



The permeation and Separation Characteristics of Polymeric Membranes Incorporated with Nanoparticles for Dye Removal and Interaction Mechanisms between Polymer and Nanoparticles: A Mini Review

Dalya D. Al-Araji^a, Faris H. Al-Ani^a , Qusay F. Alsalhy^b *

^a Civil Engineering Dept., University of Technology-Iraq, Alsina'a street, 10066 Baghdad, Iraq.

^b Chemical Engineering Dept., University of Technology-Iraq, Alsina'a street, 10066 Baghdad, Iraq.

*Corresponding author Email: qusay_alsalhy@yahoo.com

HIGHLIGHTS

- The importance of two types of Nanocomposite membrane in dye effluent treatment is reviewed
- Nanocomposite Membranes have: high dye effluent separation efficiency, anti-fouling, and stability
- The importance of the interaction mechanism between polymeric materials and nanoparticles is presented
- The influence of incorporated nanoparticles on long-term performance and stability is discussed.

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ABSTRACT

Dyes are an essential group of organic pollutants with a long history of harming aquatic life and humans. Prior to disposal, polluted dye wastewater must be adequately treated to prevent adverse impacts on persons and the environment. Although there are several techniques for dye removal, most of them share a similar drawback: they generate secondary pollution to the environment. Membrane separation is highlighted in this article because it is one of the most efficient dye removal techniques available nowadays due to its high removal capacity, ease of operation, and clean water generation. Polymeric membranes are frequently used in membrane-based separations because of their greater flexibility, ease of pore formation process, and lower cost than other membrane materials. Although polymeric membranes are preferable materials for membrane production, they are usually hydrophobic and, hence, sensitive to fouling. Therefore, much research has been done to modify the polymeric membrane. More recently, metal nanoparticles (NPs) have been introduced to the polymer matrix to minimize fouling potential and enhance membrane performance. This study describes several polymeric membranes utilized in dye separation that have been modified using nanomaterial. Also, the study illustrates how adding these components affects the membranes' performance in rejecting the dye. Additionally, it highlights the importance of membrane-nanomaterial interactions and the effect of these materials' additions on membrane performance over time.

1. Introduction

The scarcity of clean water supplies due to increased pollution from industrial pollutants has recently attracted the interest of both society and scholars. Organic dyes, which are frequently seen in a variety of industrial sectors, including textiles, medicines, leather, paper, food, printing, and cosmetics, are complex pollutant that affects living beings due to their non-biodegradability toxicity and carcinogenic effects. Dyes in water, even at extremely low concentrations (0.005 ppm), are harmful to humans and can prevent sunlight from entering the water through absorption/reflection, interacting with the development of biological activity in a body of water [1]. As a result, the scientific community, industry, and government organizations worldwide have focused on finding and developing effective treatment solutions for wastewater polluted with dyes [2]. Several techniques for removing dyes from effluents have been studied, including adsorption [3], coagulation/flocculation [4], and chemical [5] or biological degradation [6]. The researchers mentioned that each of these techniques had distinct advantages and downsides. For instance, the adsorption process is frequently quite efficient, owing to its flexibility. Coagulation and flocculation are also touted as effective procedures in the literature. However, due to the necessity to perform a later treatment of the hazardous sludge, these methods cannot be used on a large scale industrially due to their high secondary product generation rates [7].

Because of its high separation characteristics, ease of setup and operation, as well as cost-benefits, reusability, and long-term filtering characteristics, membrane filtration technology has drawn a lot of attention from the different physical and chemical removal–separation techniques [8]. One of the most difficult aspects of membrane processes is dealing with the retentate (reject) stream. Several membrane separation techniques are available and reject handling may vary based on the process and the goal feed stream. For example, surface water (such as Lake water) is used as feed for UF or MF system. In this case, the reject stream is usually sent to a municipal wastewater treatment plant for biological treatment and safe discharge into the environment [9]. In the case of dye concentrate streams, some of the sludge is disposed of in an artificial landfill. The concentrated colorant might alternatively be converted into a useful product, such as compost or brick. Furthermore, electrodeposition is one of the most popular industrial uses of membrane technology (UF membrane). It is appropriate for the recovery of electroplating and the reduction of substantial paint losses [10]. Despite the growing number of membrane filtration applications, these processes are impacted by a reduction in flux caused by membrane fouling. Membrane fouling results from complex physical and chemical interactions among fouling constituents in the feed and the membrane surface during the filtration process [11, 12]. These interactions can raise energy consumption and negatively influence the process because they raise operating costs, reduce permeated production, and shorten the membrane service period [13]. Membrane cleaning using chemicals may reduce fouling's detrimental impact on the environment. However, this might lead to deterioration of the membrane material, which would reduce the membrane's lifespan [14].

As a novel category of membrane materials, nanocomposite membranes composing inorganic nanomaterials (NPs) and organic polymers have attracted a wide research area for treating versatile wastewater effluents [15]. Several findings reported that surface modification of membranes using nanomaterials might be a potential approach for improving dye removal while also making membranes more fouling resistant [16]. This type of membrane could bestow nanomaterial's impressive characteristics presented by their large surface area to volume proportion into the targeted application. Wide range of inorganic nanostructures have been utilized for this purpose, including Zinc oxide (ZnO) [17-19], silica (SiO₂) [20, 21], alumina (Al₂O₃) [22-24], graphene oxide (GO) [7, 25-27], iron oxide (Fe₂O₃) [28], carbon nanomaterials (CNMs) [29-31], and titanium oxide (TiO₂) [32-34].

The main objective of this study is to review studies in which nanoparticles (NPs) were used as inorganic additions to increase permeation and separation characteristics of the membrane in removing various dyes from wastewater based on the percentage of dye removal. The review discusses several modification techniques for adding these compounds to membranes. Furthermore, the degree of success obtained by the nanoparticles (NPs) when added to the films will be disclosed to obtain a substantial reduction in the different dyes contained in the wastewater. Additionally, the review explains the critical role of membrane-nanomaterial interactions and the influence of these materials' additions on the long-term stability of membrane performance.

2. Nanocomposite Membranes For Dye Removal

2.1 Mixed Matrix Membranes

2.1.1 Mixed matrix membranes (embedded single nanomaterial)

Much earlier research has been conducted on modified polymeric membranes containing nanoparticles (NPs). As shown in Figure 1, the number of these studies has risen dramatically in the last five years, particularly in the field of dye-containing water treatment. As a result, we focused our research on this topic because of its importance on the performance of the modified membranes for different applications.

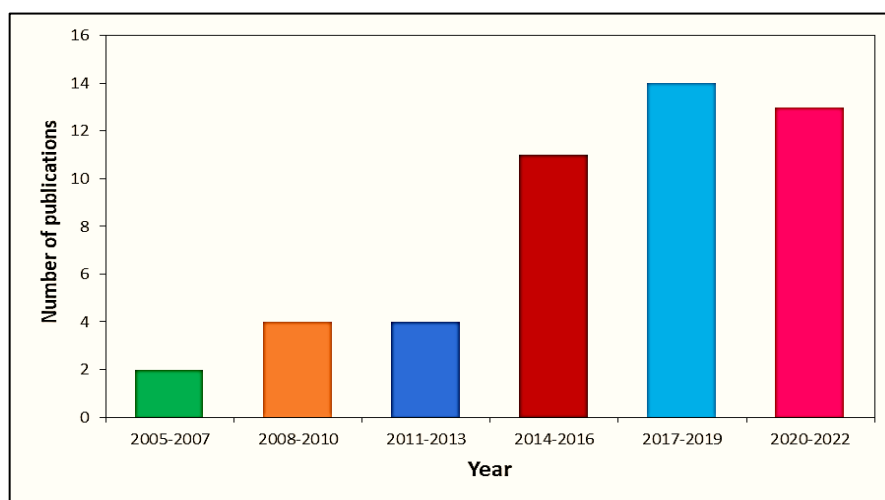


Figure 1: Published research article about dye-containing water treatment using modified polymeric membranes containing nanoparticles (NPs) within 2005-2022

For example, Krishnamoorthy and Sagadevan used iron oxide nanoparticles (FeON) as additives. The phase inversion approach was used to create a variety of polyethersulfone (PES) UF asymmetric membranes mixed with polyethylene glycol and

iron oxide nanoparticles (FeON). The sample molecules Orange II and Congo red were utilized for the rejection experiments. For the pure PES membrane, the Congo red dye rejection rate was 93.2 %, whereas for the 3 wt. % FeON composite membrane, it was 92.5 %. However, it was shown that the rejection rate fell significantly from 92.5 % to 89.8 % when the FeON concentration was increased from 3 to 4 %. Rejection of Orange II also yielded similar results. This decrease occurred because the membrane prepared with more than 3 wt% of FeON has a bigger pore size; therefore, a drop in rejection of dye was observed. Furthermore, the high permeation flux of the membranes resulted in the passage of more dye molecules across the membrane, resulting in fewer dye rejections [35].

Tavangar et al. used CeO₂ nanoparticles (NPs) as additives. Using a non-solvent induced phase separation method, loose nanofiltration nanocomposite membranes of poly(ether sulfone) (PES) were created by adding cerium oxide (CeO₂) nanoparticles (NPs). It was determined whether or not the dye particles were efficiently rejected by pristine and nanocomposite membranes by testing three colors utilizing single component dye solutions (Congo red, Direct red 23, and Direct red 243). Permeation flow and dye rejection are directly related to CeO₂ present. Fluxes of 19.1 and 105.2 L/m² h and rejections of 98.43 % and 99.36 % for Congo red dye are reported for Pristine and CeO₂ membranes with 2 wt. %, respectively. While flux grew from 19.9 to 105.4 L/m² h, rejection increased from 99.33 % to 99.78 % for pristine membranes and membranes with 2 wt. % CeO₂ in the case of Direct red 243 dye. However, when the CeO₂ concentration increased from 2 to 4 wt. %, the rejection reduced significantly, which was compatible with all types of dyes employed [36].

Polyethersulfone nanocomposite membranes with HBE-modified graphene oxide were made by Mahmoudian and Kochameshki. Membranes made of nanocomposite materials were employed to study the removal of several textile dyes, including methylene blue, methyl orange, bromothymol blue, crystal violet, and acid red 18. Compared to pure membranes, nanocomposite membranes dramatically enhanced the rate of dye rejection. Furthermore, the modified membrane with 5 wt. % additives performed better and eliminated more than 85% of all dyes. It has also been shown that using the modified membranes for an extended time does not result in a significant loss in membrane efficiency [37].

Alsahly et al. used the diffusion-induced phase inversion approach in N-methyl-pyrrolidone to make poly (phenyl sulfone) (PPSU) membranes by adding various ZnO nanoparticles (NPs). Pristine PPSU membrane rejection rates were lowered from 99 percent to 96.5 and 96.8 % using membranes made with 0.01 to 0.15 wt. % ZnO nanoparticles (NPs). However, refusal rises to 98.5 and 98.6 %, respectively, when ZnO nanoparticles (NPs) are increased to 0.02 and 0.025 %. Increasing the concentration of ZnO nanoparticles (NPs) even further reduces the separation performance to 97.3 % [17].

Kadhim et al. modified the polyethersulfone (PES) membrane with graphene oxide nanoparticles (GO-NPs) and manufactured mixed matrix membranes (MMMs). With varying quantities of GO particles (0.1, 0.2, 0.3, 0.5, 1.5, and 2 wt. %) in the casting solution, new composite membranes were created during the phase-inversion process. Two extremely hazardous dyes, Acid Black and Rose Bengal, were removed using a PES/GO flat-sheet membrane. The dye removal rate for the pure PES membrane was 88%, whereas the membrane was constructed from 0.1 wt. % GO was 99.9% effective. For any further increase in GO concentration, the removal efficiency was between 99.4 and 99.7 %. While the removal efficiency of the Rose Bengal dye by the control PES membrane was 86 %, with the addition of 0.1 wt. % GO, it increased to 96.2 %. In the casting solution, adding 0.2 wt. % GO raised the removal efficiency to 97 %, and adding more GO increased it to 98.9 % and 99 % [26].

Polyethersulfone (PES) nanofiltration membranes were prepared by Zinadini et al. using the phase inversion technique with Ocarboxymethyl chitosan/Fe₃O₄ nanoparticles (NPs). The retention of the dye Direct Red 16 was used to test nanofiltration performance. The findings revealed that adding Ocarboxymethyl chitosan/ Fe₃O₄ nanoparticles (NPs) raised the membrane's negative charge, increasing the rejection of the membrane's negative charge dye. Direct Red 16 was rejected by the pristine PES membrane with a rate of 88%. While for 0.1, 0.5, and 1 wt. % of the CC- Fe₃O₄ NPs loaded membranes. This was changed to 99.0, 99.0, and 98.5 % [38]. Tiny titanium dioxide (TiO₂) nanoparticles were incorporated into poly (vinyl alcohol) (PVA)/poly(vinylidene fluoride) (PVDF) hollow fiber composite membranes made by Li et al. [39] using a coating process. Congo red (CR), Methyl Orange (MO), and methyl blue (MB) dyes were used to test the membrane's effectiveness in separating the dyes. According to the separation results, the 1 g/L nano- TiO₂ modified membrane had the best rejection rates for CR, MO, and MB, at 94%, 52%, and 92%, respectively. The rejection efficiency of the nano- TiO₂ / PVA membrane was also examined concerning the number of layers. When the number of PVA/ TiO₂ layers is increased from 0 to 4, the rejection of CR increases considerably from 54% to 96%. At the same time, the flow of water and CR solution are significantly reduced due to the pores small size with the increase in the number of layers [39]. Kebria et al. [40] created innovative SiO₂ nanoparticle-modified PEI thin-film composite NF membranes. Membranes with positive charges were created via interfacial polymerization between PEI and TPC in the presence of nanoparticles (NPs) of SiO₂ in the PEI aqueous solution in varying concentrations (0.03, 0.05, 0.1 wt. %). Two different feed solutions were created to evaluate the efficiency of membrane separation in rejecting dyes. The first is Crystal violet mixed with water, while the second is Crystal violet mixed in 2-propanol, both at a concentration of 10 ppm. For SiO₂ nanoparticles (NPs) in an aqueous solution, 13.3 L/m² h of flux and 100% rejection were obtained at 0.1 wt. %. An adequate rejection of 99 % was achieved by raising the nanoparticles quantity (NPs) in organic solution to 0.05 and 0.1 wt. %, respectively [40]. Hosseini et al. [41] synthesized new chitosan/poly (vinyl alcohol)/SiO₂ nanocomposite electrospun nanofibrous membranes (ENMs) by electrospinning SiO₂ nanoparticles (NPs) in a doping solution at different concentrations.

Table 1: Detailed information on the membranes used to treat dye wastewater with one type of nanoparticle (NPs)

Membrane Material	Nanoparticle type	Nanoparticle content	Dye	Neat membrane rejection(%)	Rejection (%)	Permeate flux (L./m ² h)	Ref.
polyethersulfone (PES)	Iron oxide nanoparticles (FeON)	(0.1,2,3,4) wt. %	Orange II	89.5	88.4	-	[35]
polyethersulfone (PES)	Cerium oxide (CeO ₂)	(0.0,5,1,2,4) wt. %	Congo red	93.2	92.5	-	[36]
			Direct Red 23,	98.94	99.53	105.2	
			Congo Red,	98.4	99.39	105.2	
			Direct Red 243	99.33	99.78	105.4	
poly(phenyl sulfone) (PPSU)	Zinc oxide (ZnO)	(0.01,0.015, 0.02, 0.025, 0.03) wt. %	Direct red 80	99	98.6	50	[17]
polyethersulfone (PES)	Graphene oxide (GO)	(0,0.1,0.2,0.3,0.5,1.5,2) wt. %	Acid Black	88	99.7	112	[26]
			Rose Bengal	86	99	97	
polyethersulfone (PES)	Ferrosulfate oxide (Fe ₃ O ₄)	(0,0.1,0.5,1) wt. %	Direct Red 16	88	99	-	[38]
Polyvinylidene fluoride (PVDF)	Titanium dioxide (TiO ₂)	(0,1,2,3,4,5) g/L	Methyl Orange (MO)	31	52	15.3	[39]
			Congo red (CR)	86	94	9.1	
			Methyl blue (MB)	82	92	7.8	
Polysulfone	Silica (SiO ₂)	(0.03, 0.05 and 0.1) wt. %	Crystal violet	100	100	13.3	[40]
poly(vinyl alcohol) (PVA)	Silica (SiO ₂)	(0, 0.5, 1.0 and 2.0 wt. %)	Direct Red 23 (DR23)	-	98	1711	[41]
Polysulfone	Alumina (Al ₂ O ₃)	(0.204) g	disperse dye	81.7	96.4	117.8	[42]
polyethersulfone (PES)	Graphene oxide (GO)	(0,1,3,5,7)wt. %	Methylene blue	34	(85.9%)	166.9	[37]
			Methyl orange	39	(90.4%)	170.8	
			Bromothymol blue	45	(97.7%)	170.7	
			Crystal violet	38	(88.1%)	156.4	
			Acid red 18	49	(99.2%)	155.7	
			Acid yellow 36	39	(91.8%)	148.6	

The fabricated membranes were used to remove Direct Red 23 (DR23) dye from colored wastewater. The results showed that increasing the SiO₂ content to 1.0 wt. % resulted in a significant increase in both water permeability and dye rejection. Under 0.4 bar transmembrane pressure, the nanocomposite membrane with 1.0 wt. % SiO₂ content achieved 98 % Direct Red 23 rejection as well as 1711 (L/m² h) flow. While increasing the SiO₂ loading from 1.0 wt. % to 2.0 wt. % had the opposite impact on the separation of DR23, which resulted in a decrease in rejection [41]. Mojtabehi et al. [42] introduced Al₂O₃ nanoparticles (NPs) to the PSf ultrafiltration membrane structure by entrapping them in the structure and depositing them on the surface to investigate the membrane's filtration performance in dye solutions. The results revealed that nanocomposite membranes have greater dye rejection than polymeric membranes, reaching 96.4 %. This indicates that the inclusion of alumina nanoparticles (NPs) aids in enhancing dispersion dye separation quality. Furthermore, nanocomposite membranes with surface deposition have a higher rejection than membranes with incorporated nanoparticles (NPs), which may reject up to 100% of the dispersion dye despite lower flow [42]. Table 1 details the different prior studies that were given in this section.

2.1.2 Mixed matrix membranes (embedded multiple type nanomaterial)

Recently, researchers incorporated multiple types of nanoparticles (NPs) into polymeric membranes. In this regard, Kamari and Shahbazi used the phase inversion approach to create unmodified and modified NF membranes with varying amounts of Fe₃O₄@ SiO₂-NH₂ as nanofiller. Measurement of methyl red (MR) dye retention was used to assess the performance of Fe₃O₄@ SiO₂-NH₂ nanocomposite membranes. The results indicated that the adsorption characteristics of the Fe₃O₄@ SiO₂-NH₂ nanocomposite significantly improved the effectiveness of modified membranes for the removal of MR dye. The nanocomposite concentration of 0.5 wt. % exhibited the best effectiveness for removing MR dye, achieving 97 % among the nanocomposites membranes with varying doses of Fe₃O₄@ SiO₂- NH₂. It has also been shown that the modified membrane has a moderate drop in permeate flux with unchanged MR dye retention over long-term filtering, which supports the membrane's long-term stability [8].

Nanoparticles (NPs) of Ag-AgBr were attached to a polyacrylonitrile-ethanolamine (PAN-ETA) membrane with a chitosan (CS)- TiO₂ layer via vacuum filtering and in situ partial reduction, according to Wang and colleagues (2021). When the dye

rejection performance of the membranes with nanoparticles was compared to that of membranes without nanoparticles (NPs), the PAN-ETA membrane had a water flow of 120 L/m² h and a rejection of methyl orange (MO) and methyl blue (MB) of only 29 and 76 %, respectively. While the PAN-ETA/CS- TiO₂/Ag-AgBr membrane achieves a high Methyl blue (MB) rejection of 97.41 % and a methyl orange (MO) rejection of 88.22 %, the water permeability is reduced to 48 L/m².h. In addition, two other dyes (CR and RB) were used to further analyze the performance of the membranes containing nanoparticles. The dye rejection of the PAN-ETA/CS-TiO₂/Ag-AgBr membranes was relatively high, at around 95% for congo red and 99.98% for rose bengal [43]. Yu et al. successfully synthesized Ag-SiO₂ nanocomposites. They utilized 3-aminopropyltriethoxysilane (APTES) to functionalize the surface of Ag-SiO₂ to obtain better dispersion in the casting solution. The as-prepared Ag-SiO₂-APTES nanocomposite was co-blended with a poly (vinylidene fluoride) (PVDF) membrane to form the Ag SiO₂-APTES membrane. The organic dyes methylene blue (MB), rhodamine B, and direct red 28 were tested to assess how successfully the membrane removed them. Results showed that all Ag-SiO₂-APTES membranes had less flux than a clean PVDF membrane. However, all modified membranes produced in this study had greater rejection ratios than virgin PVDF membranes for various dyes. Besides, the rejection ratio rose progressively as the Ag-SiO₂-APTES concentration increased. The dye rejection ratios with 0.5g of Ag-SiO₂-APTES were 86.8 % for Methylene blue, 87 % for Rhodamine B, and 88 % for Direct Red 28. In contrast, the pure membrane dye rejection percentages for Methylene Blue, Rhodamine B, and Direct Red 28 were 74.3 %, 76 %, and 78 %, respectively. Furthermore, at pH 11, the rejection rate of MB was approximately 98.7 %. More significantly, following four cycle trials, the Ag-SiO₂-APTES membranes displayed remarkable anti-fouling capabilities and an 85 % flux recovery ratio when treating MB solution [44].

Co-precipitation was utilized by Haghghat et al. to create Ag/ TiO₂ nanoparticles (NPs), which were combined in varying proportions to create a new polyvinyl chloride (PVC) membrane. The synthesized membrane's efficiency in removing the organic dye Lanazol blue 3R, which belongs to the Azo dye family, was examined. Separation property comparisons reveal Ag/ TiO₂/PVC membrane is superior to both TiO₂/PVC membrane and pure PVC membrane. With an increase in the quantity of Ag/ TiO₂ particles from 0 wt.% to 4 wt.%, the dye rejection rose from 92.3 % to 98.6 % [45].

Percarboxylic acid-functionalized SiO₂ bound Fe₃O₄ magnetic nanoparticles (NPs) prepared by Vatanpou et al. and employed to produce PES nanocomposite UF membranes. In this study, three different dyes were used to evaluate the performance of ultrafiltration membranes in the removal of dyes (Direct Black 38, Rhodamine B, and Reactive Green 19). The findings revealed that varying the quantities of Fe₃O₄-SiO₂ nanocomposites impacted dye rejection. In addition, electrostatic repulsion between the dye and membrane surface was strengthened by the presence of nanoparticles across all membranes, leading to a rejection rate of over 85% [46].

Using ZnO NPs-decorated cGO nanosheets, Modia and Bellare created new polyethersulfone-nanohybrid HFMs. The ZnO/cGO nanohybrid was introduced to the membranes in varying weight percentages (0, 0.25, and 0.5) wt. %. HFM dye rejection performance was examined by computing rejection values for methylene blue (MB) and rhodamine B. (RhB). The results showed that for ZOGP HFMs, the rejection of MB and Rh.B solutions was considerably enhanced. Moreover, among all HFM samples, HFMs containing 0.5 wt. % ZnO/cGO nanohybrid demonstrated the highest dye rejection, with MB and Rh.B reject rates of 98.6 % and 98.5 %, respectively, while retaining PWP and anti-fouling properties [47]. Table 2 details the different prior studies that were given in this section.

Table 2: Detailed information on the membranes used to treat dye wastewater by mixing more than one nanomaterial

Membrane Material	Nanoparticle type	Nanoparticle content	Dye	Neat membrane rejection (%)	Rejection (%)	Permeate flux (L /m ² h)	Ref.
polyethersulfone (PES)	Fe ₃ O ₄ and SiO ₂	(0,0.1,0.5,1)wt. %	Methyl red	86	97	64	[8]
Polyacrylonitrile	TiO ₂ and Ag	-	Methyl blue (MB)	74	97.41	-	[43]
			methyl orange (MO)	29	88.22		
			Congo red	-	95		
			rose bengal	-	99.98		
Poly(vinylidene fluoride) (PVDF)	Ag and SiO ₂	(0,0.1,0.2, 0.5)	methylene blue (MB)	74.3	86.8	75	[44]
			Rhodamine B	76	87	70	
			Direct Red 28	78	88	67.5	
Polyvinyl Chloride (PVC)	Ag and TiO ₂	(0.25,0.5,1,2,4) wt. %	Lanasol blue 3R	92.3	98.6	-	[45]
polyethersulfone (PES)	SiO ₂ and Fe ₃ O ₄	(0.1,0.2,0.5,1)wt. %	Direct Black 38	>85	>90	-	[46]
			Reactive Green 19	>85	>90		
			Rhodamine B	>85	>90		
polyethersulfone (PES)	ZnO and GO	(0,0.25,0.5)wt. %	methylene blue (MB)	59	98.6	-	[47]
			rhodamine B. (RhB)	53	98.5		

In general, the presence of dispersed inorganic NPs in the membrane matrix improves membrane performance and properties, specifically by: (a) increasing permeability due to NPs' larger effective membrane surface area; (b) inducing a membrane with the functional properties of the nanomaterials; (c) improving a membrane's hydrophilicity and fouling resistance properties; and (d) improving the thermal and mechanical properties [48].

Previous studies indicate that regardless of the type of polymeric membranes utilized, they all behave similarly in terms of rejection after nanoparticles are embedded in them. However, the results indicated that the dye rejection rate of most of the composite nanomembranes was higher than that of the pure membranes. This is due to the nanoparticles' functional groups, which give the membrane a hydrophilic feature. This characteristic aids in forming hydrogen bonds with the surrounding water molecules, reducing or eliminating foul adherence on the membrane surface and increasing rejection. On the other hand, the nanocomposites membrane has larger pores owing to the addition of hydrophilic nanoparticles to the casting solution. This results in an increase in the permeability of the membranes and the passage of a substantial quantity of fouling species through the membrane. This is why most nanocomposite membranes have a lower rejection than unmodified films. Furthermore, through the characteristic of electrostatic interaction, the charge of nanoparticles can play a role in enhancing or decreasing dye rejection.

3. Interaction Mechanisms of Nanoparticles With Polymeric Materials

To produce the desired nanocomposite membrane, it is necessary to pick the location of nanoparticles (NPs) as building blocks and regulate the spatial arrangement of these nanoparticles (NPs) over different length scales. Nanocomposite membranes, which are made up of inorganic and organic building blocks, have the potential to mix the characteristics of their parent constituents and produce new ones. Therefore, understanding the interaction between nanoparticles (NPs) and polymers is essential for understanding the structure-property relationship in nanocomposite membranes. The strong contacts between the NPs and polymer chains affected the modulus of the nanocomposites, which was predicted by the filtration model and contributed to the mechanical reinforcement. Consequently, the interactions between filler and polymer and the network rearrangement during deformations must be described [49].

Several interaction mechanisms occur between various nanoparticles (NPs) and polymers. For instance, the mechanism of interaction between the PVC membrane and the GO in the PVC/GO membrane is illustrated in Figure 2. PVC/GO membranes typically have C–C bonds between the GO and PVC backbones and hydrogen bonds between the connected groups and water molecules. Although there is some compatibility between the polar PVC chain and the GO polar groups due to the presence of the chlorine group, these guest groups disordered the PVC chains and increased the membrane's entropy. These factors enhanced the roughness of the membrane and widened the pore diameter. Additionally, these guest groups formed hydrogen bonds with the surrounding water molecules. These factors increased the wettability and pure water flux (PWF) of the membrane, increasing its efficiency [25].

Furthermore, the interaction processes between PVC and F-MWCNTs, as well as between F-MWCNTs and water molecules, are depicted in Figure 3. The proposed interaction mechanisms revealed disordered PVC chains and improved wettability. This is due to the existence of many layers and more electronegative atoms (N atoms) in the PVC/F-MWCNTs membrane, which increases the hydrogen bonding propensity. As a result, the PWF was enhanced by increasing roughness and pore diameter [25].

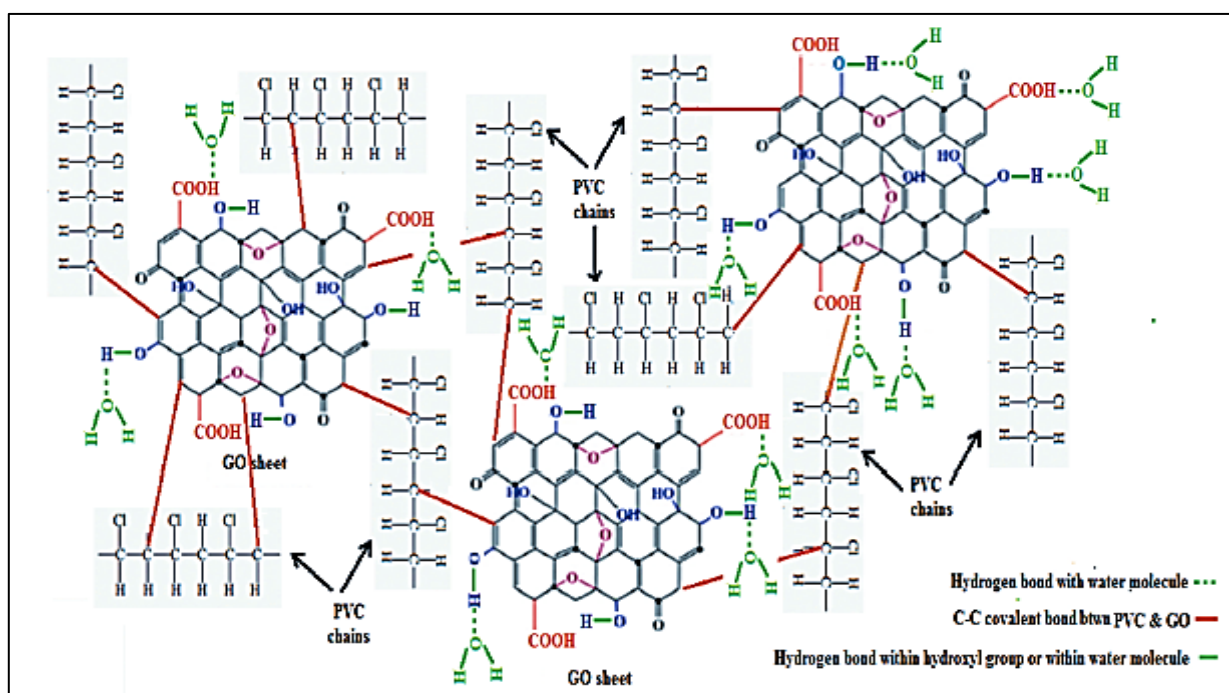


Figure 2: Interaction mechanisms between PVC/GO membrane components PVC and carbon [25]

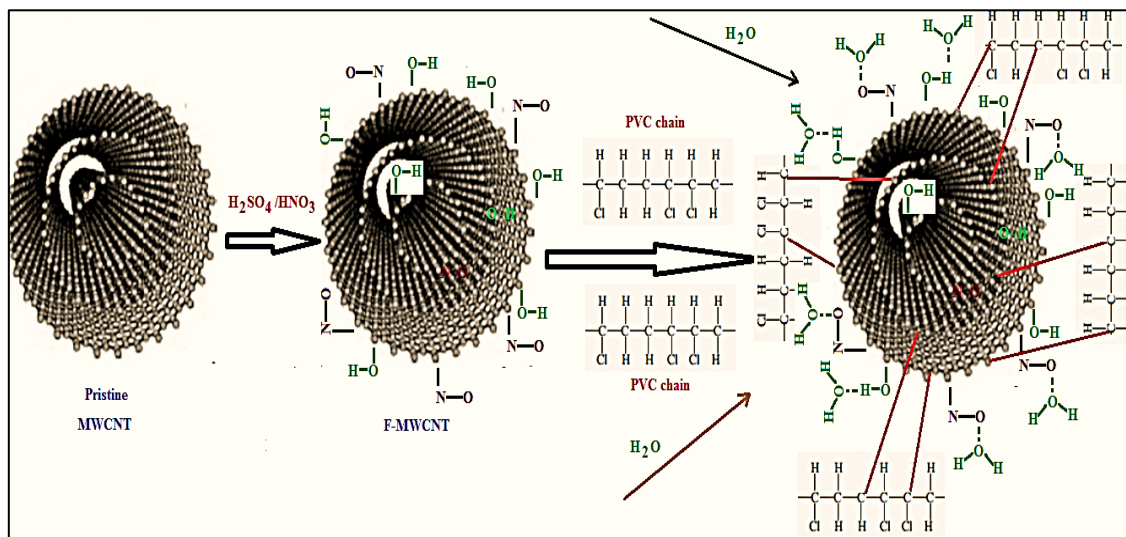


Figure 3: Described mechanisms of interaction between PVC/F-MWCNT membrane components and water molecules [25]

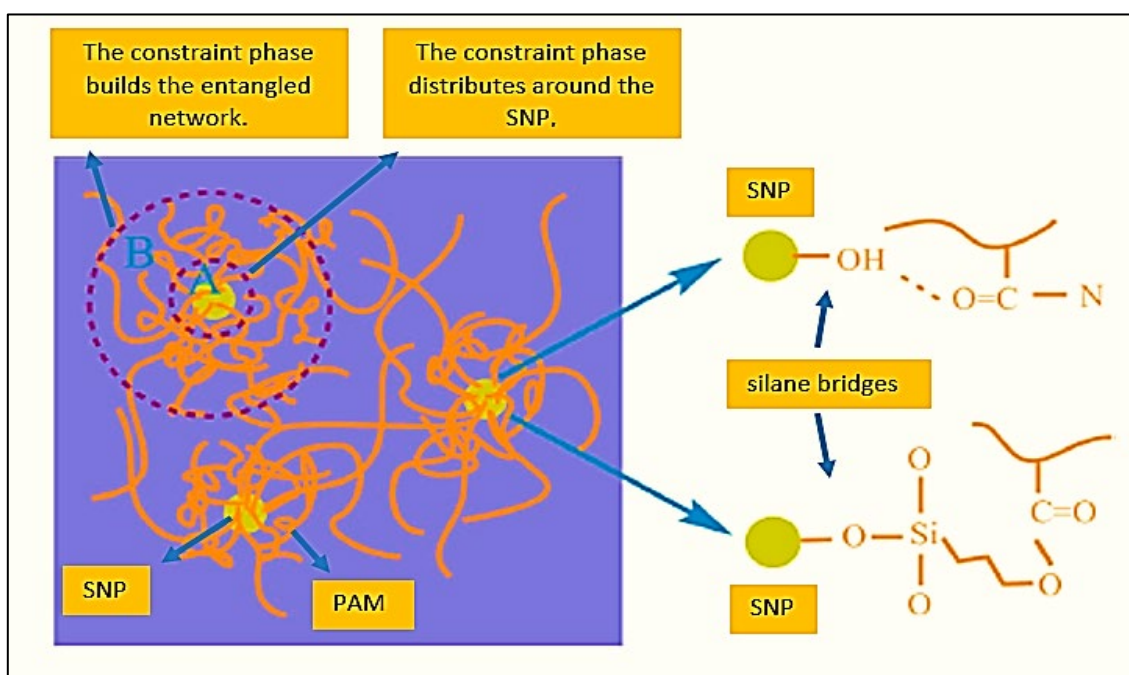


Figure 4: Interaction mechanisms between SNP/ polymer nanoparticle (NPs) [49]

In another work, the interactions between the SNP and the polymer were detailed, controlling the volume of the constrained area and improving nanocomposite hydrogels' mechanical characteristics. These interactions include covalent bonding among SNPs and PAM through silane bridges and non-covalent interactions among SNPs and polymer chains. As seen in Figure 4, these chains help to form hydrogen bonds between SiOH groups on the SNP surface and amide side groups (CONH) of polymer chains. As reversible sacrificial bonds and transient cross-links between polymer chains, these physical interactions provide limited areas of increased strength, which can postpone the onset of cracks [49].

On the other hand, these interactions may impact the removal of dyes from wastewater. For example, Yu et al. observed that the interaction between the Ag-SiO₂-APTES nanocomposite particles and the PVDF membrane resulted in the production of functional groups on the membranes, which play an essential role in the MB dye removal mechanism. Figure 5 shows that SiO₂ becomes negatively charged at high pH, resulting in the membrane having an electrically negative charge due to the membrane having silanol function groups that take hydrogen ions as acceptors. The MB, conversely, was a cation dye. Thus, the negatively charged Ag-SiO₂-APTES membrane and the MB were attracted electrostatically. On the other hand, at low pH, proton interactions occur in the amino-functional groups that act as acceptors for hydrogen ions, giving the membrane a positive charge. As a result, the removal rate of MB is extremely low due to the repulsion between the positive charge on MB and the positive charge on the membrane [44].

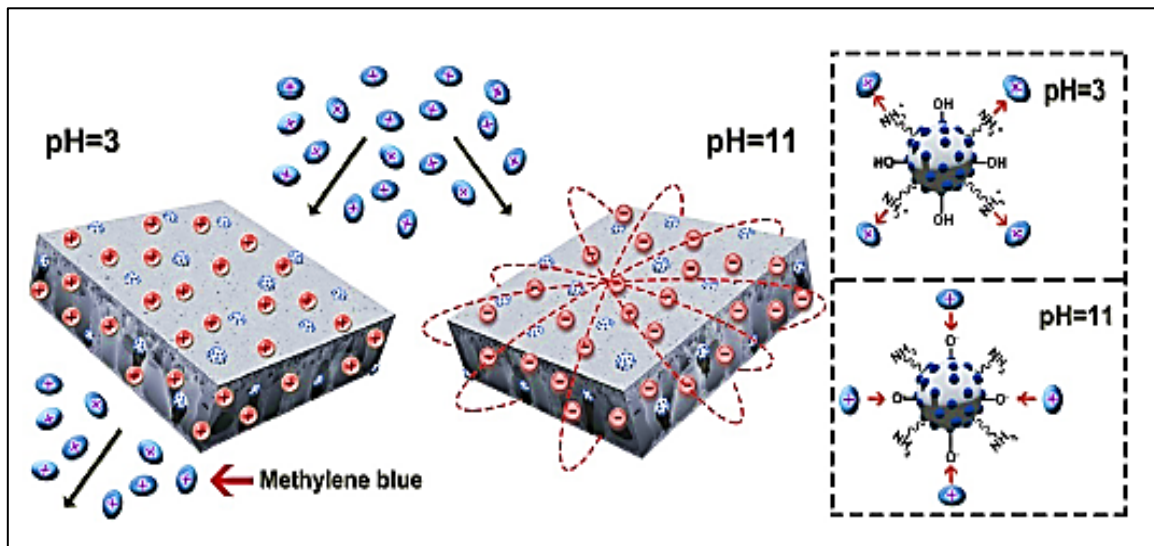


Figure 5: Mechanisms for the removal of MB [44]

4. Membrane Performance Stability After Embedding Nanoparticles in Mixed Matrix Membranes

It is well known that incorporating nanoparticles (NPs) into the polymeric matrix significantly impacts the membrane's performance stability. This has been demonstrated in several studies, which proved through long-term membrane performance tests in the treatment of dye-containing wastewater. Membranes with nanoparticle (NPs) inclusion had excellent stability and efficiency in performance compared to net membranes. For example, Kadhim et al. studied the long-term effects of two dyes processing employing membranes constructed of pure PES and PES–PVP–GO containing 0.5 wt. % GO. The findings generally indicated that the GO/PES membrane exhibited the highest performance and stability. The Acid Black solution permeation flux via the pure PES membrane remained consistent between 13 and 15.1 L/m² h for 14 days, as shown in Figure 6. Afterward, the permeation flux began to decrease. However, after 26 days, the membrane generated using 0.5 % GO with an Acid Black dye solution significantly improved in terms of long-term performance, and the permeability flux remained consistent at around 85.2 and 80 L/m² h. When the dye solution of Rose Bengal was used, the permeability flux of the pure PES membrane remained steady between 9.7 and 8 L/m² h for 14 days. Additionally, after 26 days of operation with the Rose Bengal dye solution, the membrane was modified with 0.5 wt. % GO demonstrated considerably enhanced long-term operation, with the permeation flux maintaining a constant between 50.8 and 49 L/m² h. Negative hydrophilic functional groups on the GO surface, such as hydroxyl (-OH) and carboxyl (-COOH), can create a high zeta potential by generating negative charges on the membrane surface. The negative charge of the Acid Black dye (Which is higher than the negative charge of Rose Bengal) and the negative charge on the membrane surface will increase the repulsive force, which leads to an increase in the rejection rate of the dye [26].

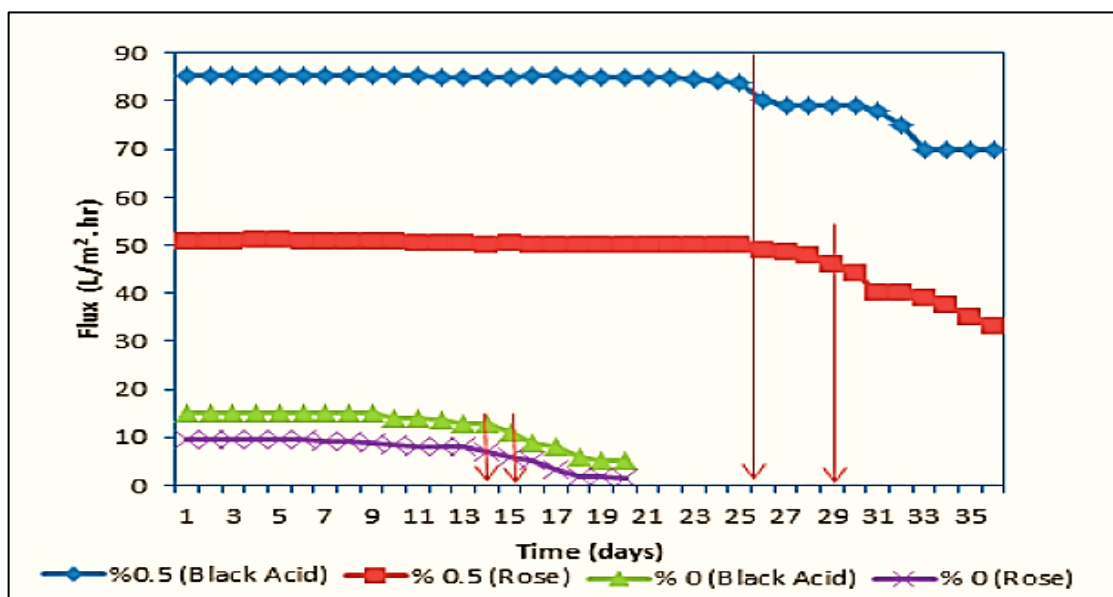


Figure 6: The influence of GO in the casting solution on the lifespan and stability of the produced membranes [26]

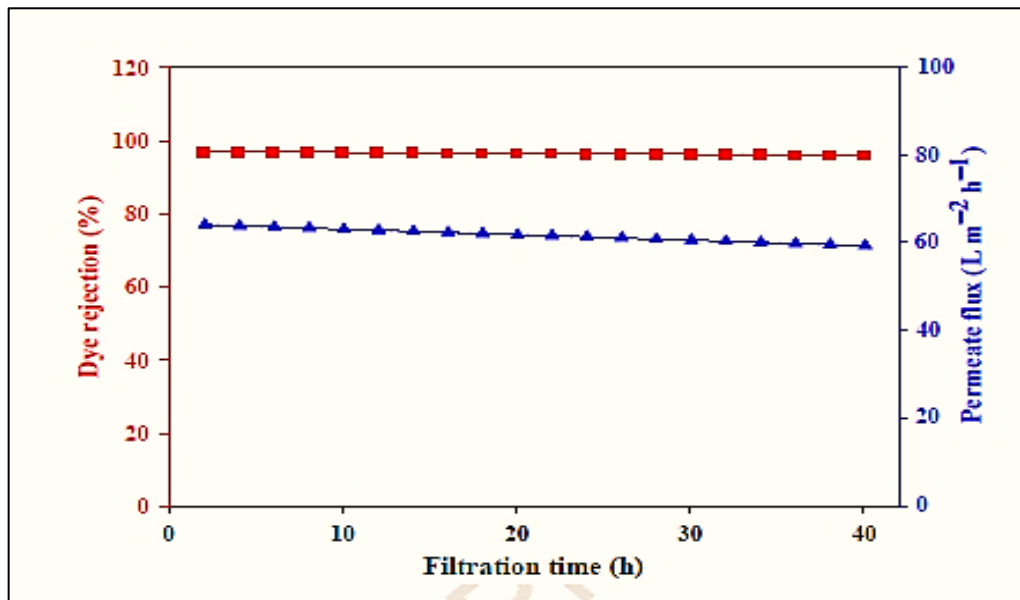


Figure 7: The influence of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ in the casting solution on the lifespan and stability of the produced membranes [8]

The $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ nanocomposite enhanced PES membranes using 0.5 wt. % $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ was utilized in another study by Kamari and Shahbazi to explore the long-term filtration of MR dyes. For approximately 40 hours of long-term operation, the membrane preserved its outstanding filtering efficiency in terms of MR dye rejection and permeated flow, demonstrating its long-term durability, as seen in Figure 7. Accordingly, the dye solution flow reduced from 64 $\text{L}/\text{m}^2 \text{ h}$ to 59 $\text{L}/\text{m}^2 \text{ h}$ over the long-term filtering process, whereas the dye removal effectiveness remained quite stable, at roughly 97%. In addition, the drop in permeation flow from the 2 to the 40 hours of filtration was around 7.5%, demonstrating that the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ had an excellent anti-contamination impact as well as could overcome the membrane's primary restriction, namely fast water flux reduction. Thus, the findings of the long-term filtering procedure validated the membrane's stability [8].

As a result of the effective performance demonstrated by the membranes with nanoparticle (NPs) inclusion in the treatment of dye-containing wastewater, and to broadly investigate the effect of nanoparticles on the long-term performance of the membrane, we touched on the presentation of some studies that were carried out in the use of membranes with nanoparticle (NPs) inclusion with other wastewater. For example, Al-Ani et al. demonstrated the effect of TiO_2 nanoparticles (NPs) on the performance stability of PVC/ TiO_2 NPs membranes in a cross-flow system at room temperature and flow rate (1.1 L/min) and pressure (1 bar). The results showed that the penetration flux of raw PVC membrane started to drop after 5 days, and the membrane operated for more than 14 days before it needed to be cleaned. While the penetration flux of the PVC/ TiO_2 membrane produced from (0.5, 1, 1.5) g TiO_2 NPs demonstrated greater stability over time. Additionally, as seen in Figure 8, all PVC/ TiO_2 membranes operated for more than 30 days before requiring cleaning [32].

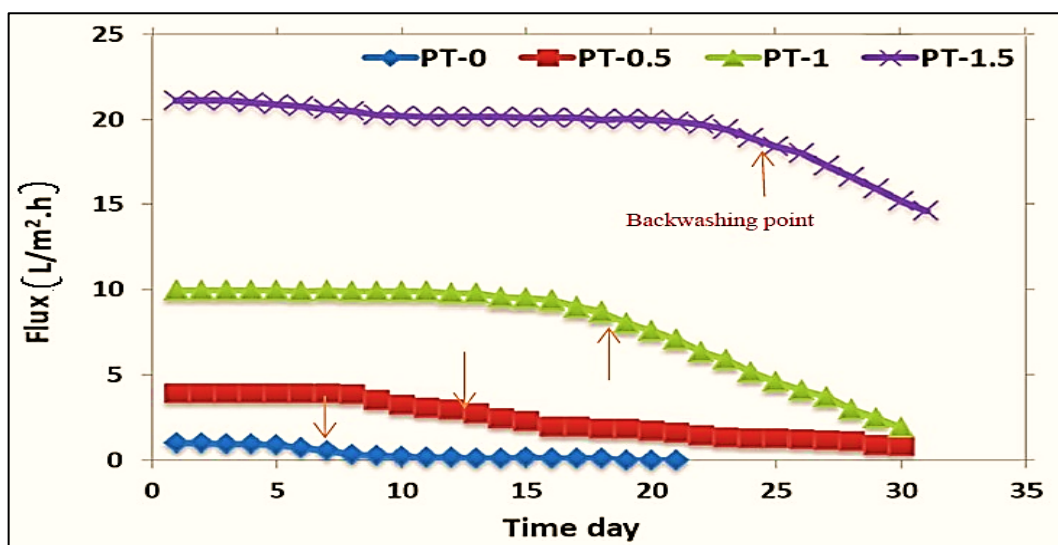


Figure 8: The influence of TiO_2 NPs in the casting solution on the lifespan and stability of the produced membranes [32]

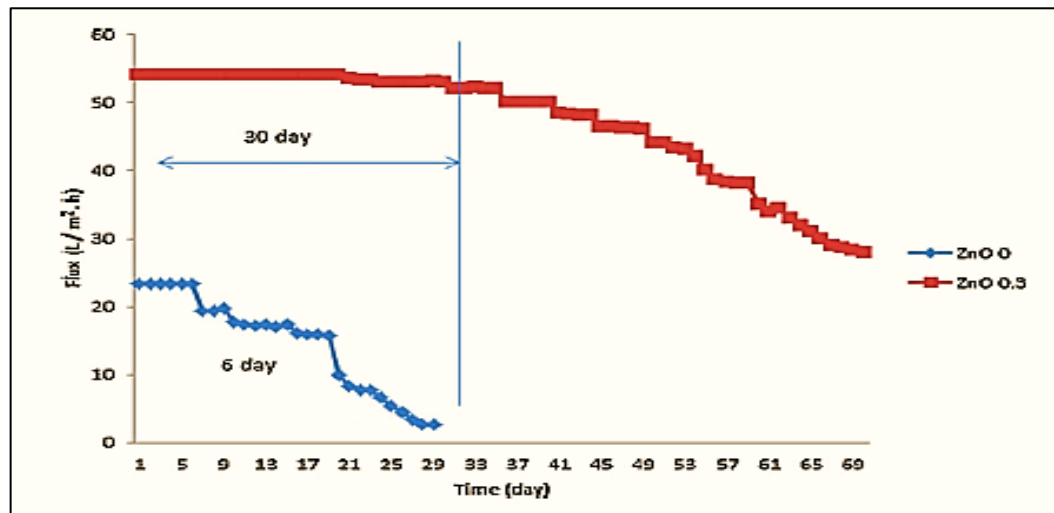


Figure 9: The influence of ZnO-NPs in the casting solution on the lifespan and stability of the produced membranes [18]

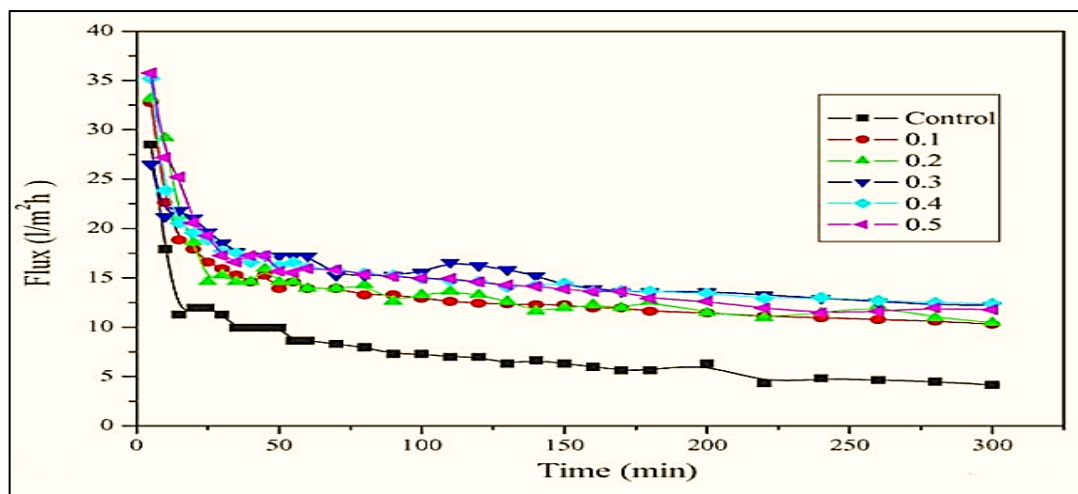


Figure 10: The influence of TiO₂ entrapped membrane on the lifespan and stability of the produced membranes [50]

Alsahy et al. used PVC membranes containing 0.3 g ZnO-NPs for long-term experiments. Figure 9 shows that after six days, the permeability flux of the membrane produced from neat PVC began to decline, and the membrane continued to run for 29 days until cleaning became required. In contrast, a PVC/ZnO-NPs membrane produced from 0.3g of ZnO-NPs began to lose permeability flux after thirty days, and then this membrane lasted 70 days before cleaning became necessary [18].

Moreover, Bae and Tak utilized pure PSf and TiO₂/PSf membranes with varying TiO₂ concentrations (0.1, 0.2, 0.3, 0.4, 0.5). According to the findings of their study, the fouling of a TiO₂ entrapped membrane was greatly decreased compared to a pristine PSf membrane. Because all of the membranes were evaluated at the same hydrodynamic condition, the variable fouling behavior indicates that nanoparticle (NPs) entrapment affected the surface property of the membrane. Due to metal oxides' increased affinity for water, the surface of a TiO₂ entrapped membrane may be more hydrophilic than that of a plain polymeric membrane. As a result, hydrophobic adsorption between sludge particles and the TiO₂ entrapment membrane was decreased, and deposited particles were easily removed by cross-flow. Consequently, TiO₂ entrapped membranes considerably enhanced the performance and stability of the membranes compared to pure membranes, as seen in Figure 10 [50].

The results of the long-term performance test indicate the feasibility of using Nanoparticles as an additive in the polymeric membrane for efficient treatment of different types of wastewater. The main reason for long and stable performance during the long-term operation was the Nanoparticles embedded in the membrane matrix, where the Nanoparticles acted as an effective anti-fouling material, which in turn protected the thickness of the membrane wall. Additionally, the reason for the stable performance was attributed to the excellent mechanical properties of Nanoparticles.

5. Conclusion

Membrane-based water treatment technologies have become more popular in recent decades due to their advantages over traditional separation methods. Due to their high hydrophobicity and fouling, classic polymeric membranes have had to be modified with organic and inorganic fillers/pore formers to improve their overall efficiency. Therefore, scientists have lately been interested in utilizing nanoparticles (NPs) as additions to the base polymeric membrane matrix to build nanocomposite membranes for dye removal applications. In fact, nanomaterials possess unique size-dependent properties related to their high

specific surface area; this feature contributes to the development of novel high-tech materials for more efficient water and wastewater treatment processes. Incorporating various kinds of NPs into polymeric membranes promotes polymeric membrane hydrophilicity and lowers fouling in water treatment. Furthermore, the polymers' mechanical, thermal, and chemical properties are enhanced. This article provides a brief overview of the research efforts conducted so far to improve membrane overall performance by adding nanoparticles (NPs). In this context, numerous nanomaterials have been added using various ways and effectively utilized in the dye removal process. This article specifically examines the role of iron oxide (FeON), cerium oxide (CeO₂), zinc oxide (ZnO), Ferrosferric oxide (Fe₃O₄), graphene (GO), titanium dioxide (TiO₂), Silica (SiO₂), Alumina (Al₂O₃), and Silver(Ag) in promoting separation of dyestuffs. These nanoparticles were revealed to be beneficial in boosting the performance of the membranes by increasing dye rejection and flux compared to bare membranes. Despite the fact that high flux membranes are invariably followed by low selectivity and vice versa. However, nanomembranes have proved to be capable of resolving this trade-off between flow and rejection and have, therefore, become an appealing choice in wastewater treatment. Furthermore, the interaction mechanisms and membrane performance stability were investigated. It is worth noting that there is relatively little information available on the interaction mechanisms in previous studies, despite the importance of these interactions, whether on membrane performance or stability. These mechanisms describe how nanoparticles (NPs) are coupled with membranes and the degree of the influence of this interconnection on the long-term stability of membrane performance.

Author contribution

All authors contributed equally to this work.

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Data availability statement

The data that support the findings of this study are available on request from the corresponding author.

Conflicts of interest

The authors declare that there is no conflict of interest.

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