Jurnal
Teknologi

Full Paper

INCORPORATION OF BACTERICIDAL NANOMATERIALS IN DEVELOPMENT OF ANTIBACTERIAL MEMBRANE FOR BIOFOULING MITIGATION: A MINI REVIEW

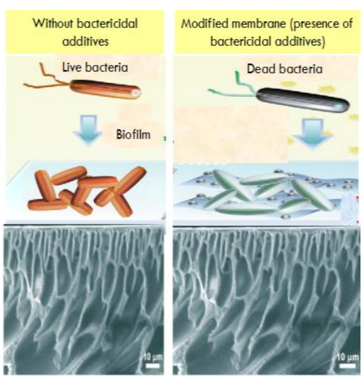
Article history
Received
24 August 2016
Received in revised form
7 October 2016
Accepted
4 November 2016

A. Nazerah[a,b], A. F. Ismail[a*], Juhana Jaafar[a]

[a]Advanced Membrane Technology Research Centre (AMTEC), Faculty of Petroleum and Renewable Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b]Universiti Kuala Lumpur - Malaysia Institute of Chemical and Bioengineering Technology (UniKL - MICET), Lot 1988, Kawasan Perindustrian Bandar Vendor, Alor Gajah, Melaka, Malaysia

*Corresponding author
afauzi@utm.my

Graphical abstract



Abstract

Biofouling has become concern issue in all pressure driven membrane technology. The attachment of microorganism to the membrane surface gave an effect to membrane life span, increased operating and maintenance costs. Therefore, this review is focusing on the development of nanocomposite membrane based on improving bactericidal properties to suppress the activity of attached organisms in order to minimize biofilm formation. This approach was done with incorporation of biocidal nanomaterials into a polymeric membrane matrix by include metal-based nanoparticles such as Titanium dioxide (TiO_2), Copper (Cu), Silver (Ag), Zinc oxide (ZnO); carbon-based nanomaterials including graphene oxide (GO) and carbon nanotubes (CNTs) and hybrid nanomaterials. Current constraints and prospective by the use of nanomaterials are discussed in order to increase antibacterial property for long term application for further implementation in membrane systems from the views of water and wastewater treatment applications.

Keywords: Biofilm, antimicrobial properties, nanoparticles, surface modification

Abstrak

Biofouling menjadi isu dalam semua teknologi membran yang berasaskan tekanan. Lampiran mikroorganisma ke atas permukaan membran telah memberi kesan terhadap jangka hayat membran serta meningkatkan kos operasi dan penyelenggaraan. Dengan itu, kajian ini memberi tumpuan kepada pembangunan membran nanokomposit dengan meningkatkan ciri-ciri bakteria untuk menyekat aktiviti pelekatan organisma dalam pembentukan biofilm. Pendekatan ini telah dilakukan dengan penambahan bahan nano biocidal ke dalam matriks membran polimer nanopartikel berasaskan logam nano partikel iaitu Titanium dioksida (TiO_2), tembaga(Cu), perak (Ag), Zink dioksida(ZnO); bahan nano berasaskan karbon termasuk graphene oksida (GO) dan nanotube karbon (CNTs) dan bahan nano hibrid. Kekangan semasa dan potensi melalui penggunaan bahan nano dalam turut dibincangkan untuk meningkatkan sifat antibakteria bagi pelaksanaan jangka panjang selanjutnya bagi sistem membran dari sudut air dan aplikasi rawatan air sisa

Kata kunci: Biofilm, ciri-ciri antimikrob, nanopartikel, pengubahsuaian permukaan

1.0 INTRODUCTION

The demand of high quality water has becomes critical concern as water resource quality degradation has been a severe social and global problem, particularly in less developed countries and causing millions of deaths annually. Moreover, severity of clean water shortage continuously increases due to the rapid growth of world population, urbanization, emergent industrial activity and water pollution. Major waste effluent sources which include domestic sewage, industrial effluent and agriculture runoff have been identified to discharge notorious anthropogenic pollutants to the aquatic system. Furthermore, the presence of pathogenic microorganisms in wastewater treatment plant such as *Escherichia coli, Vibrio, cholera, Salmonella spp* is harmful to human health and have caused water borne-disease such as diarrhea, cholera, septicemia, gastroenteritis [1].This is most probably because of the effluents are not being properly treated in wastewater treatment plants and are released into surface waters resulting in toxin accumulation, which adversely posing serious threat to the environment and health [2]. Consequently, this degradation in water quality will cause water scarcity and it is expected by the year 2025,this problem will become a major issue when global water consumption would reach to 3800 km^3/year [3].

In the last decades, the pressure driven membrane processes such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) have been widely applied in water and wastewater treatment, biotechnology, food industry and medicine [4] due to its small size, ease of maintenance, excellent separation efficiency and high water quality. Despite these advantages, organic and biological fouling still remains as one of the major obstacles to its efficient application. Biofouling based on the tendency of the organics or microorganism to attach and grow onto the surface of the membrane. These microorganisms still remain as one of the major hindrance which deters the efficiency of its application. Biofouling is based on the tendency of the organics or microorganism to attach and grow onto the surface of the membrane. Once this microorganism steadily deposited, it has tendency to produce extracellular polymeric secretions(EPS) containing 70-80% of various proteins such as glycoproteins, lipoproteins, poly saccharides and other biomolecules [5]. Eventually, biofilm formation will raised on membrane surface based on accumulation of EPS and reproduction of bacteria [6, 7]. As a result, it causes of diminishing membrane performance over time as flux reduction, rejection impairment and reduce membrane life span, consequently, increase operational and maintenance costs [7].

Hence, membrane modification is a more practical approach to overcome the biofouling since tailor ability of the membrane materials allowed specific modification to be implemented. Improving bacteriostatic properties can effectively minimize the biofilm formation via blending [8], grafting [9], surface coating [10], antimicrobial additive [11], and inorganic additives [12] has shown positive remarks. These approaches usually reduce mutual hydrophobic interactions between membrane surface, microorganisms and compounds present in the feed. Thereby reducing membrane biofouling [13].

The incorporation of nanoparticles in altering polymeric membranes has offered an innovative potential solution during the last few years in preventing membrane biofouling and enhancing water flux performance [14]. Many efforts have been focused on the nano-metals such as Ag,TiO_2 and Cu to be imparted into the polymer membrane due to its potential to act as antibacterial agent [16, 17]. The potential of these particles can be more concise in terms of their high surface area per volume and toxic to a wide spectrum of microorganisms. Interestingly, they are able to deactivate bacteria cells by different mechanism, including osmotic collapse, reciprocity with phosphorus and sulfur, a release of intracellular material, and enlargement of cell membrane permeability [17]. Hence, this mini review will discuss the improvement of antibacterial membranes through incorporation of biocidal nanomaterials on the membrane surface. Thereafter, the limitation of biocidal nanomaterials in antibacterial membrane development will be discussed and summarized.

2.0 SURFACE MODIFICATION STRATEGIES TO SUPPRESS BIOFOULING

Membrane biofouling alone responsible for 45% of all fouling occurs in membrane filtration systems [18]. Pathogenic bacteria such as *Salmonella sp., Shigella sp., Vibrio cholera, Yersinia enterocolitica, Y.pseudotuberculosis, Leptospira sp., Francis Ella tularensis, Dyspepsia coli,* enterotoxin producing *E.coli* and *Pseudomonas* is commonly found in wastewater treatment plant. In general, biofouling sequence can be summarized into four steps: (a.) adsorption of organic matters to membrane surface; (b.) microorganism adsorption and continued adhesion to the membrane surface; (c.) growth, reproduction of adhering microorganisms; (d.) subsequent secretion of extracellular polymers, mutual adhesion of the clonal cells and the formation of biofilm.

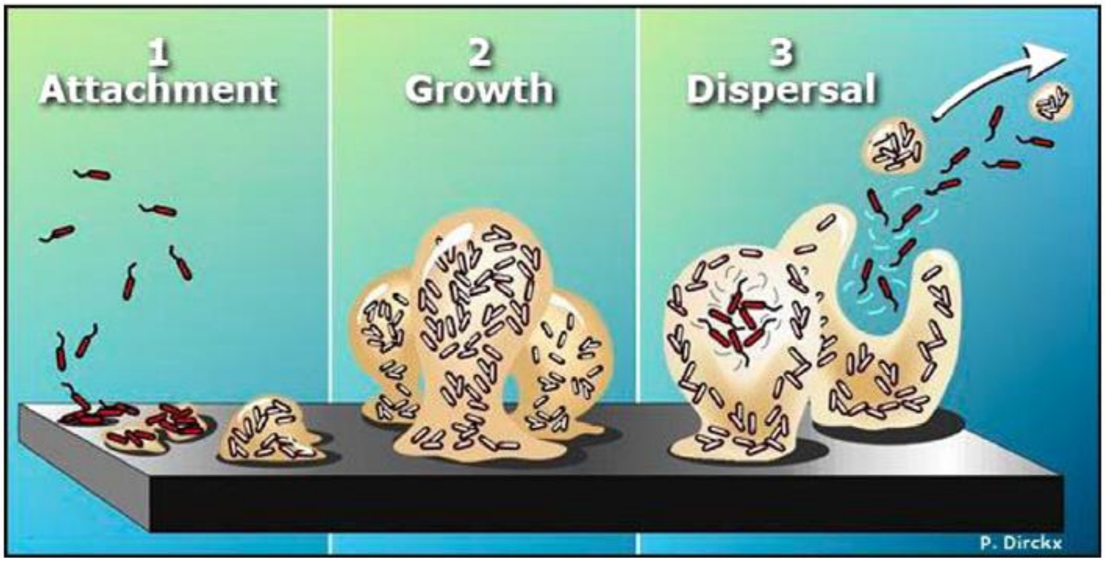


Figure 1 Stages in the formation of biofilms[5]

The attachment of microorganisms to the membrane surface is influenced by factors such as membrane material, the roughness surface and hydrophobicity and membrane surface charge. Factors affecting the adhesion of microorganisms to membrane surfaces are summarized in Table 1.

Table 1 Factors affecting microorganism adhesion to membrane surfaces [19]

Factors	Properties
Microorganism	Species Composition of mixed population Population density Growth phase Nutrient status Hydrophobicity Charges Physiological response
Surface	Chemical composition Surface charge Surface tension Hydrophobicity Conditioning film Roughness Porosity
Feed water	Temperature pH Dissolved organic matter Dissolved inorganics Suspended matter Viscosity Shear forces Boundary layer Flux

Hence, membrane surface modification is needed primarily to prevent or retard biofilm formation on one or more of these stages. For example, bacterial adhesion has been found to decrease significantly by making the surface more hydrophilic, negatively charged and/or smooth [20]. Similarly, deactivation of irreversibly adhered microorganisms can be achieved by a few different methods that include the incorporation of antimicrobial nanomaterials [21].

The incorporation biocidal nanomaterials are now becoming a favorable approach to enhance the antimicrobial activity in membrane modification to combat biofouling problem. Currently, there is increasing attention in engineering nanomaterial which possessed strong antibacterial properties which include silver nanoparticles [22], photocatalytic TIO_2 [23], copper nanoparticles [24], carbon nanotubes [25] and graphene [26] .

This technique is also considered as a potential and effective route to develop antifouling membranes. Therefore, membranes with inherent biocidal properties may be helpful in reducing fouling by means of killing bacteria either before they are able to attach to the surface or before they proliferate, ergo reducing the extent of biofilm formation.

3.0 INCORPORATION OF BACTERICIDAL NANOPARTICLES

With proper incorporation of antimicrobial nanomaterials, the dead microorganisms are incapable to develop and form a matured bio-film on the membrane surface, which is a form of irreversible fouling [27]. Silver (Ag) nanoparticles recognized as an outstanding biocidal agent due to its toxicity to a wide range of bacteria. Moreover, this material has attracted huge attention in various applications, including antimicrobial coating, plastics and wound dressings. The ability of this material has opened a great number of studies related to suppress biofouling.

For instance, Zodrow *et al.* [28] studied, about antibacterial effect of nanosilver (n)Ag incorporated into polysulfone ultrafiltration membranes (nAg-Psf)The modified membrane demonstrated excellent antimicrobial effect of a wide variety of bacteria, including *Escherichia coli K12, Pseudomonas mendocina KR1, and the MS2 bacteriophage*. It is suggested by Morones *et al.* [29] that antibacterial effects was primarily due to release of Ag^{+} ions. In addition, the functionality of the membrane also improved not only as antimicrobial but also acts as anti-adhesion. Thus, it will prevent biofilm formation. In a different study, Basri *et al.* [30] modified PES membrane by adding AgNps as the antibacterial agent and described that Ag NPs have significantly enhanced the membrane performance with increasing antibacterial activity and also improve hydrophilicity of the membrane with increasing of Ag NPs loading. The use AgNPs in wastewater was further enhanced by Yin *et al.* [31] by improving the bonding between Ag nanoparticles and surface of TFC membrane by using cross linking agent. It is observed that the modified membrane has excellence antibacterial activity as no bacteria growth on the membrane surface as shown in Figure 2.

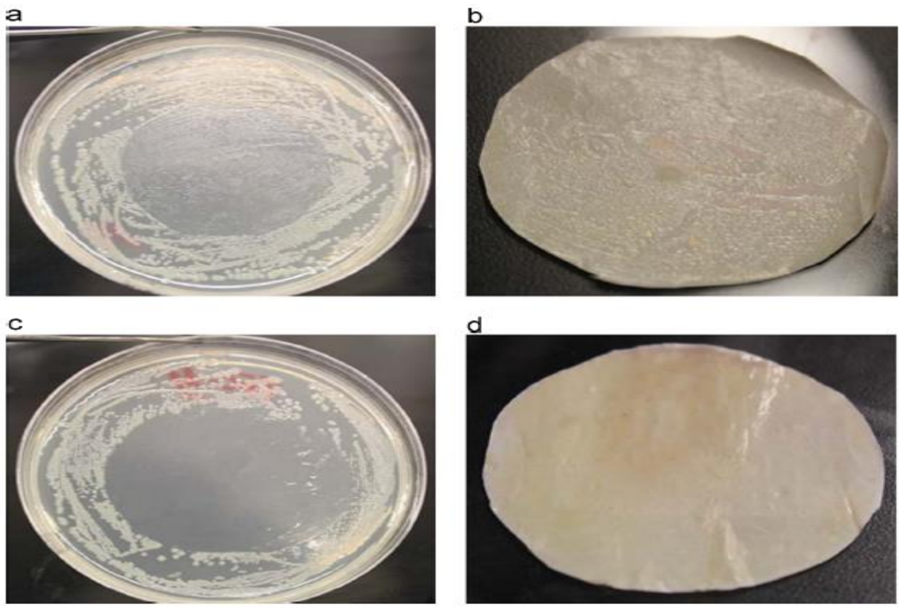


Figure 2 Difference in E.coli biofilm growth on TFC membrane and TFC-S-AgNPs membrane(a)area contacted with TFC(b)TFC surface(control)(c) area contacted with TFC-S-AgNPs (d) TFC-S-AgNPs surface[31]

On the other hand, Ben-Sasson *et al.* [32] employed simple dip coating technique to functionalize PA surface with copper suspension capped with polyethyleneimine. The positively charged polyethylenimine (PEI) enhanced Cu-NPs and create strong electrostatic attraction to the negatively charged PA surface. The number of viable of 3 model bacteria, *Pseudomonas aeruginosa*, and *Staphylococcus aureus* were respectively attached on the TFC RO membrane functionalized with Cu NPs which resulted in tremendously decreased of 87%±0.2%, 96%±3%, and 79.5%±13% , after 1 h contact relative to the control. The results were generally allied with the biocidal properties of the bound Cu-NPs.

The potential of bactericidal property TiO_2 nanoparticles was examined by depositing it onto TFC PA membrane and exposing it to the suspensions contained microbial under UV and absence of UV light[33]. As illustrated in Figure 3, the numbers of E.coli on the modified membrane are significantly decreased with the presence of UV light. Meanwhile, membrane surface without TiO_2 nanoparticles and membrane imparted with TiO_2 without UV light show high growth of bacteria. This study proved the ability of TiO_2 particle to combat biofouling which is considerably realized by the presence of UV irradiation.

In another work, the use of TiO_2 NPs in reduction of biofouling was demonstrated as it was deposited onto different UF membranes namely PS100(polysulfone), P005(polyethersulfone), C100(regenerated cellulose) under ultraviolet (UV) irradiation [20]. It can be seen that severe reduction in a quantity of *P.putida* cells on the surface of the membrane with deposits TIO_2 with antibacterial rate is about 98.1%.

Apparently, TiO_2 particles have imparted strong photo bactericidal properties on the membrane. Thus, the modified membrane demonstrated excellent flux performance with 1.7-2.3 times higher and shown more resistant to biofouling compared with control samples. Figure 4 depicted a number of *P.putida* cells on the surface of initial and TiO_2 modified membrane samples with and without UV treatment.

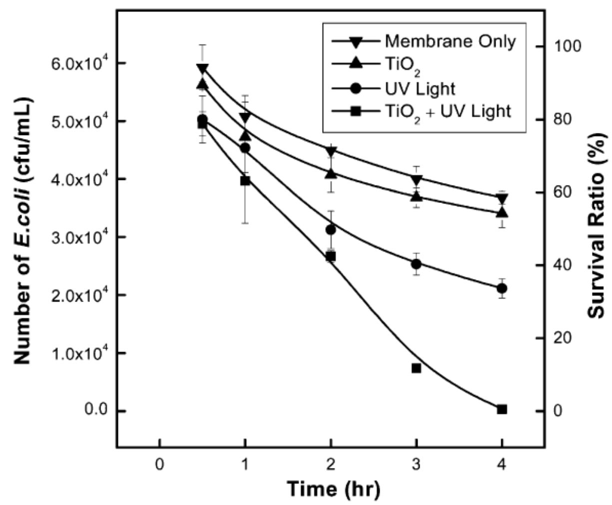


Figure 3 Cell number and survival ratio of E.coli in the hybrid and the neat TFC membranes in the dark and with UV illumination[33]

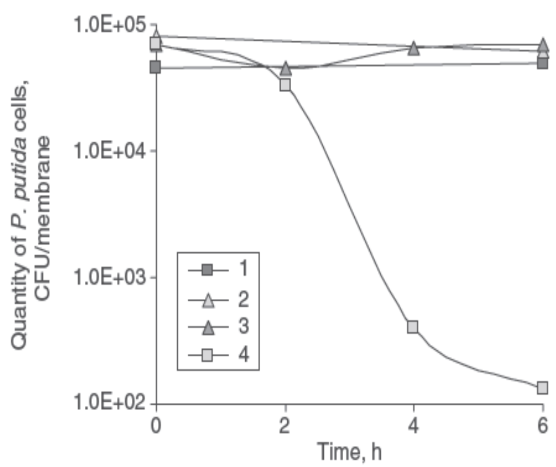


Figure 4 The number of P.putida cells on the surface of PS100 membranes vs the time of black UV-irradiation: 1- initial membrane, in the dark;2-membrane with deposited TiO_2,in the dark;3- initial membrane treated by UV;4-membrane with deposited TiO_2 treated by UV.ΔP= 3bar[20]

4.0 INCORPORATION OF CARBON BASED NANOMATERIALS

Although biocidal nanoparticles are effective to suppress microbial activity, they are not sustainable for a long period application since its antibacterial activity depleted over time [34]. Recently, carbon nanotubes (CNTs) and graphene have become favorable as biocidal agent since they have been discovered to impede grow of bacteria upon direct contact with bacterial cells [35, 36, 37]. Graphene and its derivatives like graphene oxide(GO) known have abundant oxygen containing functional groups(hydroxyl and epoxy groups on the basal planes, and carboxyl and carbonyl groups on the edges [38]. This feature has attracted huge attention in waste and wastewater treatment application since it can be easily manipulated and it assist the interaction of GO sheets with a wide variety of organic and inorganic materials.

Most studies have focused on incorporating graphene oxide(GO) into the polymer matrix in order to improved permeability, enhance antibacterial effects and high mechanical strength properties [39].Interestingly, this material can be produced at relatively low cost via oxidation of graphite. According to Liu *et al.* [40], Akhavan and Ghaderi [41], the antibacterial activity mechanism of graphene oxide acted by inducing membrane damage, mediated by physical disruption, charge transfer and formation of reactive oxygen species, and extraction of lipid from the cell membrane. Recently, efforts toward improving the membrane active layer by functionalization of graphene oxide on the TFC membrane was successfully employed by Perreault *et al.* [34]. The modified membranes showed excellent antibacterial performance compared to control-TFC membrane. SEM images as presented in Figure 5 indicated that the bacteria cells attached to the modified membranes exhibit destruction of cell structure compared to the control-TFC membrane.

Apart of GO, CNTs were also reported to exhibit antibacterial activity. The inactivation of bacteria cells performed by destruct the membranes of bacterial and disrupt their metabolic pathways based on oxidative stress [25]. The potential of CNTs function inactivation of bacteria was proved by a study conducted by Tiraferri *et al*. [35] with deposition of single-walled carbon nanotube (SWCNT) on TFC membrane. The modified membrane showed to have excellent antibacterial properties as 60% inactivation cells within 1 hour of contact time. A similar study was demonstrated by Kim *et al.* [36]) via deposition of oxidized CNTs on TFC RO membranes and stabilize by polyvinyl alcohol (PVA) coating shows excellent anti-biofouling properties as well as water flux. However, biofouling resistance property of the modified membrane was reduced due to the agglomeration formed as the amount of CNT added to the membrane increased.

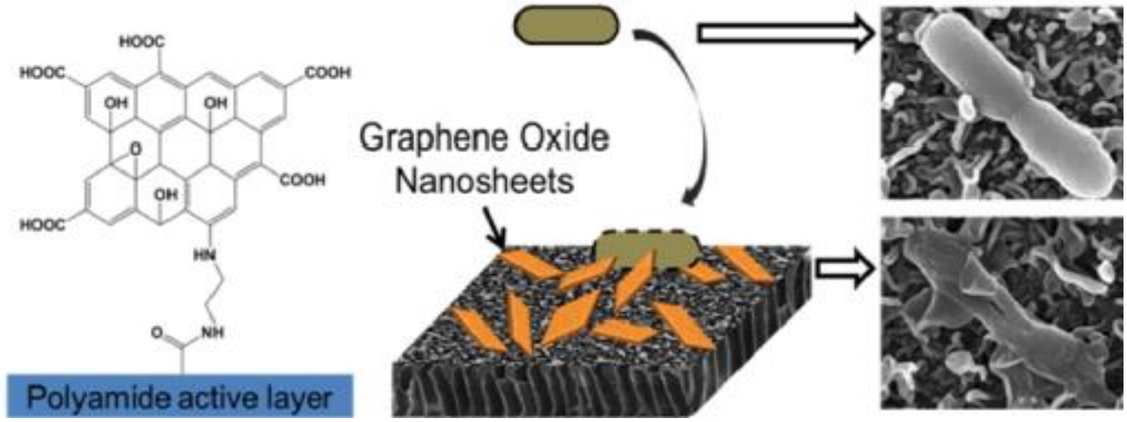


Figure 5 The existence of antimicrobial properties of functionalization of graphene oxide on the surface TFC membrane[34]

5.0 RECENT PROGRESS OF ENHANCED ANTIBACTERIAL PROPERTY AND STABILITY NANOMATERIALS IN ANTI BACTERIAL MEMBRANES

Depletion of nanoparticles is a common phenomenon when adding biocidal nanoparticles such as Ag and Cu into membranes via physical blending. Blending is a typical method widely used in surface modification and most preferable since it's simple, yet efficient in enhancing membrane morphological properties as well as its filtration performance [42, 43].

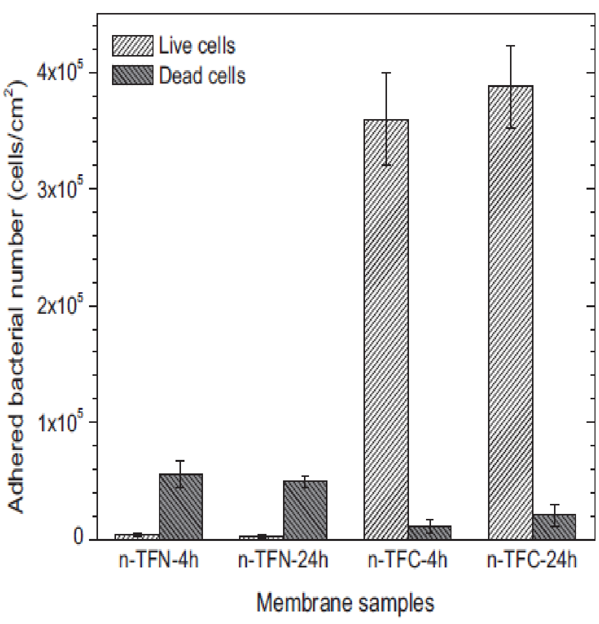


Figure 6 The adhered bacterial numbers(live and dead) on n-TFC and n-TFN membranes after 4h and 24 h immersion *in P.aeruginosa* PAO1 suspension [44]

However, due to the lack of compatibility of the nanoparticles with a polymer, it has a tendency to leach out during phase inversion process and/or filtration which will lead to a shorter antibacterial time as well as affecting the aquatic micro-organism when it is disposed and released. Moreover, this technique contributed the lack of effectiveness contact between nanoparticles and bacteria, hampered it from successfully reduce irreversible membrane fouling.

In order to improve the depletion of NPs, it is essential to create a carrier to control the NPs release by embedding specific nanoparticle within the TFN membrane as shown in Figure 6. For instance, Li *et al.* [45] proved that, the release time of silver can be controlled for a long time by imparting silver in the plasma sprayed with wollastonite coated by direct immersion of the coating specimens in $AgNO_3$ aqueous solution. In another study carried out by Liao *et al.* [42] by synthesized silver–exchanged NaY zeolite particle and blending it with PVDF to form a membrane via phase inversion technique. The hybrid membrane exhibited excellent and long lasting antibacterial activity against *Escherichia coli (E.*coli).Some substances have been used to bind silver on different materials, such as silane [46], and chitosan [47]. For instance, Zhu *et al.* [47] immobilized silver onto the surface of a chitosan membrane via the coordination between silver ions and the amino groups(nitrogen atoms) of chitosan. Table 2 shows the summary of recent studies related to stability and prolong the antibacterial activity in antibacterial membrane development.

These reported studies have demonstrated that the incorporation of nanomaterials into polymer could not only host unique functionalities such as antibacterial and photocatalytic characteristics into the membranes, but also able to tune structure and physicochemical properties such as hydrophilicity, porosity, surface charge of the membranes.

Table 2 Recent progress to improve the stability and prolong antibacterial activity of membrane

Application	Filler/ Polymer	Fabrication Method	Notable remarks	Performance	Reference
UF	HNT-Chitosan-Ag/PES	Blending/phase-inversion method	HNT acts as a carrier to enhanced antibacterial activity by control/delay silver release for a long time. The modified membrane become, more hydrophilic.	Pure water flux= 233.0% Antibacterial rates= 94.0% (*E.coli*) and (*S. aureus*)=92.6%	[16]
UF	HNT-Ag/PES	Blending/phase-inversion method	The modified HNTs were dispersed uniformly and the silver nanoparticles existed on the surface of the hybrid membrane.	Pure water flux= 251.5% Antibacterial rates against E.coli and S. aureus were about 99.9% and 99.8%, respectively.	[48]
UF	Ag-sodium zirconium phosphate (nanoAgZ)/ PES	Blending/phase-inversion method	The particles well distributed in membrane, but tend to agglomerate when increase the loading of nanoparticle. good antibacterial and antifouling property against E. coli and Pseudomonas sp.	Pure water flux= 100.6 L.m^2/hr BSA rejection= 96.7%. contact angle decrease from 71.5 ° to 52.6°	[43]
UF	Ag^+ exchanged NaY zeolite particles (AgNaY)/ PVDF	Blending/phase-inversion method	The increased of Ag^+ content led to better antibacterial activity and long lasting antibacterial activity against E. coli.	Pure water flux = 679 L.m^2/hr (12%) BSA retention rate= >92%	[42]
	Ag/MWCNT	coating	Effectively inactivate the growth of bacteria and prohibited the formation of biofilm.	relative flux drop = 6%,	[49]
	aminated polyethersulfone (NH_2-PES	phase-inversion method	Control silver release rate by 40% slower and significantly improve four times antibacterial property of modified membrane		[50]

6.0 CONCLUSION AND PERSPECTIVES

The development of anti-biofouling is in fact a critical research in membrane technology for water and wastewater treatment and it has attracted huge attention in recent years. Presently, many approaches have been employed for development of biofouling composite membranes with the incorporation of biocidal nanomaterials, including surface coating and blending. These techniques are very favorable due to improvement of antifouling property as well as membrane surface charge. However, there are issues raised from the imparted bactericidal nanomaterials in polymer membrane. The incorporation nanoparticles like silver which it has a tendency to leach from the membrane surface. As a result, the antibacterial property depleted over time and eventually can threat to aquatic life system. In order to overcome this shortcoming, there is a need for further research focusing on enhancing the silver control release rate and also devise new strategies in order to improve dispersion of nanoparticles efficiently on surface of the membrane. These improvements will eventually create better contact between bacteria cells and bactericidal nanoparticles.

Meanwhile, urged efforts are also need to be taken in order to prevent growth of silver-resistant bacterial strains. This issue can be addressed by combining potential biocidal materials from polymer with biocidal nanomaterials. This can help to impart membrane with antibacterial activity against a wide variety of bacteria and viruses and provide long term protection against biofouling. Therefore, it should be pointed out that, it is still very challenging to develop low biofouling resistance membranes without disregards separation performance as well. Thus, new advanced materials and approaches need to be explored to meet the expectation requirement needed for wastewater application.

Acknowledgement

The authors are grateful for research financial support by the Ministry of Higher Education under Higher Institution Centre of Excellence (HICoE) grant scheme (Vot no J141) and (Vot no 4J184).

References

[1] Xiao. G., X. Zhang, W. Zhang, S. Zhang, H. Su, and T. Tan. 2015. Visible-light-mediated Synergistic Photocatalytic Antimicrobial Effects And Mechanism Of Ag-nanoparticles@chitosan-TiO2 Organic-Inorganic Composites For Water Disinfection. *Applied. Catalst. B Environment.* 170-171: 255-262.
[2] Reddy D. H. K and S. M. Lee. 2012. Water Pollution and Treatment Technologies. *Journal Analytical and Environmental Toxicology*. 2(5): 5-6.
[3] Jury.W.a and H. Vaux. 2005. The Role Of Science In Solving The World's Emerging Water Problems. *Proceedings of the National Academy of Sciences of the United States of America.* 102(44): 15715-15720.
[4] Baker. R. 1995. *Membrane Technology And Applications*. Second edition. England: West Sussex.
[5] Mansouri, J., Simon Harrison, and V. Chen. 2010. Strategies For Controlling Biofouling In Membrane Filtration Systems : Challenges And Challenges And Opportunities. *Journal of Materials Chemistry.* 20: 4567-4586.
[6] Cheng, G., Z. Zhang, S. Chen, J. D. Bryers, and S. Jiang. 2007. Inhibition Of Bacterial Adhesion And Biofilm Formation On Zwitterionic Surfaces. *Biomaterials*. 28(29): 4192-4199.
[7] Zhao, Y. H., X. Y. Zhu, K. H. Wee, and R. Bai. 2010. Achieving Highly Effective Non-Biofouling Performance For Polypropylene Membranes Modified By UV-Induced Surface Graft Polymerization Of Two Oppositely Charged Monomers. *Journal Physical. Chemistry B*. 114(7): 2422-2429.
[8] Chiang, Y. C., Y. Chang, C. J. Chuang, and R. C. Ruaan. 2012. A Facile Zwitterionization In The Interfacial Modification Of Low Bio-Fouling Nanofiltration Membranes. *Journal Membrane Science*. 389: 76-82.
[9] Huang, J., H. Wang, and K. Zhang. 2014. Modification of PES membrane with Ag-SiO2: Reduction Of Biofouling And Improvement Of Filtration Performance. *Desalination*. 336(1): 8-17.
[10] Chae. S. R., S. Wang, Z. D. Hendren, M. R. Wiesner, Y. Watanabe, and C. K. Gunsch. 2009. Effects Of Fullerene Nanoparticles On Escherichia Coli K12 Respiratory Activity In Aqueous Suspension And Potential Use For Membrane Biofouling Control. *Journal Membrane Science.* 329(1-2): 68-74.
[11] Yu, C., J. Wu, A. E. Contreras, and Q. Li. 2012. Control of Nanofiltration Membrane Biofouling By Pseudomonas Aeruginosa Using D-Tyrosine. *Journal Membrane Science* 423-424: 487-494.
[12] Dong xi, L., H. Wei Yang, S. Ting Liu, X. Mao Wang, and Y. F. Xie. 2015. Fabrication And Anti-Biofouling Properties Of Alumina And Zeolite Nanoparticle Embedded Ultrafiltration Membranes. *Desalination*. 365: 70-78.
[13] Bae, T. H., and T. M. Tak. 2005. Interpretation Of Fouling Characteristics Of Ultrafiltration Membranes During The Filtration Of Membrane Bioreactor Mixed Liquor. *Journal Membrane Science.* 264(1-2): 151-160.
[14] Li. J. F., Z. L. Xu, H. Yang, L. Y. Yu, and M. Liu. 2009. Effect Of TiO2 Nanoparticles On The Surface Morphology And Performance Of Microporous PES Membrane. *Applied Surface. Science.* 255(9): 4725-4732.
[15] Sawada, I., R. Fachrul, T. Ito, Y. Ohmukai, T. Maruyama, and H. Matsuyama. 2012. Development Of A Hydrophilic Polymer Membrane Containing Silver Nanoparticles With Both Organic Antifouling And Antibacterial Properties. *Journal Membrane Science*. 387-388(1): 1-6.
[16] Chen, Y., Y. Zhang, H. Zhang, J. Liu, and C. Song. 2013. Biofouling Control Of Halloysite Nanotubes-Decorated Polyethersulfone Ultrafiltration Membrane Modified With Chitosan-Silver Nanoparticles. *Chemical Engineering Journal.* 228: 12–20.
[17] Jin. J.-C., Z.-Q. Xu, P. Dong, L. Lai, J.-Y. Lan, F.-L. Jiang, and Y. Liu. 2015. One-Step Synthesis Of Silver Nanoparticles Using Carbon Dots As Reducing And Stabilizing Agents And Their Antibacterial Mechanisms. *Carbon N. Y.* 94: 129-141.
[18] Nguyen, T., F. A. Roddick, and L. Fan. 2012. Biofouling Of Water Treatment Membranes: A Review Of The Underlying Causes, Monitoring Techniques And Control Measures. *Membranes (Basel).* 2(4): 804-840.
[19] Michelle, Chapman, and Wilbert. 1997. Enhancement of Membrane Fouling Resistance Through Water Treatment. *Technology. Progress. Report.* 22(22): 1-156.
[20] Kochkodan, V., S. Tsarenko, N. Potapchenko, V. Kosinova, and V. Goncharuk. 2008. Adhesion Of Microorganisms To Polymer Membranes: A Photobactericidal Effect Of Surface Treatment With TiO2. *Desalination*. 220(1-3): 380-385.
[21] Mauter, M. S., Y. Wang, K. C. Okemgbo, C. O. Osuji, E. P. Giannelis, and M. Elimelech. 2011. Antifouling Ultrafiltration Membranes Via Post-Fabrication Grafting Of Biocidal Nanomaterials. *ACS Applied Material Interfaces*. 3(8): 2861-2868.
[22] Abou El-Nour. K. M. M., A. Eftaiha, A. Al-Warthan, and R. A. A. Ammar. 2010. Synthesis And Applications Of Silver Nanoparticles. *Arabian Journal of Chemistry*. 3(3): 135-140.
[23] Rahimpour. A., M. Jahanshahi, B. Rajaeian, and M. Rahimnejad. 2011. TiO2 Entrapped Nano-composite PVDF/SPES Membranes: Preparation, Characterization, Antifouling And Antibacterial Properties. *Desalination*. 278(1-3): 343-353.
[24] Ren. G., D. Hu, E. W. C. Cheng, M. A. Vargas-Reus, P. Reip, and R. P. Allaker. 2009. Characterisation Of Copper Oxide Nanoparticles For Antimicrobial Applications. *International Journal of Antimicrobial Agents.* 33(6): 587-590.
[25] Kang. S., M. Pinault, L. D. Pfefferle, and M. Elimelech. 2007. Single-walled carbon Nanotubes Exhibit Strong Antimicrobial Activity. *Langmuir*. 23(17): 8670-8673.
[26] Zou. X., L. Zhang, Z. Wang, and Y. Luo. 2016. Mechanisms of the Antimicrobial Activities of Graphene Materials. *Journal of the American Chemical Society*.138: 2064-2077.
[27] Rahaman. M. S., H. Thérien-Aubin, M. Ben-Sasson, C. K. Ober, M. Nielsen, and M. Elimelech. 2014. Control Of Biofouling On Reverse Osmosis Polyamide Membranes Modified With Biocidal Nanoparticles And Antifouling Polymer Brushes. *Journal Material Chemistry. B*. 2(12): 1724-1732..
[28] Zodrow. K., L. Brunet, S. Mahendra, D. Li, A. Zhang, Q. Li, and P. J. J. Alvarez. 2009. Polysulfone Ultrafiltration Membranes Impregnated With Silver Nanoparticles Show Improved Biofouling Resistance And Virus Removal. *Water Resource.* 43(3): 715-723.
[29] Morones. M. Y., J. L. Elichiguerra, A. Camacho, K. Holt, J. B. Kouri, J. T. Ramirez. 2005. The Bactericidal Effect Of Silver Nanoparticles. *Nanotechnology*.16(10): 2346-2353.
[30] Basri, H., A. F. Ismail, and M. Aziz. 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.
[31] Yin, V., Y. Yang, Z. Hu, and B. Deng. 2013. Attachment Of Silver Nanoparticles (AgNPs) Onto Thin-Film Composite (TFC) Membranes Through Covalent Bonding To Reduce Membrane Biofouling. *Journal Membrane Science.* 441: 73-82
[32] Ben-Sasson, M., K. R. Zodrow, Q. Genggeng, Y. Kang, E. P. Giannelis, and M. Elimelech. 2014. Surface Functionalization Of Thin-Film Composite Membranes With Copper Nanoparticles For Antimicrobial Surface Properties.

Environmental Science and Technology. 48(1): 384-393.

[33] Kim. S. H., S. Y. Kwak, B. H. Sohn, and T. H. Park. 2003. Design of TiO2 nanoparticle Self-Assembled Aromatic Polyamide Thin-film-composite (TFC) Membrane As An Approach To Solve Biofouling Problem. *Journal Membrane. Science.* 211(1): 157-165.

[34] Perreaul, F., M. E. Tousley, and M. Elimelech. 2014. Thin-Film Composite Polyamide Membranes Functionalized with Biocidal Graphene Oxide Nanosheets. *Environmental Science and Technology Letter.* 1(1): 71-76.

[35] Tiraferri, A., C. D. Vecitis, and M. Elimelech. 2011. Covalent Binding Of Single-Walled Carbon Nanotubes To Polyamide Membranes For Antimicrobial Surface Properties. *ACS Applied Material Interfaces*. 3(8): 2869-2877.

[36] Kim, H. J., Y. Baek, K. Choi, D. G. Kim, H. Kang, Y. S. Choi, J. Yoon, and J. C. Lee. 2014. The Improvement Of Antibiofouling Properties Of A Reverse Osmosis Membrane By Oxidized CNTs. *RSC Advance*. 4(62): 32802-32810.

[37] Shen, L., S. Xiong, and Y. Wang. 2016. Graphene Oxide Incorporated Thin-Film Composite Membranes For Forward Osmosis Applications. *Chemical Engneering. Science.* 143: 194-205.

[38] Kuilla, T., S. Bhadra, D. H. Yao, N. H. Kim, S. Bose, and J. H. Lee. 2010. Recent Advances In Graphene Based Polymer Composites. *Progress Polymer Science*. 35(11): 1350-1375.

[39] Xia, S. and M. Ni. 2014. Preparation Of Poly(Vinylidene Fluoride) Membranes With Graphene Oxide Addition For Natural Organic Matter Removal. *Journal Membrane Science.* 473: 54-62.

[40] Liu, S., T. H. Zeng, M. Hofmann, E. Burcombe, J. Wei, R. Jiang, J. Kong, and Y. Chen. 2011. Antibacterial Activity Of Graphite, Graphite Oxide, Graphene Oxide, And Reduced Graphene Oxide: Membrane And Oxidative Stress. *ACS Nano*. 5(9): 6971-6980.

[41] Akhavan, O. and E. Ghaderi. 2010. Toxicity Of Graphene And Graphene Oxide Nanowalls Against Bacteria. *ACS Nano*. 4(10): 5731-5736.

[42] Liao, C., P. Yu, J. Zhao, L. Wang, and Y. Luo. 2011. Preparation and Characterization Of Nay/PVDF Hybrid Ultrafiltration Membranes Containing Silver Ions As Antibacterial Materials. *Desalination*. 272(1-3): 59-65.

[43] Huang. J., G. Arthanareeswaran, and K. Zhang. 2012. Effect Of Silver Loaded Sodium Zirconium Phosphate (nanoAgZ) Nanoparticles Incorporation On PES Membrane Performance. *Desalination*. 285: 100-107.

[44] Kim, E. S., G. Hwang, M. Gamal El-Din, and Y. Liu. 2012. Development Of Nanosilver And Multi-Walled Carbon Nanotubes Thin-Film Nanocomposite Membrane For Enhanced Water Treatment. *Journal Membrane Science*. 394-395: 37-48.

[45] Li, B., X. Liu, C. Cao, F. Meng, Y. Dong, T. Cui, and C. Ding. 2008. Preparation And Antibacterial Effect Of Plasma Sprayed Wollastonite Coatings Loading Silver. *Appied Surace Science.* 255(2): 452-454.

[46] Ismail, A. F., S. A. Hashemifard, and T. Matsuura. 2011. Facilitated transport Effect Of Ag+ Ion Exchanged Halloysite Nanotubes On The Performance Of Polyetherimide Mixed Matrix Membrane For Gas Separation. *Journal Membrane Science.* 379(1-2): 378-385.

[47] X. Zhu, R. Bai, K. H. Wee, C. Liu, and S. L. Tang. 2010. Membrane Surfaces Immobilized With Ionic Or Reduced Silver And Their Anti-Biofouling Performances. *Journal Membrane Science*. 363:(1-2): 278-286.

[48] Zhang, J., Y. Zhang, Y. Chen, L. Du, B. Zhang, H. Zhang, J. Liu, and K. Wang. 2012. Preparation And Characterization Of Novel Polyethersulfone Hybrid Ultrafiltration Membranes Bending With Modified Halloysite Nanotubes Loaded With Silver Nanoparticles. *Industry Engineering Chemistry Research.* 51(7): 3081-3090.

[49] Gunawan, V., C. Guan, X. Song, Q. Zhang, S. S. J. Leong, C. Tang, Y. Chen, M. B. Chan-Park, M. W. Chang, K. Wang, and R. Xu. 2011. Hollow Fiber Membrane Decorated With Ag/MWNTs: Toward Effective Water Disinfection And Biofouling Control. *ACS Nano*. 5(12): 10033-10040.

[50] Haider, M. S., G. N. Shao, S. M. Imran, S. S. Park, N. Abbas, M. S. Tahir, M. Hussain, W. Bae, and H. T. Kim. 2016. Aminated Polyethersulfone-Silver Nanoparticles (AgNPs-APES) Composite Membranes With Controlled Silver Ion Release For Antibacterial And Water Treatment Applications. *Material Science and. Engineering. C*. 62: 732-745.