POLYSULFONE/PHOTOCATALYST MEMBRANE: EFFECTS OF CATALYST, POLYMERIC ADDITIVES AND MOLECULAR IMPRINT FOR SELECTIVE FILTRATION AND PHOTODEGRADATION

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by

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LIST OF ABBREVIATIONS

APS	Ammonium persulfate
APTMS	3-aminopropyltrimethoxysilane
BSA	Bovine Serum Albumin
CB	Conduction band
COD	Chemical oxygen demand
D	Dimensional
FRR	Flux recovery ratio
HA	Humic acid
MB	Methylene blue
MIM	Molecular imprinted membrane
MIP	Molecular imprinting polymer
MO	Methyl orange
NIP	Non-Imprinted polymer
NMP	1-methyl-2-pyrrolidinone
PEG	Polyethylene glycol
PES	Polyethersulfone
PMAA	Poly(methacrylic acid)
PMR	Photocatalytic membrane reactor
PVA	Polyvinyl alcohol
PVC	Polyvinyl chlodride
PVDF	Polyvinylidene fluoride
PVP	Polyvinylpyrrolidone
PSf	Polysulfone

TEMED	N,N,N',N'-tetramethylethylenediamine
THF	Tetrahydrofuran
TiO_2	Titanium dioxide
TOC	Total organic carbon
UF	Ultrafiltration
UV	Ultraviolet
VB	Valence Band
ZnO	Zinc oxide

LIST OF SYMBOLS

C	Final concentration
C_e	Concentration at adsorption equilibrium
C_o	Initial concentration
k	Selectivity
k_1	First order rate constant
k_2	Second order rate constant
Q	Adsorption capacity
Q_e	Adsorption capacity at equilibrium
Q_t	Adsorption capacity at given time
t	Time

MEMBRAN POLISULFON/FOTOMANGKIN: KESAN MANGKIN, BAHAN TAMBAH POLIMER DAN TEKAPAN MOLEKUL UNTUK PENURASAN SELEKTIF DAN FOTODEGRADASI

ABSTRAK

Membran fotomangkin mempunyai potensi yang besar dalam rawatan air sisa kerana membran dan fotomangkin boleh digabungkan dalam satu unit. Dalam kajian ini, poli(vinil alkohol) (PVA) dan polivinil pirrolidon (PVP) digunakan untuk menstabilkan 2 wt % nanozarah fotomangkin (TiO$_2$, Mn-TiO$_2$ and ZnO) dalam membran polisulfon (PSf) sebelum penyongsongan fasa. Bahan tambah menggalakkan pembentukan jejari liang seperti yang ditunjukkan dalam imej SEM. Penambahan PVA dan fotomangkin ke dalam membran PSf membawa penambahbaikan yang ketara dalam penurasan asid humik (HA). Penambahan PVA dan fotomangkin dalam membran PSf memeningkatkan ketelapan air sebanyak 15.5~18.1 kali ganda berbanding dengan membran PSf tulen. Membran yang mempunyai prestatsi permisahan dan penerapan yang baik diperiksa dalam ujian fotodegradasi dan semua PSf/PVP/fotomangkin menunjukkan < 15 % penurunan dalam pemangkinan foto berbanding dengan nanozarah yang bebas. TiO$_2$ tulen diubahsuai menggunakan 'polimer tekapan molekul' (MIP-TiO$_2$) sebelum dimasukkan ke dalam membran PSf. MIP-TiO$_2$ mencapai selektivity sebanyak 2.06 dalam fotodegradasi methylene biru/metil jingga(MB/MO) apabila MIP-TiO$_2$ diguna bawah sinaran UV selama 1 jam. MIP-TiO$_2$ boleh digunnakan utnuk jangka masa panjang (2 jam) dan sehingga 5 kali kitaran fotodegradasi dengan seletktif MB/MO sebanyak 2.16. Penambahan MIP-TiO$_2$ ke dalam membran PSf/PVP/MIP-TiO$_2$ meningkatkan penelapan sehinnga 14.08 L/m^2.h.bar, serta pemisahan kotoran utama (MB) secara selektif sebanyak 2.83 di bawah sinaran UV.

POLYSULFONE/PHOTOCATALYST MEMBRANE: EFFECTS OF CATALYST, POLYMERIC ADDITIVES AND MOLECULAR IMPRINT FOR SELECTIVE FILTRATION AND PHOTODEGRADATION

ABSTRACT

Photocatalytic membranes exhibit great potential for wastewater treatment since they can combine filtration and photo degradation in a single unit. In this work, 2 wt % poly(vinyl alcohol) (PVA) and polyvinyl pyrrolidone (PVP) were used to stabilize 2 wt % of photocatalytic nanoparticles (TiO_2, Mn-TiO_2 and ZnO) blended into polysulfone (PSf) membrane before phase inversion. These additives affect the formation of finger-like pores as shown in the SEM images. Blending PVA and photocatalysts into PSf membrane resulted in significant improvement of humic acid (HA) rejection. The incorporation of PVP and photocatalysts into PSf membrane caused great improvement in water permeability, about 15.5~18.1 times higher than pure PSf membrane. Membranes with excellent rejection and permeation were further examined in photodegradation test, where PSf/PVP/photocatalyst showing < 15 % reduction in their photodegradation in comparison to the free nanoparticles. Pure TiO_2 nanoparticles was further modified using molecular imprinting polymer (MIP-TiO_2) before blending into PSf membrane. MIP-TiO_2 achieved a photodegradation selectivity of methylene blue/methylene orange (MB/MO) up to 2.06 under UV irradiation for 1 h. MIP-TiO_2 could be used in long duration (2 h) and up to 5 cycles of photocatalytic degradation with MB/MO selectivity of 2.16. The blending of MIP-TiO_2 into PSf/PVP/MIP-TiO_2 membrane further enhanced permeate flux up to 14.08 $L/m^2.h.bar$, while retaining the major foulant MB with a selectivity of 2.83 under UV.

CHAPTER ONE
INTRODUCTION

1.1 Photocatalyts and Their Application in Membranes

Photocatalysts assist in compound degradation when they are exposed to a light source with energy that is greater than their band gap - a gap between the conduction band (CB) and the valence band (VB) (Kaneko and Okura, 2002). The photocatalytic reactions involve several steps as illustrated in Figure 1.1
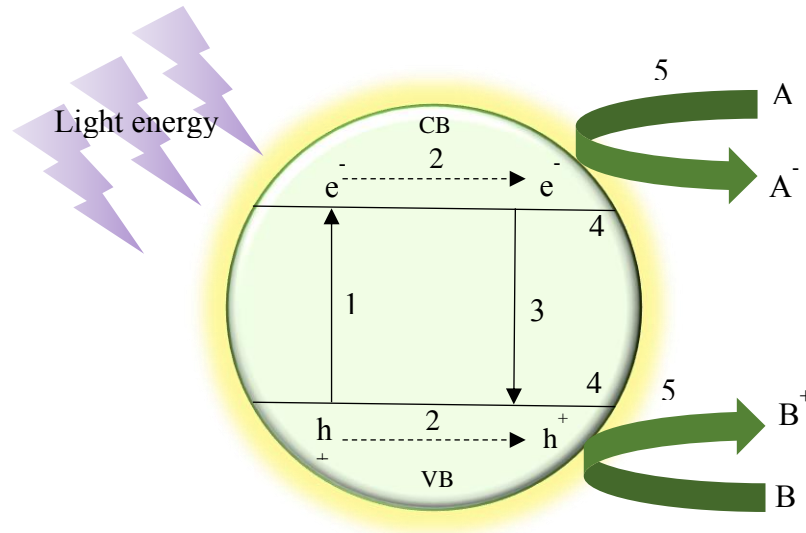
Figure 1.1 The mechanism of a common photocatalytic reaction.

The first step involves the excitation of electron from the VB to the CB. A CB electron and a VB hole are formed in the process. Secondly, the electron and hole then moves to the surface. If the recombination of electron does not occur (step 3), the electron and hole will be trapped at the surface and stabilized (step 4). Lastly, the redox reaction of the adsorbed molecules occurs on the photocatalyst (step 5) (Kaneko and Okura, 2002). The most common photocatalyst, titanium dioxide (TiO_2) can induce

the degradation of dyes and proteins in water via this redox reaction effectively under ultraviolet (UV) light (Choi *et al*., 2007; Jiang *et al*., 2014).

Besides being highly active under UV light due to a low band gap (3.2 eV), TiO_2 provides UV protection by absorbing the UV light energy. TiO_2 is also antimicrobial, hydrophilic, cheap, non-toxic as well as chemically and thermally stable (Wang *et al*., 2009). The main end user market of TiO_2 is not limited to photocatalysts only. The production of TiO_2 pigment was estimated as high as 1.16 million tons in 2015 due to their wide applications in paints and pigments, plastics, paper cosmetics, sunscreens and skin care products (Interior Department & Survey, 2016). In recent years, TiO_2 becomes more popular in wastewater treatment due to their ability to degrade wide range of synthetic dyes, such as basic dyes, and reactive dyes (Muhd Julkapli *et al*., 2014). With the presence of photocatalyst and UV light, the chemically stable synthetic dyes which derived from inorganic or organic compounds can be photodegraded and decolorized better than conventional biological treatment (Muhd Julkapli *et al*., 2014). To further enhance its photocatalysis, the doping of TiO_2 with non-metals, noble metals or transition metals has been widely reported in the literature (Pelaez *et al*., 2012). TiO_2 doped with Mn was successfully designed to shift its absorption range from the UV light region towards the visible light region (Wang *et al*., 2015). Zinc oxide (ZnO) also shows promising photocatalysis although it has a slightly larger band gap (3.3 eV), which requires higher energy to excite the electron from the valence band to conduction band (Chandran *et al*., 2014). It possesses similar properties to TiO_2 and it has been widely used in the development of membranes for waste water treatment (Nirmala *et al*., 2010; Kuriakose *et al*., 2014).

The incorporation of photocatalyst into membrane separation systems was first initiated because it is difficult to separate photocatalyst especially the photocatalytic nanoparticles from the treated water. The photocatalytic nanoparticles were either incorporated into the membrane reactor or membrane to avoid such limitation. Moreover, the incorporation of TiO_2 into membrane resulted in a boost in the membrane performance, in terms of permeability and rejection (Leong *et al*., 2014). ZnO nanoparticles were also blended into polyvinylidene difluoride (PVDF), polysulfone (PSf) and polyethersulfone (PES) membranes. The water permeability of these membranes increased one to two fold, depending on the particle loading (Bae and Tak, 2005; Liang *et al*., 2012; Rajabi *et al*., 2015). More polymeric membranes incorporated with photocatalysts were actually developed for fouling mitigation in the early years. Membrane fouling was reduced because the hydrophilic TiO_2 nanoparticles created a hydrated layer to hinder the accumulation of foulants, especially HA, on membrane surface. However, the photocatalytic activities of TiO_2 in the membrane have not been studied until recently. The accumulation of foulant on a PVDF membrane doped with TiO_2 could be effectively reduced when the filtration was coupled with photocatalytic degradation (Song *et al*., 2014). The development of polymeric membranes blended with photocatalyst has been limited only by the catalyst content so far. This is because a high content of photocatalysts could cause particle agglomeration and pore plugging (Leo *et al*., 2012).

The agglomeration of inorganic fillers, especially nanoparticles in membrane has been identified as the major challenge in the preparation of mixed matrix membranes. Strategies such as priming and in-situ synthesis of particles within the polymeric matrix have been practiced in the preparation of mixed matrix membranes

for gas separation (Dong *et al*., 2013). This similar practice was not required in the preparation of ultrafiltration membranes with nanoparticles, mainly because some additives such as polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), and polyethylene glycol (PEG) are usually blended together with photocatalysts into the polymeric solutions of ultrafiltration membranes for pore formation (Dong *et al*., 2013). These additives stabilize TiO_2 nanoparticles in the thin films or in polymer composites in order to diminish the particle agglomeration (Othman *et al*., 2012; Faure *et al*., 2013; Nia *et al*., 2015; Rajaeian *et al*., 2015).

In the recent years, the modification of photocatalyst has been extensively studied. Hydrophilic photocatalysts were converted into hydrophobic photocatalyst in order to encourage the adsorption of hydrophobic compound for further degradation. However, the selectivity was only limited to compounds containing large alkyl groups instead of specific compounds (Inumaru *et al*., 2005). The surface charge on photocatalyst was also improved to achieve selective degradation of cationic and anionic compounds. The electrostatic interactions between photocatalyst and charged compounds could be achieved by adjusting the pH of the reaction medium or surface modification using NaOH. This approach has been reported to be suitable in the selective removal of azo dyes (Liu *et al*., 2010).

Most recently, molecularly imprinting polymer (MIP) was synthesized on photocatalyst for more precise adsorption and degradation of target compound. MIP had drew attentions as it provided an attractive and unique methodology. MIP consisted 3 main steps, which are (i) preparation of bonding between the monomer and specific template molecule, (ii) polymerization, (iii) removal of the template molecule.

Although there are only 3 steps involved, there are 3 types of imprinting, namely covalent printing, non-covalent printing and hybridization of both covalent and non-covalent printing. Among these types, non-covalent is more popular although covalent imprinting is usually superior. This is because there is no need to synthesize monomer-template conjugate for non-covalent imprinting. In addition, the removal of template molecules after polymerization is very easy due to the weak non-covalent interaction. Lastly, the binding and releasing interaction of guest molecules are fast (Chen *et al*., 2011).

Poly(o-phenylenediamine) coated photocatalyst with imprinting sites was first reported by Shen *et al*. (2007) to remove 4-chlorophenol. The polymerization and the template removal were initiated photocatalytically. Although the binding selectivity of 4-chlorophenol/2-chlorophenol was not very high (1.96), but the complete removal of 4-chlorophenol from 2-chlorophenol could still be achieved after 1 h. Conductive polypyrrole was also coated on titanium oxide (TiO_2) to form the molecular imprinting sites by Deng *et al*. (2012) and He *et al*. (2014). The hydrophobic coating did not affect the imprinting purposes. The binding selectivity of molecular imprinted TiO_2 (MIP-TiO_2) towards methyl orange was 2.9 times higher than sunset yellow (Deng *et al*., 2012). The MIP-TiO_2 also showed photodegradation selectivity of rhodamine B (RhB) which was 3.6 times higher than the non-imprinted TiO_2 under visible light (He *et al*., 2014). Using polyacrylamide modified TiO_2, a dye selectivity (rhodamine B relative to rhodamine 6G) of 2.99 could be obtained as well (Bao *et al*., 2014). Though there were a few MIP-TiO_2 was synthesized successfully, the blending of the modified photocatalysts into membrane are yet to be discovered. Hence, it was crucial to study

the performance of membrane after blending with the modified photocatalyst compared to the conventional unmodified photocatalyst.

1.2   Problem Statement

There are several ways to combine both membrane system and photocatalyst, namely using photocatalytic membrane reactor, coating photocatalyst on membrane or blending photocatalyst into membrane. Photocatayst were normally dispersed in feed solution, where this heterogeneous phase was not favourable. On the other hand, membranes coated with photocatalyst or made of photocatalyst were used to study photocatalytic degradation (Bai *et al*., 2015; Kumar *et al*., 2016). Unfortunately, these studies focused more on the photocatalytic degradation since coated photocatlyst layer causing a decline in the flux. The other better alternative is to use photocatlalyst blended membrane. However, main focus in the past research of photocatalytic membrane is fouling mitigation. The full potential of these photocatalytic membranes had not been explored. For instance, fouling studies were conducted to investigate the effect of different types of TiO_2 on PVDF membrane after HA treatment (Teow *et al*., 2016). Kumar *et al*. (2016) reduced the irreversible fouling on membrane by blending photocatalyst as well. The study of antifouling of HA is important because HA is a natural organic matter in various water sources and it can reduce the separation performance of membrane significantly. The magnificent improvement in the membrane separation performance and antifouling properties had led to the oversight of the TiO_2 photocatalytic properties. Thus, a systematic investigation using different

polymeric additives and photocatalysts to investigate the photocatalytic properties of the photocatalyst in membrane are required.

Photocatalytic degradation is also rated as the most economical and environmental friendly method to remove unwanted compound, especially dyes (Liu *et al*., 2015). Unfortunately, the degradation usually involves a wide range of organic compounds without much selectivity (Lazar and Daoud, 2013; Shang *et al*., 2013). The non-selective degradation of photocatalysts limits their applications in the purification or recovery of any preferred compounds. The creation of selectivity hence became the upmost important topic in photocatalysis.

Though modification of photocatalyst shows promising results, the major drawbacks of using particles was the separation and recovery at the final stage. Few research groups had proven that the particles can be easily recovered by introducing a magnetic layer (Zhang *et al*., 2015a; Zhang *et al*., 2015b; Wei *et al*., 2015). An iron compound such as Fe_2O_3 will be used as the base support before applying MIP. By creating an extra layer of iron compound, the magnetic MIP photocatalyst could be easily collected by using a magnet. Though it showed promising results, Fe_2O_3 particles are too expensive to be used in a large scale. A cheaper alternative would be by converting the MIP photocatalyst into ceramic membrane via sol-gel method (Cai *et al*., 2008). However, ceramic membrane are hard to scale up. Hence, in this work, a simpler alternative method is proposed by blending MIP photocatalyst into polymeric membrane. Polymeric membrane is cheap and easy to scale up. Furthermore, MIP photocatalyst entrapped in the polymeric matrix will not be leached using blending method.

1.3   Objectives

(a)   To study the effects of TiO_2, ZnO and Mn-TiO_2 photocatalysts as well as the polymer additives, namely PVP and PVA on the characteristics, separation performance and photodegradation of HA using PSf membrane.

(b)   To synthesize and characterize the molecular imprinted TiO_2 photocatalyst nanoparticles to degrade methylene blue (MB) selectively via photocatalysis.

(c)   To study the effects of molecular imprinted TiO_2 in PSf membrane in terms of the characteristics, separation performance, photodegradation and selectivity of MB.

1.4 Scopes of Study

This study was divided into three parts, namely (i) the study on the effects of photocatalyst and polymer additives on membrane, (ii) synthesis and characterization of molecular imprinted photocatalyst and (iii) the study on the effects of molecular imprinting photocatalyst on PSf membrane.

The first part of the study focused on the effects of polymeric additives, PVA and PVP on different photocatalytic membrane. The synthesized membrane will be characterized to study the relationship between morphology of membrane and the photocatalytic performance. The photodegradation of HA will be carried out in batches by comparing the photocatalyst in suspension to the photocatalyst blended in the membrane. The hindrance effect was quantified by determining the final concentration

of HA at the end of experiment using UV-Vis spectrophotometer. In addition, the separation performance was included in the study to ensure that the membrane is comparable to literature while exploiting the photocatalytic properties of the photocatalyst.

The second part of the study is to synthesize a selective photocatalyst. Most of the studies were carried out to lower the band gap of the photocatalysts. In this work, MIP was used to create a selectivity towards MB instead. The selective photodegradation of MB was studied as MB which are commonly discharged from textile, plastic and printing industries can pollute and affect the ecosystem of water (Kumar *et al*., 2016). By creating selective photodegradation of MB, other valuable compound can be recycle and reuse. MO was chosen as the analog as both of the dyes have similar structure and molecular weight (327.33 g/mol) compared to MB (319.85 g/mol). These particles will be characterized to determine their morphologies changes. The performance of modified and unmodified TiO_2 will be carry out using adsorption and photodegration test. The recyclability and stability of the MIP photocatalyst will be tested as well by carrying out the photodegradation test for several cycles.

The final part of the study is to blend in the synthesized MIP photocatalyst into the membrane. The membrane was characterized to study the effect of MIP-TiO_2 on the membrane. The performance of MIP-TiO_2 membrane will be characterized and investigated. The effect of MIP-TiO_2 in the membrane will be studied in terms of permeation, rejection, photodegradation and selectivity of MB over MO.

CHAPTER TWO
LITERATURE REVIEW

2.1 Free Photocatalyst in Membrane Reactor

In order to exploit the benefits of photocatalyst and membrane in a single unit, a small amount of photocatalysts is dispersed and recycled in the membrane reactor. The setup is commonly known as photocatalytic membrane reactor (PMR). The setup normally consists of a feed tank, photoreactor and a membrane module with a recycle stream (Figure 2.1). A different setup was also introduced so that the reactor could be omitted by placing the light source in the feed tank, but required a more complex configuration at the feed tank.
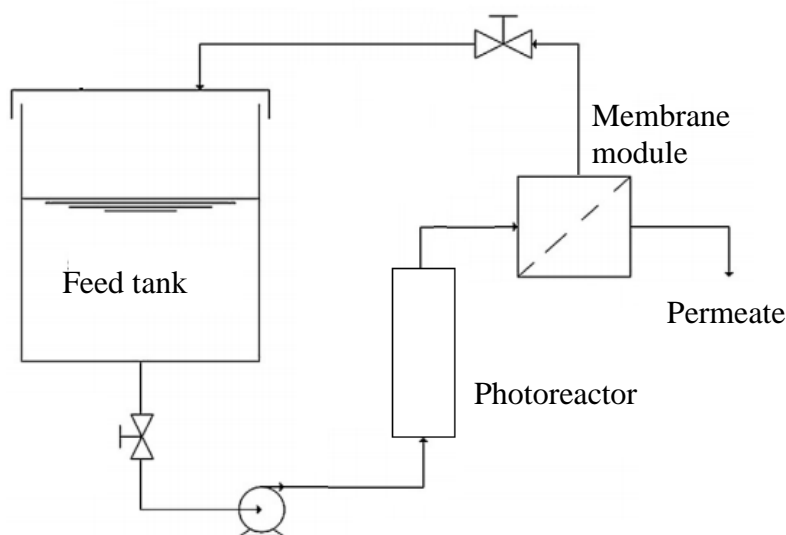

Figure 2.1 A typical photocatalytic membrane reactor.

One of the studies on PMR was carried out by circulating TiO_2 suspension in 40 mg/L of 4-nitrophenol solution (Molinari *et al*., 2001). The sum of rejection, photocatalytic degradation and adsorption of phenol achieved up to 90 %. The further