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Poly (amido amine) dendrimer based membranes for wastewater treatment – A critical review

Ahmed T. Yasir [a,b], Abdelbaki Benamor [a,b,*], Alaa H. Hawari [c], Ebrahim Mahmoudi [d]

[a] Gas Processing Center, College of Engineering, Qatar University, 2713 Doha, Qatar
[b] Department of Chemical Engineering, College of Engineering, Qatar University, 2713 Doha, Qatar
[c] Department of Civil and Architectural Engineering, Qatar University, 2713 Doha, Qatar
[d] Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia, Malaysia

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ABSTRACT

Membrane based wastewater treatment technologies in which polymeric membranes are most commonly used have been extensively applied in water/wastewater treatment to help address the issue of water shortage through water/wastewater reclamation and reuse. However, polymeric membranes due to their hydrophobic nature are subject damage caused by accumulation of organic/inorganic fouling during filtration processes, which results in a number of issues such as low water flux and low pollutant rejection. Several strategies have been considered to address these challenges and effectively improve the membrane performances. Alteration of membrane properties strategy using suitable nanofillers such us poly (amido amine) or PAMAM has been largely studied. Herein, research efforts regarding the synthesis and properties of PAMAM along with the synthesis of PAMAM multifunctional nanocomposites were concisely reviewed for the first time. Membrane performance enhancement by incorporation of PAMAM were reviewed and discussed. Results and contributions achieved in the improvement of PAMAM incorporated membranes for the treatment of different types of wastewaters has been reviewed and summarized. Furthermore, perspectives on the current challenges and future research needs in the development and application of PAMAM incorporated polymeric membranes to benefit from the potentials that offer these promising new membrane nanofiller were discussed,

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* Corresponding author at: Gas Processing Centre, College of Engineering, Qatar University, 2713 Doha, Qatar.
E-mail address: benamor.abdelbaki@qu.edu.qa (A. Benamor).

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1. Introduction

The worldwide demand for freshwater in 2019 was estimated at 4,600 km^3 and is expected to increase by 20% to 30% within the next 30 years (Boretti and Rosa, 2019; Hawari et al., 2020; Yasir et al., 2020). Wastewater reclamation and reuse could be one of the solutions to tackle the problem of limited fresh water supplies. Membrane technologies are at the forefront to implement the proposed wastewater treatment and reuse solution. Compared to other wastewater treatment technologies, membrane-based technologies are advantageous owing to their modular design, operational simplicity, energy efficiency, lack of phase change, and minimal chemical requirements (Hawari et al., 2019; Kang and Cao, 2014). However, the membrane technologies suffers from low water permeability and low selectivity.

The permeability and selectivity of the membrane depend primarily on the pore size of the membrane. Higher pore size promotes permeability at the expense of low selectivity and vice versa (Mehta and Zydney, 2005). The selectivity depends on the size of the pollutant molecule where smaller molecules can easily pass through larger membrane pores. Apart from pore radius, pore geometry, membrane thickness, and membrane hydrophilicity also affect water permeation. Chandler and Zydney studied the effect of pore geometry in microfiltration for yeast cell removal. They concluded that water permeation is better for slit-shaped pores compared to circular pores (Chandler and Zydney, 2006). Worrel et al. carried out microfiltration of SiO_2 & polystyrene particles and concluded that ellipsoidal pores promote higher membrane flux compared to cylindrical pores (Worrel et al., 2007). Wu et al. grafted varying thicknesses of poly(N-isopropyl acrylamide) on polyethylene terephthalate membrane and found that increasing thickness negatively affects the membrane permeability (Wu and Sancaktar, 2020). Membrane with high thickness has high mass transfer coefficient which reduces the membrane permeability. Along with pore geometry and membrane thickness, membrane hydrophilicity also affects the permeability and anti-fouling propensity of the membrane (Sawada et al., 2012).

During the operational period, high hydrophobicity causes excessive fouling of the membrane surface. This fouling is caused by the following four types of pollutants:

(i) particulates that physically bind on the membrane surface and pores,
(ii) organics that would attach to the membrane surface due to adsorption,
(iii) inorganics that would precipitate on the membrane surface due to a change of pH value or oxidation and
(iv) micro-biological organisms that may adhere to the membrane surface and form a bio-film (Guo et al., 2012).

According to Lee et al. cake formation is the leading cause of membrane fouling (Lee et al., 2001). This type of fouling occurs due to the deposition of larger pollutants, like sludge, flocks and colloids, on the membrane surface. Cake formation is reversible and often simple backwash is enough to regain the membrane flux. On the other hand, the adsorption of pollutants on the membrane surface is irreversible and often requires chemical treatment. According to Li and Elimelech, membrane fouling depends on feed water composition, water chemistry (ionic strength, concentration of divalent cation and pH), properties of the membrane (hydrophobicity, surface morphology, molecular weight cut-off, etc.), temperature and hydrodynamics (crossflow velocity, permeate flux, etc.) (Li and Elimelech, 2004).

To improve the anti-fouling propensity of membranes, surface modification and incorporation of nano-fillers have been suggested by researchers. Surface modification can be done by physical adsorption, atom transfer radical polymerization, photo-initiated graft polymerization and plasma graft polymerization (Xia et al., 2020). These surface modification techniques have been reviewed by Madalosso et al., Usman et al., Xu et al. and other researchers (Madalosso et al., 2021; Usman et al., 2021; Xu et al., 2013). However, according to Kim and Bruggen, the improvement in membrane performance achieved through surface modification is very limited and the incorporation of membranes with nanoparticles is more promising (Kim and Van der Bruggen, 2010). Nanoparticles allow a higher degree of control over membrane structure and fouling mechanism. These types of membranes can be prepared either by assembling the nanoparticles into the porous membrane or by blending the nanoparticles with the polymeric membranes (Bottino et al., 2002; Taurozzi et al., 2008). Metal oxides and carbon nanotubes are the most widely used nanoparticles in membrane fabrication. Metal oxides provide the membrane with built-in oxidative functionality that can decompose organic compounds on the membrane surface and mitigate fouling (Orta de Velásquez et al., 2013). Carbon-based nanomaterials cause the inactivation of viruses & bacteria and induce additional pores in the membrane (Chae et al., 2009; Verweij et al., 2007).

One of the emerging nano-polymer for membrane modification is PAMAM, more specifically polyamidoamine (PAMAM). PAMAM offers a large number of reactive sites due to the presence of a high density of amine groups on its surface. PAMAM can be modified to have multiple layers of amines and the addition of each layer increases the generation of PAMAM. By increasing the generation, the number of amine groups can be increased exponentially, which will results in improved membrane hydrophilicity for the polymeric membrane (Jin et al., 2012). During its synthesis, the PAMAM provides impressive control over the resulting structure. Consequently, PAMAM shows high iso-molecularity, precise molecular size, almost perfect spherical shape and high density of active functional groups (Sarkar et al., 2010). This makes PAMAM suitable as an adsorbent for wastewater treatment processes. However, PAMAM is water soluble and hard to regenerate. To solve this problem, Zhu et al. grafted PAMAM onto a polysulfone (PSF) membrane and achieved excellent removal of Pb^{2+} and Cu^{2+} and was also able to regenerate the membrane flux by simple cleaning regime (Zhu et al., 2015). Recently, the significance of PAMAM in the field of wastewater treatment and as a membrane modification agent has gained significant attention as identified by the increasing number of articles published on PAMAM dependent wastewater treatment technologies, shown in Fig. 1.

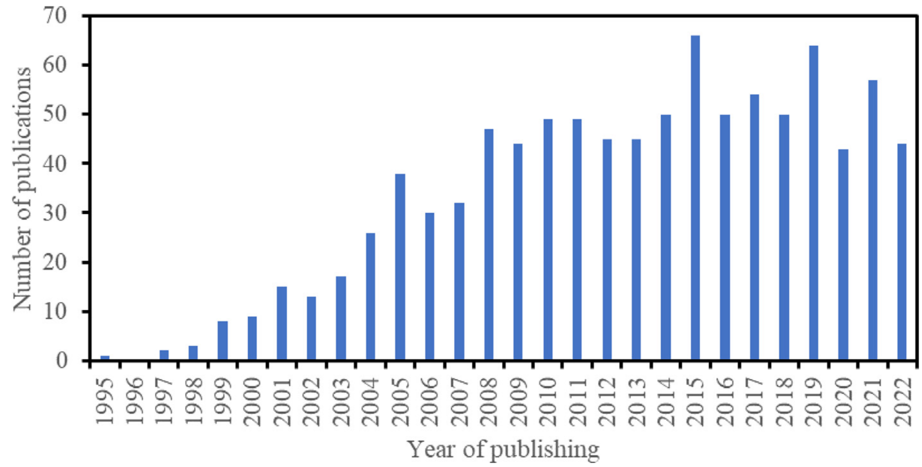

Fig. 1. The number of publications on water treatment technologies utilizing PAMAM (2004–2022). Data was obtained from Scopus by searching for articles having "PAMAM" and "Water" in their Title, Abstract and keyword.

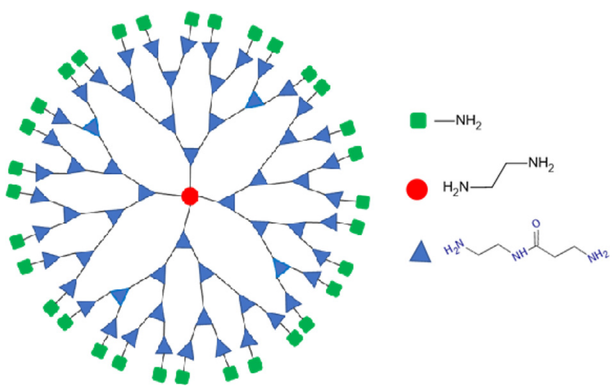

Fig. 2. G4 Poly (amido amine) dendrimer with 24 terminal functional groups.

Bouazizi et al. in their review paper summarized the application of PAMAM and functionalized PAMAM as adsorbent for water treatment and antimicrobial activities (Bouazizi et al., 2022). Furthermore, another available paper by Viltres et al. reviewed the different environmental applications of PAMAM, including anion, cation and heavy metal removal by adsorption (Viltres et al., 2021). The objectives of the two review papers mentioned here were not the use of PAMAM in membrane modification, which is the objective of our review manuscript. Hence, this paper reviews the recent advancements in polymeric membrane fabrication using PAMAM and PAMAM based multifunctional nanocomposites. The improvement in polymeric membrane performance after incorporation of PAMAM is reported. The membrane performances are analyzed in terms of pure water permeation flux, irreversible fouling and membrane hydrophilicity. The rejection of different pollutants, including salts, oils, heavy metals and others, after membrane modification with PAMAM, have been discussed. Finally, research gaps in the current PAMAM based incorporated membrane technology and recommended future works of this promising nano-filler have been discussed.

2. Poly (amido amine)

Poly (amido amine) or PAMAM are nano-sized, radially symmetric molecules with well-defined, homogeneous and monodispersed branches (Bosman et al., 1999). These branches are developed around a core of a nano molecule or a linear polymer. Polymer with these structural properties is called dendrimers. Dendrimers consist of three distinct parts; the central atom or 'core', the branches or 'dendrons' and the terminal functional groups (Sohail et al., 2020). For a PAMAM molecule, the core can be made up of ethylene diamine (EDA) or amine. Whereas the dendrons and terminal functional groups are amidoamine and amine, respectively. In PAMAM, the dendrons are grown from the central core and with the addition of each layer of dendron, the 'generation' of PAMAM increases. The size of a PAMAM molecule can range between 10 Å (G0) and 100 Å (G10). Addition of new generation increases the size linearly, however, with each additional generation, the number of terminal functional groups increases exponentially (Yen et al., 2017). The number of the terminal functional group also depends on the type of dendrimer core. The dendrimer core can be made up of ammonia, ethylenediamine (EDA) or cystamine. Fig. 2 shows G2 PAMAM ammonia and EDA core. The G2 PAMAM with EDA core has 8 terminal amine groups, whereas the G2 PAMAM with ammonia as the core has 6 terminal functional groups. The PAMAM between G0 and G4 are plane and elliptical, whereas PAMAM between G5 and G10 are spherical in shape. Unlike hyperbranched polymers that are synthesized by a one-step polymerization reaction, synthesis of PAMAM involves controlled repetition of the same reaction. Due to the presence of large number of terminal functional groups, PAMAM are suitable for modification with different functional groups which makes them physically and chemically flexible (Parquette, 2001). Low toxicity, variable size and tunability make PAMAM a suitable candidate for application in wastewater treatment. The large internal voids and external functional groups make them suitable for capturing pollutants. Moreover, customization of the terminal functional groups makes PAMAM suitable for targeting different types of pollutants.

2.1. Synthesis of PAMAM

PAMAM is primarily synthesized by divergent or convergent methods. In a divergent approach, a series of repetitive reactions extends a multifunctional core outward. For PAMAM, the starting core can either be ammonia or ethylene diamine. Depending on the core, they have three or four sites for binding with amidoamine dendrons. The amidoamine monomers have one reactive and two dormant functional groups. At the surface of the dendrons, an anime group is present. From this amino group, two additional dendrons are added. The dendrons are repeated until the required generation of PAMAM is achieved. In convergent synthesis, the

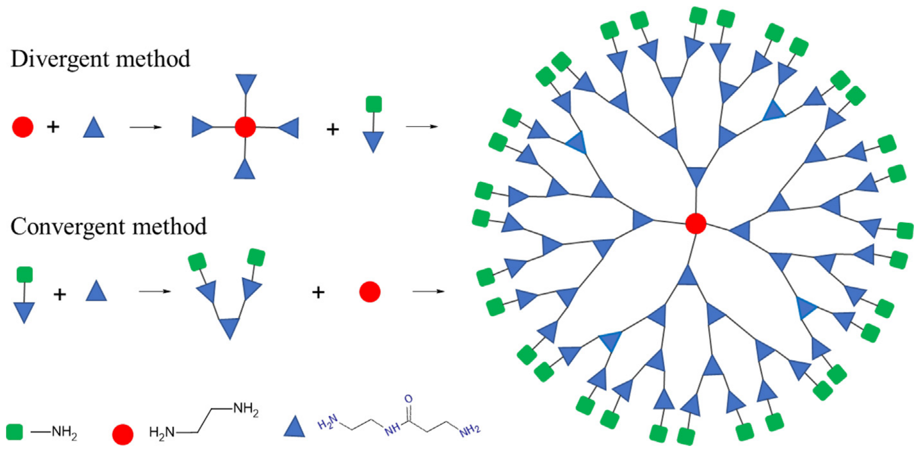

Fig. 3. Convergent and divergent approach for the synthesis of PAMAM.

Table 1
PAMAM based multifunctional composites.

Multifunctional composite	Preparation method	Advantage	Ref.
Ag-PAMAM	G5 PAMAM was functionalized with Ag by adding $AgNO_3$ and $NaBH_4$.	The nanocomposite improved the anti-bacterial properties of the PVDF membrane.	(Li et al., 2014)
PAMAM-SiO_2	PAMAM and SiO_2 were added in a sodium dodecyl solution where the nanocomposite was synthesized with ultrasonication at 40 kHz for 1 h.	The presence of SiO_2 promotes the formation of negative charges on the surface of the membrane which is deemed suitable for the treatment of oily wastewater.	(Jin et al., 2012)
PAMAM-PEG	PAMAM was functionalized with N-hydroxysuccinimide mono-functionalized polyethylene glycol (NHS-PEG) in a methyl chloride solution.	PEG functionalized PAMAM creates a cilia-like dynamic membrane surface which prevents the settling of pollutants on the membrane surface.	(Sarkar et al., 2010)
HNT-PAMAM	The HNT was first aminated in presence of APTES. The dendrons were then grown from the amine group present on the surface of HNT.	The HNT is the bond between the nanoparticle and the polymeric membrane which led to a reduction in nanoparticle leaching.	(Asempour et al., 2018)
MWCNT-PAMAM	MWCNT was functionalized with PAMAM in an aqueous solution that contained HCl and NHS. The pH of the mixture was maintained between 6 and 7.	The rigid structure of the MWCNTs made the permeate flux stable. The composite also exhibited positive zeta potential that enhanced metal ion rejection.	(Zhang et al., 2018)
PAMAM-Pal	Palygorskite (Pal) was modified with APTES and PAMAM was grown on its surface by interfacial polymerization.	Functionalization of PAMAM with Pal reduces agglomeration of the nanocomposite and enhances heavy metal removal in the membrane process.	(Zhang et al., 2019a)
Ag-GO-PAMAM	GO was prepared by modifying Hummer's method. Then G2 PAMAM was grafted onto the GO surface. Finally, the nanocomposite is functionalized with Ag by adding $AgNO_3$ and $NaBH_4$.	The oxygen based functional groups present on the surface of GO provided grafting sites for heteroatoms. This will prevent the leaching of PAMAM from the membrane matrix. Ag is expected to impart anti-microbial properties to the membrane.	(Mansourpanah et al., 2021)
HNT-PAMAM	The HNT was first aminated in presence of APTES. The dendrons were then grown from the amine group present on the surface of HNT.	HNT will stabilize PAMAM in the membrane where the amine sites of PAMAM will act as sacrificial agents during a chlorine attack.	(Asempour et al., 2021)

procedure starts from the surface of PAMAM. The surface of PAMAM consists of multiple amine groups attached to amido amine dendrons. Multiple amido amine dendrons converge to a single amine or EDA at the core of the PAMAM. The generation of dendrimer synthesized using the convergent approach has to be predetermined, whereas the step-by-step addition of functional groups makes the divergent approach more flexible in terms of the number of generations.(Gajjar et al., 2014; Hawker and Frechet, 1990). Fig. 3 shows the schematics of convergent and divergent approaches for the synthesis of a PAMAM dendrimer. From Fig. 3, in the divergent approach, EDA or ammonia is being used as the core and amine groups are being added successively until the desired generation of PAMAM is obtained. Whereas, in the convergent method, the terminal amine groups are added to the amide groups successively until the amine groups converge to a core. Apart from the divergent and convergent methods, the combined method and click method have been tested by various researchers (Bahadır and Sezgintürk, 2016). It is worth noticing that it is difficult to synthesize PAMAM beyond the 10th generation due to the steric hindrance of the dendrons. Steric hindrance of the dendrons on PAMAM higher than G6 causes a defective branching structure. This causes a reduction in synthetic yield and prevents the synthesis of PAMAM beyond G10. The higher generation of PAMAM has bigger cavities in its structure, whereas the lower generation PAMAM is more polar (Parquette, 2001).

2.2. Fabrication of multifunctional composites with PAMAM

Apart from the solo addition of Poly(amidoamine) or PAMAM in the membrane, PAMAM has also been used to synthesize multifunctional composites that have been added to the membrane matrix with the intention of reducing nanoparticle leaching, fouling reduction or enhancement of anti-bacterial activity. Different PAMAM based multifunctional activities are listed in Table 1. Li et al. grafted Ag-PAMAM nanocomposite on a PVDF membrane and observed significant activity toward *E. coli* (Li et al., 2014). Amino terminated PAMAM is cationic in nature, whereas *E. coli* is anionic in nature. This causes electrostatic interaction between PAMAM and *E. coli* resulting in disruption of the lipid bilayer and subsequent cell lysis. Li et al. argued that functionalizing PAMAM with Ag increases the durability of the anti-bacterial effect (Li et al., 2014). Jin et al. synthesized a PAMAM-SiO_2 nanocomposite and observed reduced surface zeta potential after interfacial polymerization of the nanocomposite on a PSF membrane (Jin et al., 2012). During nanofiltration (NF), the increased surface negativity improved the rejection of divalent cations. Jin et al. argue that salt rejection during NF is not only dictated by the pore size of the membrane, but also by the electrostatic interaction between the membrane and the steric hindrance (Jin et al., 2012). Sarkar et al. grafted PEG-PAMAM nanocomposite on the surface of a PA reverse osmosis membrane (Sarkar et al., 2010). The nanocomposite resulted in a dynamic membrane surface. The Brownian motion on the membrane surface created a thin layer of ultrapure water which prevented contaminants from settling (Sarkar et al., 2010). One of the major issues with PAMAM as a nanofiller for membrane processes is the solubility of PAMAM in water. Asempour et al. addressed the PAMAM leaching issue by functionalizing Halloysite nanotube (HNT) with PAMAM (Asempour et al., 2018). HNT formed a covalent bond with the membrane matrix and prevented the leaching of PAMAM into water. Zhang et al. improved heavy metal removal efficiency in UF by using PAMAM functionalized palygorskite (Pal) as membrane nano filler (Zhang et al., 2019a). Functionalization of Pal with PAMAM increases the number of active sites for adsorption and results in improved heavy metal rejection in the UF process.

3. Modification of membrane properties using PAMAM

The most important parameters that determine the efficiency of a membrane are water permeation flux, pollutant rejection and membrane fouling. These properties are primarily controlled by the crystallinity of the polymer, membrane pore size, pore structure, surface roughness, hydrophilicity and zeta potential (Lalia et al., 2013). All of these properties can be modified by incorporating poly (amido amine) (PAMAM) in the membrane matrix. In the literature, Polyvinylidene Fluoride (PVDF), Polysulfone (Psf), Polyethersulfone (PES), commercial membranes and other polymer-based membranes have been modified using PAMAM.

3.1. Modification of polyvinylidene fluoride membrane

Polyvinylidene Fluoride or PVDF membranes offer good thermal stability, excellent mechanical strength and chemical resistance (Ji et al., 2015). PVDF is semi-crystalline in nature which makes the membrane highly mechanically strong and flexible at the same time. The polymer dissolves easily in membrane casting solvents like N, N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP). However, the lack of hydrophilic functional groups in the PVDF membrane matrix makes them hydrophobic and susceptible to high membrane fouling. Li et al. carried out the first study to improve the hydrophilicity of the PVDF membrane using fifth generation PAMAM (Li et al., 2014). In the study, Ag-PAMAM nanocomposite was grafted onto the PVDF membrane. The hydrophilic amine groups present in the PAMAM dendrimer reduced the membrane contact angle from 113.4° to 45.6°. Moreover, the grafting process helped reduce the pore size and increased the surface roughness of the PVDF membranes. Moreover, the silver nanoparticle attached to the PAMAM molecule improved the anti-bacterial property of the membrane. Similar findings have been confirmed by different studies listed in Table 2.

Table 2
PAMAM incorporated PVDF membranes.

Support layer	Modified with	Modification method	Applied Pressure (bar)	Normalized flux change	Irreversible Fouling reduction	Contact angle reduction	Ref.
PVDF	PAMAM-Pal	G1, G2 and G3 PAMAM was grown on hyperbranched-nano-palygorskite. The PAMAM-Pal solution was used mixed with the casting solution and the membrane was obtained through phase inversion.	N/A	80.7%	N/A	21.1°	(Zhang et al., 2019a)
PVDF	Ag-PAMAM	PAMAM was functionalized with Ag. The PVDF membranes were modified with the synthesized nanoparticle using interfacial polymerization.	1.5	−23.3%	39.2%	67.8°	(Li et al., 2014)
PVDF	PAMAM	G0 and G1 PAMAM was added in the casting solution and mixed matrix membrane was obtained by phase inversion.	2	11,566%	N/A	31°	(Kotte et al., 2015)
PVDF-g-PAA	PAMAM	PVDF was functionalized with PAA and the PVDF-g-PAA support layer was made by phase inversion. G1-G4 PAMAM was grafted to on the surface of the membrane.	2	150%	N/A	53°	(Sun et al., 2019)
PVDF-g-PAA	SiO_2-PAMAM	PAMAM was added onto the PVDF-g-PAA membrane by interfacial polymerization method.	0.9	15,900%	99%	114.9°	(Wei et al., 2020)
PVDF-g-PAA	PAMAM	PVDF was grafted with PAA and the membrane was casted by phase inversion. Then the membrane was immersed in 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methyl morpholinium chloride solution before immersing the membrane in a G1/G2/G3/G4 PAMAM.	N/A	48.6%	N/A	48°	(Sun et al., 2022)
PVDF	PP-Si-PAMAM	PP-Si-PAMAM nanocomposite was added in the casting solution along with PVDF and the membrane was fabricated by phase inversion.	0.9	392%	~49%	52.7°	(Zhang et al., 2022)
PVDF-HFP	PAMAM	PVDF-HFP TFN membrane was prepared by phase inversion. To modify the membrane with PAMAM, appropriate amount of PAMAM was added in the casting solution.	N/A	N/A	N/A	24°	(Macevele et al., 2020)

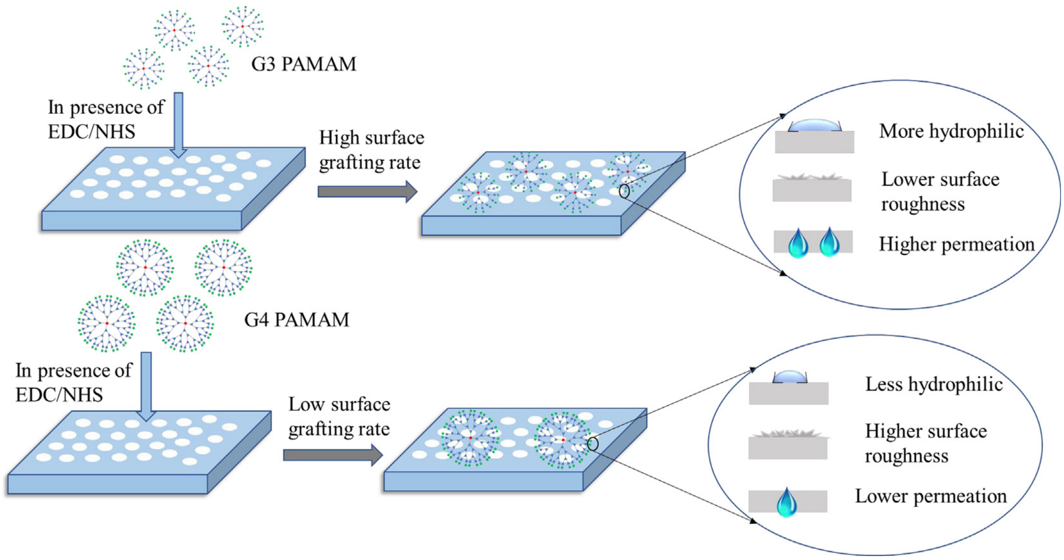

Fig. 4. Grafting of PVDF membrane with G3 & G4 PAMAM and its effect on membrane properties.

The effect of PAMAM generation on the properties of PVDF membrane was studied by Sun et al. (Sun et al., 2019). Grafting of PVDF membrane with G3 & G4 PAMAM and its effect on memrbane properties has been summerized in Fig. 4. The contact angle analysis of the study showed significant improvement in membrane hydrophilicity while grafting G1, G2, G3 and G4 PAMAM on the PVDF membrane. However, G3 PAMAM grafted PVDF membrane showed the highest hydrophilicity. Although the number of amine groups on G4 PAMAM was higher than G3 PAMAM, the grafting rate of G4 PAMAM was lower than that of G3 PAMAM. This resulted in increased amine concentration on the membrane surface while using G3 PAMAM. Thus, resulting in higher hydrophilicity for G3 grafted PVDF membrane. Moreover, grafting G3 PAMAM on the surface of the PVDF membrane also resulted in the lowest surface roughness (72.5 nm) and highest membrane flux (~250 LMH/bar) during ultrafiltration. Sun et al. carried out a similar study where they improved the hydrophilicity of the PVDF membrane while using G4 PAMAM (Sun et al., 2022). In this study 0.05 mol/L (4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methyl morpholinium chloride (DMTMM) was used for grafting instead of 0.05 mol/L 1-Ethyl-3-(3-dimethyl aminopropyl) carbodiimide hydrochloride (EDC). During this study, the generation of PAMAM varied between 1 & 4, and the effect of PAMAM generation of membrane hydrophilicity and membrane flux was studied. DMTMM improved the grafting rate and resulted in improved hydrophilicity across all the PAMAM generations. However, the highest hydrophilicity, indicated by the lowest contact angle of 23°, was observed for the membrane with G4 PAMAM. However, the highest membrane flux of 230 LMH was obtained with the G1 PAMAM grafted PVDF membrane. This is because, with increasing PAMAM generation, the size of the PAMAM molecule increased exponentially and blocked the pores of the PVDF membrane. In the previous study by Sun et al., this phenomenon was only observed when increasing PAMAM generation from 3 to 4. Zhang et al. studied the effect of G3 PAMAM concentration on the permeate flux and hydrophilicity of PVDF membrane (Zhang et al., 2022). During this study, the concentration of PP-Si-PAMAM was varied between 0 and 8 wt% and the highest membrane flux and lowest water contact angle of 3,400 LMH and 53° was obtained while using 8 wt% G3 PAMAM, respectively. The improved hydrophilicity was attributed towards additional amine groups available while using higher concentration of PAMAM. Moreover, higher concentration of PAMAM also increased the pore radius which was also responsible for the improved membrane flux. Apart from hydrophilicity and pore size, another factor that affects the membrane flux is porosity where higher porosity results in higher membrane flux. The membranes synthesized by phase inversion method, where PAMAM based nanocomposites were added in the casting solution showed improved porosity compared to membranes modified by grafting PAMAM (Sun et al., 2019; Zhang et al., 2022). This is because, the PAMAM molecules have large voids inside them, which improves porosity when incorporated inside the membrane matrix. Whereas the grating method blocks the membrane pores which results in reduction in porosity. Another impact of PAMAM based membrane modification can be seen in anti-fouling performance of the modified membrane. Regardless of the modification method, incorporation of PAMAM improves hydrophilicity of the membrane which in turn make the membrane less susceptible to organic fouling (Zhang et al., 2022). Fig. 6 shows several other advantages that can be achieved through modification of PVDF membranes using PAMAM and PAMAM functionalized nano-polymers. Table 2 summarizes the studies that have used PAMAM to improve the properties of PVDF membranes.

3.2. Modification of polysulfone membrane

Polysulfone (Psf) membranes are widely used in ultrafiltration due to their mechanical and chemical stability. Moreover, polysulfone membranes are stable in both acidic and basic conditions and possess high thermal stability (150–170 °C). However, the hydrophobic nature of Psf membranes often makes their use unfavorable as hydrophobicity results in reduced membrane flux and increased membrane fouling. Furthermore, Psf membranes have a bulky structure and low binding force among the fibers. Through surface modification, the rheological and adsorptive properties of the Psf membranes can be changed (Abdelrasoul et al., 2015; Richards et al., 2012). PAMAM and PAMAM derived nanocomposites have been extensively used to form polyamide (PA) active layer on top of Psf support layer through interfacial polymerization (IP). This, was first investigated by Deng et al. by modifying nanofiltration (NF) membranes by IP on Psf support layer using PAMAM and trimesoyl chloride (TMC) (Deng et al., 2008). The membrane surface water contact angle reduced by 38.8° indicating improved hydrophilicity of the NF membrane. The effect of

Table 3
PAMAM incorporated Psf membranes.

Support layer	Modified with	Modification method	Applied Pressure (bar)	Normalized flux enhancement	Irreversible Fouling reduction	Contact angle change	Ref.
Psf	PAMAM-PZ	Psf substrate was prepared using phase inversion. Then a solution containing G0 PAMAM and piperazine was used to carry out interfacial polymerization. Finally, the membrane was treated with trimesoyl chloride (TMC).	7	−52%	N/A	N/A	(Sum et al., 2014)
Psf	PAMAM-SiO_2	The Psf membrane was first treated with SiO_2 and G4 or G5 PAMAM solutions. Then TMC was poured on the membrane to complete interfacial polymerization which created a PA layer on Psf from PAMAM.	6	105.8%	N/A	68°	(Tang et al., 2016)
Psf	HNT-PAMAM	Psf membrane was treated with M−phenylenediamine solution before carrying out interfacial polymerization with HNT-PAMAM nano-composite dispersed in TMC solution.	20	50%	N/A	29°	(Asempour et al., 2018)
Psf	PAMAM	The Psf substrate was immersed in an aqueous solution containing G0 to G8 PAMAM. Then the substrate was treated with TMC to complete interfacial polymerization.	6	N/A	N/A	38.8°	(Deng et al., 2008)
Psf	PAMAM-TMC	Psf membrane was dipped in an aqueous PAMAM solution. The PAMAM treated membrane was then dipped in an organic solution containing TMC which produced a PA active layer on the Psf support layer through interfacial polymerization.		41.7%	N/A	~40°	(Pei et al., 2019)
Psf	PAMAM	Interfacial polymerization was carried out with a grafting solution prepared with PAMAM, TMC and ETA in methanol and acetone. Acetone was used as a co-solvent.	7	11%	N/A	12.4°	(Sum et al., 2018)
Psf	PAMAM-SiO_2	SiO_2 was dispersed in sodium dodecyl sulfate solution containing G0 and G1 PAMAM. The Psf support layer was then immersed in the solution where PAMAM-SiO_2 deposited on the Psf substrate. Then the membrane was treated with TMC to produce silica-polyamide skin layer on the Psf substrate.	6	−20%	N/A	N/A	(Jin et al., 2012)
Psf	PAMAM	On the surface of Psf membrane, a PA layer was formed by interfacial polymerization with the help of an aqueous PAMAM solution and organic TMC solution.	4	100%	N/A	14.1°	(Qiu et al., 2021b)
Psf	Ionic PAMAM	Initially, Psf membrane was soaked in an aqueous solution of ionic PAMAM. Then the interfacial polymerization was completed by soaking the membrane in an organic TMC solution.	4	157.4%	N/A	N/A	(Qiu et al., 2021a)

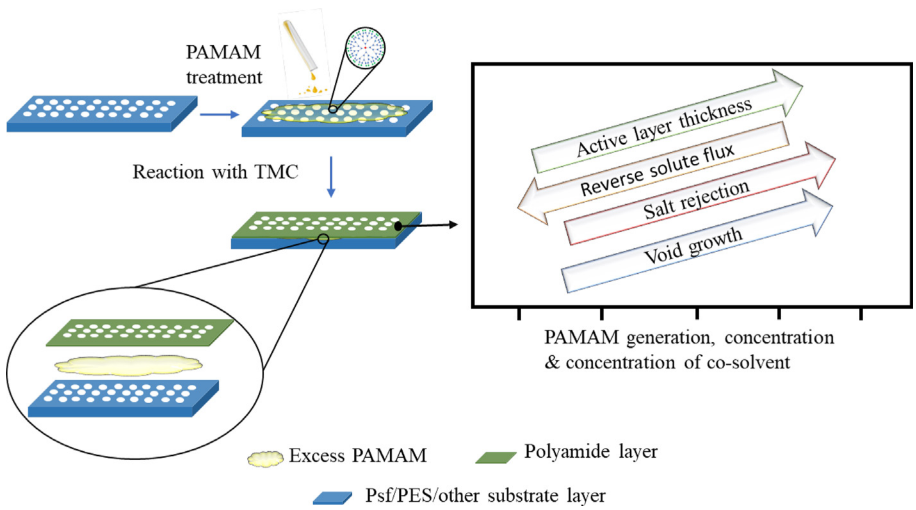

Fig. 5. Thin film membrane formation with PAMAM and the effect of PAMAM generation, PAMAM concentration & concentration of co-solvent on active layer thickness and void growth.

PAMAM generation was not observed on the membrane flux. However, usage of higher generation of PAMAM was suggested due to the presence of large number of unreacted amine group after interfacial polymerization which will improve membrane hydrophilicity, porosity, anti-fouling propensity and number of active amine sites for pollutant adsorption (Deng et al., 2008).

Pei et al. carried out a study where the concentration of PAMAM was varied during IP (Pei et al., 2019). As shown from the study, although the hydrophilicity was improved by increasing the PAMAM concentration, the water flux decreased. The presence of excess PAMAM during IP would promotes PAMAM diffusion in the organic layer and increases the thickness of the active PA layer resulting in decreased flux. To improve the availability of PAMAM in the reaction zone during IP process, the diffusion of PAMAM to the organic phase has to be improved (Sum et al., 2018). Lack of PAMAM in the reaction zone would create a loose and defective PA layer during IP. Sum et al. (2018) suggested using acetone as co-solvent during the interfacial polymerization process. It was found that the presence of acetone promoted dissociation of water and PAMAM in reaction zone and resulted in a thicker PA active layer and reduced surface roughness. However, addition of acetone increased moisture content in the organic phase of the solution

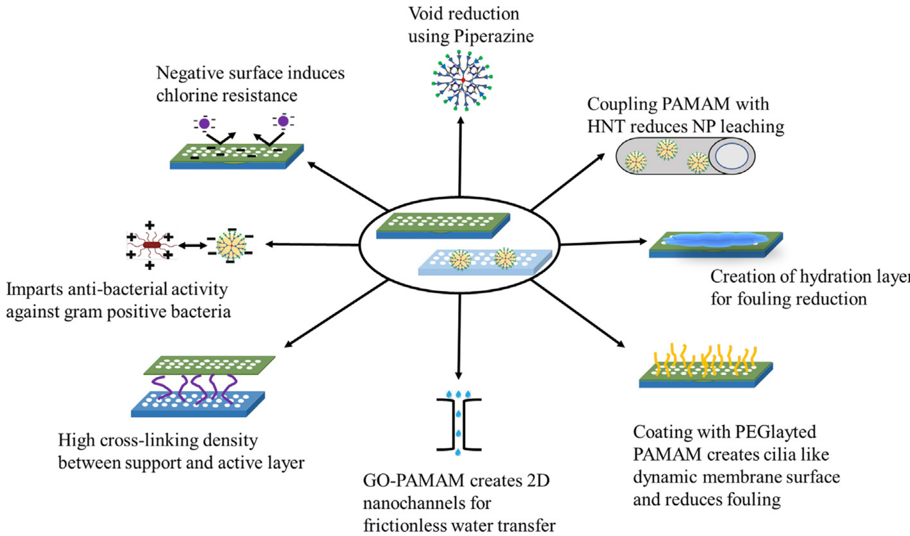

Fig. 6. Various effects of PAMAM and PAMAM derivatives on the performance of the membrane.

which resulted in gradual increment of pore size, porosity and hydrophobicity (Sum et al., 2018). Although the hydrophilicity of membranes can be improved easily using PAMAM, large voids in PAMAM have been identified as a drawback for producing NF and RO membrane that require smaller pore size. Sum et al. (2014) used piperazine to reduce the free volume in the PA active layer of RO membrane synthesized using IP of PAMAM. Although the presence of piperazine improved cross-lining in the membrane, it also reduced the membrane hydrophilicity. Asempour et al. argued that poor compatibility and adhesion between the nanoparticles are major drawbacks of thin film nanocomposite (TFN) membranes (Asempour et al., 2018). This causes uneven distribution, agglomeration, and leaching of nanoparticles from the membranes. This problem can be solved by functionalizing nanoparticles with hydrophilic functional groups such as amine, carboxylic acid, hydroxyl or sulphonic acid. Asempour et al. (2018) functionalized Halloysite Nanotubes (HNT) with PAMAM and used it for IP of PA active layer. The amine group from the nanocomposite formed covalent bonds with acryl chloride functional group of the TMC monomer during IP and was able to reduce nanoparticle leaching by 95%. Fig. 6 shows several other advantages that can be achieved through modification of Psf membranes using PAMAM and PAMAM functionalized nano-polymers. Table 3 shows all the studies where polysulfone membranes have been modified using PAMAM.

3.3. Modification of polyethersulfone membrane

Polyethersulfone or PES membranes have shown outstanding oxidative, hydrolytic and thermal stability along with good mechanical properties (Zhao et al., 2013). Like most other polymeric membranes, PES membranes also suffer from hydrophobicity which causes high membrane fouling during the filtration process. However, PES membranes are less hydrophobic than most other polymeric membranes. Apart from wastewater treatment, PES membranes are also being used in biomedical fields (Zhao et al., 2013). Thus, the current trend in PES membrane modification focus on fouling reduction and biocompatibility. PES membranes have been modified through bulk modification, surface modification and blending. Like Psf, PES has also been extensively used as support layer for NF and RO membranes where the active PA layer was deposited through IP of PAMAM. The general performance trends of PAMAM modified PES membranes can be seen in Fig. 5. The large number of amine group on PAMAM that remains unreacted during the IP process improves the hydrophilicity of the membranes (Xia et al., 2020).

Al-Gamal and Saleh used a GO-PAMAM nanocomposite to form PA active layer on PES support layer (Al-Gamal and Saleh, 2022). By using GO-PAMAM nanocomposite for IP, high hydrophilicity, high chemical stability and superior dispersion of nanoparticles were obtained. The presence of GO in the structure reduces distance between PAMAM layers and makes the membrane chlorine resistant. The presence of GO also provides frictionless water transport due to creation of 2D nanochannels and capillaries by oxidized GO. Moreover, the surface roughness is also reduced with increasing GO-PAMAM concentration which aids reducing membrane fouling. Increasing the GO-PAMAM concentration was favorable for membrane flux until 1 wt% GO-PAMAM. Above this, the pure water permeate flux declined owing to accumulation of GO-PAMAM particles on the membrane surface which decreased membrane porosity. Mansourpanah and Jafari studied the effect of using different PAMAM generation (G0, G1 and G2) for IP of PA active layer (Mansourpanah and Jafari, 2015). As found in the study, increasing PAMAM generation decreases pore size, contact angle and pure water permeation flux in FO. Using higher generation of PAMAM resulted in higher number of unreacted amine group during IP which resulted in improved hydrophilicity. Moreover, the bulky higher generation PAMAM molecules resulted in reduction in pore size. However, due to increased thickness of PA active layer while using higher generation of PAMAM, the pure water permeate flux declined while using higher generation of PAMAM. Mansourpanah et al. also varied the concentration of PAMAM and studied its effect on membrane flux and contact angle (Mansourpanah et al., 2021). As found from the study, the contact angle decreases with increasing PAMA concentration, and the highest membrane flux is found while using 0.1 wt% PAMAM during phase inversion. Above 0.1 wt%, the pure water permeation flux declines.

The diffusion of PAMAM in PA is low due to skin compactness and molecular size of the nanoparticle (Sum et al., 2014). This results in uneven distribution of PAMAM during IP and lower membrane flux. Incorporating annular supermolar CB6 and PAMAM in PA enlarges polyamide tunnels and created hydrophobic rotaxane tunnels in the membrane due to large steric effect. This improves the water flux by 400% (Cai et al., 2020). The large voids inside the structure of PAMAM makes it unstable during high pressure operation. Thus, Sum et al. (2014) suggested using piper-

Table 4
PAMAM incorporated PES membranes.

Support layer	Modified with	Modification method	Applied Pressure (bar)	Normalized flux enhancement	Irreversible Fouling reduction	Contact angle change	Ref.
PES	PAMAM	PES support layer was synthesized by non-solvent induced phase inversion process. The membrane was modified with G0, G1 and G2 PAMAM using interfacial polymerization.	7	−75%	32%	17.7°	(Mansourpanah and Jafari, 2015)
PES	PA-PAMAM	PES membrane surface was modified with G0, G1 and G2 PAMAM with the surface grafting method.	15	25.8%	N/A	18°	(Zhu et al., 2015)
PES	PAMAM-MWCNT	G4 PAMAM were used to synthesize PAMAM-MWCNT. PA support layer were modified with PAMAM-MWCNT using interfacial polymerization.	4	81.5%	N/A	42°	(Zhang et al., 2018)
PES	PAMAM	PES membranes were fabricated using nonsolvent induced phase separation. G0, G3 & G5 PAMAM modified PA film were then deposited on the PES membrane with interfacial polymerization.	N/A	~4.5%	~15%	~25°	(Duong et al., 2017)
PES	Ag-GO-PAMAM	Thin film composite (TFC) membrane was prepared by first treating PES membrane with an aqueous Ag-GO-G2 PAMAM solution. Then interfacial polymerization was completed by treating the membrane with an organic TMC solution. The study also fabricated thin film nanocomposite (TFN) membrane by adding Ag-GO-G2 PAMAM nanocomposite with the membrane casting solution.	8	~11.9%	~9%	31°	(Mansourpanah et al., 2021)
SPES	PAMAM	SPES membrane was synthesized via a non-solvent induced phase-separation process. A PA layer was formed on the surface of the SPES support layer by interfacial polymerization. Finally, G0 to G3 PAMAM was grafted onto the PA active layer.	N/A	−3.0%	N/A	12°	(Bao et al., 2019)
SPES	PAMAM	SPES substrate was produced by phase inversion. PA active layer was formed on the membrane surface by interfacial polymerization. Finally, the surface of PA was grafted by G2 PAMAM. Three different methods were studied for grafting PAMAM.	N/A	−9.1%	~4%	30°	(Bao et al., 2021)
PES	GO-PAMAM	On the surface of a PES membrane, an aqueous solution of GO-PAMAM nanocomposite was allowed to sit for 5 min. Then an organic TMC solution was allowed to sit on the modified membrane surface for 2 min to complete interfacial polymerization of.	10	63.2%	N/A	30°	(Al-Gamal and Saleh, 2022)

Table 5
PAMAM incorporated commercial membranes.

Membrane name	Modified with	Modification method	Applied Pressure (bar)	Normalized flux change	Irreversible Fouling reduction	Contact angle reduction	Ref.
PA	PEGlayted PAMAM	N-hydroxysuccinimide mono-functionalized polyethylene glycol was functionalized with G2 PAMAM. This PEGlayted PAMAM was used to coat the PA support layer.	7	−35.2%	N/A	24°	(Sarkar et al., 2010)
PA 6	PAMAM	PA 6 membrane was fabricated following the electro spinning method. The membrane was then crosslinked with G5 PAMAM with a microwave assisted reaction.	N/A	N/A	N/A	N/A	(Johal et al., 2013)
PA	GO and PAMAM	PA support layer was modified with PAMAM using interfacial polymerization. Then GO nanoplates were grafted on the modified membrane.	15	35%	6.1%	15.4°	(Vatanpour and Sanadgol, 2020)
PS35	HNT-PAMAM	The surface of PS35 membrane was treated with and organic solution containing HNT-PAMAM nanocomposite. Then the membrane was treated with NaOCl to complete the chlorination process.	20	380%	N/A	26°	(Asempour et al., 2021)
PTFE	GO-PAMAM	A solution was made with GO and G0, G1 and G2 PAMAM. The solution was then filtered in a dead-end cell containing a PTFE membrane at 4.8 bar. The used PTFE membrane was then considered as the modified membrane.	N/A	−40%	N/A	N/A	(Song et al., 2019)

azine in the PA membrane in order to fill the voids in PAMAM nanostructure. However, for higher generation of PAMAM, piperazine alone is not suitable. Thus, Tang et al. proposed usage of piperazine and SiO_2 to fill the void (Tang et al., 2016). Duong et al. fabricated a upportide membrane using PDA and PAMAM on PES support layer (Duong et al., 2017). The study found that high hydrophilicity of PAMAM in the copolyimide structure created hydration layer on the surface which led to reduction in membrane fouling. Pei et al. synthesized a hyperbranched PAMAM/TMC RO membrane for treatment of oily seawater (Pei et al., 2019). Theupportt layer suffered from reduced fouling due to reduced roughness and increased hydrophilicity caused by incorporation of PAMAM. Fig. 6 shows several other advantages that can be achieved through modification of PES membranes using PAMAM and PAMAM functionalized nano-polymers. Table 4 summarizes all the studies that have modified PA membranes using PAMAM.

3.4. Modification of commercial membranes

PAMAM has been generally used to modify commercially available Polyamide (PA) membranes. In reverse osmosis, the current state of art membrane is the thin film composite PA membrane. However, the membrane suffers from low salt rejection, irreversible cationic surfactant fouling, chemical oxidation, high fouling and structural degradation under high pressure. Polyamide membranes have good water flux and salt rejection rate. However,

Table 6
Other PAMAM incorporated membranes.

Support layer	Modified with	Modification method	Applied Pressure (bar)	Normalized flux enhancement	Irreversible Fouling reduction	Contact angle change	Ref.
Acrylic UF	PAMAM	Acrylic UF membranes were prepared by phase inversion. The prepared membranes were then amidoximated by reacting with hydroxylamine. The amine groups added on the surface of the membrane were then used to grow G0-G3 PAMAM following Michael addition.	3	46.1%	59.3%	28.4°	(Bojaran et al., 2019)
Acrylic UF	PAMAM	Acrylic UF membranes were prepared by phase inversion. The prepared membranes were then amidoximated by reacting with hydroxylamine. The amine groups added on the surface of the membrane were then used to grow G0-G2.5 PAMAM.	3	∼100%	N/A	27.2°	(Cao et al., 2020)
PVA/PAA	PAMAM	PVA/PAA membrane was prepared by electrospinning. G3 PAMAM was grafted on the surface of the membrane via amide formation with carboxylic group present on the surface.	N/A	N/A	N/A	N/A	(Amariei et al., 2017)
Polyimide	PAMAM	Polyimide membrane was immersed in an aqueous solution containing G0/G1/G2 PAMAM, cucurbit [6]uril and piperazine. The membrane was then immersed in an TMC solution that completed the interfacial polymerization process.	6	330%	99.43%	∼10°	(Cai et al., 2020)
BPPO	PAMAM	The bromide group of bromomethylated poly(2,6-dimethyl-1,4-phenyleneoxide) (BPPO) hollow fiber membrane was functionalized with anime group. Then G3 PAMAM was synthesized on the surface of BPPO from this amine.	N/A	N/A	N/A	N/A	(Zhang et al., 2013)
PEK-C	PAMAM-TMC	PEK-C membrane was prepared by phase inversion. Then the membrane was immersed in an aqueous solution of G0 PAMAM and sodium dodecylsulfate (SDS). Then the membrane was treated with an organic solution of TMC where PA layer was formed by interfacial polymerization.	6	74.0%	N/A	21°	(Lianchao et al., 2006)
Polyurethane	MWCNTs/PAMAM	In the casting solution α,ω-telechelic poly(ε-caprolactone) diols and MWCNT-PAMAM nanocomposite were added and the membrane were obtained by phase inversion.	3	700%	N/A	N/A	(Antolín-Cerón et al., 2021)
PAN	PAMAM	PAN membrane was treated with PAMAM before completing interfacial polymerization using TMC.	8	−97%	N/A	14°	(Xu et al., 2012)
PAN	PAMAM	PAMAM was added to the casting solution containing PAN. The mixed matrix membrane was obtained with phase inversion.	1	400%	−15%	∼50°	(Jiang et al., 2020)

the aromatic nature of the membrane results in severe organic and biofouling problems. In the industry, frequent cleaning of the PA membrane is done to sustain the flux for a longer period of time (Zhang et al., 2019b). Often, chlorine is added to the feed to prevent biofouling (Camacho et al., 2013). However, diffusion of chlorine in the membrane matrix can compromise the integrity of the membrane.

By grafting GO-PAMAM nanoplates on PA membrane surface, chlorine resistance of the membrane can be improved (Vatanpour and Sanadgol, 2020). The PAMAM layer was found to repel negative charged chlorine particles and reduces the possibility of reaction between PA and chlorine. Moreover, Vatanpour & Sanadgol (2020) achieved smoother membrane surface by grafting PAMAM on the PA layer. This along with improved hydrophilicity resulted in reduction of organic fouling. However, the zeta potential analysis showed that, although at neutral and basic conditions, the modified membrane shows negative zeta potential, at acidic conditions, the zeta potential would be positive. This indicates that if the pH of water is acidic, organic fouling may still occur. Below a pH of 6.5, the presence of carboxylic acid group in the membrane results in negative surface charge. However, above a pH of 6.5, deprotonation of PAMAM takes place which makes the membrane surface positively charged. Moreover, the improved hydrophilicity improved the membrane flux by 35% when PAMAM was grafted onto the PA membrane surface. However, a different trend was observed in the work of Sarkar et al. where grafting PEGlayted PAMAM on PA membrane reduced the membrane flux by 35% (Sarkar et al., 2010). Sarkar et al. (2010) attributed this loss of membrane flux to higher crosslinking density and argued that by reducing the cross-linking density, the membrane flux can be improved. The available literature work featuring PA membrane modification using PAMAM dendrimer is summarized in Table 5.

In addition to PA membranes, commercial Psf UF and polytetrafluoroethylene (PTFE) UF membranes have also been modified through interfacial polymerization and surface grafting using PAMAM, respectively. The Psf UF membrane, PS 35, was used as support layer where a PA active layer was formed by interfacial polymerization using PAMAM and TMC (Asempour et al., 2021). The modified membrane showed increased hydrophilicity and porosity which resulted in doubling of the membrane flux while showing ∼ 4% reduction in NaCl rejection. However, the main outcome of this study was, improved chlorine resistance of the modified membrane. The amine and amide group present in PAMAM acted as chlorine scavengers. The increased number of amine and amide group in G2 and G3 PAMAM modified membranes made them more chlorine resistant. Song et al. modified a hydrophilic polytetrafluoroethylene (PTFE) membrane using GO-PAMAM nanocomposite (Song et al., 2019). By using PAMAM, the interlayer distance between GO nanosheets is reduced. This happened due to creation of covalent bonds between amine and oxygen containing functional groups on GO. Although the modification results in loss of flux by ∼40%, the pollutant rejection improves significantly. Fig. 6 shows several other advantages that can be achieved through modification of commercial membranes using PAMAM and PAMAM functionalized nano-polymers.

3.5. Modification of other membranes

In addition to the membranes discussed earlier, other membranes have also been modified with PAMAM. Some of these membranes have been used as support layer for a PA active layer, while others have been modified directly using PAMAM either through surface grafting or during phase inversion. Table 6 lists these membranes along with their properties. Among the listed membranes, PAN, PEK-C and polyimide membrane has been used as support layers for PA RO membrane where the IP was carried out using PAMAM. Whereas Acrylic UF, BPPO, PVA/PAA, polyurethane and PAN has been modified using PAMAM whether by surface grafting or during phase inversion. As seen in Table 6, PAN has been used in both the scenarios. PAN has good hydrophilicity, costs less and has mild forming condition (Xu et al., 2012). Alkaline hydrolysis of the nitrile groups in PAN results in formation of carbonyl group which enhances the hydrophilicity further. When modified with PAMAM, the terminal nitrile groups of PAMAM will form strong and stable cross links with PAN support layer (Xu et al., 2012). The formation of the PA layer on the PAN surface reduced the membrane flux by ~80%. However, it improved the hydrophilicity, as indicated by 15° reduction in contact angel. This will reduce organic fouling of the membrane surface, although such study was not carried out by the authors. Jiang et al. found that, PAN-PAMAM composite membranes are suitable for acidic wastewater systems (Jiang et al., 2020). By studying surface tension and XDLVO theory it was found that addition of ETA in PAN-PAMAM composite membrane enhances Lewis acid-base interaction at the membrane surface which further enhances antifouling properties of the membrane. However, adsorption of BSA on the membrane (due to presence of ETA) caused irreversible membrane fouling.

The best anti-fouling performance was obtained by fabricating NF membrane using polyimide as support layer where PAMAM, cucurbit[6]uril (CB6) and piperazine (PIP) were used to form PA active layer using IP (Cai et al., 2020). While using this membrane, 99% flux recovery rate was possible due to two main reasons: (1) absence of nodal structures on the membrane surface due to large size and PIP diffusion resistance action of G2 PAMAM and (2) increased hydrophilicity of the membrane surface due to the presence of amine and amide groups on the membrane surface due to the presence of PAMAM. The combination of CB6 and PAMAM created dilated polyamide tunnels and hydrophobic rotaxane tunnels due to the host guest chemistry between PAMAM, PIP and CB6. This created enhanced permeability and perfect electivity. This also made the membrane suitable for treatment of both organic and inorganic pollutants. For PAMAM grafted membranes, the highest irreversible fouling reduction of 59% was observed when acrylic UF membrane was modified with G3 PAMAM (Bojaran et al., 2019). The study also found higher pure water permeate flux while using G3 PAMAM compared to G0, G1 and G2 PAMAM. The improved water flux and reversible fouling resulted from increased hydrophilicity, pore size and porosity.

Alariei et al. used electro-spinning to modify poly (vinyl alcohol) (PVA) and poly (acrylic acid) (PAA) membrane with PAMAM (Amariei et al., 2017). The membrane was modified with PAMAM to improve its anti-bacterial properties. The gram-positive bacteria used in the study could not colonize the membrane surface due to negative surface charge of the bacteria which interacted with the positive surface charge of the PAMAM dendrimer present on the surface of PVA/PAA membrane. This study indicated that modifying the membrane surface with PAMAM can be an effective way to prevent bacterial growth on any other polymeric membrane surface. Fig. 6 shows several other advantages that can be achieved through modification of these membranes using PAMAM and PAMAM functionalized nano-polymers.

4. Application of PAMAM incorporated membranes

The polymeric membranes developed and modified using PAMAM were used to treat monovalent salts, multivalent salts, oil, heavy metals and other types of pollutants from wastewater. This section discusses the use of PAMAM modified membranes in microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) processes to treat different types of pollutants.

4.1. Removal of salts

The membranes that have been modified with PAMAM and tested for NaCl rejection are listed in Table 7. We observe that membranes modified with PAMAM have shown good NaCl rejection rate during RO, NF and FO. Asempour et al. achieved the highest NaCl rejection rate of 99.4% by synthesizing an RO membrane using HNT-PAMAM nanocomposite (Asempour et al., 2018). Whereas, Mansourpanah and Jafari prepared a NF membrane using PAMAM and was able to reduce >90% NaCl from the saline solution (Mansourpanah and Jafari, 2015). Furthermore, Duong et al. deposited a PA layer on PES membrane using PAMAM and used the membrane for FO (Duong et al., 2017). The membrane was able to reduce NaCl by >90%. However, increasing the PAMAM concentration above 20% creates pin holes on the membrane surface and increases the reverse salt flux and reduces NaCl rejection. The thickness of the PA layer directly affects the NaCl rejection rate. For a dense active layer, higher PAMAM diffusion rate, higher PAMAM generation and higher PAMAM concentration during the interfacial polymerization is required. Using higher PAMAM generation and higher PAMAM concentration increases the number of amine and amide groups on the membrane during interfacial polymerization and enhances the IP reaction resulting in denser active

Table 7
Removal of monovalent ions with membranes modified with PAMAM.

Support layer	Modified with	Applied for	Pollutant Removal	Ref.
PVDF-g-PAA	PAMAM	NF	60% NaCl	(Sum et al., 2018)
PAN	G0 PAMAM	NF	48.1% NaCl	(Xu et al., 2012)
	G1 PAMAM		47.2% NaCl	
PA	GO-PAMAM	RO	95.5% NaCl	(Vatanpour and Sanadgol, 2020)
PES	PAMAM	NF	>90% NaCl	(Mansourpanah and Jafari, 2015)
PES	PAMAM	FO	>90% NaCl	(Duong et al., 2017)
PES	PAMAM-MWCNT	NF	49.4% NaCl	(Zhang et al., 2018)
Psf	HNT-PAMAM	RO	99.1% NaCl	(Asempour et al., 2018)
Psf	PAMAM	NF	43.7% NaCl	(Deng et al., 2008)
PEK-C	PAMAM	NF	72.55 NaCl	(Lianchao et al., 2006)
PS35	HNT-PAMAM	RO	95.5% NaCl	(Asempour et al., 2021)
Psf	PAMAM	NF	16.1% Na^+	(Qiu et al., 2021b)
			53.2% Cl^-	
PES	GO-PAMAM	RO	87.37% Cl^-	(Al-Gamal and Saleh, 2022)
Psf	Ionic PAMAM	NF	34.5% NaCl	(Qiu et al., 2021a)

Table 8
Removal of divalent ions with membranes modified with PAMAM.

Support layer	Modified with	Applied for	Pollutant Removal	Ref.
PVDF-g-PAA	G0 PAMAM	NF	87% $MgCl_2$ 80% $MgSO_4$	(Sum et al., 2018)
PAN	G0 PAMAM	NF	86.4% $MgSO_4$ 47.1% $MgCl_2$	(Xu et al., 2012)
	G1 PAMAM		87.0% $MgSO_4$ 48.5% $MgCl_2$	
PES	PAMAM-MWCNT	NF	90.2% $MgSO_4$ 88.5% $MgCl_2$	(Zhang et al., 2018)
Psf	PAMAM-PZ	NF	>97.5% $MgSO_4$	(Sum et al., 2014)
Psf	PAMAM	NF	86.6% $MgCl_2$ 82.9% $MgSO_4$	(Deng et al., 2008)
PEK-C	PAMAM	NF	77.2% $MgCl_2$ 67.6% $MgSO_4$	(Lianchao et al., 2006)
Psf	PAMAM	NF	96.8% Mg^{+} 96.1% Ca^{+} 96.8% SO_4^{-}	(Qiu et al., 2021b)
PES	GO-PAMAM	RO	92.79%SO_4^{-} 92.08% Mg^{2+} 100% Ca^{2+}	(Al-Gamal and Saleh, 2022)
Psf	Ionic PAMAM	NF	91.2% $MgSO_4$ 45.7% $MgCl_2$	(Qiu et al., 2021a)
Polyimide	PAMAM	NF	>90% Na_2SO_4	(Cai et al., 2020)
Psf	Ionic PAMAM	NF	99.5% Na_2SO_4	(Qiu et al., 2021a)

layer. Diffusion of PAMAM to the organic layer during IP also improves the number of amine and amide groups during IP and creates a denser active layer. However, increasing the thickness of the active layer would also reduce the membrane flux. Although pore radius is an important factor in salt rejection, this factor has not been explored in detail by the researchers in case of NaCl rejection. The effect of PAMAM concentration and generation on salt rejection can be seen in Fig. 5.

Apart from NaCl, Na_2SO_4, $MgCl_2$, $CaCl_2$ and other multivalent salts have to be removed as well during desalination. Removal of multivalent salts are slightly less challenging than removing NaCl due to their larger particle diameter. The salt rejection usually in the following order: $Na_2SO_4 > MgSO_4 > MgCl_2 > NaCl$. Due to larger size of these multivalent salts, high salt rejection can be obtained during NF. Table 8 includes the membranes that have been modified with PAMAM and have been tested for multivalent salt rejection. As seen from Table 8, most membranes can remove >90% of the multivalent salts during NF. The PAMAM generation, concentration and diffusion rate have similar effect on NF membranes as discussed in section 4.1. For instance, Xu et al. used G0 and G1 PAMAM to synthesize NF membranes (Xu et al., 2012). The G1 NF membrane had a denser active layer and resulted in better $MgSO_4$ and $MgCl_2$ rejection rate compared to G0 NF membrane. In some studies, the large voids in PAMAM have been considered as a drawback for the PAMAM modified NF membranes in terms of salt rejection. Sum et al. used piperazine to fill the voids in PAMAM and improved the salt rejection by 30%–40% (Sum et al., 2014). The study also varies the concentration of PAMAM during interfacial polymerization and shows improvement in salt rejection. As seen in the study, increasing PAMAM concentration increases the salt rejections. This occurred due to denser membrane structure that resulted from increased PAMAM concentration during interfacial polymerization.

4.2. Removal of heavy metals

Heavy metals have become one of the major pollutants in industrial wastewater and disposal of untreated heavy metal rich wastewater can cause catastrophic destruction of the ecosystem. The abundance of amine groups on PAMAM makes them suitable for heavy metal adsorption during MF and UF process. Daillo et al. studied the EOB (extent of binding, moles of metal ions per mole dendrimer) of Cu^{2+} with PAMAM and found it to be 8, 13, 29, 46, 83 and 153 for G3, G4, G5, G6, G7 and G8, respectively

Table 9
Removal of heavy metals with membranes modified with PAMAM.

Support layer	Modified with	Applied for	Model pollutant	Adsorption capacity enhancement	Ref.
PVDF-g-PAA	G1 PAMAM G2 PAMAM G3 PAMAM G4 PAMAM	UF	Cu(II)	6,900% 74,00% 9,900% 8,900%	(Sun et al., 2019)
PVDF	G0 PAMAM G1 PAMAM	UF	Cu(II)	5,900% 5,400%	(Kotte et al., 2015)
PES	PA-PAMAM	RO	Pb(II)Cd (II)Cu (II)As (V)	36.8% 10.4% 209.7% 49.1%	
PVDF	G3 PAMAM-Pal	MF	Ni(II)Cd (II)Cu (II)	550% 500% 650%	(Zhang et al., 2019a)
BPPO	PAMAM	UF	Cu(II)Pb (II)	1,166% 1,566%	(Zhang et al., 2013)
PVDF-g-PAA	PAMAM	MF	Cu(II)	1,070%	(Sun et al., 2022)
PVDF-HFP	PAMAM	MF	Cd(II)	10.3%	(Macevele et al., 2020)

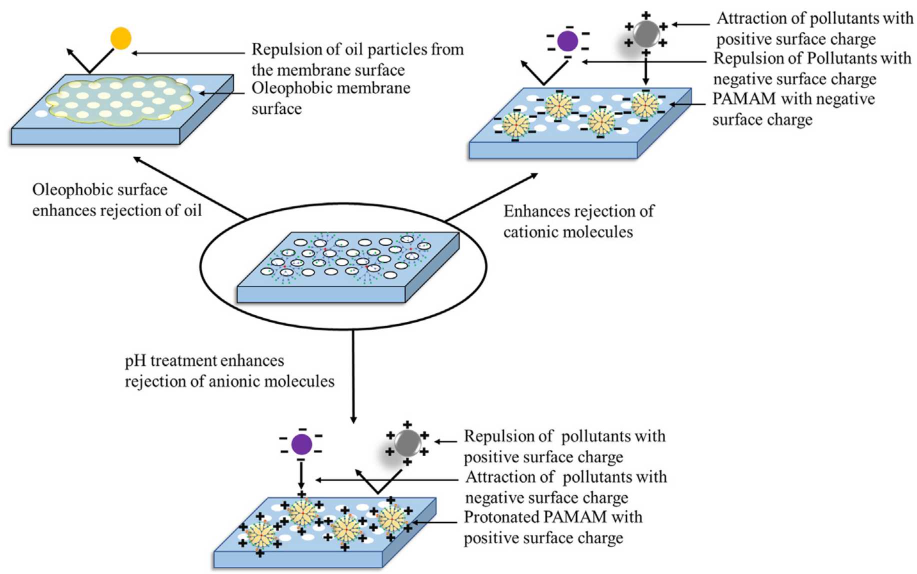

Fig. 7. General principle of pollutant rejection enhancement of PAMAM modified membranes.

Table 10
Treatment of oil emulsion with membranes modified with PAMAM.

Support layer	Modified with	Applied for	Reduction in oil conc.	Ref.
PVDF-g-PAA	SiO_2-PAMAM	MF	>99% n-hexadecane/water >99% n-dodecan/water >99% soyabean/water	(Wei et al., 2020)
Psf	PAMAM-SiO_2	NF	60% oily wastewater	(Jin et al., 2012)
PVDF	PP-Si-PAMAM	MF	>99% oily wastewater	(Zhang et al., 2022)
PES	GO-PAMAM	RO	100% Pentane 100% Nonane 100% Decane 100% Toluene	(Al-Gamal and Saleh, 2022)

(Diallo et al., 1999). The tertiary amine groups of PAMAM have a negative surface charge. This negative surface charge promotes the formation of coordinate bonds with Cu^{2+}, resulting in chemisorption of Cu^{2+} (Diallo et al., 2005; Ottaviani et al., 1994). However, at low pH, protonation of amine groups occurs and results in reduced cation adsorption. Similar adsorption mechanism has been suggested for Pb(II), Ag(I), Au(III), Pd(IV), Ni(II), Zn (II) and other heavy metals (Barakat et al., 2013; Barakat et al., 2014; Diallo et al., 2005; Yen et al., 2017; Zarghami et al., 2016).

Zhang et al. synthesized a PAMAM and multi-walled carbon nanotube (MWCNT) embedded NF membrane with high rejection rate of divalent anions and cations (Zhang et al., 2018). The $-NH_2$ group attached with PAMAM resulted in creation of positive sites in the membrane. Both positive sites offered by MWCNT & PAMAM and narrow pores resulted in electrostatic repulsion and size exclusion which enhanced heavy metal rejection rate. Incorporation of PAMAM in PES membrane reduces the pore size and increases the number of positively charged functional groups on the membrane surface. This will result in almost 99% rejection of heavy metals like Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+} and As^{3+}. The rejection of heavy metal is also aided by adsorption of heavy metals by PAMAM nano particles (Zhu et al., 2015). PAMAM possesses abundant number of terminal amine groups (Bao et al., 2019). The electrostatic repulsion between protonated amine layer and NH_4^+ and concentration induced diffusion resistance improves NH^{4+} rejection and reverse solute flux in FO. Moreover, during this study the PAMAM attracted the negatively charged organic foulants and repulsed the positively charged metals ions which also reduced membrane fouling (Bao et al., 2019). Zhang et al. synthesized PAMAM dendronized BPPO hollow fiber membrane for recovering heavy metal (Zhang et al., 2013). The nanoparticles in membrane showed superior binding quality with Cu^{2+}, Pb^{2+} and Cd^{2+}. Sun et al. studied the effect of PAMAM generation on the adsorption capacity of a PVDF membrane (Sun et al., 2022). The study found that increasing PAMAM generation up to generation 3, the Cu(II) adsorption capacity of the membrane increases. This is because, at higher PAMAM generation, there are more adsorption sites for Cu(II) adsorption. Moreover, generation 3 PAMAM has lower static hindrance which makes it better than generation 4 PAMAM where higher static hindrance reduces the number of active adsorption sites. Table 9 lists all the studies that have modified membranes with PAMAM and used them for heavy metal rejection. The mechanism of heavy metal removal from wastewater while using PAMAM modified membranes can be seen in Fig. 7.

4.3. Removal of oils

The oil and gas industry produces a large quantity of produced water during their production. These produced waters are rich with oils and disposing them without proper treatment can cause environmental issues. By MF and UF, the oil content of the wastewater or oil emulsions can be reduced by >99%. However, the main drawback of this process is in the oleophilic nature of the polymeric membranes. This causes reduction of oil removal efficiency and increased irreversible membrane fouling. Reducing the oleophilicity of the polymeric membranes through modification of the membrane surface with PAMAM showed significant improvement in oil removal efficiency and membrane fouling.

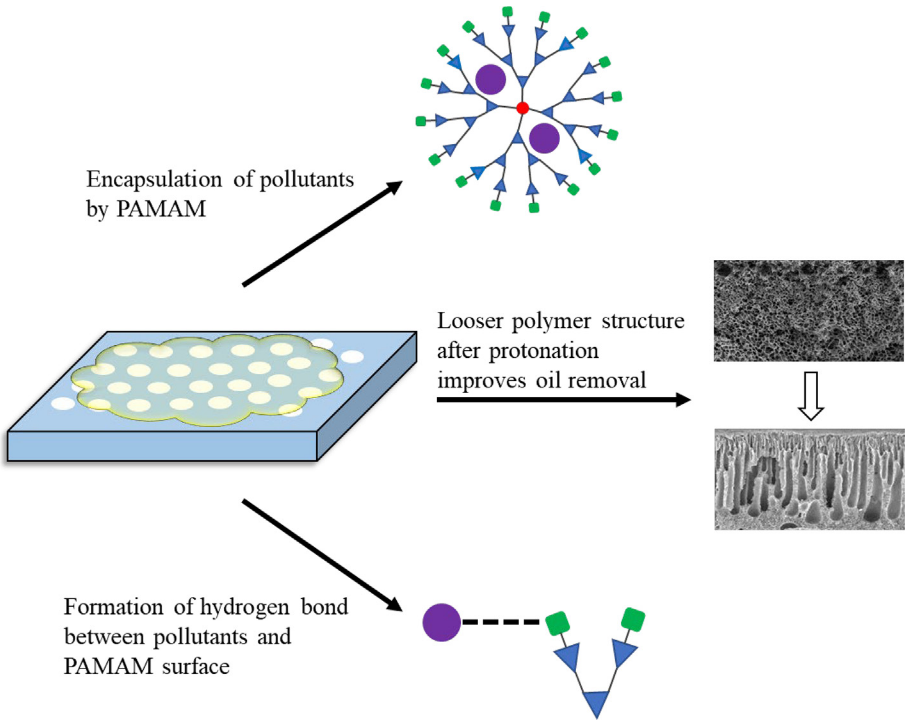

Fig. 8. Miscellaneous mechanism of pollutant removal due to the presence of PAMAM.

Table 11
Removal of other types of pollutants with membranes modified with PAMAM.

Support layer	Modified with	Applied for	Pollutant Removal	Ref.
SPES	PAMAM	FO	93% NH^{4+}-N	(Bao et al., 2019)
PTFE	GO-PAMAM	Pervaporation	82.79% EtOH 91.87% *i*-PrOH 90.86% BuOH 93.53% *i*-BuOH	(Song et al., 2019)
PVA/PAA	PAMAM	MF	>95% Toluene	(Amariei et al., 2017)
Acrylic UF	PAMAM	UF	82.5% Lasalocid A 87.3% Salinomycin 91.3% Semduramicin	(Cao et al., 2020)
Acrylic UF	PAMAM	UF	91.4% tulathromycin	(Bojaran et al., 2019)
PES	Ag-GO-PAMAM	UF	98.7% $Cr(NO_3)_3$	(Mansourpanah et al., 2021)
SPES	PAMAM	FO	>99% NH_4^+-N	(Bao et al., 2021)
PA 6	PAMAM	UF	78% Li^+	(Johal et al., 2013)

The PAMAM enhanced membranes used for removal of oils and treatment of oil emulsions are listed in Table 10. Al-Gamal & Saleh have achieved 100% removal of different oils using GO-PAMAM enhanced RO membrane. The smaller pore size of the RO membrane aided in removing 100% of the oils. Similar oil rejection could be obtained by the MF process as shown by Zhang et al. who achieved >99% removal of oils from oily wastewater during MF using a PAMAM enhanced MF membrane (Zhang et al., 2022). In this study, the concentration of G3 PAMAM was varied between 0 and 8 wt% and its effect on the oil separation efficiency was studied. By adding PAMAM to the membrane matrix, the separation efficiency was improved by almost 20%. The author attributed this improvement on improved hydrophilicity of the membrane. Similar trend was observed by Wei et al. (Wei et al., 2020). Zhang et al. (2022) observed significant improvement in oil/water separation during filtration tests in acidic medium where protonation of the amine groups take place and changes the polymers to a loose state from a dense state. This promotes lower oil adhesion and promotes oil–water separation. The mechanism of oil removal while using PAMAM modified membrane has been summarized in Fig. 7 and Fig. 8.

4.4. Removal of other types of pollutants

In addition to salts, oils and heavy metals, PAMAM modified membranes were used to remove bacteria, organic pollutants and pharmaceutical pollutants. Table 11 lists the different available studies carried out using PAMAM modified membranes to remove these pollutants. Cao et al. grafted PAMAM on to the commercial UF membrane to treat veterinary antibiotics (Cao et al., 2020). The modified membrane showed >90% rejection of Lasalocid A, Salinomycin and Semduramicin. Along with reduced pore size and negative surface charge, negatively charged PAMAM branches aided in rejection of these antibiotics. Amariei et al. functionalized PVA-PAA membrane with G3 PAMAM to remove microbes and low molecular weight non-polar pollutant from wastewater (Amariei et al., 2017). The composite electro-span membrane was found to be suitable for removing gram positive microbes. Through docking studies, it was found that low molecular weight nonpolar molecules like toluene are encapsuled by PAMAM due to host–guest chemistry, thus resulting in their enhanced removal. Johal et al. developed a composite membrane with PAMAM and Nylon 6 for removing Li^+ from wastewater (Johal et al., 2013). The large surface area and good mechanical strength made the membrane suitable for water UF. Bojaran et al. synthesized PAMAM membrane on acrylic UF membrane for treating veterinary wastewater (Bojaran et al., 2019). Veterinary antibiotics drugs like macrolides and pleuromutilins have positive surface charge which makes negatively charged PAMAM ideal nanofiller for treating veterinary antibiotics. Bao et al. used PAMAM modified membranes for removing NH^{4+} from the wastewater (Bao et al., 2019). PAMAM possesses abundant number of terminal amine groups. The electrostatic repulsion between protonated amine layer and NH^{4+} and concentration induced diffusion resistance improves NH^{4+} rejection and reverse solute flux in FO. Moreover, the PAMAM attracted the negatively charged organic foulants and repulsed the positively charged metals ions which also reduced membrane fouling (Bao et al., 2019). The mechanism of enhanced pollutant rejection while using PAMAM modified membrane has been summarized in Fig. 7 and Fig. 8.

Apart from the above discussed pollutants, PAMAM modified membranes can also be used to remove other organic pollutant and dyes. Although removal of these pollutants using these membranes is still scarce in the literature, the pollutant removal mechanism would be similar. For example, the adsorption of anions depends on two factors, hydrophobicity of anions and polarity of the solvent. PAMAM with hydrophobic cavities and positively charged internal groups are deemed suitable for adsorption of anions (Diallo et al., 2007). At low pH, protonation of PAMAM takes place and promotes development of positive electrostatic attraction for anions (Diallo et al., 2007). At pH 4 and 11, EOB of ClO_4^- on PAMAM was found to be 9 and 1.5, respectively (Diallo et al., 2007). We should also note that, below pH equals 2, anions oxidizes and become neutral molecules which cannot be adsorbed on PAMAM electrostatically (Zhao et al., 2015). PAMAM was also used to adsorb anionic and cationic dyes at acidic and basic conditions, respectively (Eskandarian et al., 2014; Salimpour Abkenar et al., 2015). Cationic dye BB9 and anionic dye DR23 were adsorbed by PAMAM at pH of 11 and 3, respectively. In the adsorption process of cationic dye, hydrogen bonding, electrostatic interaction and trapping of dye molecules in the cavities of PAMAM was found responsible for the enhanced adsorption performance (Salimpour Abkenar et al., 2015). In case of adsorption of anionic dies, anionic dye ions have to be first formed in the water and then will bind with protonated PAMAM (Eskandarian et al., 2014). Dendrimers have also been used for adsorption of organics from wastewater through modification of titania with PAMAM (Hayati et al., 2016). The nanohybrid contains positively charged PAMAM and negatively charged titania. During treatment of phenolic wastewater, formation of hydrogen bonds between phenolic hydroxide and PAMAM/titania nanohybrid has been observed. The presence of oppositely charged hydrogen forming molecule made the adsorption process pH independent. The above discussion suggests that low pH is suitable for adsorption of anionic molecules whereas high pH is suitable for adsorption of cationic molecules on PAMAM. The basic of pollution adsorption mechanism can be seen in Fig. 7.

5. Research gap and conclusions

Membrane technologies are among the most suitable wastewater reclamation technologies due to their low energy requirement and simplicity of operation. However, the membrane technologies suffer from low water permeation flux and high membrane fouling due to the hydrophobic nature of the polymeric membranes. The presence of amine groups in high density, makes PAMAM a suitable hydrophilic nano-filler for polymeric membranes. In this review, we analyzed the performance of different PAMAM and PAMAM nanocomposite incorporated polymeric membranes in terms of membrane flux enhancement, irreversible fouling reduction and improvement in hydrophilicity. We have also reviewed the effect of PAMAM incorporation on different pollutant rejection efficiency and the pollutant rejection mechanism.

The review showed that three primary methods of PAMAM incorporation have been used for membrane modification, (i) surface grafting, (ii) PA actively layer formation and (iii) blending with polymer during phase inversion. Incorporation of PAMAM using all three methods has shown significant improvement in polymeric membrane hydrophilicity which has resulted in improved permeate flux and reduced membrane fouling. For microfiltration applications, surface grafting of PAMAM has shown up to 114.9° reduction in water contact angle which resulted in 160 times higher water flux and 99% reduction in irreversible membrane fouling. However, the sustainability of these improvements has not been addressed. Nanoparticle leaching from the surface grafted membranes is one of the major concerns in the surface grafting technology. The solubility of PAMAM in water adds an additional layer to this problem.

Usage of PAMAM to form the PA active layer during interfacial polymerization process has resulted in up to 68° reduction in water contact angle, which led to 105% improvement in water permeation flux during reverse osmosis. However, this trend was not observed in all the studies as 97% water permeation flux reduction has also been observed in the study by Xu et al (2012). Apart from the PAMAM addition, the performance of reverse osmosis membrane also depends on various other factors, including the thickness of the active layer. Although a clear indication was not observed in terms of flux enhancement, the improved porosity of the reverse osmosis membrane was reported in many experimental works. Moreover, the fouling performance of PAMAM incorporated reverse osmosis membranes has not been extensively studied and details of interaction between surface active PAMAM with different salts is also missing in the literature.

Blending functionalized PAMAM in the polymeric membrane matrix has reduced the contact angle by 52.7° which resulted in 392% permeation flux enhancement and 49% reduction in irreversible fouling. However, there are not enough experimental work done on PAMAM and PAMAM nanocomposite blended membranes. In addition, more experimental work has to be done to verify the improvements in membrane performance achieved using the PAMAM blended membranes.

So far the research showed promising improvements in polymeric membranes after incorporation of PAMAM nanofillers. However, a lot of work is yet to be done on PAMAM incorporated polymeric membranes including the following:

- PAMAM are well known to be soluble in water, hence, they easily leach from the membrane matrix (Beezer et al., 2003). However, most studies available in the literature ignored the implication of nanoparticle leaching from the fabricated membrane. For longevity of the membrane process, the integrity of the membrane must be conserved. Therefore, additional studies on leaching of dendrimers toned to be undertaken. Dendrimers can be anchored on other more stable nanoparticles before they are incorporated in the membrane matrix (Cui et al., 2019). This would not only make the membrane more stable, but also add new characteristics to the membrane that need to be revealed.
- High viscosity of polymers prevents appropriate dispersion of nano-fillers in the membrane matrix. This can lead to agglomeration of nanoparticles and deteriorate membrane properties.

Moreover, the surface charge of PAMAM depends on its terminal functional group where –NH2 terminated PAMAM exhibits positive surface charge, whereas –OH terminated PAMAM exhibits negative surface charge. The polymers generally exhibit negative surface charge. Detailed investigation is needed to understand the interaction between different polymers and PAMAM which will help to optimize PAMAM dispersion in the membrane matrix. Without proper dispersion of nano-polymers, reproducible performance cannot be obtained for the membrane. Inadequate dispersion of nano-polymers would also reduce the longevity of the membrane.

- The surface active PAMAM molecules can easily adsorb pollutants on its surface which makes PAMAM incorporated membranes highly efficient in pollutant removal from wastewater. However, the adsorption sites have to be regenerated on the membrane surface to ensure longevity of the membrane process. Regeneration of this adsorption sites on the membrane surface has not been experimentally studied. Depending on the pollutant type, special cleaning regimes has to be developed for the PAMAM incorporated membranes.
- Another challenging aspect of developing a dendritic membrane is to ensure the scalability of the membrane process. Currently, synthesis of dendrimer is harder than synthesis of many other nanoparticles, which makes controlling the membrane synthesis process difficult. More research is needed on synthesis of dendrimers to ease the membrane synthesis process and improve its scalability. This will also make the process more cost effective which is another important aspect missing from the literature and requires more investigations.
- Improvement in water permeation flux and reduction in fouling is expected to reduce the operating cost of the membrane technologies. However, the cost of PAMAM is still very high and detailed life cycle cost analysis of a PAMAM incorporated membrane processes would give a better indication of the advancement on current state of art membrane technologies.
- Finally, PAMAM is the only dendrimer that has been used for fabricating new membranes. Other dendrimers; such as Poly (propylene imine) (PPI), Carboxymethyl chitosan-modified magnetic-cored dendrimers (CCMDs), tris(hydroxymethyl) aminomethane (TRIS), polar nano-dendritic adsorbent containing amine groups (SAPAMAA) and others; contain a large number of hydrophilic functional groups that showed promising pollutant removal efficiency and have not had sufficient attention from researchers (Wazir et al., 2020). It is recommended that these dendrimers should be tested as nanofillers for polymeric membranes.

CRediT authorship contribution statement

Ahmed T. Yasir: . **Abdelbaki Benamor:** Writing – review & editing, Project administration. **Alaa H. Hawari:** Writing – review & editing, Project administration. **Ebrahim Mahmoudi:** Conceptualization, Visualization.

Data availability

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

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.

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