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항생제 분해용 광촉매막: 리뷰

라비아 카갈니* · 라즈쿠마 파텔**,†

*연세대학교 언더우드학부 융합과학공학부 나노과학공학, **연세대학교 언더우드학부 융합과학공학부 에너지환경융합전공

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Photocatalytic Membrane for Degradation of Antibiotics: A Review

Rabea Kahkahni* and Rajkumar Patel,†**

*Integrated Science and Engineering Division, Underwood International College, Yonsei University, Incheon 21983, Korea
**Energy and Environmental Science and Engineering, Integrated Science and Engineering Division, Underwood International College, Yonsei University, Incheon 21983, Korea

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요 약: 활성 의약품 성분(APIs)의 존재가 수생 생태계와 인간의 건강에 위험하다는 증거가 있다. 물에 항생물질인 테트라사이클린과 같은 API가 존재하면 미생물에 항균제 내성(AMR)이 발생해 개인과 사회에 막대한 비용이 발생한다. TiO_2 또는 비스무트 기반 촉매와 같은 촉매가 내장된 막은 유기 유출물을 분해하고 폐수로부터 분리한다. 촉매의 광촉매 활성은 귀금속 도핑 및 탄소성 물질의 첨가 및 다른 반도체와의 헤테로 접합 형성으로 향상될 수 있다. 광촉매의 회수는 고분자 막에서 광촉매의 고정화를 통해 가능하다. 이 검토에서는 물 속 항생제의 분해가 논의된다.

Abstract: There is evidence that the presence of active pharmaceutical ingredient (APIs) are a danger for aquatic ecosystems and the human health. The presence of APIs such as tetracycline, an antibiotic, in water causes antimicrobial resistance (AMR) in microorganisms inflicting enormous costs on individuals and society. Membranes embedded with catalysts such as TiO_2 or bismuth based catalysts degrade and separate the organic effluents from wastewater. The photocatalytic activity of the catalysts can be enhanced with noble metal doping and addition of carbonaceous materials and formation of heterojunction with other semiconductors. The recollection of photoctalysts is possible through the immobilization of the photocatalysts in polymeric membranes. In this review, the degradation of antibiotics in water is discussed.

Keywords: *photocatalytic membrane, antibiotics, wastewater, antimicrobial resistance*

1. Introduction

Due to the rising concern of wastewater pollution with antibiotics, photocatalytic membranes application in wastewater treatment are increasingly investigated. The technology incorporates photocatalysts such as TiO_2 and BiOCl into the membrane, which solves problems related to membrane fouling and photocatalytic efficiency[1-2].

TiO_2 is either used in suspension or immobilized over the surface of the membrane in the membrane photocatalytic reactor (PMR) system. The suspension of TiO_2 has higher degradation efficiency of the pollutant because of the increased surface area of the photocatalyst available for degradation. However, the suspension of TiO_2 causes fouling of the membrane due to the formation of dense layer of TiO_2 during the process of oxidation. The immobilization of TiO_2 in membranes solves the problem of fouling due to the

†Corresponding author(e-mail: rajkumar@yonsei.ac.kr; http://orcid.org/0000-0002-3820-141X)

oxidation of the pollutant on the surface of the membrane and within its pores. In addition, the membrane shows more stability after many cycles of use. However, the oxidation efficiency of suspended TiO_2 is higher than that of immobilized TiO_2[3]. Carbonaceous material such as graphene is added to TiO_2. The semiconductor's photocatalytic activity can be enhanced due to the important properties of graphene that facilitates the charge transportation and electron-hole separation in TiO_2[4]. The coupling of TiO_2 with other materials can enhance its photocatalytic activity further. For example, when TiO_2 is coupled with carbon material, its band gap is reduced so that it can be active under visible light. Furthermore, the addition of carbon improves the charge transfer of TiO_2 and increases the conductivity of TiO_2. In addition, carbon can be fabricated from ecofriendly materials and is low cost and stable[5].

Ceramic membranes are used in PMR due to their excellent chemical resistance against strong oxidants formed during the photocatalytic activity. The control of structural characteristics of the photocatalyst film and the morphology of the photocatalytic membrane account for the improvement of the membrane's performance[6]. It is also possible to enhance the catalytic activity of TiO_2 by doping it with noble metal nanoparticles such as Au, Ag, and Pd. Since it is difficult to recollect the nanoparticles from a slurry medium due to their small size, supports such as PVDF are used to immobilize the particles[7]. Fibers such as nanowires and electrospun nanofibers are also efficient carriers of catalysts. They have high flexibility and high surface area[8].

Bismuth oxyhalides are also one of the most promising photocatalysts because of their high photocatalytic ability and environmental friendliness. Bismuth oxyhalides such as BiOI, BiOCl and BiOBr prevent electron hole recombination due to their unique crystal arrangement of the$[BiO_2]^{2+}$ and halide ion[9]. 2-D layered materials enhance the separation and transfer of electron-hole pairs generated in the photocatalytic process. $BiOCl/TiO_2$ and TiO_2/BiOBr heterojunctions are examples of 2D/2D heterojunctions with high photocatalytic activity and efficient separation of electron hole pairs[10]. To improve the photocatalytic performance of the heterojunction further, nitrogen carbon quantum dots (NQCDs) are added. They improve activity under the visible light and the electron transmission efficiency[11]. *E. coli* degradation by BiOCl/Br heterojunction was found unaffected by HO radicals and $^1O_2$. The inactivation of *E. coli* is mainly due to the direct contribution of photogenerated holes with the activity of the heterojunction being most efficient under UV light[12]. This review is divided mainly into three section. In the first section, the degradation of tetracycline by TiO_2 based membranes is discussed. In the second section, antibiotics degradation by bismuth-based membrane is described. In the final section, alternative membranes are discussed. Fig. 1 represents the schematic classification and Table 1 summarizes the photocatalytic membrane.

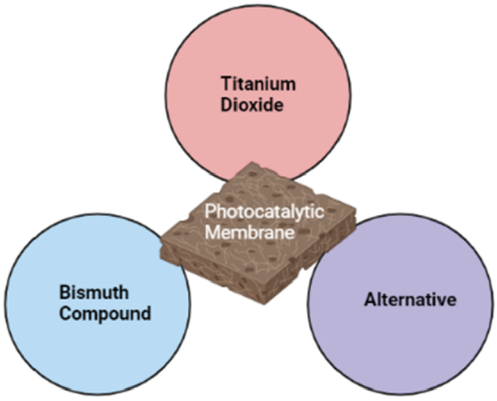

Fig. 1. Schematic presentation of classification of the table.

2. Titanium Oxide Based Membrane

TiO_2 and bismuth oxyhalides are considered as one of the most promising photocatalysts because of their non-toxicity, stability, high photocatalytic activity and biocompatibility. In this study, the photodegradation of Tetracycline (TC) under visible light by AgS_2/TiO_2 composite nanofiber membranes made through electrospinning and hydrothermal method was investigated[13]. The results showed that compared to TiO_2

Table 1. Summary of the Photocatalytic Membrane

Membrane	Filler	Water flux ($L\ m^{-2}\ h^{-1}$)	Contaminants	Degradation rate	Reference
PVDF	AgS_2/TiO_2	-	TC	70.54%	[13]
LLDPE	TiO_2-modified ZnO QDs	-	TC	89.45%	[14]
SCMPR	TiO_2	-	AMX	80.3%	[15]
CA	Au/Ag /TiO_2	-	TC	80%	[16]
pDA coated PVDF	Au/TiO_2	-	TC	92%	[17]
PPTD	TiO_2	243.44	SD	91.4%	[18]
PVDF	g-C_3N_4 BiOI	30.688	TC	94.6%	[19]
PVDF	Bi_2WO_6/CeO_2	TC: 49.2 HA:41.65	TC, HA	TC: 82% HA: 78%	[20]
CF	Ag_3PO_4 BiOBr	-	TCH	90%	[21]
g-C_3N_4	g-C_3N_4	-	Cr (VI), TCH	83.3%	[22]
PVDF	$ZnIn_2S_4$	26.09	TC	92%	[23]
CA	$H_4SiW_{12}O_{40}$	-	TC, MO	TC: 63.8% MO: 94.6%	[24]
PVDF	$CoFe_2O_4$–(rGO)	927.28	TC	85%	[25]

Abbreviations: LLDPE: linear low-density polyethylene polymer, SCMPR: submerged ceramic membrane photocatalytic reactor, PVDF: polyvinylidene fluoride; pDA: polydopamine, PPTD: PVDF-PVP-TiO_2-Dopamine blend ultrafiltration membrane, b-phase PVDF: beta-phase polyvinylidene fluoride membrane, CA: cellulose acetate, TC: tetracycline, HA: Humic acid, MO: Methyl orange, AMX: amoxicillin, SD: sulfadiazine, TCH: Tetracycline hydrochloride, CA: Cellulose acetate, CF: Carbon Fiber

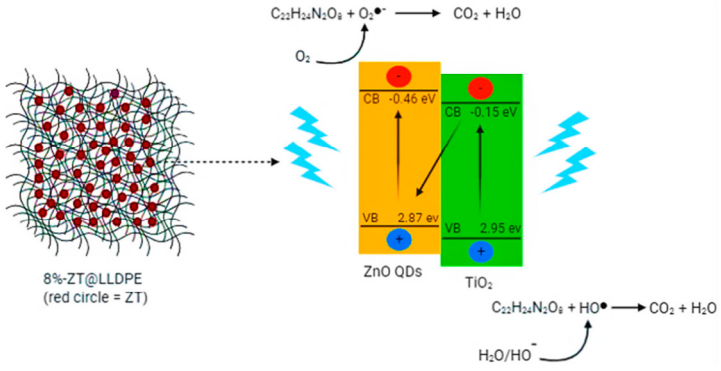

Fig. 2. Proposed mechanism for the photocatalytic degradation of TC using 8%-ZT@LLDPE under visible light irradiation (Reproduced from Iqbal *et al.*[14], 2021, MDPI).

and Ag_2S the photocatalytic performance of the composite membrane was excellent reaching 70.54% photodegradation rate. It was due to the high charge transfer property of the heterojunction of Ag_2S and TiO_2 and its enlarged band gap, which increases the photocatalytic performance under visible light. To understand the mechanism of the photocatalysis the trapping experiment and degradation intermediates analysis revealed that O_2^- and h^+ are the major species involved in the photodegradation. Finally, the membrane showed high recyclability potential after five cycles.

Through solution casting method, Mesoporous TiO_2-modified ZnO quantum dots (QDs) were immobilized on a linear low-density polyethylene (LLDPE) polymer[14].

The generated film photodegradation performance

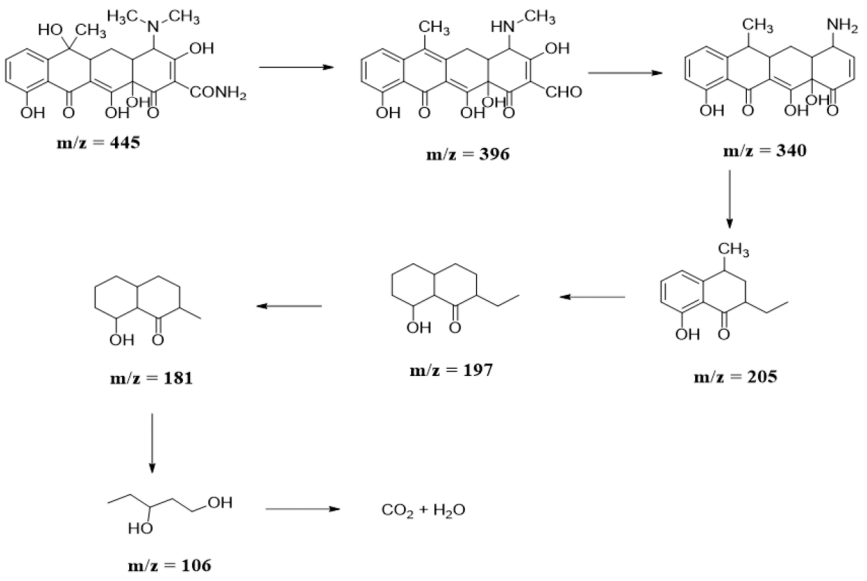

Fig. 3. Proposed possible pathways for the photodegradation of TC in the presence of 8%-ZT@LLDPE (Reproduced from Iqbal *et al.*[14], 2021, MDPI).

was investigated using Tetracycline (TC) as an antibiotic model. Under optimal conditions of pH value of 9 and TC concentration of 40 mg/ml, and 90 min time period, the photodegradation efficiency reached a percentage of 89.5%. It was due to improved water uptake by the film that has a rough surface. Furthermore, heterojunction of the QDs and TiO_2 lower the probability of recombination of the photoinduced charge carriers. The displacement of the conduction band of ZnO to more negative values compared to TiO_2, which is due to quantum confinement effect, leads to the formation of more reactive species. The main species in photodegradation is O_2^- investigated using the scavenging test. Finally, the film demonstrates good recyclability potential after 8 cycles of use.

Submerged ceramic membrane photocatalytic reactor (SCMPR) coupled with TiO_2 nanocatalyst was developed for the treatment of refractory antibiotic organic compounds[15]. The ceramic membrane acts as a support of TiO_2, which enables its easy separation from wastewater. The results of the study show that the membrane has high photocatalytic performance and stability under a wide interval of pH that ranges from 6.5 to 9.0. The aeration system increased the contact of the TiO_2 with UV light, which enhanced the photocatalytic process. The membrane has a high level of stability owing to its self-cleaning capability resulting from the aeration system. Furthermore, the membrane has good resistance to oxidants resulting from the photocatalytic process. Finally, through Q-TOF LC/MS system, AMX photodegradation process was investigated. The intermediates of the photodegradation reactions turned into CO_2, water, and inorganic ions due to hydroxyl radicals.

Bimetallic Au/Ag decorated TiO_2 nanocomposite membrane was developed for degradation of antibiotics (tetracycline, TC) and bacteria elimination[16]. TiO_2 nanorods were first decorated with bimetallic $Au_{0.1}Ag_{0.9}$ (mass ratio of Au or Ag to TiO_2) nanoparticles. The decorated nanorods $Au_{0.1}Ag_{0.9}/TiO_2$ NRs were then incorporated into the cellulose acetate (CA) matrix using the phase inversion method. The incorporation of $Au_{0.1}Ag_{0.9}/TiO_2$/ into the CA matrix did not change the membrane's structure with high hydrophilicity and porosity. The incorporation of the composite enhanced the membrane's photocatalytic activity under visible light due to the presence of Ag and Au. Furthermore, Ag has good antibacterial efficiency. The results show

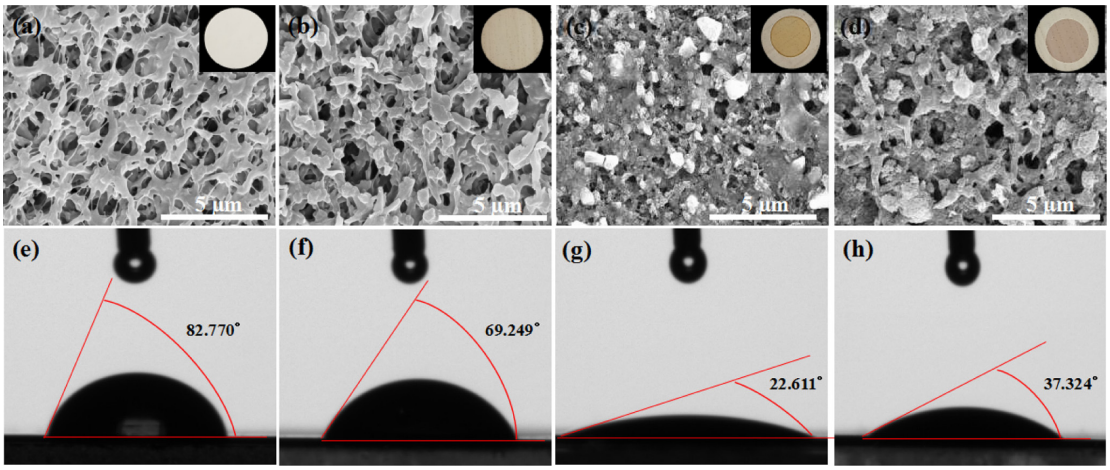

Fig. 4. SEM images and the corresponding photographs of membranes, (e, f) images of water contact angle on the membrane surfaces, and the angle in the figure is the average. (a, e) original PVDF, (b, f) pDA/PVDF, (c, g) TiO_2/pDA/PVDF, (d, h) Au-TiO_2/pDA/PVDF (Reproduced with permission from Wang *et al.*[17], Copyright 2017, American Chemical Society).

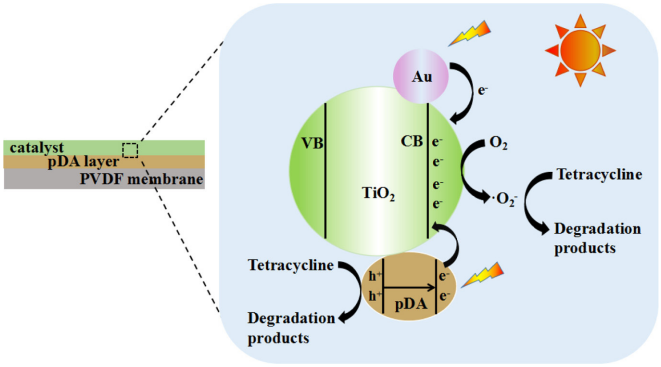

Fig. 5. Photocatalytic mechanism of degradation of tetracycline for Au-TiO_2/pDA/PVDF membranes (Reproduced with permission from *Wang et al.*[17], Copyright 2017, American Chemical Society).

that the membrane operated optimally with a ratio of composites being $Au_{0.1}Ag_{0.9}/TiO_2$/CA-1.5. In the static degradation system, the rate of degradation reached 80 % after 120 min exposure to visible light and in dynamic photodegradation system, it increased to 90%.

A photocatalytic nanocomposite membrane was made by immobilizing vacuum-filtrated Au-TiO_2 nanocomposites into polydopamine (pDA)-coated poly(vinylidene fluoride) (PVDF) membrane[17].

The Au-TiO_2 structure enhances the photocatalytic activity under visible light. Moreover, pDA coating acts as a photosensitizer of TiO_2. The pDA is also the bioadhesion material that strengthens the bond between the nanocatalysts and the PVDF substrate. The results of the study show that under visible light for 120 min the photodegradation efficiency of tetracycline (TC) reached 92%, which is 26% more than that of Au-TiO_2 powder and 51% more than that of TiO_2/pDA/PVDF. The equilibrium adsorption percentage of Au-TiO_2/pDA/PVDF membrane reached a maximum value of 30% for the tetracycline within 80 min. Finally, the membrane showcases good recyclability and reusability potential with a stable degradation efficiency of 90% after 5 cycles.

A PVDF-PVP-TiO_2-Dopamine membrane (PPTD) was synthesized by physical blending for photodegradation of sulfadiazine (SD) in water under UV light[18]. PVP-TiO_2-Dopamine increased the hydrophilicity of the PVDF membrane by increasing its pore size and it improved the pure water flux by 56%.

In pure water the photodegradation efficiency of SD reached 91.4% under optimal condition of pH, concentration of SD, time interval and UV intensity, while in the real sample, the water quality parameters, NO_3^-, SO_4^{2-}, Cl^- and HA, influenced the photocatalytic process by improving the degradation of SD. Furthermore, ESR characterization showed that OH radicals played a major role in the photodegradation of SD. In the photodegradation process of the membrane OH^-, O^{2-}, HO_2^-, H_2O_2 and $^1O_2$ could be formed; also, the TiO_2-Dopamine synergetic structure involves bidentate structure or the chelated structure.

3. Bismuth Compound Based Membrane

Z-scheme 2D/3D g-C_3N_4/BiOI heterojunction immobilized in beta-phase polyvinylidene fluoride membrane (b-phase PVDF) was synthesized through solvent crystallization and phase inversion technique[19]. The photocatalytic performance of the membrane was investigated using tetracycline (TC) degradation experiment and was compared to that of CN/BI heterojunction, CN/PVDF and BiOI/PVDF photocatalytic membranes (PMs). It was reported that the Z-scheme 2D/3D g-C_3N_4/BiOI PVDF photocatalytic membrane achieved higher degradation percentage of TC reaching 94.6% in 120 min. In dynamic degradation system, the percentage increased to 94.8% in a span of 80 min. the membrane showed great stability and reusability potential after five cycles, as well as great permeability and self-cleaning ability. The excellent photocatalytic performance of CN/BI/PVDF PMs was possible owing to scheme Z-2D/3D nanostructure that eased the charge transfer and prevented the recombination of electron-hole pair. The porosity of PVDF enabled the transport of the nanostructures to the surface with more advantageous exposure to the light source. ESR revealed that O^{2-} and OH radicals, which were generated by the pure-beta PVDF membrane, participated in the photodegradation of TC. Water flux recovery rate was studied and found out that the composite membrane under visible light emission recover 92%.

Nanocomposites with two different ratios of the photocatalytic nanomaterial Bi_2WO_6 and CeO_2 were synthesized, 1:1 and 2:1 Bi_2WO_6/CeO_2, through the facile sono-dispersion method[20]. The nanocomposites were grafted onto the PVDF membrane. FTIR and XPS analysis demonstrated the strong bonding between the nanocomposite and the membrane through showing the presence of carboxylic acid functional group and Bi, W, and Ce elements. The grafted acrylic acid and Bi_2WO_6/CeO_2 improved the hydrophilicity of the membrane. Furthermore, CeO_2 prevented the recombination of photo-generated charge carriers. Bi_2WO_6/CeO_2- PVDF with 1 wt% of PVP and 0.5 wt% of photocatalytic nanomaterials had permeate flux of 49.2 L m^{-2} h^{-1} for tetracycline and 41.65 L m^{-2} h^{-1} for humic acid. With PVDF - 2:1 Bi_2WO_6/CeO_2 the photodegradation rate of tetracycline and the humic acid solution was 82% and 78% respectively after 90 min under visible light, with a total resistance of 1.43×10^{10} m^{-1} and 1.64×10^{10} m^{-1} respectively and 83.5% and 77% flux ratio respectively. These results make the 2:1 Bi_2WO_6/CeO_2 nanocomposite grafted a better photocatalytic membrane with high permeate flux.

Ag_3PO_4 and BiOBr nanocomposites were grown on the carbon fiber (CF) film through solvothermal-chemical deposition two-step process[21]. The heterojunction Ag_3PO_4/BiOBr has widened the photoabsorption edge of the film from 430 nm to 520 nm due to the presence of Ag_3PO_4 and the nanoparticle improved the electron-hole separation. The Ag_3PO_4/ BiOBr/ CF is a flexible porous film with excellent visible light absorption whose performance reached 90% degradation efficiency of Tetracycline hydrochloride (TCH) under visible light in 30 min. Degradation of TCH increases by 76.8% from first grade to sixth grade of the degradation. The main reaction species of the photodegradation were investigated and revealed to be h^+ and O^{2-}.

4. Alternative Membrane

Photocatalytic composite membranes embedded with other catalysts such as metal sulfides were proven ef-

fective for the degradation of tetracycline. Ultrathin nanosheets of g-C_3N_4 was synthesized through the exfoliation of bulk raw graphitic carbon nitride by edible glucose syrup[22]. Through the exfoliation, g-C_3N_4 acquired advantageous characteristics such as large surface area, homogeneous dispersion and enhanced exposure of active sites. The thin layers of g-C_3N_4 exhibited excellent photocatalytic performance on Cr(VI) and Tetracycline hydrochloride TCH. Compared to raw g-C_3N_4, the thin film reduction of Cr(VI) was 18-fold improved, and the reduction of TCH was 3-fold improved under visible light because the thin layers of g-C_3N_4 have a larger surface area and have more exposed active sites. The g-C_3N_4 were obtained from carbon nitride nanosheet dispersion through its direct vacuum filtration.

The dynamic photocatalytic membrane reactor is $ZnIn_2S_4$ is deposited on polyvinylidene fluoride (PVDF) membrane[23]. With effluent circulating to the photocatalytic membrane reactor the total organic carbon removal efficiency reaches a maximum value of 57% after 3 h degradation with 1.88 mg cm^{-2} photocatalyst and under conditions of 84.06 L m^{-2} h^{-1} flux and 50 mW cm^{-2} light intensity. With continuous influent and effluent circulating to the photocatalytic membrane, the average removal efficiency reached 50% after 24 h degradation with 1.88 mg cm^{-2} catalyst under conditions of 26.09 L m^{-2} h^{-1} flux and light intensity of 50 mW cm^{-2} and initial concentration of tetracycline of 10 mg L^{-1}. To reach a higher efficiency of 92% under the same circumstances, the time of exposure was extended to 36 h and the initial concentration of tetracycline was decreased to 100 μg L^{-1}.

$H_4SiW_{12}O_{40}$ (SiW_{12})/cellulose acetate (CA) composite nanofibrous membrane was synthesized through electrospinning. Fourier transformation infrared spectroscopy (FT-IR), Energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) confirmed that SiW_{12} has immobilized into the CA membrane and its Keggin structure was preserved[24]. The optimal mass ratio of SiW_{12} to CA was 1:4, it exhibited excellent photocatalytic degradation of Tetracycline (TC) and Methyl orange (MO) under ultraviolet light. The degradation of TC reached 63.8% and the degradation of MO reached 94.6%. The difference in degradation efficiency between the two pollutants comes from the fact that CA played a different role in the degradation of each of the pollutants. For MO the CA membrane did not only provide contact between the pollutant and the SiW_{12} but also donated electron to SiW_{12} in the photocatalytic process, which lead to a greater efficiency in the photodegradation of MO compared to the photodegradation of TC. Finally, the membrane has good reusability potential due the water-insolubility of CA and stability of SiW_{12} on CA stemming from their hydrogen bond.

A photocatalytic composite membrane (PCM) was synthesized by coating a carbon fiber cloth with $CoFe_2O_4$–rGO and PVDF, after adding the $CoFe_2O_4$–rGO into the PVDF casting solution[25]. With the $CoFe_2O_4$–rGO coated PCM, the membrane played the role of the cathode membrane in a photocatalysis-assisted Microbial Fuel Cells (MFC)- Membrane Bio-Reactor (MBR) system. Tests with four types of MFe_2O_4 (M = Ni, Fe, Co, Zn) were carried out; results show that $CoFe_2O_4$ had the highest oxygen reduction reaction (ORR) activity. Furthermore, the coupling of GO and $CoFe_2O_4$ enhanced the photocatalytic activity. The PCM achieved a maximum power density of 942 mW m^{-3} under visible light irradiation and performed efficient degradation of tetracycline (TC).

5. Conclusions

Pharmaceutical industries' effluents contain a wide range of antibiotics that can end up in the aquatic environment. Their presence in wastewater breeds resistant bacteria. Thus, the effluent needs to be purified before being released into the stream. Degradation of the organic pollutants through photocatalytic membranes is a well-known process. However, there are still challenges in the use of the method related to cost, effectiveness, and reusability of the catalysts. This review concentrated on TiO_2 and Bismuth based photo-

catalysts and addressed the different challenges related to the process.

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