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PRELIMINARY STUDY OF NANOMATERIALS EFFECTS TOWARDS MEMBRANE SALT REJECTION IN REVERSE OSMOSIS DESALINATION PROCESS

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Abstract

Fresh water or also known as potable water is the water that is safe to drink and to use for a food preparation. However, fresh water is not always potable water because a lot of the fresh water on earth is unsuitable for human consumption without some treatment. It can be seen that around 1 to 2 billion people lack of safe water which causes 30,000 deaths each week in which more people die from unsafe water than from war. As the world is expanding with a new technology every day, it is possible to make a desalination process around the world. A finding suggested that nanomaterial will be used in membrane technology and reverse osmosis (RO) to improve the attractiveness of the membrane without changing the mechanical properties of membrane. This literature review provides an overview analysis of several nanoparticles (NPs) such as titanium dioxide (TiO2), silver (Ag) and silica (SiO2) on effect towards performance of the thin film nanocomposite (TFNC) membranes in terms of RO desalination process. These NPs show a significant effect in terms of salt rejection and anti-fouling properties of TFNC membranes compared to the thin film composite (TFC) composite membranes during the process of RO desalination process. From this current review, an average 98.28% of the salt rejection was found in the application of TiO2. This result happens due to the mechanism of the TiO2 which it can block the salt ions from going across the membrane. Other than that, another NP which is silver has found an average salt rejection at 91.32%. This is because due to an approximately 1000-fold increase in surface area per unit weight, silver nanoparticle is more desired over micro particles, which allows for more chemical interactions. Lastly, silica nanoparticle has an average of salt rejection at 98.05%. These results can be achieved due to the mechanism of the silica nanoparticles which is increase the hydrophobicity of the membrane surface and decrease the membrane surface roughness. In conclusion, these nanoparticles have shown a significantly impacts towards of the salt rejection performance on the TFNC membranes in desalination process. For the further understanding, more studies should be done to gain more and in-depth knowledge in this RO desalination process.

Keywords: Desalination; nanomaterials; titanium dioxide; *silver; silica*

1.0 INTRODUCTION

Clean water is an important source of all life on earth and it is an important food source in a variety of key industries including food and industry [1]. From an article written by Teow and Mohammed, this problem happens because the world is facing some challenge on continuously meeting the demand of the people around the world and the rapid growth of the industrial every year [2]. From Mohammed final technical report, a prediction from United Nations (UN) that states by the middle of the 21st century, approximately between two billion to seven billion people will face a water crisis [1]. Furthermore, water crisis can bring a huge impact on the world such as economic growths and human health since it affects industrial production and shrinks the availability of hygienic foods and drinks that causing a variety of epidemic diseases such as vomit, diarrhea, and dehydration [1]. From article written by Teow, a report endorsed by the World Health Organization in the year 2002 stated that the deficiency of clean and safe water accounted for 3.1% of death worldwide [1]. This trend is forecasted to rise over the years [1].

Next, Mallick et al. have reported that diarrhea is the most common disease that happens in the developing countries [3]. From the same report in 2013, it was reported globally around 0.58% children died under five years due to this disease. From this percent, India has totally contributed of one fifth of the whole cases of diarrhea in that year [3]. Based on their study, diarrhea is commonly happened in India because due to lack of clean water. The country did not make major improvement of sanitation facilities [3]. It was also reported in 2015 that 663 million people have no improvement of drinking water availability and 2.4 billion have not improved on sanitation facility which 946 million were forced to practice in an open place [3]. The authors conclude that the government must take serious action towards this disease before they lack of the new generation for the future purpose [3].

Teow and Mohammed wrote, around 70% of earth's surface is being covered by water but the fresh water that can be consumed by the human is around 3% only [1]. This is because most of the water that can be drank is being stored in a frozen form or will be collected in deep underground [1]. In terms of meeting the demand from the people around the world, some extensive efforts are being made to use the rest of water which is the ocean water using some technology that being called desalination process [4]. Qasim et al. have said that, this desalination process is a simple method and will be a main source to clean fresh water [4]. Desalination refers to a process of removing salt and contaminations from the seawater using membrane technology which suitable for human daily usage [5].

Desalination process was chosen for this study because currently desalination is acknowledged as a credible and readily available source of clean water [6]. Desalination has good characteristics such as easiness in operation, economical, no or less requirement of chemical additives, greater productivity, no need of phase changing, simple scaling up and superior removal ability [7]. Kavitha et al. stated, starting from 50 years ago, desalination has been one of the potential technologies to fulfill the demand for fresh water supplies [8].

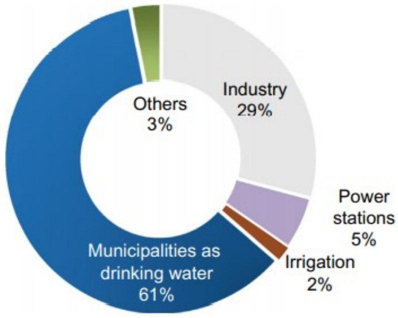

Fig. 1. *Percentage of online desalination capacity[9].*

In Qatar and Kuwait, water is sourced through desalination process. This water is used for domestic and industrial use [10]. 60% of all online desalination capacity provides municipalities with drinking water, and more than 30% covers industrial water demand based on Fig. 1 [9].

Generally, there are two methods in desalination process, which are thermal method and pressure method. The study from the Qasim et al, have conclude that thermal desalination is no longer efficient to be use in the 21st century [4]. It is because they stated that, thermal process use around 10,000 tons of fossil fuels to produce 1000m^3 per day [4]. In advance of technology, the authors found that fresh water can be produce using membrane science which can give the most promising and give high efficiency when using desalination process [4]. The advantage of using membrane desalination is this process used low space requirement and proven operation simplicity [11]. Pressure-driven membrane-based processes operate semipermeable membrane where water molecules diffuse through the membrane while the salts are rejected to be purify [12]. Furthermore, there are several membrane-based processes that widely used for seawater and brackish water treatment such as reverse osmosis (RO), nanofiltration (NF), and membrane distillation (MD) [13,14].

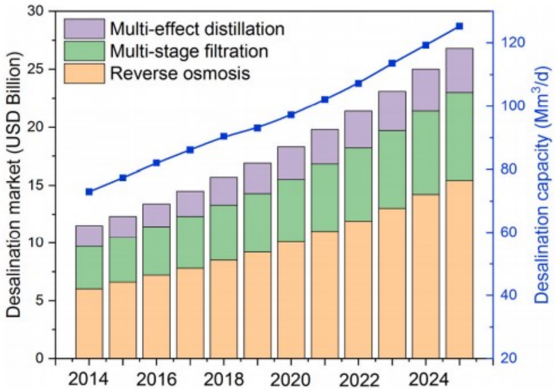

Fig. 2. *Estimation desalination market and capacity from 2014 to 2024 [15].*

A report by Zhao [15], it mention that 16,880 desalination plants are supplying freshwater of 97.2 million m^3/day in 2020 globally [16]. Since 2000, the total production capacity of freshwater has tripled up from less than 30 million m^3/day [17]. As shown in Fig. 2 the estimation of desalination growth in terms of capacity and market for the next few years based on the recent growth [16]. Analysis from the figure it point out that desalination market will be double up between 2015 and 2025 [15]. On top of that, from figure above, RO was the most used for global desalination market in both of section which revenue and installed numbers (14,360, accounting for 85% of existing desalination plants [16]).

Fig. 3. *Technologies usage for desalination capacity world widely [15].*

In addition, Fig. 3 shows the total technology installation for desalination capacity for worldwide. RO is the most dominant technology shown as its percentage is 60% which more than half. This figure showed how essential and useful RO process in desalination industry [15].

Additionally, Marcovecchio et al., reported RO processes have become the most common separation method used in the production of potable water from seawater and brackish [18]. RO is able to reduce energy consumption compared to thermal separations [18]. Advances in researches have been focused on producing new membranes, enhancing the rejection processes and flux [18]. Qasim et al. have said RO is the most dependent technique for seawater and brackish water desalination [4]. RO also has been chosen as another source for producing water to minimize the cost of desalination-associated [16,17]. Since 1950s, the utilization of RO for desalination has drastically increased [4]. Safarpour and others also stated that RO desalination process is the most efficient desalination technology thus it has developed significantly over the last three decades as the main membrane-based desalination technique [21].

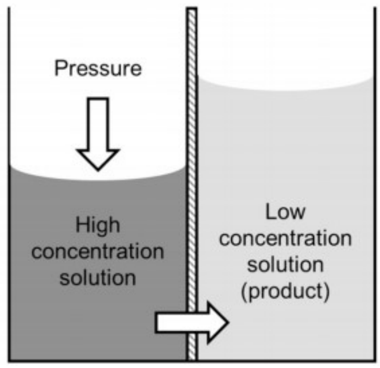

Fig. 4. *Mechanism of RO [4].*

The mechanism of RO being explained in Fig. 4 [4]. When pressure was added in high concentration solution, the flow of water molecular can be stopped or reversed [4]. The water molecules were forced to flow in from high concentration solution to low concentration solution which the opposite of natural osmosis phenomenon [4]. The important condition for this process to occur is applied pressure differences must greater in magnitude than the osmotic pressure differences across the membrane [4].

A wide range of polymers, such as cellulose acetate (CA), acrylic, polysulfone (PSf) and other patented non-cellulosic polymers, are widely used for porous membranes. Polycarbonate (PC), polyvinyl chloride (PVC), polyvinylidene fluoride (PVDF), polyamide (PA) and polyacrylates have also been prepared for porous membranes [22]. Polymer choice affects the characteristics and properties of the membrane, such as charge, adsorption, stability and hydrophilicity of porous membranes [23]. Solubility and diffusivity also depend on the chemical structure of the membranes for non-porous membranes such as RO [23]. The RO membrane consists of three layers, a bottom layer made of 100-200 µm thick unwoven polyester cloth to support the entire membrane [24]. At the middle layer consisting of 30-50 µm thick PSf or polyethersulfone (PES) and a top layer of 100-200 nm thick PA or polyetherimide

(PEI) supported by PSF or PES that is used to separate solutes from feed water [24]. One such RO membrane is an industrial product called FT-30, which has a high salt rejection rate of more than 99 % at 1.55 MPa for 2000 ppm NaCl [24]. Many kinds of RO membranes have thus been developed.

Leading to the rise in production and application of their specific physicochemical properties and their possible threats to the natural environment, nanoparticles have gained a lot of interest in recent decades [22–24]. Nanoparticles (NPs) are one of the substances most commonly studied, contributing to the development of a new branch of study, ''nanotechnology''. NPs are classified as particles with at least one dimension ranging in diameter from 1 to 100 nm [28] that can change their physicochemical properties compared to their parent bulk material [26,27]. NPs are commonly used in different aspects of everyday life and energy efficiency due to their special characteristics and novel features [29]. NPs can be synthesized from a number of bulk materials, and both their chemical composition and the size and/or form of the particles depend on their behaviour [31].

Haleema and Syed have stated the production of thin-film nanocomposite (TFNC) membranes using nanoparticles creates huge potential in the desalination industry [7]. The latest research on TFNC membranes incorporating nanoparticles used for the purification of water has been reviewed [7]. The broadly tested nanoparticles include metal and oxide-based metals (silver, copper, titanium dioxide, zinc oxide, alumina and metal-organic frameworks), carbon-based (carbon nanotube, graphene-oxide), and other nano-sized fillers such as silica, halloysite-based, zeolite-based and cellulose-nanocrystals [7]. These nanoparticles demonstrate major effects in terms of salt rejection, water flow, anti-fouling properties and chlorine resistance of TFNC membranes relative to the thin-film composite membrane (TFC) [7]. The environmental effects, commercialization and reach of TFNC membranes will show in the future that nanomaterials have unique properties that can lead to the development of high-tech nanocomposite membranes with improved desalination capability [7].

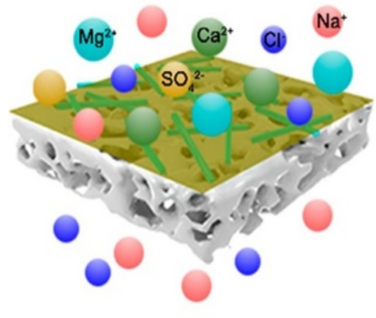

Fig. 5. *Schematic illustration ions at PA layer [32].*

Fig. 6. *Separation different types of salt at PA layer. [32]*

From the research by Huang et al. bacically, PA-membrane based are invented by few process which are interfacial polymerization of piperazine (PIP) and trimesoyl (TMC) on an ultrafiltration substrate to form a TFNC structure [32]. From the Fig. 5 above it shows that PA membrane can reject variety types of salt such as NaCl, $MgSO_4$, Na_2SO_4, $MgCl_2$ and $CaCl_2$. As Fig. 6 NaCl is the lowest rejection percentage due to Donnan effect and size effect. The meaning of Donnan effect is the equilibrium and interaction between soluble charged molecule and charge existing on membrane [33]. The outcome from dissociation of different ionic groups present on membrane are assume as charges that existing on membrane [33]. It may also come from porous conformation of membrane [33].

In this study, several nanoparticles will be review to determine the effectiveness towards the performance of membrane desalination for salt rejection capability. NPs that have been chosen are titanium dioxide (TiO_2), silver (Ag) and silica (SiO_2).

2.0 LITERATURE REVIEW

A. Titanium Dioxide (TiO_2)

A study by Ike et al. stated that titania or commonly called as titanium dioxide (TiO_2) is a crystalline solid that may exist in a number of polymorphs such as brookite, anatase, and rutile [9]. Out of these, rutile known as the most stable phase for TiO_2 as crystalline solid. On top of that, anatase and brookite phases can change irreversibly to the rutile when at high temperature. Haleema and Syed also mention that TiO_2 has receives much research consideration, as the great characteristics own such as antimicrobial coatings, photo-catalysis, pigment and oxygen sensors [31,32]. Among them, the main characteristic for this research is photo-catalytic features to separate the organic compounds could be used in the filtration membranes to decrease the fouling process in the membranes [33,34].

From Safarpour study [21], she reported that TiO_2 is widely used as nanomaterial because of its feauture as mention by Haleema plus it is low cost and non-toxic [38]. That is why it commonly used in different industries for instance wastewater desalination and as water [39]. The other benefits of TiO_2 are high chemical stability. The negative impact of TiO_2 as nanomaterial are incorporating into membrane matrix, the negative effect of NPs may be observed on the morphology and performance of the resulted membranes due to the aggregation and agglomeration of titanium dioxide nanoparticles (TiO_2-NPs) [38,39]. Agglomeration may happen due to their large surface are or particle size ratio. It is also may affect degradation of material properties when incompatibility of inorganic particles with polymer subtract happen [21].

Regarding TiO_2 effects towards salt rejection performance, several studies have been conducted to analyze the effectiveness of TiO_2 in helping the improvement of salt rejection in desalination process [42–44]. For instance, a study have been reported by Lee to show relationship between TiO_2 concentration and percentage of salt rejection [42].

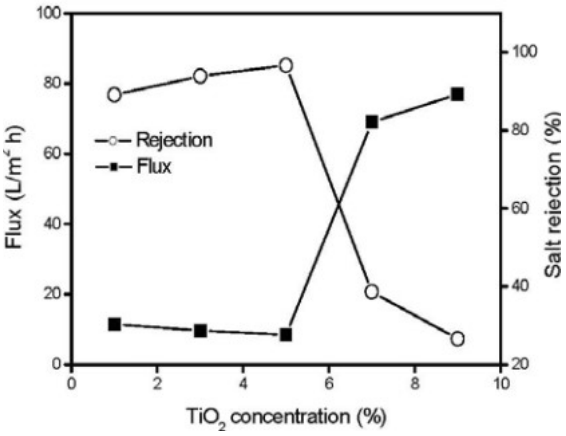

Fig. 7. *Effect of TiO_2 concentration on the membrane performance of water flux and MgSO4 rejection [42].*

Based on Fig. 7, the experiment started with concentration of $MgSO_4$ 2000 ppm and operating pressure 0.6 MPa. As concentration of TiO_2 increased to 4.0 wt%, salt rejection slightly increase but decrease drastically starting 5.0 wt%. It is because above the critical concentration, the performance of membrane will decrease eventually [42]. The authors suspect PA-TiO_2 layer tend to peel-off from PES substrate at above critical concentration after the filtration experiment. On the other hand, at high concentration of TiO_2, it will interfere the interfacial polymerization (IP) affect to degree of polymerization in the PA surface. Therefore, the membrane cannot be functioned fully after 5% TiO_2 concentration [42].

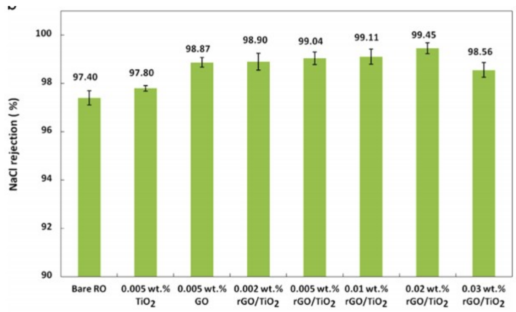

Fig. 8. *Salt rejection of the prepared RO membranes [21].*

According to Fig. 8 percentage of salt rejection has increased with TiO_2-NP at 97.80% and rGO/TiO_2 99.04% while bare RO only at 97.40%. The highest salt rejection from the experiment mention in the article was 0.02wt% rGO/TiO_2/RO membrane which with 99.45% [21]. Based on salt rejection 0.02wt% rGO/TiO_2 has selected as the optimum content of nanocomposite [21]. From the result, it had shown that modification of TiO_2 helps in increase the salt rejection and quality of TFC-RO membrane [21].

A recent study by Akalili et al. have shown that incorporation of titania nanosheet (TNS) onto the membrane surface have improve the salt rejection [43]. For this experiment TNS was used with TFC and TFN to define the optimum number of TNS-TFC to have highest NaCl rejection as Fig. 9.

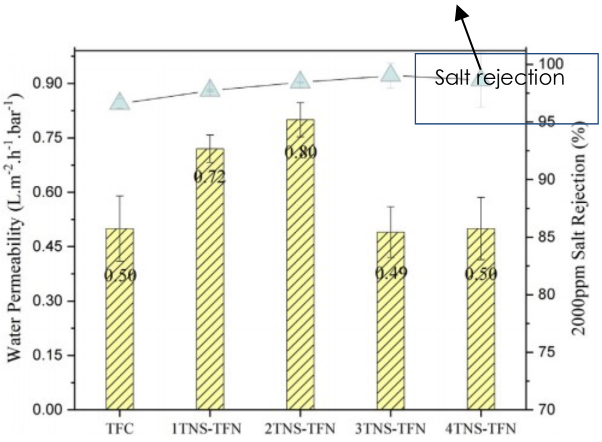

***Fig. 9**. NaCl rejection of various TNS-PA TFN membranes [43].*

***Table 1.** Percentage of salt rejection based on the layers [43].*

Layer	Percentage of salt rejection (%)
TFC	96.65
2TNS-TFN	98.19
3TNS-TFN	99.03

Based on Table 1, the authors reported that this phenomenon happen because of additional coating layer and high PA crosslinking effect that permissible more resistive diffusion of salt passage [43]. Water molecules on the TFN were trapped efficiently in membrane surface because of the interaction between water molecules and metal-hydroxyl group of TNS surface through hydrogen bonding [43].

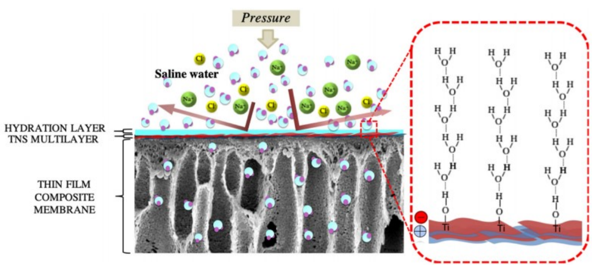

***Fig. 10**. The mechanism of hydration layer formation on TNS-PA TFN membrane [43].*

As shown as Fig. 10, the hydration barrier layer could act as a foulant-resistance medium [43]. The salt will separate into two ions which are Na^+ and Cl^- in feed water[43]. When ions were blocked from direct contacting with the membrane surface, it will increase performance of membrane for salt rejection [43]. On top of that, the surface charges of the membrane played important roles in ion adsorption an ion transmission effect [43]. As well known, the ions adsorption occurred when the negative charged OH^- group from TNS adsorbed the Na^+ regarding on the electrostatic interaction between them [43]. Concentration polarization significantly took place because of the retention of ions in the boundary layer and indirectly increase the salt rejection [44–46].

To be summarize, it is believe that TiO_2 is a good nanomaterial that helps to improve the performance of salt rejection in desalination. Modifications of TiO_2 also bring a bigger impact to increase percentage of salt rejection such as TiO_2-COOH and rGO/TiO_2. By using TiO_2, the membrane can be long lasting and concentration of TiO2 was not changed greatly, implying a robust, stable nanocomposite membrane [42]. The agglomeration is less happen in TiO_2. Hence, this is why TiO_2 used to be the most common and well-known nanomaterial before.

B. Silver (Ag)

Silver nanoparticles (Ag-NPs) have antimicrobial properties due to their large surface area, small size and their ability to become lodged into matrixes [48]. 20 years ago, numerous studies have concentrated on the immobilization of Ag-NPs on the exterior of the membrane to provide long-lasting, effective and direct anti-bacterial performance of the polyamide TFC membrane [48–50]. For example, pre-synthesized Ag-NPs have been inserted on the exterior of the membrane to enhance the TFC membrane's anti-bacterial performance (ex-situ formation) [48,50]. Several studies have indicated that Ag-NPs should be located at the interface of the membrane feed to allow immediate contact between Ag and bacterial cells in order to achieve superior antimicrobial capacity [51,52]. Ag-NPs are less than 100 nm in size, while silver ions, commonly oxidized from metallic Ag, are in the ionic form [54]. There is an increased surface-to-volume ratio for smaller NPs that allows more interaction sites between ions and bacteria [43,44]. Photocatalytic and surface features of Ag-NPs are ideal towards biocidal activities and are much more toxic than Ag^+ ions [54]. Due to an approximately 1000-fold increase in surface area per unit weight, NPs are more desirable over microparticles, which allows more chemical interactions [44,45]. The properties of NPs depend on size, the extent of dispersion and structure [58].

For antimicrobial use, many kinds of NPs have been used, such as zinc, titanium, magnesium and copper, but Ag remains the most effective against viruses, bacteria and other eukaryotic microorganisms [59]. Ag-NPs are chemically stable, more antimicrobial than other metals and have catalytic and conductive properties [48–50]. Ag is bacteriostatic [63], thereby deactivating but not actually killing cells.

Three probable mechanisms for the antimicrobial properties of Ag include damage to microbial cell membranes and intracellular components which is through protein thiol group interaction and enzyme inactivation, adsorption to microbial cell walls, and formation of reactive oxidative species (ROS) [52–54]. In addition, gram-negative bacteria have lipopolysaccharide surfaces that are negatively charged, forming electrostatic attractions between the Ag and bacteria.

Studies have shown that Ag-NPs can bind to the thiol groups of bacterial cysteine groups, leading to enzyme inactivation and replication [45,55,56]. When bacterial cell walls contain proteins with -SH groups due to Ag^{+} interactions, the cell walls are likely to have their functionality compromised [69]. By forming complexes with silver released from the NPs [42,52], cysteine will make Ag^{+} ions unavailable. Owing to the development of complexes, this reduces the antimicrobial aspects of the Ag-NPs in the first place. Size, shape, zeta potential, pH, etc., are the main factors regulating Ag-NP antimicrobial activity [44,45,52,55]. In addition, in the presence of moisture, metallic Ag-NPs can be oxidized, which enhances silver ion leaching from surfaces to minimize surface antimicrobial properties [67].

By creating reduced forms of oxygen, ROS is able to increase the rate at which cells are conditioned to die by disrupting the aerobic respiration process [48]. It is sufficient to separate electrons from other types of oxygen molecules (donors) in the presence of metals and increase the presence of ROS derivatives [48]. Overall, oxidative stress on the cells [48] is produced. Generated from oxidizing hydrogen peroxide (H_2O_2), hydroxyl radicals (OH.) are extremely strong oxidizing radicals and can react with almost all biomolecules [70]. Oxidative damage to the cell is caused by biomolecules deprived of their hydrogens, and a shortened life span [41].

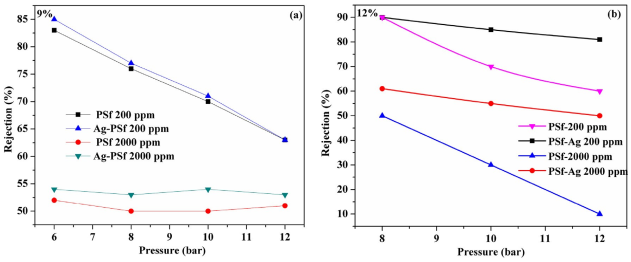

Fig. 11. *Rejection of Sulfate Solution using (a) 9% PSf and Ag-PSf (b) 12% PSf and Ag-PSf [64].*

A study by Angeline et al, the rejection of 200 ppm sulfate and 2000 ppm sulfate solution through the 9% and 12% membranes is shown in Fig. 11. As the pressure increases, rejection gradually started to decrease, as the solute is more likely to come into the filtrate at higher pressures. The rejection rate for 12% Ag-PSf membranes is comparably higher than 9% PSf membranes, 9% Ag-PSf membranes and 12% PSf membranes for both 200 ppm and 2000 ppm solute concentrations [71].

At all pressure ranges, the rejection rate decreased for 2000 ppm compared with 200 ppm, regardless of membrane concentrations (9% or 12%). This may be due to the polarization effect of the concentration, i.e. the increase in the concentration of the solute at the membrane surface at which the feed solution comes in contact [64–67]. The rejected solute forms a layer when the sulfate encounters the surface of the membrane, thus maintaining salt rejection. The concentration of the solutes at the surface of the membrane will be 20-50 times higher than the feed solution due to concentration polarization [73]. Therefore, for such a high sulfate concentration (2000 ppm), the rejection at all pressures was comparatively lower than the lower concentration (200 ppm).

The rejection rates of 9% and 12% of membranes (PSf and Ag-PSf), irrespective of pressure, are summarized in Table 2. The rejection of $MgSO_4$ using 12% Ag-PSf is 85% for 200 ppm and 73% for 2000 ppm which can include the concentration of the feed with 200 pm has been lowered to 30 ppm in the permeate and 2000 ppm has been lowered to 540 ppm [71].

Table 2. *Rejection of Magnesium Sulfate ($MgSO_4$) Solution [71].*

Concentration of $MgSO_4$ (ppm)	9% PSf (%)	9% Ag-PSf (%)	12% PSf (%)	12% Ag-PSf (%)
200	76 ± 1.78	77.6 ± 4.57	30 ± 3.50	85 ± 2.65
2000	50.6 ± 3.12	53.6 ± 3.35	62 ± 4.27	73 ± 4.77

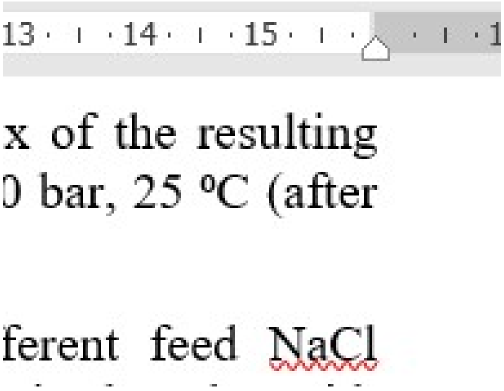

Fig. 12. *Effect of salt concentration on the salt rejection rate and water flux of the resulting Ag/PSf/PA membrane [76].*

A study by Shawky et al., the salt rejection rate of the Ag/PSf/PA membrane is measured at 12 bar and 25°C under various feed NaCl concentrations and the results are shown in Fig. 12. It is clear that the rejection rate of the membranes mainly being taken at lower salt concentration with the feed concentration increasing and then betake down when the salt concentration reaches approximately 2,000 mg/L [76]. In addition, the Ag/PSf/PA membrane is also typically sufficient for the processing of aqueous solutions with low salt concentrations, such as brackish water [79–83].

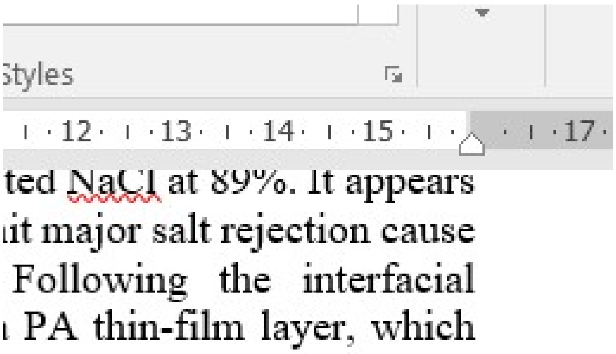

Fig. 13. *Effect of AgNPs concentration on salt rejection and water flux of the resulting Ag/PSf/PA membrane testing with 2000 mg/L NaCl aqueous solution at 10 bar, 25 ºC (after 60 min) [76].*

Salt rejections of PSf/PA and Ag/PSf/PA membranes from 2,000 mg/L NaCl an aqueous solution were measured at 10 bar based on Fig. 13. Ag/PSf/PA membrane rejected NaCl at 89%. The maximum salt rejection of NaCl at 92.5%. It appears that the PSf support layer's nano-porous constitution did not allow major salt rejection, causing permeate flux to be significantly higher than salt rejection [76]. These nanopores were covered by a PA thin-film layer after the IP process, which served as a salt ion reject [76]. With increasing Ag-NPs loading, the decrease in salt rejection could occur through the accumulation of Ag-NPs, which could occur more simply at a higher concentration [79–83].

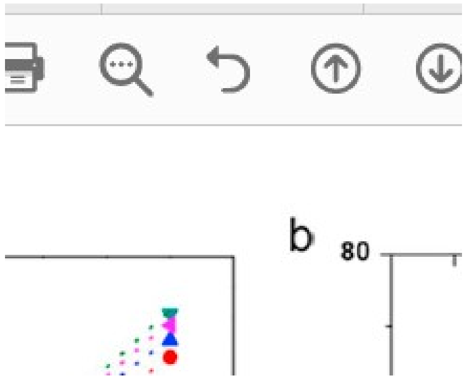

Fig. 14. *Solution flux and salt rejection [50].*

Table 3. *Effect of membrane on the NaCl rejection rate [50].*

Types of Membrane	TFC	TFC-SH	TFC-S-AgNPs
NaCl Rejection (%)	95.9 ± 0.6	93.4 ± 0.1	93.6 ± 0.2
Performance Drop (%)	-	2.5	2.3

A study by J. Yin et al., Ag-NPs immobilization was verified by cross-sectional TEM, SEM and energy dispersive X-ray spectroscopy (EDS) analyses. The thiol-terminated thin-film composite membrane (TFC-SH) and silver nanoparticle grafted membrane (TFC-S-AgNPs) showed a partially lower salt rejection compared to the virgin TFC membrane [50]. Figure 14 shows the salt rejection of the membranes. The NaCl rejection of control TFC, TFC-SH and TFC-S-AgNPs were 95.9 ± 0.6%, 93.4 ± 0.1% and 93.6 ± 0.2% respectively based on Table 3, at 300 psi constant transmembrane pressure. The performance drop happened to TFC-SH by 2.5% and TFC-S-AgNPs by 2.3%. Overall, the performance drop for TFC-SH was higher than TFC-S-AgNPs. It should be noted that the lower rejection of salt could be due to the impact of the ethanol solution used in the grafting process for the thiol-terminated membrane and TFC-S-AgNPs [50]. The grafted membrane of the Ag-NPs had an increased antibacterial capacity to inhibit Escherichia coli development (E. coli). As tested by both flow-through and batch strategies, the leaching of Ag from the grafted membrane surfaces of Ag-NPs was noted to be negligible. Also, the generation of biofilm on the TFC membrane surface was observed following a 7-day biofilm growth experiment, while the surface of the TFC-s-AgNPs was comparatively clear with no biofilm growth [50].

In a nutshell, Ag-NPs has proven very beneficial towards salt rejection of PSf membranes in desalination process. The results have proved that Ag-NPs can reduce the activity of bacteria due to a synergistic effect between direct particle specific biological effects and the release of Ag^+ ions [82]. Furthermore, Ag-NPs can stick to the bacterial cell which influences negatively the permeability and respiration of the bacteria, but particles affecting the cell membrane resulting in cell lysis. In this way, the Ag-NPs can go through the bacterial cytoplasm, causing damage to the DNA. Modification of Ag bring the impact in increasing the percentage of salt rejection such as silver oxide (Ag_2O), biogenic AG-NPS grafted membrane ($TFC - S - BioAg^0$) and Ag based-metal-organic framework (Ag-MOF). Ag_2O may help to develop a comparatively thicker rejection PA layer, which improved salt rejection. $TFC - S - BioAg^0$ increased the hydrophilicity of the PSf membranes while maintaining the relatively high salt rejection including showing the more excellent and longer-lasting antibacterial property. Recently, the use of Ag-MOF has been aiming to mitigate the biofouling in TFNC. Ag-MOF nanocrystals provided a biocidal activity during six months, showing an improvement in biofouling resistance, with increase in rejection. Typically, the addition of the fillers tend to change the surface properties of membranes influencing the separation performance such as excellent salt rejection against foulants and better antifouling behavior [88–90]. With widely dispersed immobilized Ag-NPs, these membranes possessed better antimicrobial properties and salt rejections than conventional membranes or membranes blended with Ag-NPs.

C. Silica Dioxide (SiO_2)

The silica nanoparticles (SiO_2-NPs) are examples of the main types of the nanomaterial that can be used in RO membrane systems that able to provide higher efficiency in the process of salt rejection to obtain clean fresh water from saline water [5,72]. Kim et al. have made several studies by adding SiO_2 nanomaterials into the specific membranes to increase the effectiveness of the salt rejection. The study from the authors provides that SiO_2-NPs can express some microporous frameworks but these microporous cannot survive in long term because as sea water or saline water passes through these pores, the pores can resize in much larger proportions as compared to before the process due to the interaction of the sea water with the saline group [88]. Therefore, based on the author's study, adding SiO_2 as a NP to membrane layer can be a starting point for creating chemical stability membranes and mechanical systems on it [74].

The problem with these SiO_2-NPs is that these NPs can be categorized as hydrophilic NPs which means that the salt rejection cannot be enhanced to a high level because the NPs cannot block more salts due to their characteristic limitations [89]. Pang et al. have discovered that the salt rejection problem can be solved when they concluded that using hydrophobic fluorinated SiO_2-NPs as special filler in TFNC could improve the salt rejection in the desalination process. Based on the authors experiment, these fluorinated SiO_2-NPs can distribute among organic phase because several IP process happen on the particles. The results of these fluorinated SiO_2-NPs loading towards the membrane on the impacts of salt rejection and water flux have been reveal in the Fig. 15.

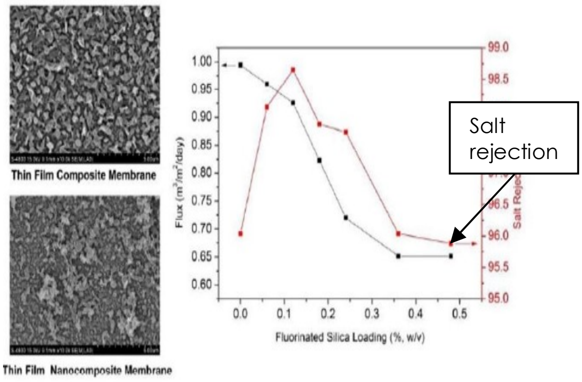

Fig. 15. *Impacts of fluorinated silica loading on membrane desalination performance which adding fluorinated silica in organic phase.*

Based on the Fig. 15 which is impacts of fluorinated SiO_2 loading on membrane desalination performance when adding fluorinated SiO_2 in organic phase, it was found that the salt rejection on the membrane has improve immediately in the beginning of the fluorinated SiO_2 loading and through the end, with the addition of fluorinated SiO_2-NPs from time to time can makes the salt rejection slightly decreases.

In addition, Pang and Zhang claimed that these combinations of the new technology of fluorinated SiO_2-NPs have change the surface of the membrane. The authors have concluded that the surface of membrane hydrophobicity has increased while the surface of membrane roughness has decreased from time to time. Other than that, the authors also observed at the time of organic solvent removal and IP reaction time on these NPs. From the data that have been provided from the authors, based on reading at optimal fluorinated SiO_2-NPs, which is at 0.12% (w/v), the rejection of salt increase significantly from 96% to 98.6%. According to the authors, this process where adding fluorinated SiO_2-NPs into TFNC-RO can be apply successfully because it can be done with a simple integration into the current membrane procedure. Also, this new hydrophobic SiO_2 technology may be a perfect way to solve the current problem about the salt rejection and produce a unique of performance TFNC-RO membrane [75].

Subsequently, Shen et al. have proved that they can demonstrate a simple technique for the fluorinated silica nanoparticles membrane through a process that is being called in-situ IP where the process of aqueous amine as well as acid chloride/silicon tetrachloride ($SiCl_4$) solutions, as shown in the Fig. 16 [90]. Shen et al. said that using this process can maintain the higher salt rejection [90]. They claimed that with the additional of 0.02% w/v $SiCl_4$, water permeability will increase around 171% while rejection of the NaCl in this process can maintain at the same value above the requirement which is above 97%. SiO_2-NPs is a good choice to conduct in-situ filler which will improve the surface of membrane and membrane performance in this process. Higher water flux and higher salt rejection can be achieved when further study has been made to discuss in detail about this process.

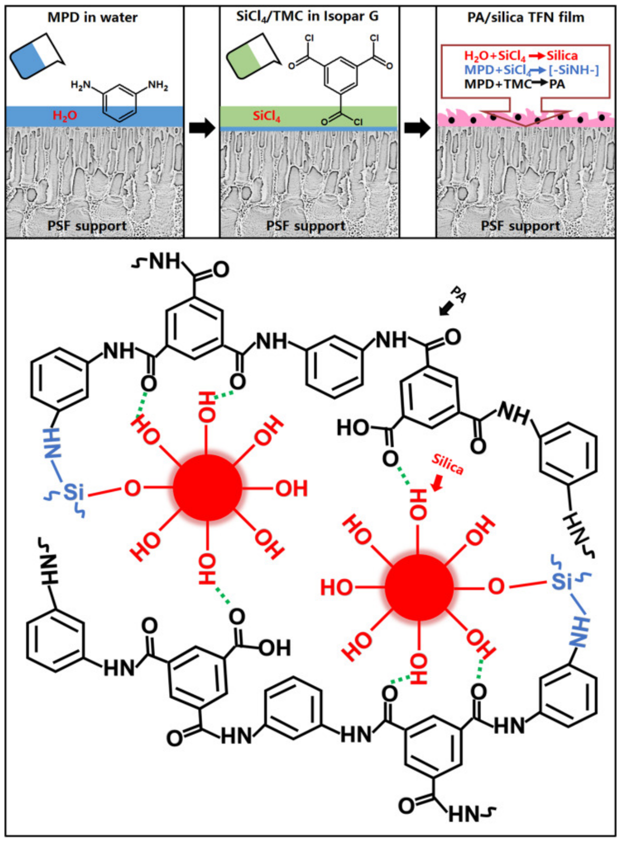

Fig. 16. *Schematic of silica TFN membranes via an in-situ IP reaction. Green dotted lines indicated hydrogen bonds whereas red circles with rich hydroxyl groups indicated silica nanoparticles and blue -Si-NH- indicated covalent bonds between silica nanoparticles and the polyamide.*

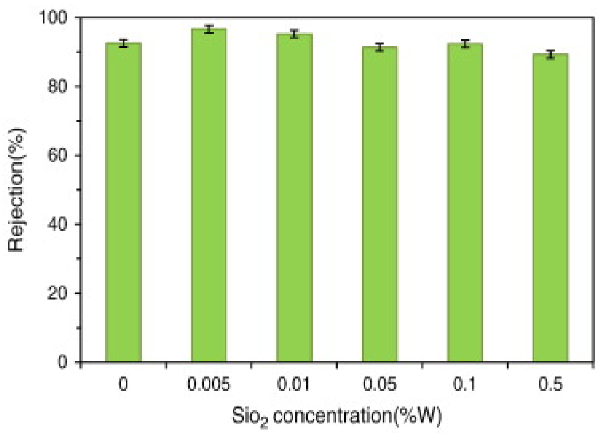

Fig. 17. *Rejection of unmodified and modified membranes versus silica content during reverse osmosis tests with aqueous salt solutions (11,000 ppm).*

Next, a study from Mary L. Lind et al. showed the effect of SiO_2-NPs on salt rejection from modified RO membranes in Figure 17 [91]. Based on the Fig. 17, the salt rejection was increased at lower contents of SiO_2 which is between 0.005 to 0.01 wt.% and then decreased with increasing of SiO_2-NPs content. The authors claim that lower contents of SiO_2, will give more compact structure which lead to increment of the salt rejection.

Based on the previous articles, it proved that SiO_2-NPs could be considered as effective nanomaterials that able to improve the performance of salt rejection in desalination membranes. Modifications of SiO_2-NPs to become hydrophobic fluorinated SiO_2-NPs also bring a huge impact to increase percentage of salt rejection to higher value such as 97% and above [75]. Hence, this review has shown that SiO_2-NPs are very beneficial towards salt rejection of the PSf membrane in RO process.

3.0 DISCUSSION

Based on the studies, it is shown that all nanomaterials brought an average increment towards the salt rejection performance compare to bare membrane. TiO_2 and Ag can reject both NaCl and MgSO4 while SiO_2 can reject NaCl only. Each of nanomaterials has their own criteria and mechanism to increase the salt rejection. Table 4 explain the comparison among the three nanomaterials.

Table 4. *Comparison result of salt rejection of each nanomaterials.*

Nanomaterial	Percentage of salt rejection for Bare Membrane/ 0% Concentration (%)	Highest salt rejection percentage (%)	Percentage difference (∆%)	Reference	Average highest salt rejection (%)
TiO_2	90	98	8	[42]	98.28
	97.4	97.8	0.4	[21]	
	96.65	99.03	2.38	[43]	
Ag	33.50	87.67	54.17	[71]	91.32
	89	92.5	3.5	[76]	
	96.5	93.8	-2.70	[50]	
SiO_2	95.8	98.6	2.8	[89]	98.05
	94	97.5	3.5	[91]	

From the data, TiO_2 have the highest average salt rejection which 98.28% while SiO_2 the second highest with 98.05% and Ag is the lowest. TiO_2 has the highest salt rejection because it has the ability to block salt ions from moving across the membrane [43]. TiO_2 can crosslinking in PA membrane as to reject the salt from water [43].

SiO_2 also have a good mechanism using in-situ IP reaction. It is because lower contents of silica, give more compact of structure which lead to increasing the salt rejection [91]. Therefore, SiO_2-NPs could be considered as effective nanomaterials as much as TiO_2 that able to improve the performance of salt rejection in desalination.

The performance drop has happened to TFC-SH by 2.5% and TFC-S-AgNPs by 2.3%. Overall, the performance drop for TFC-SH was higher than TFC-S-AgNPs. It should be noted that the lower rejection of salt could be due to the impact of the ethanol solution used in the grafting process for the thiol-terminated membrane and Ag-NPs grafted membrane.

On the other hand, there are some disadvantages of NPs that is challenging towards salt rejection in nanotechnology. Firstly, the greatest difficulty in the commercialization of TFNC membranes is leaching out of NPs into the downstream (retentate and permeate streams). The loss of chemical interaction between the PA matrix and nanomaterials will likely cause the NPs to readily leach out at the time of IP or filtration, thus reducing the productivity of NPs use at the time of production [7]. Haleema and Syed [7] showed that NPs agglomeration in the PA layer is another difficulty in the manufacture of TFNC membranes. Increasing water safety and ecological concerns, membrane degradation and property damage over time, and the generation of deformities inside the membrane structure are caused by these difficulties [7].

Despite that its disadvantages, NPs are more beneficial to the industry especially for increasing the salt rejection performance plus it is low cost and non-toxic. The mission to treat water with higher salt rejection in desalination process can be achieved by using nanotechnology.

4.0 CONCLUSION

In order to meet demand of clean water, desalination process has been implemented to treat the seawater by separating the salt from the water. Many improvements have been conducted to optimized desalination process to increase the salt rejection from seawater. Implementation of nanomaterial in the membrane is one of the approaches.

In average, all three nanomaterials improve salt rejection by having the percentage of rejection above 90%. Every NPs have positive characteristics and strengths of their own. TiO2-NPs is a low-cost and non-toxic NPs. That is why it is widely used, for example, as wastewater desalination and as water in various industries. High chemical stability is among the other advantages of TiO2. Next, Ag-NPs are chemically stable, have catalytic and conductive properties and are more antimicrobial than other metals. Ag is bacteriostatic, thereby deactivating cells but not fully destroying them. As a delivery carrier, SiO2-NPs have special properties, including excellent biocompatibility, high hydrophobicity, systemic stability and resistance to changes in pH, as well as great multi-functionality. From the overview, it is evident that the nanomaterials possess exclusive properties which can contribute to the advancement of high-tech NPs membranes with improved capabilities for desalination.

Overall, in order to truly understand and maximize the capabilities of NPs, the impact of NPs towards salt rejection performance, further study should be conducted such as long-term testing and huge range of concentration NPs. A long-term period of study should be done to determine the effectiveness of NPs towards membrane performance as only one-shot study had been done. In addition, studies in this field are required to produce TFNC membrane with increased performance for commercial application.

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