

Short Review of Ultrafiltration of Polymer Membrane As a Self-Cleaning and Antifouling in the Wastewater System

Siti Hawa Mohamad^{1,a}, M. I. Idris^{2,b}, H. Z. Abdullah^{3,c}, A.F. Ismail^{4,d}

^{1,2,3} Faculty of Mechanical & Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia (UTHM), Parit Raja 86400, Batu Pahat, Johor, Malaysia

⁴Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 UTM, Skudai, Johor, Malaysia

^acthawamd@gmail.com (corresponding author), ^bizwana@uthm.edu.my, ^chasan@uthm.edu.my, ^dafauzi@utm.my

Keywords: Ultrafiltration; Antifouling; Self-cleaning; TiO₂; UV radiation

Abstract This paper focuses on ultrafiltration polymer membrane for wastewater systems as a self-cleaning and antifouling. Fouling is one of the most important problems in almost all membrane processes. In this review, membrane antifouling and self-cleaning properties can be improved by using titanium dioxide (TiO₂) particles and UV radiation on membrane structure and surface. Coating TiO₂ particles on membrane surface is an advanced method to minimize membrane fouling. Hence, these properties can be improved the membrane performance.

Introduction

Over the years, the development of wastewater treatment technology has been driven by the need to protect public health and the environment. As population continues to increase, people put increasing pressure on the natural system. Many communities are struggling to find solutions to lack of clean water for direct human consumption, irrigation and groundwater recharge to mitigate saltwater issues [1]. In order to restrain the worsening of clean water shortage, development of advanced with low-cost and high efficiency water treatment technologies to treat the wastewater is desirable [2]. One of a few attractive options is the possible reuse of onsite rural wastewater or the treated municipal wastewater from treatment plants or agricultural and industrial activities [3-4]. The two most successful commercial water purification techniques are involving thermal and membrane systems. Membrane separation processes are also widely used in biochemical processing, in industrial wastewater treatment, in food and beverage production and pharmaceutical applications [5].

Overview of Membrane

Membrane technology has become an important separation technology over the past decades. Today, membrane technologies has a unique place in any industrial, water management applications, chemical technology and are used in aboard range of applications [6-7]. The word membrane technology is applied to a number of separation processes, each using a membrane but differing in the details of the method [8]. Industrial applications of membrane separation are reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), pervaporation (PV), gas permeation, dialysis, electrodialysis and liquid membranes [7].

In general, membranes are thin layers that can have significantly different structures, but all have the common feature of selective transport to different components in a feed. Membranes may be homogeneous or heterogeneous, symmetrical or asymmetrical and porous or non-porous [8]. Membranes suited for technical applications may be classified by the following characteristics [8-11]:

- Membrane materials: Organic polymers, inorganic materials (oxides, ceramics, metals), mixed matrix or composite materials

- Membrane cross-section: Isotropic (symmetric), integrally anisotropic (asymmetric), mixed matrix composite
- Preparation method: Phase separation (phase inversion) of polymer, sol-gel process, interface reaction, stretching, extrusion, track-etching and micro-fabrication
- Membrane shape: Flat sheet, hollow fiber, capillary, tubular and capsule.

Membrane nowadays have gained wide acceptance and made significant in many areas because of flexibility and performance reliability of membrane system, cost competitiveness, increasing demand and environmental awareness. Polymer membranes are also good production and low operating cost and modular design [12].

Ultrafiltration Membrane Ultrafiltration (UF) membrane separation process used in a wide range of application, including water/wastewater treatment, reverse osmosis pretreatment and separations in the food, dairy, paper, textile, chemical and biochemical industries [9,13-14]. UF uses a finely porous membrane to separate water and microsolute from macromolecules and colloids [9]. Ultrafiltration is separating process of extremely smaller suspended particles and dissolved macromolecules (surface pore size in the range of 50 to 1 nm) pass through the membranes [15]. UF membranes are often operated in a tangentially across the upstream surface of membranes as filtration occurs. Numerous polymer membranes have been developed for ultrafiltration applications. Polyethersulfone (PES) has been developed as a common employed material in ultrafiltration processes for protein separation due to its favorable mechanical strength and physicochemical stability [16-17]. Polysulfone (PSf) is an excellent UF membrane material because of its film and membrane forming properties and high mechanical and chemical stability [18].

Ultrafiltration Membrane Fouling Ultrafiltration is a novel and powerful technique that can be used to concentrate or fractionate protein and aqueous solutions. However, a major challenge of these operations is membrane fouling by proteins and other biomolecules in the feed stream [13-14]. Protein has been identified as one of the major membrane foulants in wastewater treatment and reclamation applications [19-20]. The accumulation of protein on membrane surface or inside membrane pores decreases flux greatly, affects the quality and quantity of product and eventually shortens the membrane lifetime [21]. Some of the rejected molecules absorb or deposit on membrane surface causing considerable membrane fouling [22]. In general, fouling occurs on hydrophobic surfaces as a result of protein adsorption, denaturation and aggregation at the membrane solution-interface [23]. Flux decline in membrane processes is due to two main sources which are concentration polarization and membrane fouling. Table 1 shows the detail explanations of concentration polarization and membrane fouling.

Table 1 : Explanations of concentration polarization and membrane fouling [6,9,14,24-25]

Concentration polarization	-irreversible accumulation of rejected molecules close to membrane surface -decreases the driving force of water flow across the membrane due to local increase foulant concentration -completely reversible and can be reduced by modifying the membrane flow
Membrane fouling	-includes reversible and irreversible fouling -can be removed by hydrodynamic methods, if cannot be removed is defined as irreversible fouling -can occur in two ways which are cake formation and adsorption of foulants -cake fouling is generally reversible by water flushing or backwashing -adsorption of foulants is irreversible and can only be counteracted to a certain extent by aggressive chemical cleaning, occur on the membrane selective layer surface and pore walls

Development of UF Membrane with Antifouling and Self-Cleaning Properties

Various approaches have been performed to reduce fouling. An increase in membrane hydrophilicity appears to be a good way to improve the membrane resistance to fouling. The techniques include addition of hydrophilic polymers to the casting solution [26-27], immobilization of polymers with hydrophilic segments by photo- or plasma-polymerization [28-30] and surface coating [31-32]. Recently establish method to improve the membrane antifouling properties is using titanium dioxide (TiO_2) nanoparticles on membrane structure and surface. TiO_2 has been focus of numerous studies in recent years, because of its photocatalytic and superhydrophilicity effects, that can decompose organic chemicals and kill bacteria [33]. Therefore, it has been applied to surface modification of several membranes. There are growing interests on photocatalytic degradation of recalcitrant pollutant in wastewater. Various semiconductors can be used for photocatalytic reaction, but TiO_2 have attracted great attention among the semiconductors due to of its stability under harsh conditions, commercial availability and ease of preparation [34-35].

TiO_2 particles can degrade chemicals especially organic compounds effectively with UV light [36]. Among different applications of photoactive TiO_2 thin films, one concerns self-cleaning surfaces, which depend both on photocatalysis and photo-hydrophilicity mechanisms. One of the most interesting aspects of TiO_2 is that types of photochemistry responsible for photocatalysis and hydrophilicity are completely different, even though both can occur simultaneously on the same surface [37]. This is the reason that the film has a self-cleaning effect.

Some papers have demonstrated the good antifouling properties of membranes with TiO_2 . For example, Kim *et al.* prepared a hybrid thin film-composite (TFC) membrane by self-assembly of the TiO_2 nanoparticles through interaction with the COOH functional groups of aromatic polyamide thin-film layer. This hybrid membrane was shown to posses the dramatic photobactericidal effect on *E. coli* under UV light illumination [38]. By means of an ion-assisted deposition method, a TiO_2 photocatalyst was prepared on porous Teflon sheet (PTS) by Yamashita *et al.* [39]. Madaeni and Ghaemi have been studied the effects of coating of membrane surface with TiO_2 particles and UV radiation in creating self-cleaning membrane. Coating the membrane surface with TiO_2 particles not only creates photocatalytic property but also increases membrane hydrophilicity. Surface coating was carried out by self-assembly of TiO_2 particles through coordinance bonds with OH functional groups of polymer on the membrane surface [40]. After the radiation of the membrane by UV light, two phenomenons are carried out photocatalytic and ultrahydrophilicity. As a result of photocatalysis, groups of active oxidant reagents are appear on the surface of membrane which lead to decomposition and removal of the membrane foulants. Ultrahydrophilicity not only provides self-cleaning through dirt removal, but also increases the membrane flux.

A comparison between UV-irradiated TiO_2 -entrapped and deposited membrane was reported by Rahimpour *et al.* [36]. Their results proved that coating TiO_2 on membrane surface is a superior technique for the modification of PES membranes to minimize membrane fouling. The performance and antifouling property of UV-irradiated TiO_2 -deposited membrane is higher than UV-irradiated TiO_2 -entrapped membrane. In summary coating the membrane surface by TiO_2 is a superior technique compared to entrapping TiO_2 nanoparticles for modification of PES membrane and the minimization of membrane fouling.

Conclusions

Consider for a moment the entire water resources issue on a global scale. Various aspects of the water problem need to be considered not only by developing nations but also by developed countries. Water is required for urban, development, industrialization and agriculture. An increase in the world population results in an increase in water usage. So, the development of antifouling and self-cleaning properties are an important research in ultrafiltration membrane technology for water and wastewater treatment and it has attracted wide attention in recent years. This paper critically reviews of ultrafiltration membranes as antifouling and self-cleaning, the superior technique for creating those properties have been discussed.

References

- [1] Water Environment Federation (WEF). Membrane systems for wastewater treatment. 2006. WEF Press, McGraw-Hill.
- [2] M.N. Chong, Jin B., Chow, C.W.K., Saint, C., Recent development in photocatalytic water treatment technology: A review. *Water Research*. 44 (2010) 2997-3027.
- [3] B.R. Bradley, G.T. Daigger, R. Rubin, G. Tchobanoglous, Evaluation of onsite wastewater treatment technologies using sustainable development criteria. 2002. *Clean Technol. Environ. Policy* 4, 87-99.
- [4] L. Lapen, M., Cerezo, P. Garcí'a-Augustin, Possible reuse of treated municipal wastewater for Citrus spp. plant irrigation. 1995. *Bull. Environ. Contam. Toxicol.* 55, 697-703.
- [5] R. Singh and J. Tembrock, Effectively controlled reverse osmosis systems, September (1999) 57-66.
- [6] Z.F. Cui, and H.S. Muralidhara *Membrane Technology: A Practical Guide to Membrane Technology and Applications in Food and Bioprocessing*. Elsevier. 2010.
- [7] J.D. Seader, and E.J. Henley, *Separation Process Principles*. Second Edition, John Wiley & Sons, Inc. 2006.
- [8] T.D. Naylor, *Polymer Membranes-Materials, Structures And Separation Performance*. Vol.8, No.5, Rapra Technology Ltd. 1995.
- [9] R.W. Baker, *Membrane Technology and Applications*. Second Edition, John Wiley & Sons, Inc. 2004.
- [10] E. Drioli, and L. Giorno, *Membrane Operations: Innovative Separations And Transformations*. Wiley-VCH. 2009.
- [11] S. Ramakrishna, Z. Ma, T. Matsuura, *Polymer Membrane In Biotechnology: Preparation, Fictionalization And Application*. London: Imperial College Press. 2011.
- [12] K. Scott, and R. Hughes, *Industrial Membrane Separation Technology*. Chapman & Hall. 1996.
- [13] M.F.A. Goosen, S.S. Sablani, H. Al-Hinai, S. Al-Obeidani, R., Al-Belushi, D. Jackson, Fouling of reverse osmosis and ultrafiltration membranes: a critical review, *Sep. Sci. Technol.* 39 (2004) 2261–2298.
- [14] A.D. Marshall, P.A. Munro, G. Tragardh, The effect of protein fouling in microfiltration and ultrafiltration on permeate flux, protein retention and selectivity-a literature-review, *Desalination* 91 (1993) 65–108.
- [15] B.K. Chaturvedi, A.K. Chosh, Ramachandhan, M.K. Trivedi, M.S. Hanra, B.M. Misra, Preparation, Characterization And Performance Of Polyethersulfone Ultrafiltration Membranes, *Desalination*. 2001. 133: 31-40.
- [16] W.F. Jones, R.L. Valentine, V.G.J. Rodgers, Removal of suspended clay from water using transmembrane pressure pulsed microfiltration, *J. Membr. Sci.* 157 (1999) 199–210.
- [17] J. Pieracci, J.V. Crivello, G. Belfort, Photochemical modification of 10 kDa polyethersulfone ultrafiltration membranes for reduction of biofouling, *J. Membr. Sci.* 156 (1999) 223–240.
- [18] R. Guan, H.D. Cuihua, "Effect of casting solvent on the morphology and performance of sulfonated polyethersulfone membranes. *J. Membr. Sci.* 277, 148-156.
- [19] Q. She, C.Y. Tang, Y.-N. Wang, Z. Zhang, The role of hydrodynamic conditions and solution chemistry on protein fouling during ultrafiltration. *Desalination* 249 (3), (2009).1079–1087.

- [20] H.K. Shon, S. Vigneswaran, I.S. Kim, J. Cho, H.H. Ngo, Fouling of ultrafiltration membrane by effluent organic matter: a detailed characterization using different organic fractions in wastewater. *J. Membr. Sci.* 278 (1–2), (2006) 232–238.
- [21] J. Mueller, R.H. Davis, Protein fouling of surface-modified polymeric microfiltration membranes. *J. Membr. Sci.* 116 (1), (1996) 47–60.
- [22] I.H. Huisman, P. Pradanos, The effect of protein and protein membrane interactions on membrane fouling in ultrafiltration. *J. membrane science* 179,79-90(2000).
- [23] J.A. Koehler, M. Ulbricht, G. Belfort, Intermolecular forces between proteins and polymer films with relevance to filtration, *Langmuir* 13 (1997) 4162–4171.
- [24] P. Mikulasek, Methods to reduce concentration polarization and fouling in membrane filtration, *Collect. Czechoslovak Chem. Commun.* 59 (1994) 737–755.
- [25] J. Pieraccia, J.V. Crivello, G. Belfort, Increasing membrane permeability of UV-modified poly(ether sulfone) ultrafiltration membranes, *J. Membr. Sci.* 202 (2002) 1–16.
- [26] M. Ulbricht, M. Ridel, U. Marx, Novel photochemical surface functionalization of polysulfone ultrafiltration membranes for covalent immobilization of biomolecules, *J. Membr. Sci.* 120 (1996) 239–259.
- [27] A. Rahimpour, S.S. Madaeni, Polyethersulfone (PES)/cellulose acetate phthalate (CAP) blend ultrafiltration membranes: preparation, morphology, performance and anti-fouling properties, *J. Membr. Sci.* 305 (2007) 299–312.
- [28] S. Bequet, J.-C. Remigy, J.C. Rouch, J.-M. Espenan, M. Clifton, P. Aptel, From ultrafiltration to nanofiltration hollow fiber membranes: a continuous UV-photografting process, *Desalination* 144 (2002) 9–14.
- [29] Z.P. Zhao, J. Li, D.X. Zhang, C.X. Chen, Nanofiltration membrane prepared from polyacrylonitrile ultrafiltration membrane by low-temperature plasma. I. Graft of acrylic acid in gas, *J. Membr. Sci.* 232 (2004) 1–8.
- [30] C. Qiu, F. Xu, Q.T. Nguyen, Z. Ping, Nanofiltration membrane prepared from cardo polyetherketone ultrafiltration membrane by UV induced grafting method, *J. Membr. Sci.* 255 (2005) 107–115.
- [31] S.P. Nunes, M.L. Sforca, K.V. Peinemann, Dense hydrophilic composite membranes for ultrafiltration, *J. Membr. Sci.* 106 (1995) 49–56.
- [32] A. Asatekin, A. Menniti, S. Kang, M. Elimelech, E. Morgenroth, A.M. Mayes, Antifouling nanofiltration membranes for membrane bioreactors from self assembling graft copolymers, *J. Membr. Sci.* 285 (2006) 81–89.
- [33] A. Mills, S.L. Hunte, An overview of semiconductor photocatalysis, *J. Photochem. Photobiol. A: Chem.* 1 (1997) 108.
- [34] Z. Baolong, C. Baishun, S. Keyu, H. Shangjin, L. xiaodong, D. Zongjie, Y. Kelian, Preparation and characterization of nanocrystal grain TiO₂ porous microsphere, *Appl. Catal. B: Environ.* 40 (2003) 253–258.
- [35] W. Xi, S.U. Geissen, Separation of titanium dioxide from photocatalytically treated water by cross-flow microfiltration, *Water Res.* 35 (2001) 1256–1262.
- [36] A. Rahimpour, S.S. Madaeni, A.H. Taheri, Y. Mansourpanah, Coupling TiO₂ Nanoparticles With UV Irradiation For Modification Polyethersulfone Ultrafiltration Membranes. *Journal of Membrane Science.* 2008. 313: 158-169.
- [37] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis. *J. Photochem. Photobiol. C* 1 (2000) 1-21.

-
- [38] S.H. Kim, S.Y. Kwak, B.H. Sohn, T.H. Park, Design of TiO₂ nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane as an approach to solve biofouling problem, *J. Membr. Sci.* 211 (2003) 157–165.
- [39] H. Yamashita, H. Nakao, M. Takeuchi, Y. Nakatani, M. Anpo, Coating of TiO₂ photocatalysts on super-hydrophobic porous teflon membrane by an ion assisted deposition method and their self-cleaning performance, *Nucl. Instrum. Methods Phys. Res. B* 206 (2003) 898–901.
- [40] S.S. Madaeni, N. Ghaemi, Characterization of Self-Cleaning RO Membranes Coated With TiO₂ Particles Under UV Irradiation, *J. Membr. Sci.* 303 (2007) 221-233.