

Article

Photocatalytic Degradation of Sulfamethoxazole and Enrofloxacin in Water Using Electrospun Composite Photocatalytic Membrane

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Abstract: Photocatalysis has emerged as a promising technology for the removal of emerging contaminants such as antibiotics from water. Fixing photocatalytic materials on polymers to prepare applicable membranes is a feasible method for applying photocatalysis. This study explored the preparation of composite PAN-TiO₂ and PAN-TiO₂-rGO (PAN-rGTi) photocatalytic membranes by combining TiO₂, TiO₂-reduced graphene oxide (rGO) and polyacrylonitrile (PAN) using electrospinning. Characterization through SEM and EDS analysis confirms the composite membrane's microstructure and elemental composition. The electrospun PAN-TiO₂ and PAN-rGTi composite membranes exhibit a stable and efficient photocatalytic performance in degrading sulfamethoxazole (SMX) and enrofloxacin (ENR), two typical antibiotics commonly found in water bodies. Photocatalytic degradation experiments under simulated solar light reveal the superior performance of the composite photocatalytic membranes compared to PAN alone, with a notable increase in the reaction rate constants of PAN-TiO₂ (1.8 to 2.2 times for SMX and 3.2 to 4.0 times for ENR) and even higher enhancements for PAN-rGTi (2.8 to 3.0 times for SMX and 5.4 to 6.5 times for ENR) compared to PAN alone. Despite minor decreases (from 97.6% to 90.4%) in activity over five cycles, the photocatalytic composite membranes remain effective, showcasing their stability and recyclability. This study highlights the potential application of PAN-TiO₂ and PAN-rGTi composite membranes as sustainable and effective materials for removing emerging contaminants from water. Further exploration should focus on optimizing materials for specific emerging contaminants and improving their application feasibility for wastewater and water treatment and water purification in water bodies.

Keywords: photocatalytic degradation; sulfamethoxazole; enrofloxacin; polyacrylonitrile; composite membrane



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1. Introduction

In recent years, emerging contaminants, mainly including antibiotics, endocrine-disrupting chemicals (EDCs) and microplastics, have attracted increasing attention and concern due to the high detection frequency in aquatic environments [1–4] and the associated risks to ecosystems and public health. To mitigate the risks from emerging contaminants, various technologies, including adsorption [5], advanced oxidation [6,7], and biological treatment [8], have been studied and developed in recent years. Among these technologies, photocatalytic oxidation has shown high efficiency and promising potential in removing various emerging contaminants, thanks to its advantages of high removal efficiency, a simple process, easy operation, and no secondary pollution [9,10]. Marvelous studies on photocatalytic materials, especially semiconductor materials, have been conducted and reported. Common photocatalytic materials, such as TiO₂, ZnO, SiO₂, SnO₂,

WO₃, Fe₂O₃, InO₃, ZnS, CdS, etc. [11,12], exhibit excellent photocatalytic performance in removing emerging contaminants from water. Moreover, by harnessing the exceptional photocatalytic properties of materials like TiO₂ and ZnO and combining them with carbon materials such as graphene oxide (GO) [13], carbon nanotubes [14], C₃N₄ [15], mesoporous carbon materials [16], etc., the specific surface area and conductivity of carbon materials are fully exploited, enhancing the photocatalytic activity and application potential of the materials. Existing research has demonstrated the significant advantages of these composite materials in removing emerging contaminants in water. However, current photocatalytic materials are usually studied and applied in the form of powder or particles. Powdered or particulate materials disperse readily in water, allowing for enhanced interaction with contaminants in water, thereby demonstrating excellent photocatalytic performance [17,18]. Nevertheless, powdered or granular photocatalytic materials face challenges in applications, such as being easy to agglomerate in the preparation process and difficult to recycle from water [9,19,20], limiting their usability and engineering application.

To address the limitations of conventional photocatalytic materials, researchers have explored innovative approaches for immobilizing photocatalytic materials [21–23], enhancing their stability and reusability. One promising strategy involves the development of photocatalytic nanocomposites, where photocatalytic materials are incorporated into a stable matrix or support material. Polymer-based carriers offer a viable solution for stabilizing photocatalytic materials and facilitating their separation from treated water [24–26]. In numerous studies, the removal efficiency of pollutants in dyes such as methyl orange and rhodamine B through photocatalytic degradation has been reported to reach 70–100% [25,27]. Polymers like polyethylene (PE), polytetrafluoroethylene (PTFE), polypropylene (PP), polyacrylonitrile (PAN), polyaniline (PANI), polyethersulfone (PES) and polydimethylsiloxane (PDMS) have also drawn attention as common polymer matrices for photocatalysts [28–30]. Among various methods for immobilizing photocatalysts in polymers, electrospinning, recognized for its effectiveness and versatility, has gained substantial attention in wastewater treatment. This is due to its capability to produce nanofibers with high surface area and porosity, as well as its convenience for separation, recovery, and reuse operations [31,32]. Recent studies have demonstrated successful applications of electrospun nanofibers as carriers for photocatalysts [31,33].

Despite the progress made in using polymer-based carriers for fixed-bed photocatalytic systems, there are still some challenges that need to be addressed. Existing studies predominantly focused on a limited range of pollutants or polymer materials, necessitating further exploration of more composite materials and their applicability to a broader spectrum of contaminants. While many studies confirm the efficacy of these photocatalytic composite membranes in degrading pollutants like dyes [34,35], further investigation into emerging contaminants, such as antibiotics, remains inadequate. Additionally, careful consideration is required in the selection and design of suitable polymer materials and photocatalysts as specific contaminants require careful consideration to achieve optimal removal efficiency. Furthermore, the stability and reusability of polymer-based carriers and immobilized photocatalysts warrant further investigation.

Consequently, this study aims to develop PAN-TiO₂ and PAN-TiO₂-rGO (PAN-rGTi) composite photocatalytic membranes by combining TiO₂, TiO₂-reduced graphene oxide (rGO) and polyacrylonitrile (PAN) using electrospinning. The objective is to evaluate their performance in degrading sulfamethoxazole (SMX) and enrofloxacin (ENR) in water. The key innovations of this research include: (1) the use of electrospinning to immobilize TiO₂ nanoparticles and TiO₂-rGO on PAN nanofibers, creating a stable and efficient photocatalytic membrane; (2) investigating the recyclability and stability of the composite membrane over multiple cycles of SMX and ENR degradation, effectively addressing emerging contaminants in wastewater treatment and water reclamation in wastewater treatment plants and water purification in rivers and lakes.

2. Methods and Materials

2.1. Materials and Regents

SMX (analytic standard) and ENR (analytic standard) were purchased from Sigma-Aldrich. Acetonitrile, methanol, and ethyl acetate of at least HPLC grade were obtained from Sigma-Aldrich (St. Louis, MO, USA). PAN (Mw = 150,000) was acquired from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). *N,N*-dimethylformamide (DMF, analytical reagent, 99.5%) and ethanol absolute were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Moreover, 3-Methacryloxypropyltrimethoxysilane (MEMO, analytic reagent) was procured from Tianjin BaiMa Technology Co., Ltd. (Tianjin, China). Graphene oxide (GO) powder (lateral size of 0.5–5 μm and thickness of 1–3 nm) was synthesized using the Hummers method and provided by Nanjing XFNANO Materials Tech Co., Ltd. (Nanjing, China). The Chemical Abstracts Service (CAS) numbers of the major chemicals are listed in Table S1. Ultrapure water (resistivity $18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$ at 25°C) was produced by a Merck Millipore water purification system (Darmstadt, Germany) and was used in related experiments.

2.2. Preparation of PAN Membrane and Composite Membrane

The PAN membrane and composite membrane were prepared using an electrospinning machine (TL-Pro-BM, Tongli Tech, Shenzhen, China), similar to in our previous study [36]. A 6% PAN solution was prepared by dissolving 1.8 g PAN in 30 mL DMF and stirred by magnetic stirring overnight before electrospinning. Additionally, 0.5 g P25 TiO_2 was weighed and added into a beaker containing 40 mL methanol and 10 mL ethanol, with the addition of 0.1 mL of MEMO reagent. The mixture was stirred by magnetic stirring overnight.

Two injection pumps were installed on the same side of the drum collector, and the injection tube was fixed on the same mobile platform. The PAN solution and TiO_2 dispersion were loaded into two 10 mL syringes, respectively. The speed of the mobile platform was maintained at 50 mm/s, with the scanning starting point at 30 mm and the scanning endpoint at 300 mm. Both the PAN solution and TiO_2 dispersion were fed at a constant rate through a 20# stainless steel needle (inner diameter 0.99 mm). The voltage set on the needle was 13 kV, the voltage set on the drum was -2 kV , and the distance from the tip of the needle to the collector was 15 cm. The drum speed was set to 500 rpm/min and the collection time was 10 h. During this process, the electrospun PAN nanofibers and the electro-sprayed TiO_2 nanoparticles were simultaneously collected on the drum collector to form a composite membrane of nanoparticles and fibers. Finally, the composite membrane was dried in a vacuum oven at 50°C for 12 h to remove the residual solvent and then placed in a dry box for use.

The preparation of TiO_2 -rGO (rGTi) material has been reported by some related studies [37–39]. Similarly, it was prepared by a hydrothermal method in this study. Initially, a certain amount of GO powder was dispersed in a 90 mL ultrapure water/ethanol solution (volume ratio of 2:1). The dispersion underwent ultrasonic treatment for 3 h in an ultrasonic bath to obtain a well-dispersed GO solution. Subsequently, 800 mg of P25 TiO_2 powder was added to the 90 mL GO dispersion, and the mixture was stirred at 500 rpm for 30 min. The resulting mixture was then transferred to a 150 mL Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment at 180°C for 6 h, followed by cooling to room temperature. The reaction mixture was centrifuged at 3900 rpm for 15 min to obtain a centrifugal precipitate. The precipitate was washed several times with anhydrous ethanol and ultrapure water, and finally, it was dried in a vacuum oven at 60°C for 8 h. In the synthesis of materials, the mass ratios of GO to P25 were set at 1% and 2%, denoted as rGTi-1 and rGTi-2, respectively. During the electrospinning stage, the main processes and parameters are essentially the same as those in the preparation method of the PAN- TiO_2 composite membrane.

2.3. Characteristics of PAN Membrane and Composite Membrane

A scanning electron microscope (SEM, ZEISS Gemini 300, Carl Zeiss, Jena, Germany) was used to analyze the surface microstructure and morphology, and the element mapping was carried out by an energy-dispersive X-ray spectrometer (EDS, Oxford Xplore, Oxford Instruments, Abingdon, UK) equipped with an SEM.

2.4. Photocatalytic Degradation of SMX and ENR Using Photocatalytic Membrane

The prepared PAN membrane and composite membrane were employed in the photocatalytic degradation of two common antibiotics in water. This study investigates the efficacy of PAN-TiO₂ and PAN-rGTi composite membranes in the photocatalytic degradation of typical antibiotics. Photodegradation experiments of SMX and ENR were conducted under simulated solar light provided by a photochemical reactor (Phchem III, NBeT, Beijing NBET Technology Co., Ltd., Beijing, China) equipped with a 500 W Xenon lamp, as stated in a previous study [40]. In the experiment, approximately 1.8 cm × 10 cm membranes were cut and placed in a quartz test tube. To support the morphology of the membrane in water, the metal mesh of the membrane collected during the spinning process was placed together with the membrane, ensuring a stable state in the test tube. The control group with just the PAN membrane was set to explore the difference in the photocatalytic degradation effect of the composite membrane loaded with TiO₂ and rGTi. At the same time, due to the introduction of metal mesh as a support structure, a blank control group with only metal mesh was set up in the experiment to eliminate the possible interference of metal mesh on the reaction. The experimental process included the dark adsorption stage (30 min) and photocatalytic reaction stage (60–180 min). In this group of experiments, the device used is the light reactor mentioned above. The light source used to simulate the solar light source was a 500 W xenon lamp light source, and the current was set to 8 A. The initial concentration of SMX or ENR was set as 5 mg/L, the samples were taken at certain time points during the reaction process, and the concentrations of SMX or ENR antibiotics were analyzed using high-performance liquid chromatography (HPLC) (Agilent HPLC 1200, Agilent Technologies, Santa Clara, CA, USA) using a variable wavelength detector (VWD) and a Shim-pack VP-ODS column (250 mm × 4.6 mm), with the analytic method similar to the previous study [40].

3. Results and Discussion

3.1. The Characteristics of PAN and Composite Membrane

The SEM images in Figure 1 depict the morphologies of the PAN, PAN-TiO₂ and PAN-rGTi membranes. The PAN membrane, fabricated through electrospinning without a photocatalyst, showcases a typical PAN nanofiber structure. Upon the introduction of the TiO₂ material, visible changes occur, with some TiO₂ nanoparticles sprayed onto the surface of PAN nanofibers. This process results in the creation of surface roughness and a defect structure, as shown in Figure 1e. It is noteworthy that not all TiO₂ nanoparticles were uniformly integrated with the PAN surface; some remained either loosely associated or were not loaded into the material. The resulting rough and defective structure of TiO₂ particles on the PAN nanofiber surface, along with the formation of a nanofiber structure composed of TiO₂ and PAN, plays a crucial role in enhancing the photocatalytic activity sites of the PAN membrane. This, in turn, allows the composite membrane to exhibit notable photocatalytic performance.

The element analysis of the PAN membrane and PAN-TiO₂ composite membrane was carried out by energy-dispersive spectrometer surface-scanning analysis mapping, and the corresponding elements were observed. As shown in Figure 2, the elemental surface sweeping results of the PAN-TiO₂ composite membrane offered the distribution of C, Ti, O, and N elements and the corresponding element weight ratios. The weight ratio of elements C, N, Ti, and O differs more from the theoretical value for PAN and less for TiO₂; thus, the accuracy of weight percentages may be lower for low-mass elements. The characterization of this elemental ratio primarily aims to confirm the combination of the two materials.

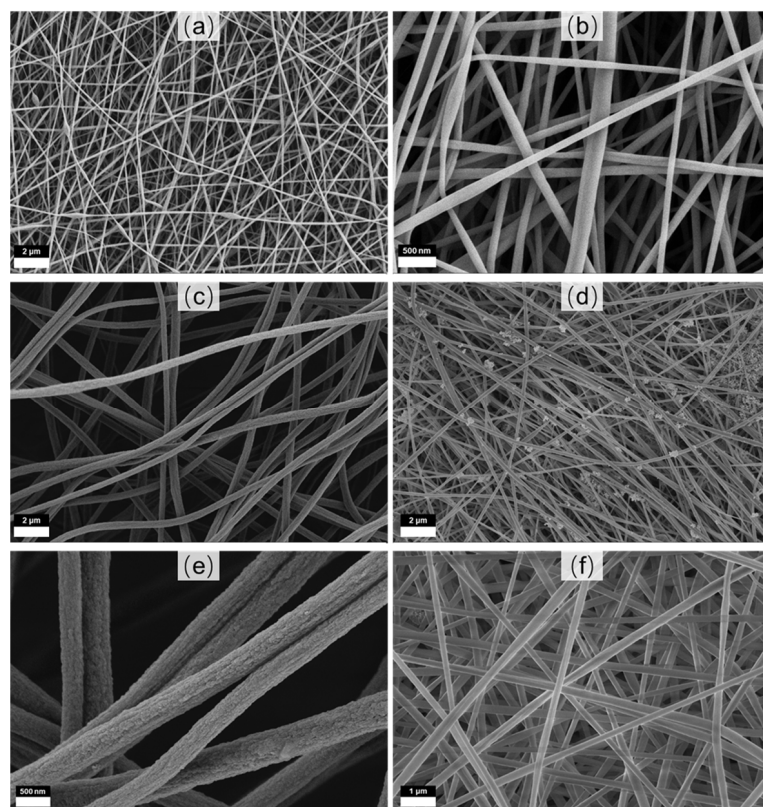


Figure 1. SEM images of PAN membrane under (a) 2 μm and (b) 500 nm scale, PAN-TiO₂ composite membrane under (c) 2 μm , (d) 2 μm and (e) 500 nm scale and PAN-rGTi composite membrane under (f) 1 μm scale.

3.2. Photocatalytic Degradation of SMX and ENR

The concentration variations of SMX and ENR during the reaction and corresponding kinetic fittings for the photocatalytic reaction stage are shown in Figures S1 and 3. A previous study [40] established that the degradation reactions of both SMX and ENR adhere to pseudo-first-order kinetics, a pattern consistent with the photocatalytic degradation stage in this study. Following the dark adsorption stage, the metal mesh has a small amount of adsorption (7.4%) for SMX in the reaction system, and the adsorption of SMX on the PAN membrane was more obvious (18.7%), which may account for a larger adsorption area. The PAN composite membrane loaded with TiO₂ had the largest adsorption capacity for SMX, with the PAN-TiO₂-2 composite membrane adsorbing 34.2% of SMX and the PAN-TiO₂-4 composite membrane adsorbing 37.3% of SMX. This indicated that the PAN membrane composed of a large number of fibers could adsorb and retain a certain number of pollutants in its structure, and after TiO₂ particles were loaded on the PAN fiber, the structural pores were smaller, which helped to increase the capacity of adsorption and retention of pollutants. Similar trends are observed in the dark adsorption and photocatalytic degradation phases of ENR. While the PAN membrane adsorbs more ENR than the group with just a metal mesh, both groups exhibit a comparable final total removal ratio for ENR by the end of the photochemical reaction phase. In the PAN-TiO₂-2 and PAN-TiO₂-4 systems, a noticeable photocatalytic degradation effect is evident compared to the PAN membrane and the metal mesh groups. The reaction rate constants during the photochemical reaction phase are increased by 3.2 to 4.0 times.

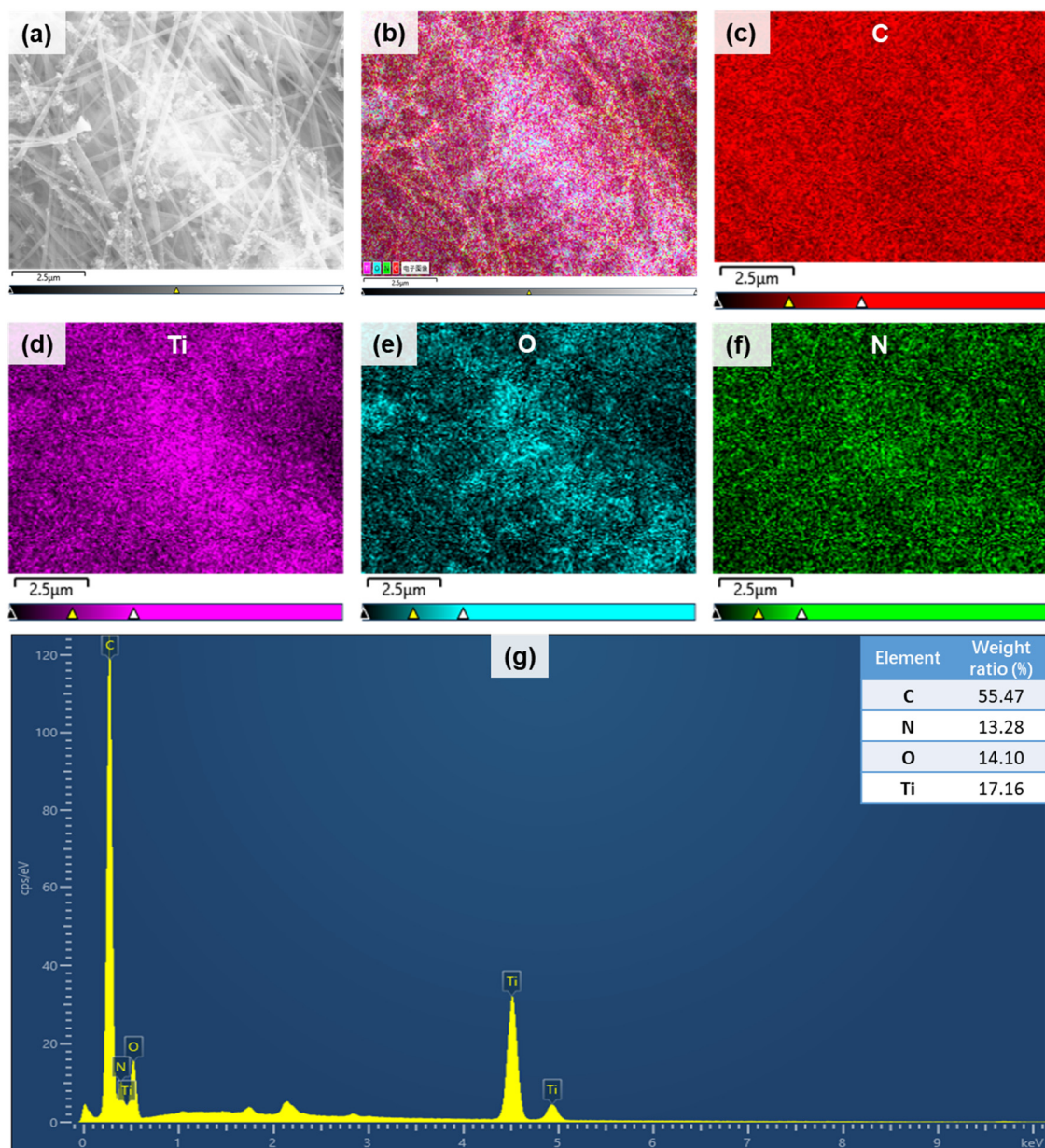


Figure 2. (a) SEM micrograph, (b) energy-dispersive X-ray spectroscopy (EDS) layered image, corresponding EDS elemental mapping for (c) C, (d) Ti, (e) O, (f) N, and (g) EDS pattern of of PAN-TiO₂ composite membrane.

In the photocatalytic reaction, although the PAN membrane adsorbs more SMX than the group with metal mesh alone, the total removal efficiencies of SMX in both groups were close, indicating that the PAN membrane had no significant catalytic effect on the photodegradation of SMX. Moreover, the photodegradation rate of SMX in the PAN membrane group was even slightly lower than that in the metal mesh group during the photocatalytic reaction stage. This may be attributed to the PAN membrane affecting the light transmission in the reaction system, thereby reducing the photodegradation rate of SMX and resulting in a lower total removal rate.

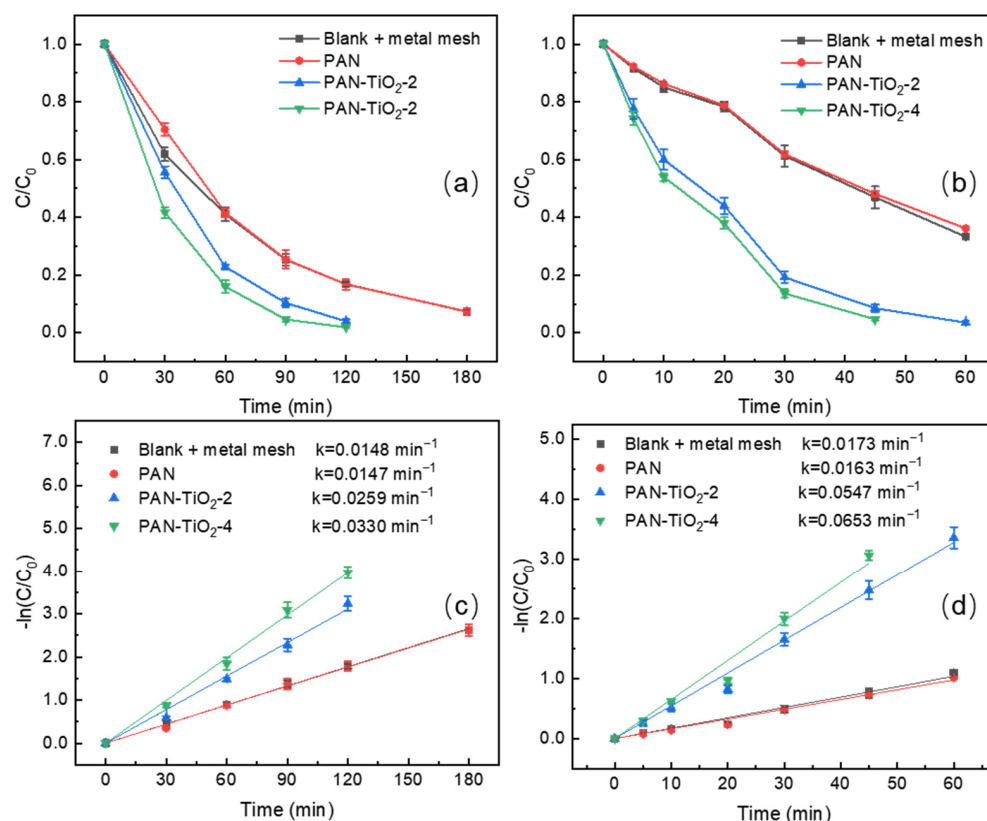


Figure 3. The concentrations of (a) SMX and (b) ENR in the photocatalytic degradation stage with PAN-TiO₂ composite membrane and the corresponding kinetic curves of (c) SMX and (d) ENR with the initial concentration of 5 mg/L and uncontrolled pH at room temperature (20 °C).

The PAN-TiO₂ composite membrane, with the addition of TiO₂, played a catalytic degradation role in the photoreaction process. The reaction constants of PAN-TiO₂-2 and PAN-TiO₂-4 relative to the PAN membrane and the blank group increased by 1.8–2.2 times. Su et al. [41] prepared TiO₂/PAN composite nanofiber membranes by electrospinning, demonstrating commendable air filtration performance and photocatalytic capabilities. Notably, as the mass ratio of TiO₂ to PAN increased, the efficiency of photocatalytic toluene removal exhibited a corresponding rise. The optimal performance was achieved at a TiO₂/PAN mass ratio of 4:1, yielding a toluene conversion rate of 97.9%. While the specific pollutants targeted differed, Su et al.'s findings showcased robust photocatalytic performance in the composite membrane, aligning with our study. Similarly, in the investigation conducted by Xu et al. [42] on PAN/TiO₂/PANI, it was observed that augmenting the TiO₂ ratio in the composite membrane led to an enhancement in photocatalytic performance.

A parallel investigation was conducted to assess the photocatalytic application of the PAN-rGTi composite membrane. A reaction tube with only a metal mesh served as the blank control group, while a tube with only a PAN membrane served as the control group. Tubes containing PAN-rGTi-1 and PAN-rGTi-2 were placed into separate test tubes, undergoing a dark adsorption stage followed by a photoreaction stage under xenon lamp illumination. The concentration changes and reaction constants for the photoreaction process of SMX and ENR are illustrated in Figure 4a–d. Following the dark adsorption stage, the PAN membrane adsorbed more pollutants compared to the metal mesh alone. However, during the photoreaction stage, the photocatalytic degradation rate of pollutants in tubes containing the PAN membrane was slightly lower than that of the group with only the metal mesh. In contrast, the PAN-rGTi composite membrane demonstrated excellent performance in both adsorption and photocatalytic properties. Analyzing the removal efficiency of SMX during the dark adsorption and photoreaction stages, as well as the reaction constants during the photoreaction stage for the PAN membrane, PAN-TiO₂ membrane, and PAN-

rGTi composite membrane (Table 1), reveals that the adsorption performance of the PAN-TiO₂ composite membrane is improved compared to the PAN membrane, reaching 2.2 to 2.5 times. The adsorption capacity of PAN-rGTi is further enhanced, increasing to around three times. Comparing the experimental group with the PAN-TiO₂ composite membrane to the blank group and the photodegradation reaction rate constant of SMX and ENR in the PAN membrane, the PAN-TiO₂ composite membrane exhibited an increase of 1.8 to 2.2 times and 3.2 to 4.0 times during the photoreaction stage, respectively. The photocatalytic activity of the PAN-rGTi composite membrane was even higher, showing an enhancement of 2.8 to 3.0 times and 5.4 to 6.5 times. These results highlight the excellent photocatalytic performance of the photocatalytic composite membrane.

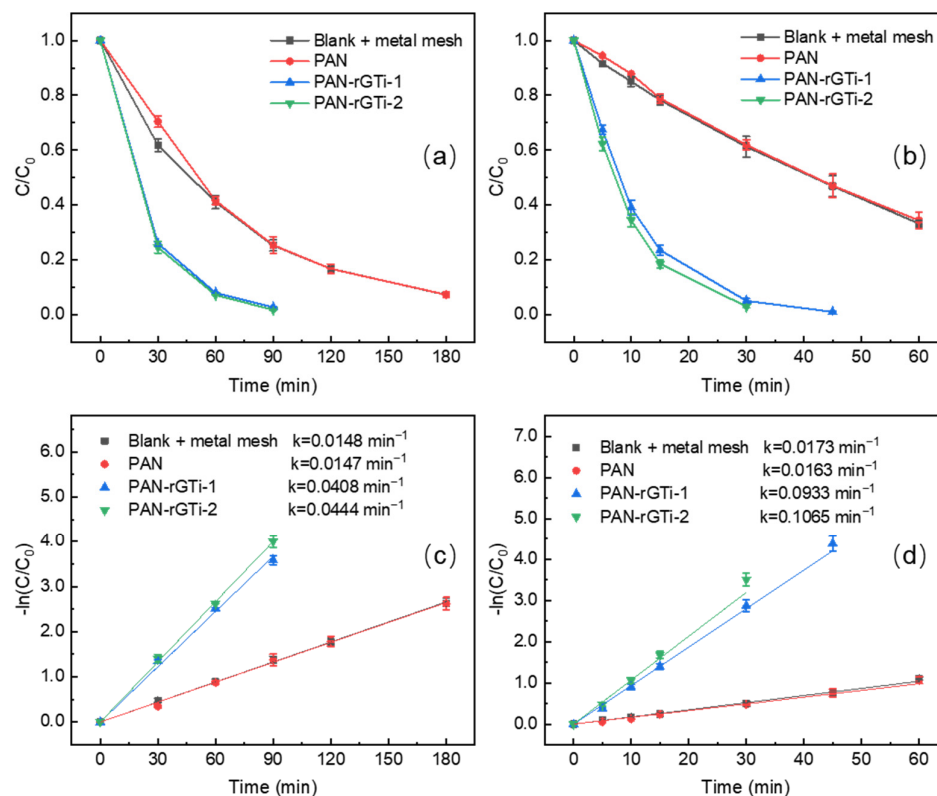


Figure 4. Adsorption and photocatalytic degradation of (a) SMX and (b) ENR with PAN-rGTi composite membrane and kinetic curves of (c) SMX and (d) ENR with the initial concentration of 5 mg/L and uncontrolled pH at room temperature (20 °C).

Table 1. The removal of SMX by PAN-TiO₂ and PAN-rGTi composite membrane in different reaction stage with the initial concentration of 5 mg/L and uncontrolled pH at room temperature (20 °C).

	Blank + Metal Mesh	PAN Membrane	PAN-TiO ₂ -2	PAN-TiO ₂ -4	PAN-rGTi-1	PAN-rGTi-2
Removal efficiency in adsorption stage	2.86%	16.82%	37.72%	42.61%	47.96%	50.85%
Removal efficiency in photocatalytic degradation stage	92.7%	92.6%	~100%	~100%	~100%	~100%
Total removal efficiency	92.9%	93.8%	~100%	~100%	~100%	~100%
Reaction constant in photocatalytic degradation stage (min ⁻¹)	0.148	0.147	0.259	0.330	0.408	0.444

3.3. Recyclability and Application Feasibility of Photocatalytic Composite Membrane

To assess the application potential of the prepared photocatalytic composite membrane, the feasibility of membrane reuse was investigated using ENR as the research target. The PAN-TiO₂ composite membrane underwent repeated application under nearly identical conditions for five cycles to evaluate its photocatalytic removal efficiency of ENR. After each adsorption and photoreaction stage, the membrane underwent thorough washing and ultrapure water soaking before being dried for the subsequent cycle. As shown in Figure 5, after five cycles, the removal efficiency of ENR by the PAN-TiO₂ composite membrane for photocatalytic degradation gradually decreased from 97.6% to 90.4%. Despite this reduction, the PAN-TiO₂ composite membrane maintained high photocatalytic activity. The reaction constant during the photocatalytic reaction process decreased from 0.064 min^{−1} in the first cycle to 0.039 min^{−1} in the fifth cycle, remaining more than twice as high as the experimental group without a photocatalytic composite membrane. This demonstrated the stability of the electrospun PAN-TiO₂ composite membrane, showcasing its ability to be reused multiple times. In the study of Su et al. [41], the removal efficiency of toluene by PAN-TiO₂ composite membrane was only slightly reduced when it was reused five times and still maintained a high removal efficiency. Shi et al. [43] also reused the PAN@TiO₂/Ag composite nanofiber membrane five times under visible light to remove methylene blue and found that the removal efficiency of photocatalytic degradation was slightly reduced from 99.0% to 93.0% after five cycles.

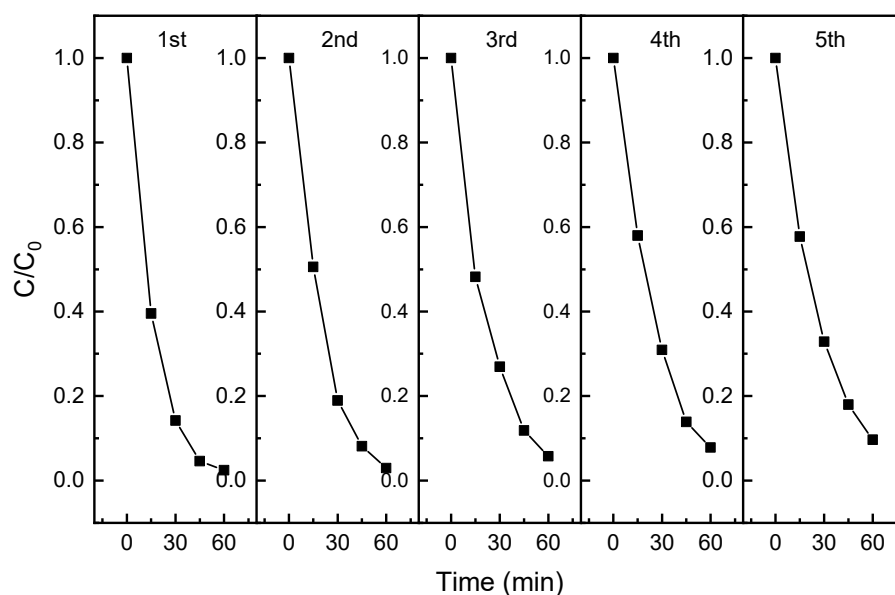


Figure 5. Five circling runs for photocatalytic degradation of ENR with PAN-TiO₂ membrane.

It is important to note that the vertical positioning of the membrane during experiments may lead to slight changes in the light contact area due to water flow disturbances and potential accidental damage. This could result in wrinkles or local defects, leading to a corresponding decrease in catalytic performance during subsequent uses. Similar observations by Sun et al. [44] also indicated that the prepared PAN/TiO₂ composite membrane still kept good stability after 10 cycles of reuse, but it suffered slight damage during deionized water cleaning. Due to the particularity of the preparation process, they also realized that the damaged membrane could be dissolved in DMF again and reshaped, and a new membrane could be prepared again, and the photocatalytic activity was not significantly reduced, which helped to further reduce the cost of photocatalytic materials and avoid the pollution caused by discarding material.

Cleaning and maintenance during the reuse process emerged as a critical factor influencing photocatalytic membrane performance. While pollutants in the aqueous phase were nearly completely removed during the photocatalytic reaction, the residual incomplete

photodegradation of pollutants within the membrane and adsorbed products from the photodegradation stage could affect catalytic performance in subsequent reuse cycles. In comparison to photocatalytic powders, the photocatalytic composite membrane exhibited a slight reduction in catalytic reaction rates due to factors such as the contact area and degree between the catalyst and pollutants. However, it maintained excellent catalytic performance, making it more suitable for practical engineering applications due to advantages like easy recovery, reuse, flexible application forms, and stable performance.

Figure 6 presents the conceptual scenarios for the application of photocatalytic composite membranes in the engineering practice of reclaimed water reuse in rivers, including ultraviolet (UV) disinfection tanks in wastewater treatment plants and actual urban rivers. UV disinfection, as an essential disinfection process before reclaimed water replenishment into rivers, provides a UV light source that can be further utilized. With the deepening of subsequent research, photocatalytic composite membranes are expected to play an effective photocatalytic role in ultraviolet disinfection tanks, further removing emerging contaminants from reclaimed water [45]. In actual urban rivers, photocatalytic membranes can be fixed on the water surface, utilizing sunlight to catalyze reactions. When combined with various ecological restoration technologies such as biological filters and submerged plants in existing water bodies, they can further purify water quality, ensuring the safety of reclaimed water reuse and overall water body quality. Therefore, photocatalytic composite membranes have promising applications, and conducting more in-depth research is essential to advance their practical use.

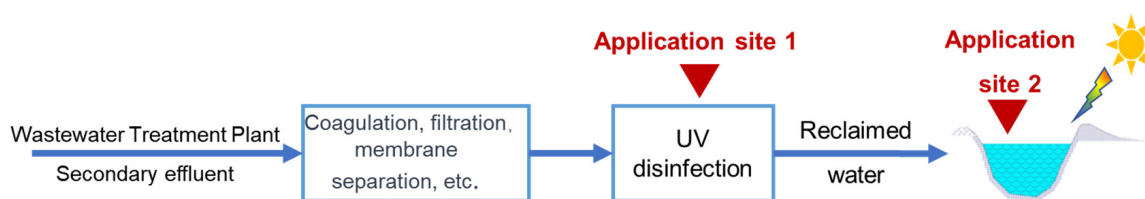


Figure 6. Proposed application sites for photocatalytic membranes.

4. Conclusions

The study investigated the preparation and application of PAN-TiO₂ and PAN-rGTi composite photocatalytic membranes prepared by electrospinning for the degradation of emerging contaminants: SMX and ENR. Electrospinning technology effectively immobilizes TiO₂ nanoparticles and rGTi onto PAN nanofibers, resulting in the preparation of a stable photocatalytic composite membrane. SEM and EDS images reveal the microstructure of the PAN-TiO₂ composite fiber membrane. After the electrostatic spraying of TiO₂, a multilayered TiO₂-coated coating forms on PAN nanofibers, exhibiting a well-defined defective structure. In the photocatalytic degradation of SMX and ENR, the reaction rate constants of PAN-TiO₂ increased by approximately 1.8 to 2.2 times and 3.2 to 4.0 times, respectively, compared to the PAN membrane system. PAN-rGTi demonstrated even better photocatalytic effects, with reaction rate constants increasing to approximately 2.8 to 3.0 times and 5.4 to 6.5 times, respectively, compared to the PAN membrane system. Cyclic experiments indicate that after five repeated uses, the catalytic performance of the photocatalytic composite membrane remains excellent. Taking ENR as an example, the removal efficiency of the PAN-TiO₂ composite membrane gradually decreased from 97.6% to 90.4%, maintaining high photocatalytic activity. The slight decrease in activity is attributed to minimal localized damage and wrinkles during repeated use, indicating that the composite membrane exhibits good catalytic activity and stability.

This research highlights the potential of PAN-TiO₂ and PAN-rGTi composite membranes as effective and sustainable materials for the removal of emerging contaminants from water. Further improvement can be achieved through additional research and an exploration of applications. Future research should focus on optimizing materials for a wider range of emerging contaminants and enhancing their feasibility for wastewater and water treatment in diverse environmental conditions. The developed membranes, with

their stable photocatalytic activity and recyclability, hold promise for practical engineering applications in water purification and treatment. Additionally, this study envisions the application of these membranes in UV disinfection tanks and urban rivers, contributing to the overall improvement of water quality and the safety of reclaimed water reuse. The continued exploration and refinement of these innovative photocatalytic membranes, as well as the stability, reusability, scalability, and cost-effectiveness of this technology, are crucial for advancing their real-world applicability and addressing emerging water quality challenges.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w16020218/s1>, Figure S1: Adsorption and photocatalytic degradation of (a) SMX and (b) ENR with PAN-TiO₂ composite membrane with the initial concentration of 5 mg/L and uncontrolled pH at room temperature (20 °C); Table S1: Chemical Abstracts Service (CAS) Numbers of the major chemicals.

Author Contributions: Conceptualization, X.L.; methodology, X.L., D.S. and J.X.; software, X.L., D.S. and G.Z.; validation, X.L., G.Z. and J.X.; resources, H.F., L.W. and J.X.; data curation, X.L.; writing—original draft preparation, X.L.; writing—review and editing, X.L. and J.X.; visualization, X.L.; supervision, J.X.; project administration, H.F. and J.X.; funding acquisition, H.F., L.W. and J.X. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: All relevant data are included in the paper or its Supplementary Materials.

Conflicts of Interest: Authors X.L., H.F. and L.W. are employed by the company PowerChina Huadong Engineering Corporation Limited, and author G.Z. is employed by the company Shanghai Urban Construction Design & Research Institute (Group) Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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