The Effect of Membrane Modification Using TiO₂, ZnO, and GO Nanoparticles: Challenges and Future Direction in Wastewater Treatment

TD Kusworo¹,², R E Nugraheni¹, N Aryanti¹,²

¹) Department of Chemical Engineering, Faculty of Engineering, Universitas Diponegoro
²) Membrane Research Center (MeR-C), University of Diponegoro, Semarang, Indonesia

*Corresponding author: tdkusworo@che.undip.ac.id

Abstract. Since a long time ago, membrane technology has been applied in the field of wastewater treatment. This technology is considered effective, environmentally-friendly, and does not require a large amount of space in operation. Fouling, either caused by microorganisms or non-living organisms, are the biggest problems that often occur in this technology. Most of the time, organic compounds can cause cake formation and fouling problems. If left untreated, it can increase the maintenance costs and shorten the durability of the membrane. Hence, a membrane-modification effort is needed to be done. In previous studies, nanoparticles such as TiO₂, ZnO, and GO were utilized. They are considered affordable and able to prevent the fouling problem. However, some problems occur due to the addition of nanoparticles. In this paper, we will elaborate on the effect of adding various kinds of nanoparticles towards the modified membrane and evaluate its morphology, performance, and photocatalytic abilities. This article is expected to provide both a new and broad perspective in the future.

1. Introduction

One of the issues currently faced is the global water crisis [1]. The high demand for clean water, decreasing water quality, and the transmission of water-borne diseases are very threatening to human life today [2]. The use of membrane technology in the last few decades is believed to be able to overcome this problem. Membrane technology is widely used for water purification and waste treatment [3], [4]. However, the presence of organic matter in wastewater [5]–[7] and seawater [8] is something that cannot be avoided. Several conventional water treatment methods [9], [10] have been used to reduce this problem. However, byproducts such as activated sludge [11] will cause new problems that can increase the operating costs. Researchers have been trying to improve membrane performance through membrane modification [12]. This effort has been made so that fouling would not reduce the quality of the membrane [13]–[16] which occurred due to the clogging of pores [17], [18].

In its development, the membrane modification method is divided into two. Namely membrane surface modification and polymer membrane modification. Efforts to modify the surface of the membrane include the ozone induction process [19], photografting induction [20], and plasma grafting (21, 22, 23). Meanwhile, the polymer membrane modification is done by combining inorganic
materials [22]–[26] or hydrophilic polymer [27]–[29] in the casting solution. Between these two methods, the polymer membrane modification method is preferred because it is simple and can maintain a stable membrane performance [22], [30]. In addition, some inorganic materials such as TiO$_2$ [1], [31], ZnO [32], [33], and GO [34], [35] are chosen to improve the morphology and performance of the modified membrane because they have good performance compared to other nanoparticles. In this paper, the effect of TiO$_2$, ZnO, and GO nanoparticles addition will be discussed more deeply to make new perspectives related to future studies of polymer membrane modification. Besides, an explanation related to the photocatalytic property of TiO$_2$ and ZnO nanoparticles will also be discussed.

2. Effects of Titanium Dioxide (TiO$_2$) on Modified Membranes

2.1. Regarding the membrane morphology

Modifying polymer membrane using TiO$_2$ nanoparticles can affect the pore size, porosity, and membrane structure. The addition of TiO$_2$ nanoparticles in the casting solution reduces the thickness of the cast solution which will affect the demixing process or the solvent and non-solvent exchange process [22]. Generally, the lower the viscosity of the cast solution, the faster the solvent and non-solvent exchange rates are [36]. As a result, the porosity of the modified membrane will increase [37].

At the same time, according to Yang (2007) [22], the presence of TiO$_2$ in the cast solution would increase the membrane pore size. TiO$_2$ nanoparticles would stick to the membrane layer and created a new "prospective holes". This "prospective holes" would form new pores on the membrane surface during the demixing process. This phenomenon occurred because TiO$_2$ came out of the solvent to the non-solvent. For this reason, the presence of TiO$_2$ nanoparticles in the casting solution is proven to increase the size of the membrane pores.

The demixing process can also affect the shape of the membrane support layer. In some cases, the membrane support layer is known to widen after TiO$_2$ is added to the casting solution [38]–[41]. The membrane structure under the skin layer turns into a sponge because of the presence of TiO$_2$ nanoparticles in the casting solution. Modified membrane thickness is increased [22] because of the TiO$_2$ deposition process in the membrane matrix [42]. This phenomenon shows that the addition of TiO$_2$ in casting solutions can improve membrane structure [22], [43].

However, based on previous research, the amount of TiO$_2$ added to the casting solution needs to be considered [22], [37], [44]. Some studies explained that excessive amounts of TiO$_2$ could cause increased viscosity of casting solutions. This was due to the high surface area and energy that the nanoparticles had [45]. As a result, the exchange rate of solvents and non-solvents became slower and the membrane porosity decreased. Excessive TiO$_2$ would also cause clumping [36], [42], [46] because TiO$_2$ could not mix well in casting solutions [37]. As a result, large pores around the TiO$_2$ clumping area would be formed [37].

2.2. Regarding the membrane performance

In general, TiO$_2$ nanoparticles are thought to increase membrane hydrophilicity [47]. This happens because TiO$_2$ can emerge hydrophilic groups such as -COOH and -OH [43]. Increased hydrophilicity has an impact on increasing the amount of permeate flux. This situation occurs because water molecules are drawn into the membrane and pass through its transportation path. Water transport routes are formed due to the presence of TiO$_2$ in casting solutions that increases membrane porosity. On that account, the membrane pores that are in line with the water transport space will increase [22], [43].

Previous studies also explained that TiO$_2$ could improve the antifouling property of the membrane [36], [37], [43], [48]. TiO$_2$ nanoparticles would increase membrane hydrophilicity which affected hydration layer formation. Later, the hydration layer would weaken the interaction between the impurity molecule and the membrane polymer [43]. This caused the impurity molecules to be swept...
away when the membrane cleaning process was carried out hydraulically. As a result, the cake layer that caused membrane surface fouling was not easily formed [37].

Deposition on the membrane surface caused by the excessive amount of TiO$_2$ can significantly reduce membrane performance [37]. So, the amount of permeate flux will decrease. According to Yang et al. (2007) [22], flux decrease could also be caused by a clump of nanoparticles which made the structure turned symmetrical. That way, the membrane density increased, resulting in less water passing through the membrane.

3. Effects of Zinc Oxide (ZnO) on Modified Membranes

3.1. Regarding the membrane morphology
Adding ZnO to the casting solution can have a strong effect on the demixing process or the solvent and non-solvent exchange process. The hydrophilic nature of ZnO causes water molecules to be easily attracted when the demixing process occurs. The exchange rate of solvent and non-solvent increases so that the morphology of the membrane changes significantly [49]–[51]. According to Mahlangu et al. (2017) and Leo et al. (2012) [52], [53], ZnO increased the size of membrane pores. It is caused by possible aggregation processes due to the presence of ZnO nanoparticles [54].

ZnO nanoparticles aggregation process in the membrane layer is considered as a good phenomenon in improving membrane morphology. However, if the amount of ZnO added to the casting solution is more than 4% weight [53], this can cause membrane pore blockage [55]. Severe pore membrane blockage can create fragility in the membrane. If this continues, the membrane becomes easily broken [54], [56] and can not work optimally. Therefore, the homogeneity of the casting solution must be maintained properly aided by an ultrasonic device [57].

In his research, Lingou Shen et al. (2012) [58] explained that changes in membrane pore size could be influenced by the thickness of the casting solution and the ZnO hydrophilicity factor. In the low composition of nanoparticles (less than 2% weight) [53], the ZnO hydrophilicity factor was more dominant. This phenomenon took place because the casting solution had a low viscosity. So ZnO hydrophilicity accelerated the demixing process and increased the size of the membrane pores. Conversely, if the ZnO composition in the casting solution was high, the ZnO hydrophilic factor became less dominant. That way, the process of solvent and non-solvent exchange slowed down and the size of the membrane pores decreased.

3.2. Regarding the membrane performance
The presence of ZnO in a casting solution can increase membrane hydrophilicity [53], [58]–[60]. This factor is influenced by the high polarity and abundance of hydroxyl groups in ZnO nanoparticles [61]. The presence of ZnO in the casting solution is considered to increase membrane surface energy. This phenomenon has an impact on water distribution during the contact angle measurement process. The scattered water causes lower contact angle value, so that membrane hydrophilicity increases [62]. The process of reducing the value of the contact angle is likely to occur because ZnO is successfully embedded in the membrane matrix [63].

Measurement of low contact angle value is often associated with increased anti-biofouling membrane capability [64]. In previous studies, ZnO was proven effective in killing bacteria Bacillus subtilis, Escherichia coli (E. coli) [65], and Enterobacter sp. [66]. Therefore, ZnO is often added to several types of membranes to improve its biofouling capability [67]. Usually, to kill microbes, ZnO makes direct contact with bacterial cell walls. After that, the bacteria will release components of hydrogen peroxide, hydroxide anion, and superoxide which can kill their cells [68]. That way, the formation of cake on the membrane surface can be prevented [57].

Cake formation on the membrane surface not only causes the biofouling process but also reducing the amount of permeate flux. Generally, the amount of permeate flux decreases sharply at the beginning of the filtration cycle due to the adsorption of the feed solution, thereby affecting the internal pore blocking [69], [70]. To overcome this problem, ZnO nanoparticles are added to the
casting solution to increase the pore size of the membrane [60]. However, Gebru and Das (2017) [71] reminded that the presence of ZnO did not always affect membrane porosity. Sometimes, the pore size of the membrane did not change significantly after ZnO was added. As a result, the feed solution remained inhibited as it passed through the pores of the membrane [72].

4. Comparison of the photocatalytic ability of TiO\(_2\) and ZnO

TiO\(_2\) and ZnO are two types of nanoparticles that are often added to casting solutions. Both of these nanoparticles were chosen because they have good photocatalytic properties. Their photocatalytic ability can work well under UV irradiation or sunlight [48]. TiO\(_2\) is considered to have high photoactivity [73], economic [74], and non-toxic to humans [75]. Whereas ZnO has a large bandgap (3.37 eV) [34], low toxicity [76], and good photocatalytic activity [77]. TiO\(_2\) and ZnO have good photocatalytic dye degradation [77]. Therefore, these two nanoparticles are often used to reduce the content of dyes in liquid waste [1], [32], [78]–[80].

Membrane modification using TiO\(_2\) and ZnO under UV light may affect the morphology and performance of the membrane. For example, membranes can experience increased roughness [81], hydrophilic property [60], chemical change [81], or changes in porosity [82]. Changes in membrane hydrophilicity generally occur due to the formation of hydrophilic groups from methyl oxidation. While membrane chemical changes are caused by the separation of chemical bonds or cutting of chains. This event can form a C-O bond [83], [84], benzene sulfonic acid [84], and the C = O group [85]. However, in reality, the formation of these groups does not always increase the rejection rate or permeate flux. This might occur because UV irradiation is not considered to have an effect on changes in membrane morphological structure [60].

The duration of exposure to UV light is one of the things that can change the porosity of the membrane [82]. Normally, the longer the UV exposure duration, the membrane porosity will decrease [82]. While the higher the membrane porosity, the membrane thickness will increase [82]. Increased membrane thickness is considered beneficial because it can increase the number of photons absorbed in the membrane layer [82]. If the number of photons increases, the permeate flux will also increase. But what needs to be underlined, this phenomenon only applies to membranes that have thicknesses below 300 nm [82].

The charge type between the modified membrane and the feed solution must be properly maintained so that membrane adsorption takes place maximally. Otherwise, there will be a repulsion which affects the membrane adsorptivity value. The resistance occurs because the membrane and feed solution have the same charge. Thus, to prevent this from happening, the pH of the feed solution must be maintained in such a way. Membranes containing TiO\(_2\) are more effective at pH<6 [86]. While membranes containing ZnO are more effective in alkaline conditions [87]. This happens because under acidic conditions, especially at pH<4.5 [88], membranes tend to experience photo corrosion which can drastically reduce photocatalytic activity [89].

The decreased photocatalytic activity can also take place due to an increased concentration of feed solution. For this matter, Bechembmi et al. (2005) [32], Hu et al. (2020) [90], and Borker and Desai Gaokar (2020) [91] split it into two possibilities. The first possibility might be due to an increase in the concentration of the feed solution which was not followed by an increase in the number of free radicals. As a result, cell regeneration did not occur and the number of active sites decreased [92]. Secondly, perhaps due to an increase in the concentration of the feed solution, the active membrane site was covered by the ions contained therein [93], so the photon interaction decreased [94].

In addition, photocatalytic activity is closely related to the disability of the nanostructure of particles [95] and powder size [96] added to the casting solution. Nanoparticles defect may occur due to improper preparation methods [97]. While the nanoparticles powder is better to be small and uniform in size so that the photocatalytic activity of the membrane increases [96]. This causes the photocatalytic surface area to increase because the small size of the powder causes the molecules to be easily adsorbed inside the membrane [96]. The process of maximizing photocatalytic surface area can be done by the addition of doping [32] which can cause photoexcitation [95].
5. Effects of Graphene Oxide (GO) on Modified Membranes

5.1. Regarding the membrane morphology

Broadly speaking, the addition of GO to the casting solution has a large impact on changes in membrane surface roughness [60] and the thickness of the casting solution [98]. Generally, the membrane surface becomes smoother after GO has successfully dispersed [99] and well embedded in the membrane matrix [100]. This ability supports the membrane to increase the ability of antifouling by limiting the penetration of foulants into the pore [45], [101] and limit foulant adhesion to the top of the membrane [102], [103]. However, if GO cannot be dispersed homogeneously into the casting solution [104], [105], the ability of the antifouling membrane will decrease [60].

The thickness of the casting solution increases with the presence of GO nanoparticles [35], [98]. As a result, the process of exchanging solvents and non-solvents in the coagulation bath slows down. So the pore size decreases [106–108] and membrane porosity increases [109]. Solvent and non-solvent exchange processes also affect the size of the macro void on the membrane surface. If the process is rapid, then the size of the macro void increases, and the water flow increases [35]. However, if the process is slow, small macro voids will form [40], [110].

5.2. Regarding the membrane performance

The addition of GO nanoparticles to the membrane matrix may reduce the value of the contact angle [98], [111]. This means GO nanoparticles may increase membrane hydrophilicity. Increased membrane hydrophilicity can be influenced by the presence of oxygenate groups [112], carboxyl, epoxy, and hydroxyl groups [98]. The presence of oxygenate groups can increase membrane hydrophilicity because it can create hydrogen bonds between the membrane surface and water [112]. Increased membrane hydrophilicity is considered good because it can increase pure water flux [113], [114]. However, pure water flux will decrease if the composition of GO in the membrane matrix is excessive. As a result, nitrate content causes deposition and interferes with the placement of hydrophilic groups [55].

GO nanoparticles that are well embedded in the membrane matrix affect the membrane rejection value. The carbon-based affinity of GO carbon particles absorbs fouling agents well and increases membrane rejection [55]. Adsorption of proteins in carbon structures [115] and an increase in water permeability causes increased protein rejection [116], [117]. In some cases, for example, the rate of membrane rejection on a pigment [118], [119], pore size, or membrane porosity is more dominant than the effect of its hydrophilicity [100]. So to increase the rate of membrane rejection, membrane defects need to be minimized by adding GO nanoparticles [120].

GO nanoparticles are considered effective in reducing fouling and biofouling problems [121], [122]. After GO is present in the membrane matrix, there is a decrease in interface energy because hydrogen bonds are formed [116]. Furthermore, water molecules enter the membrane and increase the ability of antifouling or anti-biofouling [123], [124]. Generally, fouling is easy when membranes have large pore sizes and porous structures such as sponges [125]. The chance of fouling on the porous membrane is five times greater than that of the pore membrane [126].

Table 1. The effect of adding TiO2, ZnO and GO nanoparticles to the membrane matrix

| Polymer type | NP type | Variation of NP addition | Type of solvent | Duration of agitation | Membrane thickness | Conditions of the demixing process | Effect on membranes | Source |
|--------------|---------|--------------------------|-----------------|----------------------|-------------------|-----------------------------------|---------------------|--------|
| PSF (18% w)  | TiO2    | 0, 0.5 and 1% w         | NMP             | 20 minutes           | 200 µm            | 12 hours, at room temperature, using demineralized water | • The membrane has more pores in the top layer and more pores in the underlayer • Hydrophilicity of | [43]   |
The permeation of PDF/MWCNT membranes is greater than that of pure PSF and PSF/TiO$_2$.

PSF (1.5 g) GO 0.25, 0.5, 0.75 and 1% w NMP 12 hours at room temperature, using demineralized water 150 µm 12 hours, 0.5 NaCl solution, at room temperature, using demineralized water

- The addition of GO can form small macrovoids, increase the roughness of the membrane, and decrease the contact angle of the membrane.
- The addition of the composition GO 0.25 and 0.5% by weight will increase the size of the pores of the membrane distribution. However, the addition of 0.75% by weight of composition GO will reduce the pore size of the membrane distribution.
- The addition of 0.75% by weight of composition GO decreased the value of the membrane flux.
- The addition of 1% by weight of composition GO can interfere with the placement of hydrophilic groups on the surface of the membrane.

[98]
- Rejection of membrane with GO composition 0.5% by weight increased then decreased.

| Material | GO Composition | NMP | Time | Temperature | Content |
|----------|----------------|-----|------|-------------|---------|
| PSF      | (15, 18, and 20% w) | 0.125, 0.25, 1%w | 24 hours, 300 rpm, 50°C | 10 minutes, 20-30°C, using demineralized water |

- The incorporation of GO on the PSF can increase the porosity of the membrane.
- The addition of GO makes the top layer of the membrane less dense.
- The increase in the GO composition causes an increase in the porous channel and a decrease in the contact angle.
- The highest pure water flow belonged to membranes PSF 15% and GO 1%.
- Increasing the working pressure increases the flow of all membranes.

| Material | GO Composition | NMP | Time | Temperature | Content |
|----------|----------------|-----|------|-------------|---------|
| PSF      | (1.8 g) GO and CGO | 0, 9, 27 mg GO or CGO | NMP 8.1 g + PVP 0.1 g | 24 hours, 60°C | Using demineralized water |

- A high concentration of GO in NMP (>1 mg/ml) means that the diffusion of GO is not maximal and creates aggregates.
- High concentrations of GO (3.3 mg/ml) can propagate well in the PSF membrane.
- The GO/CGO composition above 3% causes GO/CGO to be above the membrane surface, and vice versa.
- Addition of nanoparticles results in a smoother membrane surface.
• The roughness of the membrane is reduced due to the presence of GO/CGO in the membrane.

• The porosity of the PSF/CGO membrane affects the water permeability more than the hydrophilicity of the membrane.

• BSA rejection values were almost the same for all test membranes (almost 100%).

• The reject value MO is inversely proportional to the water flow.

| PSF (18% w) | Fe-TiO$_2$ | DMAC 74%, NMP (4:1), 8% PEG | 20 minutes, 5000 ppm | Using demineralized water |
|------------|------------|-----------------------------|----------------------|-------------------------|

- The higher the ratio of Fe-TiO$_2$ catalyst, the larger the membrane pores.
- At an Fe-TiO$_2$ catalyst ratio greater than 0.1, there is a thickening of the skin membrane layer.
- Addition of Fe-TiO$_2$ to a certain limit will increase the hydrophilicity of the membrane.
- The flux ratio of Fe-TiO$_2$ <0.2 is greater than that of pure PSF.
- Fe-TiO$_2$ increases the reactivity of the membrane to visible light.

[44]

| PSF (18% w) | TiO$_2$ | DMAC: NMP = 4:1 | 1 to 2 days, at room temperature, with deionized water |
|------------|--------|----------------|---------------------------------------------------|

- The number of membrane pores increases on the skin layer after the
addition of TiO$_2$

- A composition of TiO$_2$ > 3% causes lumps
- The porosity of the membrane will increase and then decrease with the addition of the concentration of TiO$_2$ nanoparticles
- The maximum permeability value occurs when the TiO$_2$ concentration is 2% by weight

| PSF (15% w) TiO$_2$-PDA | 100 µm | 24 hours, at 30°C, using distilled water |
|-------------------------|--------|----------------------------------------|
| TiO$_2$-PDA increases membrane hydrophilicity, pore size, membrane permeability and roughness
- Adding an excess of TiO$_2$-PDA (>0.8% w) causes lumps but the surface becomes smoother. To improve antifouling performance
- Addition of TiO$_2$ and TiO$_2$-PDA to the PSF membrane can increase the maximum decomposition temperature
- Addition of TiO$_2$-PDA (<0.8%) increases water flow up to 1.5 times compared to regular PSF
- The addition of TiO$_2$-PDA did not have a significant impact on the release of BSA
- TiO$_2$/PSF membranes exhibit extreme reduction in
rejection after exposure to UV light

| PSF (18% w) | TiO$_2$, 0.5%w | 6 hours, 250 rpm, 50°C | 100 µm, 5 hours, with deionized water |

- There is no negative effect caused by NP because the membrane surface is smooth and flat without microscopic defects.
- Addition of NP results in the expansion of the support layer compared to pure PSF.
- NRGT-PSF membranes have higher porosity and larger pore sizes than PSF, TiO$_2$-PSF, GO-PSF and RGT-PSF membranes.
- The roughness of the hybrid membrane gradually decreased after the addition of NP.
- The addition of NP gradually decreases the value of the contact angle.
- NRGT-PSF membranes have a lower contact angle due to their higher porosity values than other membranes.
- The addition of NP in low composition has no significant effect on the adsorption capacity of the membrane.
- Addition of NP results in a relatively slower decrease in flux.
- TiO$_2$-PSF and GO-
| PSF (3 g) TiO\textsubscript{2} | NMP | 24 hours, 60°C | 24 hours, at room temperature, with demineralized water |
|---|---|---|---|
| 0, 0.3, 0.4, and 0.5% w | (16 ml) | | |

- The increase in the concentration of nanowires causes lumps
- Efficient Cr removal occurs at lower pH
- TiO\textsubscript{2} is well distributed on the membrane surface
- Agglomerates do not form on membranes with a TiO\textsubscript{2} concentration of 0.5 to 1.0% w
- At TiO\textsubscript{2} concentrations greater than 2% p, NP agglomeration occurs
- The addition of NP TiO\textsubscript{2} increases the thickness of the membrane
- Addition of NP TiO\textsubscript{2} at 1.5% w will increase the pore size of the membrane and decrease it to a concentration of 2% w
- The contact angle of the PSf-TiO\textsubscript{2} membrane decreases as the number of TiO\textsubscript{2} nanoparticles increases
- Adding 0.5% w TiO\textsubscript{2} decreases the contact angle and adding 1.5% w TiO\textsubscript{2} decreases the contact angle value
- The membranes of 1.5% by weight and w

| PSF (19% w) TiO\textsubscript{2} | PEG | 8 hours | 150 μm | 24 hours, in an oven at 50°C |
|---|---|---|---|---|
| PEG 2% w + NMP | | | |

- The increase in the concentration of nanowires causes lumps
- Efficient Cr removal occurs at lower pH
- TiO\textsubscript{2} is well distributed on the membrane surface
- Agglomerates do not form on membranes with a TiO\textsubscript{2} concentration of 0.5 to 1.0% w
- At TiO\textsubscript{2} concentrations greater than 2% p, NP agglomeration occurs
- The addition of NP TiO\textsubscript{2} increases the thickness of the membrane
- Addition of NP TiO\textsubscript{2} at 1.5% w will increase the pore size of the membrane and decrease it to a concentration of 2% w
- The contact angle of the PSf-TiO\textsubscript{2} membrane decreases as the number of TiO\textsubscript{2} nanoparticles increases
- Adding 0.5% w TiO\textsubscript{2} decreases the contact angle and adding 1.5% w TiO\textsubscript{2} decreases the contact angle value
- The membranes of 1.5% by weight and w
2.0% by weight of TiO$_2$ show a marked decrease in flux.

- The release rates of COD and NH$_3$ were higher than those of TDS.

| PSF (18.5, 18, 17.5% w) | TiO$_2$ | NMP | 24 hours | 24 hours, at 25°C, using deionized water |
|--------------------------|---------|------|----------|-----------------------------------------|
| 1.5, 2.5% w              | 2       | 16 ml|          |                                         |

- TiO$_2$ can increase the roughness of the membrane.
- The PSF/TiO$_2$ membrane will increase its roughness after UV exposure.
- TiO$_2$ nanoparticles can increase water flow.
- The increase in the concentration of NP leads to the formation of agglomerates at too high a dose of NP and can reduce the membrane flux.

| PSF (19% w) | TiO$_2$/GO | NMP | 24 hours, remove solvent/PVP residual | 70-90 µm |
|-------------|------------|-----|--------------------------------------|----------|
| 0, 1.0, 0.5:0.5, 1:0 (TiO$_2$:GO ratio) | 81% w | Until homogeneity, 60°C | |

- The addition of TiO$_2$ and GO results in greater water permeability.
- In some cases, the release of membrane salts is disturbed by a high water flow.

| PSF (19% GO-ZnO w) | NMP | 24 hours, at room temperature, with distilled water | 100 µm |
|---------------------|-----|-----------------------------------------------|-------|
| 0.01-0.03% w        | 81% w | Until homogeny, 60°C | |

- The morphology of the GO-ZnO-S and TFN-RO membrane is denser and smoother.
- As the concentration of GO-ZnO increases, the thickness of the polyamide layer also increases.
- The contact angle of the modified membrane with
Water decreases with increasing GO-ZnO charge.

- Increasing the GO and/or GO-ZnO load to 0.02% by weight will increase the water flow.
- Water permeability and salt rejection decrease at relatively high levels of GO/GO-ZnO (e.g., 0.03 wt%).
- Increased anti-fouling property during membrane modifications.

| PSF | ZnO | NMP, PVA | 4.5 hours, 400 rpm, 75°C | 150 µm, 30 minutes, at room temperature, with ultrapure water | [53] |
|-----|-----|----------|--------------------------|---------------------------------------------------------------|-----|

- Addition of ZnO nanoparticles to the PSF membrane resulted in a larger average pore size than pure PSF.
- The addition of large nanoparticles can also cause a strong aggregation of nanoparticles resulting in severe fragility of the membrane 4% w ZnO.
- The contact angle with water of composite membranes (Pf-1, Pf-2, Pf-3 and Pf-4) is generally lower than that of pure PSF membranes (Pf-0).
- The contact angle with water decreases with increasing ZnO concentration to 2% by weight and subsequently increases due to the agglomeration of ZnO.
The addition of 2% by weight of ZnO nanoparticles did not show a significant impact on the morphology of the membrane except for the thickness of the membrane.

Composite membranes mixed with ZnO nanoparticles have increased water permeability.

Pf-2 membranes have the highest permeability.

Pf-4 membranes with 4 wt% NP ZnO showed a similar flow reduction pattern to Pf-0 membranes due to severe agglomeration events.

The content of ZnO at 1% by weight is not sufficient to reduce fouling, while the concentration of ZnO at 3% is slightly high to prevent agglomeration.

The surface roughness of the nanocomposite membrane is lower than that of pure PVDF membranes.

Increasing the GO from 0.75% w to 1% w results in an increase in the roughness of the membrane surface.

| PVDF (18% w) | GO, GO-g, PMSA | 0.75&1% GO, 0.5&0.5% GO-g-PMSA | DMF 82% | 24 hours, 200 µm | 24 hours, at 30°C, using distilled water | [99] |
|--------------|----------------|--------------------------------|---------|------------------|-----------------------------------------|-----|
|              |                |                                |         |                  |                                          |     |
• Tendency to decrease in static contact angle after incorporation of GO-g-PMSA
• The resistance to reversible and irreversible fouling of mixed GO-g-PMSA membranes is much lower than that of pure membranes and mixed GO membranes

| Membrane Composition | Treatment | Contact Angle | Pore Radius | Permeate Flux |
|----------------------|-----------|---------------|-------------|---------------|
| PES (18% w, SiO$_2$, 25% w) | NMP, 1.5% w, + PEG, 2% w | 12 hours, 150 µm | 24 hours, at 30°C, using distilled water |
| PES (18% w, CuO, ZnO) | DMAc, 0.2% w | 150 µm | Dry PES membranes which have been dried after immersion in ethanol have greater resistance to fouling than similar mixed membranes |

[60] [52]
The modification of the water solvent to isopropanol increases the antifouling properties with CZN and dried

- Porosity increases and decreases with increasing ZnO
- The addition of hydrophilic ZnO nanoparticles increased the hydrophilicity of the PES membrane
- The number of pores increases with the increase in the weight of added ZnO
- When the weight of ZnO added is more than 0.2 g, the number of pores tends to stabilize and causes a slight change in the size of the pores
- When the weight of the added ZnO nanoparticles was greater than 0.2 g, the volume of macrovoid started to decrease
- The water flow of all ZnO/PES hybrid membranes is higher than that of PES membranes
- All ZnO/PES hybrid membranes have a lower flow reduction than PES membranes
- The 0.2g PES/ZnO hybrid membrane showed the highest antifouling capacity

| PES (8% w) | ZnO 0; 0.1; 0.2; 0.3; 0.4%w | NMP + g 2 | 72 hours, 70°C | 3 hours, at room temperature |
|------------|-----------------|-----------|-----------------|-----------------------------|
6. Conclusions and Future View

Researches related to the modification of polymer membranes using nanoparticles TiO$_2$, ZnO, and GO are still conducted. They are popular because it has been shown to significantly influence membrane morphology and performance. Although mixing nanoparticles into a casting solution is very simple, problems such as the clumping of nanoparticles are very likely to occur if the composition of nanoparticles is excessive. Unfortunately, until now there has been no research that can ensure the maximum number of nanoparticles that can be added to the membrane matrix. Therefore, in future research, modeling the composition of nanoparticles to the membrane matrix is encouraged to determine the maximum membrane performance of the composition of nanoparticles. In addition, a combination of one type of nanoparticles and another can be developed to create a membrane that is more stable and has the best antifouling ability. The application of membrane modification to various types of waste needs to be expanded to test the efficiency and stability of the membrane. The photocatalytic ability of the membrane needs to be tested more deeply as well to determine its effect on morphology and membrane performance.

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