Membrane Water Treatment, *Vol. 8, No. 5 (2017) 463-481*
DOI: https://doi.org/10.12989/mwt.2017.8.5.463

Modified membrane with antibacterial properties

P.T.P. Aryanti[1a], M. Sianipar[2b], M. Zunita[3c] and I.G. Wenten[*3]

[1]*Chemical Engineering Department, Jenderal Achmad Yani University, Jl. Terusan Jend. Sudirman, Cimahi, Indonesia*
[2]*Research Center of Nanosciences and Nanotechnology, ITB, Jl. Ganesa 10, Bandung - 40132, Indonesia*
[3]*Chemical Engineering Department, ITB, Jl. Ganesa 10, Bandung - 40132, Indonesia*

(*Received September 9, 2016, Revised March 28, 2017, Accepted May 17, 2017*)

Abstract. Bacteria have been considered as a major foulant that initiates the formation of biofilm on the polymeric membrane surface. Some polymeric membranes are naturally antibacterial and have low fouling properties, however, numerous efforts have been devoted to improve their antibacterial performance. These modifications are mostly carried out through blending the membrane with an antibacterial agent or introducing the antibacterial agent on the membrane surface by chemical grafting. Currently, a significant number of researches have reported nanocomposite membrane as a new approach to fabricate an excellent antibacterial membrane. The antibacterial nanoparticles are dispersed homogenously in membrane structure by blending method or coating onto the membrane surface. Aim of the modifications is to prevent the initial attachment of bacteria to membrane surface and kill bacteria when attached on the membrane surface. In this paper, several studies on antibacterial modified membranes, particularly for water treatment, will be reviewed comprehensively. Special attention will be given on polymeric membrane modifications by introducing antibacterial agents through different methods, such as blending, grafting, and coating.

Keywords: antibacterial membrane; biofouling; membrane modification; antibacterial agents; water treatment

1. Introduction

The application of polymeric membrane in water treatment fields has grown significantly due to its low cost production, easy preparation and adjustable pore structure, high quality of product, easy scale up, lower energy consumption, and environmentally friendly (Ariono *et al.* 2017, Ariono *et al.* 2016, Khoiruddin *et al.* 2014, Wenten *et al.* 2016, Wenten *et al.* 2013). However, applications of the membrane are limited by fouling formation that contributes to flux loss, increasing of trans-membrane pressure, and change in membrane selectivity (Khoiruddin *et al.* 2014, Wenten 1995, Wenten *et al.* 2002). As the major component of microorganisms in water, bacteria contributes to biofilm formation on the membrane surface that initiates adsorption

*Corresponding author, Professor, E-mail: igw@che.itb.ac.id
[a]Ph.D., E-mail: p.teta@lecture.unjani.ac.id
[b]MsC., E-mail: sianipar.merry@yahoo.com
[c]Ph.D., E-mail: m.zunita@che.itb.ac.id

http://www.techno-press.org/?journal=mwt&subpage=7 ISSN: 2005-8624 (Print), 2092-7037 (Online)

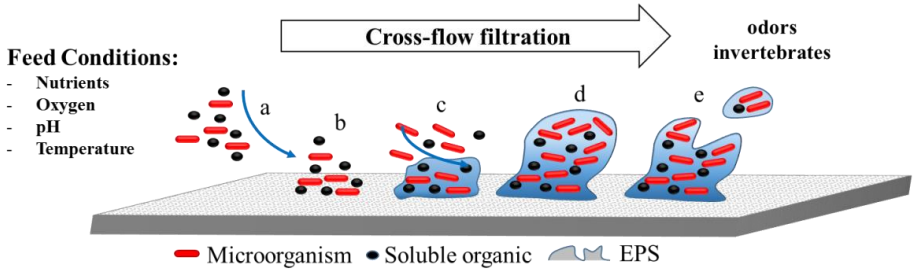


Fig. 1 The growth of biofilm on membrane surface: (a), (b) adsorption of microorganism (bacteria), (c) EPS formation, (d) growth of biofilm, and (e) dispersal of microorganism from EPS

interaction of other organic molecules into the film and forms extracellular polymeric secretions (EPS) (Guo *et al.* 2012, Saeki *et al.* 2016). The matrix of biofilm leads to the entrapment of inorganic particles and form an irreversible fouling layer on the membrane surface (Fig. 1). Furthermore, the presence of biofilm induces concentration polarization on the membrane surface and leads to the increase of hydrodynamic pressure as well as operational cost (Ferrando *et al.* 2017, Zhang *et al.* 2013).

The growth of biofilms formation on the membrane surface is controlled by some parameters, such as feed water conditions, i.e., nutrients, oxygen concentration, pH, and temperature. pH of solution contributes to its isoelectric point (IEP) properties on the substance electrical charge (Qiu *et al.* 2009, Wu *et al.* 2016). When the pH of solution was higher than IEP substance, the bacteria has negative charge. Since most commercial membrane surfaces are hydrophobic and have positive charge, the adsorption of bacteria become more severe towards the membrane surface and forms biofilm.

Numerous strategies have been proposed to prevent biofouling formation on the membrane surface, such as pretreatments and cleaning methods (Friedman *et al.* 2016, Hakizimana *et al.* 2016, Pramanik *et al.* 2016). Even though 99% of bacteria could be eliminated by these methods, the remaining bacteria are able to reproduce them self and grow rapidly on the membrane surface. Therefore, biocide dosing or UV irradiation is generally used to control the bacteria growth during membrane operation (Maddah *et al.* 2016). Many efforts have also been devoted by choosing polymers with natural antibacterial property, e.g., chitosan (CS) and polymethyl acrylate (PMA), as a membrane material (Wang *et al.* 2016). The antibacterial polymers kill bacteria when attached to the membrane surface and reduce the formation of biofouling significantly. Although the polymers have antibacterial property, some modifications are performed to improve the membrane performance by blending polymer with polycationic biocides (e.g., phosponium and ammonium quaternized polymer) (Xue *et al.* 2015). Currently, coating the polycationic biocide onto the anionic polymer membrane (e.g., zwitterionic polymers) has became a preferred method to produce antibacterial membrane coupled with antifouling property (Weng *et al.* 2016).

A significant number of researches consider nanocomposite membrane as a new approach to fabricating an excellent antibacterial membrane with high permeability and selectivity (Goh *et al.* 2015). There are two types of nanocomposite membrane, namely mixed matrix membrane, can be prepared by dispersing the nanoparticles into polymeric membrane structure, (Chung *et al.* 2017) and thin film nanocomposite, prepared by coating the nanoparticles on the membrane support (Zinadini *et al.* 2017). Most of the nanocomposite membranes showed a greater antibacterial property compared than unmodified antibacterial membranes (Kamal *et al.* 2016, Ozay *et al.*

2016). Although these nanocomposite membranes offer some advantages, these nanocomposite membranes are limited by its incompatibility with a polymeric membrane, which led to the loss of nanoparticle from membrane matrix during fabrication and filtration process. Some techniques have been proposed to overcome the challenge (Yang *et al.* 2016).

The membrane modifications with reliable antibacterial properties are still challenging for widespread application of membrane technologies, especially in water treatment application. In this paper, the antibacterial membrane for water treatment will be reviewed comprehensively. Special attention will be given to membrane modification by introducing antibacterial agents (polymer, nanoparticle, and biomaterial) into membrane matrix through several methods, such as blending and surface modification (chemical grafting and coating).

2. Polymeric antibacterial membrane

Some polymer materials have naturally antibacterial properties, such as chitosan (CS) and polymethyl acrylate (PMA) (Muñoz-Bonilla *et al.* 2012). Most of these antibacterial polymers are positively charged, which kill bacteria by disrupting cell of bacteria membrane. CS is known as cationic biopolymer that offers some advantages including good antibacterial activity, biodegradability, nontoxicity, reactivity, film and fiber forming capacity, and favorable hydrophilicity (Liu *et al.* 2016). In water treatment field, the CS membranes have been used as an adsorbent membrane to remove hazardous materials such as dyes and heavy metal ions, mainly in trace amounts, from water resources.

In spite of its advantages, the application of CS as membrane material is limited by its insoluble character in most of organic solvents and low mechanical strength (Pillai *et al.* 2009). Therefore, CS is mostly blended with other polymers or coated on the appropriate membrane support, which is mostly utilized any cross-linking agent as well as any post-preparation treatment (Reiad *et al.* 2012, Waheed *et al.* 2014). In recent years, modification of CS polymer has been performed by some techniques to improve the antibacterial property with a good solubility. Tan *et al.* (2013) immobilized a quaternary ammonium group on a dissociative hydroxyl group or amino group of the CS. They found that the quaternized CS (QCh) had stronger antibacterial activity than unmodified CS over an entire range of pH values. When the QCh blended into hydrophilic polymer-based membranes (such as poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) (PVP)), the modified membrane showed higher antibacterial activity against the gram-positive bacteria (S. aureus) and gram-negative bacteria (E. coli) (Ignatova *et al.* 2007). The antibacterial membrane can also be prepared by directly blending a quaternary ammonium compound (QAC) into polymeric membrane solution, as has been done by Zhang *et al.* (2016).

Other CS derivatives (e.g., N-phthaloyl chitosan (NPHCs), N,O-carboxymethyl chitosan (NOCC), and N-succinyl chitosan (NSCS)) also attracted many researchers (Xu *et al.* 2015). These CS derivatives showed a good antibacterial activity and have been used as an additives in the most polymeric membranes, such as polythersulfone (PES), polysulfone (PSf), polyvinylidene fluoride (PVDF), and cellulose acetate (CA) (Kausar 2016, Rajesha Kumar *et al.* 2013, Luo *et al.* 2012). Some modifications of antibacterial polymeric membranes and the membrane preparation techniques are shown in Table 1.

3. Surface modification of antibacterial membrane

Table 1 Polymeric-based antibacterial membranes

Polymeric mixture materials	Preparation technique	Bacteria test	Antibacterial activity	Reference
CS-PCL	Electrospinning	*S. aureus* (ATCC 25693)	CFU= 2.02 cell number/cm^2 (after 8h of filtration)	(Cooper *et al.* 2013)
QCh/PVP	Electrospinning	*S. aureus* and *E. coli*	Excellent kill S. *aureus* and 98.8% reduction of E. coli	(Ignatova *et al*. 2007)
Nylon-6/CS	Electrospinning	*E.coli*	Efficiency of 96% (30/70-CS/ Nylon ratio)	(Jabur *et al.* 2016)
PA	Electrospinning	*S. aureus* and *E. coli*	*S. aureus* removal= 5.8 $\log_{10}$ CFU/100 mL E.coli removal= 4.0 $\log_{10}$ CFU/100 mL	(Daels *et al.* 2011)
CA/PEG600/CS	Solvent evaporation phase separation	*E.coli*	negligible bacterial growth	(Sidra Waheed *et al.* 2014)
PE/PEO/GO-NH_2	Melt mixing with twin extruder	*E. coli*	Efficiency of 90% (90/10 PE/PEO with 1%wt of GO-NH_2)	(Mural *et al.* 2014)
PS-MSP	Co-precipitation method	*E. coli and P. aeruginosa*	CFU= 26 - 28/ml	(Khan *et al.* 2012)

Abbreviation: CS = chitosan; PCL= polycaprolactone; CA = cellulose acetate; PEG = polyethylene glycol; QCh = quaternized chitosan derivative; PVP = poly(vinyl pyrrolidone); PA = polyamide; PS = polystyrene; MSP = magnesium-strontium phosphate;

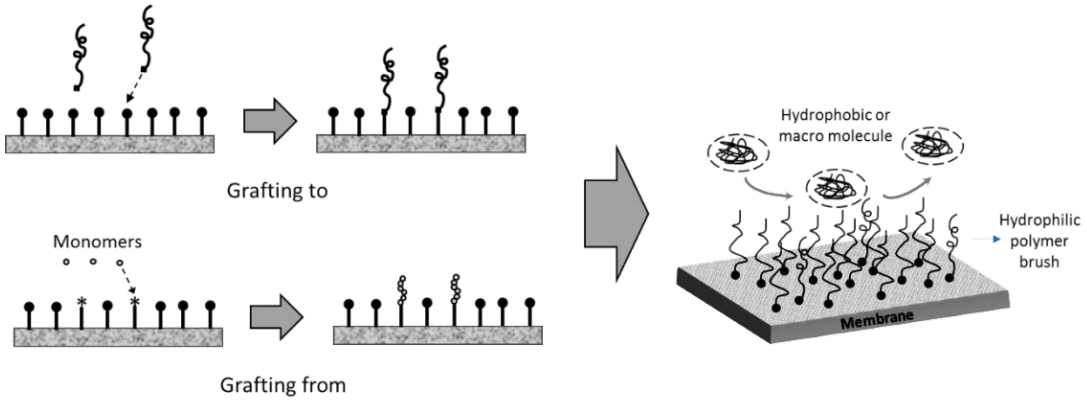


Fig. 2 Anchoring polymer chains techniques on the membrane surface

Considerable works on polymeric membrane surface modifications have been conducted. The modification of the membrane surface with an antibacterial property is more effective in killing bacteria without the release of active molecules that contribute to the second contamination in the environment. The most widely used method to introduce an antibacterial agent on the membrane surface is chemical grafting method. This grafting method can generated via a “grafting to” or

"grafting from" technique (Krishnamoorthy *et al.* 2014). Both of mentioned techniques are shown in Fig. 2. In "grafting to" technique, end functionalized polymer chain, or polymer brush, is directly anchored (or immobilized) onto the membrane surface through chemical reaction. While in "grafting from" method, initiators are introduced on the membrane surface, after that followed by polymerization of monomers. The length of polymer chain and antibacterial efficiency can be adjusted by changing the reaction time (Yao *et al.* 2008). Several types of antibacterial agents have been coated on the membrane surface by grafting methods, such as cationic biocides or polymers (Nikkola *et al.* 2013, Shen *et al.* 2015) and functionalized graphene oxide (Huang *et al.* 2016).

Polydopamine (PDA), which contains both catechol and primary amine functional groups, has been successfully coated on a commercial reverse osmosis (RO polyamide (PA) membrane surface by Karkhanechi *et al.* (2014). Although the PDA active layer reduced the membrane flux, but antiadhesion and antibacterial was improved due to the presence of protonated amine groups in the layer structure. When the PDA active layer is further modified with PVPiodine complex via multiple hydrogen bonding interactions, the PDA/PVP/I active layer kills the attached bacteria up to 99.9% (Jiang *et al.* 2013). In addition to RO membrane modification, the mitigation of biofilm in RO membrane system may also be performed by coating or embedding the spacer surface with antibacterial agents (Ronen *et al.* 2016). Further strategy has also been developed by coating antibacterial polymers onto an anionic polymers, such as zwitterionic polymers, to produce antibacterial as well as antiadhesion or antifouling polymeric membrane. (Mi *et al.* 2014). For example, the combination of CS and betaine showed stronger antibacterial activity and a broader range of inhibition as compared with the CS alone (Tada *et al.* 2009).

Layer-by-layer self-assembly (LbL) of polyelectrolytes is another technique to easily attach antibacterial agents and antiadhesive agents on the membrane surface. The multilayer thin film membrane may be formed by electrostatic interactions (Jiang *et al.* 2006), charge transfer (Shimazaki *et al.* 1997), hydrogen bonds (Kharlampieva *et al.* 2009), or step by step reactions (Bergbreiter *et al.* 2007). These techniques are shown in Fig. 3. Fu *et al.* (2005) fabricated anti-adhesive and antibacterial multilayer membranes by interacting CS (as polycation) and heparin (as polyanion) on a poly(ethylene terephthalate) (PET) membrane surface. They studied the effect of charge density of the polyelectrolytes to the thickness of the formed layer by changing the pH of

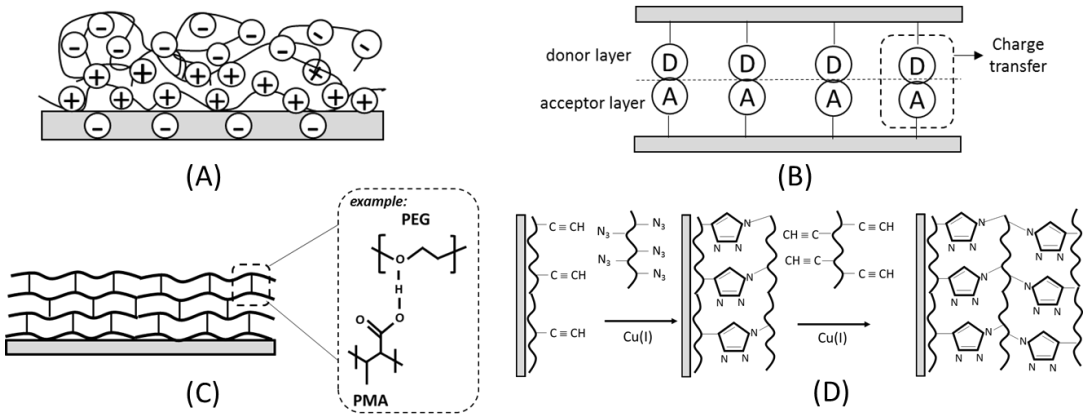


Fig. 3 Schematic of multilayer membrane preparation: (a) electrostatic interaction, (b) charge transfer, (c) hydrogen bonding, and (d) click chemistry

Table 2 Surface modification techniques of antibacterial membranes.

Surface modification techniques	Support membrane	Antibacteria agent	Bacterial test	Anti-bacteria efficiency	Ref.
Plasma-induced grafting	Polyethylene (PE) hollow fiber	poly(methacryloxyethyl benzyl dimethyl ammonium chloride) (PDMAE-BC)	*E.coli*	92.4%	(Li *et al.* 2015)
Plasma-induced grafting	PVC	PDMAE-BC	*E. coli*	96.3%	(Li *et al.* 2016)
Photografting	PES (150 kDa)	MEDSAH	P. putida	±100%	(Razi *et al.* 2012)
UV-induced grafting	PP	polySBMA	- *E. coli* - *S. aureus* - *P. fluores-cens*	E.coli and S. aerus: 100% P. fluorescens: 98%	(Yang *et al.* 2010)
UV-induced grafting	PP	PDMAEMA	- *E. coli,* - *S. aureus*	100%	(Yang *et al.* 2011)
Genipin-induced crosslinking reaction	Aminolyzed silicone	Blending pSBMA and HTCC	- *E.coli* *P. mirabilis;* - *S. aureus* - *P. aeruginosa*	>99%	(Wang *et al.* 2015)
radical graft polymerizations	PVDF	PDMAEMA	*E.coli*	99%	(Sui *et al.* 2014)
Grafting polymerization	PA (RO)	PDA (composition: 5 kg/m^3 of dopamine)	- *E.coli* - *P. putida*	± 46%	(Karkhanechiet al. 2014)
Grafting polymerization	PP	PDA-PVP-I	*S. aureus*	99.9%	(Jiang *et al.* 2013)
Layer-by-layer polyelectrolyte	PSf	PAH / PAA polyelectrolyte	*E. coli*	99%	(Tang *et al.* 2013)
Layer-by-layer Polyelectrolyte	polyamide (RO)	PAA/Ag-PEI	*E. coli*	95%	(Rahaman *et al.* 2014)
Chemical grafting	polyamide (RO)	PVA/CA/PEG	*Staphylococcus sp.*	±99%	(Hassanien *et al.* 2013)
Spray- and spin-assisted layer-by-layer assembly	polyamide (RO)	Copper (Cu)	*E. coli*	94.3% - ±100%	(Ma *et al.* 2016)
In-situ generation on TFC layer	Polyamide (RO)	TA-Fe-PEI/Ag	*E. coli and B. subtilis*	100%	(Dong *et al.* 2017)

Abbreviation: MEDSAH=[2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide; PP=polypropylene, PVC=polyvinyl chloride ; PDMAE-BC=poly(methacryloxylethyl benzyl dimethyl ammonium chloride); PSf=polysulfone, PA=polyamide, SBMA=polysulfobetaine methacrylate, PDMAEMA=Poly(2-(dimethylamino) ethyl methacrylate), PAH=poly(allylamine hydrochloride), PDA=polydopamine, PP = polypropylene, I = iodine ; pSBMA= poly(sulfobetaine methacrylate), HTTC=N-[(2-hydroxy-3-trimethylammonium)propyl] chitosan chloride, PAA=poly(acrylicacid), PEI=poly(ethylene imine); PDMAEMA= poly(N,N-dimethylamino-2-ethylmethacrylate), PRP=platelet-rich plasma;

solution. At higher pH, CS, as a weak polyelectrolyte, tend to adsorb as a thicker layer, while heparin, as a strong polyelectrolyte, tend to form a thin layer. In another research, Tang *et al.* (2013) have assembled polyelectrolyte multilayers on polysulfone membrane by interacting poly (allylamine hydrochloride) (PAH)/poly(acrylicacid) (PAA) and efficiency of bacteria removal to 99% was achieved. Several methods of membrane surface modifications are shown in Table 2.

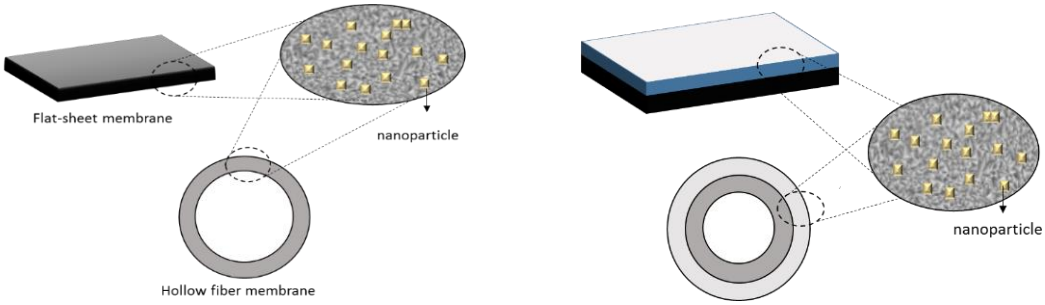
Up to this time, the surface modification of polymeric membranes has been continuously developed. Kinetics and electrostatic cognition assembly mechanism of polyelectrolytes on the membrane surface by chemical reaction and LbL method are needed to design over thickness, topology, and local chemical composition as well as final properties. Furthermore, multilayer membrane design methods have also been continue developed by using a range of simple and accessible processing operation for commercialization.

4. Nanocomposite antibacterial membrane

Nanocomposite membranes, which are increasingly fabricated by incorporating nanoparticles (NPs) into polymeric membrane matrix, have been increasing used in water treatment field due to their superior physicochemical properties (e.g., hydrophilicity, porosity, charge density, and thermal and mechanical stability) (Khoiruddin *et al.* 2016, Wenten *et al.* 2016). A few NPs have been progressively used as antibacterial agents (disinfectant) and then incorporated on or into polymeric membrane structure, i.e., metals (such as: silver/Ag, copper/Cu) (Tamayo *et al.* 2016), metal oxides (such as: ZnO, CuO,TiO_2) (Aruoja *et al.* 2009), metal salts (such as: $CuSO_4$) (McCarrell *et al.* 2008), metal hydroxides (such as: $Cu(OH)_2$, $Ca(OH)_2$, $Mg(OH)_2$, ZnOH) (Karkhanechi *et al.* 2013), polymers (such as: P-4VP) (Ozay *et al.* 2010), carbon nanotubes (CNT) (Tiraferri *et al.* 2011), and hybrid NPs (Jung *et al.* 2011).

Based on the NPs location in membrane structure, nanocomposite membranes can be divided into two types, i.e., conventional nanocomposite and surface located nanocomposite. In conventional nanocomposite membrane, the NPs are dispersed in the membrane structure by blending method. Meanwhile in surface located nanocomposite, the NPs are deposited on the surface of the membrane by grafting or interfacial polymerization method. The types of nanocomposite membrane are shown in Fig. 4. The first composite membrane type is referred as hybrid or mixed matrix membrane, meanwhile the second type is referred as thin film nanocomposite (TFN) membrane. There are two techniques to disperse the NPs in membrane structures, including in-situ generation (precursor blending followed by NPs generation in membrane solution) and NPs blending (ex-situ). It has been reported that the nanocomposite membrane prepared by ex-situ method had higher NPs density and bigger particles size, which preferentially located in the skin membrane layer (Taurozzi *et al.* 2008). Conversely, in situ method resulted in low density and smaller NPs that homogenously distributed along the membrane cross-section. Lower density of NPs is attributed by the limited particles availability for NPs growth under condition of developing porosity in membrane structure (Taurozzi. 2008).

The NPs position in membrane structure may also be controlled by adjusting the viscosity of polymer solutions during membrane preparation (Sile-Yuksel *et al.* 2014). Higher viscosity of polymer solution retarded the motion of NPs during membrane structure formation led to the collocation of NPs in the sub-layer of the membrane. On the contrary, the lower polymer solution allowed the NPs to move towards the membrane surface, which contributes to higher antibacterial performance. Beside the position of NPs, particle size and concentration of NPs in membrane



(a) (b)

Fig. 4 Nanocomposite membrane types based on nanoparticle location: (a) conventionalnanocomposite (mixed matrix) and (b) surface located nanocomposite

structure also become important parameters. It has been reported that the antibacterial activity is improved by the increasing of particles concentration and decreasing of particle size (Pan *et al.* 2016). Silver (Ag) NPs is the most used of antibacterial agent to improve the antibacterial membrane preparation. It has been reported that 70% of gram negative bacterium *E. coli* growth can be inhibited in the presence of the Ag particles at a concentration of 10 μgcm^{-3} bacterium (Sondi *et al.* 2004). It is estimated that the interaction of building elements of bacteria with Ag^{+} ions induced a structural changes and degradation, after that attributed to the bacteria cell death. Another study reported that Ag generated a reactive oxygen species (ROS), which contributed to toxic condition to bacterial strains (Dallas *et al.* 2011).

As a photocatalyst, TiO_2 also showed an excellent performances to degrade many environmental pollutants and possess an effective antibacterial property (Leong *et al.* 2014). The antibacterial property of TiO_2 depends on crystallinity degree of the particle. It has been reported that TiO_2 composed by 100% anatase crystalline type allows the formation of aggregate particles in the membrane matrix, which has high tendency to clog the membrane pores and reduce the membrane performance (Vatanpour *et al.* 2012). Modification technique with TiO_2 has been purposed to prevent the particles aggregation and increase its stability in polymeric membrane matrix, such as chemical modification with a coupling agent and mechanical modification by increasing the density of the bulk or reducing the particle size being a fine powder (Altan *et al.* 2012). In water treatment processing, the utilization of TiO_2 nanocomposite membranes are generally coupled with UV-light exposure to enhance the inactivity bacterial. The presence of reactive oxygen generated by TiO_2 and direct UV illumination of the cells attributed to excellent bactericidal effect. Impregnated TiO_2 in membrane matrix followed with UV-light irradiation produces an excellent anti-bacterial membrane coupled with anti biofouling due to its superhydrophilicity. The anti-biofouling activity of TiO_2 is improved due to the hydroxyl (-OH) groups on the membrane surface (Madaeni *et al.* 2011). In contrast to TiO_2, the UV-light irradiation induces reduction of Ag^{+} into silver elementary substance (Ag(0)), either on the surface or inside of the template (Chen *et al.* 2013).

Incorporated of two or more types of NPs into membrane solution to enhance the antibacterial membrane performance has been progressively proposed. As reported by Youssef *et al.* (2013), TiO_2 had less antibacterial effect than Ag over all tested of bacteria (Candida, Staph. Aurous and Pseudomonas) except with Staphylococcus. The synthesized Ag-TiO_2 thin film showed better bactericidal activities compared with the neat TiO_2 nanofilm. Some examples of modifications of

polymeric membranes by introducing NPs in membrane structure, both single and hybrid NPs, and its antibacterial performances are shown in Table 3.

Table 3 Nanocomposite antibacterial membranes

Nanoparticle materials	Polymer membrane	Modification Method	Bacteria test	Antibacterial membrane performance	Ref.
Silver (Ag)	PES + PVP	Blending	*E. coli* *S. aureus*	100% inhibition	(Basri *et al.* 2011)
	CS (DD 89± 2%)	In-situ synthesis of Ag NPs	*S. aureus*	Almost complete (~100%)	(Regiel *et al.* 2013)
	PES	Plasma-induced Grafting	*S. Typhimuri-um*	Almost complete (~100%)	(Cruz *et al.* 2015)
	PSBMA-zwitterionic brush	In-situ synthesis of Ag NPs on membrane surface	*P. aeruginosa*	Efficiency of 97%	(Liu *et al.* 2017)
TiO_2	PVDF	Blending	*E. coli*	Almost complete (~100%)	(Damodar *et al.* 2009)
	PVDF/SPES	Blending	*E. coli*	Inhibited bacteria effectively	(Rahimpour *et al.* 2011)
	PVDF/PEG	Surface adhesion	*E. coli*	Almost complete (~100%)	(Younas *et al.* 2016)
ZnO	CA	Blending	*S. auereus* *E. coli,*	Inhibited bacteria effectively	(Anitha *et al.* 2013)
	CA	Blending	*E.coli*	1.07-0.75% bacterial adherence on the membrane surface	(Khan *et al.* 2015)
	CS	Blending	*E. coli* *S. aureus*	Inhibited bacteria effectively	(Li *et al* . 2010)
Cu	PES	Blending	*E.coli*	Inhibited bacteria effectively	(Ozay et al. 2016)
	PA	In-situ synthesis of Ag-NPs	*E.coli*	90% reduction	(Ben-Sasson *et al.* 2016)
Functionalized CNT	CA	Blending	*E.coli*	60% inactivation	(Tiraferri et al. 2011)
Ag-SiO_2 hybrid particles	PVDF	Chemical grafting	*E. coli*	Inhibited bacteria effectively	(Pan et al. 2016)
	PA	Chemical grafting	*E. coli* *P.aeruginosa* *S. aureus*	Almost complete	(Park *et al.* 2016)
Ag/MWNTs hybrid particles	PAN	Deposited on membrane surface by filtration	*E. coli (initial concentration* 2×10^6 *CFU/mL)*	180×10^6 CFU/mL after 80h of filtration compared to 18 h for unmodified membrane	(Booshehri *et al.* 2013)

Abbreviation: CA=cellulose acetate; Cu=copper, CS=chitosan, DD=deacetylation degree, MWNTs=multi-walled carbon nanotubes; PA = polyamide; PAN=polyacrylonitrile; PEG=polyethylene glycol, PES=polyethersulfone, PSBMA=polysulfobetaine methacrylate; PVP= Polyvinylpyrrolidone, PVDF= poly (vinylidene fluoride), SPES= sulfonated polyethersulfone

TFN membrane is a new type of composite membranes that mostly prepared via interfacial polymerization (IP). The NPs are introduced within the thin polyamide (PA) dense layer of the thin film composite (TFC) membrane. In-situ and ex-situ methods of TFN membrane preparation have been proposed, either in aqueous or an organic phase (Mollahosseini *et al.* 2013). In in-situ preparation, the synthesized porous support was dipped in aqueous m-phenylenediamine (MPD) solution, subsequently immersed in trimesoyl chloride (TMC) solution containing NPs for the polymerization process. Meanwhile in ex-situ preparation, NPs are embedded onto the porous support surface prior to interfacial polymerization of monomers on the membrane surface (Mollahosseini *et al.* 2014).

Besides agglomeration of the NPs in film membrane structure, the main problem in TFN membrane application for water treatment is the release of deposited NPs from coating layer, which contribute to the potential toxicity risk of NPs when they enter the environment and organisms (Ashutosh Kumar *et al.* 2013). In addition, the antibacterial performance of the membrane declines in proportion to the total number of NPs released from the coating layer. Some techniques have been proposed to minimize the particle release, such as improvement in the grafting methods to enhance the NPs stability in membrane matrix. Isawi *et al.* (2016) have been successfully incorporated ZnO into the active grafting layer over PA(TFC) membrane. The zinc leaching from the ZnO NPs modified PMAA-g-PA(TFC) was minimal, which indicated the stabilization of the ZnO NPs on the membrane surface. Park *et al.* (2016) attached AgNP-SiO_2 hybrid particles (AgNP-SiO_2), in which AgNPs (±30 nm in dia.) were robustly and uniformly grown on the aminopropyl moiety-functionalized SiO_2 particles (±400 nm in dia.), on the membrane surface using cysteamine as a covalent linker. The hybrid particles were well distributed over the entire membrane surface without severe aggregation and showed a great leaching stability. Meanwhile, Mural *et al.* (2017) proposed a strategy to control the release of Ag from polyethylene (PE)-based membrane surface by modifying the membrane surface with a polyethylene imine (PEI) before depositing silver on the surface Mural *et al.* (2017). They found that the presence of PEI allowed controlled leaching of silver ions in the permeate (less than 0.1 $mg.l^{-1}$ of silver ions in the final permeate. Basri et al. added PVP (15.000 Da) and 2, 4, 6-triaminopyrimidine (TAP) during the membrane preparation, which resulted in silver leaching reduction up to 57% and respectively 63%. The increase of PVP molecular weight reduced the membrane pore size, thus contributed to higher entrapped of Ag particles in the membrane matrix. Since hydrophilic polymers (such as: PVP, PEG,and CS) are effective in reducing fouling in membrane structure (Aryanti *et al.* 2016, Aryanti *et al.* 2015), blending them with antibacterial agent to polymeric membrane can be used to produce an excellent anti fouling and antibacterial membrane (Alpatova *et al.* 2013).

Recently, deposition of multilayer nano-sheet, such as graphene oxide (GO), on polymeric membrane has been developed by layer-by-layer (LbL) assembly method as an alternative to composite membrane (Fig. 6). Zhang *et al.* (2015) deposited GO layers on polypropylene (PP) membrane surface through click chemistry technique. Polypropylene (PP) is one of the most used polymers in membrane fabrication due to its good thermal and chemical stability (Himma *et al.* 2017, Himma Nurul *et al.* 2016). Anti-fouling and antibacterial of the modified PP membrane was enhanced due to the presence of GO, which has prominent antibacterial properties. Hu *et al.* (2013) crosslinked GO nanosheet layers on polydopamine coated polysulfone membrane support through 1,3,5-benzenetricarbonyl trichloride (TMC). Flux water of the modified membrane was found 4-10 times higher than that of the most commercially available TFC membrane.

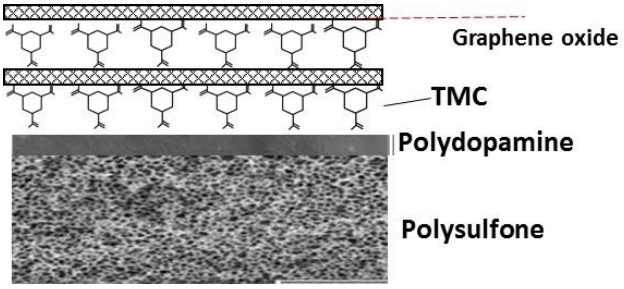


Fig. 5 Schematic of cross-linked GO nanosheet layers on polydopamine-coated polysulfone support (Nair *et al.* 2012)

5. Bio-antibacterial membrane

Due to the sensitivity towards environmental problems, biomaterials-based antibacterial agents have been used as a nontoxic strategy on biofouling mitigation instead of chemical treatment. Immobilization of antibacterial substances produced by living microorganisms, such as antimicrobial peptides and bacteriolytic enzymes, have been developed to improve anti adhesion property of microbial (Glinel *et al.* 2012). These biomaterials can be immobilized onto the membrane supports either physically (e.g., via adsorption or layer by layer assembly) or chemically (via covalent bonding). The use of covalent-based immobilization methods of biomaterials on surfaces minimizes biomaterial leaching from the modified surface and overcoming short-term antimicrobial protection problems inherent in physical immobilization methods (Onaizi *et al.* 2011).

Several important parameters should be considered during immobilization of enzyme, including reaction time, pH value, temperature, buffer, and inhibitor (Cordeiro *et al.* 2011). The characteristics of immobilized enzyme depend on the properties of both enzyme and support material (Tischer *et al.* 1999). Saeki *et al.* (2013) immobilized lysozyme onto ACA-modified polyamide RO membrane by an amine coupling reaction using 1-ethyl-3-(3-dimethyl amino propyl) carbodiimide (EDC) and N-hydroxysuccinimide (NHS) at pH 8.0. The modified RO membrane showed sufficient antibacterial activity up to 91% against the gram-positive bacteria, *Micrococcus lysodeikticus* and *Bacillus subtilis*, which was remained active after being stored for 5 months at 5^{o}C.

Antimicrobial peptide (AMP) is known as a cationic active compound that can resist bacteria, viruses, protozoa and fungi (Giuliani *et al.* 2008). Immobilizing techniques of AMP on the support surface have been reported, such as covalent bonding (Bagheri *et al.* 2009) and self-assembly monolayer (SAM) method (Wang *et al.* 2008). Due to its physicochemical characteristics, AMP tends to associate with a negatively charged membrane. Generally, a PEG linkage or other reactive groups is used to immobilize peptide on a polymer surface. (Gao *et al.* 2011) conjugated Cysteine functionalized cationic antimicrobial peptide on the copolymers brushes using a maleimide thiol addition reaction, which has a good antimicrobial activity against Pseudomonas aeruginosa (P. aeruginosa) PA01. Peptide density and graft density are two important parameters in achieving the optimum antimicrobial properties of the peptide grafted polymer brush. Although almost of biomaterial based modified membranes are used for medical applications up to the present time, this modified type of membrane could be considered as a new strategy of non-toxic and environmentally friendly in antifouling and antibacterial technology.

6. Conclusions

As the major component of microorganisms in water, bacteria contribute to biofilm formation on the membrane surface. Therefore, many efforts have been devoted to inactivate the activity of bacteria during the filtration process by introducing antibacterial agent in the membrane structure. Several antibacterial agents have been used in antibacterial membrane preparation, i.e., polymers, nanoparticles (NPs), and biomaterial. These antibacterial agents are introduced into the membrane matrix through different methods, such as blending, grafting, and coating. The Aim of these modifications is to kill the bacteria when it attached on the membrane surface.

Some of polymer materials have naturally antibacterial and low fouling properties, such as chitosan (CS) and zwitterionic polymers. CS has attracted considerable attention to be used as antibacterial membrane-based material, either single or blended with other polymer materials. The antibacterial properties of CS are influenced by intrinsic and environmental factors, such as degree of polymerization, degree of acetylation, and solution pH. Several researches have also been performed to improve the antibacterial properties of polymer by introducing polycationic biocides, such as phosphonium and quaternary ammonium salts.

Numerous surface modification methods of the membrane have also been devoted to inhibit biofilm formation. These modifications are mostly carried out through physical adsorption, chemical grafting, and coating methods. Grafting is a method wherein monomers are bonded covalently onto the end of membrane polymer chains by chemical, radiation, photochemical and plasma-induced techniques. Furthermore, antibacterial membrane may also be prepared by coating antibacterial agent and charged material on the membrane support surface. Recently, layer by layer (LBL) assembly method has been reported to fabricate multilayer thin film membrane, which can be driven by electrostatic interactions, charge transfer, hydrogen bonds, and step by step reactions.

Significant numbers of researchers have considered nanocomposite membrane as a new approach to fabricate an excellent antibacterial membrane. The NPs are dispersed homogenously in the membrane by blending method or coating onto the membrane surface. The antibacterial efficiency of the nanocomposite membrane depends on location of NPs, which is influenced by synthesizing technique of NPs and viscosity of the polymer membrane during the preparation. Blending of two or more types of nanoparticles into membrane solution has been progressively proposed to enhance the antibacterial membrane performance. A few strategies to control the loss of NPs have been proposed to improve the entrapment of NPs in membrane structure, such as PVP or PEG addition into the membrane solution during membrane preparation and modification of the membrane surface before depositing silver on the surface.

Due to the sensitivity towards environmental problems, biomaterials-based antibacterial agents have been used as a nontoxic strategy on biofouling mitigation instead of chemical treatment. These biomaterials can be immobilized onto the membrane supports either physically (e.g., via adsorption or layer by layer assembly) or chemically (via covalent bonding). Several important parameters should be considered during immobilization of biomaterials, including reaction time, pH value, temperature, buffer, and inhibitor. Although almost of biomaterial-based modified membranes are used for medical applications up to this time, this modified type of membrane could be considered as a new strategy of non-toxic and environmental friendly in anti fouling and antibacterial technology.

Further research in development of antibacterial membrane, with good anti-fouling properties, high permeability and selectivity, as well as long term stability, is still continuously conducted, particularly in nanocomposite membrane. Although many efforts have been made to develop

antibacterial membrane using various nanoparticles (NPs), incorporation between nanoparticle into polymeric membrane becomes a challenge in the design of nanocomposite membranes. Therefore, many researches have been focused on surface modification of the particles before it is mixed into a polymer solution. Furthermore, due to the potential toxicity risk of nanoparticles when they enter the environment and organisms, recently, the use of "green" synthetic NPs have begun proposed.

References

Alpatova, A., Kim, E.S., Sun, X., Hwang, G., Liu, Y. and Gamal El-Din, M. (2013), "Fabrication of porous polymeric nanocomposite membranes with enhanced anti-fouling properties: Effect of casting composition", *J. Membr. Sci*., **444**, 449-460.

Altan, M. and Yildirim, H. (2012), "Mechanical and antibacterial properties of injection molded Polypropylene/TiO_2 nano-composites: effects of surface modification", *J. Mater. Sci. Technol.*, **28**(8), 686-692.

Anitha, S., Brabu, B., John Thiruvadigal, D., Gopalakrishnan, C. and Natarajan, T.S. (2013), "Optical, bactericidal and water repellent properties of electrospun nano-composite membranes of cellulose acetate and ZnO", *Carbohydr Polym.*, **97**(2), 856-863.

Ariono, D., Aryanti, P.T.P., Subagjo, S. and Wenten, I.G. (2017), "The effect of polymer concentration on flux stability of polysulfone membrane", *AIP Conference Proceedings*, **1788**(1), 030048.

Ariono, D., Purwasasmita, M. and Wenten, I.G. (2016), "Brine effluents: Characteristics, environmental impacts, and their handling", *J. Eng. Technol. Sci.*, **48**(4), 367-387.

Aruoja, V., Dubourguier, H.C., Kasemets, K. and Kahru, A. (2009), "Toxicity of nanoparticles of CuO, ZnO and TiO2 to microalgae Pseudokirchneriella subcapitata", *Sci. Total Environ.*, **407**(4), 1461-1468.

Aryanti, P.T.P., Joscarita, S.R., Wardani, A.K., Subagjo, S., Ariono, D. and Wenten, I.G. (2016), "The influence of PEG400 and acetone on polysulfone membrane morphology and fouling behaviour", *J. Eng. Technol. Sci.*, **48**(2), 135-149.

Aryanti, P.T.P., Yustiana, R., Purnama, R. and Wenten, I.G. (2015), "Performance and characterization of PEG400 modified PVC ultrafiltration membrane", *Membr. Water Treat.*, **6**(5), 379-392.

Bagheri, M., Beyermann, M. and Dathe, M. (2009), "Immobilization reduces the activity of surface-bound cationic antimicrobial peptides with no influence upon the activity spectrum", *Antimicrob. Agents Chemother.*, **53**(3), 1132-1141.

Basri, H., Ismail, A.F. and Aziz, M. (2011), "Polyethersulfone (PES)-silver composite UF membrane: effect of silver loading and PVP molecular weight on membrane morphology and antibacterial activity", *Desalination*, **273**(1), 72-80.

Ben-Sasson, M., Lu, X., Nejati, S., Jaramillo, H. and Elimelech, M. (2016), "In situ surface functionalization of reverse osmosis membranes with biocidal copper nanoparticles", *Desalination*, **388**, 1-8.

Bergbreiter, D.E. and Chance, B.S. (2007), ""Click"-based covalent layer-by-layer assembly on polyethylene using water-soluble polymeric reagents", *Macromolecules*, **40**(15), 5337-5343.

Booshehri, A.Y., Wang, R. and Xu, R. (2013), "The effect of re-generable silver nanoparticles/multi-walled carbon nanotubes coating on the antibacterial performance of hollow fiber membrane", *Chem. Eng. J.*, **230**, 251-259.

Chen, M., Zhao, Y., Yang, W. and Yin, M. (2013), "UV-irradiation-induced templated/in-situ formation of ultrafine silver/polymer hybrid nanoparticles as antibacterial", *Langmuir*, **29**(51), 16018-16024.

Chung, Y.T., Mahmoudi, E., Mohammad, A.W., Benamor, A., Johnson, D. and Hilal, N. (2017), "Development of polysulfone-nanohybrid membranes using ZnO-GO composite for enhanced antifouling and antibacterial control", *Desalination*, **402**, 123-132.

Cooper, A., Oldinski, R., Ma, H., Bryers, J.D. and Zhang, M. (2013), "Chitosan-based nanofibrous membranes for antibacterial filter applications", *Carbohyd. Polym.*, **92**(1), 254-259.

Cordeiro, A.L. and Werner, C. (2011), "Enzymes for antifouling strategies", *J. Adhes. Sci. Technol.*, **25**(17),

2317-2344.
Cruz, M.C., Ruano, G., Wolf, M., Hecker, D., Castro Vidaurre, E., Schmittgens, R. and Rajal, V.B. (2015), "Plasma deposition of silver nanoparticles on ultrafiltration membranes: Antibacterial and anti-biofouling properties", *Chem. Eng. Res. Des.*, **94**, 524-537.
Daels, N., De Vrieze, S., Sampers, I., Decostere, B., Westbroek, P., Dumoulin, A., Dejans, P., De Clerck, K. and Van Hulle, S.W.H. (2011), "Potential of a functionalised nanofibre microfiltration membrane as an antibacterial water filter", *Desalination*, **275**(1-3), 285-290.
Dallas, P., Sharma, V.K. and Zboril, R. (2011), "Silver polymeric nanocomposites as advanced antimicrobial agents: classification, synthetic paths, applications, and perspectives", *Adv. Colloid Interface Sci.*, **166**(1), 119-135.
Damodar, R.A., You, S.J. and Chou, H.H. (2009), "Study the self cleaning, antibacterial and photocatalytic properties of TiO2 entrapped PVDF membranes", *J. Hazard Mater.*, **172**(2-3), 1321-1328.
Dong, C., Wang, Z., Wu, J., Wang, Y., Wang, J. and Wang, S. (2017), "A green strategy to immobilize silver nanoparticles onto reverse osmosis membrane for enhanced anti-biofouling property", *Desalination*, **401**, 32-41.
Ferrando, D., Ziemba, C. and Herzberg, M. (2017), "Revisiting interrelated effects of extracellular polysaccharides during biofouling of reverse osmosis membranes: Viscoelastic properties and biofilm enhanced osmotic pressure", *J. Membr. Sci.*, **523**, 394-401.
Friedman, L., Harif, T., Herzberg, M. and Mamane, H. (2016), "Mitigation of biofilm colonization on various surfaces in a model water flow system by use of UV treatment", *Water Air Soil Pollut.*, **227**(2), 1-16.
Fu, J., Ji, J., Yuan, W. and Shen, J. (2005), "Construction of anti-adhesive and antibacterial multilayer films via layer-by-layer assembly of heparin and chitosan", *Biomaterials*, **26**(33), 6684-6692.
Gao, G., Yu, K., Kindrachuk, J., Brooks, D.E., Hancock, R.E.W. and Kizhakkedathu, J.N. (2011), "Antibacterial surfaces based on polymer brushes: investigation on the influence of brush properties on antimicrobial peptide immobilization and antimicrobial activity", *Biomacromol.*, **12**(10), 3715-3727.
Giuliani, A., Pirri, G., Bozzi, A., Di Giulio, A., Aschi, M. and Rinaldi, A. (2008), "Antimicrobial peptides: natural templates for synthetic membrane-active compounds", *Cell. Mol. Life Sci.*, **65**(16), 2450-2460.
Glinel, K., Thebault, P., Humblot, V., Pradier, C.M. and Jouenne, T. (2012), "Antibacterial surfaces developed from bio-inspired approaches", *Acta Biomaterialia*, **8**(5), 1670-1684.
Goh, P., Ng, B., Lau, W. and Ismail, A. (2015), "Inorganic nanomaterials in polymeric ultrafiltration membranes for water treatment", *Sep. Purif. Rev.*, **44**(3), 216-249.
Guo, W., Ngo, H.H. and Li, J. (2012), "A mini-review on membrane fouling", *Bioresour. Technol.*, **122**, 27-34.
Hakizimana, J.N., Gourich, B., Vial, C., Drogui, P., Oumani, A., Naja, J. and Hilali, L. (2016), "Assessment of hardness, microorganism and organic matter removal from seawater by electrocoagulation as a pretreatment of desalination by reverse osmosis", *Desalination*, **393**, 90-101.
Hassanien, A., El-Hashash, M., Mekewi, M., Guirguis, D. and Ramadan, A. (2013), "Fabrication of polyvinyl alcohol/cellulose acetate (PVA/CA/PEG) antibacterial membrane for potential water purification application", *Hydrol Current Res*., **4**, 1-6.
Himma, N.F., Wardani, A.K. and Wenten, I.G. (2017), "Preparation of superhydrophobic polypropylene membrane using dip-coating method: the effects of solution and process parameters", *Polym. Plast. Technol. Eng.*, **56**(2), 184-194.
Himma, N.F., Anisah, S., Prasetya, N. and Wenten, I.G., "Advances in preparation, modification, and application of polypropylene membrane", *J. Polym. Eng*., **36**(4) (2016) 329.
Hu, M. and Mi, B. (2013), "Enabling graphene oxide nanosheets as water separation membranes", *Environ. Sci. Technol*., **47**(8), 3715-3723.
Huang, X., Marsh, K.L., McVerry, B.T., Hoek, E.M.V. and Kaner, R.B. (2016), "Low-fouling antibacterial reverse osmosis membranes via surface grafting of graphene oxide", *ACS App. Mater. Interf.*, **8**(23), 14334-14338.
Ignatova, M., Manolova, N. and Rashkov, I. (2007), "Novel antibacterial fibers of quaternized chitosan and

poly (vinyl pyrrolidone) prepared by electrospinning", *European Polym. J.*, **43**(4), 1112-1122.
Isawi, H., El-Sayed, M.H., Feng, X., Shawky, H. and Mottaleb, M.S.A. (2016), "Surface nanostructuring of thin film composite membranes via grafting polymerization and incorporation of ZnO nanoparticles", *App. Surf. Sci.*, **385**, 268-281.
Jabur, A.R., Abbas, L.K. and Moosa, S.A. (2016), "Fabrication of electrospun Chitosan/Nylon 6 anofibrous membrane toward metal ions removal and antibacterial effect", *Adv. Mat. Sci. Eng.*, **2016**, 10.
Jiang, J., Zhu, L., Zhu, L., Zhang, H., Zhu, B. and Xu, Y. (2013), "Antifouling and antimicrobial polymer membranes based on bioinspired polydopamine and strong Hydrogen-Bonded Poly (N-vinyl pyrrolidone)", *ACS App. Mater. Interf.*, **5**(24), 12895-12904.
Jiang, S.P., Liu, Z. and Tian, Z.Q. (2006), "Layer-by-Layer Self-Assembly of composite polyelectrolyte-nafion membranes for direct methanol fuel cells", *Adv. Mater.*, **18**(8), 1068-1072.
Jung, J.H., Hwang, G.B., Lee, J.E. and Bae, G.N. (2011), "Preparation of airborne Ag/CNT hybrid nanoparticles using an aerosol process and their application to antimicrobial air filtration", *Langmuir*, **27**(16), 10256-10264.
Kamal, T., Ali, N., A Naseem, A., B Khan, S. and M Asiri, A. (2016), "Polymer nanocomposite membranes for antifouling nanofiltration", *Recent Pat Nanotechnol.*, **10**(3), 189-201.
Karkhanechi, H., Takagi, R. and Matsuyama, H. (2014), "Biofouling resistance of reverse osmosis membrane modified with polydopamine", *Desalination*, **336**, 87-96.
Karkhanechi, H., Takagi, R., Ohmukai, Y. and Matsuyama, H. (2013), "Enhancing the antibiofouling performance of RO membranes using Cu (OH) 2 as an antibacterial agent", *Desalination*, **325**, 40-47.
Kausar, A. (2016), "Scientific potential of chitosan blending with different polymeric materials: A review", *J. Plast. Film Sheeting*, 8756087916679691.
Khan, M.M.A. and Rafiuddin (2012), "Preparation, electrochemical characterization and antibacterial study of polystyrene-based magnesium-strontium phosphate composite membrane", *Mater. Sci. Eng. C*, **32**(5), 1210-1217.
Khan, S.B., Alamry, K.A., Bifari, E.N., Asiri, A.M., Yasir, M., Gzara, L. and Ahmad, R.Z. (2015), "Assessment of antibacterial cellulose nanocomposites for water permeability and salt rejection", *J. Ind. Eng. Chem.*, **24**, 266-275.
Kharlampieva, E., Kozlovskaya, V. and Sukhishvili, S.A. (2009), "Layer-by-Layer Hydrogen-Bonded polymer films: from fundamentals to applications", *Adv. Mater.*, **21**(30), 3053-3065.
Khoiruddin, Hakim, A.N. and Wenten, I.G. (2014), "Advances in electrodeionization technology for ionic separation-A review", *Membr. Water Treat.*, **5**(2), 87-108.
Khoiruddin, Widiasa, I.N. and Wenten, I.G. (2014), "Removal of inorganic contaminants in sugar refining process using electrodeionization", *J. Food Eng.*, **133**, 40-45.
Khoiruddin, K. and Wenten, I.G. (2016), "Investigation of electrochemical and morphological properties of mixed matrix Polysulfone-Silica anion exchange membrane", *J. Eng.Technol. Sci.*, **48**(1), 1-11.
Krishnamoorthy, M., Hakobyan, S., Ramstedt, M. and Gautrot, J.E. (2014), "Surface-initiated polymer brushes in the biomedical field: Applications in membrane science, biosensing, cell culture, regenerative medicine and antibacterial coatings", *Chem. Rev.*, **114**(21), 10976-11026.
Kumar, A. and Dhawan, A. (2013), "Genotoxic and carcinogenic potential of engineered nanoparticles: an update", *Arch Toxicol.*, **87**(11), 1883-1900.
Kumar, R., Isloor, A.M., Ismail, A.F. and Matsuura, T. (2013), "Synthesis and characterization of novel water soluble derivative of chitosan as an additive for polysulfone ultrafiltration membrane", *J. Membr. Sci.*, **440**, 140-147.
Leong, S., Razmjou, A., Wang, K., Hapgood, K., Zhang, X. and Wang, H. (2014), "TiO_2 based photocatalytic membranes: A review", *J. Membr. Sci.*, **472**(0), 167-184.
Li, L.H., Deng, J.C., Deng, H.R., Liu, Z.L. and Xin, L. (2010), "Synthesis and characterization of chitosan/ZnO nanoparticle composite membranes", *Carbohydr. Res.*, **345**(8), 994-998.
Li, M.S., Wang, M.X., Wu, F.Y. and Chu, X.Z. (2016), "Construction of antibacterial layer on polyvinylchloride three-channel hollow fiber membranes", *J. Ind. Eng. Chem.*, **39**, 181-187.

Li, M.S., Zhao, Z.P., Wang, M.X. and Zhang, Y. (2015), "Controllable modification of polymer membranes by LDDLT plasma flow: Antibacterial layer onto PE hollow fiber membrane module", *Chem. Eng. J.*, **265**, 16-26.

Liu, C., de Faria, A.F., Ma, J. and Elimelech, M. (2017), "Mitigation of biofilm development on thin-film composite membranes functionalized with zwitterionic polymers and silver nanoparticles", *Environ. Sci. Technol.*, **51**(1), 182-191.

Liu, T.M., Wu, X.Z. and Qiu, Y.R. (2016), "Enhanced biocompatibility and antibacterial property of polyurethane materials modified with citric acid and chitosan", *J. Biomater Sci Polym Ed.*, 1-21.

Luo, Z., Wu, Q. and Zhang, M. (2012), "The synergistic antibacterial effects of water soluble N-succinyl-chitosan with ceftriaxone against Escherichia coli", *Lett. Drug Des. Discov.*, **9**(9), 848-852.

Ma, W., Soroush, A., Van Anh Luong, T., Brennan, G., Rahaman, M.S., Asadishad, B. and Tufenkji, N. (2016), "Spray- and spin-assisted layer-by-layer assembly of copper nanoparticles on thin-film composite reverse osmosis membrane for biofouling mitigation", *Water Res.*, **99**, 188-199.

Madaeni, S., Zinadini, S. and Vatanpour, V. (2011), "A new approach to improve antifouling property of PVDF membrane using in situ polymerization of PAA functionalized TiO_2 nanoparticles", *J. Membr. Sci.*, **380**(1), 155-162.

Maddah, H. and Chogle, A. (2016), "Biofouling in reverse osmosis: phenomena, monitoring, controlling and remediation", *Appl. Water Sci.*, 1-15.

McCarrell, E.M., Gould, S.W., Fielder, M.D., Kelly, A.F., El Sankary, W. and Naughton, D.P. (2008), "Antimicrobial activities of pomegranate rind extracts: enhancement by addition of metal salts and vitamin C", *BMC Complement Altern. Med.*, **8**(1), 64.

Mi, L. and Jiang, S. (2014), "Integrated antimicrobial and nonfouling zwitterionic polymers", *Angew. Chem. Int. Ed.*, **53**(7), 1746-1754.

Mollahosseini, A. and Rahimpour, A. (2013), "A new concept in polymeric thin-film composite nanofiltration membranes with antibacterial properties", *Biofouling*, **29**(5), 537-548.

Mollahosseini, A. and Rahimpour, A. (2014), "Interfacially polymerized thin film nanofiltration membranes on TiO2 coated polysulfone substrate", *J. Ind. Eng. Chem.*, **20**(4), 1261-1268.

Muñoz-Bonilla, A. and Fernández-García, M. (2012), "Polymeric materials with antimicrobial activity", *Prog. Polym. Sci.*, **37**(2), 281-339.

Mural, P.K.S., Banerjee, A., Rana, M.S., Shukla, A., Padmanabhan, B., Bhadra, S., Madras, G. and Bose, S. (2014), "Polyolefin based antibacterial membranes derived from PE/PEO blends compatibilized with amine terminated graphene oxide and maleated PE", *J. Mater. Chem. A*, **2**(41), 17635-17648.

Mural, P.K.S., Jain, S., Madras, G. and Bose, S. (2017), "Antibacterial membranes for water remediation with controlled leaching of biocidal silver aided by prior grafting of poly (ethylene imine) on to Ozone-Treated polyethylene", *Chem. Select*, **2**(2), 624-631.

Nair, R., Wu, H., Jayaram, P., Grigorieva, I. and Geim, A. (2012), "Unimpeded permeation of water through helium-leak-tight graphene-based membranes", *Science*, **335**(6067), 442-444.

Nikkola, J., Liu, X., Li, Y., Raulio, M., Alakomi, H.L., Wei, J. and Tang, C.Y. (2013), "Surface modification of thin film composite RO membrane for enhanced anti-biofouling performance", *J. Membr. Sci.*, **444**(0), 192-200.

Onaizi, S.A. and Leong, S.S.J. (2011), "Tethering antimicrobial peptides: Current status and potential challenges", *Biotechnol. Adv.*, **29**(1), 67-74.

Ozay, O., Akcali, A., Otkun, M.T., Silan, C., Aktas, N. and Sahiner, N. (2010), "P(4-VP) based nanoparticles and composites with dual action as antimicrobial materials", *Colloid. Surf. B Biointerf.*, **79**(2), 460-466.

Ozay, Y., Dizge, N., Gulsen, H.E., Akarsu, C., Harputlu, E., Ozer, E., Unyayar, A. and Ocakoglu, K. (2016), "Investigation of electroactive and antibacterial properties of polyethersulfone membranes blended with copper nanoparticles", *CLEAN-Soil, Air, Water*, **44**(8), 930-937.

Pan, Y., Yu, Z., Shi, H., Chen, Q., Zeng, G., Di, H., Ren, X. and He, Y. (2016), "A novel antifouling and antibacterial surface-functionalized PVDF ultrafiltration membrane via binding Ag/SiO_2 nanocomposites", *J. Chem. Technol. Biotechnol.*, **92**(3), 562-572.

Park, S.H., Ko, Y.S., Park, S.J., Lee, J.S., Cho, J., Baek, K.Y., Kim, I.T., Woo, K. and Lee, J.H. (2016), "Immobilization of silver nanoparticle-decorated silica particles on polyamide thin film composite membranes for antibacterial properties", *J. Membr. Sci.*, **499**, 80-91.

Pillai, C., Paul, W. and Sharma, C.P. (2009), "Chitin and chitosan polymers: Chemistry, solubility and fiber formation", *Prog. Polym. Sci.*, **34**(7), 641-678.

Pramanik, B.K., Kajol, A., Suja, F. and Md Zain, S. (2016), "Effect of biological and coagulation pre-treatments to control organic and biofouling potential components of ultrafiltration membrane in the treatment of lake water", *Environ. Technol.*, **38**(5), 579-587.

Qiu, S., Wu, L., Pan, X., Zhang, L., Chen, H. and Gao, C. (2009), "Preparation and properties of functionalized carbon nanotube/PSF blend ultrafiltration membranes", *J. Membr. Sci.*, **342**(1), 165-172.

Rahaman, M.S., Thérien-Aubin, H., Ben-Sasson, M., Ober, C.K., Nielsen, M. and Elimelech, M. (2014), "Control of biofouling on reverse osmosis polyamide membranes modified with biocidal nanoparticles and antifouling polymer brushes", *J. Mater. Chem. B*, **2**(12), 1724-1732.

Rahimpour, A., Jahanshahi, M., Rajaeian, B. and Rahimnejad, M. (2011), "TiO_2 entrapped nano-composite PVDF/SPES membranes: Preparation, characterization, antifouling and antibacterial properties", *Desalination*, **278**(1-3), 343-353.

Razi, F., Sawada, I., Ohmukai, Y., Maruyama, T. and Matsuyama, H. (2012), "The improvement of antibiofouling efficiency of polyethersulfone membrane by functionalization with zwitterionic monomers", *J. Membr. Sci.*, **401-402**, 292-299.

Regiel, A., Irusta, S., Kyzioł, A., Arruebo, M. and Santamaria, J. (2013), "Preparation and characterization of chitosan-silver nanocomposite films and their antibacterial activity against Staphylococcus aureus", *Nanotechnol.*, **24**(1), 015101.

Reiad, N.A., Salam, O.E.A., Abadir, E.F. and Harraz, F.A. (2012), "Adsorptive removal of iron and manganese ions from aqueous solutions with microporous chitosan/polyethylene glycol blend membrane", *J. Environ. Sci. (China)*, **24**(8), 1425-1432.

Ronen, A., Resnick, A., Lerman, S., Eisen, M.S. and Dosoretz, C.G. (2016), "Biofouling suppression of modified feed spacers: Localized and long-distance antibacterial activity", *Desalination*, **393**, 159-165.

Saeki, D., Karkhanechi, H., Matsuura, H. and Matsuyama, H. (2016), "Effect of operating conditions on biofouling in reverse osmosis membrane processes: Bacterial adhesion, biofilm formation, and permeate flux decrease", *Desalination*, **378**, 74-79.

Saeki, D., Nagao, S., Sawada, I., Ohmukai, Y., Maruyama, T. and Matsuyama, H. (2013), "Development of antibacterial polyamide reverse osmosis membrane modified with a covalently immobilized enzyme", *J. Mem. Sci.*, **428**, 403-409.

Shen, X., Zhao, Y. and Chen, L. (2015), "Polycation-Grafted poly (vinylidene fluoride) membrane with biofouling resistance", *Chem. Eng. Technol.*, **38**(5), 859-866.

Shimazaki, Y., Mitsuishi, M., Ito, S. and Yamamoto, M. (1997), "Preparation of the layer-by-layer deposited ultrathin film based on the charge-transfer interaction", *Langmuir*, **13**(6), 1385-1387.

Sile-Yuksel, M., Tas, B., Koseoglu-Imer, D.Y. and Koyuncu, I. (2014), "Effect of silver nanoparticle (AgNP) location in nanocomposite membrane matrix fabricated with different polymer type on antibacterial mechanism", *Desalination*, **347**(0), 120-130.

Sondi, I. and Salopek-Sondi, B. (2004), "Silver nanoparticles as antimicrobial agent: a case study on E. coli as a model for Gram-negative bacteria", *J. Colloid Interf. Sci.*, **275**(1), 177-182.

Sui, Y., Wang, Z. and Gao, C. (2014), "A new synthetical process of PVDF derivatives via atom transfer radical graft polymerizations and its application in fabrication of antifouling and antibacterial PVDF ultrafiltration membranes", *Desalination Water Treat.*, **52**, 6377-6388.

Tada, S., Inaba, C., Mizukami, K., Fujishita, S., Gemmei-Ide, M., Kitano, H., Mochizuki, A., Tanaka, M. and Matsunaga, T. (2009), "Anti-Biofouling properties of polymers with a carboxybetaine moiety", *Macromol. Biosci.*, **9**(1), 63-70.

Tamayo, L., Azócar, M., Kogan, M., Riveros, A. and Páez, M. (2016), "Copper-polymer nanocomposites: An excellent and cost-effective biocide for use on antibacterial surfaces", *Mater. Sci. Eng.: C*, **69**, 1391-1409.

Tan, H., Ma, R., Lin, C., Liu, Z. and Tang, T. (2013), "Quaternized chitosan as an antimicrobial agent: antimicrobial activity, mechanism of action and biomedical applications in orthopedics", *Int. J. Mol. Sci.*, **14**(1), 1854.

Tang, L., Gu, W., Yi, P., Bitter, J.L., Hong, J.Y., Fairbrother, D.H. and Chen, K.L. (2013), "Bacterial anti-adhesive properties of polysulfone membranes modified with polyelectrolyte multilayers", *J. Membr. Sci.*, **446**, 201-211.

Taurozzi, J.S., Arul, H., Bosak, V.Z., Burban, A.F., Voice, T.C., Bruening, M.L. and Tarabara, V.V. (2008), "Effect of filler incorporation route on the properties of polysulfone-silver nanocomposite membranes of different porosities", *J. Membr. Sci.*, **325**(1), 58-68.

Tiraferri, A., Vecitis, C.D. and Elimelech, M. (2011), "Covalent binding of Single-Walled carbon nanotubes to polyamide membranes for antimicrobial surface properties", *ACS Appl. Mater. Interf.*, **3**(8), 2869-2877.

Tischer, W. and Wedekind, F. (1999), *Immobilized Enzymes: Methods and Applications, Biocatalysis-from discovery to application: Volume 200 of the series Topics in Current Chemistry*, Springer Berlin Heidelberg

Vatanpour, V., Madaeni, S.S., Khataee, A.R., Salehi, E., Zinadini, S. and Monfared, H.A. (2012), "TiO_2 embedded mixed matrix PES nanocomposite membranes: influence of different sizes and types of nanoparticles on antifouling and performance", *Desalination*, **292**, 19-29.

Waheed, S., Ahmad, A., Khan, S.M., Gul, S.E., Jamil, T., Islam, A. and Hussain, T. (2014), "Synthesis, characterization, permeation and antibacterial properties of cellulose acetate/polyethylene glycol membranes modified with chitosan", *Desalination*, **351**, 59-69.

Waheed, S., Ahmad, A., Khan, S.M., Gul, S.E., Jamil, T., Islam, A. and Hussain, T. (2014), "Synthesis, characterization, permeation and antibacterial properties of cellulose acetate/polyethylene glycol membranes modified with chitosan", *Desalination*, **351**, 59-69.

Wang, M.-z., Wang, T., Yuan, K. and Du, J. (2016), "Preparation of water dispersible poly (methyl methacrylate)-based vesicles for facile persistent antibacterial applications", *Chinese J. Polym. Sci.*, **34**(1), 44-51.

Wang, P., Hadjar, O., Gassman, P.L. and Laskin, J. (2008), "Reactive landing of peptide ions on self-assembled monolayer surfaces: an alternative approach for covalent immobilization of peptides on surfaces", *Phys. Chem. Chem. Phys*., **10**(11), 1512-1522.

Wang, R., Neoh, K.G. and Kang, E.T. (2015), "Integration of antifouling and bactericidal moieties for optimizing the efficacy of antibacterial coatings", *J. Colloid Interf. Sci.*, **438**, 138-148.

Weng, X.D., Ji, Y.L., Ma, R., Zhao, F.Y., An, Q.F. and Gao, C.J. (2016), "Superhydrophilic and antibacterial zwitterionic polyamide nanofiltration membranes for antibiotics separation", *J. Membr. Sci.*, **510**, 122-130.

Wenten, I.G. and Khoiruddin (2016), "Recent developments in heterogeneous ion-exchange membrane: preparation, modification, characterization and performance evaluation", *J. Eng. Sci. Technol.*, **11**(7), 916-934.

Wenten, I.G. (1995), "Mechanisms and control of fouling in crossflow microfiltration", *Filtr. Separat.*, **32**(3), 252-253.

Wenten, I.G. and Khoiruddin (2016), "Reverse osmosis applications: Prospect and challenges", *Desalination*, **391**, 112-125.

Wenten, I.G., Khoiruddin, Arfianto, F. and Zudiharto (2013), "Bench scale electrodeionization for high pressure boiler feed water", *Desalination*, **314**, 109-114.

Wenten, I.G. and Widiasa, I.N. (2002), "Enzymatic hollow fiber membrane bioreactor for penicilin hydrolysis", *Desalination*, **149**(1-3), 279-285.

Wu, B., Wang, R. and Fane, A.G. (2016), "The roles of bacteriophages in membrane-based water and wastewater treatment processes: A review", *Water Res.*, **110**, 120-132.

Xu, N. and Ding, D. (2015), "Preparation and antibacterial activity of chitosan derivative membrane complexation with iodine", *RSC Adv*., **5**(97), 79820-79828.

Xue, Y., Xiao, H. and Zhang, Y. (2015), "Antimicrobial polymeric materials with quaternary ammonium and phosphonium salts", *Int. J. Mol. Sci.*, **16**(2), 3626-3655.

Yang, H.C., Hou, J., Chen, V. and Xu, Z.K. (2016), "Surface and interface engineering for organic-inorganic composite membranes", *J. Mater. Chem. A*, **4**, 9716-9729.
Yang, Y.F., Li, Y., Li, Q.L., Wan, L.S. and Xu, Z.K. (2010), "Surface hydrophilization of microporous polypropylene membrane by grafting zwitterionic polymer for anti-biofouling", *J. Membr. Sci*., **362**(1), 255-264.
Yang, Y.F., Hu, H.Q., Li, Y., Wan, L.S. and Xu, Z.K. (2011), "Membrane surface with antibacterial property y grafting polycation", *J. Membr. Sci.*, **376**(1-2), 132-141.
Yao, F., Fu, G.D., Zhao, J., Kang, E.T. and Neoh, K.G. (2008), "Antibacterial effect of surface-functionalized polypropylene hollow fiber membrane from surface-initiated atom transfer radical polymerization", *J. Membr. Sci.*, **319**(1-2), 149-157.
Younas, H., Fei, Y., Shao, J. and He, Y. (2016), "Developing an antibacterial super-hydrophilic barrier between bacteria and membranes to mitigate the severe impacts of biofouling", *Biofoul.*, **32**(9), 1089-1102.
Youssef, A.M., Kamel, S. and El-Samahy, M.A. (2013), "Morphological and antibacterial properties of modified paper by PS nanocomposites for packaging applications", *Carbohydr. Polym.*, **98**(1), 1166-1172.
Zhang, X., Wang, L. and Levanen, E. (2013), "Superhydrophobic surfaces for the reduction of bacterial adhesion", *RSC Adv.*, **3**(30), 12003-12020.
Zhang, X., Wang, Z., Chen, M., Liu, M. and Wu, Z. (2016), "Polyvinylidene fluoride membrane blended with quaternary ammonium compound for enhancing anti-biofouling properties: Effects of dosage", *J. Membr. Sci.*, **520**, 66-75.
Zhang, Z.B., Wu, J.J., Su, Y., Zhou, J., Gao, Y., Yu, H.Y. and Gu, J.S. (2015), "Layer-by-layer assembly of graphene oxide on polypropylene macroporous membranes via click chemistry to improve antibacterial and antifouling performance", *Appl. Surf. Sci.*, **332**, 300-307.
Zinadini, S., Rostami, S., Vatanpour, V. and Jalilian, E. (2017), "Preparation of antibiofouling polyethersulfone mixed matrix NF membrane using photocatalytic activity of ZnO/MWCNTs nanocomposite", *J. Membr. Sci.*, **529**, 133-141.

RJ