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Effect of metal and metal oxide nanoparticle impregnation route on structure and liquid filtration performance of polymeric nanocomposite membranes: a comprehensive review

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ABSTRACT

Nanocomposite membranes benefit from both flexibility and processability of polymers and the thermal and mechanical stability of nanoparticles at the same time. This paper discusses the effect of the presence of various nanoparticles on the morphology and efficiency of the polymeric membranes in the separation of liquid phase. The presence of nanoparticles usually increases the hydrophilicity and decreases the fouling of polymeric membranes during the filtration process. The presence of TiO_2, Al_2O_3, ZrO_2, SiO_2, Fe_3O_4, Ag, and Fe nanoparticles increases the mechanical and thermal resistant of the polymeric membranes. The TiO_2 and Ag result in anti-bacterial characteristics, ZrO_2 and Fe create catalytic properties, SiO_2 nanoparticle causes conductivity properties, and Fe_3O_4 nanoparticle gives magnetic characteristics to polymeric membranes. Understanding the synthesis method (in situ or ex situ) and the combination routes (blending with polymeric matrix or deposition on the surface) of the used nanoparticles is very important in determining the structure and performance of the composite membranes during liquid filtration. Findings from such studies are highlighted and the future possibility of nanocomposite membrane application in liquid filtration is also discussed.

Keywords: Polymeric nanocomposite membrane; Nanoparticle; Blending; Deposition

1. Introduction

Developments in nanotechnology and material science, in addition to the need for specific separations with high efficiency, have resulted in the synthesis of nanocomposite membranes. Membrane structures obtained from the presence of nanoparticles in a polymeric matrix can be considered as multi-functional compounds because they possess both the specific properties of nanoparticles and the polymeric matrix at the same time. This review studies the presence of various metal and metal oxide nanoparticles in the synthesized polymeric membranes to be used in filtration processes with pressure as the driving force. In addition to giving their own properties to the nanocomposite membrane, nanoparticles can be used as additives in order to modify the membrane if they are

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synthesized in controlled conditions. The properties of nanocomposite membranes are different from those of the membranes without nanoparticles to the extent that various nanoparticles are used in many researches in order to modify polymeric membranes. It must be pointed out that there are numerous methods for the modification of polymeric membranes depending on the type of the polymer and on its application. However, as will be discussed later, the specific properties of nanoparticles have encouraged the researchers to study their application for the modification of the structure and performance of the membranes. Table 1 lists various methods to modify polymers whose modification with nanoparticles has been studied as well.

2. Membrane modification in the presence of nanoparticles

Nanoparticles are particles with the dimensions about 1–10 nm. While switching from micro-particles to nanoparticles, the ratio of surface area to volume increases and the particle size is affected by quantum effects, resulting in some physical changes. Some different types of metal and metal oxide nanoparticles that have applications in the field of nanocomposite membranes and the specific properties of the nanoparticles have been listed in Table 2.

Except metal and metal oxide nanoparticles (listed in Table 2), the presence of nanostructures, such as nanotubes [12,29–34,185–187], zeolite nanoparticles [35,61,188], clay [36,94,180,189], and fullerene [27,28,87,88,124,149], in the structure of polymeric membranes has been studied too.

Possessing the specific properties listed in Table 2, the metal and metal oxide nanoparticles make a big change in the performance of the nanocomposite membranes by creating changes in the structure and properties of the synthesized membrane or by changing the synthesis process when they enter the structure of the polymer. Mechanical and thermal properties, hydrophilicity, and crystallinity of the polymeric films vary when nanoparticles are added to polymeric membranes. Catalytic, anti-bacterial, and magnetic properties as well as conductivity are among the characteristics that are added to the nanocomposite membranes in the presence of nanoparticles. Permeability, anti-fouling properties, and selectivity are among the most important properties of polymeric membranes during the filtration and are extremely affected by the type, size, and amount of the nanoparticle, and, most importantly, how the nanoparticle has been added to the polymeric matrix.

3. Effect of nanoparticle impregnation method on structure and filtration performance of polymeric nanocomposite membranes

The effect of nanoparticles on the structure and filtration performance of nanocomposite membranes depends more on the size [2,93,119,190] and amount of nanoparticles and how they were added to the polymeric matrix than the type of the nanoparticles (see Fig. 1). There are typically two different methods to use nanoparticles for membrane modification: adding nanoparticles to the casting solution before phase inversion process [1,2,4–10,16–27,40,44,46,47,49,50, 67,87,88,101, 106,111,115] and deposition of nanoparticles on the surface of the pre-synthesized polymeric membrane [2,3,11,40–43,45,48,54–56,58,59,70,76]. Studies were carried out in order to compare the two modification methods. Results showed that the deposition on the surface is a more effective method to modify the membrane although the stability of nanoparticles entrapped in the polymeric bed is much longer [2,40]. Each of the methods may include using pre-synthesized nanoparticles or *in situ* synthesis of nanoparticles in polymeric matrix [10,11,17,26,59,70,115]. Addition of nanoparticle precursors to casting solution before phase inversion in appropriate ambient (temperature and pH) deduced *in situ* synthesis of nanoparticles in membrane matrix. Based on nanoparticle nature, a variety of methods such as sol–gel [10,17], ion exchange and reduction [11], and chemical reduction [26,59,70,115] can be used for *in situ* nanoparticle fabrication.

3.1. Blending of nanoparticles with casting solution

The use of additive in the casting solution changes the rate of phase separation and, consequently, changes the structure and filtration performance of the synthesized nanocomposite membranes. Changes in demixing rate are caused by thermodynamic and kinetic variations. In any polymeric system, there are controllable trade-off relations between thermodynamic and kinetic variation [191]. Additives can play a thermodynamic enhancer or rheological deterrent role during phase inversion process. Similar to other additives, nanoparticles cause simultaneous thermodynamic enhancement and rheological hindrance during the phase separation process. The presence of nanoparticles enhances phase separation and shows prohibitive effects. From a thermodynamic point of view (enthalpy), nanoparticles, as additives, decrease the compatibility of the polymer with the solvent. Therefore, less non-solvent is required for the happening of phase inversion. This fact induces instantaneous phase separation and creates a porous structure.

Table 1
Various methods for modification of polymers whose modification with nanoparticles has been studied

Membrane material	Nanoparticle used for membrane modification	Other methods for membrane modification
Polyvinylidene fluoride PVDF	TiO_2 [1–4] Al_2O_3 [5,6] ZrO_2 [7] SiO_2 [8–10] Fe/Pd [11] Carbone nanotube [12]	Blending with poly(styrenealtmaleic anhydride) (SMA) to fabricate surface hydrophilic PVDF membrane [3] The addition of hydrophilic polymethyl methacrylate (PMMA) improves the membrane pore size distribution and pore structure [5] Modification by chitosan solution for reducing protein fouling [13] poly(3,4-dihydroxy-l-phenylalanine) (DOPA) coating and heparin immobilization [14] Surface modification of microporous PVDF membranes by atom transfer radical polymerization (ATRP) [15]
Polysulfone PSf	TiO_2 [2,16–18] ZrO_2 [19] SiO_2 [20–22] Fe_3O_4 [23] Fe [24] Ag [25,26] C60 [27,28] Carbone nanotube [29–34] Zeolite [35] Clay [36]	Hydrophilic modification of microporous polysulfone membrane via surface-initiated atom transfer radical polymerization of acrylamide [37] Grafting with poly(ethylene glycol) for application as biomaterial coatings [38] Grafting with zwitterionic copolymer via UV-initiated polymerization for enhancing anti-fouling property of polysulfone [39]
Polyethersulfone PES	TiO_2 [40–49] Al_2O_3 [50] ZrO_2 [51]	UV photo-grafting of hydrophilic monomers for improving surface properties of nano-porous PES membranes [52] Surface irradiation with UV light (254 rmr) in the presence of N-vinyl-2-pyrrolidine (NVP), 2-acrylamidoglycolic acidmonohydrate (AAG) and 2-acrylamido-2-methyl- lpropanesulfonic acid (AAP) to improve PSf membrane filtration performance [53] Blending with polysulfone-based amphiphilic polymer polysulfone-graft-poly (ethylene glycol) methyl ether methacrylate (PSf-g-POEM) to tune the hydrophobicity and fouling-liable properties of PES membranes [52]
Polyamide PA	TiO_2 [55–58] Ag [59–61] Zeolite [62]	Surface modification of polyamide membranes by dendrimer-based coatings [63] Graft polymerization of 3allyl5, 5dimethylhydantoin on polyamide membrane to improve its chlorine resistance and anti-biofouling property [64] Grafting of poly(ethylene glycol) diglycidyl ether onto polyamide surface to enhance membrane fouling resistance [65] Radical grafting of methacrylic acid and polyethylene glycolmethacrylate [66] Electrostatic self-deposition of polycations (polyethylenimine) for improved fouling resistance of polyamide membrane [67]
Polyimide PI	TiO_2 [41,58,68,69] SiO_2 [70] Ag [71,72] MgO [73]	Vapor-phase ethylenediamine (EDA) treatment of polyimide surface for hydrogen purification [74] UV irradiation on polyimide dope solution for cross-linking and chemical gelation of casting solution for membrane controlled structures synthesis [75] Chemical cross-linking of 6FDA-durene onto polyimide membranes for thermal stability in gas separation [76]

(*Continued*)

Table 1 (*continued*)

Membrane material	Nanoparticle used for membrane modification	Other methods for membrane modification
Polyvinyl alcohol PVA	TiO_2 [77,78] ZrO_2 [79] SiO_2 [80–82] Carbone nanotube [32,83]	Modification of poly(vinyl alcohol) by copolymerization with carboxylic monomers [84] Novel approach to the chemical modification of poly(vinyl alcohol): phosphorylation [85] Modification of poly(vinyl alcohol) using maleic acid for application in the pervaporation [86]
Poly phenylene oxide PPO	SiO_2 [87] C60 [88,89]	Structural modification of polyphenyene oxide by oxidation curing [90] Benzoylation of polyphenylene oxide (PPO) with aromatic acid chlorides [91] Nitration and amination of polyphenylene oxide for improving membrane gas selectivity [92]
Polyether ether ketone PEEK	TiO_2 [93] ZrO_2 [93,94] SiO_2 [93] Clay [95]	Electron beam deposition of titanium on polyetheretherketone for enhanced biological properties [96] Surface functionalization of PEEK by covalent coupling and photografting [97] Modification of poly(etheretherketone) by ion irradiation [98]
Polyacrylonitrile PAN	TiO_2 [2]	Hydrophilic modification of polyacrylonitrile membranes by oxyfluorination [99] Surface modification of ultrafiltration membranes by low temperature plasma [100] Surface glycosylation of polyacrylonitrile to improve its anti-fouling performance [101]
Chitosan	ZnO [102]	Modification of chitosan by argon plasmas [103] Graft copolymerization of 2 hydroxyethylmethacrylate (HEMA) onto chitosan using 60Co-ray irradiation for controlled release of glucose [104] Surface modification by chondroitin sulfate (CS) for biomedical applications [105] Maleic anhydride surface-modification of cross-linked chitosan [106]
Polyphthalazine ether sulfone ketone PPESK	TiO_2 [107]	Coating with silicone rubber and with sol–gel polytrifluoropropylsiloxane for hydrophobic modification [108] PPESK-g-PEG graft copolymers blending into PPESK for hydrophilic modification [109] Surface-initiated atom transfer radical polymerization (ATRP) to graft hydrophilic polymer onto PPESK [110] surface immobilization of poly(ethylene glycol) acrylates for hydrophilic modification of PPESK [111]
Polyetherimide PEI	SiO_2 [112]	Coating with brominated poly(vinylpyrrolidone) (BrPVP) for hydrophilization of PEI [113] Modification of PEI with poly(butylene terephthalate) for rubber toughening [114] Surface modification of PEI with poly(ethylene glycol) for fouling lowering [115]
Cellulose acetate CA	Ag [116]	Modification of cellulose acetate membrane via low-pressure plasma polymerization [117] Blending of CA and hydrophobically modified methylcellulose [118] Incorporating of cellulose acetate membranes with poly (amide–imide) [119]

(*Continued*)

Table 1 (*continued*)

Membrane material	Nanoparticle used for membrane modification	Other methods for membrane modification
Vinyl ester VE	Al_2O_3 [120]	UV radiation modifications of vinyl ester network [121] Reinforcement of vinyl ester by glass fiber with nanotube integration [122] Toughening vinyl ester networks with polypropylene meso-fibers [123]
Polystyrene PS	TiO_2 [124] C60 [125]	Hydrophilic modification of polystyrene with hydrophobin for immobilizing antibodies [126] Ammonium surfactant modification for improving oil removal capability of polystyrene [127] Modification of polystyrene with a highly reactive cold oxygen plasma [128]
Poly 4-methyl-2-pentyne PMP	SiO_2 [129–131]	Surface modification of poly(4-methyl-2-pentyne) membrane by plasma treatment [132] PMP crosslinking by UV irradiation or thermal treatment for higher gas selectivities [133]
Polyphthalazinone ether ketone PPEK	SiO_2 [134,135]	Modification of poly(phthalazinone ether ketone) with inorganic particles for membrane fuel cell [136] Sulfonation of poly(phthalazinone ether ketone) membranes for direct methanol fuel cell [137]
Epoxy	SiO_2 [138]	Modification of epoxy resin system with different elastomers [139] Modification of commercial epoxy resin using cardanol-based phenolic resins [140] Thermal and radio-oxidation of epoxy coatings [141]
Polybenzimidizole PBI	SiO_2 [142]	Functionalization of polybenzimidizole membranes to change surface charge and hydrophilicity [143] Blending of PBI with inorganic oxides for improving membrane conuctivity [144]
PolyMethylMethAcrylate PMMA	AgCl [145]	Surface modification of PMMA by direct-current (DC) glow discharge and microwave plasma for the improvement of coating adhesion [146] Functionalization of PMMA thin films by 157 nm laser irradiation for sensing applications [147] Modification of the PMMA by UV-radiation [148]
Polydimethylsiloxane PDMS	Ag [149] C60 [150]	Plasma and chemical treatments for the formation of hydrophilic surfaces of PDMS [151] PDMS surface modification using atmospheric pressure plasma [152], UV-irradiation induced modification of PDMS [153]
Polyvinyl chloride PVC	Ag [154]	Modifications on PVC films by ultrasound [155] Selective surface modification of PVC in solvent–non-solvent mixtures [156]
Nafion	TiO_2 [157–161] Al_2O_3 [159,162] ZrO_2 [158,159,162,163–168]	Formation of self-polymerized dopamine nano-layer to enhance the methanol barrier property of Nafion membrane [182]
	$Zr(HPO_4)_2 \cdot H_2O$ [169,170]	Modification of Nafion membrane using interfacial polymerization [183]
	SiO_2 [158–160,162,166, 168,171–178] Ag [179,180] WO3 [160,161]	Chemical modification of Nafion membrane with *in situ* chemical polymerization of 3,4-ethylenedioxythiophene [184]
	Clay [181]	Modification of Nafion membranes with ternary composite material (polyvinyl alcohol (PVA), polyimide (PI), and 8-trimethoxysilylpropyl glycerin ether-1,3,6-pyrenetrisulfonic acid (TSPS)) [185]

Table 2
The intrinsic properties and structural effects of metal and metal oxide nanoparticles used for modification of polymer membranes

Nanoparticle	Property	Ref.
TiO_2	Photocatalyst, pollution removal ability, anti-fouling property, stability in harsh condition, good mechanical resistance, low cost	[1–4,16–18,40–49,55–58, 68,69,77,78, 93, 107,124,157–161]
Al_2O_3	Anti-fouling property, improvement of mechanical property of polymeric membranes, antibacterial activity	[5,6,50,120,159,162]
ZrO_2	Suitable for high-temperature catalytic reactions and oily wastewater filtration, high chemical stability	[7,19,51,79,93,94,158,159,162,163–168]
SiO_2	Improvement of chemical and mechanical stability, increasing conductivity and improvement of physicochemical stability of polymer films	[8–10,20–22,70,80–82,87,93,112,128–131,134,135,138,142,158–160,162,166,168,171–178]
Fe	Improvement of mechanical, electrical, and thermal properties and permeability behavior of polymers	[11,24]
Fe_3O_4	Magnetic improvement of thermal stability of polymers	[23]
Ag	Anti bacterial, disinfection ability, wastewater filtration ability, and anti-biofouling ability	[25,26,59–61,71,72,116,145,149,154]

In many studies [2,5,44,46,47,49,50], the hydrophilicity of nanoparticles was considered as the main reason for the reduction in the compatibility of the polymer with the solvent. According to this theory, the hydrophilicity of nanoparticles results in the tendency of the non-solvent (water) to the structure of the polymeric film, increases the penetration velocity of water into nascent membrane, speeds up the phase separation, and, finally, creates porous nanostructures.

In many other studies [1,6–8,20–23,26,43,87,88,111], nanoparticles are considered as inorganic compounds that reduce the need for non-solvent to complete the phase inversion process. As a result, the structures with high porosity and permeability are synthesized.

From a rheological (entropic) point of view, nanoparticles decrease the diffusion factor of the casting solution, reduce the rate of solvent and non-solvent exchange during the phase inversion, and, consequently, induce the delay of demixing and form a dense structure.

The reduction in the rate of exchange between solvent and non-solvent due to the presence of nanoparticles has been considered in many studies to be caused by an increase in the viscosity of the casting solution [4,43,67,106]. However, the effect of nanoparticles is studied as a factor to involve polymeric chains in other reports [9,24,40,115].

There exist thermodynamic enhancement and kinetic hindrance caused by nanoparticles at the same time. Thermodynamic enhancement is usually dominant at low concentrations of nanoparticles, and nanoparticles increase the rate of precipitation and create a porous structure. However, rheological hindrance increases as the concentration of nanoparticles increases, and dense structures with low permeability are formed. There is usually an exclusive threshold concentration for any specific casting solution (polymer/solvent/nanoparticle) which is calculated through nanoparticle concentration increment in casting solution in constant polymer and solvent concentration [5,10,18,27,46]. Thermodynamic enhancement is dominant at concentrations lower than the threshold, while rheological hindrance is dominant at higher concentrations than the threshold. This threshold was calculated 3 wt.% of nanoparticle for polyvinylidene fluoride (PVDF)/DMF(dimethylformamide)/dimethylacetamide (DMAC)/SiO_2 system by Lu et al. [10]. In their study, they showed that at concentrations lower than 3 wt.% of nanoparticle and due to the hydrophilicity of nanoparticles, an increase in the amount of nanoparticles enhances thermodynamic variation of the phase inversion process, promotes instantaneous demixing, creates finger-like pores, and increases porosity and permeability of the nanocomposite membrane. When the concentration of nanoparticles becomes higher than the threshold concentration, an increase in the amount of nanoparticle increases the viscosity of the casting solution and slows down the phase inversion process, elimination of finger-like pores and creation of a sponge-like structure, and reduction in porosity and permeability of the nanocomposite membrane. Moreover, the threshold concentration was reported to be 9.3 wt.%, 4 wt.%, 5 wt.%, 3 wt.%, and 2 wt.% for [PSf/DMAC/N-methyl-2-

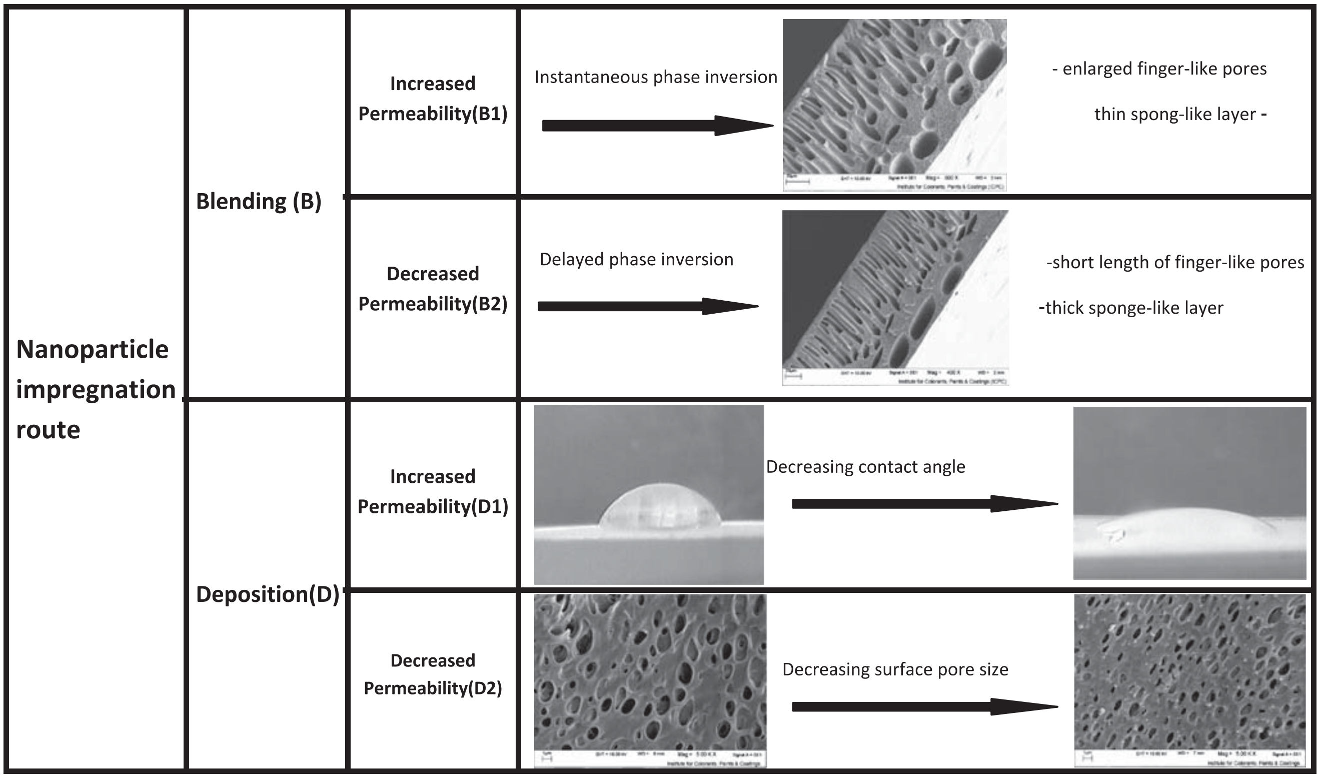

Fig. 1. Effect of the nanoparticle impregnation method on structure of polymeric nanocomposite membranes.

pyrrolidone (NMP)/TiO_2] [18], [Poly ether sulfones (PES)/DMAc/TiO_2] [46], [PSf/NMP/PVP/C60] [27], [PVDF/DMAC/DMF/SiO_2] [10], and [PVDF/DMAC/Al_2O_3] [5] systems, respectively.

3.2. Deposition of nanoparticles on the surface of polymeric membranes

The effect of stabilization of nanoparticles on the surface of the prepared polymeric membranes can be studied from two different points of view. Nanoparticles, on the one hand, increase the diffusion factor of the membrane for hydrophilic feeds by increasing the hydrophilicity and roughness and, on the other hand, they decrease the permeability and increase the selectivity of the nanocomposite membranes by reducing the membrane surface pore size.

Pre-synthesized or *in situ* synthesized nanoparticles are used in the fabrication of the nanocomposite membrane. Self-assembly of the coated layer has been reported in some cases [3,41–43,45,48,54,56,76]. Lee et al. [64] showed in a research that as the concentration of the colloidal solution of titanium dioxide increases, the flux of water decreases and the separation of magnesium sulfate increases due to the reduction in the pore size of the membrane surface. This process continues until the concentration of the colloidal solution of titanium dioxide reaches 5 wt.%. At concentrations above this critical concentration, hydrophilicity and roughness of the surface rise, and it results in an increase in the flux and a decrease in the separation of magnesium sulfate and mechanical resistance of the membrane. Therefore, such surface modification process may increase or decrease the permeability of the nanocomposite membrane. Reduction in the permeability is seemingly caused by the reduction in the pore size of the membrane surface according to many studies [2,11,45,55,58,59]. The increase in permeability may be caused by an increase in hydrophilicity or an increase in the roughness and contact area between the fluid and the membrane [3,40–43,48,54,56,58,76].

4. Effect of different nanoparticles on structure and performance of membrane nanocomposites

Here, the effect of different metal and metal oxide nanoparticles on membrane structure and liquid filtration performance have been reviewed (see Table 3). The TiO_2, Al_2O_3, ZrO_2, SiO_2, Fe and Ag-based nanoparticles have been used as additive in polymeric matrixes and the properties of fabricated

Table 3
Various nanoparticle impregnation routes for fabricating nanocomposite membranes

			MF	PVDF/TiO_2 [1], PES/TiO_2 [47], ZrO_2/PES [51]
	Blending (B)	B1	UF	PVDF/TiO_2 [1], PVDF/PSf/PAN/TiO_2 [2], PVDF/Al_2O_3 [5,6], PVDF/ZrO_2 [7], PVDF/SiO_2 [8,10], PSf/TiO_2 [16,18], PSf/ZrO_2 [19], SiO_2/PSf[21,22], PSf/Fe_3O_4 [23], PSf/Ag [25,26*], PES/TiO_2[44,48], PES/Al_2O_3 [50]
			NF	Not studied
			RO	Not studied
Nanoparticle		B2	MF	PVDF/SiO_2 [9], PES /TiO_2 [47]
			UF	PVDF/TiO_2 [4], PVDF/Al_2O_3 [5], PVDF/SiO_2 [10], PSf/TiO_2 [17,18], PES/TiO_2 [40], PPESK/TiO_2 [107], CA/Ag [116*],
			NF	PI /TiO_2 [68]
			RO	CA/Ag [116*]
Impragnation route	Deposition (D)	D1	MF	PES /TiO_2 [43**,46]
			UF	PVDF/TiO_2 [3], PES/TiO_2 [40**,42,49**]
			NF	PES/PI/TiO_2 [41**]
			RO	PA/TiO_2 [55**,57]
		D2	MF	PVDF/Fe/Pd [28*]
			UF	PVDF/PSf/PAN/TiO_2 [2], PES/TiO_2 [45**]
			NF	PA/TiO_2 [56], PA/Ag[59]
			RO	PA/Ag [60*]

B: Blending.B1: Increased permeability.B2: Decreased permeability.D: Deposition.D1: Increased permeability.D2: Decreased permeability.*In situ synthesized nanoparticle.**Self-assembled nanoparticle.RO: Reverse osmosis.MF: Microfiltration.UF: Ultrafiltration.NF: Nanofiltration.

nanocomposites have been reported. Besides this, other nanoparticles including magnesium-based [72,192] and zinc-based [101] nanoparticles were also synthesized and their application was studied in gas separation processes.

4.1. Effect of TiO_2

Numerous studies have been carried out in the presence of TiO_2 nanoparticles in various polymeric membranes. Titanium dioxide has received much attention due to its photocatalytic properties that cause chemical decomposition of organic materials and elimination of the bacteria [193,194] and its reducing effect on the membrane fouling. In addition to possessing photocatalytic and anti-bacterial characteristics, membranes that contain TiO_2 nanoparticles have self-cleaning properties. In addition to liquid phase separation [1–4,16–18,40–48,54–56,67,76,106,195] that is the main subject of this paper, nanocomposite membranes have applications in gas separation [57,68], ion exchange process and fuel cells [92,156–160], and pervaporation [77].

Titania nanoparticles enter the polymeric matrix through the two methods of dissolving in the casting solution or deposition on the surface. Rahimpour et al. [40] added titania nanoparticles to the structure of a nanocomposite membrane through the both methods of dissolving in the casting solution and deposition, and compared the properties of the obtained nanocomposite membranes in milk ultrafiltration. Results of the study showed that although the stability of nanoparticles that were dissolved in the structure of the nanocomposite membrane was longer than that of the deposited nanoparticles, deposition method was a more effective one for the modification of membrane surface. Deposited membranes had better anti-fouling properties and higher flux in comparison with membranes containing entrapped nanoparticles. The effect of the method to synthesize nanocomposite membranes on sludge filtration in membrane bioreactor (MBR) systems was studied in another research by Bae et al. [2]. Results of the study confirmed that the deposited membranes had a higher hydrophilicity, anti-fouling, and flux than the membranes synthesized through entrapment method. The results also confirmed the results obtained by Rahimpour et al. [40] that the deposition method was more successful than the entrapment method. Except for the two above-mentioned studies that compared the effect of various methods for the synthesis of nanocomposite membranes on the membranes performance, in most of the studies that have so far been carried out, titanium dioxide nanoparticles have been added to the structure of the nanocomposite membrane through one of the methods "entrapping in the polymeric bed" or "deposition on the surface."

4.1.1. *Blending of titanium dioxide nanoparticles with polymeric matrix*

Synthesis of nanocomposite membranes includes the addition of prepared titania nanoparticles to the casting solution before the phase inversion. Introduction of titania nanoparticles as an additive to the casting solution changes the rate of phase inversion process. In some cases, as the rate of phase inversion increases, the porosity and permeability increase too. In some other cases, however, the reduction in the rate of phase separation process results in the formation of dense structures with low permeability. As was discussed in the Introduction section, speeding up or slowing down the phase inversion process by nanoparticles depends on the threshold composition of the nanoparticle for every individual polymeric system. Although researchers have used in most of researches a specific composition of the casting solution and reported the behavior and properties of the nanocomposite membrane without calculating the threshold concentration of the nanoparticle, Li et al. [46] reported a threshold concentration of 4 wt.% for [PES/DMAc/TiO_2] system. They observed an increase in the membrane flux as the amount of nanoparticle increased up to 4 wt.%. At higher concentrations, because of rheological hindrance effect of nanoparticles, an increase in the amount of nanoparticle reduced the porosity and the flux of the membrane. The threshold concentration was reported to be 9.3 wt.% for [PSf/DMAC/NMP/TiO_2] system by Yang et al. [18]. According to the reports, the behavior of the nanocomposite membranes can be classified in the two zones of "concentrations lower than the threshold concentration" and "concentrations higher than the threshold concentration" although the threshold concentration was not calculated in any of the studies. Nanocomposite membranes synthesized at concentrations lower than the threshold concentration have a higher porosity that results in a higher permeability. However, the synthesis of membranes at concentrations higher than the threshold concentration forms denser membranes with lower permeability.

4.1.1.1. Adding titanium dioxide nanoparticles at concentrations lower than the threshold concentration to the casting solution. Effects of the presence and the size of TiO_2 nanoparticles on the performance of PVDF membrane were studied by Cao et al. [1]. Less than 2 wt.% of TiO_2 nanoparticles were used in the two forms of rutile (initial diameter of 26–30 nm) and anatase (initial diameter of 10 nm). Results obtained from filtration tests and other analyses showed that the nanometric size of particles affected the performance and structure of PVDF membranes. Moreover, nanoparticles in anatase phase have a greater effect on the increase in the hydrophilicity of the membrane surface. Prepared membranes also have a smaller pore average size, more pores, higher anti-fouling characteristic, and higher crystallinity. By increasing the hydrophilicity properties and by increasing the precipitation rate and creating a membrane with more porosity, these nanoparticles increase the flux, but do not have a significant effect on the separation of protein by the nanocomposite membrane.

In another study, Yang et al. [16] investigated the effect of TiO_2 as nanofiller on the morphology and properties of PSf ultrafiltration membrane. As was mentioned before, the threshold concentration had been already calculated as 9.3 wt.% for this very polymeric system by the group [18]. Therefore, the synthesis conditions in this study (2 wt.% of TiO_2 with particle size of 20–30 nm) were below the threshold concentration, and the obtained composite membranes had more pores in number, perfect permeability of water, and higher protein separation due to instantaneous phase separation. In addition, high hydrophilicity, high mechanical resistance, and desirable anti-fouling characteristic were reported for the nanocomposite membranes. Due to an increase in the surface hydrophilicity, the obtained nanocomposite membranes increased noticeably the rate and efficiency of the separation of oil in water emulsions. Higher concentrations of TiO_2 (more than 2 wt.%) result in the accumulation of nanoparticles and increase viscosity significantly. As a result, the efficiency of [PSf/TiO_2] membranes decreases.

Razmjou et al. [44] studied the effect of mechanical and chemical modification of TiO_2 nanoparticles on the surface, structure, and fouling performance of PES ultrafiltration membranes. They showed that the mechanical and chemical modification of nanoparticles resulted in an appropriate distribution, reduction in the size of particles from 380 nm to less than 100 nm, increase in glassy transition temperature, reduction in the free energy of surface, reduction in roughness, increase in the pores size of the surface, resistance against protein absorption, increase in the hydrophilicity of the surface, and higher anti-fouling characteristic. An increase in the length and widening of micro voids in the structure of the membrane were observed due to the use of nanoparticles at a concentration less than the threshold concentration. It indicates the occurrence of instantaneous phase separation mechanism that results in an increase in the porosity and flux of the membrane and in a small reduction in protein separation by the membrane.

The effect of TiO_2 nanoparticles on the morphology and performance of PES membranes was studied by Wu et al. [47]. They observed an increase in porosity and hydrophilicity of the surface, which consequently increased the flux of the obtained nanocomposite membranes. In addition, mechanical resistance, thermal decomposition temperature, and anti-fouling characteristic of the nanocomposite membranes increased too. It was also reported that the composite membrane showed the best possible performance by adding 0.5 wt.% of nanoparticle, while at higher concentrations, the membrane had a poorer performance due to nanoparticle accumulation.

4.1.1.2. Adding titanium dioxide nanoparticles at concentrations higher than the threshold concentration to the casting solution. Soroko et al. [67] studied the effect of TiO_2 nanoparticles on the morphology and performance of polyimide (PI) nanofiltration membranes. Results showed that an increase in the amount of nanoparticle increased the viscosity of the casting solution, increased the delayed phase separation, decreased the porosity of the nanocomposite membrane, decreased the flux, and increased the separation of ethanol. Among other characteristics of the said nanocomposite, mention can be made of an increase in the hydrophilicity and the tensile and thermal strength.

Li et al. [106] studied the characteristics of polyphthalazinone ether sulfone ketone (PPESK) ultrafiltration membrane containing entrapped TiO_2 nanoparticles. As TiO_2 nanoparticles are added to the casting solution, the viscosity of the casting solution increases. As a result, delayed phase separation occurs and it reduces the number of macro voids in the membrane, increases the thickness of the skin layer, and shortens the length of finger-like pores in the sub layer. Due to such structural changes, it is expected that the flux of the membrane decreases, but an increase in the flux and in the protein separation has been reported for this membrane. The increase in the membrane flux was explained by an increase in the hydrophilicity of the membrane surface in this research. The results also reported significant improvement in the mechanical and anti-fouling properties of [PPESK/TiO_2] ultrafiltration membranes.

The [PVDF/TiO_2] membrane was studied in order to modify the fouling resistant by Oh et al. [4]. The surface of the synthesized nanocomposite has a less roughness than that of the raw membrane. An increase in the viscosity of the casting solution and a delay in phase separation occur when nanoparticles are added to the solution, while the porosity and water permeability decrease.

In situ synthesis of titania nanoparticles in the casting solution was carried out by Yang et al. [17] before the phase inversion process. An increase in the viscosity of the casting solution due to the presence of nanoparticles and, consequently, a decrease in the rate of precipitation and the transformation of finger-like pores to sponge-like ones were reported in the research. The shrinkage of the polymeric network in the presence of nanoparticles creates tension and forms pores that cause an increase in the total porosity of the membrane. Therefore, the nanocomposite membranes have a higher permeability than the raw membranes. The sponge-like structure that is formed due to the specific type of the precipitation mechanism maintains the amount of protein separation efficiency. An increase in hydrophilicity and thermal and mechanical resistant was reported for the nanocomposite membranes.

4.1.2. Deposition of titanium nanoparticles on the surface of polymeric membranes

Deposition is one of the most common methods for the synthesis of nanocomposite membranes that contain nanoparticles [123,196]. This method includes immersing the prepared membrane in the colloidal solution of titanium oxide nanoparticles. Nanoparticles cover the membrane surface in the form of a thin layer. In some cases [3,41–43,45,48,54,56,76], the hydroxyl group that is connected to titania nanoparticles helps the self-assembly of titania nanoparticles on the membrane surface by reacting with the functional groups of the base membrane. The self-assembly of TiO_2 takes place in the structure of the polymer in two different ways. One way is the bond between TiO_2 and two oxygen atoms of the carboxylate group in the form of Ti^{4+} cation and the other way is the formation of a hydrogen bond between the carbonyl group and the surface of the hydroxyl group of TiO_2. In a research carried out by Lee et al. [55], titania nanoparticles were deposited on the polyamide (PA) membrane through an interfacial polymerization and by using a strong coordination or a hydrogen bond between the TiO_2 and the COOH group of polyamide. Results showed that as the concentration of titanium dioxide colloidal solution increases, the water flux decreases and magnesium sulfate separation increases due to a decrease in the pores size on the membrane surface. It continues until the concentration of titanium dioxide colloidal solution reaches 5 wt.%. At concentrations higher than this critical point, the hydrophilicity and roughness of the membrane surface increase, and it causes an increase in the flux and a decrease in magnesium sulfate separation and mechanical resistance of the surface. Therefore, two different behaviors for the nanocomposite membrane can be expected due to the deposition of titania nanoparticles on the membrane surface: "increase in the permeability of the nanocomposite membrane" due to the hydrophilicity of titania nanoparticles and an increase in the roughness of the membrane surface [3,40–43,48,54,56,76], and "decrease in the permeability of the membrane" due to the reduction in pores size of the membrane [2,45,55].

4.1.2.1. Deposited nanocomposite membrane with increased permeability. The self-assembly of TiO_2 nanoparticle in an aromatic polyamide thin film composite (TFC) membrane was studied by Kim et al. [54] in order to solve its biological fouling problem.

The TiO_2 nanoparticles, 10 nm or less in size, were synthesized in an anatase crystalline structure through controlled hydrolysis of titanium tetra-isopropoxide. Becoming able to terminate micro-organisms by the photocatalytic characteristic, the TFC membrane, formed by the self-assembled TiO_2 nanoparticles, was introduced as a novel object to reduce the biologic fouling of membranes. The presence of TiO_2 nanoparticles in the membrane surface also increased the hydrophilicity, and therefore, increased the flux and rejection of sodium chloride.

Li et al. [3] studied the self-assembly of TiO_2 nanoparticles (10 nm or less in size and with anatase crystalline structure) on the surface of SMA/PVDF membrane. Results showed that the self-assembly of TiO_2 nanoparticles reduces the contact angle and gives a perfect hydrophilicity to the nanocomposite membrane. Among other characteristics of the synthesized nanocomposite membranes, mention can be made of an increase in hydrophilicity and flux and a decrease in protein separation and resistance against biological fouling.

The formation of appropriate sites for the arrangement of the photocatalytic TiO_2 nanoparticles on the surface of nanofiltration membrane was studied by Mansourpanah et al. [41], and its effects on the performance and resistance of the membranes against fouling were analyzed. The TiO_2 nanoparticles (25 nm in size) were placed on two different groups of membranes: (1) PES/PI non-modified composite membrane and (2) PES/PI composite membrane modified with OH functional group by various concentrations of diethanol amine (DEA). The non-modified membrane displayed a relatively homogenous and smooth surface with high porosity. The presence of titania nanoparticles on its surface increases the flux due to an increase in the hydrophilicity of the surface, while it does not change the separation of the salt solution. The modification of surface with DEA created a dense surface with low porosity, and it formed some indention in the surface. Therefore, a considerable increase was observed in the salt rejection. The surface of the membrane modified with DEA provides a suitable surface for the self-assembly of titania nanoparticles. The photocatalytic characteristic of nanoparticles, decomposition of organic materials by the membrane, and the remaining of the leftovers from the decomposition of organic materials in the voids cause the flux and the salt separation not to vary, while those nanocomposite membranes successfully prevented the fouling.

The hydrophilicity modification of the surface of PES ultrafiltration membrane by using the self-assembly of TiO_2 nanoparticles on the membrane surface was studied by Luo et al. [42]. The TiO_2 nanoparticles (5–42 nm in size) were synthesized with an anatase crystalline structure. Results showed that the composite membrane had acceptable separation efficiency, and it could be used as an anti-fouling membrane. As the concentration of nanoparticles increased, the hydrophilicity, flux, and polyethylene glycol rejection increased, while the membrane fouling decreased.

The self-assembly of TiO_2 nanoparticles (4–7 nm in size) and the anti-fouling behavior of polyether sulfone nanocomposite membranes in a membrane bioreactor system were studied by Bae et al. [43]. The sulfonation of polyether sulfone was used in the research to help the self-assembly of titania nanoparticles on the membrane surface. As long as the addition of nanoparticles increases the hydrophilicity of the surface of the polymeric membrane, the resistance against the formation of cake layer decreases considerably and, consequently, the amount and rate of fouling in the nanocomposite membranes decrease as well.

Madaeni et al. [76] determined the self-cleaning properties of the reverse osmosis TFC membranes coated by TiO_2 under UV radiation. The self-assembly of titania nanoparticles took place via the interaction between the hydroxyl group in the polyvinyl alcohol layer and the hydroxyl group of nanoparticle. Results showed that the presence of nanoparticles increased the hydrophilicity of the surface, and the UV radiation modified the photocatalytic characteristic of the membrane. Hydrophilicity and photocatalytic properties aggravate each other and give self-cleaning ability to the membrane. The flux of the coated membrane is higher than that of the untouched membrane because of the hydrophilicity, roughness, and photocatalytic properties of the nanocomposite membrane. When SiO_2 nanoparticles are added to TiO_2 in the coating of the membrane, the acidity of the surface increases, and it results in an increase in ultra-hydrophilicity, photocatalytic, and self-cleaning characteristics of the membrane.

Luo et al. [48] reported self-assembly of titania nanoparticles through the interactions between the hydroxyl group of nanoparticles and ether and the sulfone groups of the polyether sulfone membrane. Adding nanoparticles to the membrane surface increased the hydrophilicity and the roughness of the membrane surface. As a result, the permeability of the membrane increased. Moreover, a decrease in the fouling and an increase in the polyethylene glycol separation for the nanocomposite membrane were reported as well.

The self-assembly of titania nanoparticles on the surface of polyamide membrane via the hydroxyl groups on their surface was studied too [56]. An increase in hydrophilicity and permeability was observed in the nanocomposite membranes, while the amount of chloride sodium separation remained constant. In addition, an anti-bacterial characteristic, that is a result of the photocatalytic properties of titania nanoparticles, was observed in the study as well.

4.1.2.2. Deposited nanocomposite membrane with reduced permeability. The effect of the deposition of titanium dioxide nanoparticles on the three PSf, PVDF, and AN membranes was studied [2]. The presence of titania nanoparticles on the surface and the void walls of the membrane reduces the flux, but increases polyethylene oxide separation by the nanocomposite membranes. It also resulted in an increase in hydrophilicity of the nanocomposite membrane and a decrease in the fouling of the membrane in MBR systems.

Bae et al. [45] prepared fouling-resistant nanocomposite membranes by using the electrostatic self-assembly between TiO_2 nanoparticles and sulfonic acid groups on the membrane surface. Results showed that the deposition of titania nanoparticles on the membrane surface reduced the pores size on the surface. As a result, the flux decreased but polyethylene oxide separation by the nanocomposite membrane increased. In addition, an increase in hydrophilicity of the membrane surface was reported as an effective factor on the modification of anti-fouling characteristic of the nanocomposite membrane in MBR systems.

Taking into account the above-mentioned studies, which have been briefly listed in Table 3, it can be concluded that in addition to giving their own antibacterial characteristic to the synthesized nanocomposite membranes, TiO_2 nanoparticles create polymeric films with modified mechanical, thermal, and crystalline properties, and they facilitate the filtration operation by increasing the hydrophilicity and by decreasing the fouling due to hydrophilicity.

4.2. *Effect of Al*

The Al_2O_3 nanoparticles are usually used in the synthesis of the nanocomposite membrane due to their desirable anti-fouling and mechanical properties. The obtained nanocomposite membranes have many applications in ion-exchange membranes and fuel cells [158,161] and liquid separation [5,6,49]. Alumina nanoparticles were added to the casting solution in all researches that have been carried out so far, and then the nanocomposite membrane was synthesized via the phase inversion process. The presence of alumina nanoparticles changes the phase inversion process and affects the structure and performance of the obtained nanocomposite membrane. Similar to what was observed in titania nanoparticles, there is a threshold concentration for alumina nanoparticles. At concentrations of alumina nanoparticles less than the threshold concentration, a membrane with more porosity and permeability is formed, while the use of nanoparticles at concentrations higher than the threshold concentration results in the formation of a denser membrane with lower permeability.

The effect of Al_2O_3 nanoparticles (10 nm in size) on the efficiency of PVDF ultrafiltration membrane was studied by Yan et al. [5]. According to their study, the threshold concentration is 2 wt.% for [PVDF/DMAC/Al_2O_3] system. As the concentration of Al_2O_3 nanoparticles increases up to 2 wt.%, an increase in hydrophilicity, water flux, anti-fouling behavior, tensile strength, and elongation at the break point is observed. However, when the concentration of nanoparticles becomes higher than the threshold concentration, a reverse effect happens.

Maximous et al. [49] investigated the performance of polyether sulfone (PES) ultrafiltration membrane with entrapped 48-nm Al_2O_3 nanoparticles in the filtration of the active sludge. They found out that the use of Al_2O_3 nanoparticles increases the rate of the phase inversion process due to its high hydrophilicity, and consequently, it forms a membrane with high pore size, porosity, and permeability. The surface of the entrapped membrane Al_2O_3 is more hydrophilic than that of the pure polymeric membrane. Therefore, the hydrophobic adsorption between the sludge particles and the entrapped membrane Al_2O_3 decreases, and the fouling is less in the nanocomposite membranes than that in the pure PES membrane. Taking into consideration the fact that nanoparticles were used at a concentration range of [$PES/Al_2O_3 = 0.01$–0.05], it is predicted that this concentration range is less than the threshold concentration for this very polymeric system. Therefore, an increase in porosity and permeability was reported for the nanocomposite membrane. The best behavior of the membrane was reported at [$PES/Al_2O_3 = 0.05$].

The effect of the presence of alumina nanoparticles on the performance of PVDF ultrafiltration membrane in the purification of wastewater polluted with petroleum wastage was studied by Yan et al. [6]. They observed an increase in hydrophilicity and anti-fouling properties of the nanocomposite membrane as well as an increase in the permeability, while the separation percentage of the membrane remained constant when nanoparticles were added at a concentration range of 0–4 wt.%.

Generally speaking, the presence of Al_2O_3 nanoparticles increases the water flux and modifies the permeability and anti-fouling characteristic of the membrane due to an increase in the pore size, porosity, and hydrophilicity. It also augments the mechanical and thermal resistance of the synthesized nanocomposite membranes.

As was mentioned before, polymer/alumina nanocomposite membranes have so far been synthesized by adding nanoparticle to the casting solution [5,6,49]. Therefore, the deposition or self-assembly of alumina nanoparticles through immersing the pre-prepared polymeric membrane in a colloidal solution of alumina nanoparticles is proposed as an approach for future investigations.

4.3. *Effect of Zr*

The ZrO_2 nanoparticle is a common catalyst with high potential for high-temperature catalytic reactions, and it is used in order to increase the membrane permeability. The ZrO_2 nanoparticles have a higher chemical stability than Al_2O_3 and TiO_2 nanoparticles, so they are more suitable for liquid phase applications in harsh conditions. Moreover, the toxicity of ZrO_2 nanoparticles is higher than that of the TiO_2 nanoparticles [50]. In addition to their application in liquid separation [7,19,50,162], nanocomposite membranes made of ZrO_2 nanoparticles are also used for the improvement in the performance of fuel cells [92,157,158,161,163–169] because they increase the conductivity of the nanocomposite membrane [78].

A common method including the addition of titania nanoparticles to the casting solution before the phase inversion operation has so far been used in order to synthesize polymer/zirconia nanocomposite membranes. Maximous et al.[50] studied the performance of [PES/ZrO_2] nanocomposite membrane in the filtration of wastewater in MBR systems. As the concentration of [PES/ZrO_2] increases, water diffuses into the casting solution faster due to the hydrophilicity of zirconia nanoparticles. Therefore, a porous structure is formed due to instantaneous phase inversion. As the concentration of [PES/ZrO_2] increases, the density of particles, the viscosity of the casting solution, thickness, resistance against fouling, and the permeability of the membrane increase, while the molecular weight cut-off (MWCO) does not change. Such increase continues up to [PES/ZrO_2]=0.05. When the concentration of [PES/ZrO_2] goes higher than 0.05, a meaningful decrease is observed in the porosity and permeability of the membrane. In fact, passing the threshold concentration changes the phase inversion mechanism from instantaneous to the delayed. Therefore, a denser structure with lower permeability is formed.

Bottino et al. [7] studied the specifications of the porous [$PVDF$-ZrO_2] composite membrane and the effect of the presence and composition of $PVDF/ZrO_2$ in the membrane. An increase in the concentration of ZrO_2 resulted in an increase in porosity and flux and in a decrease in protein rejection of the membrane due to the weak interactions between the polymer and the nanoparticles.

In another study, the effect of the presence of zirconia nanoparticles on the polysulfone matrix was studied by Genne et al. [19]. An increase in the total porosity of the membrane and, consequently, an increase in the permeability and a decrease in protein separation by the membrane were observed in the study. Considering the above-mentioned studies, it can be concluded that the ZrO_2 nanoparticles increase the resistance, anti-fouling characteristic, flux, and the permeability of the membrane, but they decrease rejection of the membrane. They also create a catalytic membrane that is resistant against heat and mechanical tensions.

The calculation of the threshold concentration for various polymeric systems is proposed for future investigations in order to determine the best nanocomposite membrane with optimized properties and also to synthesize polymer/zirconia nanocomposite membranes through deposition or self-assembly on the membrane surface method.

4.4. Effect of Si

The SiO_2 nanoparticles are conductive. Therefore, nanocomposite membranes made of such particles can be used in separation systems with electrical driving force. In addition to conductivity, silica nanoparticles have thermal and chemical stability and electrostatic characteristic. They are also compatible with biological molecules [177]. The presence of silica nanoparticles improves the application of polymeric membranes in various fields such as pervaporation [79,86,128], ion exchanging and fuel cell membranes [9,69,80,92, 133,134,141,157–159,161,165,167,170–177], gas separation [20,81,111,128–130,137,197], and liquid separation [8–10,21,22].

Nanocomposite membranes made of silica nanoparticles were synthesized in various polymeric matrixes by dissolving nanoparticles in the casting solution before the phase inversion operation [8–10,21,22]. Except in the study carried out by Lu et al. [10] in which the threshold concentration was calculated for the polymeric system, the silica nanoparticles were added to the casting solution at higher [9] or lower [8,21,22] concentrations than the threshold concentration in other researches. Lu et al. used *in situ* synthesis of silica nanoparticles in the casting solution. According to their calculation, the threshold concentration for [PVDF/DMF/DMAC/SiO_2] system was 3 wt. %. Results showed that due to the hydrophilicity of the nanoparticles, at concentrations lower than 3 wt.%, an increase in the concentration of nanoparticles enhances the thermodynamic variation of the phase inversion phenomenon. Thermodynamic variation works in favor of the enhancement of demixing in the casting solution, so it speeded up the phase separation, created finger-like pores, and increased the porosity and permeability of the nanocomposite membrane. At concentrations higher than the threshold concentration, with the kinetic hindrance offsetting the thermodynamic effect for phase separation enhancement, demixing of the cast solution was delayed, terminated the finger-like pores and created sponge-like ones, and decreased the porosity and the permeability of the nanocomposite membrane. It was also observed that an increase in the concentration of nanoparticles up to 3 wt.% improved the mechanical and thermal properties, while a decrease in the mechanical and thermal properties was reported at higher concentrations.

Bottino et al. [8] investigated the characteristics of the porous nanocomposite membranes with a homogenous distribution of SiO_2 nanoparticles in the structure of PVDF. Results showed that the thermal properties of [PVDF/SiO_2] nanocomposite membranes are very similar to those of PVDF membranes, while they have less mechanical resistance. Adding SiO_2 nanoparticles to the thin solution of PVDF increased the flux and decreased the rejection, while no effect on the performance of the membrane was observed by adding SiO_2 nanoparticles to the thick solution of PVDF.

Ahmad et al. [21] functionalized the [PSf/SiO_2] nanocomposite membrane for the separation of oil from water. Results showed that the presence of nanoparticles increased the pore size, created interconnected pores, and increased the porosity, permeability, and the anti-fouling characteristic of the nanocomposite membrane.

Zhang et al. [22] studied the preparation and characterization of polysulfone (PSf) nanocomposite membrane containing SiO_2 nanoparticles (Ce-doped). As the concentration of nanoparticles increased, an increase in the tensile strength and reduction in the contact angle and resistance against the fouling of the nanocomposite membrane was observed. The synthesized nanocomposite membranes also displayed a significant increase in the flux and efficiency of the separation of wastewater polluted by petroleum wastage.

The SiO_2 nanoparticles have general effects on the thermal stability, modification of mechanical properties, increasing the hydrophilicity and conductivity of the membrane, increasing gas permeability, and decreasing the rejection of the membrane. It is suggested that other methods for the synthesis of nanocomposite membranes, such as *in situ* synthesis of nanoparticles in the casting solution and deposition or self-assembly of silica nanoparticles on the polymeric bed, are used in the future investigations.

4.5. Effect of Fe

Iron-based nanoparticles possess magnetic and catalytic properties, but they are not used in pure form due to their high activity. Due to their paramagnetic properties, the Fe_3O_4 nanoparticles are used in magnetic solutions, magnetic memories, magnetic polymeric microspheres, and so forth. When nanoparticles are placed in a magnetic field, they move alongside the magnetic force line and when the field is removed, they can rapidly go back to their initial place. Likewise, metallic particles and iron nanoparticles control the permeability of the nanocomposite membrane by filling the space between polymeric chains. Iron-based nanoparticles have been also used in ion-exchanging membranes with applications in fuel cells [198] and also in liquid phase separation [11,23].

Xu et al. [11] studied the stabilization of [Pd/Fe] nanoparticles in the voids of PAA/PVDF microfiltration membrane. In their study, the [Pd/Fe] nanoparticles were synthesized through *in situ* method by using carboxylic acid groups of polyacrylic acid deposited on the surface of PVDF membrane. Catalytic dechlorination of toxic organic materials is one of the important applications of membranes containing metallic nanoparticles. They showed that the presence of iron nanoparticles reduces the porosity and flux, but increases the separation factor. Moreover, it increases the thermal resistance of the nanocomposite membranes.

Jian et al. [23] studied [PSf-Fe_3O_4] composite ultrafiltration membrane and its behavior in a magnetic field by determining the lysosome rejection. The [PSf-Fe_3O_4] nanocomposite membrane was prepared by using phase inversion method and by adding 8–12 nm Fe_3O_4] nanoparticles to the casting solution. The surface of the particles was bonded with oleic acid in order to modify the dispersion of iron oxide nanoparticles in the membrane structure. The presence of nanoparticles reduced glass transition temperature, increased thermal stability, decreased hydrophilicity (due to the oleic acid coating on nanoparticles), and increased the porosity of nanocomposite membranes. When nanocomposite membrane is exposed to magnetic field, Fe_3O_4 nanoparticles may change the skin layer and the void structure. Therefore, the diffusion of soluble materials into [PSf-Fe_3O_4] composite membrane can be very easy or difficult. According to the results, the magnetic field does not have a significant effect on the pure water flux of the composite membrane, but the lysosome rejection of the composite membrane decreases in a magnetic field.

Magnetic Fe_3O_4 nanoparticles have general effects of reduction in glass transition temperature, modification of thermal and mechanical stability, and increase in porosity and permeability of the membrane.

The specific characteristic of nanocomposite membranes containing iron oxide magnetic nanoparticles enables them to act as a valuable tool in filtration operations in which a magnetic field is used as the driving force. Selective separation of various materials can be carried out by such membranes due to the possibility of creating reversible changes in the microstructure of the membranes. Iron nanoparticles can be used in various applications in catalytic membrane reactors due to their catalytic characteristic. Generally speaking, iron-based nanoparticles can be used in ion-exchanging membranes, and many researches can be carried out on the synthesis of nanocomposites based on iron nanoparticles, no matter what their application is.

4.6. Effect of Ag

Taking into account their specific physical and chemical properties, the Ag nanoparticles have many applications in the fields of electronics, optics, medicine, hygiene, and catalysts. The Ag nanoparticles have anti-bacterial characteristic and they are also used for disinfection purposes [59,199–208]. Nanocomposite membranes containing silver nanoparticles are used as adsorbent [144], and have applications in gas separation [71,148,153,207,208], ion-exchanging membranes [178,179], and liquid separation [25,26,58,59,70,115,209]. Silver nanoparticles enter the structure of the polymeric membrane through the two methods of dissolving in the casting solution [25,26,115] or deposition on the surface [58,59,70].

Zodrow et al. [25] studied the effect of the presence of silver nanoparticles on the increase in biofouling resistance and the elimination of viruses by PSf ultrafiltration membrane. Nanoparticles entered the membrane structure after being dissolved in the casting solution, and they caused an increase in hydrophilicity, a decrease in fouling, and an elimination of the bacteria and separation of viruses. Results also showed a small increase in the permeability of the nanocomposite membrane.

By using a similar method, silver nanoparticles were used in order to synthesize [PSf/Ag] nanocomposite membrane after they were dissolved in polysulfone casting solution [26]. In the research, silver nanoparticles were either prepared or produced through *in situ* reduction of silver ions within casting solution during the phase inversion process. Results showed that the arrangement of *in situ* synthesized nanoparticles caused the obtained nanocomposite membrane to have a higher protein separation and anti-fouling characteristic than membranes containing individually synthesized nanoparticles.

In another study carried out by Chou et al. [115], cellulose acetate/silver nanoparticle hollow fiber membrane was synthesized for water purification. In situ synthesis of nanoparticles took place in the casting solution, and the obtained nanocomposite hollow fibers had a semi sponge-like structure and dense outer and inner surfaces. The reason was the happening of delayed phase separation due to the use of silver nanoparticles at a concentration higher than the threshold concentration. Nanocomposite membranes have less tensile strength, elongation, and thickness, but they possess more permeability and anti-bacterial activity.

Lee et al. [58] synthesized nanocomposite membranes through interfacial polymerization that resulted in the deposition of silver nanoparticles and polyamide layer on the surface of PES membrane. Due to a decrease in the pore size of the membrane, the presence of Ag nanoparticles resulted in a small decrease in the flux and a small increase in the rejection of magnesium sulfate. Moreover, an improvement in the biological anti-fouling characteristic of the nanocomposite membrane was reported too.

In another research, Yang et al. [59] studied the modification of the surface of reverse osmosis membrane with the Ag nanoparticles in order to reduce biological fouling in seawater desalination. In situ synthesis of spherical Ag nanoparticles with diameter of approximately 100 nm was carried out on the membrane surface through chemical reduction method. Results showed that the nanocomposite membranes had less flux but more separation due to the smaller pore size on their surface. In addition, they did not make the duration of biological fouling longer but also decreased the fouling as well.

Silver nanoparticles were synthesized through *in situ* method on the surface of PI membrane by Deng et al. [70] Results showed that most of nanoparticles settled on the walls of the membrane pores. Taking into account the more distribution of the pores in the lower part of the membrane and more nanoparticles settled on this part. The filtration behavior of nanocomposite membranes was not studied in this research.

Results of the studies show that the Ag nanoparticles generally result in a reduction in flux, an increase in rejection and anti-bacterial activity, and an increase in the thermal and mechanical resistance of the membrane.

5. Conclusion

Various methods have so far been developed to change the structure and improve the performance of polymeric membranes, among which structural modification with nanoparticles is one of the novel ones. This method has been used on some polymers, such as PSf, PES, PA, PI, PAN, PVDF, and CS, in the recent years. Nanoparticles are able to give some properties such as electrical conductivity (SiO_2), and magnetic (Fe_3O_4), catalytic (ZrO_2 and Fe), and anti-bacterial (Ag, ZnO, and TiO_2) properties to membrane structures that do not possess such properties in the absence of nanoparticles. The entrance of nanoparticles to the structure of nanocomposite membrane can result in the modification of physical properties such as mechanical and thermal resistance, hydrophilicity, and crystallinity of nanocomposite films. Moreover, the presence of nanoparticles in membrane structure changes the synthesis process, porosity, and size and form of the membrane pores, and it results in changes in operational parameters such as permeability, rejection, and fouling. Apart from all mentioned parameters, structural and functional specifications of nanocomposite membranes depend on the amount (more or less than the threshold concentration) and on how (entrapment or deposition) the nanoparticles are added to the polymeric matrix. Variety of membrane polymers, the need for specific separations in various industries, structures and various types of nanoparticles, and the methods for the synthesis of nanocomposite membranes introduce this field of study as an open path for future investigations.

Generally speaking, there are numerous unknown subjects to be investigated in future, such as comparing the efficiency of the modification of one characteristic by using a specific nanoparticles with other modification methods, combining other modification methods with the present method in order to increase the efficiency of optimization process, investigating the simultaneous use of both nanoparticles in a polymeric matrix, using two different nanoparticles simultaneously in order to take advantage of the properties of both structures in the modification process, studying the properties of nanocomposite membranes with special porous structure for specific separations such as separation of biological materials or metallic complexes, using nanoparticles such as quantum dots and studying the specific characteristics and performance of the obtained nanocomposite film in ultrafiltration, using the properties reported in previous studies in order to improve the efficiency of filtration process, and technical and economical evaluation of the use of this method for industrial applications.

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