

Technical Note

Photocatalytic membrane reactors for water and wastewater treatment applications: process factors and operating conditions review

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ABSTRACT

This paper aimed to overview of coupling photocatalytic process and membrane, known as photocatalytic membrane reactors (PMRs) and their potential applications in wastewater treatment, especially application for the decomposition of persistent organic matters. Mechanisms of PMRs for organic removal by photocatalytic and membrane processes are described. PMRs with suspended and immobilized TiO₂ on/in the membrane are intensively reviewed. Several operating factors such as pH, initial TiO₂ concentration, the concentration of pollutants, dissolved oxygen and aeration, hydraulic retention time as well as light intensity have been intensively discussed. Advantages and disadvantages of two types of PMRs are illustrated. This review is benefit to further future works such as up-scale PMRS to the industrial level, and the operating and maintenance needs for the effective PMRs.

1. Introduction

From past, membrane technology received tremendous interesting from engineers and researchers globally due to the versatile functions and varied application of membrane processes. Applications of membrane include desalination of sea water and brackish water, production of potable water, and, removal of various pollutants from wastewater. Many advanced technologies occurred from a combination of the membrane to other conventional technologies to produce the technology with energy efficiency, high performance in pollutant removal, and minimum negative impacts on the environment.

The combination of membrane and catalysts as the hybrid process was first introduced in 2002 by Molinari and his coworker (Molinari et al., 2002a, b). The first hybrid process was applied for the removal of organic pollutants. In this process, membrane not only plays a role as a barrier for molecules separation but also for catalyst separation. A year later, Sun et al. (2003) combined inorganic membrane and photocatalyst in a single module to treat *E. coli* in water. Nanofiltration (NF) membrane was used in their systems with relatively high catalyst recover efficiency. The efficiency of removal organic pollutants and deactivation of *E. coli* was increasing.

On the early stage of the hybrid process of membrane and photocatalyst or photocatalytic membrane reactors

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(PMRs), the TiO_2 photocatalyst has been applied in water treatment as powders suspended in the slurry. Submerged membrane photocatalysis reactor with TiO_2 suspended catalyst was firstly designed for the removal of fulvic acid in drinking water by Fu et al. in 2005 and 2006 (Fu et al., 2005, 2006). Air was bubbled and withdrawn by the suction pump to prevent membrane fouling. The overpressure in the submerged membrane was applied to deal with membrane fouling problems. However, the rate of photocatalytic reaction can be reduced by increasing scattering UV light, when turbidity of suspension increases (Fu et al., 2005). The limitation of this system arose from the declination of membrane flux, membrane fouling, and deformation of the membrane from UV irradiation.

During 2005, many works have reported the immobilized of photocatalyst on the supports and its application in pollutant removal (Kajitvichyanukul et al. 2005; Lepore et al., 1996; Loddo et al., 1998). This innovation led to the initiation of immobilized or coated photocatalyst on the surface of the membrane. Bosc et al. (2005) coated anatase on the membrane surface for the coupling of membrane and photocatalysis systems. Zhang et al. (2003) conducted experiments using a tubular photocatalytic reactor with the light source inside the tube. The pronounce advantage of the immobilized catalyst on the membrane surface is high efficiency in contaminant removal with the prevention of nanoparticle detachment (Molinari et al., 2002a). Benefits of immobilized catalyst on the membrane are the promising key in applying this system in continuous flow photocatalytic processes with the advantage in improving pollutants removal, and avoiding losing or adding catalyst during the process. The PMRs hybrid system is tentative to be a promising technology for applying in water and wastewater treatment in nearly future.

Taking into account that there are numerous recent reports about PMRs during past few years and the potential practical application on novel configurations of PMRs have been described in the literature. Currently, less work demonstrated the practical way to apply PMRs effectively in contaminant removal from wastewater treatment. In this review work, the mechanisms of PMRs are reviewed. Different configurations of PMRs are described. Several operating factors such as pH, initial TiO_2 concentration, the concentration of pollutants, dissolved oxygen and aeration, hydraulic retention time as well as light intensity have been intensively discussed. This article aimed to gather those significant data and discuss the appropriate parameters in operating and controlling PMRs that can lead to the promising application of this technology for water and wastewater treatment.

2. Pollutant removal mechanism using PMRs

PMRs are the advanced technology from the combination of membrane and photocatalysis which are intensively investigated during past few years. To understand the mechanism in pollutant removal by this technology, fundament concept in contaminant removal using both membrane and photocatalyst should be known.

In membrane processes, the pressure difference, the concentration difference, partial pressure difference or electrical potential difference can be the driving force for separation of particles and organic molecules. However, the pressure difference and the concentration difference are the major driving forces of the membrane used in PMRs (Mozia et al., 2010). In the pressure driven membrane processes (which are microfiltration, ultrafiltration, nanofiltration and reverse osmosis), the solvent and various solute molecules infuse through the membrane, whereas other molecules or particles are rejected as shown in **Fig. 1**. The extent of the rejected molecule is based on the type of membrane. The microfiltration membrane (MF) can reject the particles and dissolve molecules larger than $0.1\mu\text{m}$. The particles and dissolved molecules with the size in the range of $0.1\mu\text{m} - 2\text{nm}$ can be separated from the water stream using ultrafiltration membranes (UF). The nanofiltration membranes (NF) can reject the particles and dissolved molecules smaller than 2nm . For the reverse osmosis (RO), almost complete separation of all particles and molecules occur by the trans-membrane pressure with osmotic pressure difference (Koros et al., 1996).

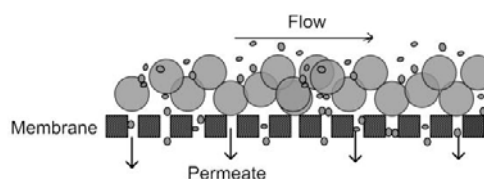


Fig. 1. Principle mechanism of pollutant removal by membrane process.

For the concentration difference driven membrane, three types of membrane included dialysis, evaporation and direct contact membrane distillation are used in PMRs (Mozia et al., 2010). In dialysis, the solute separation occurs from the difference in diffusion rates across the membrane arising from the differences in molecular size and solubility (Mulder, 1996). Pervaporation membrane is a dense membrane, in which a binary or multicomponent liquid mixture is separated by partial vaporization. The different chemical potentials of the permeants, acrossing the membrane from the feed side to the permeated side is the driving force of this

membrane (Kujawski and Krajewski, 2007). In direct contact membrane distillation, the driving force of the mass transfer through the membrane pores is a vapor pressure difference on both sides of the membrane (Gryta et al., 2006).

Membrane technology draw attentions from many scientists and engineers due to their several advantages include low energy consumption, low chemicals consumption, production of water of stable quality, automatic control and steady operation, low maintenance costs, and easy scale up by simple connecting of additional membrane modules. However, membrane technology also has the major drawback of membrane fouling due to particles and colloids existing in the feed and limited lifetime of the membrane (Mozia et al., 2010).

For photocatalysis, the photoinduced reactions including photocatalytic reduction and photocatalytic oxidation are activated by absorption of a photon with sufficient energy of the photocatalyst. Among many photocatalysts used in photocatalysis process, TiO₂ is the most widely used semiconductor for this process. When a TiO₂ absorbs a photon of energy, the generation of an electron/hole (e⁻ - h⁺) pair is occurred (Eq.1). Electron (e⁻) is generated from the promotion of an electron from the valence band (VB) to the conduction band (CB) upon the irradiation with energy equal to or greater than the bandgap energy as shown in Fig. 2. The electron vacancy in the valence band is called "hole (h⁺)". Both electrons and holes are charge carriers and can migrate to the surface of TiO₂. The valence band holes are powerful oxidants (+1.0 to +3.5V vs. NHE depending on the semiconductor and pH), while the conduction band electrons are good reductants (+0.5 to -1.5 V vs. NHE) (Grätzel, 1989). These charge carriers can subsequently either recombine and dissipate the input energy as heat, get trapped in metastable surface states, or react with electron donors and acceptors adsorbed on the surface or bound within the electrical double layer (Bahnmann, 2004).

In the presence of electron acceptors such as oxygen, the superoxide radical anions O₂^{•-} can occur from the reaction of oxygen and electron (e⁻) on the surface of TiO₂ (Eq.2). This reaction is so called photocatalytic reduction. In the presence of electron donors such as H₂O or OH⁻, the hydroxyl radical OH[•] occur from the photocatalytic oxidation between the hole (h⁺) and those surface-bond electron donor species (Eq.3). Many reactions consequently occur during these redox reactions (Eqs. (2) - (12) with different species adsorbed on the catalyst surface. All reactions are written below (Mozia et al., 2010).

Most organic photodegradation reactions utilize the oxidizing power of the holes either directly or indirectly

from the OH[•]. The OH[•] is expected to be the primary oxidizing species for the degradation of organic molecules via the photocatalytic oxidation processes (Eq.10). As a result, hydroxyl radical and oxidative radical react with organic matters to generate intermediates, and eventually to form CO₂, H₂O and degradation products.

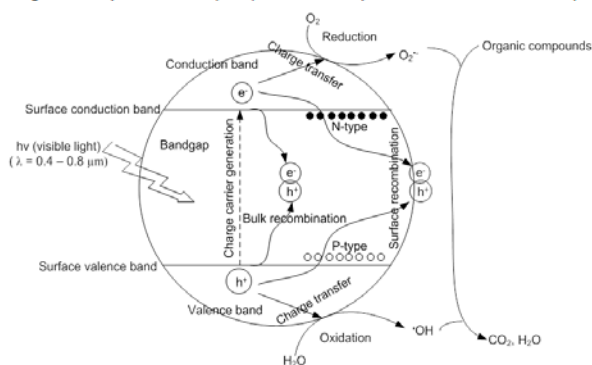
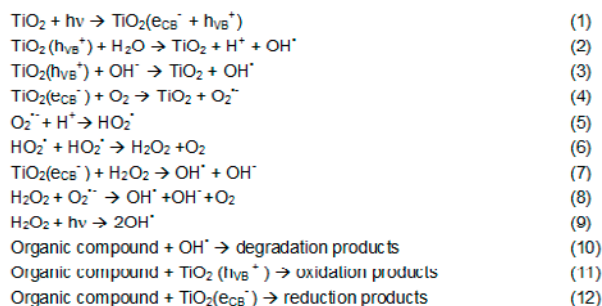


Fig. 2. Principle mechanism of photocatalysis in removal of organic compounds and the reactions during photo-degradation process which are oxidation-reducing reactions and electron-hole recombination.

The PMRs are the combination of membrane and photocatalysis with the enhancement in organic contaminant removal. The organic molecules can be degraded by the photocatalysis resulting small derivative molecule which can be separated from water by the membrane. In another hand, the membrane can separate the larger molecule out of the smaller molecules which can be consequently degraded by the photocatalyst. The configuration and the unit design are required to get high output from the PMRs.

The PMRs can be divided into two main groups, (I) reactors with photocatalyst suspended in a solution mixture and (II) reactors with photocatalyst immobilized in/on the supported membrane. To achieve high performance in contaminant removal using both PMRs configuration, many specific parameters of the PMRs regarding organic degradation rate, membrane fouling, permeate flux and permeate quality have to be taken in concern.

3. Process factors and operating conditions for PMRS with suspended and immobilized TiO₂

3.1. PMRs with suspended TiO₂

Reactor configurations of PMRs with suspended TiO₂ include photocatalytic reactor coupling with membrane outside of photocatalytic oxidation reactor and membrane submergence inside the reactor (submerged membrane photocatalytic reactor) as shown in **Fig. 3**. TiO₂ suspensions in the reactor are controlled by stirrer or mixer. The position of the light source in this reactor can be located in three different positions. The light can be located in the feed tank, at an additional reservoir (photoreactor), or at the membrane module. Also, in some cases, the irradiation of light source can be positioned at both above membrane module and feed tank, or inside them in case of immersed used UV lamps.

For the PMRs with membrane outside the photocatalytic reactor, the reactor is usually made of the glass to allow UV light penetration inside reactor when the photocatalytic reaction is taking place. Molinari et al. (2002a) have designed the simple reactor configuration with UV lamp with emitting wavelength 365 nm (ultraviolet light) that placed outside the reactor and oxygen gas supplied instead of air as bubbling gas. The plug flow photoreactor was also initiated by Augugliaro et al. (2005) to increase the reaction rate between OH^{*} and organic molecules on the catalyst surface, and hindering recombination of electrons and holes.

The PMRs with membrane submergence inside is also widely introduced due to the advantage in preventing membrane fouling by TiO₂ slurry. In one work, reactor configuration of PMR with TiO₂ suspension was designed by placement one more UV lamp with emitting wavelength 300 - 400 nm above membrane (Shon et al., 2008). In this type of PMRs, the membrane is submerged in photocatalytic reactor separated from photocatalytic oxidation zone. Membrane separation zone is connected to photocatalytic oxidation zone by bottom flow channel and an overflow channel. In some experiment, the settling tank is placed between the photocatalytic reactor and submerged membrane reactor (Ho et al., 2009). Several types of lamps have been used in this PMRs configuration. For the submerged membrane photocatalytic reactor, a suitable program for filtration and backwashing leads to low membrane fouling and can increase organic removal efficiency (Patsios et al., 2013; Sarasidis et al., 2011). Nano structured TiO₂ photocatalysts with larger particles size than P25 is less membrane fouling and increasing permeate flux to compare with P25 TiO₂ photocatalysts (Fu et al., 2006).

In both types of PMRs with suspended TiO₂, membrane plays a role to separate TiO₂ molecule to return slurry reactor, and also plays as a selective barrier to remove initial compounds or product degradation. The permeate quality of PMRs with suspended TiO₂ depends on membrane process and the application of membrane module. Each part of PMRs including photocatalytic reaction and membrane separation process have specific effecting factors for their performances. Several factors such as TiO₂ loading, TiO₂ morphologies (Zhang et al., 2009), pH, temperature (Augugliaro et al., 2005; Chong et al., 2010; Mozia, 2010), dissolved oxygen, contaminants and their loading, hydraulic residence time (Chin et al., 2007; Shon et al., 2008; Wang et al., 2013), air supply rate (Chin et al., 2007), turbidity water (Azrague et al., 2006), and membrane processes (Azrague et al., 2006; Camera-Roda et al., 2007; Damszel et al., 2009; Molinari et al., 2002a; Mozia et al., 2009) have effects on photocatalytic membrane reactor performances. A setting suitable operating condition for PMRs with different organic matters can optimize system productivity as shown in Table 1.

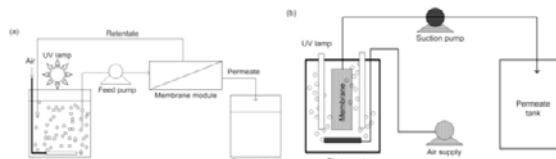


Fig. 3. Reactor configurations for PMRs with suspended TiO₂ (a) PMRs with membrane outside the photocatalytic reactor and (b) PMRs with membrane submergence inside reactor.

3.2 PMRs with immobilized TiO₂

In PMRs with immobilized TiO₂, the TiO₂ particles can be coated on the membrane surface where the photocatalytic reaction can occur. Different materials such as polymer and ceramic membranes and synthesis methods can be used to coat TiO₂ particles on/in membranes to improve physical membrane properties. TiO₂ particles are trapped on/in membranes during the membrane fabrication processes or coated on the neat membrane surface. Coated TiO₂ methods on polymer membranes include blending method, surface coating, surface coating via interfacial polymerization, photo-induced grafting, gamma ray and electron/ion beam-induced grafting, plasma treatment and plasma-induced grafting, thermal-induced method, and surface-initiated atom transfer radical polymerization (Zhao et al., 2013). Increasing photocatalyst surface ratio enhances organic removal efficiency and improves photocatalyst stability by entrapped or coated photocatalyst on membrane leading to the promising application of PMRs with immobilized

photocatalytic in water and wastewater treatment (Lin et al., 2012; Papageorgiou et al., 2012). Membrane physical

membrane surface of feed side by photocatalytic reactions. In contrast, a membrane with photocatalyst coated on permeate side, the feed side of membrane

Table 1. Summary configuration of PMRs, operating condition and performance in the removal of pollutants using PMRs with suspended TiO₂.

Organic matters	PMRs with TiO ₂ suspension configuration				Operating condition					Performance		References	
	Reactor Volume (L)	Membrane area (m ²)	Membrane Process	Weight length (nm)	OC (mg/L)	TiO ₂	pH	Aeration rate (L/min)	HRT (h)	Flux (L/m ² /h)	Experiment time (h)		Removal efficiency (%)
Humic acid	9.00	0.4700	UF	365	5.00	0.75	5.5	18.5	2.0	14.0	48	83.1	Patsios (2015)
2,4 Dibromophenol	0.21	0.0092	-	254	15.0	1.00	6.89	-	-	7.6	80	98.0	Gao (2013)
Polysaccharide	9.00	0.4700	UF	365	2.19	0.75	6-7	20.0	2.1	100	48	77.6	Sarasidis (2011)
Bisphenol A	-	0.0041	-	355	10.0	0.50	4.0	0.50	2.0	48.0	5	97.0	Chin (2007)
Fulvic acid	3.20	0.2000	MF	253.7	11.59	0.50	6.5	1.00	4.1	322	8	73.1	Fu (2006)
Organic matter	4.00	0.0043	MF	300-400	9.40	2.00	~7	-	4.0	220	3	97.0	Shon (2008)
Cabamazepine	1.00	0.0023	MF	450	5.00	1.00	5.1	-	2.0	64.0	74	69.0	Wang (2013)
Reactive Black 5	3.00	0.0152	MF	254	100	0.60	5.0	-	-	-	8	95.0	Danodara (2012)
Acid Red 18	4.50	0.0015	Membrane Distillation	355	10	0.30	6.5	-	0.05	-	8	100	Damszel (2009)
Direct Green 90												94.0	
Acid Yellow 36												91.9	
Acid Red 1	5.00	0.940	UF	254	15	0.5	3.0	3.0	-	4.0	10	93.78	Kertesz (2013)
2,4 dihydroxybenzoic acid	4.00	0.126	MF	380	200	1.00	-	-	-	-	16	>90	Azragua (2006)
4-chlorophenol	3.00	0.016	Membrane prevaporatio	365	200	0.0625	-	8.0	-	0.107	30	~57	Camera-Roda (2007)
Lincomycin	47	2.510	NF	Sunlight	75μM	-	6.3	-	-	-	-	97.78	Augugliaro(2005)
Trichloroethylen	0.7	0.0021	MF	365	100	1-1.5	4.5	-	2.5	146-219	8.5	>60	Choo (2008)
Acid Red B	1.2	0.0069	UF	365	50	1.5	2.0	-	-	353	2	>70	Jiang (2010)
NOM	2.5	0.00257	MF	254	2.5	0.1	4.5	4	-	-	2	90	Le-Clech (2006)

NOM: Natural Organic Matter

characteristics are improved by coated or entrapped photocatalysts on/in the membrane that can overcome with disadvantages of PMRs such as catalyst losing, and membrane fouling (Table 2) (Li et al., 2013; Shi et al., 2013; Wei et al., 2011). Coated TiO₂ on the polymer membrane also enhances the hydrophilic property of the membrane due to the replacement of OH groups on the empty site producing by losing oxygen atom on the membrane surface (Rahimpour et al., 2008).

Table 2. Improvement physical characteristics of membranes in PMRs by coated or entrapped photocatalysts on/in membrane.

Membrane characteristics	Improvement of physical characteristics	References
Porosity	Increasing 7-12%	Li et al., (2013)
Pore size	Reducing pore size 7 – 30nm	Shi et al., (2013)
Contact angle	Reducing 23-48%	Wei et al., (2011)
Tensile strength	Increasing 50 – 105%	
Elongation at break	Increasing 5 MPa	
Retention to BSA	Increasing 19-22%	
	Increasing avoid protein retention on membrane 21-27%	
Stability of coated catalysis on membrane	TiO ₂ stability on membrane after 72 hours for filtration	

In the membrane with an immobilized photocatalyst, the light source can be located above the membrane either at feed or permeate side depending on the configuration of PMRs. Photocatalyst coated on feed side is known as the photoactive skin layer and non-photoactive support and the non-photoactive skin layer and photoactive support for photocatalyst coating on permeate side. Unlike the mechanism of PMRs with suspended TiO₂, the mechanism in pollutant removal of PMRs with immobilized TiO₂ in/on membrane takes place on the membrane surfaces or in its pores. Membranes with photocatalyst coating on feed side not only play as separation player but also as a photocatalytic reaction. Organic compounds can be decomposed on the

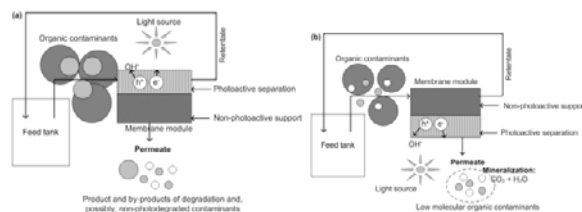


Fig. 4. Reactor configurations for PMRs with immobilized TiO₂. (a) TiO₂ coated on feed side, (b) TiO₂ coated on permeate side.

Two configurations of the PMRs with immobilized TiO₂ showing the mechanism in destroying organic molecules of each type are shown in Fig. 4. In the first configuration (Fig. 4a), the light source should be located on the separative and photoactive layer side which is in contact with the feed solution containing the organic molecules. For the second configuration (Fig. 4b), a non-photoactive separative top layer is deposited on a photoactive porous support. The light source should be provided on the opposite side of the membrane. In this configuration, a photoactive coating is on the grain surface of the membrane support. This configuration is suitable for the wastewater treatment with a low ultrafiltration membrane allowing the retention of the colloids or of the macromolecules, and allowing the permeation of small molecules (or VOCs) which would be photo-oxidized on the other side of the membrane (Bosc et al., 2005).

The major disadvantage of this type is a loss of photoactivity of the immobilized photocatalyst (Geissen et al., 2001). In comparison with PMRs with suspended TiO₂, the photooxidation efficiency of the contaminants was reported to be higher when an immobilized PMRs was used, rather than in the case of PMRs with

suspended catalyst particles (Molinari et al., 2004). However, the immobilizing of the photocatalyst particles might cause severe destruction to the membrane structure owing to their close contact with both UV light and hydroxyl radicals (Chin et al., 2006). The major problem of the PMRs is membrane fouling. In the case of PMRs with immobilized catalyst, the membrane fouling due to TiO₂ particles could be avoided. However, the efficiency of photodegradation was found to be lower than in the case of the PMRs with the suspended catalyst. The operating conditions of PMRs with TiO₂ immobilized in/on membrane have effects on the oxidation rates and efficiency of the photocatalytic system. The suitable operating condition of PMRs with different organic removal does not only optimize organic removal efficiency but also stabilize permeate flux. Summary of some configuration of PMRs, operating conditions and performance in removal of pollutants using PMRs with immobilized TiO₂ is shown in **Table 3**.

Table 3. Summary of configuration of PMRs, operating conditions and performance in the removal of pollutants using PMRs with immobilized TiO₂.

Organic matter	PMR with immobilized configuration		Operating condition		Removal efficiency (%)	Reference
	Membrane type	Coated TiO ₂	Weight length (nm)	Organic concentration		
AR 18	Immobilized catalyst beb	1.45 (mg/L)	508	10 mg/L	60.3	Damszel (2009)
DG 99			628		76.5	
AY 36			414		78.1	
MO	Y-Alumina UF tube	41.6 (Wt%)	365	2 μ M	18	Papageorgiou (2012)
RB5dye	AL ₂ O ₃ supported		383	100 mg/L	100	Lin (2012)
MB	Alumina supported	3.8 (g/cm ³)	350	5 mg/L	100	Bose (2005)
Phenol	Polymer membrane	1.29 (Wt%)	365	10 mg/L	32.5	Yang (2011)
2,4 D	PET filer cloth	1 (Wt%)	254	30 mg/L	100	Liu (2009)
AR 4	Ceramic tube membrane	0.29 (Fe/TiO ₂) (g)	365	0.013 mol/m ³	51	Wang (2008)
AC	Ceramic tube membrane	11.4 (mg/m ²) (P/TiO ₂)	254	5.5 mg/L	100	Zhang (2003)

Note: AR18 (Acid Red 18); AR 36 (Acid Yellow 36); MO (Methyl Orange); RB5 dye (Reactive Red 5); MB (Methyl Blue); 2,4 D (2,4 dichlorophenol); AR 4 (Acid Red 4)

4. Effects of operating factors on PMRs performance

4.1 Effect of solution pH

Solution pH plays an important role for the adsorption of pollutants onto the surface of the photocatalyst. The point zero charge of TiO₂ or pH_{pzc} is in the range of 6 - 8 in which pH_{pzc} of Degussa P25 TiO₂ particles is around pH 6.3 (Kajitvichyanukul et al. 2001). If solution pH is less than point zero charge (pzc) of TiO₂, the catalyst surface charge is induced to represent as a positive charge. On another hand, if the TiO₂ is in an alkaline media with pH higher than the pH_{pzc} of the catalyst, the surface catalyst

exhibits the negative charge. Most of the organic molecules have pK_a in the basic region, and the negative charge is normally presented in the wide range of solution pH. Thus, in an acidic solution, the opposite-charge attractions between TiO₂ and organic molecules become dominant, and the surface adsorption is favorable. As the like-charge repulsions become predominant as the solution pH approaches the pH_{pzc}, the adsorption of the organic molecules on the catalyst surface is decreased and become minimal in a basic solution. The photocatalytic ability is greatly depended on the amount of TiO₂. Organic molecules absorbed on the catalyst surface. The higher amount of pollutants on the adsorbed surface is the greater photocatalytic activity of the photocatalyst leading to the high efficiency of the PMRs. It is noted that the solution pH in the operating condition of PMRs for organic molecules presented in Table 1 is in an acidic region. For the removal of acid red 1, humic acid, acid red B, and natural organic matter using PMRs, the removal efficiency in basic pH is obviously lower than those in acidic pH (**Table 4**).

Table 4. pH effects on organics removal for PMRs with suspended and immobilized TiO₂.

Organic matter	Type of PMRs	pH	Photocatalytic oxidation			Reference
			Removal efficiency (%)	Initial degradation (mg/L.min)	Degradation rate constant, k (min ⁻¹)	
Carbamazepine	TiO ₂ suspension	3.0			0.0179	Wang (2013)
		6.0			0.0215	
		9.0			0.0238	
		12			0.0269	
Acid red1	TiO ₂ suspension	3.0	93.78			Kerteze (2013)
		7.0	65.43			
		11	48.79			
Humic acid	TiO ₂ suspension	3.5	66.10			Sarasidis (2011)
		5.5	77.20			
		7.0	52.50			
Bisphenol A	TiO ₂ suspension	4.0		0.225		Chin (2007)
		7.0		0.187		
		10		0.124		
Acid red B	TiO ₂ suspension	2.0	73.0			Jiang (2010)
		3.0	64.0			
		4.0	52.0			
		5.0	28.0			
		7.0	5.0			
		8.0	5.0			
		9.0	2.0			
11	2.0					
MON	TiO ₂ suspension	3.0	81.0			Le-Clech (2006)
		4.5	90.0			
		6.5	87.0			
		8.0	62.0			
C.I. Disperse Red 73	TiO ₂ suspension	4.0	98.88			Buscio (2015)
		6.0	72			
		10				
2,4 D	TiO ₂ immobilization	2.0	90.0			Liu (2009)
		4.0	96.0			
		6.0	100			
		8.0	93.0			
		10	70.0			
Acid Orange 7	TiO ₂ immobilization	4.0				Mendret (2013)
		6.0				
		8.0				

The solution pH also exerts an effect on the agglomeration of the photocatalyst. The electrostatic

repulsions among photocatalysts are less pronounced when the solution pH approached the pH_{pzc} value. Petosa et al. (2010) reported that the largest titania aggregate sizes are encountered at pH values closest to the pH_{zpc} . The reducing of catalyst surface area according to the agglomeration of the photocatalyst is consequently one factor affected on the photocatalytic activity and the yield of pollutant removal by PMRs. Also, the effects of solution pH on membrane fouling that is due to either the formation of a TiO_2 layer in membrane surface or the intrusion of TiO_2 inside membrane pores are also reported (Wang et al., 2013).

4.2 TiO_2 initial concentration

Effect of TiO_2 dosing of is mainly on the photocatalytic reaction rate. Small amounts of TiO_2 in PMRs provide the limited available active site for the photocatalytic reaction leading to low organic removal efficiency. However, the excess TiO_2 in the system can be a cause of membrane fouling and lower permeate flux due to the formed layer of TiO_2 cake on the membrane surface (Shon et al., 2008). The high concentration of TiO_2 is also a cause of the scattering of UV-light by bare TiO_2 particles (Chin et al., 2007; Shon et al., 2008), and increasing solution turbidity that can lead to reducing UV light absorption coefficient (Fu et al., 2006). Effecting TiO_2 concentration on photocatalytic oxidation rate and membrane resistant is shown in Table 5.

According to the configuration of PMRs with immobilized TiO_2 , the catalyst was fixed or supported on/into the membrane. Consequently, the amount of catalyst loading depends on the catalyst layer thickness, and it is one of the important parameters in photocatalytic degradation. Kajitvichyanukul et al. (2005) demonstrated that the effect of the catalyst loading on the efficiency of chromium (VI) removal using the immobilized TiO_2 . As the thickness of the catalyst increased, the amount of deposited titanium dioxide was increased resulting in high activity of the photocatalytic process. With the high catalyst loading, the decomposition ratio increases because the surface area available for reaction also increases.

However, the photocatalytic efficiency was reduced with the application of five cycle coatings of thin film TiO_2 (Kajitvichyanukul et al., 2005). When the film thickness increases with the photon flux remains the same resulting in the decreasing of transparency of the TiO_2 film, and the available electron-hole will decrease. Wang et al. (2008) reported that the global rate constants increase as the catalyst loading increase until reaching some constant value at higher catalyst loading (Wang et al., 2008). In this situation, the light cannot penetrate deep

into the catalyst layer and cannot activate the whole inner surfaces, but only can penetrate into a certain depth.

4.3 Characteristic and concentrations of pollutants

The characteristics and initial concentration of pollutants in feeding solution are one of the major factors in operating the PMRs. The size of the pollutants can exert effects on the PMRs performance. Lin et al. (2012) reported the membrane fouling from two different sizes of dextran. It was found that the dextran fouling resistance at 450kDa was larger than that at 70 kDa. This result is because the higher-MW dextran was not as readily decomposed by the TiO_2 membrane as the lower-MW dextran when the membrane was exposed to UV light, leading to greater fouling resistances from the 450-kDa dextran solution. The degree of fouling resistance was reduced when the membrane was exposed to UV light when compared with those that were in the dark. It was reported that the dextran foulants were reduced due to the effect of photodegradation, resulting in a decrease in fouling resistance (Lin et al., 2012).

Table 5. TiO_2 concentration effects on organics removal.

Organic matter	TiO_2 (g/L)	Photocatalytic oxidation			Reference
		Removal efficiency (%)	Initial degradation (mg/L.min)	Degradation rate constant, k (min ⁻¹)	
Carbamazepine	0.3	44.0			Wang (2013)
	0.5	60.0			
	1.0	68.0			
Acid red1	0.01			2.67	Kerteze (2013)
	0.05			2.17	
	0.25			2.00	
	0.50			1.17	
	1.00			1.34	
	2.00			1.50	
Polysaccharide	0.25	32			Sarasidis (2011)
	0.50	51			
	0.75	75			
	1.00	72			
	1.25	70			
	1.50	65			
Bisphenol A	0.2		0.220		Chin. (2007)
	0.5		0.264		
	1.0		0.235		
	2.0		0.240		
Acid red B	0.5			0.030	Jiang (2010)
	1.0			0.059	
	1.5			0.113	
	2.0			0.069	
MON	0.05	79			Le-Clech (2006)
	0.10	81			
	0.50	79			
Acid red 18	0.1	50			Mozia (2005)
	0.3	86			
	0.5	90			
Trichloroethylen	0.0	42			Choo (2008)
	0.5	35			
	1.0	68			
	1.5	68			
	2.0	30			

For the effect of initial concentration of pollutants, the high concentration or large amounts of a pollutant can cause a low permeate flux due to the formation of thick fouling layers in front of the TiO_2 membrane. This behavior was seen in the removal of three different

concentrations of humic acids (HA) by the TiO₂ membrane in the dark. The HA removals at the initial concentrations of 1, 2, and 4 ppm were 58%, 65%, and 72%, respectively. The high concentration of HA led to an increase in the removal of HA due to the formation of a thicker cake layer in the dark. This layer formed a penetration barrier for HA in passing through the TiO₂ membrane, leading to an increase in HA removal (Lin et al., 2012). During irradiation, the pore and cake fouling resistances were both effectively reduced by the illumination of the TiO₂ membranes with UV light. However, a thick cake layer of high concentration of organic molecules can hinder the incidence of UV light on the TiO₂ membrane, resulting in a decrease in the photocatalytic activity of TiO₂.

Table 6. Effects of initial concentrations of the organic molecule on removal efficiency using PMRs with suspended and immobilized TiO₂.

Organic matter	Type of PMRs	Initial concentration of pollutants (ppm)	Photocatalytic oxidation		Reference
			Removal efficiency (%)	Degradation rate constant, k (min ⁻¹)	
Bisphenol A	TiO ₂ suspension	10		0.0569	Chin. (2007)
		20		0.0223	
		30		0.0160	
		50		0.0104	
Diclofenac	TiO ₂ suspension	10		0.3000	Kanakaraju (2014)
		30		0.2500	
		50		0.2200	
		60		0.2000	
		70		0.1500	
Diclofenac	TiO ₂ suspension	2.5	53.9		Sarasidis. (2014)
		8	39.7		
C.I. Disperse Red 73	TiO ₂ suspension	50	88.20		Buscio (2015)
		70	81.17		
		100	80.80		
Reactive black5	TiO ₂ suspension	75	86.00		Damodar (2010)
		225	52.00		
MON	TiO ₂ suspension	5		0.0290	Huang (2008)
		10		0.0180	
2,4 dichloroph enol	TiO ₂ immobilization	10	100		Liu (2009)
		30	100		
		50	66		
		100	60		
Humic acid	TiO ₂ immobilization	1	83		Lin (2012)
		2	90		
		4	82		
Acid yellow 36	TiO ₂ immobilization	10	99		Mozia. (2009)
		30	50		

In the application of a composite membrane of Fe⁰, activated carbon, and TiO₂, it was found that at low concentration of a pollutant, the adsorption and diffusion are the rates limiting steps. As the concentration of pollutant increased, the catalytic reaction becomes the overall conversion rate-limiting step, rather than adsorption or diffusion resulting in the low photocatalytic activity of the composite membrane (Liu et al., 2009). Consequently, the low initial concentration of organic molecules can be removed effectively than the high initial concentration. Effects of the initial concentration of the

organic pollutants on the removal efficiency are shown in Table 6.

4.4 Dissolved oxygen and aeration rate

Dissolved oxygen plays an important role as an electron acceptor in photocatalysis process. It can react with an electron from the conduction band of TiO₂ and provides the superoxide anion radicals (O₂^{-•}) that can further oxidize the organic molecules. The recombination of electron and hole is also limited in the presence of oxygen. The high aeration rate can prevent the catalyst agglomeration resulting in maintaining the available surface area of the catalyst to be reacted with the organic molecules in the PMRs. Consequently, a high efficiency in removal of organic pollutants from PMRs can be achieved. Lower aeration leading to more catalyst agglomeration reduces available active site and lowers the organic degradation rate. Also, the aeration also increases the liquid film mass transfer coefficient around the aggregates leading to a higher degradation rate. However, providing aeration at an extremely high rate can cause the formation of the bubble cloud that can attenuate the UV light transmission and subordinate the light intensity yielding the low photodegradation rate. The aeration rate also controls the membrane fouling resulting in a working performance of membrane in PMRs. Thus, the optimum aeration rate should be taken into account for the balancing of the competing mass transfer and light attenuation effects (Chin et al., 2007). For example, the degradation rate of bisphenol A by PMRs under UV irradiation showed that highest removal efficiency at air aeration 0.5 L/min with the set up aeration 0.2, 0.5, 1.0 and 4.0 L/min (Chin et al. 2007).

4.5 Hydraulic retention time

The hydraulic retention time (or HRT) is an important factor to be controlled to obtain the high efficiency of PMRs. The longer the HRT is provided for the photocatalytic reaction, the higher the photodegradation rate of the organic molecule could be obtained. Chin et al. (2007) demonstrated that optimum control of HRT resulted in a good degradation efficiency of high concentration of the organic substance with low permeate flux and less membrane fouling due to TiO₂ photocatalyst. It was reported that the optimum HRT at 1.95-4.87 hours could provide the TOC concentration in the range of 1.5-6 ppm after 3 hours of photocatalytic reaction (Chin et al., 2007). Rivero et al. (2006) also reported that the mineralization of organic molecules was achieved at low permeate fluxes. The percentage removal of chemical oxygen demand (COD) was 78-83%

for 15 L/m² h and 70-73% for 55 L/m² h. Molinari et al. (2000) conducted the hybrid photocatalysis –NF processes for 4-nitrophenol removal. It was reported that the degraded amount of 4-NP was slightly higher for less permeable membranes due to longer contact time.

From previous reports, it is clearly that the long period of photocatalytic oxidation process can enhance the transformation of the parent organic molecules to be the smaller intermediate products and finally reach the mineralization with the CO₂ and water as the final products. For the membrane, the high HTR causes the membrane fouling and low permeate flux (Shon et al., 2008). Hence, the debate of the pros and cons of the PMRs working performance has to be stated.

4.6 Light intensity

In PMRs process, light intensity has a great effect on photocatalytic efficiency and reaction rate. Zhou and Ray (2003) reported that the reaction rate constant is proportional to the square root of the light intensity at high intensity. At sufficiently low intensity, the reaction rate constant follows first-order dependence (Zhou and Ray, 2003). Wang et al. (2008) demonstrated that the relationship between the reaction rate and light intensity. The experiments were conducted in a one pass dead-end system with light intensities of 1.1, 4.0 and 6.0 mW/cm². It was found that the decomposition ratio increases sharply initially with an increase of the light intensity, and then the rise becomes less gradual at a light intensity of 6.0 mW/cm². Decomposition ratio is defined as 1 minus the ratio of the permeate concentration to the feed concentration or $1 - C_A/C_{A0}$ (Wang et al., 2008).

Mehrotra et al. (2005) conclude that at low light intensities (catalyst dependent, surface reaction limited) the rate is linearly proportional to the light intensity. At medium–high values, the rate becomes proportional to the square root of the light intensity and at higher values. Thus, the rate would not be affected by the increase of the light intensity (zero order). It was explained that at lower illumination intensities, the photon flux is insufficient to excite all of the available active TiO₂ sites on the surface of the ceramic membrane. An increase in the light intensity leads to more excitation and more electron-hole pair generation (Choi et al., 2000), along with the corresponding increase in OH species and the pollutant degradation rate. However, according to Ollis et al. (1991), as the light intensity increases, it should enhance the recombination processes (second-order) faster than oxidation processes (first-order in excited oxidant), regardless of the photochemistry involved. Under these

conditions, the degradation rate becomes independent of light intensity.

For the PMRs with catalyst immobilized in a polymer membrane, the membrane damaging by the light can occur. The stronger the light intensity is; the high potential of the membrane damage should be considered. The resistant of the membrane destruction by UV light irradiation should be conducted for this PMRs configuration.

5. Summary and prospective research in the future

A coupling process of photocatalyst and membrane is an emerging technology known as photocatalytic membrane reactors (PMRs) which are intensively investigated for application in treating organic matters in water and wastewater. Two major configurations of this technology are the PMRs with catalyst suspension in reactor or immobilization in/on the membrane. In PMRs with suspended TiO₂, membrane plays a role in separating TiO₂ molecule to return slurry reactor, and also plays as a selective barrier to remove initial compounds or product degradation. The permeate quality of PMRs with suspended TiO₂ depends on membrane process, and membrane module applied. Each part of PMRs including photocatalytic reaction and membrane separation process has specific effecting factors for their performances. Unlike the mechanism of PMRs with suspended TiO₂, the mechanism in pollutant removal of PMRs with immobilized TiO₂ in/on membrane takes place on the membrane surfaces or in its pores. TiO₂ coating on/ membrane reduces the initial membrane pore sizes leading to resistance the pollutant molecules passing membrane and enhances permeate quality. The major problem of the PMRs is usually membrane fouling and damage organic membrane by UV light. In the case of PMRs with immobilized catalyst, the membrane fouling due to TiO₂ particles could be avoided. However, the efficiency of photodegradation was found to be lower than in the case of the PMRs with suspended catalyst. These factors need to be considered for the upscaling PMRs to industrial level.

Several operating factors exerted either positive or negative influence on the PMRs system. The appropriate parameters in operating and controlling PMRs can lead to the promising application of this technology for water and wastewater treatment as shown in this review. From overall operating condition considerations, it could be concluded that PMRs can provide high efficiency in pollutant removal from water and wastewater. However, further investigations are still needed to improve the PMRs performance regarding permeate flux and to

overcome the difficulty arisen from membrane fouling. It is important to emphasize that all parameters are gathering in this review mainly using synthetic wastewater as model solutions. The number of reports concerning the appropriate optimum conditions for the treatment of natural waters and real wastewaters is still limited. It is necessary to investigate the PMRs in the real systems to obtain the limitation and overcome the obstacle of the processes. As a result, this process can eventually be the valid promising technology for water and wastewater treatment. To prevent damaged organic membrane by UV light, more application of PMRs under visible irradiation will be studied.

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