in the nanomaterial form have been incorporated in PES membrane matrix. The importance of nanomaterial choice has been emphasized with low-cost and non-toxic materials such as chitosan and iron-based nanomaterials being recommended based on sustainability aspects.

From the literature, it is evident that while membranes incorporating NPs and to a lesser extent, NFs, have been investigated extensively for MBR applications, there are limited studies on membranes based on other NMs (NCS, NTs, NSS). This is possibly because NFs can be readily manufactured since electrospinning is a well-established process; also nanoparticles and CNTs are widely available commercially. Nanoparticles anchored on polymeric membranes and electrospun nanofiber membrane surface has demonstrated long-term permeability and better antifouling ability. Moreover, though NMs such as nanospheres, nanorods, and quantum dots-based membranes have been applied for wastewater treatment, they have not yet been used in MBR applications. Among these, quantum dots-based membrane could be one of the most effective membranes for MBR applications due to better hydrophilicity, permeability and fouling resistance properties.

The cost of NMs-based membranes needs to be established. Bjorge et al. estimated NFs membranes cost to be 20€/m² that is cheaper than commercial membranes (50€/m²). Fatarela et al. estimated the production cost of NFs membranes to be 5€/m², with the major cost component (75%) coming from the non-woven support. Indeed, the use of cheaper supports can reduce the total cost. This cost is much lower than the cost of traditional cast polymeric membranes, which run to 14–50€/m² (refs. 9,90). However, the cost of raw materials for the development of NMs membranes can be quite varied. For example, reports suggest that clay-based NMs membranes enhance the pollutants removal capacity from wastewater in a sustainable way but there is a huge inequality in price between clays and some polymers (Supplementary Table S1). However, more detailed cost-benefit analyses are required for the future development of NMs-MBR systems.

EMERGING APPLICATIONS OF NMS-MBR TECHNOLOGY

This review focuses on wastewater treatment applications of novel NMs-MBR technology. However, based on the previous success of conventional MBRs, NMs-MBR technology can also be employed in other emerging areas. The treatment of landfill leachates is one of the critical issues in environmental pollution control. A high concentration of organic and inorganic compounds, including micropollutants can be found in landfill leachates thereby threatening the quality of surface and groundwater sources. There have been a number of successful studies on the treatment of landfill leachates using MBR technology, thus, NMs-MBRs can be readily employed in this application. - 54. Dabaghian et al. reported a comprehensive review of the potentiality of nanostructured membranes for landfill leachate treatment, and suggested that NMs membrane could lead to greater benefits than commercial membranes. Yet another prospect is in the area of anaerobic digestion (biomethanation) of organic wastes (including excreta) that includes the steps of hydrolysis, acidogenesis, acetogenesis and methanogenesis. Addition of nanomaterials helps to accelerate the digestion process, resulting in a high amount of volatile fatty acids (VFAs) and biogas being produced. Instead of biogas production, alternatives such as hydrogen generation, recovery of VFAs for chemicals production etc. are being increasingly explored. MBRs are being employed in this application and thus NMs-MBRs also have potential. With the increasing shift from waste treatment to resource recovery, nutrients (nitrogen and phosphorus) recovery is another key area; in this context, hybrid systems including MBR-based hybrids have been recommended. With an emphasis on reducing energy use and recovering resources, anaerobic MBRs are being investigated extensively. NMs-MBRs especially have a role in this sector considering the more serious membrane fouling that is encountered in anaerobic MBR systems.

CHALLENGES AND FUTURE PERSPECTIVE

In spite of the progress in the application of nanomaterials-based MBR systems for wastewater treatment, there are challenges to be addressed for accelerating the practical application of NMs-MBR technology. It is necessary to justify the possible environmental threats that may be associated with this technology. Leaching of nanomaterials into aquatic environments can occur during long-term operation of such NMs-MBR, during the membrane synthesis process itself as well as due to inappropriate disposal of used membranes. The nanomaterials so released can undergo an environmental transformation, be taken-up by various aquatic organisms and could potentially pose a risk to both human health and environmental systems. Assessment of nanomaterials membrane stability and understanding the dynamics of the release of nanomaterials from the membrane matrix is, therefore, a crucial part of the long-term NMs-MBR operation; besides the environmental implications, leaching of nanomaterials from the membrane surface could adversely impact membrane performance and its lifespan. For instance, the antimicrobial properties
Table 4. Applications of nanocrystals membrane bioreactor (NCs-MBR), nanowires membrane bioreactor (NWs-MBR), and nanosheets membrane bioreactor (NSs-MBR) system.

| Types of Membrane reactors | Membrane materials | Membrane characteristics | Wastewater type/characteristics | Configuration | Operational conditions | Performance | Ref. |
|---------------------------|-------------------|--------------------------|-------------------------------|---------------|------------------------|-------------|------|
| NCs-MBR                   | Polyvinylidene difluoride (PVDF)/graphene oxide (GO)-cellulose nanocrystal (CNC) | Membrane area = 72 cm² | Municipal wastewater | MBR | $V = 3.43 \, L$, HRT = 24 h, SRT = 300 d, MLVSS = 4000–5000 mg L⁻¹, flux = 45 ± 1 L m⁻² h⁻¹, $T = 20–25 ^\circ C$ | High flux recovery ratio (FRR) | 61 |
|                           |                   |                          | COD = 378 ± 30 mg L⁻¹, BOD₅ = 207 ± 15 mg L⁻¹, NH₄⁺-N = 42 ± 4.5, SS = 195 ± 10 mg L⁻¹, TN = 42 ± 4.5 mg L⁻¹, PO₄³⁻ = 4 ± 1.5 | |                   | | |
|                           |                   |                          | Sewage wastewater | MBR/MFC | HRT = 24 h, aeration = 0.5 m³ m⁻² h⁻¹ | Stable membrane flux COD (99%), NH₄⁺-N (88%) | 62 |
| NWs-MBR                   | Cu-NW6             | Membrane area = 2.5 × 5.8 cm² | Municipal wastewater | SEF-MBR | $V = 0.028 \, L$, $T = 30 ± 1 ^\circ C$ | High membrane flux COD (93.3%), TN (76.1%), TP (82.3%) | 63 |
|                           |                   | Membrane pore size = 0.1 ± 0.01 µm | COD = 756.1 ± 9.1 mg L⁻¹, TN = 40.3 ± 1.5 mg L⁻¹, TP = 4.7 ± 0.7 mg L⁻¹ | | | | |
| NSs-MBR                   | Single-layer graphene oxide (SLGO)/polyethersulfone (PES) | Membrane area = 10 cm² | Metropolitan wastewater | Submerged MBR | $V = 1 \, L$, MLSS = 8000 mg L⁻¹, $T = 7$ | Low fouling resistance | 64 |
|                           |                   |                          | COD:N:P ratio = 100:5:1, organic loading rate (OLR) = 4.8 kg m⁻³ d⁻¹ | | | | |
|                           | PVDF/GO nanosheets | Membrane area = 0.0162 m² | Municipal wastewater | MBR | $V = 10 \, L$, HRT = 12 h, SRT = 40 d, aeration = 2–3 m³ m⁻² h⁻¹, MLSS = 4000–5000 mg L⁻¹, flux = 10–12 L m² h⁻¹, $T = 20–25 ^\circ C$ | High critical flux COD (87.1%), NH₄⁺-N (93.7%) | 65 |
|                           |                   |                          | COD = 13.1 ± 5.3 mg L⁻¹, BOD₅ = 1.535 mg L⁻¹, TN = 273 mg L⁻¹, TP = 80.2 mg L⁻¹ | | | | |
|                           |                   | Dairy wastewater | Submerged MBR | $V = 2 \, L$, MLSS = 6140 mg L⁻¹ | FRR (57.5%) | | 150 |
|                           | PES/Ag₃PO₄/g-C₃N₄ | Membrane area = 25 cm² | Milk processing wastewater | MBR | $V = 6.45 \, L$, HRT = 6 h, MLSS = 14000 mg L⁻¹, $pH = 7–8$ | Greater fouling resistance COD (95.4%), BOD₅ (95.1%), TN (66.8%), TP (76.1%) | 151 |
|                           |                   |                          | DO = 3–4 mg L⁻¹, BOD₅ = 1.535 mg L⁻¹, TN = 273 mg L⁻¹, TP = 60.2 mg L⁻¹ | | | | |
|                           |                   | Synthetic wastewater | Submerged MBR | $V = 7 \, L$, HRT = 24 h, MLSS = 6000–6500 mg L⁻¹, SRT = 25 d, TMP = 0.1 bar, aeration = 2–2.5 m³ m⁻² h⁻¹, $T = 25 ^\circ C$ | FRR (80.81%) | 152 |
|                           | PVDF/PVP-GO nanosheet | Membrane area = 14.7 cm² | High ammonia nitrogen wastewater | MPBR | $V = 24 \, h$, SRT = 30 d, TMP = 0.1 bar, aeration = 1.5 m³ m⁻² h⁻¹, $T = 25–30 ^\circ C$, $pH = 7.5–8$ | Higher permeability and flux recovery rate COD (97.8%), NH₄⁺-N (96.8%), NO₃⁻-N (76.9%) | 154 |
|                           |                   |                          | COD = 1996 mg L⁻¹, NH₄⁺-N = 71.9 mg L⁻¹ | | | | |

V: working volume, HRT: hydraulic retention time, SRT: sludge retention time, T: temperature, COD: chemical oxygen demand, TP: total phosphorus, TN: total nitrogen, N (NH₄-N): ammonium, NO₃-N: nitrate nitrogen, DO: dissolved oxygen, MLVSS: mixed liquor volatile suspended solids, MLSS: mixed liquor suspended solids, FR: flux recovery, FRR: flux recovery ratio.
of the membrane could be improved by the addition of silver nanoparticles as biocidal agents but if continuously leached into water bodies, the desirable properties would not be achieved\textsuperscript{48,182,183}.

Yet another challenge is the large-scale manufacture of the NMs membranes. Various techniques such as roll-to-roll, phase inversion, interfacial polymerization, stretching, track-etching and electrospinning process are in use. The roll-to-roll technique is

Fig. 7 Conceptual illustration of nanowires membrane bioreactor (NWs-MBR) technology. Nanowires membrane was also prepared by following the phase inversion method. A variety of polymeric materials and nanowires were gradually mixed to obtain a homogeneous solution and cast on non-woven support, which is termed as nanowires membrane. Finally, the as-prepared nanowires membrane was used in the MBR configurations for purifying water.

Fig. 8 Conceptual illustration of nanosheets membrane bioreactor (NSs-MBR) technology. At first, GO nanosheet was prepared by adding a known amount of graphite powder and mixed with a polymeric solution. After sonication, a homogeneous solution was observed and placed on a non-woven cloth by a casting knife. Then, the formed membrane was placed in the water bath for 24 h for using in the MBR module. Moreover, clean water was collected for further use.

Fig. 9 Fouling mechanism in nanomaterials membrane bioreactor (NMs-MBR) operation. There are three types of membranes were chosen for understanding the fouling mechanism. Pristine PVDF membrane, the attachment of EPS, sludge flocs and suspended particles are higher than CNC/PVDF membrane, while a very few opportunities were observed for GO-CNC/PVDF membrane. More water molecules pass through the GO-CNC/PVDF membrane and less fouling occurred sequentially.
still preferable for manufacturing of membranes, but it is a time-consuming process with low selectivity and difficulty in membrane pore size tuning\(^{184}\). Phase inversion and interfacial polymerization are widely used membrane fabrication techniques to obtain low-surface roughness, which is of primary interest to develop low-fouling membranes. However, phase inversion and interfacial polymerization induced membranes have low water permeability that would have to be enhanced through functionalization approaches\(^{185}\). The stretching method is useful to fabricate hydrophobic membranes but organic and biofouling propensity restricts its application. The track-etched method-based membrane offers some unique features such as low-surface roughness, but the low flux due to small porosity and high cost makes them less attractive\(^{186}\). Electrospinning technique is increasingly becoming popular as it offers a simple preparation method and different sizes of membranes can be produced; the challenge lies in jet instability, use of toxic solvents and adjustment of various operation parameters that are required to obtain membranes of adequate quality\(^{89,187}\). According to our knowledge, many companies have started large-scale production of membranes/filters incorporating nanomaterials targeted at various applications (Table 5). Though this is not exactly what we proposed (use of such membranes in MBRs), considering the widespread applications of nanomaterials-based membranes/filters in water and wastewater segment, it can be expected that the MBR segment will subsequently be covered comprehensively by such products.

In short, it is imperative to find out the best possible solutions for the NMs-MBRs technology by mitigating the challenges as described previously. Efforts to prevent leaching of nanomaterials would involve more robust methods of fixing the nanomaterials on the membrane matrix such as chemical grafting. Advanced fabrication options that are both scalable and cost-effective need to be investigated; in this context additive (3D) manufacturing holds promise\(^{188}\). Additionally, operation parameters, feed characteristics and reactor configurations need to be suitably adjusted with effective protocols for NMs-MBR systems. In particular, maintenance practices including cleaning procedures have to be evolved and implemented regularly to control the operating cost and output. Consequently, the assessment of techno-economic analysis data available specifically on NMs-MBRs technology, but it can follow models for conventional MBRs, which have been published in recent years\(^{190-192}\). It is of importance to control fouling by adopting different strategies. Lab-scale to real-scale transition must be started by maintaining the potential benefits such as sustainability and energy consumption. These aspects would, therefore, be key in promoting NMs-MBR technology for wastewater treatment.

### CONCLUSION

This paper has critically reviewed the progress in the development of NMs-MBR applications for wastewater treatment. The possibility of synthesizing nanomaterials incorporated novel membranes with specific properties opens up opportunities for their use in MBR systems for wastewater treatment. While the use of NMs-MBR technology demonstrates good performance in terms of lower fouling and enhanced removal efficiency of pollutants, there are several aspects that are poorly understood presently. These include the cost of large-scale manufacture of such membranes, their lifespan in full-scale applications, the possibility of leaching of the nanomaterials in the wastewater/sludge etc. These issues should be further investigated before integration of nanomaterials membranes with MBRs, which will assist in designing next-generation MBRs technologies.

### DATA AVAILABILITY

The datasets generated during the current study are available from the corresponding author on reasonable request (Prof. Vincenzo Naddeo, V.N.).

### CODE AVAILABILITY

No code was attempted or used during the current manuscript.

Received: 14 May 2020; Accepted: 12 October 2020; Published online: 05 November 2020

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