The Impacts of Iron Oxide Nanoparticles on Membrane Properties for Water and Wastewater Applications: a Review

Nadiene Salleha Mohd Nawi[1,2] · Woei Jye Lau[1,2] · Norhaniza Yusof[1,2] · Ahmad F. Ismail[1,2]

Abstract

The sustainability of clean water supply remains as one of the grand crises faced by today's world. The rapid expansion of membrane technology has opened up the opportunities for its applications in the sector of water and wastewater treatment. However, the commercial polymeric membranes are suffered from low degree of hydrophilicity and prone to different types of surface fouling. The incorporation of inorganic nanomaterials as nanofillers within polymeric matrix to produce nanocomposite membranes has received enormous attention because of its ability to resolve underlying issues encountered by conventional polymeric membranes. Among various nanoparticles, iron oxide (Fe_3O_4) nanoparticles have sparked great interest in the fabrication of nanocomposite membranes owing to its intrinsic properties that could improve not only the membrane surface hydrophilicity and antifouling properties but also its removal rates against pollutants via sieving and/or adsorption mechanisms. This review aims to provide insights on the recent advances of Fe_3O_4-modified microporous membranes for both water and wastewater treatment. Novel strategies such as surface functionalization and nanohybridization of Fe_3O_4 nanoparticles and its impacts on membrane physicochemical properties and separation performances have been explored and critically reviewed. Finally, the technical challenges in utilizing Fe_3O_4-modified microporous membranes for potential applications in real operation are also discussed.

1 Introduction

As water reclamation has become critical to relieve clean water scarcity, membrane technology has emerged as a promising alternative that could overcome the limitations of the conventional water treatment methods due to its high separation performance, reliability, small footprint, ease of operation and cost-effectiveness [1]. Polymeric membranes in particular have gained widespread attention owing to its ease of fabrication, good balance between water flux and rejection, as well as low manufacturing cost [2, 3].

Among various pressure-driven membrane filtration processes, ultrafiltration (UF) membranes are widely used to remove organic matters, colloidal particles and macromolecules present in water and wastewater. UF membranes offer several unique advantages such as high separation efficiencies against particles/molecules of micron size, promising water production rate, minimum energy requirement (due to its low operating pressure) and low maintenance cost [4–6]. Various polymers have been used as the main material for the development of UF membranes, and some of the commonly used materials for commercial UF membrane manufacturing are polyvinylidene fluoride (PVDF), polysulfone (PSf) and polyethersulfone (PES). Although the membranes made of these polymeric materials do not encounter major issues in the industrial operation, their low degree of surface hydrophilicity which is prone to different types of fouling could lead to flux declination and increase in operation cost [3, 7].

In order to mitigate fouling phenomenon such as colloid and organic fouling, focus has been placed on surface modification of polymeric membrane via inorganic nanoparticles incorporation, aiming to develop nanocomposite membranes with improved surface characteristics. The research on this

✉ Woei Jye Lau
  lwoeijye@utm.my; lau_woeijye@yahoo.com

1 Advanced Membrane Technology Research Centre
   (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai,
   Johor, Malaysia

2 School of Chemical and Energy Engineering, Universiti
   Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

topic had sparked great interest as the presence of inorganic materials in the polymeric matrix could offer synergistic effects to the resultant membrane, improving not only the membrane fouling resistance but also its water permeation rate without compromising solute rejection [8]. In certain cases, the presence of nanoparticles in polymeric matrix was found to promote the membrane chemical, thermal and mechanical stability, making them suitable for use in harsh conditions such as corrosive and high temperature environments [9–13].

One of the popular nanoparticles that have been always reported as the promising nanofillers in modifying microporous membrane is iron oxide (Fe_3O_4) nanoparticles [14–17]. Similar to other commonly used nanoparticles such as titanium oxide (TiO_2) [18–20], zinc oxide (ZnO) [21–23] and silica (SiO_2) [24–26], Fe_3O_4 also shows promising results in enhancing the characteristics of microporous membranes for water applications [27–29]. In general, Fe_3O_4 can be used to modify either top surface of membrane (via coating technique) or its bulk structure (via blending method during dope preparation) and its quantity introduced varies depending the applications. Besides exhibiting good hydrophilicity and good thermal and chemical stability, Fe_3O_4 also possesses outstanding magnetic properties, low toxicity and adsorption ability that make it suitable for membrane modification [30–32]. A literature search indicated that the Fe_3O_4-modified membranes have been studied for wide range of applications. These include palm oil mill effluent treatment [33, 34], dye removals [35, 36], high strength wastewater such as oily wastewater and food industrial wastewater [16, 37, 38], as well as heavy metal removal [39–41].

We have seen a significant number of review articles published over the years on the development of nanocomposite membranes incorporated with different types of nanomaterials including TiO_2, ZnO, carbon nanotubes (CNTs), graphene oxide (GO) and metal organic frameworks (MOF) [42–46], but a comprehensive review of Fe_3O_4-modified microporous membranes is still limited despite its extensive scientific literature. Figure 1 shows the number of research articles related to Fe_3O_4-modified membranes for water and wastewater treatment published over the past decade with an upward trend observed in recent two years. Many studies have proved that the membranes incorporated with Fe_3O_4 are able to compete if not surpassing the conventional polymeric membranes performances. Thus, there is a need to review these developments in order to lead further studies in the near future.

This paper aims to review the recent progress of Fe_3O_4-modified microporous membranes for both water and wastewater treatment. The impacts of different types of Fe_3O_4 such as typical, functionalized, hybrid Fe_3O_4 on the surface properties and filtration performance of the
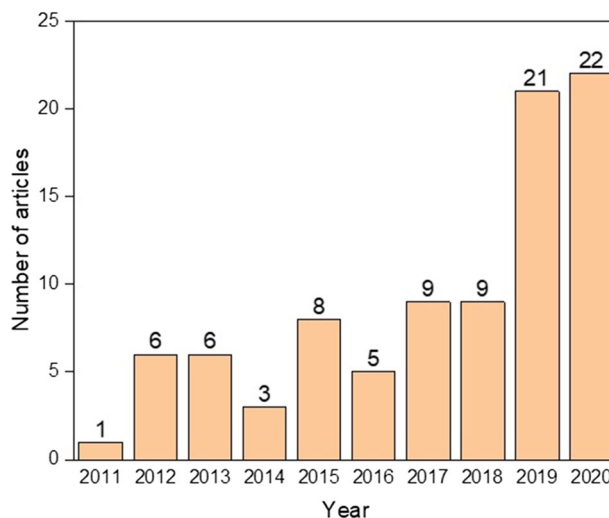

Fig. 1 Number of relevant research articles published in refereed journals between 2011 and 2020 for water and wastewater treatment (Data from Scopus, Assessed on May 16, 2021. Search: Fe_3O_4 membrane water or iron oxide membrane water; Field: Article title, abstract, keywords; Limit to: Top 20 most relevant source titles with further screening on the article contents)

membranes will be reviewed for both pressure-driven and adsorptive processes. At last, the technical challenges of making Fe_3O_4-modified microporous membranes will also be discussed to provide insights into development of better nanocomposite membranes.

2 Characteristics of Iron Oxide Nanoparticles

Iron oxide nanoparticle, which is composed of iron (Fe) and oxygen (O) atoms, has molecular weight of 159.69 g/mol. It has many forms in nature, among which are the commonly known phase magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3) as shown in Fig. 2. Magnetite has a cubic inverse spinel structure with Fe^{3+} ions randomly distributed between octahedral and tetrahedral sites, and Fe^{2+} ions in octahedral sites. Maghemite meanwhile has the similar cubic structure but with a defect spinel, where the absence of Fe^{2+} ions in its structure is composed of Fe^{3+} and O^{2-} ions. In hematite, O^{2-} ions are in rhombohedral/hexagonal close-packed arrangement, with Fe^{3+} ions occupying octahedral sites [32, 47, 48].

Magnetite is the most preferred material as it exhibits several promising properties such as great biocompatibility and chemical stability, low toxicity, ease of synthesis/surface functionalization and excellent magnetic properties due to its symmetrical structure sites [32, 49, 50]. It is worth noting that different properties of Fe_3O_4 nanoparticle such as its size, shape, morphology, dispersibility and magnetism can affect its application as nanofillers in polymeric membrane [31,
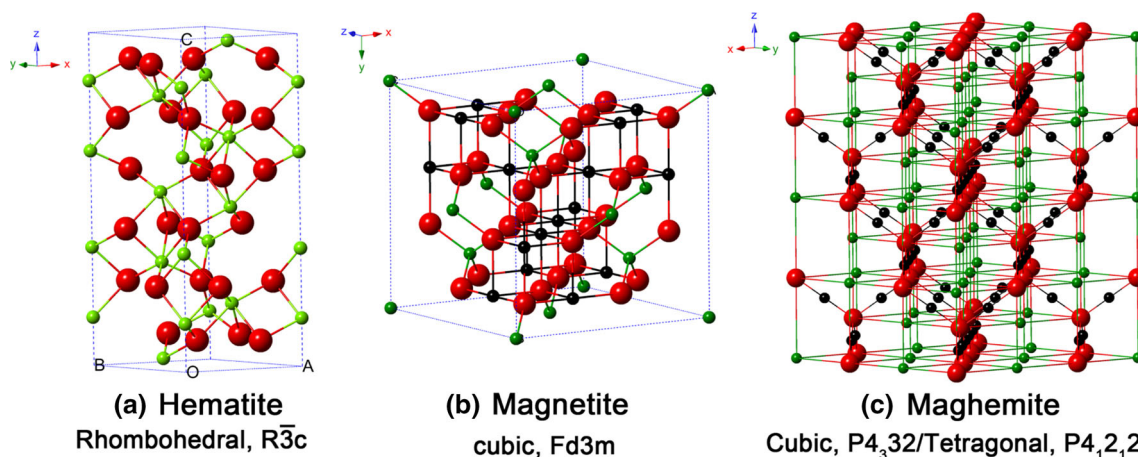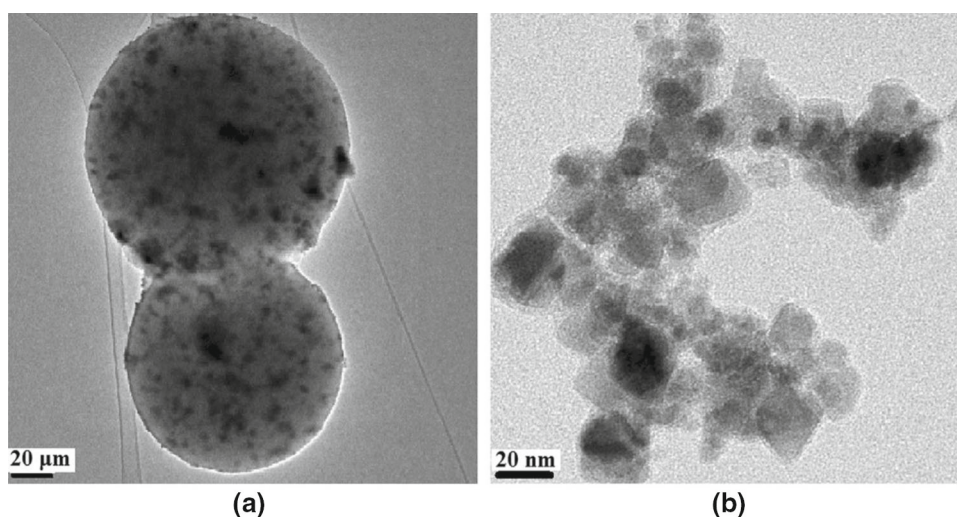
Fig. 2 Crystal structure of Fe_3O_4, **a** hematite, **b** magnetite and **c** maghemite (Note: black ball: Fe^{2+}, green ball: Fe^{3+} and red ball: O^{2-}) [30]

Fig. 3 TEM images of **a** micro-sized Fe_3O_4 and **b** nano-sized Fe_3O_4 [60]

51]. Hence, many efforts have been focused on developing different synthesis methods to produce Fe_3O_4 nanoparticles with desirable properties. Some of the synthesis methods are co-precipitation, hydrothermal reactions, thermal decomposition, microemulsion, sol–gel reactions and electrochemical method. Among them, co-precipitation and sol–gel reactions are the most extensively used methods due to their simplicity and ease of particle size control [52, 53].

Fe_3O_4 can appear in two different scales as shown in Fig. 3. Micro-sized Fe_3O_4 (0.2–1.5 µm) usually possesses Brunauer–Emmett–Teller (BET) surface area of between 6 and 29.23 m^2/g, while nano-sized Fe_3O_4 (5–37 nm) could show significantly higher BET surface area of 165.05–286.9 m^2/g [54–57]. Besides showing different surface area, both particles also display different magnetic properties, surface energy level and dispersibility [57, 58]. As the particle size decreases, the surface area-to-volume ratio tends to increase which allows more molecules to attach on its active surface sites. Nevertheless, the nanoparticles tend to aggregate more compared to the microparticles due to its larger surface

area. Since nanoparticles are commonly used in membrane fabrication, the issues associated with aggregation and ununiformed nanoparticles are one of the main concerns as it could lead to microdefects which affect separation rate [2, 59]. In view of this, surface modification is recommended as a strategy to improve nanoparticles dispersion and stability in the membrane matrix. In addition, surface functionalization could also be useful to enhance biocompatibility of nanoparticles with the membrane which as a consequence leads to better performance [30–32].

Fe_3O_4 nanoparticles have been extensively used as nanofillers in nanocomposite membranes, taking advantage of its hydrophilicity, superparamagnetic and excellent adsorptive capacity. The abundance of hydroxyl groups available on the large surface of Fe_3O_4 is the main factor making this nanomaterial highly hydrophilic in nature and important in attracting water molecules during water filtration process. This as a result improves membrane water permeability [2, 61–63]. Due to the superparamagnetic behavior of Fe_3O_4 nanoparticles (at zero net magnetization), the use of external

Table 1 Important characteristics of Fe_3O_4 nanoparticles for membrane fabrication [15, 52–54, 61, 62, 67–69]

Physical property	Chemical property	Biocompatibility
High surface area to volume ratio Small particles size	Highly hydrophilicity Antifouling characteristics Excellent absorptivity Superparamagnetism	Good biocompatibility Low toxicity

magnetic field can enhance membrane properties and performances by rearranging the alignment orientation of Fe_3O_4 nanoparticles closer to membrane surface, producing membrane with sturdy sublayer and more hydrophilic top surface [15, 57, 64–66]. It also demonstrates excellent adsorptivity toward heavy metal contaminants. For instance, the maximum adsorptive capacity of Fe_3O_4 against copper(II) ions was reported to be 18.61 mg/g and such value was further improved to 59.6 mg/g upon integrating it with carboxylate multi-walled carbon nanotubes (MWCNTs) [67–69]. The good adsorptive performance of Fe_3O_4 nanoparticles is due to its small size coupled with the electrostatic attraction between the nanoparticles and metal ions that facilitates ion exchange. The key characteristics of Fe_3O_4 nanoparticles that would be useful in improving membrane properties are listed in Table 1.

3 Impact of Iron Oxide Nanoparticles on Membrane Properties

While nanocomposite membranes are known to be plagued with some significant bottlenecks such as nanofiller loadings, dispersibility and leaching, the technical progress and the accompanying knowledge in the development of membranes incorporated with Fe_3O_4 nanoparticles have grown rapidly to address the underlying problems. The addition of nanofillers at its optimum loading is generally known to bring an improvement in membrane permeability and selectivity without affecting its structural integrity [2, 3, 70, 71], but tendency of the nanoparticle to agglomerate at an excessive loading might cause severe problems including poor membrane mechanical property, significant reduction in water flux (due to pore blocking) and extremely rough membrane surface which is prone to surface fouling. All these issues could restrict the applications of resultant membranes. Thus, it becomes essential to improve Fe_3O_4 nanoparticles dispersion in the polymeric membrane matrix [3, 70, 72].

It has been reported in the literature that surface functionalization of Fe_3O_4 nanoparticles has a substantial influence

in boosting not only its dispersion in membrane matrix, but also its biocompatibility, surface activity and physicochemical properties [30–32]. Aside from modifying nanoparticles, the development of hybrid nanomaterials has also garnered attentions in an effort to reduce the aggregation effects of Fe_3O_4 nanoparticles. By coupling the Fe_3O_4 with a different nanoparticle, a synergistic effect could be created, hence producing hybrid nanoparticles that are good for the nanocomposite membrane development [70, 73, 74].

3.1 Conventional Pressure-Driven Membranes

Conventional pressure-driven UF membranes have been a leading separation technology for a wide range of water and wastewater treatment applications. The following subsections will provide a review the impacts of different types of Fe_3O_4 nanoparticles on the properties of microporous UF membranes.

3.1.1 Typical Fe_3O_4

One of the earliest works that incorporated Fe_3O_4 nanoparticles in the membrane matrix was reported by Jian et al. [65]. In this study, oleic acid-treated Fe_3O_4 nanoparticles were blended into PSf solution and the resultant modified membrane was used for lysozyme rejection (molecular weight of lysozyme: 14,300 g/mol). Due to its superparamagnetic properties, Fe_3O_4 nanoparticles can be manipulated to arrange along the force magnetic line when it is magnetized. The behavior of Fe_3O_4-modified membrane was observed under magnetic field influence to examine whether it would affect the rejection performance. Figure 4 shows the surface and cross section structures of the membranes with and without 0.27 wt% Fe_3O_4 incorporation. It was apparent that the nanoparticles were uniformly distributed across the membrane surface, inner pores and walls. With respect to contact angle, the Fe_3O_4-modified membrane showed higher value (73°) compared to the neat PSf membrane (58°), owing to the use of oleic acid to modify Fe_3O_4 nanoparticles. This in turn improved membrane surface hydrophilicity.

As Fe_3O_4 nanoparticles possess magnetic property, the use of it for membrane modification could lead to different lysozyme rejection rates when a different magnetic field intensity was used during filtration process. Jian et al. [65] showed that the membrane rejection against lysozyme was recorded at 88% when magnetic field of 0.18 Tesla (T) was used. This was significantly higher compared to the rejection (55%) achieved at higher magnetic field (0.4 T). When stronger magnetic field was used, it tended to cause lysozyme molecules to move in a circle that could weaken the membrane sorption and decrease boundary layer thickness, leading to lower rejection. When compared with the neat PSf membrane, the magnetic field has little to no effect on

Fig. 4 SEM micrographs of surface (top) and cross section (bottom) of **a**, **c** neat PSf membrane and **b**, **d** Fe$_3$O$_4$-modified PSf membrane [65]
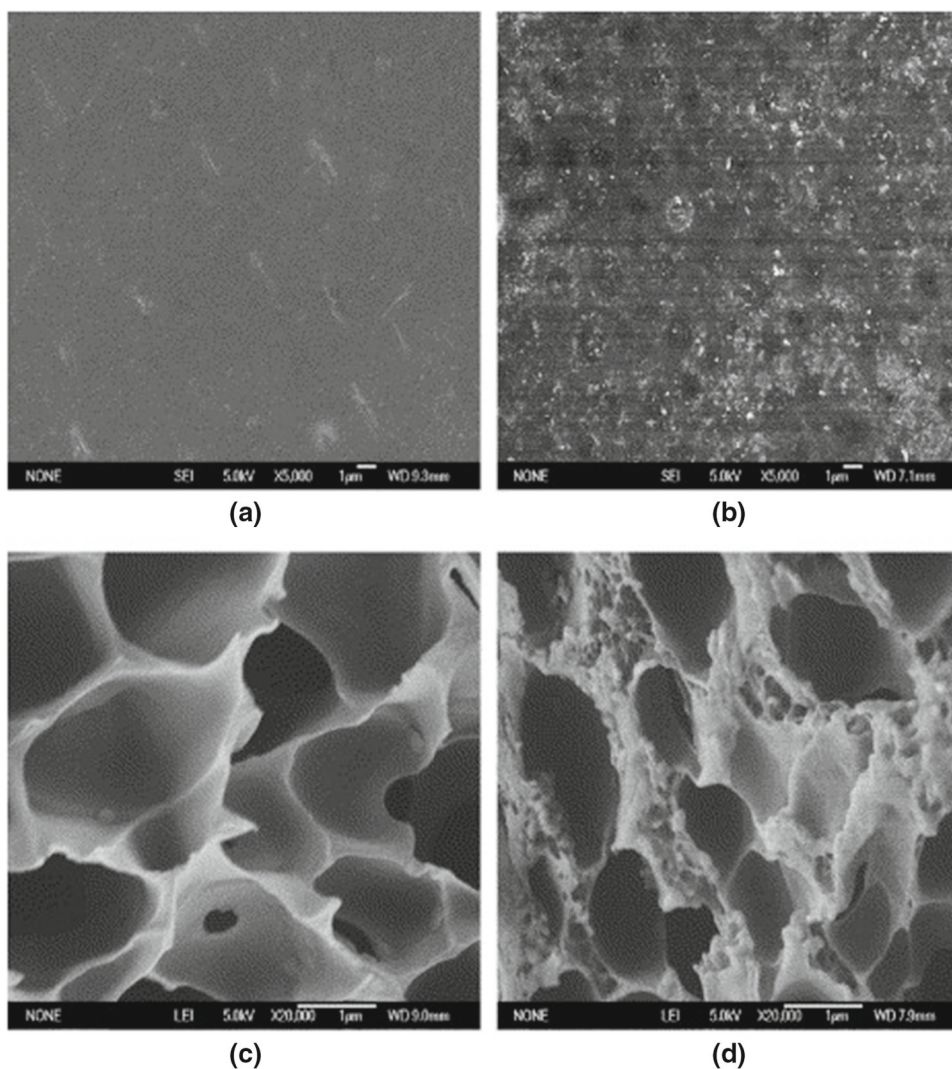
the lysozyme rejection due to the absence of Fe$_3$O$_4$ nanoparticles in the membrane matrix.

Rambabu and Velu [75] modified PES-based membranes using Fe$_3$O$_4$ nanoparticles (0–4 wt%) and used the resultant membranes for removal of Orange II and Congo Red. Compared to the pristine PES membrane, it was found that the presence of nanofillers tended to increase the surface pore size and porosity of the membrane. In addition, the surface hydrophilicity of membrane was also improved which could be attributed to the decrease in water contact angle upon Fe$_3$O$_4$ incorporation. As shown in Fig. 5, the membrane blended with 3 wt% Fe$_3$O$_4$ nanoparticles showed 4 times higher pure water flux than that of pure PES membrane, recording 64 L/m^2.h at 2.76 bar. Nevertheless, it must be noted that the separation efficiency of the membrane was negatively affected when large amount of Fe$_3$O$_4$ nanoparticles was used (>3 wt%). With respect to thermal stability, the Fe$_3$O$_4$-modified membranes showed improved thermal

resistance as uniform distribution of Fe$_3$O$_4$ nanoparticles in the membrane matrix increased the thermal stability of the membrane.

Bagheripour et al. [77] reported an improvement in salt separation and antifouling performance of PES membrane upon incorporation of Fe$_3$O$_4$ nanoparticles. Based on the atomic force microscopy (AFM) images, the introduction of Fe$_3$O$_4$ nanoparticles (<3 wt%) was found to be able to reduce the number of peaks and valleys on the membrane surface, creating a smoother surface. This is due to the filling of Fe$_3$O$_4$ on the membrane surface that significantly reduces the surface roughness. Despite the improved surface hydrophilicity upon Fe$_3$O$_4$ nanoparticles incorporation, the flux of the Fe$_3$O$_4$-modified membrane was still lower (23 L/m^2.h) than that of pure PES membrane (35 L/m^2.h) when both membranes were tested at 5.5 bar. This might be due to pore blockage by the Fe$_3$O$_4$ nanoparticles which increased water transport resistance and thus reduced water permeation
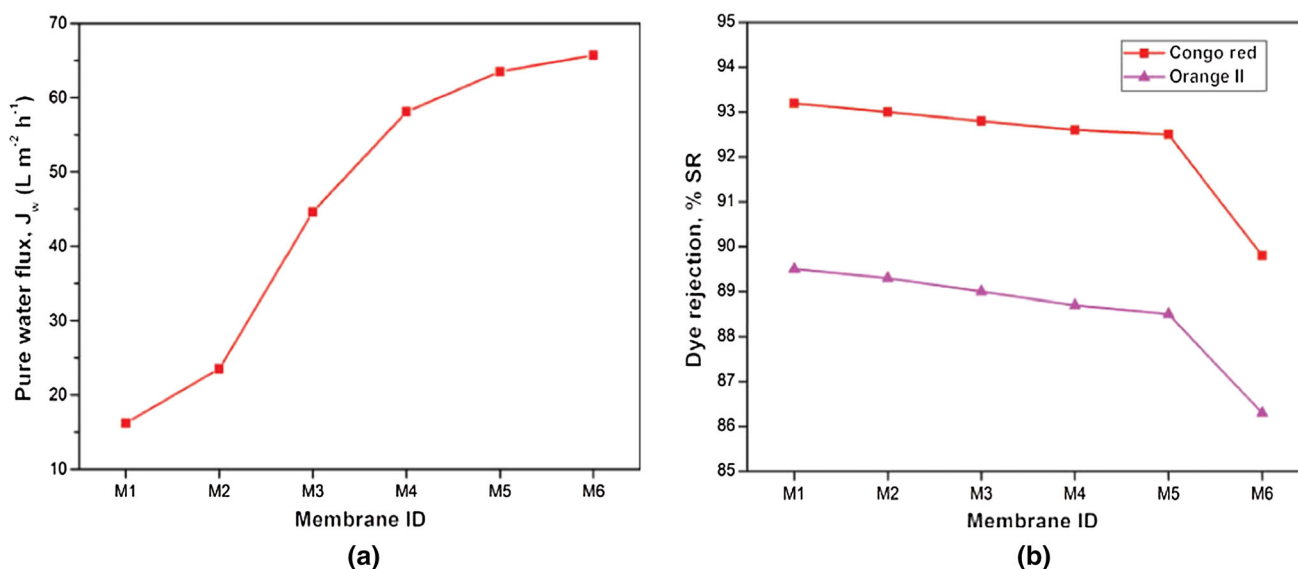
Fig. 5 Performance of PES and Fe$_3$O$_4$-modified PES membranes, **a** pure water flux and **b** dye rejection (Note: M1: pure PES membrane, M2: PES membrane with PEG, M3–M6: PES membrane with 1, 2, 3 and 4 wt% Fe$_3$O$_4$ in the presence of PEG) [76]

rate. Nevertheless, the improved surface hydrophilicity of the modified PES membrane was found to be effective in enhancing antifouling performance against milk solution as high flux recovery rate (FRR) of 87.4% was achieved by Fe$_3$O$_4$-modified membrane in comparison with 38.1% shown in the pristine membrane. The FRR of modified membrane, however, was dropped to 71.1% when 4 wt% Fe$_3$O$_4$ was introduced into the membrane matrix as increase in membrane surface roughness made it more susceptible to organic fouling.

Gholami et al. [78], on the other hand, reported the positive effect of Fe$_3$O$_4$ nanoparticles on the hydrophilicity of membrane made of polyvinyl chloride (PVC). With the incorporation of only 0.1 wt% Fe$_3$O$_4$, the water content of the modified membrane was found to increase (corresponding to improved hydrophilicity) in comparison to the pure PVC membrane. When tested at 5 bar, the modified membrane also showed 50% greater water flux (75 L/m^2.h) than that of pure membrane (50 L/m^2.h). However, flux was reported to decrease when high loading of Fe$_3$O$_4$ nanoparticles was introduced (1 wt%). This is likely due to membrane pore blockage caused by the excessive use of nanomaterial. Although the Fe$_3$O$_4$-modified membrane showed much higher lead (Pb) ion removal (14%) than the pure membrane (4%), the removal rate was still very low to meet the industrial expectation.

Huang et al. [79], Ansari et al. [80] and Mehrnia and Homayoonfal [81] also separately reported that incorporating the membrane with small quantity of Fe$_3$O$_4$ nanoparticles (< 0.3 wt%) could improve not only the membrane water permeability but also solute rejection. Huang et al. [79] found that the flux of 0.3 wt% Fe$_3$O$_4$-modified PES membrane was 75% better than the unmodified PES membrane. Upon incorporation of 0.05 wt% and 0.07 wt% Fe$_3$O$_4$ into poly(phenylene ether–ether sulfone) (PEES) and PSf membrane matrix, respectively, Ansari et al. [80] and Mehrnia and Homayoonfal [81] reported the water flux of resultant membranes was enhanced by 60–150%. The improvement in the membrane properties was attributed to the higher level of surface hydrophilicity, increased structural porosity and greater water content. Excessive use of Fe$_3$O$_4$ (e.g., > 1 wt%) for membrane modification had been reported to negatively affect structural integrity of membrane, leading to formation of large pore size and high membrane porosity which consequently reduced membrane separation efficiency [79]. In terms of mechanical strength, the reduction in membrane tensile strength at higher loading of Fe$_3$O$_4$ can be attributed to the increased membrane porosity that negatively affects its mechanical resistance against tear [80, 81].

Instead of evaluating Fe$_3$O$_4$-modified membranes for synthetic feed solution, Mehrnia and Homayoonfal [81] examined the potential of the 0.07 wt% Fe$_3$O$_4$-modified PSf membranes for activated sludge treatment. The modified membrane was reported to achieve much greater chemical oxygen demand (COD) and removal rate (97%) than that of pristine PSf membrane (73%). The authors attributed the better removal performance to the adsorption property of Fe$_3$O$_4$ nanoparticles toward organic pollutants in the activated sludge. The water flux recorded at 3 bar for PSf membrane with 0.07 wt% Fe$_3$O$_4$ was about 100 L/m^2.h, while the neat PSf membrane only achieved 75 L/m^2.h. The elevated flux obtained was due to increased membrane hydrophilicity in response to the presence of Fe$_3$O$_4$ nanoparticles.

Using electrospinning technique, Al-Husaini et al. [28] fabricated a nanofiber membrane incorporating 1.04 wt% Fe_3O_4 and used it for oily wastewater treatment. The authors showed that the introduction of Fe_3O_4 in nanofiber mat could improve the pure water flux of pristine PES nanofiber membrane by 17%, reaching a value >3200 L/m^2.h (at 1 bar). The flux enhancement was primarily credited to increased membrane hydrophilicity, as can be observed from contact angle results, where Fe_3O_4-modified PES membrane recorded 21.78° compared to pristine PES membrane of 105.61°. The Fe_3O_4-modified PES membrane also possessed greater oil–water separation performance as it achieved 94.01% rejection which is better than that of pristine PES membrane at 87.16%. The improved rejection rate of modified membrane is largely attributed to its smaller pore size that improved membrane selectivity. With respect to fouling resistance, the authors found that the hydrophilicity of Fe_3O_4 nanoparticles was effective in weakening the interaction between hydrophobic oily particles and hydrophilic membrane surface, leading to higher FRR in the Fe_3O_4-modified PES membrane (79.50%) compared to the neat PES membrane (61.46%).

3.1.2 Surface Functionalized Fe_3O_4

Despite its advantages, Fe_3O_4 nanoparticles tend to agglomerate which leads to poor distribution and dispersion in membrane matrix and limits the applications of nanocomposite membranes for water applications. Several strategies have been performed to increase the stability and affinity of Fe_3O_4 nanoparticles within membrane body. Prior to the addition of Fe_3O_4 nanoparticles into membrane matrix, Daraei et al. [82] performed coating on the surface of Fe_3O_4 nanoparticles using polyaniline (PANI). As PANI is considerably more hydrophilic compared to Fe_3O_4 nanoparticles, the use of it as coating layer could improve membrane hydrophilicity and show positive impact against whey protein separation. The water contact angle of membrane was decreased in the order of pristine PES (71.45°) > PES with Fe_3O_4 (53.38°) > PES with PANI-coated Fe_3O_4 (51.12°). The reduction in contact angle was corresponded to the increase in membrane hydrophilicity which led to the increase in membrane water flux in the order of PES = PES with Fe_3O_4 (33–36 L/m^2.h at 4 bar) < PES with PANI-coated Fe_3O_4 (45 L/m^2.h). When tested with whey protein solution, the PES membrane with PANI-coated Fe_3O_4 exhibited significantly greater FRR (80%) compared to other two membranes (52–68%), suggesting its high degree of antifouling properties. Superior hydrophilicity of PANI-coated Fe_3O_4 tended to reduce the irreversible fouling ratio by minimizing adhesion of foulants on the hydrophilic membrane surface.

The addition of O-carboxymethyl chitosan (OCMCS)-coated Fe_3O_4 nanoparticles into membrane matrix as reported in the work conducted by Rahimi et al. [83] and Zinadini et al. [35] also showed promising results in producing membranes with improved flux and rejection abilities as shown in Fig. 6. The former work attempted to incorporate 0.05–1 wt% OCMCS/Fe_3O_4 into PVDF membranes and evaluated the separation performance using BSA solution. It was found that the membrane flux at 1 bar was enhanced with increasing OCMCS/Fe_3O_4 loading, where at a lower dosage (0.05 wt%), the flux was recorded at 1164.6 L/m^2.h compared to 314.2 L/m^2.h by pure PVDF membrane. The dramatic increase in flux ($>10,000$ L/m^2.h.bar) at the highest OCMCS/Fe_3O_4 dosage (1 wt%) was attributed to the defects formed in the produced membrane caused by poor dispersion of nanoparticles. The separation performance of 0.05 wt% OCMCS/Fe_3O_4-modified PVDF membrane against BSA solution (48%) was found to be far more superior than the neat membrane (18%) and commercial microfiltration membrane (pore size: 0.22 μm, Millipore Corporation) (6%). The antifouling assessment using activated sludge suspensions revealed the FRR of modified PVDF membrane (incorporated with the lowest loading of OCMCS/Fe_3O_4) was at 95.7% and the result was significantly better compared to the neat PVDF membrane at 64.3%. This made 0.05 wt% the optimum loading for the incorporation of OCMCS/Fe_3O_4 into PVDF membrane.

In the latter work by Zinadini et al. [35], OCMCS/Fe_3O_4 nanoparticles at a loading of 0.1, 0.5 and 1 wt% were, respectively, incorporated into PES membranes to study the filtration performance against Direct Red 16 dye. It is noteworthy that regardless of the nanofiller concentration, the membrane hydrophilicity was greatly enhanced due to the hydrophilic properties of the modified nanoparticles. The contact angle of pure PES membrane and PES membrane with 0.5 wt% OCMCS/Fe_3O_4 is 64.4° and 53.2°, respectively. Although the 1 wt% OCMCS/Fe_3O_4-modified PES membrane displayed the highest hydrophilicity (contact angle of 52.5°), its pure water flux at 4 bar dropped significantly from 36 L/m^2.h (0.5 wt% OCMCS/Fe_3O_4-PES membrane) to 29 L/m^2.h. The is likely due to nanoparticles agglomeration caused by high loading that resulted in pore blockage. The rejection capability of the OCMCS/Fe_3O_4-modified PES membrane displayed much greater performance with an average of 99% rejection compared to 88% reported in the pure PES membrane. The authors ascribed that since both the nanoparticles and dye have negative charges which resulted from the dissociation of sulfonic group of the dye and carboxylic group of the OCMCS/Fe_3O_4, respectively, the creation of electrostatic repulsion force could lead to higher rejection and alleviate membrane antifouling property simultaneously.

The effect of Fe_3O_4 nanoparticles grafted with polyacrylic acid (PAA) on the morphology and separation performance of PES membranes was studied by Bagheripour et al. [84]. The authors observed apparent difference in the structure
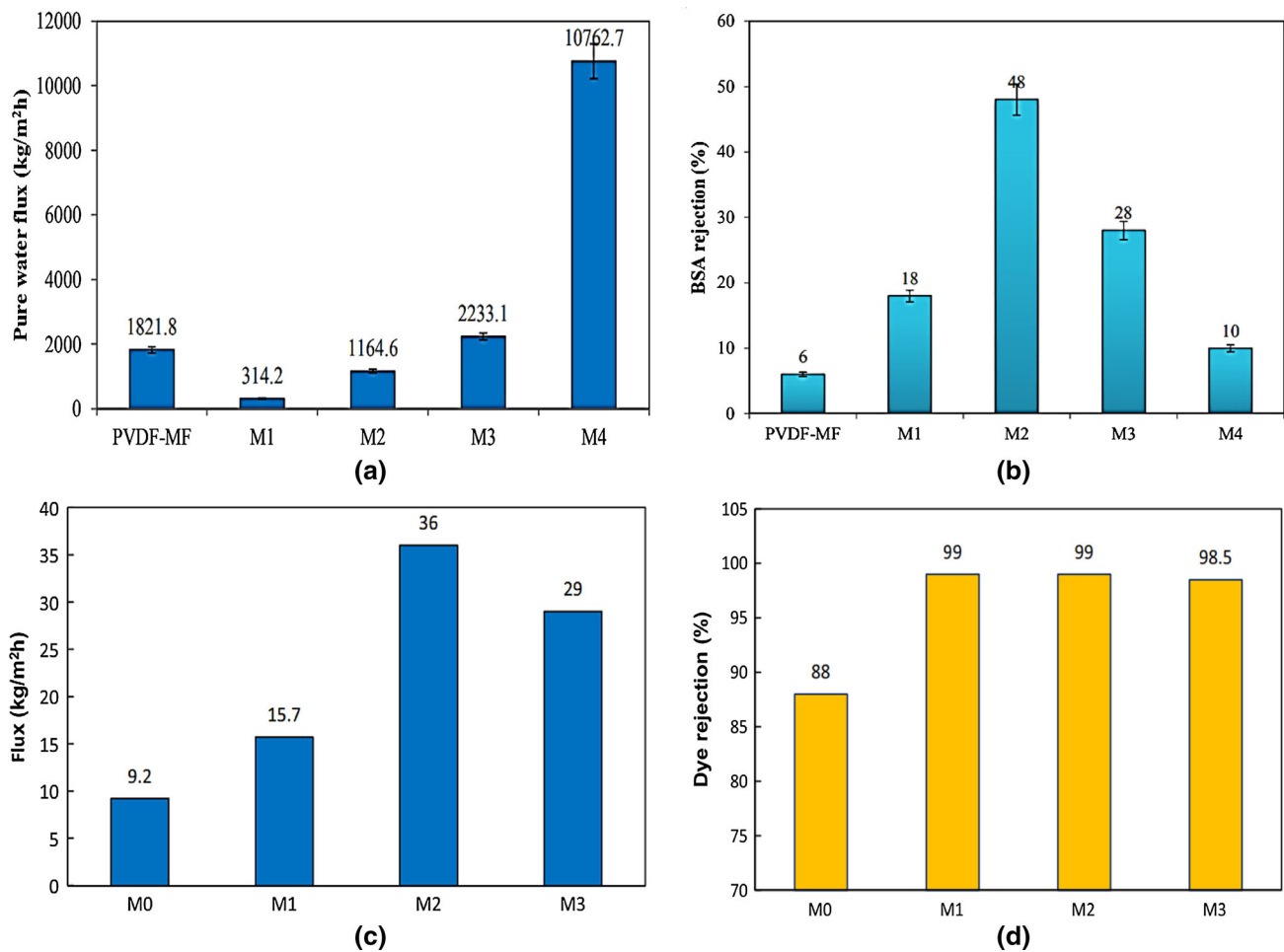
Fig. 6 Performance in terms of flux (Left) and rejection (Right) of, **a**, **b** Pure PVDF and OCMCS/Fe$_3$O$_4$-modified PVDF membranes (Note: PVDF-MF: Commercial MF, M1: Pure PVDF, M2–M4: PVDF membranes with 0.05, 0.1, 1 wt% OCMCS/Fe$_3$O$_4$) [83], and **c**, **d** Pure PES membrane and OCMCS/Fe$_3$O$_4$-modified membranes (Note: M0: Pure PES, M1–M4: PVDF membranes with 0.1, 0.5, 1 wt% OCMCS/Fe$_3$O$_4$) [35]

of PES membrane before and after the incorporation of PAA-grafted Fe$_3$O$_4$ nanoparticles in which the pores and channels radius at top and membrane sublayer increased upon 1 wt% nanofiller incorporation. As presented in Fig. 7, at the threshold loading (1 wt%), agglomerated PAA-grafted Fe$_3$O$_4$ nanoparticles were detected within the membrane matrix and this could cause obvious pore blockage and pore size reduction. This study revealed that the membrane with 0.5 wt% PAA-grafted Fe$_3$O$_4$ nanoparticles exhibited higher flux (8.71 L/m^2.h at 6 bar) than the pristine PES membrane (2.68 L/m^2.h). As a result of strong interfacial bonding of 0.5 wt% PAA-grafted Fe$_3$O$_4$ with PES polymer, the modified membrane has better endurance for load stress (4825 kPa) compared to the neat PES membrane (3874 kPa). However, it must be pointed out that the water flux of the best performing membrane in this work is still significantly lower compared to the performance of UF membranes reported in the literature.
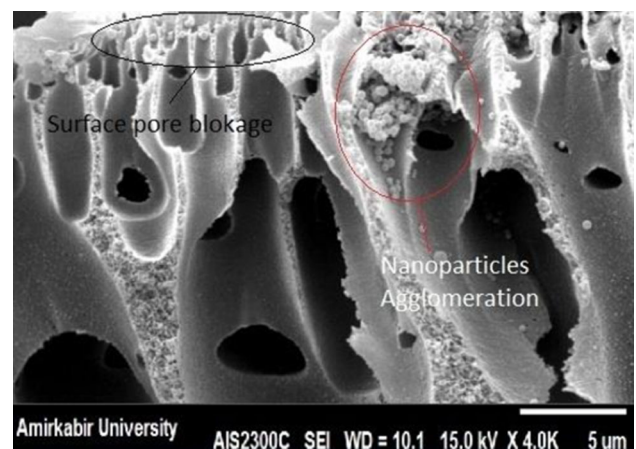

Fig. 7 SEM cross-sectional images of PES membrane with 1 wt% of PAA-grafted Fe$_3$O$_4$ nanoparticles [84]

3.1.3 Hybrid Fe_3O_4

The incorporation of hybrid nanomaterials into polymer matrix to develop nanocomposite membranes has demonstrated a synergistic effect to improve membrane performance [85]. Tan et al. [34] and Subramaniam et al. [33] incorporated coupled zinc–iron oxide nanohybrid (ZnO/Fe_3O_4) into PVDF and PES membranes, respectively, and reported the resultant membranes could attain high removal efficiency when they were used to treat aerobically treated palm oil mill effluent (AT-POME). ZnO and Fe_3O_4 nanoparticles are widely used as photocatalytic nanofillers as they can induce self-cleaning under the illumination of UV and visible light. A slight increase in membrane hydrophilicity was observed by Tan et al. [34] where the contact angle of PVDF membrane decreased from 78° to 73° upon the addition of 0.5 wt% ZnO/Fe_3O_4. The increased hydrophilicity improved the water flux of PVDF membrane by 50%, reaching 170 L/m^2.h (at 1 bar). The ZnO/Fe_3O_4-modified PVDF membrane also improved the color removal rate of neat PVDF membrane by 17%. This achievement was mainly attributed to the negatively charged membrane surface that minimized foulant deposition on membrane surface and improved membrane antifouling properties.

Despite being the commonly used polymeric materials for membrane fabrication, the hydrophobic nature of PES is always associated with poor fouling resistance [7]. In view of this, Subramaniam et al. [33] improved the membrane hydrophilicity by embedding 0.5 wt% ZnO/Fe_3O_4 into PES matrix. The contact angle of the nanocomposite membrane was 87.6°, a slight improvement from the neat PES membrane at 99.5°. Besides developing more membrane pores, the addition of hydrophilic ZnO/Fe_3O_4 into PES membrane also improved the negative membrane surface charge and played a significant role in the decolorization of AT-POME by repelling the color pigments. Consequently, the modified membrane exhibited better color rejection (76.2%) compared to the neat membrane (32.5%).

The superior hydrophilicity of 2D GO nanosheets makes it highly suitable for Fe_3O_4 nanoparticles to be attached on its surface, forming GO/Fe_3O_4 nanohybrid [86]. Xu et al. [87] and Huang et al. [53] studied the properties of GO/Fe_3O_4-modified PVDF membranes that were fabricated under magnetic field. Xu et al. [87] found that GO/Fe_3O_4 nanohybrids were able to migrate toward the top surface of PVDF membrane due to magnetic attraction (0.2 T), thus producing membrane with improved contact angle and water flux (55° and 595.39 L/m^2.h at 1 bar). The GO/Fe_3O_4-modified PVDF membrane prepared without magnetic field influence only showed 62° and 446.74 L/m^2.h, respectively. The neat PVDF membrane meanwhile only demonstrated 74.5° and 200 L/m^2.h, respectively. The separation performance of PVDF membranes was tested against BSA solution,

where all membranes have a rejection of more than 92%. The FRR of the modified membranes, however, were better compared to the neat membrane with the order of modified PVDF under magnetic field influence (86.4%) > modified PVDF without magnetic field influence (82.1%) > neat PVDF membrane (43.3%). This suggested that inducing magnetic field during membrane casting was able to enhance membrane performance in terms of membrane hydrophilicity, flux and antifouling properties.

The performances of PVDF membranes incorporated with 1 wt% GO/Fe_3O_4 were reported by Huang et al. [53] under magnetic field influence of 0.05 T. The deflection and orientation behavior of GO/Fe_3O_4 nanohybrids in the presence of magnetic field were observed under the microscope, as shown in Fig. 8. With the aid of the magnetic field, the GO/Fe_3O_4 could be arranged along the direction of the field and be embedded on membrane top surface. This, as a result, modified the surface properties of membrane. The modified membrane also exhibited greater pure water flux (484 L/m^2.h at 1 bar) than the pristine PVDF membrane (320 L/m^2.h) with slight reduction in the BSA rejection. With respect to fouling resistance, the modified membranes displayed high FRR of 83.0% compared to the pristine membrane of 47.9%, indicating that the nanohybrid modified membrane has better antifouling performance.

As reported in the work of Chai et al. [73], the blending of GO/Fe_3O_4 into PSf membrane increased the membrane permeability and hydrophilicity but with the compensation of humic acid rejection due to enlarged pore size. The contact angle of PSf membrane with 1 wt% GO/Fe_3O_4 was greatly reduced from 75.86° to 43.98°, showing its hydrophilicity improvement. This is due to the presence of nanohybrid that contains abundance of hydroxyl group to promote water passage through membrane. The flux of modified membrane was also greatly enhanced and achieved 156.99 L/m^2.h.bar, i.e., much higher than the PSf membrane (51.78 L/m^2.h.bar). Although pore enlargement occurred upon the addition of GO/Fe_3O_4, the modified membrane could still achieve reasonably good rejection against humic acid, i.e., close to 85% rejection.

Fe_3O_4 and MWCNT nanohybrids have been proven to possess excellent properties in electrochemistry, magnetism and adsorption [88]. Upon incorporation of 0.65 wt% $MWCNT/Fe_3O_4$ into PVC membrane, Wang et al. [89] observed an enhancement in membrane morphologies, surface hydrophilicity and filtration performance against BSA. The addition of $MWCNT/Fe_3O_4$ was found to increase membrane pore size and its pore number as well as hydrophilicity, which subsequently promotes water permeability. Comparing with the flux of neat PVC membrane, the flux of modified PVC membrane was increased by 31%, reaching 118.3 L/m^2.h.bar.
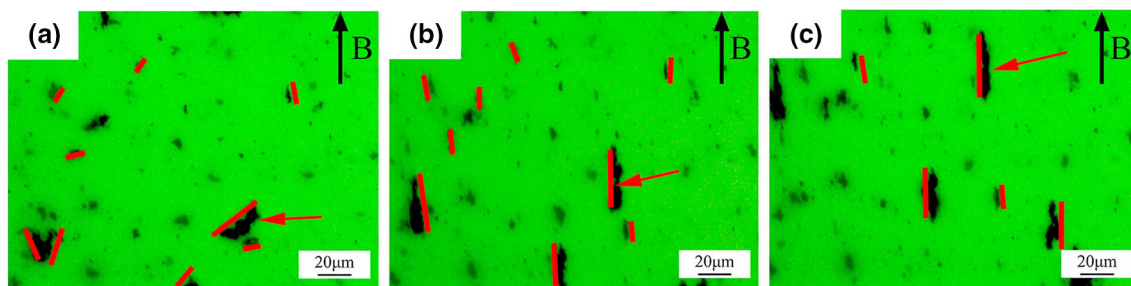
Fig. 8 Microscope images of GO/Fe$_3$O$_4$ in the presence of magnetic field; **a** after 0 s, **b** after 5 s and **c** after 7 s [53]

The surface modification of ZrO$_2$/Fe$_3$O$_4$ nanohybrid was performed by Noormohamadi et al. [90], in which the synergistic effect of Fe$_3$O$_4$ nanoparticles helped in increasing membrane pore size and ZrO$_2$ nanoparticles reduced PAN membrane surface roughness and hydrophobicity. Upon the blending of 1 wt% ZrO$_2$/Fe$_3$O$_4$ into PAN membrane, the contact angle decreased by 51% compared to neat PAN membrane, from 72° to 35°. The flux of 1 wt% ZrO$_2$/Fe$_3$O$_4$-modified PAN membrane at 0.3 bar was doubled (29 L/m^2.h) than that of pure PAN membrane (13 L/m^2.h). The separation capability of PAN membranes was evaluated using activated sludge with microorganism population of 12,000 mg/L. The modified PAN membrane recorded COD removal of 93%, a slight increase from 86% by the neat PAN membrane. The authors attributed the increased FRR from 35 to 58% to the enhanced membrane surface roughness and hydrophilicity due to the addition of ZrO$_2$/Fe$_3$O$_4$ into PAN membrane.

Table 2 summarizes the key findings related to the use of Fe$_3$O$_4$ for modification of polymeric membranes for water application. Their performances were compared with the respective pristine membrane, and the results generally indicated that the Fe$_3$O$_4$-modified membranes always yield better filtration performances.

3.2 Adsorptive Membranes

The combination of membrane filtration and adsorption process has been proven to be an effective alternative in removing ions (e.g., metal or salt ions) from water/wastewater at relatively low operating pressure [92]. In this case, polymeric membranes act as a host for the adsorptive nanoparticles in which the adsorption ability of nanoparticles can be manipulated to selectively remove targeted ions. Zainol Abidin et al. [62] blended PSf membrane with 5 wt% Fe$_3$O$_4$ for adsorptive removal of phosphate (PO$_4^{3-}$). Figure 9 shows the microscopic images of PSf membranes with and without Fe$_3$O$_4$. For the modified PSf membrane, Fe$_3$O$_4$ was found to distribute uniformly throughout the membrane, indicating good interaction between the nanoparticles and the polymer matrix. Upon the incorporation of Fe$_3$O$_4$, the contact angle of pristine membrane was decreased from 73.5° to 63.9° and

its pure water flux was increased by 5 times, reaching 55.2 L/m^2.h.bar. With respect to the phosphate adsorption, the results revealed that the Fe$_3$O$_4$-modified membrane could achieve maximum adsorption capacity of 73.5 mg/g.

Rowley and Abu-Zahra [93] modified Fe$_3$O$_4$ nanoparticles with 3-aminopropyltriethoxysilane (APTES) before adding it into PES membranes. It was found that the membrane with 3 wt% APTES-modified Fe$_3$O$_4$ recorded much lower contact angle (63.68°) than that of neat PES membrane (74.8°). The presence of hydroxyl groups on APTES/Fe$_3$O$_4$ boosted the membrane surface hydrophilicity and permeability. In addition, the APTES/Fe$_3$O$_4$-modified membrane exhibited arsenic adsorption rate of 14.6 mg/g due to the role of nanomaterials in adsorbing arsenic ions. The pristine PES membrane meanwhile showed almost zero adsorption rate. When tested using 1 ppm of arsenic solution, the APTES/Fe$_3$O$_4$-modified membrane was able to remove 76% of arsenic ions. Nevertheless, the low arsenic removal rate could be due to the relatively low adsorption rate of the membrane itself.

Fe$_3$O$_4$ nanoparticles also show potential for Pb(II) ions removal. Moradihamedani et al. [94] modified PSf membrane by incorporating 7–13 wt% talc-modified Fe$_3$O$_4$ nanoparticles. Optimum loading was reported at 9 wt% in which the resultant membrane could achieve 89.4% Pb(II) ions removal. The authors attributed the results to the electrostatic attraction between positively charged Pb(II) ions and negatively charged silanol group on the surface of talc/Fe$_3$O$_4$ that led to efficient adsorption of ions.

Using 0.1 wt% SiO$_2$-coated Fe$_3$O$_4$ nanoparticles, Ghaemi et al. [61] fabricated a new type of composite membrane that showed improvement in the membrane hydrophilicity and rejection rate. The reduced water contact angle of the modified PES membrane (69°) compared to the neat PES membrane (78°) was ascribed to increased surface hydrophilicity and smoothness. Flux improvement of more than 3 times was achieved by the modified PES membrane (27.8 L/m^2.h at 4 bar) in comparison to the pure PES membrane (8.8 L/m^2.h). The separation efficiency of PES membranes was tested against copper (Cu(II)) ion, where the modified PES membrane demonstrated a rejection of 92%, a

Table 2 Summary of Fe_3O_4 incorporation into pressure-driven membranes

Class	Type of NPs	Particle size (nm)	Type of polymer	Application	Operating pressure (bar)	Key findings		Refs.
						Pristine membrane	Best Fe_3O_4-modified membrane	
Fe_3O_4	–	8–12	PSf	Lysozyme removal	1	Flux: n/a Porosity: 0.41 Rejection: 70% Contact angle: 58°	Flux: 13 L/m^2.h Porosity: 0.50 Rejection: 88% Contact angle: 73° (Note: 0.27 wt% Fe_3O_4)	[65]
	–	20	PES	Dye removal (Congo Red dye)	2.76	Flux: 16 L/m^2.h Rejection: 93.2% Contact angle: 67°	Flux: 64 L/m^2.h Rejection: 92.5% Contact angle: 52° (Note: 3 wt% Fe_3O_4)	[75]
	–	60	PES	Na_2SO_4 rejection	5.5	Flux: 35 L/m^2.h Rejection: 68.4% Contact angle: 65° Flux recovery rate: 38.1%	Flux: 23 L/m^2.h Rejection: 90% Contact angle: 52° Flux recovery rate: 87.4% (Note: 2 wt% Fe_3O_4)	[77]
	–	60	PVC	Lead rejection	5	Flux: 50 L/m^2.h Rejection: 14% Water content: 19 wt%	Flux: 75 L/m^2.h Rejection: 45% Water content: 35 wt% (Note: 0.1 wt% Fe_3O_4)	[78]
	–	n/a	PES	BSA rejection	1	Flux: 41 L/m^2.h Rejection: 98% Contact angle: 85.9°	Flux: 70 L/m^2.h Rejection: 98% Contact angle: 78.6° (Note: 0.3% Fe_3O_4)	[79]
	–	60	PEES	$MgSO_4$ rejection	6	Flux: 5.58 L/m^2.h Rejection: 65% Water content: 70.25%w	Flux: 13.95 L/m^2.h Rejection: 90% Water content: 83.25%w (Note: 0.05 wt% Fe_3O_4)	[80]

Table 2 continued

Class	Type of NPs	Particle size (nm)	Type of polymer	Application	Operating pressure (bar)	Key findings		Refs.
						Pristine membrane	Best Fe_3O_4-modified membrane	
	–	60–70	PSf	Activated sludge treatment	0.3	Flux: 75 L/m².h; COD Rejection: 73%; Contact angle: 85°	Flux: 100.1 L/m².h; COD Rejection: 97%; Contact angle: 51° (Note: 0.07 wt% Fe_3O_4)	[81]
	–	n/a	PES	Copper ion removal	4.14	Flux: 5 L/m².h; Rejection: 95%; Contact angle: 62.22°	Flux: 18 L/m².h; Rejection: 93.5%; Contact angle: 41.37° (Note: 4 wt% Fe_3O_4)	[75]
	–	4.5	PES	Oily wastewater separation	1	Flux: 2675.6 L/m².h; Rejection: 87.16%; Contact angle: 105.61°; FRR: 61.46%	Flux: 3227.8 L/m².h; Rejection: 94.01%; Contact angle: 21.78°; FRR: 79.50% (Note: 1.04 wt% Fe_3O_4)	[28]
Functionalized Fe_3O_4	PANI-coated Fe_3O_4	11.73	PES	Protein rejection (Whey protein)	4	Flux: 33 L/m².h; Rejection: 98%; Contact angle: 71.45°; FRR: 52%	Flux: 45 L/m².h; Rejection: 98%; Contact angle: 51.12°; FRR: 80% (Note: 0.1 wt% PANI/Fe_3O_4)	[82]
	OCMCS-coated Fe_3O_4	60–90	PVDF	BSA rejection	1	Flux: 314.2 L/m².h; Rejection: 18%; Contact angle: 67.5°; FRR: 64.3%	Flux: 1164.6 L/m².h; Rejection: 48%; Contact angle: 53.1°; FRR: 95.7% (Note: 0.05 wt% OCMCS/Fe_3O_4)	[83]
	OCMCS-coated Fe_3O_4	60–90	PES	Dye removal (Direct Red 16)	4	Flux: 9.2 L/m².h; Rejection: 88%; Contact angle: 64.4°; FRR: 83%	Flux: 36 L/m².h; Rejection: 99%; Contact angle: 53.2°; FRR: 91.7% (Note: 0.5 wt% OCMCS/Fe_3O_4)	[35]

Table 2 continued

Class	Type of NPs	Particle size (nm)	Type of polymer	Application	Operating pressure (bar)	Key findings		Refs.
						Pristine membrane	Best Fe_3O_4-modified membrane	
	PAA-grafted Fe_3O_4	60	PES	Na_2SO_4 rejection	6	Flux: 2.68 $L/m^2.h$ Rejection: 50% Water content: 72.04%	Flux: 8.71 $L/m^2.h$ Rejection: 75% Water content: 75.67% (Note: 0.5 wt% PAA/Fe_3O_4)	[84]
Hybrid nanomaterials	ZnO/Fe_3O_4	5.72	PVDF	AT-POME treatment	1	Flux: 85.92 $L/m^2.h$ Color removal: 59.25% Contact angle: 78°	Flux: 170 $L/m^2.h$ Color removal: 69.53% Contact angle: 73° (Note: 0.5 wt% ZnO/Fe_3O_4)	[34]
	ZnO/Fe_3O_4	n/a	PES	AT-POME treatment	1	Flux: 0.75 $L/m^2.h$ Color removal: 32.5% Contact angle: 99.5°	Flux: 2.16 $L/m^2.h$ Color removal: 76.2% Contact angle: 87.6° (Note: 0.5 wt% ZnO/Fe_3O_4)	[33]
	GO/Fe_3O_4	n/a	PVDF	BSA rejection	1	Flux: 200 $L/m^2.h$ Rejection: 99% Contact angle: 75° FRR: 44%	Flux: 595.39 $L/m^2.h$ Rejection: 92% Contact angle: 55° FRR: 86.4% (Note: 1 wt% GO/Fe_3O_4)	[87]
	GO/Fe_3O_4	9.5	PVDF	BSA rejection	1	Flux: 320 $L/m^2.h$ Rejection: 80% Contact angle: 80° FRR: 47.9%	Flux: 484 $L/m^2.h$ Rejection: 77.7% Contact angle: 61.9° FRR: 83.0% (Note: 1 wt% GO/Fe_3O_4)	[53]

Table 2 continued

| Class	Type of NPs	Particle size (nm)	Type of polymer	Application	Operating pressure (bar)	Key findings		Refs.
						Pristine membrane	Best Fe_3O_4-modified membrane	
	GO/Fe_3O_4	5	PSf	Humic acid removal	1	Flux: 51.78 $L/m^2.h$ Rejection: 89% Contact angle: 75.86°	Flux: 156.99 $L/m^2.h$ Rejection: 84% Contact angle: 43.98° (Note: 1 wt% GO/Fe_3O_4)	[73]
	GO/Fe_3O_4	n/a	PSf	Dye removal (Congo Red)	1	Flux: 51.82 $L/m^2.h$ Rejection: 85% Contact angle: 78° FRR: 73%	Flux: 112.47 $L/m^2.h$ Rejection: 97% Contact angle: 69.97° FRR: 95% (Note: 0.4 wt% GO/Fe_3O_4)	[91]
	$MWCNT/Fe_3O_4$	n/a	PVC	BSA rejection	1	Flux: 90.4 $L/m^2.h$ Rejection: 64.5% Contact angle: 72.5°	Flux: 118.3 $L/m^2.h$ Rejection: 74.6% Contact angle: 63.5° (Note: 0.65 wt% $MWCNT/Fe_3O_4$)	[89]
	ZrO_2/Fe_3O_4	35	PAN	Activated sludge treatment	0.3	Flux: 13 $L/m^2.h$ COD rejection: 86% Contact angle: 72° FRR: 35%	Flux: 29 $L/m^2.h$ COD rejection: 93% Contact angle: 35° FRR: 58% (Note: 1 wt% ZrO_2/Fe_3O_4)	[90]
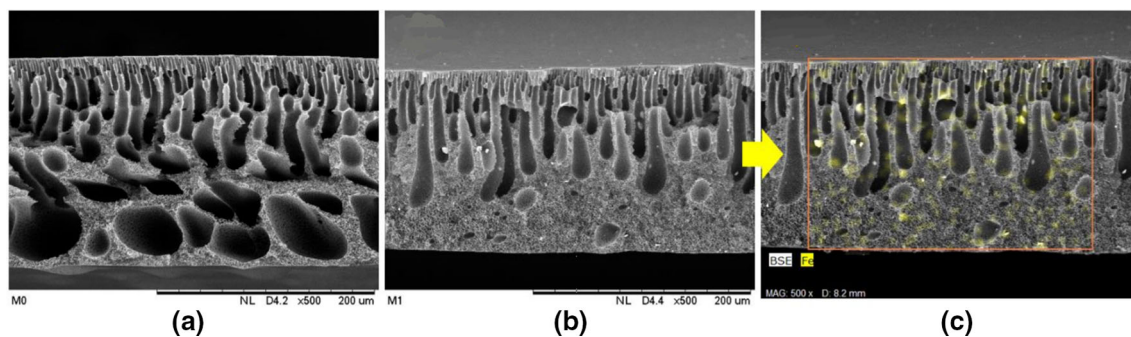
Fig. 9 SEM images of cross section of **a** neat PSf membrane, **b** PSf membrane with Fe_3O_4 nanoparticles and **c** EDX mapping of Fe element on PSf membrane [62]

significant increase from 25% by the pristine PES membrane. The dual modification of Fe_3O_4 nanoparticles with silica and metformin tended to increase the available membrane surface active sites, leading to increased membrane rejection ability.

Daraei et al. [41] also explored the potential of using PES membrane incorporating PANI-coated Fe_3O_4 nanoparticles for the adsorption process of Cu(II) ion. As previously mentioned, the coating of Fe_3O_4 using PANI could significantly improve membrane hydrophilicity. Nevertheless, despite the enhanced hydrophilicity, the addition of nanofillers led to reduction in membrane flux due to the reduced pore size and pore blockage caused by migration of PANI/Fe_3O_4 to membrane top surface. The PANI/Fe_3O_4-modified membrane only exhibited 25 L/m^2.h (at 4.5 bar), while pristine PES at 50 L/m^2.h. Although the authors reported the modified membrane could achieve 85% Cu(II) ions removal rate (Fig. 10), the flux reduction and extremely low adsorption capacity of the membrane (i.e., 1.6 mg/g) could indicate the separation mechanism is mainly governed by sieving effect rather than adsorption mechanism.

In addition to heavy metal ions removal, Modi and Bellare [95] studied the potential of 0.5 wt% GO/Fe_3O_4-modified PSf membrane for the adsorptive removal of contaminant of emerging concern—2,4-dichlorophenol (2,4-DCP). The modified membrane was reported to have much lower contact angle (37.1°) compared to neat PSf (76.3°), and this had caused the membrane to exhibit better surface hydrophilicity and subsequently higher water flux. A remarkable removal of 2,4-DCP was achieved by GO/Fe_3O_4-modified membrane (96.5%), a significant improvement from the bare PSf membrane (55%). With respect to the adsorption capacity, the modified and the neat PSf membrane recorded 0.0192 and 0.0385 mg/g, respectively. Based on the data, it must be pointed out that the low adsorption capacity of membrane (< 1 mg/g) is not the main factor causing the membrane to have good separation rate.

The PVDF membrane blended with various loadings (0.1–0.8 wt%) of Fe_3O_4 modified with halloysite nanotubes (HNT/Fe_3O_4) was developed by Liu et al. [59] and used for Congo Red dye removal. Figure 11 displays the TEM images of pure HNT and HNT/Fe_3O_4 nanohybrids, where Fe_3O_4 nanoparticles were uniformly attached on the top surface of HNT. Owing to the presence of Fe_3O_4 on the HNT surface, the specific surface area of the nanocomposites is boosted and its adsorption ability is enhanced accordingly. The contact angle of all membranes gradually declined with the increasing HNT/Fe_3O_4 loading. Due to its hydrophobicity, the bare PVDF membrane recorded contact angle of 80.1°, while the lowest contact angle of 60.7° was achieved by the PVDF membrane with 0.4 wt% HNT/Fe_3O_4. This modified membrane also exhibited the highest flux of 39.8 L/m^2.h (at 3 bar), an increase of 104.6% from 19.45 L/m^2.h by the pure PVDF membrane. The enhancement of Congo Red removal by the modified membrane (92.1%) compared to the pure PVDF membrane (82.1%) was attributed to the adsorption ability of HNT/Fe_3O_4. Furthermore, the FRR of the modified PVDF membrane was reported to increase, revealing the improved antifouling behavior upon HNT/Fe_3O_4 incorporation (Table 3).

4 Technical Challenges of Fe_3O_4-Modified Membranes Fabrication

Although Fe_3O_4 nanoparticles have demonstrated its potential as nanofillers for nanocomposite membrane fabrication for laboratory-scale water and wastewater treatment, there are several key challenges related to the membrane fabrication and these limitations should be addressed in order to produce more cost competitive and high-performing Fe_3O_4-modified membranes for possible use in the industrial applications.

One major challenge of Fe_3O_4-modified membrane fabrication is the agglomeration of Fe_3O_4 nanoparticles in membrane matrix. Fe_3O_4 nanoparticles have high aggregation effect due to van der Waals forces that disrupt its uniform distribution and cause low dispersion ability throughout membrane matrix. Due to having large surface-to-volume
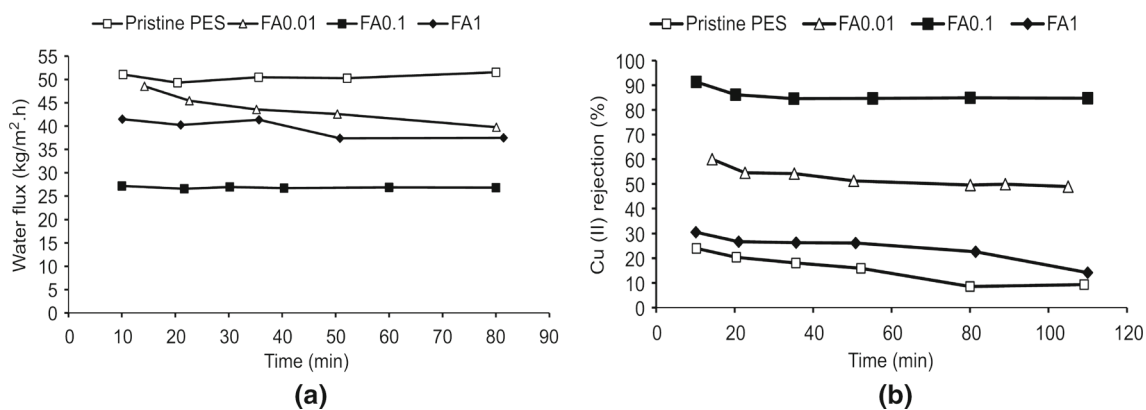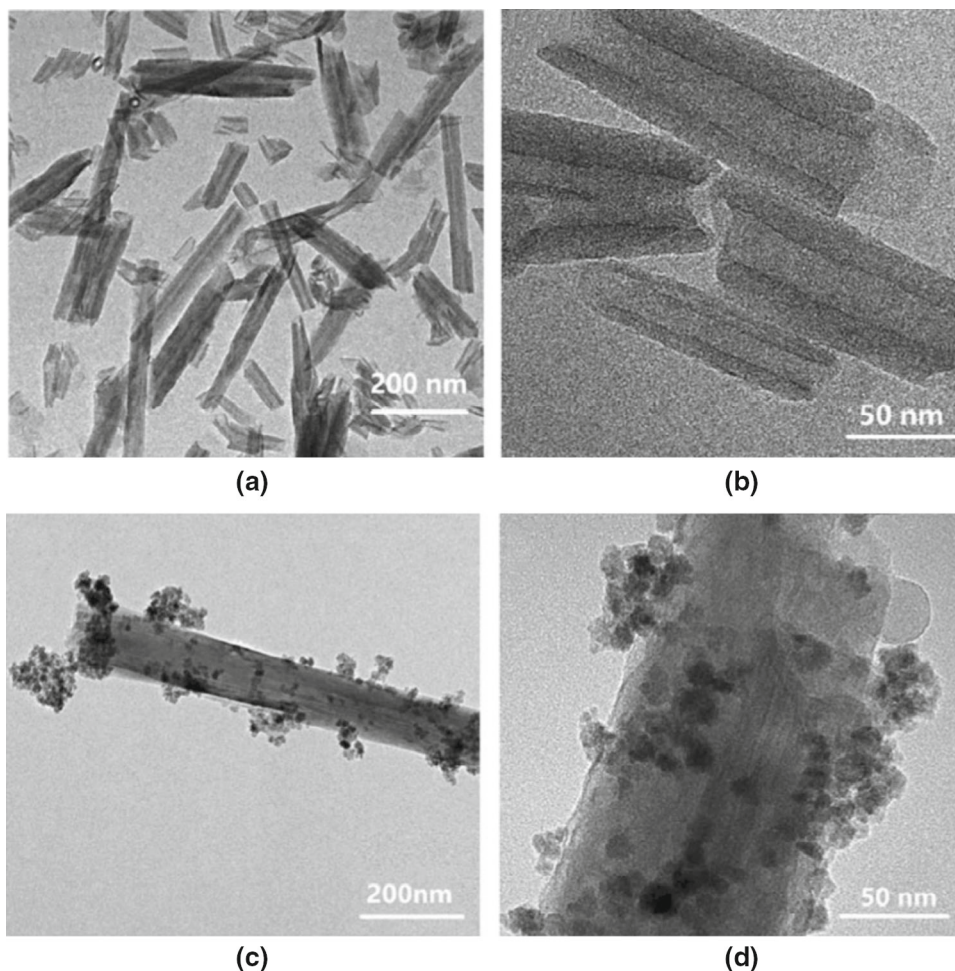
Fig. 10 Performance in terms of **a** water flux and **b** Cu(II) rejection of neat PES membranes and PES membranes incorporated with 0.01, 0.1 and 1 wt% PANI/Fe$_3$O$_4$ nanoparticles [41]

Fig. 11 TEM images of **a**, **b** pure HNTs and **c**, **d** HNT/Fe$_3$O$_4$ nanocomposites [59]

ratio, Fe$_3$O$_4$ possesses high surface tension. In order to reduce the surface energies, these nanoparticles tend to aggregate. Nanoparticle agglomeration and non-uniformed dispersion are generally reported as the factors leading to incompatibility between nanofillers and polymers, causing voids and non-selective defects in membrane structure and negatively affecting the membrane filtration capabilities [72,

96, 97]. Incorporating Fe$_3$O$_4$ nanoparticles at a higher loading (>4 wt%) normally would cause severe agglomeration that results in poor integrity of membrane structure. Consequently, the membranes exhibit poor filtration performance and/or low mechanical property [2, 98, 99].

Although reports on Fe$_3$O$_4$ nanoparticles leaching from nanocomposite membranes are rare, the phenomenon of

Arabian Journal for Science and Engineering (2022) 47:5443–5464

Table 3 Summary on Fe_3O_4 modification into adsorptive membranes

Class	Type of NPs	Particle size (nm)	Type of polymer	Application	Operating pressure (bar)	Key findings — Pristine membrane	Key findings — Best Fe_3O_4-modified membrane	Refs.
Fe_3O_4	–	20	PSf	Phosphate removal	1	Flux: 10 L/m².h Contact angle: 73.5° Rejection: n/a Adsorption capacity: n/a	Flux: 55.2 L/m².h Contact angle: 63.9° Rejection: 37% Adsorption capacity: 73.5 mg/g (Note: 5 wt% Fe_3O_4)	[62]
Modified Fe_3O_4	APTES-modified Fe_3O_4	50–100	PES	Arsenic removal	3.4	Flux: 16.15 L/m².h Contact angle: 74.8° Rejection: n/a Adsorption capacity: 0	Flux: 23.9 L/m².h Contact angle: 63.68° Rejection: 76% Adsorption capacity: 14.6 mg/g (Note: 3 wt% APTES/Fe_3O_4)	[93]
	Talc-modified Fe_3O_4	n/a	PSf	Lead ion removal	3	Flux: 0 L/m².h Contact angle: 74° Rejection: n/a	Flux: 11 L/m².h Contact angle: 62° Rejection: 89.4% (Note: 9 wt% Talc/Fe_3O_4)	[94]
	Metformin-modified silica coated Fe_3O_4	40–45	PES	Copper ion removal	4	Flux: 8.8 L/m².h Rejection: 25% Contact angle: 78°	Flux: 27.8 L/m².h Rejection: 92% Contact angle: 69° (Note: 0.1 wt% SiO_2-Met/Fe_3O_4)	[61]
	PANI-modified Fe_3O_4	12–28	PES	Copper ion removal	4.5	Flux: 50 L/m².h Water content: 285 wt% Rejection: n/a Adsorption capacity: n/a	Flux: 25 L/m².h Water content: 307 wt% Rejection: 85% Adsorption capacity: 1.6 mg/g (Note: 0.1 wt% PANI/Fe_3O_4)	[41]
Hybrid Fe_3O_4	GO/Fe_3O_4	n/a	PSf	2,4-dichlorophenol removal	1	Flux: 61.5 L/m².h Contact angle: 76.3° Rejection: 55% Adsorption capacity: 0.0192 mg/g FRR: 55.1%	Flux: 339.8 L/m².h Contact angle: 37.1° Rejection: 96.5% Adsorption capacity: 0.0385 mg/g FRR: 95.8% (Note: 0.5 wt% GO/Fe_3O_4)	[95]
	HNT/Fe_3O_4	100	PVDF	Dye removal (Congo Red)	3	Flux: 19.45 L/m².h Rejection: 82.1% Contact angle: 80.1° FRR: 64.8%	Flux: 39.8 L/m².h Rejection: 92.1% Contact angle: 60.7° FRR: 70.7% (Note: 0.4 wt% HNT/Fe_3O_4)	[59]

Fe_3O_4 nanoparticles leaching from membrane during fabrication and filtration process is likely to occur. It has been previously reported that the possible nanomaterials leaching is very small and is normally found during early stage of permeation in the case where nanomaterials are not strongly attached to membrane [100–103]. However, it must be noted that the frequent use of chemical agents during cleaning process could attack the polymeric membrane surface which leads to nanoparticle leaching during operation. Besides affecting membrane performance, the nanoparticles leaching from membrane could also pose risk of water poisoning if such membrane is used in drinking water purification process [2, 3]. The leaching process may be caused by physical damage on membrane or improper nanoparticle incorporation techniques that results in lack of proper anchor points for the nanomaterials embedded within the membrane matrix [104, 105].

Manufacturing cost is another main concern that governs the commercial readiness of Fe_3O_4-modified membranes. Nanocomposite membranes are typically considered more expensive to produce compared to conventional polymeric membrane [3, 106]. While Fe_3O_4 nanoparticles are known for its relatively low cost, the cost involved in the development of membranes incorporated with Fe_3O_4 nanoparticles still remains as an obstacle for its commercial deployment. Despite extensive research on Fe_3O_4-modified membranes was conducted in laboratory scales over the past years, the industrial applications of Fe_3O_4-modified membranes for water and wastewater treatment are yet to be found, largely due to increased production costs of high-quality Fe_3O_4 nanoparticles and its surface functionalization. Recent development in synthesis of nanomaterials may enable the large-scale manufacturing of high-quality Fe_3O_4 nanoparticles at a low price [107, 108], but still an in-depth cost analysis study is needed to prove its cost competitiveness.

5 Conclusions

The development of Fe_3O_4-modified membrane can address the limitations posed by typical polymeric membrane by outperforming it with respect to permeability/selectivity and antifouling properties. This review focuses on the recent advancement of membranes incorporated with different types of Fe_3O_4 nanoparticles including unmodified Fe_3O_4, surface functionalized Fe_3O_4 and hybrid Fe_3O_4 for water and wastewater treatment, classified according to pressure-driven and adsorptive membranes. The introduction of Fe_3O_4 nanoparticles into polymer matrix could improve membrane hydrophilicity, separation performance, adsorption capacity as well as fouling resistance. Despite these progresses, several challenges were identified in utilizing Fe_3O_4 nanoparticles as nanofillers for nanocomposite membrane

fabrication and its process. These include agglomeration within membrane pores, ununiformed dispersion and lack of affinity between nanofillers and polymer matrix, water permeability/rejection trade-off effect, nanoparticles leaching, as well as manufacturing cost concern. These limitations might restrict the applications of modified membranes. Some strategies were proposed by researchers to effectively improve Fe_3O_4 nanoparticles employment into membrane such as incorporation of Fe_3O_4 nanoparticles at a low loading (< 1 wt%), surface modification of nanoparticles and use of external magnetic field to manipulate the nanoparticles orientation. Although some Fe_3O_4-modified membranes have shown good potential in treating water and wastewater, e.g., high rejection against protein [79, 82] and good adsorption capacity against phosphate and arsenic [62, 93], more reliable studies in the application of Fe_3O_4 nanoparticles as nanofillers are needed in order to develop Fe_3O_4-modified membranes with greater yet stable performance for industrial application. With the continuous and further exploration carried out by scientists for functionalizing Fe_3O_4 and designing membrane structure, the nanocomposite membranes are possible to become attractive option for commercial water and wastewater treatment in the future.

References

1. Chen, X.; Su, Y.; Shen, F.; Yinhua, W.: Antifouling ultrafiltration membranes made from PAN-b-PEG copolymers: effect of copolymer composition and PEG chain length. Fuel Energy Abstr. **384**, 44–51 (2011). https://doi.org/10.1016/j.memsci.2011.09.002m

2. Ng, L.Y.; Mohammad, A.W.; Leo, C.P.; Hilal, N.: Polymeric membranes incorporated with metal/metal oxide nanoparticles: a comprehensive review. Desalination **308**, 15–33 (2013). https://doi.org/10.1016/j.desal.2010.11.033

3. Goh, P.S.; Ng, B.C.; Lau, W.J.; Ismail, A.F.: Inorganic nanomaterials in polymeric ultrafiltration membranes for water treatment. Sep. Purif. Rev. **44**(3), 216–249 (2015). https://doi.org/10.1080/15422119.2014.926274

4. Baker, R.W.: Ultrafiltration. In: Membrane Technology and Applications. pp. 237–274. Wiley, West Sussex, England (2004). https://doi.org/10.1002/0470020393

5. Al Aani, S.; Mustafa, T.N.; Hilal, N.: Ultrafiltration membranes for wastewater and water process engineering: a comprehensive statistical review over the past decade. J. Water Process. Eng. **35**, 101241 (2020). https://doi.org/10.1016/j.jwpe.2020.101241

6. Van Der Bruggen, B.; Vandecasteele, C.; Van Gestel, T.; Doyen, W.; Leysen, R.: A review of pressure-driven membrane processes in wastewater treatment and drinking water production. Environ. Prog. **22**(1), 46–56 (2003). https://doi.org/10.1002/ep.670220116

7. Zhao, X.; Ma, J.; Wang, Z.; Wen, G.; Jiang, J.; Shi, F.; Sheng, L.: Hyperbranched-polymer functionalized multi-walled carbon nanotubes for poly (vinylidene fluoride) membranes: from dis-

person to blended fouling-control membrane. Desalination **303**, 29–38 (2012). https://doi.org/10.1016/j.desal.2012.07.009

8. Akar, N.; Asar, B.; Dizge, N.; Koyuncu, I.: Investigation of characterization and biofouling properties of PES membrane containing selenium and copper nanoparticles. J. Membr. Sci. **437**, 216–226 (2013). https://doi.org/10.1016/j.memsci.2013.02.012

9. Yu, S.; Zuo, X.; Bao, R.; Xu, X.; Wang, J.; Xu, J.: Effect of SiO_2 nanoparticle addition on the characteristics of a new organic–inorganic hybrid membrane. Polymer **50**(2), 553–559 (2009). https://doi.org/10.1016/j.polymer.2008.11.012

10. Souza, V.C.; Quadri, M.G.N.: Organic-inorganic hybrid membranes in separation processes: a 10-year review. Braz. J. Chem. Eng. **30**, 683–700 (2013)

11. Cao, X.; Ma, J.; Shi, X.; Ren, Z.: Effect of TiO_2 nanoparticle size on the performance of PVDF membrane. Appl. Surf. Sci. **253**(4), 2003–2010 (2006). https://doi.org/10.1016/j.apsusc.2006.03.090

12. Kayvani Fard, A.; McKay, G.; Buekenhoudt, A.; Al Sulaiti, H.; Motmans, F.; Khraisheh, M.; Atieh, M.: Inorganic membranes: preparation and application for water treatment and desalination. Materials **11**(1), 74 (2018)

13. Agboola, O.; Fayomi, O.S.I.; Ayodeji, A.; Ayeni, A.O.; Alagbe, E.E.; Sanni, S.E.; Okoro, E.E.; Moropeng, L.; Sadiku, R.; Kupolati, K.W.; Oni, B.A.: A review on polymer nanocomposites and their effective applications in membranes and adsorbents for water treatment and gas separation. Membranes **11**(2), 139 (2021)

14. Darabi, R.R.; Peyravi, M.; Jahanshahi, M.; Qhoreyshi Amiri, A.A.: Decreasing ICP of forward osmosis (TFN-FO) membrane through modifying $PES-Fe_3O_4$ nanocomposite substrate. Korean J. Chem. Eng. **34**(8), 2311–2324 (2017). https://doi.org/10.1007/s11814-017-0086-1

15. Huang, Z.Q.; Chen, Z.Y.; Guo, X.P.; Zhang, Z.; Guo, C.L.: Structures and separation properties of $PAN-Fe_3O_4$ ultrafiltration membranes prepared under an orthogonal magnetic field. Ind. Eng. Chem. Res. **45**(23), 7905–7912 (2006). https://doi.org/10.1021/ie0603013

16. Moatmed, S.M.; Khedr, M.H.; El-dek, S.I.; Kim, H.-Y.; El-Deen, A.G.: Highly efficient and reusable superhydrophobic/superoleophilic polystyrene@ Fe_3O_4 nanofiber membrane for high-performance oil/water separation. J. Environ. Chem. Eng. **7**(6), 103508 (2019). https://doi.org/10.1016/j.jece.2019.103508

17. Abegunde, S.M.; Idowu, K.S.; Sulaimon, A.O.: Plant-mediated iron nanoparticles and their applications as adsorbents for water treatment—a review. J. Chem. Rev. **2**(2), 103–113 (2020). https://doi.org/10.33945/sami/jcr.2020.2.3

18. Razmjou, A.; Mansouri, J.; Chen, V.: The effects of mechanical and chemical modification of TiO_2 nanoparticles on the surface chemistry, structure and fouling performance of PES ultrafiltration membranes. J. Membr. Sci. **378**(1), 73–84 (2011). https://doi.org/10.1016/j.memsci.2010.10.019

19. Sotto, A.; Boromand, A.; Zhang, R.; Luis, P.; Arsuaga, J.M.; Kim, J.; Van der Bruggen, B.: Effect of nanoparticle aggregation at low concentrations of TiO_2 on the hydrophilicity, morphology, and fouling resistance of $PES-TiO_2$ membranes. J. Colloid Interface Sci. **363**(2), 540–550 (2011). https://doi.org/10.1016/j.jcis.2011.07.089

20. Bae, T.H.; Tak, T.M.: Effect of TiO_2 nanoparticles on fouling mitigation of ultrafiltration membranes for activated sludge filtration. J. Membr. Sci. **249**(1), 1–8 (2005). https://doi.org/10.1016/j.memsci.2004.09.008

21. Li, X.; Li, J.; Van der Bruggen, B.; Sun, X.; Shen, J.; Han, W.; Wang, L.: Fouling behavior of polyethersulfone ultrafiltration membranes functionalized with sol–gel formed ZnO nanoparticles. RSC Adv. **5**(63), 50711–50719 (2015). https://doi.org/10.1039/C5RA05783C

22. Zhao, S.; Yan, W.; Shi, M.; Wang, Z.; Wang, J.; Wang, S.: Improving permeability and antifouling performance of polyethersulfone ultrafiltration membrane by incorporation of ZnO-DMF dispersion containing nano-ZnO and polyvinylpyrrolidone. J. Membr. Sci. **478**, 105–116 (2015). https://doi.org/10.1016/j.memsci.2014.12.050

23. Hong, J.; He, Y.: Polyvinylidene fluoride ultrafiltration membrane blended with nano-ZnO particle for photo-catalysis self-cleaning. Desalination **332**(1), 67–75 (2014). https://doi.org/10.1016/j.desal.2013.10.026

24. Muhamad, M.S.; Salim, M.R.; Lau, W.J.; Hadibarata, T.; Yusop, Z.: Removal of bisphenol A by adsorption mechanism using $PES-SiO_2$ composite membranes. Environ. Technol. **37**(15), 1959–1969 (2016). https://doi.org/10.1080/09593330.2015.1137359

25. Shen, J.N.; Ruan, H.M.; Wu, L.G.; Gao, C.J.: Preparation and characterization of $PES-SiO_2$ organic–inorganic composite ultrafiltration membrane for raw water pretreatment. Chem. Eng. J. **168**(3), 1272–1278 (2011). https://doi.org/10.1016/j.cej.2011.02.039

26. Huang, J.; Zhang, K.S.; Wang, K.; Xie, Z.L.; Ladewig, B.; Wang, H.T.: Fabrication of polyethersulfone-mesoporous silica nanocomposite ultrafiltration membranes with antifouling properties. J. Membr. Sci. **423–424**, 362–370 (2012). https://doi.org/10.1016/j.memsci.2012.08.029

27. Alam, J.; Dass, L.A.; Ghasemi, M.; Alhoshan, M.: Synthesis and optimization of $PES-Fe_3O_4$ mixed matrix nanocomposite membrane: application studies in water purification. Polym. Compos. **34**(11), 1870–1877 (2013). https://doi.org/10.1002/pc.22593

28. Al-Husaini, I.S.; Yusoff, A.R.M.; Lau, W.J.; Ismail, A.F.; Al-Abri, M.Z.; Wirzal, M.D.H.: Iron oxide nanoparticles incorporated polyethersulfone electrospun nanofibrous membranes for effective oil removal. Chem. Eng. Res. Des. **148**, 142–154 (2019). https://doi.org/10.1016/j.cherd.2019.06.006

29. Jiang, Z.; Tijing, L.D.; Amarjargal, A.; Park, C.H.; An, K.J.; Shon, H.K.; Kim, C.S.: Removal of oil from water using magnetic bicomponent composite nanofibers fabricated by electrospinning. Compos. B Eng. **77**, 311–318 (2015). https://doi.org/10.1016/j.compositesb.2015.03.067

30. Wu, W.; Wu, Z.; Yu, T.; Jiang, C.; Kim, W.-S.: Recent progress on magnetic iron oxide nanoparticles: synthesis, surface functional strategies and biomedical applications. Sci. Tech. Adv. Mater. **16**(2), 023501 (2015). https://doi.org/10.1088/1468-6996/16/2/023501

31. Zhu, N.; Ji, H.; Yu, P.; Niu, J.; Farooq, M.U.; Akram, M.W.; Udego, I.O.; Li, H.; Niu, X.: Surface modification of magnetic iron oxide nanoparticles. Nanomaterials (Basel) **8**(10), 810 (2018). https://doi.org/10.3390/nano8100810

32. Noqta, O.A.; Aziz, A.A.; Usman, I.A.; Bououdina, M.: Recent advances in iron oxide nanoparticles (IONPs): synthesis and surface modification for biomedical applications. J. Supercond. Nov. Magn. **32**(4), 779–795 (2019). https://doi.org/10.1007/s10948-018-4939-6

33. Subramaniam, M.N.; Goh, P.S.; Tan, Y.H.; Chiong, S.J.; Lau, W.J.; Ng, B.C.; Ismail, A.F.; Chuah, J.Y.; Lai, S.O.: Antifouling improvement of polyethersulfone membrane incorporated with negatively charged zinc–iron oxide for AT-POME colour removal. Arab. J. Sci. Eng. **44**(6), 5571–5580 (2019). https://doi.org/10.1007/s13369-019-03858-y

34. Tan, Y.H.; Goh, P.S.; Ismail, A.F.; Ng, B.C.; Lai, G.S.: Decolourization of aerobically treated palm oil mill effluent (AT-POME) using polyvinylidene fluoride (PVDF) ultrafiltration membrane incorporated with coupled zinc-iron oxide nanoparticles. Chem. Eng. J. **308**, 359–369 (2017). https://doi.org/10.1016/j.cej.2016.09.092

35. Zinadini, S.; Zinatizadeh, A.A.; Rahimi, M.; Vatanpour, V.; Zangeneh, H.; Beygzadeh, M.: Novel high flux antifouling nanofiltration membranes for dye removal containing carboxymethyl

chitosan coated Fe_3O_4 nanoparticles. Desalination **349**, 145–154 (2014). https://doi.org/10.1016/j.desal.2014.07.007

36. Koulivand, H.; Shahbazi, A.; Vatanpour, V.: Fabrication and characterization of a high-flux and antifouling polyethersulfone membrane for dye removal by embedding Fe_3O_4-MDA nanoparticles. Chem. Eng. Res. Des. **145**, 64–75 (2019). https://doi.org/10.1016/j.cherd.2019.03.003

37. Rahimi, Z.; Zinatizadeh, A.A.; Zinadini, S.: Milk processing wastewater treatment in a bioreactor followed by an antifouling O-carboxymethyl chitosan modified Fe_3O_4/PVDF ultrafiltration membrane. J. Ind. Eng. Chem. **38**, 103–112 (2016). https://doi.org/10.1016/j.jiec.2016.04.011

38. Zarghami, S.; Mohammadi, T.; Sadrzadeh, M.: Preparation, characterization and fouling analysis of in-air hydrophilic/underwater oleophobic bio-inspired polydopamine coated PES membranes for oily wastewater treatment. J. Membr. Sci. **582**, 402–413 (2019). https://doi.org/10.1016/j.memsci.2019.04.020

39. Li, L.; Wang, F.; Lv, Y.; Liu, J.; Zhang, D.; Shao, Z.: Halloysite nanotubes and Fe_3O_4 nanoparticles enhanced adsorption removal of heavy metal using electrospun membranes. Appl. Clay Sci. **161**, 225–234 (2018). https://doi.org/10.1016/j.clay.2018.04.002

40. Koushkbaghi, S.; Zakialamdari, A.; Pishnamazi, M.; Ramandi, H.F.; Aliabadi, M.; Irani, M.: Aminated-Fe_3O_4 nanoparticles filled chitosan/PVA/PES dual layers nanofibrous membrane for the removal of Cr(VI) and Pb(II) ions from aqueous solutions in adsorption and membrane processes. Chem. Eng. J. **337**, 169–182 (2018). https://doi.org/10.1016/j.cej.2017.12.075

41. Daraei, P.; Madaeni, S.S.; Ghaemi, N.; Salehi, E.; Khadivi, M.A.; Moradian, R.; Astinchap, B.: Novel polyethersulfone nanocomposite membrane prepared by PANI/Fe_3O_4 nanoparticles with enhanced performance for Cu(II) removal from water. J. Membr. Sci. **415–416**, 250–259 (2012). https://doi.org/10.1016/j.memsci.2012.05.007

42. Ma, J.; Ping, D.; Dong, X.: Recent developments of graphene oxide-based membranes: a review. Membranes **7**(3), 52 (2017). https://doi.org/10.3390/membranes7030052

43. Bet-Moushoul, E.; Mansourpanah, Y.; Farhadi, K.; Tabatabaei, M.: TiO_2 nanocomposite based polymeric membranes: a review on performance improvement for various applications in chemical engineering processes. Chem. Eng. J. **283**, 29–46 (2016). https://doi.org/10.1016/j.cej.2015.06.124

44. Abdullah, N.; Yusof, N.; Ismail, A.F.; Lau, W.J.: Insights into metal-organic frameworks-integrated membranes for desalination process: a review. Desalination **500**, 114867 (2021). https://doi.org/10.1016/j.desal.2020.114867

45. Ihsanullah: Carbon nanotube membranes for water purification: Developments, challenges, and prospects for the future. Sep. Purif. Technol. **209**, 307–337 (2019). https://doi.org/10.1016/j.seppur.2018.07.043

46. Sheikh, M.; Pazirofteh, M.; Dehghani, M.; Asghari, M.; Rezakazemi, M.; Valderrama, C.; Cortina, J.: Application of ZnO nanostructures in ceramic and polymeric membranes for water and wastewater technologies: a review. Chem. Eng. J. **391**, 123475 (2019). https://doi.org/10.1016/j.cej.2019.123475

47. Teja, A.; Koh, P.Y.: Synthesis, properties, and applications of magnetic iron oxide nanoparticles. Prog. Cryst. Growth Charact. Mater. **55**, 22–45 (2009). https://doi.org/10.1016/j.pcrysgrow.2008.08.003

48. Dar, M.I.; Shivashankar, S.A.: Single crystalline magnetite, maghemite, and hematite nanoparticles with rich coercivity. RSC Adv. **4**(8), 4105–4113 (2014). https://doi.org/10.1039/C3RA45457F

49. Ghazanfari, M.R.; Kashefi, M.; Shams, S.F.; Jaafari, M.R.: Perspective of Fe_3O_4 nanoparticles role in biomedical applications. Biochem. Res. Int. (2016). https://doi.org/10.1155/2016/7840161

50. Can, M.M.; Coşkun, M.; Fırat, T.: A comparative study of nanosized iron oxide particles; magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3), using ferromagnetic resonance. J. Alloy. Compd. **542**, 241–247 (2012). https://doi.org/10.1016/j.jallcom.2012.07.091

51. Jeong, U.; Teng, X.; Wang, Y.; Yang, H.; Xia, Y.: Superparamagnetic colloids: controlled synthesis and niche applications. Adv. Mater. **19**(1), 33–60 (2007). https://doi.org/10.1002/adma.200600674

52. Petcharoen, K.; Sirivat, A.: Synthesis and characterization of magnetite nanoparticles via the chemical co-precipitation method. Mater. Sci. Eng. B **177**(5), 421–427 (2012). https://doi.org/10.1016/j.mseb.2012.01.003

53. Huang, Y.; Xiao, C.F.; Huang, Q.L.; Liu, H.L.; Hao, J.Q.; Song, L.: Magnetic field induced orderly arrangement of Fe_3O_4/GO composite particles for preparation of Fe_3O_4/GO/PVDF membrane. J. Membr. Sci. **548**, 184–193 (2018). https://doi.org/10.1016/j.memsci.2017.11.027

54. Sarno, M.; Ponticorvo, E.; Cirillo, C.: High surface area monodispersed Fe_3O_4 nanoparticles alone and on physical exfoliated graphite for improved supercapacitors. J. Phys. Chem. Solid **99**, 138–147 (2016). https://doi.org/10.1016/j.jpcs.2016.08.019

55. Ma, J.H.; Wang, L.L.; Wu, Y.L.; Dong, X.S.; Ma, Q.L.; Qiao, C.; Zhang, Q.F.; Zhang, J.L.: Facile synthesis of Fe_3O_4 nanoparticles with a high specific surface area. Mater. Trans. **55**(12), 1900–1902 (2014). https://doi.org/10.2320/matertrans.M2014184

56. Wang, H.; Pu, X.; Zhou, Y.; Chen, X.; Liao, X.; Huang, Z.; Ying, G.: Synthesis of macroporous magnetic Fe_3O_4 microparticles via a novel organic matter assisted open-cell hollow sphere assembly method. Materials **11**(9), 1508 (2018). https://doi.org/10.3390/ma11091508

57. Blaney, L.: Magnetite (Fe_3O_4): properties, synthesis, and applications. Lehigh Rev. **15**, 33–81 (2007)

58. Duriagina, Z.A.; Tepla, T.L.; Kulyk, V.V.: Evaluation of differences between Fe_3O_4 micro- and nanoparticles properties. Acta Phys. Pol. A **133**, 869 (2018). https://doi.org/10.12693/APhysPolA.133.869

59. Liu, X.; Chen, Y.; Deng, Z.; Yang, Y.: High-performance nanofiltration membrane for dyes removal: blending Fe_3O_4-HNTs nanocomposites into poly(vinylidene fluoride) matrix. J. Dispers. Sci. Technol. (2019). https://doi.org/10.1080/01932691.2019.1662308

60. Akın Sahbaz, D.; Yakar, A.; Gündüz, U.: Magnetic Fe_3O_4-chitosan micro- and nanoparticles for wastewater treatment. Part. Sci. Technol. **37**(6), 732–740 (2019). https://doi.org/10.1080/02726351.2018.1438544

61. Ghaemi, N.; Madaeni, S.S.; Daraei, P.; Rajabi, H.; Zinadini, S.; Alizadeh, A.; Heydari, R.; Beygzadeh, M.; Ghouzivand, S.: Polyethersulfone membrane enhanced with iron oxide nanoparticles for copper removal from water: application of new functionalized Fe_3O_4 nanoparticles. Chem. Eng. J. **263**, 101–112 (2015). https://doi.org/10.1016/j.cej.2014.10.103

62. Zainol Abidin, M.N.; Goh, P.S.; Ismail, A.F.; Said, N.; Othman, M.H.D.; Hasbullah, H.; Abdullah, M.S.; Ng, B.C.; Sheikh Abdul Kadir, S.H.; Kamal, F.: Polysulfone/iron oxide nanoparticles Ultrafiltration membrane for adsorptive removal of phosphate from aqueous solution. J. Membr. Sci. Res. **5**(1), 20–24 (2019). https://doi.org/10.22079/jmsr.2018.87665.1195

63. Said, N.; Hasbullah, H.; Ismail, A.F.; Othman, M.H.D.; Goh, P.S.; Zainol Abidin, M.N.; Sheikh Abdul Kadir, S.H.; Kamal, F.; Abdullah, M.S.; Ng, B.C.: Enhanced hydrophilic polysulfone hollow fiber membranes with addition of iron oxide nanoparticles. Polym. Int. **66**(11), 1424–1429 (2017). https://doi.org/10.1002/pi.5401

64. Frey, N.A.; Peng, S.; Cheng, K.; Sun, S.: Magnetic nanoparticles: synthesis, functionalization, and applications in bioimaging

and magnetic energy storage. Chem. Soc. Rev. **38**(9), 2532–2542 (2009). https://doi.org/10.1039/B815548H

65. Jian, P.; Yahui, H.; Yang, W.; Linlin, L.: Preparation of polysulfone–Fe$_3$O$_4$ composite ultrafiltration membrane and its behavior in magnetic field. J. Membr. Sci. **284**(1), 9–16 (2006). https://doi.org/10.1016/j.memsci.2006.07.052

66. Koseoglu, Y.; Kavas, H.: Size and surface effects on magnetic properties of Fe$_3$O$_4$ nanoparticles. J. Nanosci. Nanotechnol. **8**, 584–590 (2008). https://doi.org/10.1166/jnn.2008.B012

67. Chang, Y.C.; Chen, D.H.: Preparation and adsorption properties of monodisperse chitosan-bound Fe$_3$O$_4$ magnetic nanoparticles for removal of Cu(II) ions. J. Colloid Interface Sci. **283**(2), 446–451 (2005). https://doi.org/10.1016/j.jcis.2004.09.010

68. Zhang, J.; Lin, S.; Han, M.; Su, Q.; Xia, L.; Hui, Z.: Adsorption properties of magnetic magnetite nanoparticle for coexistent Cr(VI) and Cu(II) in mixed solution. Water **12**(2), 446 (2020)

69. Xiao, D.L.; Li, H.; He, H.; Lin, R.; Zuo, P.L.: Adsorption performance of carboxylated multi-wall carbon nanotube-Fe$_3$O$_4$ magnetic hybrids for Cu(II) in water. New Carbon Mater. **29**(1), 15–25 (2014). https://doi.org/10.1016/S1872-5805(14)60122-0

70. Saraswathi, A.S.A.; Nagendran, A.; Rana, D.: Tailored polymer nanocomposite membranes based on carbon, metal oxide and silicon nanomaterials: a review. J. Mater. Chem. A **7**(15), 8723–8745 (2019). https://doi.org/10.1039/C8TA11460A

71. Kim, J.; Van der Bruggen, B.: The use of nanoparticles in polymeric and ceramic membrane structures: review of manufacturing procedures and performance improvement for water treatment. Environ. Pollut. **158**(7), 2335–2349 (2010). https://doi.org/10.1016/j.envpol.2010.03.024

72. Zahid, M.; Rashid, A.; Akram, S.; Rehan, Z.A.; Razzaq, W.: A comprehensive review on polymeric nanocomposite membranes for water treatment. J. Membr. Sci. Technol. (2018). https://doi.org/10.4172/2155-9589.1000179

73. Chai, P.V.; Mahmoudi, E.; Teow, Y.H.; Mohammad, A.W.: Preparation of novel polysulfone-Fe$_3$O$_4$/GO mixed-matrix membrane for humic acid rejection. J. Water Process. Eng. **15**, 83–88 (2017). https://doi.org/10.1016/j.jwpe.2016.06.001

74. Ma, D.L.: Chapter 1 - Hybrid nanoparticles: an introduction. In: Mohapatra, S., Nguyen, T.A., Nguyen-Tri, P. (eds.) Noble metal-metal oxide hybrid nanoparticles. pp. 3–6. Woodhead Publishing, (2019)

75. Rambabu, K.; Velu, S.: Polyethylene glycol and iron oxide nanoparticles blended polyethersulfone ultrafiltration membrane for enhanced performance in dye removal studies. E-Polymers **15**, 151–159 (2015). https://doi.org/10.1515/epoly-2014-0214

76. Rambabu, K.; Velu, S.: Iron nanoparticles blended polyethersulfone ultrafiltration membranes for enhanced metal ion removal in wastewater treatment. Int. J. ChemTech Res. **6**, 4468–4470 (2014)

77. Bagheripour, E.; Moghadassi, A.R.; Parvizian, F.; Hosseini, S.M.; Van der Bruggen, B.: Tailoring the separation performance and fouling reduction of PES based nanofiltration membrane by using a PVA/Fe$_3$O$_4$ coating layer. Chem. Eng. Res. Des. **144**, 418–428 (2019). https://doi.org/10.1016/j.cherd.2019.02.028

78. Gholami, A.; Moghadassi, A.R.; Hosseini, S.M.; Shabani, S.; Gholami, F.: Preparation and characterization of polyvinyl chloride based nanocomposite nanofiltration-membrane modified by iron oxide nanoparticles for lead removal from water. J. Ind. Eng. Chem. **20**(4), 1517–1522 (2014). https://doi.org/10.1016/j.jiec.2013.07.041

79. Huang, Z.Q.; Chen, Y.S.; Chen, Z.W.; Nie, L.H.; Zhang, Z.; Xu, H.T.; Zhou, K.M.: Effect of the mass ratio of Fe$_3$O$_4$/PAA on separation properties and the extractive amount of Fe$_3$O$_4$ during the formation of Fe$_3$O$_4$-PES ultrafiltration membranes. J. Appl. Polym. Sci. **129**(6), 3558–3565 (2013). https://doi.org/10.1002/app.39128

80. Ansari, S.; Bagheripour, E.; Moghadassi, A.; Hosseini, S.M.: Fabrication of mixed matrix poly(phenylene ether-ether sulfone)-based nanofiltration membrane modified by Fe$_3$O$_4$ nanoparticles for water desalination. J. Polym. Eng. (2016). https://doi.org/10.1515/polyeng-2015-0392

81. Mehrnia, M.R.; Homayoonfal, M.: Fouling mitigation behavior of magnetic responsive nanocomposite membranes in a magnetic membrane bioreactor. J. Membr. Sci. **520**, 881–894 (2016). https://doi.org/10.1016/j.memsci.2016.08.046

82. Daraei, P.; Madaeni, S.S.; Ghaemi, N.; Khadivi, M.A.; Astinchap, B.; Moradian, R.: Fouling resistant mixed matrix polyethersulfone membranes blended with magnetic nanoparticles: study of magnetic field induced casting. Sep. Purif. Technol. **109**, 111–121 (2013). https://doi.org/10.1016/j.seppur.2013.02.035

83. Rahimi, Z.; Zinatizadeh, A.A.; Zinadini, S.: Membrane bioreactors troubleshooting through the preparation of a high antifouling PVDF ultrafiltration mixed-matrix membrane blended with O-carboxymethyl chitosan-Fe$_3$O$_4$ nanoparticles. Environ. Technol. **40**(26), 3523–3533 (2019). https://doi.org/10.1080/09593330.2018.1480665

84. Bagheripour, E.; Moghadassi, A.R.; Hosseini, S.M.: Incorporated polyacrylic acid-co-Fe$_3$O$_4$ nanoparticles mixed matrix polyethersulfone based nanofiltration membrane in desalination process. Int. J. Eng. Trans. C Asp. **30**, 821–829 (2017)

85. Silva Valentim, A.C.; da Silva, E.O.; da Silva, P.S.R.C.; Garcia, D.S.; Bruno Tavares, M.I.: Synergistic effect between hybrid nanoparticles of TiO$_2$ and Nb$_2$O$_5$ in the nanostructured materials based on eva matrix. Polym. Test. **70**, 111–116 (2018). https://doi.org/10.1016/j.polymertesting.2018.06.033

86. Wu, H.; Tang, B.; Wu, P.: Development of novel SiOR GO nanohybrid/polysulfone membrane with enhanced performance. J. Membr. Sci. **451**, 94–102 (2014)

87. Xu, Z.; Wu, T.; Shi, J.; Wang, W.; Teng, K.; Qian, X.; Shan, M.; Deng, H.; Tian, X.; Li, C.; Li, F.: Manipulating migration behavior of magnetic graphene oxide via magnetic field induced casting and phase separation toward high-performance hybrid ultrafiltration membranes. ACS Appl. Mater. Interfaces **8**(28), 18418–18429 (2016). https://doi.org/10.1021/acsami.6b04083

88. Li, S.Z.; Gong, Y.B.; Yang, Y.C.; He, C.; Hu, L.L.; Zhu, L.F.; Sun, L.P.; Shu, D.: Recyclable CNTs/Fe$_3$O$_4$ magnetic nanocomposites as adsorbents to remove bisphenol A from water and their regeneration. Chem. Eng. J. **260**, 231–239 (2015). https://doi.org/10.1016/j.cej.2014.09.032

89. Wang, C.; Wu, H.; Qu, F.; Liang, H.; Niu, X.; Li, G.: Preparation and properties of polyvinyl chloride ultrafiltration membranes blended with functionalized multi-walled carbon nanotubes and MWCNTs/Fe$_3$O$_4$ hybrids. J. Appl. Polym. Sci. (2016). https://doi.org/10.1002/app.43417

90. Noormohamadi, A.; Homayoonfal, M.; Mehrnia, M.R.; Davar, F.: Employing magnetism of Fe$_3$O$_4$ and hydrophilicity of ZrO$_2$ to mitigate biofouling in magnetic MBR by Fe$_3$O$_4$-coated ZrO$_2$/PAN nanocomposite membrane. Environ. Technol. **41**(20), 2683–2704 (2020). https://doi.org/10.1080/09593330.2019.1579870

91. Chai, P.V.; Mahmoudi, E.; Mohammad, A.W.; Choy, P.Y.: Iron oxide decorated graphene oxide embedded polysulfone mixed-matrix membrane: Comparison of different types mixed-matrix membranes on antifouling and performance. IOP Conf. Ser. Earth Environ. Sci. **463**, 012174 (2020). https://doi.org/10.1088/1755-1315/463/1/012174

92. Madaeni, S.S.; Heidary, F.; Salehi, E.: Co-adsorption/filtration of heavy metal ions from water using regenerated cellulose UF membranes modified with DETA ligand. Sep. Sci. Technol. **48**(9), 1308–1314 (2013). https://doi.org/10.1080/01496395.2012.735741

93. Rowley, J.; Abu-Zahra, N.H.: Synthesis and characterization of polyethersulfone membranes impregnated with (3-aminopropyltriethoxysilane) APTES-Fe$_3$O$_4$ nanoparticles for As(V) removal from water. J. Environ. Chem. Eng. **7**(1), 102875 (2019). https://doi.org/10.1016/j.jece.2018.102875

94. Moradihamedani, P.; Kalantari, K.; Abdullah, A.H.; Morad, N.A.: High efficient removal of lead(II) and nickel(II) from aqueous solution by novel polysulfone/Fe$_3$O$_4$–talc nanocomposite mixed matrix membrane. Desalin. Water Treat. **57**(59), 28900–28909 (2016). https://doi.org/10.1080/19443994.2016.1193449

95. Modi, A.; Bellare, J.: Efficient removal of 2,4-dichlorophenol from contaminated water and alleviation of membrane fouling by high flux polysulfone-iron oxide/graphene oxide composite hollow fiber membranes. J. Water Process. Eng. **33**, 101113 (2020). https://doi.org/10.1016/j.jwpe.2019.101113

96. Chen, F.; Dong, S.; Wang, Z.; Xu, J.; Xu, R.; Wang, J.: Preparation of mixed matrix composite membrane for hydrogen purification by incorporating ZIF-8 nanoparticles modified with tannic acid. Int. J. Hydrog. Energy **45**(12), 7444–7454 (2020). https://doi.org/10.1016/j.ijhydene.2019.04.050

97. Sri Abirami Saraswathi, M.S.; Nagendran, A.; Rana, D.: Tailored polymer nanocomposite membranes based on carbon, metal oxide and silicon nanomaterials: a review. J. Mater. Chem. A **7**(15), 8723–8745 (2019). https://doi.org/10.1039/C8TA11460A

98. Liu, J.; Li, Y.; Wang, X.; Zhang, Q.; Yang, J.: Preparation and properties of nano-composite films based on polyethersulfone and surface-modified SiO$_2$. J. Macromol. Sci. Part B **50**(12), 2356–2365 (2011). https://doi.org/10.1080/00222348.2011.562825

99. Turcheniuk, K.; Tarasevych, A.V.; Kukhar, V.P.; Boukherroub, R.; Szunerits, S.: Recent advances in surface chemistry strategies for the fabrication of functional iron oxide based magnetic nanoparticles. Nanoscale **5**(22), 10729–10752 (2013). https://doi.org/10.1039/C3NR04131J

100. Said, N.; Hasbullah, H.; Abidin, M.N.Z.; Ismail, A.F.; Goh, P.S.; Othman, M.H.D.; Kadir, S.H.S.A.; Kamal, F.; Abdullah, M.S.; Ng, B.C.: Facile modification of polysulfone hollow-fiber membranes via the incorporation of well-dispersed iron oxide nanoparticles for protein purification. J. Appl. Polym. Sci. **136**(21), 47502 (2019). https://doi.org/10.1002/app.47502

101. Agbaje, T.A.; Al-Gharabli, S.; Mavukkandy, M.O.; Kujawa, J.; Arafat, H.A.: PVDF/magnetite blend membranes for enhanced flux and salt rejection in membrane distillation. Desalination **436**, 69–80 (2018). https://doi.org/10.1016/j.desal.2018.02.012

102. Chai, P.V.; Mahmoudi, E.; Mohammad, A.W.; Choy, P.Y.: Iron oxide decorated graphene oxide embedded polysulfone mixed-matrix membrane: comparison of different types mixed-matrix membranes on antifouling and performance. IOP Conf. Ser. Earth Environ. Sci. **463**, 012174 (2020). https://doi.org/10.1088/1755-1315/463/1/012174

103. Patel, S.; Hota, G.: Iron oxide nanoparticle-immobilized PAN nanofibers: synthesis and adsorption studies. RSC Adv. **6**(19), 15402–15414 (2016). https://doi.org/10.1039/C5RA20345G

104. Mahmoudi, E.; Ng, L.Y.; Ang, W.L.; Chung, Y.T.; Rohani, R.; Mohammad, A.W.: Enhancing morphology and separation performance of polyamide 6,6 membranes By minimal incorporation of silver decorated graphene oxide nanoparticles. Sci. Rep. **9**(1), 1216 (2019). https://doi.org/10.1038/s41598-018-38060-x

105. Li, Y.; Huang, S.; Zhou, S.; Fane, A.G.; Zhang, Y.; Zhao, S.: Enhancing water permeability and fouling resistance of polyvinylidene fluoride membranes with carboxylated nanodiamonds. J. Membr. Sci. **556**, 154–163 (2018). https://doi.org/10.1016/j.memsci.2018.04.004

106. Wen, Y.; Yuan, J.; Ma, X.; Wang, S.; Liu, Y.: Polymeric nanocomposite membranes for water treatment: a review. Environ. Chem. Lett. **17**(4), 1539–1551 (2019). https://doi.org/10.1007/s10311-019-00895-9

107. Pendergast, M.M.; Hoek, E.M.V.: A review of water treatment membrane nanotechnologies. Energy Environ. Sci. **4**(6), 1946–1971 (2011). https://doi.org/10.1039/C0EE00541J

108. Ali, A.; Zafar, H.; Zia, M.; Ul Haq, I.; Phull, A.R.; Ali, J.S.; Hussain, A.: Synthesis, characterization, applications, and challenges of iron oxide nanoparticles. Nanotechnol Sci Appl **9**, 49–67 (2016). https://doi.org/10.2147/NSA.S99986