Polymer-based TiO$_2$ nanocomposite membrane: synthesis and organic pollutant removal

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ABSTRACT
Titanium dioxide (TiO$_2$) nanoparticles are efficient photocatalysis for treating organic pollutants in water. Immobilizing TiO$_2$ nanoparticles not only enables the reuse of nanoparticles but also prevents the harmful impact of releasing nanoparticles into the aquatic environment. In this study, a porous composite microfiber membrane based on polyacrylonitrile (PAN) with TiO$_2$ nanoparticles has been synthesized by electrospinning technique. The new membrane system has exhibited excellent adsorptive-photocatalytic property to degrade Methylene blue (MB). Using the nonlinear form of the pseudo-first-order, pseudo-second-order, Elovich, and Intra-particle diffusion models, the adsorption mechanism was analyzed. Coupling with adsorption and photocatalysis, the efficiency of this membrane system was illustrated via the multistage linear form of the pseudo-first-order kinetic; and the electrical energy per order (EEO) confirmed the lowest energy requirements to transfer selected pollutants. Combining the results of SEM, BET, FTIR, XRD and TGA, it revealed the relationship of microstructure, composition, and MB decomposition performance. The finding presents new knowledge for material design and evaluation of polymers/oxides membrane systems for remediating organic pollutants in water.

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Introduction
Titanium dioxide (TiO$_2$), the most widely studied photocatalytic material for water treatment, occurs in three major crystal structures: rutile, anatase, and brookite [1,2]. These crystal structures have different lattice parameters, resulting in different physical and chemical properties. The most commonly used commercial TiO$_2$ powder is anatase, or a mixture of rutile and anatase, as anatase has the highest photocatalytic activity among all three crystal structures. To obtain a high photocatalytic efficiency, nanoscale materials are often preferred because of their large surface area and high chemical activities. However, the release of nanoparticles in the environment may cause severe genotoxicity and cytotoxicity to aquatic organisms and human beings [3,4]. Therefore, methods that can fix and reuse nanomaterials should be implemented during the photocatalyst designing process.

Immobilizing TiO$_2$ nanoparticles on macro carriers provides a simple way to separate the photocatalyst from the solution, preventing the harmful effects of nanoparticles from entering the environment. Various carrier materials have been reported to immobilize TiO$_2$ nanoparticles, including glass, metals, ceramics, polymers, and other porous carriers [5–9]. Nevertheless, choosing the best carrier is not an easy task. Because it must resist the oxidizing environment, allow penetration of ultraviolet rays, and permit good contact of pollutants and photocatalyst [10]. To that end, the use of materials with adsorptive properties as the carrier of TiO$_2$ nanoparticles is more advantageous as the combined actions of adsorption and degradation of pollutants will improve the photodecomposition efficiency of TiO$_2$.

Polyacrylonitrile (PAN) is a synthetic organic polymer that is widely used as protective materials, automated tools, medical care, filtration process, environmental technology, energy, textiles, and agriculture industries [11]. It has good chemical stability, optical transparency, thermal stability, low density, high strength, good elasticity, and low cost. With the cyano group on its surface, it can be modified by introducing various functional groups, making it an ideal membrane substrate.

The electrospinning technique uses an electric field to draw fibers from precursor solutions and is an economical and efficient method to produce polymer fibers and membranes. Controlled morphology [12–16] and composition [17–21] of fibers can be obtained by adjusting the solution and process parameters, and environmental conditions [22]. In this study, we aimed to develop an effective photocatalytic and adsorptive membrane system using TiO$_2$ nanoparticle and PAN for environmental applications. The electrospinning technique was used to prepare polymer-based TiO$_2$ microfiber membranes, i.e. PAN-TiO$_2$ composite microfiber membranes, with porous structures, followed by selective dissolution of the materials. Adsorption and photo-decomposition kinetics of methylene blue (MB), an organic dye, were investigated. The relationships of fiber composition, microstructure, and MB removal performance were examined.

Experimental
Chemical and reagents
Polyacrylonitrile (PAN, $M_w = 150,000$), N, N-dimethylformamide (DMF), polyvinylpyrrolidone (PVP, $M_w = 55,000$), TiO$_2$ nanoparticles (21 nm primary particle size),
methylene blue (MB), and methyl orange (MO) were purchased from Sigma Aldrich (St. Louis, MO, United States). Sodium polyphosphate (SP) was purchased from ECP (Birkenhead, Auckland, New Zealand). Deionized water is used for reagent preparation.

**Synthesis of PAN-TiO₂ composite microfiber membrane**

The electrospinning solution was prepared through the following procedure. PAN and PVP with mass ratios of 1:0, 4:1, 2:1, and 1:1 were mixed with 10 ml DMF. The solution was magnetically stirred at 750 rpm and 75°C for 3 h to obtain completely dissolved solution and left for 12 h to fully swell. Certain amounts of TiO₂ nanoparticles and sodium hexametaphosphate (as a dispersant) were then added to this solution (Table 1). The mixture was loaded into a 10-ml syringe with a needle inner diameter of 0.91 mm.

The precursor solution was injected under a voltage of 11 kV with a speed of 0.8–1.0 ml/h onto the Al foil covered drum collector which was placed at 20 cm and rotated at 150 rpm. After operating for 5 h at room temperature, a piece of non-woven mat was obtained. The mat was dried in an oven at 75°C for 12 h to remove residual solvent, followed by removing PVP to generate porosity. Sample No.1–4 were immersed into deionized water for 24 h at 4°C, while sample No.5–9 were washed several times with deionized water for 15 min each time to remove PVP [23]. The as-prepared samples were dried and shaped in an oven at 80°C for 12 h.

**Materials characterization**

Microstructure and composition analysis of fibers and membrane were performed using scanning electron microscope (SEM, FEI Philips XL30 S-FEG). The surface functional group was identified by Fourier Transform Infrared Spectroscopy (FTIR, Spectrum 100, Perkin-Elmer). The crystalline structure was measured by X-ray diffractions (XRD, Bruker D2-phaser). Thermogravimetric analysis (TGA, Shimadzu GA-50) was used to determine the change of sample mass (TiO₂ content). The specific surface area and aperture distribution of fibers were measured by BET (Brunauer-Emmett-Teller) and BJH (Barrett-Joyner-Halenda) methods from the nitrogen adsorption-desorption isotherm data using Micromeritics TriStar 3000 [24].

| No. | Name   | PAN Copolymer (g) | PVP Copolymer (g) | TiO₂ (g) | SP (g) |
|-----|--------|-------------------|-------------------|----------|--------|
| 1   | EF     | 1                 | 0                 | 0.5      | 0.05   |
| 2   | EF 4–1 | 1                 | 0.25              | 0.5      | 0.05   |
| 3   | EF 2–1 | 1                 | 0.5               | 0.5      | 0.05   |
| 4   | EF 1–1 | 1                 | 1                 | 0.5      | 0.05   |
| 5   | M 10-0-0 | 1             | 0                 | 0        | 0      |
| 6   | M 10-0-7 | 1            | 0                 | 0.7      | 0.07   |
| 7   | M 10–2.5-7 | 1           | 0.25              | 0.7      | 0.07   |
| 8   | M 10-5-7 | 1             | 0.5               | 0.7      | 0.07   |
| 9   | M 10–10-7 | 1           | 1                 | 0.7      | 0.07   |
Contaminant removal experiments

Adsorption experiments
The adsorption performance of the membranes was evaluated in a water bath heated shaker (BS-31, Acorn Sci.) with a frequency of 100 rpm at 25°C. Dye concentration was determined by UV-VIS spectrophotometer (UV-2500, Shimadzu) [25].

Adsorption kinetics: 50 mg membrane was added into 50 ml of MB or MO dye solution with the initial concentration of 5 mg/L for adsorption kinetics test. Reacted solution was taken periodically to determine the solute concentration during the adsorption/photocatalysis process. Equation (1) is used to calculate the amount of adsorbed dyes on fiber membranes at different time points. The adsorption kinetics of the synthesized membrane was simulated graphically using first order, second order, Elovich model, and intraparticle-diffusion model.

\[ q_e = \frac{C_0 - C_e}{m} V \]  
(1)

where \( q_e \) is the adsorption capacity (mg/g); \( C_e \) is the equilibrium dye concentration (mg/L); \( C_0 \) is the initial dye concentration (mg/L); \( m \) is the mass of membranes (g); and \( V \) is the volume of dye solution (L).

Adsorption selectivity: As-prepared 5 mg membrane was added to the mixed solution of 20 mL MB (cationic dye, 2.5 mg/L) or MO (anionic dye, 2.5 mg/L) until adsorption saturation. The adsorption capacity of the membrane to the different types of dyes was determined [26].

Photocatalytic experiments
The photocatalytic activity of the membrane was assessed by the removal efficiency of MB from aqueous solution (\( V_0 = 50 \) ml, \( C_0 = 5 \) ppm) under simulated sunlight radiation (300 W, Ultra Vitalux 230 V E27). The experiments were performed in a closed system with 50 mg of PAN-TiO\(_2\) microfiber membranes (3.5 \( \times \) 2.5 cm\(^2\)) mounted on a wire mesh frame and hung inside a 100 ml glass beaker. For examining combined adsorption and photocatalysis activities, experiments were performed by exposing the reaction system to simulated sunlight for 120 min without prior adsorption/desorption equilibrium in dark.

Photocatalytic reaction kinetics: The absorbance of MB (lambda peak Max = 664 nm) is measured using a UV-visible spectrophotometer according to the Beer–Lambert law:

\[ A = \varepsilon b C \]  
(2)

where \( C \) is solution concentration; \( A \) is solution absorbance; and \( \varepsilon, b \) are constants. The degradation rate was calculated using:

\[ Y(%) = \frac{C_0 - C_t}{C_0} \cdot 100\% = \frac{A_0 - A_t}{A_0} \cdot 100\% \]  
(3)

where \( C_0 \) is initial concentration; \( C_t \) is the concentration at time \( t \); \( A_0 \) is initial absorbance; and \( A_t \) is the absorbance at reaction time \( t \).

Photocatalytic energy consumption: Electrical energy per order (EEO) is used to describe the energy requirements of light irradiation-based advanced oxidation processes (AOPs). The parameter \( E_{EO}(\text{kWh/m}^3/\text{order}) \) is defined as the energy
required to reduce the concentration of the target pollutant by one order of magnitude (90%) per unit volume ($1 \text{ m}^3$) [26][27]. The arithmetic expression is:

$$E_{EO}(\text{kWh/m}^3/\text{order}) = \frac{E \cdot \left(\frac{1}{60}\right)}{V \cdot \log\left(\frac{C_0}{C_t}\right)}$$

(4)

This equation can also be simplified by a pseudo-first-order kinetic constant ($k$, min$^{-1}$) (Equations 3–6). $k$ is obtained by fitting the first-order kinetic equation (Equations 3, 4).

$$\ln\left(\frac{C_0}{C_t}\right) = kt$$

(5)

$$E_{EO}(\text{kWh/m}^3/\text{order}) = \frac{E}{V \cdot 60 \cdot 0.4343 \cdot k} = \frac{E}{26.058 \cdot V \cdot k}$$

(6)

where $E$ is the power of light source (kWh); $t$ is irradiation time (min); $V$ is treated solution volume ($\text{m}^3$); $C_0$ and $C_t$ are the concentrations of initial and when time is $t$; $k$ is pseudo-first-order reaction rate constant (min$^{-1}$)

**Results and discussion**

**Characterization of PAN-TiO$_2$ composite microfibre membrane**

The microstructure and composition of PAN-TiO$_2$ microfiber membrane play a critical role in the removal efficiency of water organic pollutants [27][28]. Due to the high surface energy, TiO$_2$ nanoparticles can easily aggregate to form larger clusters that significantly reduce the photocatalytic activity (Figure 1(a)). The SEM micrographs revealed that TiO$_2$ nanoparticles distributed uniformly on PAN microfibers (Figure 1(c-f)), demonstrating the effectiveness of immobilization to prevent TiO$_2$ nanoparticles from aggregation and embeddedness. This is probably because that the processing used to spin the polymer solution prevent the agglomeration of TiO$_2$ nanoparticles.

TiO$_2$ nanoparticles exposed on the polymer surface would be more accessible to light, solvent and contaminants in solution, resulting in good photocatalytic activity [29]. To our knowledge, this is the first-time report that TiO$_2$ nanoparticles can be uniformly distributed on the surface of fibres instead of embedding/agglomerating inside the substrate materials in electrospinning immobilization field. The microfiber membrane also demonstrated excellent flexibility (Figure 1(h)).

Samples EF1-1, EF2-1, EF4-1 were synthesized from the solutions with different PVP concentrations. The BET analysis on these samples revealed that the total pore volume increased with PVP content under the same process condition (Table 2). The specific surface area seemed to relate to an optimal PVP content. Comparing with EF4-1 and EF 1–1, EF2-1 (PAN: PVP = 2:1) has a higher specific surface area. Also, PVP seemed to facilitate the immobilization of TiO$_2$ nanoparticles as more evenly distributed TiO$_2$ nanoparticles are visible on the fiber surface in the samples with PVP (EF1-1, EF2-1, EF4-1) than those without PVP (EF) (Figure 1(b)).
The slight increase of TiO$_2$ nanoparticles and SP was unlikely to affect the total pore volume and the specific surface area of composite fibers. Instead, the post-synthesis wash step exerted more significant effects as M10-10-7 showed notably higher specific surface area and pore volume than samples EF1-1, EF2-1, and EF4-1.

Figure 1. SEM images: (a) TiO$_2$ nanoparticles, (b) EF, (c) EF 4–1, (d) EF 2–1, (e) EF 1–1, (f) (g) M 10–10-7, and (h) flexible membrane M 10–10-7. Note: The denotation of EF, EF 4–1, EF 2–1, EF1-1, and M10-10-7 is listed in Table 1.
Table 2. BET specific surface area and total pore volume of composite fibers.

| Sample    | \( S_{\text{BET}} \) (m\(^2\)/g) | \( V_{\text{por}} \) (cm\(^3\)/g) \times 10\(^{-2} \) |
|-----------|-----------------------------------|-------------------------------------------------|
| EF 4–1    | 11.35                             | 4.29                                            |
| EF 2–1    | 12.63                             | 4.52                                            |
| EF 1–1    | 11.51                             | 6.89                                            |
| M 10–10-7 | 23.17                             | 8.96                                            |

N\(_2\) adsorption–desorption curve of M 10–10-7 showed low N\(_2\) adsorption at the low relative pressure (0.0–0.1) (Figure 2(a)). This low N\(_2\) adsorption capacity indicates weak interaction between fibers and the adsorbent. The H3 hysteresis loop appeared at the medium relative pressure area (0.1–0.9) and a large amount of N\(_2\) adsorbed at high relative pressure area (0.9–1.0), corresponding to the existence of slit-like pores in fiber, and agree with the SEM micrographic image in Figure 1(g). The pore distribution analysis of M10-10-7 indicated a mesoporous structure containing pores with diameter ranging from 5 to 40 nm (Figure 2(b)). The peak size of pores is around 22 nm, suitable for the storage and nailing of nano-sized titanium oxide particles used in this study.

FTIR was used to characterize the chemical compositions of the composite membrane by identifying the molecular fingerprint and quantifying the intensity of the functionality present in the samples. The pure PAN fiber displayed the same infrared absorption spectra with powder PAN at 2242 cm\(^{-1}\), 2942 cm\(^{-1}\), and 1451 cm\(^{-1}\), which can be attributed to the stretching vibration of the nitrile group (-C≡N-), tensile vibration, and bending vibration of the methylene group (-CH\(_2\)-), respectively (Figure 3(a)). In the FTIR spectra of PVP, the characteristic peaks at 1660 cm\(^{-1}\), 1290 cm\(^{-1}\), and 1425 cm\(^{-1}\) correspond to the C = O and C-N stretching vibration and -CH\(_2\) bending vibration, respectively. The peaks around 3371 cm\(^{-1}\) and 2954 cm\(^{-1}\) show the O-H stretching vibration and asymmetric stretching
vibration of C-H. The FTIR spectrum of TiO$_2$ shows a sharp decrease intensity after 1000 cm$^{-1}$, revealing the existence of O-Ti-O bond.

Compared with the untreated samples in Figure 3(b), the stretching vibration of the C = O bond of PVP at 1660 cm$^{-1}$ of the treated samples was significantly decreased, indicating that PVP in the samples was successfully removed to produce porosity. Meanwhile, samples EF 4–1, EF 2–1, and EF 1–1 contained different proportions of PVP (Figure 3(c)) with PVP higher than treated samples in Figure 3(b). An explanation could be that there was a film-forming effect of PVP when the sample was soaked in water for a long time [30].

Figure 4(a) shows the XRD patterns of pure PAN and TiO$_2$ modified membranes with different weight ratios of polymer substrate. Two small peaks were found in the pure PAN sample at 16.8° and 27.8°, corresponding to (100) plane and (110) plane of PAN hexagonal structure. However, the shape of peaks indicates that the PAN has mainly an amorphous structure with a small amount of crystal feature.

The fibers loaded with TiO$_2$ can be identified by the XRD patterns. The peaks at 25.3°, 37.1°, 37.8°, 48.1°, 53.9°, 55.1°, 62.1°, and 68.8° are indexed as (101), (103), (004),
and crystal planes of anatase, respectively, while the unique diffraction peaks at 27.4°, 41.2° are from the rutile phase (110) and (111) crystal planes. These results revealed that TiO\textsubscript{2} modified membranes were successfully prepared via electrospinning with the same TiO\textsubscript{2} phases in different polymer matrices.

The concentration of TiO\textsubscript{2} incorporated in the polymer matrix was measured by using thermogravimetric analysis (TGA) with a heating rate of 10 K/min under an oxygen atmosphere (75% O\textsubscript{2}). Figure 4(b, c) shows the TGA/DSC curves of samples M 10-0-7, M 10–2.5–7, M 10-5-7, and M 10–10-7, indicating that the reaction proceeded at 300 °C with an exothermic reaction of polymer oxidation. And they all had a similar weight loss of about 55%, and the weight of remaining determines the TiO\textsubscript{2} loading around 45%, while the pure PAN fiber membrane (M 10-0-0) was oxidized entirely and decomposed. These results prove that there is negligible TiO\textsubscript{2} nanoparticle loss during the fabrication and treatment processes.

### Adsorption of organic dyes by PAN-TiO\textsubscript{2} composite microfiber membranes

The adsorption kinetics of MB onto EF, EF4-1, EF2-1, and EF1-1 was examined (Figure 5). The adsorption occurred instantaneously; the adsorption capacity increased rapidly in the first 30 min and then reached equilibrium in approximately 180 min. EF2-1 exhibited the highest adsorption capacity and the removal of MB achieved 98.9% (Table 3). Compared with EF2-1, the adsorption capacity reduced to 90.5% for EF1-1 and 85.7% for EF4-1, consistent with the BET specific surface area.

Among the four kinetics models used, the nonlinear form of the pseudo-first-order and the pseudo-second-order kinetics demonstrate the correlation coefficients (R\textsuperscript{2}) around 0.99, indicating better simulation of these models than Elovich and intra-particle diffusion model (Figure 6, Table 3). It is possible that the adsorption rate depends on the available sites in the adsorbent for both the physisorption and chemisorption processes. The calculated kinetics constants indicate that EF sample had the highest adsorption rate, while it was accompanied by the lowest equilibrium adsorption capacity.
The Elovich model is based on the chemisorption nature of adsorption, which assumes that the actual solid surface is energetically heterogeneous, and neither interaction nor desorption among adsorbed substances influences adsorption at the low surface occupation of species. This model fits the adsorption data fairly well with the correlation coefficients ranging from 0.948 to 0.982 for four samples.

The intra-particle diffusion model usually fits best the adsorption process involving a rate-limiting step caused by external diffusion (the movement of solutes from solution to the adsorbent), internal diffusion (the direction of solutes from the surface to the pores inside the adsorbent), or surface adsorption (rapid adsorption between the solute and the active sites). The data fitted poorly to this model with low $R^2$ values. It is speculated that the internal diffusion is not the rate-limiting step. There may exist multiple steps that control the adsorption process.

The effect of organic dye charge on the adsorption efficiency of PAN-TiO$_2$ composite microfiber membranes was investigated using negatively charged MB and positively charged MO (Figure 7(a)). As illustrated in Figure 7(b), the MO concentration did not change with time after the adsorption test, while the MB concentration significantly decreased at the end of the adsorption experiments (Figure 5). To further verify the selective adsorption of MB, membrane EF2-1 was soaked in a mixed MB and MO solution. The UV-Vis absorption spectroscopy indicated that the MB characteristic peak at 664 nm was significantly reduced after adsorption equilibrium, while the peak of MO at 464 nm was retained (Figure 7(c)). These results reveal that the dye sorption is highly charge-dependent. The adsorption of positively charged dyes is likely due to the electrostatic attraction of the membrane surface.

**Figure 5.** Adsorption of MB by four electrospun nanomembranes.
Table 3. Adsorption kinetics fitting parameters of four electrospun membrane to MB (T = 25°C).

| Samples | Removal rate | The pseudo-first-order kinetic | The pseudo-second-order kinetic | Adsorption Capacity | Elovich model | Intra-particle diffusion model |
|---------|--------------|---------------------------------|---------------------------------|--------------------|---------------|---------------------------------|
|         |              | \( q_t = q_e \left( 1 - \frac{1}{e^{kt}} \right) \) | \( q_t = \frac{k_1 q_e t}{1 + k_1 q_e t} \) | \( q_e = \frac{C_r - C_t}{m} t \) | \( q_e = a + b \log t \) | \( q_t = k_{int} t^{1/2} \) |
|         |              | \( k_1 \times 10^{-2} \) (mg·g⁻¹) \( q_e \) (cal) \( R^2 \) | \( k_2 \times 10^{-2} \) (g·mg⁻¹·min⁻¹) \( q_e \) (cal) \( R^2 \) | \( q_e \) (exp) | \( a \) (mg·g⁻¹) | \( b \) (mg·g⁻¹) | \( R^2 \) | \( k_{int} \) (mg·g⁻¹·min⁻¹) | \( R^2 \) |
| EF      | 84.9         | 7.55                            | 4.11                            | 0.993              | 3.46          | 4.33                            | 0.998            | 4.25      | 2.34 | 0.80 | 0.982 | 0.293 | −8.267          |
| EF 4–1  | 85.7         | 3.11                            | 4.17                            | 0.998              | 0.92          | 4.66                            | 0.989            | 4.29      | −0.076 | 1.83 | 0.950 | 0.287 | 0.375          |
| EF 2–1  | 98.9         | 5.22                            | 4.92                            | 0.999              | 1.71          | 5.27                            | 0.990            | 4.95      | 1.83 | 1.36 | 0.948 | 0.346 | −2.377          |
| EF 1–1  | 90.5         | 4.96                            | 4.42                            | 0.995              | 1.72          | 4.77                            | 0.995            | 4.53      | 1.42 | 1.32 | 0.960 | 0.312 | −1.635          |
Figure 6. Adsorption kinetics of four electrospun nanomembranes to MB.

Figure 7. (a) The chemical structure of MB and MO, (b) Adsorption of MO by EF 2–1 membrane, and (c) UV-Vis spectra of MB/MO mixed solution before and after adsorption.
Photocatalytic performance of PAN-TiO$_2$ composite microfiber membranes

The overall removal efficiencies of MB using M10-2.5-7, M10-5-7, and M10-10-7 under visible light by coupling adsorption and photocatalysis were determined. These results agree with the pseudo-first-order kinetics. As shown in Figure 8(a, b), the degradation process of MB can be divided into two stages in line with the pseudo-first-order kinetics, and the three samples showed similar degradation behavior. In the first stage (0–30 min), the kinetics of MB removal was much higher than the second stage (90–120 min). Sample M 10-5-7 had the best performance of decreasing the MB to more than 90% after 30 min of irradiation.

This result implies a synergistic action of the polymer matrix and TiO$_2$ nanoparticles during the degradation of MB. The effect can be ascribed to the combination of adsorption and photocatalytic processes that can increase the molecular surface contact of MB with TiO$_2$ nanoparticles and therefore facilitating a more efficient mass transfer of MB from the solution to the surface of photocatalysts. This factor can reduce the concentration difference of targeted pollutants between the active sites and bulk liquid, reducing the effect of the mass transfer step on the overall rate of photocatalytic reaction. The multiple kinetics also provide understanding on synergy of adsorption and photocatalysis. Adsorption is not the key function to removal MB in our designed adsorbent-photocatalyst system. Its main role is to accelerate the speed of pollutants moving from solution liquid to catalyst surface. If the adsorption capacity of the adsorbent is too strong, the pollutants tend to combine with it rather than migrate to the photocatalyst surface, which would have a negative effect on photocatalytic activity.

Table 4 summarizes the rate constant $K$ and energy consumption for various materials at different reaction stages. It was observed that sample M 10-5-7 had a faster reaction rate and lower energy consumption. Table 5 compares the removal efficiency of MB in the literature. Note that our specimen (M 10-5-7) exhibited the highest TiO$_2$ loading and
excellent removal rate. The compositions of M 10−2.5-7, M 10-5-7, and M 10−10-7 showed a negligible difference between before and after the photocatalytic oxidation in the FTIR analysis (Figure 8(c)), implying excellent stability of the PAN-TiO$_2$ microfiber membrane under simulated sunlight. Possibly, the polymer matrix can prevent the damage caused by strong oxidant species generated by photocatalyst, possessing good reusability of the membrane.

### Conclusions

We have developed a novel technique to immobilize TiO$_2$ nanoparticles on the surface of polymer microfiber membrane through the electrospinning technique. The effects of polymer composition and post-synthesis treatment on the resulted composite membranes were examined. Both the PVP content and the post-synthesis treatment process for removing PVP play essential roles in forming the porous structures and exposing TiO$_2$. Unlike the conventional TiO$_2$ nanoparticles, immobilized TiO$_2$ nanoparticles were uniformly dispersed on the porous polymer matrix and did not need an additional separation process. This PAN-TiO$_2$ composite microfiber membrane system combined the functions of selective adsorption and photocatalysis, possessing a superior property for contaminant removal. The kinetics results provide a further understanding on the coupling adsorption and photocatalysis process. The functionalities of the membrane are closely related to the physicochemical properties, including porosity, electrostatic attraction, and a synergistic effect of the polymer matrix and TiO$_2$ nanoparticles. The successful preparation of these polymer-based TiO$_2$ microfiber membranes provides a new direction for designing and developing a promising adsorbent-photocatalyst for environmental applications.

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Table 5. The report of photocatalytic contaminants removal rate by immobilized TiO$_2$ on different substrates.

| No. | Catalyst | Target compound | Substrate | Light source | TiO$_2$ content (wt %) | Loading | Initial target concentration (ppm) | Removal rate (min$^{-1}$) $\times 10^{-2}$ | Synthesis method | Ref |
|-----|----------|-----------------|-----------|--------------|-----------------------|---------|------------------------------------|---------------------------------------------|------------------|-----|
| 1   | TiO$_2$  | MB              | PAN       | Simulated solar irradiation | 45 % | 50 mg/50 ml | 5.0 | 7.8 | Electrospinning | This study |
| 2   | TiO$_2$  | MB              | PVDF      | UVA          | 26 % | 20 cm$^2$/50 mL | 3.2 | 5.0 | Electrospinning | [31] |
| 3   | TiO$_2$  | MG              | PAN       | UVC          | 25 % | 1.2 mg/3 ml | 3.2 | 1.1 | Electrospinning | [32] |
| 4   | TiO$_2$  | MB              | PAN       | Simulated solar irradiation | - | 3 cm$^2$/3 ml | 10.0 | 1.3 | Electrospinning | [33] |
| 5   | TiO$_2$  | MB              | PMMA      | UVC          | - | 9 cm$^2$/50 mL | 10.0 | 0.13 | Electrospinning | [34] |
| 6   | TiO$_2$  | MB              | Carbonized PANI | Simulated solar irradiation | - | 50 mg/50 ml | 3.2 | 3.5 | Polymerization and heating | [35] |
| 7   | TiO$_2$  | MB              | PVDF/PMMA | UV           | - | 16 cm$^2$/400 mL | 3.2 | 1.2 | Phase-inversion | [36] |
Disclosure statement

No potential conflict of interest was reported by the authors.

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