A REVIEW OF NANOTECHNOLOGY APPLICATION FOR SEAWATER DESALINATION PROCESS

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Abstract

As freshwater resource decreasing rapidly due to high rate of human population growth, many researchers have done studies to develop methods for producing freshwater supply. Seawater desalination is one of the method that has the credibility to be implemented. However, conventional seawater desalination processes suffer from a number of problems related to energy efficiency and cost. In spite of this, nanotechnology has been applied to the process. In this paper, we give an overview and explanations concerning the roles of nanotechnology in seawater desalination processes which consist of pretreatment, reverse osmosis (RO), and disinfection. In addition, the comparisons between conventional and nanotechnology-applied processes as related to its efficiency and effectiveness are also provided.

Keywords: Seawater desalination process, pretreatment, reverse osmosis, disinfection

Dewasa ini, sejumlah penelitian telah dilakukan untuk mengembangkan metode produksi sumber air bersih yang dapat diandalkan seiring dengan penyusutan sumber air bersih secara signifikan akibat tingginya angka pertumbuhan penduduk. Salah satu metode yang kredibel untuk diimplementasikan adalah desalinasi air laut. Meskipun demikian, metode desalinasi konvensional memiliki beberapa kelemahan, seperti tingginya biaya yang dibutuhkan dan efisiensi proses yang rendah. Oleh sebab itu, aplikasi teknologi nano mutlak diperlukan untuk meningkatkan efektivitas dan efisiensi proses tersebut. Dalam jurnal ini, penulis akan menyajikan ikhtisar dan penjelasan mengenai peran teknologi nano dalam proses desalinasi air laut yang terdiri dari pretreatment, reverse osmosis (RO), dan desinfeksi serta perbandingan efektivitas dan efisiensi antara proses desalinasi konvensional dengan proses desalinasi yang telah mengaplikasikan teknologi nano.

Kata kunci: Proses desalinasi air laut, pretreatment, reverse osmosis, desinfeksi

Introduction

Water plays an important role for maintaining sustainability of all lives on earth, especially human civilization. Nowadays, reliable access to clean water is one of the major challenge that humanity has to face. Although 70% part of earth is water, there is only 0.003% that can be used by human directly (Diallo, *et al.*, 2009). In addition, the rate of population growth is constantly rising. As a result, about 11% of population still lack access to clean water (Qu, *et al.*, 2013). Specifically in Indonesia, about thirty nine million people do not have access to clean water (UNICEF, 2014).

Several studies have been conducted to create practical and applicable water treatment techniques, such as distillation, filtration, microbial fuel cell, and seawater desalination (Karagiannis & Soldatos, 2007). Seawater desalination is one of water treatment techniques that has high

credibility to be applied in Indonesia due to its long coastal line. Furthermore, Indonesia's geographical position (on the equator) inflicts low salinity level of its seawater (about 3.5%) so desalination process is more reasonable to be applied (Karsidi & Rahardjo, 1996).

In fact, seawater desalination process has been applied in Israel, Iran, and several countries in Asia, including Indonesia. However, this technique is challenged by some problems related to energy efficiency, pollution, and cost. In general, conventional desalination has low energy efficiency, high level of pollution, and expensive operating cost (Karagiannis & Soldatos, 2007). Hence, several new methods have been established to increase the efficiency and effectiveness of this technique, one of them is nanotechnology application for seawater desalination.

Nanotechnology is the materials engineering and manufacturing at the atomic, molecular, and supramolecular scale (1 – 100 nm in size). This technology encompasses the understanding and fundamental of physics, chemistry, biology, and technology of nanometer-scale objects (Farokhzad & Langer, 2009). In seawater desalination process, nanotechnology is possible to be applied to the whole processes of the technique. The processes consist of pretreatment, reverse osmosis, and disinfection (Qu, *et al.*, 2013). In this paper, we provide an overview of the role of nanotechnology in the three processes mentioned above. In addition, we also examine the comparison between conventional and nanotechnology-applied processes related to its efficiency and effectiveness.

Seawater Desalination Process

Conceptually, seawater desalination process is a process of removing salts and minerals from saline water. This process separates saline seawater into two kind of streams; the first stream is fresh water containing low concentration of dissolved salts and the second stream is the concentrated brine stream (high concentration of salts) (Khawaji, *et al.*, 2007).

There are three major processes occurring in seawater desalination process: pre-treatment, reverse osmosis, and conditioning-disinfection. Specifically, reverse osmosis (RO) is the main process of seawater desalination. In this process, certain type of molecules and ions from the saline water are removed. Applied pressure is used to overcome osmotic pressure and semipermeable membrane removes undesirable particles from the solution (Lu, *et al.*, 2006). In case to perform a high quality reverse osmosis process, pre-treatment is conducted to prevent membrane fouling (major problem in reverse osmosis process) since the accumulated materials cannot be removed from the membrane surface systems (Brehant, *et al.*, 2002). Furthermore, disinfection process is used to remove harmful particles contained in the fresh water as the product of seawater desalination process (Tanaka, *et al.*, 1994).

Figure 1. Seawater desalination process chart (Toray Industries, 2006).

1. Pre-Treatment

For a successful desalination by seawater reverse osmosis (SWRO), a good and high quality pretreatment process is necessary. Pretreatment process in desalination by SWRO works by preventing fouling on the reverse osmosis (RO) membrane. Fouling is the main problem that need to be dealt with on the pretreatment process, since it has a degrading effect that cause a reduced lifetime to the condition of RO membrane elements, which will further lead to increasing operational costs and energy demand for maintenance and cleanings. Therefore, a good and cost-effective antifouling method is needed to prevent fouling from occurring, hence extending the lifetime of RO membrane and lowering the operational costs and energy demand for SWRO plants.

Besides fouling, a poor feed water can also cause a reduced lifetime of RO membrane elements, because the constant quality of the feed water is the main factor for a successful SWRO desalination operation. During pretreatment, the unnecessary material for the main process (e.g. suspended solids, dissolved organic contaminants, immiscible liquid, and soluble salts) in feed water also need to be removed or reduced to at least the maximum allowable level of contaminants (Alawadhi, 1997).

Pretreatment technologies for preventing fouling and extending lifetime of RO membrane are generally divided into two categories: conventional pretreatment, which includes coagulation, acidity (pH) adjustment, scaling inhibition, filtration with granular media, and disinfection, and non-conventional pretreatment, which includes beachwell system and pressure-driven membranes such as microfiltration, ultrafiltration, and nanofiltration. Both of those categories are widely applied in SWRO plants in the world. The technology used in each SWRO plants vary from conventional and non-conventional depending on the quality of the feed water (Prihasto, *et al.*, 2009).

1.1. Conventional Pretreatment

a. Coagulation

Coagulation causes small particle in the feed water to combine and form a larger mass of the particles. The aggregation is caused by the neutralization of electrical charges on the surface of the particles. As such, the coagulation occurs to prevent biomass from bio-mineralization

of some minerals such as iron and silica to form on the RO membrane surface as shown in figure below.

Figure 2. SEM of the RO surface of biosorption formation: (a) adsorption of organic matter onto the RO surface; (b) growth of organic matrix and inorganic biosorption on the organic matter; (c) growth of the biomass (Ma, *et al.*, 2007).

Other than being used in conventional pretreatment, coagulation have also been used for low pressure membrane pretreatment such as microfiltration (MF) and ultrafiltration (UF). However, coagulation as a pretreatment for desalination process needs a suitable coagulant, optimal dosage, and coagulation strategies for a successful process. A study conducted by Ma *et al.* showed that using potassium polymer ferrate (VI) as a coagulant and pre-oxidant prior to ultrafiltration cause an increase to algae and microbial removal up to 98% and therefore reducing the biomass formed on RO membrane (Ma, *et al.*, 2007).

b. Acidity (pH) Adjustment

Acidity (pH) adjustment can prevent scaling on the RO membrane elements through controlling the formation of certain scaling that depends on the acidity of the feed water such as calcium carbonate scaling. The solubility of calcium carbonates depends on the acidity of the solution, which can be explained as the equilibrium reaction below:

If more H^+ ion as an acid is added, the reaction will shift to the left in which the calcium carbonate is soluble. The acid used can be carbon dioxide, sulfuric acid, or hydrochloric acid (Prihasto, *et al.*, 2009).

c. Filtration

Filtration are commonly used in many pretreatment processes including desalination process. It mostly depends on the complex physical and chemical mechanism, including adsorption. As the feed water passes the filtration bed, the suspense particle will contact and stick to the

surface of the media or to the previously deposited particles (Chua, *et al.*, 2003). Furthermore, filtration can be grouped into three category based on the media used:

- Single media filtration; single-media filtration only use one media as the filter bed. Small-grained silica sand is the media that is often used for single media filtration, while other media such as anthracite or greensand may be used to remove specific substance or compounds from the feed water;
- Dual media filtration; dual media filtration use two media with different specific gravity as the filter bed, which will create two-layer separation effect. This will allow higher amount of material to be filtered;
- Mixed media filtration; mixed media filtration use three media with slightly intermixing between layers. The gradual change from this layers provide necessary flow pattern to get a low silt density index from feed water. Silica sand, garnet, and greensand are mostly used in mixed media filtration.

1.2. Pressure-Driven Membrane as Non-Conventional Pretreatment

Membrane separation technologies have been used in industries because of their adaptability and selectivity. Membrane is a thin barrier that permits selective mass transport of solutes and solvents across the barrier. Membrane have many differences in configurations, compositions, and characteristics that enable these processes to be used in various applications in industries. The rate of transfer of solutes or solvents across a membrane is controlled by a driving force, while the rate of solute rejection is controlled by the size and shape of the solute molecules. The types of driving forces include mechanical pressure, concentration or chemical potential, and temperature or electrical potential (Mortazavi, 2008).

Table 1. Pressure-driven membrane separation processes (Mortazavi, 2008).

Membrane	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse Osmosis (RO)
Thickness	1 - 150 micron	1 micron 150 - 250 micron	1 micron 150 micron	1 micron 150 micron
Rejection	Particles, clay, bacteria	Macromolecules, proteins, polysaccharides, vira	High molecular weight compounds (mono-, di-, and oligosaccharides, polyvalent ions)	High and low molecular weight compounds (NaCl, glucose, amino acids)
Materials	Ceramic, Polysulfonic (PS), Polyvinylidenefluoride (PVDF), Cellulose Acetate (CA) Thin Film	Ceramic, Polysulfonic (PS), Polyvinylidenefluoride (PVDF), Cellulose Acetate (CA) Thin Film	Cellulose Acetate (CA) Thin Film	Cellulose Acetate (CA) Thin Film
Pore Size	0.02 - 4 micron	0.02 - 0.2 micron	< 0.002 micron	< 0.002 micron
Module Configuration	Tubular hollow fiber	Tubular hollow fiber spiral wound, plate-and-frame	Tubular spiral wound, plate-and-frame	Tubular spiral wound, plate-and-frame
Operating Pressure	< 2 bar	1 - 10 bar	5 - 35 bar	15 - 150 bar

Pressure-driven membrane separation (PDMS) processes are applicable for treating mining-influenced water (MIW). Pressure-driven membrane separation are distinguished from each other by the molecular size of the contaminants of solutes that will be removed. Pressure-driven membrane separation processes use semipermeable membranes to reduce the concentration of the selected solutes in a feed solution, which contains the materials that filtered out of the feed solution.

a. Microfiltration (MF)

Microfiltration is a pressure-driven membrane separation process which removes contaminants from a fluid by part through a microporous membrane. Microfiltration is typically used to separate suspended solids (Mortazavi, 2008) and can be applied to waters that are easy to treat. Such clear cold water is known for being susceptible to microbial contamination. Microfiltration process uses low pressures and higher porosity, the membranes are unable to remove smaller compounds (Scott & Hughes, 1996).

b. Ultrafiltration (UF)

In ultrafiltration process, solvent and salts of low molecular weight pass through the membranes but large molecules are rejected. Ultrafiltration membrane effective at recovering floatation agents, surfactants and organometallic complexes. UF is sometimes used as a pretreatment option for feed solutions that is intended to be treated by NF or RO (Mortazavi, 2008).

c. Nanofiltration (NF)

Nanofiltration used for disinfecting feed water are challenged with problems such membrane fouling. Nanofiltration systems operated at a lower pressure than that of RO systems have higher fluxes across the membrane surfaces and the quality of permeate is lower than that of permeate from RO systems. Nanofiltration can be used to remove smaller particles than ultrafiltration and also used in the desalination process. This process can remove multivalent ions and dissolved compounds containing sulfate, phosphate, magnesium, and calcium according to the size and shape of the compounds (Mortazavi, 2008).

d. Reverse Osmosis (RO)

Reverse Osmosis uses thin-film composite membranes that are used for water purification or desalination process. Reverse Osmosis uses higher pressures than the other processes to force a feed solution through a semipermeable membrane. This process is used to remove ionic solutes, metals, and macromolecules from feed solution that used for desalination process but

not only desalination, the other applications in industrial waste water and mine water treatment.

Combined with other separation technologies such as UF, evaporation, and distillation, treatment hybrids can result in highly effective and selective separation process (Williams, 2013). Ideal properties of Reverse Osmosis membrane include resistance to chemical and microbial agents, structural stability over long operating periods, and appropriate separation selectivity for the feed solution.

2. Reverse Osmosis

Reverse osmosis (RO) is one of the key component in desalination (Diallo, 2009) and membrane has the major role in reverse osmosis system, especially in desalination which is the most complex (Roth, *et al.*, 2009). Hence, the performance and effectiveness of reverse osmosis system is depends on the membrane characteristics. Membrane performance are assessed by water flux, salt rejection, mechanical stability, and fouling resistance. On the other hand, capital costs, energy costs, and operation costs are the parameters of reverse osmosis efficiency (Balcajin, *et al.*, 2009). Generally, membrane-based process has several advantages such as continuous, low energy consumption due to no heating and phase changing, chemical-free, easy to scale up, and automated process control but unfortunately, membrane process has a short lifetime, limited chemical selectivity, concentration polarization, and membrane fouling. Specifically, conventional reverse osmosis process needs high performance pretreatment to reduce fouling, low flux operation, frequent cleaning and control, and high energy consumption (Hoek & Ghosh, 2009).

Table 2. Performance comparison of RO membrane.

Materials	Membrane Size	Salt Rejection	Water Flux	Description	Source
MFI Zeolite	0.56 nm ^a	76%	0.112 kg.m ⁻² .h ⁻¹	under 20.7 bar	Li, <i>et al.</i> , 2004
Modified Zeolite	2 µm ^b	90.60%	1.129 kg.m ⁻² .h ⁻¹	50:50 (Si:Al); under 28 bar	Rodriguez-Calvo, <i>et al.</i> , 2014
rGO/TiO ₂ /RO Membrane	-	99.45%	51.3 L.m ⁻² .h ⁻¹	0.02 wt.% rGO/TiO ₂	Safarpour, <i>et al.</i> , 2015
MWNTs MMM	-	95%	14-17 L.m ⁻² .h ⁻¹	for aqueous solution of polyethyleneoxide 100,000	Choia, <i>et al.</i> , 2006
MWNTs MMM	-	35-75%	>40 L.m ⁻² .h ⁻²	for aqueous solution of polyvinylpyrrolidone (PVP) 55,000	Choia, <i>et al.</i> , 2006
CNTs TFC	47 mm ^c	97.69%	44 L.m ⁻² .day ⁻¹ .bar ⁻¹	CNT diameter: 0.8 nm	Rodriguez-Calvo, <i>et al.</i> , 2014
Aquaporin MMM	-	97%	4 L.m ⁻² .h ⁻¹ .bar ⁻¹	-	Tang, <i>et al.</i> , 2012

^aPore Size

^bMembrane Thickness

^cMembrane Disc Diameter

At this point, nanotechnology seems promising in enhancing membrane performance and efficiency due to the unique properties and geometry of nanomaterial (Chae, *et al.*, 2009). Nevertheless, the infancy of nanotechnology brings out an issue of how to apply it. It still needs quantitative evaluation of major membrane characteristics such as fouling properties (Balcájin, *et al.*, 2009). Regardless of the limited data set for fouling properties, the novel and nanostructured membranes including zeolite membranes, thin film nanocomposite membranes, carbon nanotube membranes, and biomimetic membranes are discussed in this review.

2.1. Nanostructured Ceramic Membranes

Ceramic membranes are commonly made of alumina, silica, titanium, zirconia, or mixture of these material (Lee, *et al.*, 2011) which have mechanical stability to undergo the high pressure processed and higher fouling resistance than current polymeric membranes due to its chemical stability (Hoek & Ghosh, 2009). Generally, ceramic membranes consist of a macro-porous support layer and a mesoporous or microporous active layer where nanoparticles such as zeolite or other nanoparticles are embedded inside (Rodríguez-Calvo, *et al.*, 2014). Currently, ceramic membranes are commonly used in micro- and ultrafiltration application (Lee, *et al.*, 2011). Nevertheless, the concern about optimizing functional membrane still going on research for expanding their functionalities. Each of nanoparticles as coating material has their own functionalities for fabricating ceramic membranes (Kim & Bruggen, 2010).

a. Zeolite-Coated Ceramic Membranes

Naturally, through hydrothermal synthesis, zeolite contains aluminosilicate with nano sized crystalline structure. The inert characteristic of aluminosilicate crystal equipped these membrane with the thermal and chemical stability to prevent fouling (Hoek & Ghosh, 2009). Its material potential be examined with molecular dynamic simulation of a perfect all-SI ZK-4 zeolite membrane show 100% ion rejection. This theoretical calculation showed that zeolite membranes has smaller pore size than the hydrated ion.

Synthetic A-type zeolite has 0.4 nm pores and MFI zeolite has 0.56 nm pores (Lee, *et al.*, 2011). The experiment of MFI zeolite on RO showed a result of 76% Na⁺ rejection from 0.1 M NaCl solution with a water flux of 0.112 kg.m⁻².h⁻¹ under 20.7 bar pressure. This low ion rejection was caused by nanometer-sized intercrystalline pores which diminish the efficiency of ion rejection for high concentration and multivalent cations contained solutions. These result also shows that the filtration mechanism is not only depending on size exclusion, but also on charge (Donnan) exclusion which less dominant for monovalent ions due to the charged double layer induced by the adsorbed ions on the intercrystalline walls (Li, *et al.*, 2004). However, zeolite performance to reject salt with high water flux could be improved by changing the ratio of Al and Si composition which affect the wettability and the membrane

surface charge. Affinity with water which depends on surface hydrophilicity could be controlled by the Al composition.

Figure 3. Flow diagram of the in-situ crystallization method for the synthesis of zeolite membrane (Wee, *et al.*, 2008).

Moreover, the growth of secondary layer of zeolite on zeolite seeded onto a porous α -alumina substrate could minimize the defect in the crystal structure (Lee, *et al.*, 2011). A tremendous improvement was gained by resetting the composition ratio of Al and Si into 50:50. A membrane with 2 μm thick could increase the water flux from 0.112 to 1.129 $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at 28 bar. Besides, when 2.0 % mole a Si^{4+} in zeolite framework replaced by Al^{3+} , the ion rejection increased from 90.6 % to 92.9%. As the experiment continues, zeolite membrane thickness was reduced up to 0.7 μm and capable of rejecting more organic (>99%) and salts (97.3%) with 4 times improvement in water flux (Rodríguez-Calvo, *et al.*, 2014).

Figure 4. Micro-porous ceramic membrane structure: micro-porous site in the crystalline structure (a) Type A Zeolite; and (b) MFI Zeolite (Baerlocher, *et al.*, 2007).

If compared to polymeric membrane, zeolite membrane showed a better performance in permeability and selectivity. Chemical stability of zeolite membrane could resist the harsh chemicals condition and the mechanical stability of zeolite membrane could withstand high pressure and temperature (Li & Wang, 2010). These characteristics are highly favorable for desalination. Nevertheless, the challenges for zeolite membrane comes from the economical and performance issue due to its thickness that at least 3 times higher than current polymeric membranes. As a result, to generate the same result of production capacity, inorganic membranes require at least 50 times area higher than polymeric membranes (Lee, *et al.*, 2011). Finally, further development specifically in nanotechnology for enhancing zeolite membrane performance is necessary to be continue.

2.2. Inorganic-Organic Membranes

a. Mixed Matrix Membranes (MMM)

The concept of mixed matrix membranes is to the combination of the low cost and ease of fabrication from organic materials with the mechanical stability and functional properties from inorganic materials (Hoek & Ghosh, 2009). Since 1980, mixed matrix membranes made from silicalite-cellulose acetate were developed for the gas separation which exhibit a better selectivity than conventional polymeric membranes (Kulprathipanja, *et al.*, 1988). However, the development of combining inorganic materials into organic RO Thin-Film Composite (TFC) was started in the early 2000's (Lee, *et al.*, 2011) which was due to most research and development in mixed matrix membranes are for gas separations, pervaporation, and fuel cell application that seek the most efficient combination of matrix and filler materials (Diallo, 2009). Nevertheless, the current development of nanotechnology offers new degree of freedom in RO membranes development with a better mechanical, chemical, biological, and thermal stability.

b. Nanoparticle/Polymeric membranes

Nanoparticle/polymeric membrane is a conventional or a macroscopic material (the “matrix”) that is enhanced by adding a nanocomposite material (the “filler”) into it (Komarneni, 1992). The membrane performance enhancement from nanocomposite material covers mechanical properties (e.g., strength, modulus, and dimensional stability), thermal and chemical stability, permeability, electrical and thermal conductivity, surface properties, optical properties, and dielectric properties. Generally, the nanophase is dispersed into the matrix during the fabrication, but the mass fraction of nanocomposite is low (mostly less than 5 percent) due to its high specific surface area (Diallo, 2009). Fig. 5 below compares polymerization of Thin Film Nanocomposite (TFN) membrane to conventional TFC membrane. As it is shown

below, nanoparticles are dispersed into TMC/n-hexane solution to synthesize TFN membrane.

The common nanomaterial used in TFN synthesis is TiO_2 due to its unique properties (i.e., high chemical stability, low toxicity, defouling and photocatalytic properties and availability) (Safarpour, *et al.*, 2015). In spite of that, the negative effect of nanoparticles observed on the morphology and performance due to the aggregation and agglomeration of TiO_2 particles (Ganesh, *et al.*, 2013). In order to overcome this issue, carbon based materials has been investigated frequently in recent years. Previous studies on graphene and graphene oxide (GO) for preparing TFN membranes shows tremendous improvement (i.e., high surface area, compatibility, prominent electron transport, great mechanical properties and superior hydrophilicity) (Wang, *et al.*, 2012). High hydrophilicity of GO emerged from the presence of several oxygen functional group (e.g., hydroxyl, epoxide, carbonyl and carboxyl) on its surface. Moreover, the high surface area of GO allows other nanoparticles such as TiO_2 to be dispersed in (Safarpour, *et al.*, 2015).

Figure 5. Schematic depiction of TFC/TFN membrane fabrication. Note: MPD = m-phenylene diamine; TMC = trimesoyl chloride; TFC = thin film composite (pure polyamide), and TFN = thin film nanocomposite (inorganic–organic mixed matrix) (Diallo, 2009).

The latest reduced graphene oxide (rGO)/ TiO_2 /RO membrane evaluation for desalination performance that was done by Mahdie Safarpour in February 2015 shows water flux performance of $51.3 \text{ L.m}^{-2}.\text{h}^{-1}$ and salt rejection of 99.45% with 0.02 wt.% rGO/ TiO_2 . A composition of 0.02 wt.% rGO/ TiO_2 in RO membrane had the best antifouling property in Bovine Serum Albumin (BSA) solution filtration. Also, after chlorination the 0.02 wt.% rGO/ TiO_2 membrane, only decrease 3% of salt rejection that indicates a remarkable improvement compared to bare RO membrane that plummeted from 95.40 to 65.38% due to conformational deformation of polyamide chains. This chlorine resistance characteristics of rGO/ TiO_2 /RO membrane might improve hydrophilicity and rGO/ TiO_2 layer able to protect polyamide layer (Safarpour, *et al.*, 2015).

Another nanomaterial which embedded into TFC membranes is zeolite (Figure 6). Zeolite nanoparticle might enhance separation performance, reduced fouling, antimicrobial activity, and other novel functionality of TFC membrane (Hoek & Ghosh, 2009). These advantages comes from zeolite nanoparticle which synthesized via complex processes involving templated hydrothermal reaction, template removal, carbonization, sodium exchange, and calcination. These processes produces a highly hydrophilic particles (contact angle $<5^\circ$), and highly repulsive to anions by negatively charged 0,4 nm pores (Lee, *et al.*, 2011).

Figure 6. Schematic cross-section of zeolite nanocomposite membrane (Lee, *et al.*, 2011).

The NaA-type zeolite particles with Si / Al ratio of 1,5 and size range of 50-150 nm are dissolved into TMC in hexane solution, and ultrasonication process carried out to homogenized the zeolite particles dispersion before the interfacial polycondensation reaction take place. The various amount of zeolite filler might affect the RO membrane characteristics, i.e. as amount of zeolite filler is increased, the membrane becomes smoother, more hydrophilic, and negatively charged. This MMM membrane shows 90% of flux and slight enhancement of salt rejection compared to conventional TFC membrane. This improvement might be the result of enhanced charge (Donnan) exclusion by the zeolite nanoparticles and changes of membrane morphology (Jeong, *et al.*, 2007).

c. Carbon Nanotube/Polymeric Membranes

Mixed-CNT membrane is an upgrade for UF with nanotubes. The MMM synthesis implicate MWNTs ($>5\%$ by weight volume) which embedded into polysulfone. The experiment intended to measure water flux and salt rejection under an operating pressure 1-4 bar (Choia, *et al.*, 2006). The result shows two contrary data for water flux and salt rejection according to the molecular weight of the solute. For an aqueous solution of polyethyleneoxide 100,000, the water flux was $14-17 \text{ L/m}^2 \cdot \text{h}$ and 95% of solute rejection. In contrast, for an aqueous solution of poly-vinylpyrrolidone (PVP) 55,000, the solute rejection decreased by 20-60%,

while the water flux was increased to $> 40 \text{ L/m}^2\text{.h}$ (Ahn, *et al.*, 2012). It shows that another method needed to accomplish high solute rejection and high water flux at once.

Figure 7. Molecular structure of SWNT (Single-Walled Nano-Tube) and MWNT (Multi-Walled Nano-Tube) (Rodríguez-Calvo, *et al.*, 2014).

Figure 8. Schematic cross-section of CNTs embedded TFC membrane (Rodríguez-Calvo, *et al.*, 2014).

A US patent invented (Ratto, *et al.*, 2011) might overcome this issue. They blend CNTs into cross-linking agent solution (trimesoyl of isophthalic chloride) as the formulation. The CNTs were embedded onto barrier layer formed by conventional interfacial polymerization on micro-porous polysulfone support (Figure 8) (Rodríguez-Calvo, *et al.*, 2014). According to (Lee, *et al.*, 2011), the CNTs need to be functionalized to achieve better solubility in organic solvent, and octadecylamine was used in the patent. The resulting membrane can be easily adapted into RO system with 0.8 nm CNTs diameter were used (Rodríguez-Calvo, *et al.*, 2014).

After the test, the result of membrane with and without CNTs were compared. From the result, (Lee, *et al.*, 2011) concluded that membrane with enhancement from CNTs exhibit a slightly higher salt rejection (97.69% as compared with 96.19%) and almost twice of water flux was obtained ($44 \text{ L/m}^2\text{.day.bar}$ as compared with $26 \text{ L/m}^2\text{.day.bar}$) (Rodríguez-Calvo, *et al.*, 2014). Nonetheless, the membrane disc tested was only synthesized with 47 mm in diameter,

further studies on larger surface area are needed so that larger scale manufacturing method can be applied.

2.3. Biomimetic RO Membranes

Biomimetic membranes are designed to imitate biological membrane that possess highly selective transport of water and solutes. Previous studies on membrane nanotechnologies, biomimetic RO membrane such as aquaporin-based, was exhibited the best performance for desalination (Tang, *et al.*, 2012). Characteristics and performance of aquaporin membranes will be discussed concisely in the next section.

a. Aquaporin Membranes

Figure 9. Schematics stopped-flow measurement (Tang, *et al.*, 2012).

Aquaporins are a kind of protein with pore and exists in living cells. Under certain conditions, they form ‘water channels’ to exclude ionic species, but water permeability and solute rejection of single aquaporin is arduous to measure. Molecular dynamics simulation of aquaporin disclose that water permeability of aquaporin is in the range $3\text{-}30 \times 10^{-14} \text{ cm}^3/\text{s}$ (Jensen & Mouritsen, 2006). The other method to achieve aquaporin water permeability is stopped-flow method (Fig. 9). Based on stopped-flow measurement, water permeability of aquaporin is in the range of $2\text{-}20 \times 10^{-14} \text{ cm}^3/\text{s}$ which exhibits similar results compared to molecular dynamics simulation results (Tang, *et al.*, 2012). Comparison of aquaporin water permeability with several membranes are summarized on figure 10 below:

Figure 10. Comparison water permeability of polymer vesicles with Aquaporin (AqpZ-ABA) or without Aquaporin (ABA) to those of polymeric membranes. FO is a commercial forward osmosis membrane; RO is a commercial reverse osmosis membrane, and EE-EO is a polyethylenepolyethylene oxide diblock polymer (Kumar, *et al.*, 2007).

Even though it has high water permeability, aquaporin has several obstacles in the production phase, due to its complex structure, hydrophobic transmembrane regions, host toxicity, time consuming, and requiring low efficiency steps. Nonetheless, recent development of high-expression system might resolve aquaporin large scale production issue (Tang, *et al.*, 2012). Several strategies have been proposed to scale-up nano-constructed aquaporin to m^2 dimension which is more suitable for industrial application. One of the strategies is to treat aquaporin-containing vesicles as the filler in mixed matrix membrane method (Fig. 11). In the first stage, the microporous substrate is soaked into aqueous solution of *m*-phenylene-diamine (MPD) that contains given amount of aquaporin-containing vesicles. The soaked substrates were then reacted with trimesoyl chloride (TMC) to form interfacially polymerized polyamide rejection layer, where the vesicles were scattered in the thin rejection layer. In this method, aquaporin-containing vesicles could provide favorable water paths through the polyamide layer and thus significantly increase the water permeability of the membrane (Tang, *et al.*, 2012). Moreover, the crosslinked polyamide might support and protect the aquaporin-containing vesicles in the environment. This resulting membrane showed a water permeability of $4 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ with NaCl rejection of 97% under applied pressure 5 bar (Zhao, *et al.*, 2012).

Figure 11. Preparation of aquaporin based biomimetic membranes by interfacial polymerization. The polymerization results in a thin matrix (yellow) with aquaporin-containing forming the active layer supported by a microporous substrate (Zhao, *et al.*, 2012).

3. Disinfection

The development of nanotechnology in the process of desalination, especially in the disinfection process is in great need to improve the efficiency and effectiveness of water disinfection. There is also the potential of application of nanotechnology in this process, such as the use of nanomaterials that can replace conventional applications. Conventional applications such as UV disinfections, chemical disinfections, and ozone disinfections have been known to produce unknown organic reactions while the infection is still occurring after the separation process is done (Amin, *et al.*, 2014). So, the separation process with the advancement of technology needs to overcome these problems. There are several advantages of nanomaterials, among others, it can reproduce or recycle nanoparticles, and it is easily separated from the water. But these are in need of long-term research to examine the negative effects resulting from nanoparticles that can happen. There are many applications of nanotechnology used in the disinfection process, such as titanium dioxide nanoparticles (TiO_2), silver nanoparticles (Ag), and carbon nanotubes (CNT).

3.1. Titanium dioxide nanoparticles (TiO_2)

TiO_2 nanoparticles and nanocrystallines irradiated with UV visible light exhibited strong bactericidal activity against *E. coli* (Maness, *et al.*, 1999). TiO_2 nanoparticle can inactivate

microorganisms under UV/solar irradiation by forming some reactive oxygen species (ROS) such as hydroxyl radical (OH), superoxide radical (O_2^-) and hydrogen peroxide (H_2O_2) (Sunada, *et al.*, 1998). ROS are formed by reaction of surface oxygen and water with positive cavities formed on TiO_2 crystal lattice during UV/solar irradiation (Huang, *et al.*, 2005). When energy (derived from photon) that is equal to or is greater than the bandgap energy of the TiO_2 , electrons are released from valance band leaving holes and forming the so-called exciton. At that time, a suitable electron scavenger (for example O_2) is necessary to protect the recombination of valance band holes and conduction band electrons. The valance band holes and the conduction band electrons are powerful oxidants and reductants. By preventing the recombination, successive redox reactions may form the ROS in the matrix (Hoffman, *et al.*, 1995).

Deckers found that TiO_2 NP was very effective to inactivate *E. coli* but *Cupriavidus metallidurans* CH_{34} exhibited some resistance (Deckers, *et al.*, 2009). There was no significant inactivation of *C. metallidurans* but *E. coli* inactivation was noticeable after 24 h of contact time. The authors concluded that TiO_2 nanoparticles may penetrate the peptidoglycan (PG) layer while PG layer of *C. metallidurans* has more stability when contacted to these nanoparticles. Additionally, some plasma membrane properties of *C. metallidurans* may repair or replace the damaged cell membrane very quickly, a process that can explain its enhanced resistance to TiO_2 . Therefore, bacteria death was depending not only on the availability of ROS but also on the membrane integrity in presence of ROS (Deckers, *et al.*, 2009). Additionally, Cho, *et al.* (2005) applied the TiO_2 nanoparticles to inactivate the *E. coli* as well as MS-2 phase. They found that OH was responsible for inactivating two of the targeted microorganisms but it was depending on the type of OH (for example bulk phase OH and surface phase OH). MS-2 phase was sensitive to bulk phase free OH, while *E. coli* was inactivated by both surface and bulk phase OH, including minor interaction with H_2O_2 and O_2^- .

Nanostructured TiO_2 films and membranes are capable of disinfecting microorganisms in addition to the decomposition of organic pollutants under UV and visible light irradiation (Choi, *et al.*, 2009). Due to its stability in water, TiO_2 can be incorporated in thin film or membrane filters for water filtration. TiO_2 nanorods and nanofilms exhibited a higher photocatalytic activity than commercial TiO_2 nanoparticles and TiO_2 thin films.

Based on the above considerations, it becomes evident that TiO_2 can be a promising alternative candidate for water disinfection. Smaller particles, exhibiting large specific surface area can effectively release free radicals to facilitate the inactivation process.

3.2. Silver nanoparticles (Ag)

Silver is the most widely used material due to its low toxicity and microbial inactivation in water with well-reported antibacterial mechanism (Yamanaka, *et al.*, 2005). The size of the antibacterial effect is dependent, smaller Ag nanoparticles (8nm) were most effective, while larger particle size (11-23 nm) results in lower bactericidal activity (Makhluf, *et al.*, 2005). The shape of the antibacterial effect is also dependent, truncated triangular silver nanoplates exhibited better antibacterial effects than the spherical and rod-shaped nanoparticles (Pal, *et al.*, 2007).

The author (Feng, *et al.*, 2000) and (Sondi & Sondi, 2004) suggested possible inactivation of bactericidal mechanism, involving protein denaturation caused by bringing of functional groups of protein with Ag⁺ (Feng, *et al.*, 2000) and severe cell structural change and degradation that was induced by the nanoparticles interaction with cell component. Ag⁺ caused irreversible cell damage by accumulating nanoparticles in the cytoplasm (Sondi & Sondi, 2004).

Ag nanoparticles are also incorporated into different types of polymers for the production of antimicrobial nanofibers and nanocomposites (Botes & Cloete, 2010). Poly (ϵ -caprolactone-) based polyurethane nanofiber mats containing Ag nanoparticles were prepared as antimicrobial nanofilters in a study (Jeon, *et al.*, 2008). Different types of nanofibers containing Ag nanoparticles are prepared for antimicrobial application and exhibited very good antimicrobial properties. Water filters prepared by polyurethane's foam coated with Ag nanofibers have shown good antibacterial properties against *Escherichia coli* (*E. coli*). Ag nanocatalyst alone and incorporate with carbon covered in alumina has been demonstrated as efficient for degradation of microbial contaminants in water (Chaturvedi, *et al.*, 2012).

Alternatively, doping of Ag nanoparticles with other metallic nanoparticles or its composites with metaloxide nanoparticles can solve the issue and this could also lead to the parallel removal of inorganic/organic compounds from water/wastewater. Although Ag concentration that meet drinking water quality standards is not determined by WHO or other water regulating authorities, immobilized Ag can be a good alternative as disinfectant because of higher surface area to volume ratio and its tremendous antimicrobial properties (Hossain, *et al.*, 2014). Ceramic filter and Membrane or paper impregnated Ag nanoparticles can be applied in POU (point-of-use) water treatment process in case of emergency (Dankovich TA, 2011). Furthermore, Ag nanoparticles can enhance the inactivation efficiency while reducing the time and nano disinfectant requirement for a system (Hossain, *et al.*, 2014). The practical application of nanoscale silver, however, is limited by probable side-effects caused by the release of nanoscale silver particles and/or dissolved Ag species in water, which would play a detrimental effect on the impacted aqueous environment. A careful evaluation of the physical and chemical stability of immobilized silver in an aqueous media (natural or effluents) will be then necessary for its prudent use.

3.3. Carbon nanotubes (CNT)

CNTs have proved to be very effective in removing bacterial pathogens. CNT which have been used for removal of biological impurities have received special attention for their excellent capabilities of removing biological contaminant from water (Savage & Diallo, 2005). CNTs possess antimicrobial characteristics against a wide range of microorganisms including bacteria and virus.

Filtration membranes containing radially aligned CNTs are very effective in removing both bacteria and viruses in very short time due to size exclusion and depth filtration (Vecitis, *et al.*, 2011) and thus enable such filters to be used as cost effective and point of use water disinfection devices. CNTs can also reduce membrane biofouling and a nanocomposite membrane of single-walled CNTs and polyvinyl-N-carbazole showed high inactivation of bacteria upon direct contact in a study (Ahmed, *et al.*, 2012). Another example of controlling the biofouling in thin film nanocomposite membranes is the single-walled CNTs covalently bonded to thin film composite membrane surface which have exhibited moderate antibacterial properties (Tiraferri, *et al.*, 2011).

The effectiveness of multi-walled carbon-nanotubes (MWNTs) compared to single-walled carbon-nanotubes (SWNTs) to inactivate *E. coli* has been observed as well. SWNTs were more efficient than MWNTs as bactericidal agent due to SWNT's smaller diameter and cylinder-like shape. Bacteria in SWNT suspension exhibited a severe structural damage and became flattened whereas bacteria in MWNT suspension did not exhibit any inhibiting effect and maintained their membrane structure. Other bio-chemical reactions including glycolysis, fatty acid beta-oxidation and fatty acid biosynthesis might also be effected by CNT. Furthermore, oxidative stress caused by CNT can also be considered a pathway of bacteria inactivation (Kang, *et al.*, 2008).

The CNT efficiency can be affected by the characteristics of the aqueous matrix such as the presence of salts, natural organic matter and characteristics of CNT itself. Performance of CNT can be evaluated according to length, diameter, matrix quality and species of microorganisms to get valuable knowledge about potential application. Although CNT has some adverse effects on human health and the environment, organized research can increase its benefit and decrease its unfavorable effects. CNT as a nanoadsorbent can simultaneously remove other contaminants from water.

In particular, SWNT and MWNT (Kang, *et al.*, 2008) may have important use in membrane technology. These two nanomaterials can be used in short and flexible form homogenously dispersed in a membrane matrix to limit their unintentional release into the water media. Although these nanotubes have shown significant antimicrobial efficiency, it is still indispensable to improve our understanding of their antimicrobial activity, stability, durability, exposure and negative health effect. These nanotubes can be used as a benign biofilm growth

catalyst for biological wastewater treatment. Therefore, it seems feasible to achieve synergistic use of these nanomaterials as water filtering and antimicrobial agents in membrane process. Although CNT-based nanofilters can be used to derive potable water from sea water, their performance still needs to be improved to meet water quality requirements (Hillie T, 2007).

4. Post-treatment

Post-treatment consists of preparing the water for distribution after filtration. Reverse osmosis is an effective barrier to pathogens, but post-treatment provides secondary protection against compromised membranes and downstream problem. Reactor catalyst offers the way to modify the surface properties of nanoparticles.

Figure 12. The scheme of reverse osmosis system (Dominic, 2015).

They have very high surface-to-volume ratio and porosity, and are very active against waterborne pathogens, less toxic with minimum health risks, as well as provide solutions to ensure safe water (Amin, *et al.*, 2014). It is very easy to dope functional nanomaterials to form multifunctional media/membrane filters with increased reactivity and selectivity for different contaminants. The use of nanofibrous composites membranes for water/wastewater treatment is very limited and a stand-alone system is proposed for removing all types of contaminants including bacteria/viruses, heavy metals and ions, and complex organic compounds (Amin, *et al.*, 2014).

Figure 13. Schematic of a proposed composite nanofibrous media/membrane filters for complete removal of contaminants from water/wastewater (Amin, *et al.*, 2014).

Conclusion

Nanotechnology has the credibility to be applied in seawater desalination process. Nanoengineered materials, such as nanoadsorbents and nanomembranes offer high potential for novel water treatment technologies, they are easy-to-apply and are able to be integrated into conventional processes. Furthermore, nanomaterials result in a higher efficiency process due to its unique properties.

However, there are still several drawbacks that have to be considered; environmental effects since they might be released and emitted to the ecosystem, and it is difficult to produce nanomaterials due to its molecular size so higher production cost would be needed. Finally, nanotechnology is reasonable to apply in laboratory scales but it may be difficult to be scaled up for an industrial scale. This will remain a challenge that must be solved through substantial research and development efforts.

Endnotes

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