

TiO₂-PES Fibrous Composite Material for Ammonia Removal Using UV-A Photocatalyst

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Abstract

This study focused on the development and characterization of TiO₂-PES composite fibers with varying TiO₂ loading amounts using a phase inversion process. The resulting composite fibers exhibited a sponge-like structure with embedded TiO₂ nanoparticles within a polymer matrix. Their photocatalytic performance for ammonia removal from aqueous solutions under UV-A light exposure was thoroughly investigated. The findings revealed that PeTi8 composite fibers displayed superior adsorption capacity compared to other samples. Moreover, the study explored the impact of pH, light intensity, and catalyst dosage on the photocatalytic degradation of ammonia. Adsorption equilibrium isotherms closely followed the Langmuir model, with the results indicating a correlation between q_m values of 2.49 mg/g and the porous structure of the adsorbents. The research underscored the efficacy of TiO₂ composite fibers in the photocatalytic removal of aqueous NH₄⁺ under UV-A light. Notably, increasing the distance between the photocatalyst and the light source resulted in decreased hydroxyl radical concentration, influencing photocatalytic efficiency. These findings contribute to our understanding of TiO₂ composite fibers as promising photocatalysts for ammonia removal in water treatment applications.

Keywords

Ammonia Removal, Photocatalyst, TiO₂-PES Composite Fiber, Fibrous Material

1. Introduction

Ammonium-nitrogen (NH₄-N) serves as a nitrogen source conducive to plant growth, and it constitutes an integral component of fertilizers, which invariably

contain nitrogen in the form of either ammonia or its $\text{NH}_4\text{-N}$ derived compounds. Numerous origins contribute to $\text{NH}_4\text{-N}$ pollution, with municipal sewage serving as one notable source [1], industrial wastewater [2], landfill leachate [3] and agriculture discharges as well as agricultural residues [4]. The excessive release of $\text{NH}_4\text{-N}$ into the environment via aquatic drainage gives rise to discernible repercussions on both aquatic ecosystems and human health. Elevated $\text{NH}_4\text{-N}$ concentrations in water foster the proliferation of photosynthetic microorganisms, thus precipitating eutrophication, a phenomenon with potentially severe consequences. This process can engender a reduction in dissolved oxygen levels as a result of $\text{NH}_4\text{-N}$ oxidation in water, thereby diminishing water quality and leading to the development of discolored and malodorous water bodies. These deleterious conditions can ultimately lead to mortality among aquatic flora and fauna. Moreover, the depletion or contamination of water resources due to pollution may exert adverse effects on economic growth and employment opportunities. Consequently, the imperative need for wastewater treatment and reuse has emerged as one of the most critical global water resource concerns.

To address this concern, extensive research endeavors have been undertaken to explore various ammonia removal techniques, encompassing biological processes [5], stripping [6], chemical precipitation [7], as well as the utilization of diverse separation materials such as ion exchange [5], adsorbents [8] [9], and membranes [10]. Each of these methods possesses its inherent advantages and disadvantages. For instance, biological processes necessitate substantial water volumes and stringent requirements pertaining to pH, carbon content, and dissolved oxygen conditions. Air stripping processes exhibit high efficacy in removing $\text{NH}_4\text{-N}$ from wastewater; however, they may lead to the release of gaseous ammonia into the environment, potentially causing secondary pollution concerns [11]. The chemical precipitation method for $\text{NH}_4\text{-N}$ removal has demonstrated an impressive capacity to achieve removal efficiencies exceeding 92% within a brief reaction timeframe. Furthermore, the by-products generated through this process hold potential utility as fertilizers. However, it is essential to note that this method entails substantial operational expenses and demands a considerable quantity of sediment agents. [12]. In contrast, adsorbents and membrane-based approaches impose significant energy consumption [13] [14]. When juxtaposed with the aforementioned methodologies, photocatalysis emerges as a highly promising pollution control technology, characterized by its environmentally friendly attributes and remarkable efficacy in $\text{NH}_4\text{-N}$ removal [15] [16] [17]. The pioneering utilization of TiO_2 photocatalysis for $\text{NH}_4\text{-N}$ oxidation dates back to 1979, and since then, it has garnered substantial attention [17]-[22]. Furthermore, TiO_2 has consistently been employed as a photocatalyst for redox reactions and has been extensively documented in scientific literature [23] [24] [25] [26]. However, it is imperative to acknowledge that the use of TiO_2 particles as photocatalysts, particularly in slurry systems, poses challenges concerning the recovery of TiO_2 particles from the treated water medium [27]. The uncollected slurry can introduce environmental contamination concerns, which

necessitate resolution. Additionally, investigations into the toxicological aspects of TiO₂ have revealed its potential harm to both plants and animals [28]. Elevated concentrations of this material in surface water bodies could pose a substantial threat to aquatic ecosystems and environmental health.

The choice of an ideal substrate for immobilizing photocatalysts is paramount, as it must provide stable anchoring to prevent catalyst leaching and exhibit selective affinity for the targeted contaminants. Various materials have been explored as supports for photocatalysts, including glass, silica, ceramics, polymers [29] [30], activated carbon, alumina, zeolite, natural fiber composite [31], and stainless steel [32]. Notably, polymers such as Polyether Sulfone (PES) hold promise as substrates due to their high chemical and mechanical stability [33]. Furthermore, the hydrophobic nature of PES facilitates the concentration of inorganic contaminants on its surface, where photocatalysts are anchored. The substrate's architecture is critical in providing a high surface area. Wet spinning, as a method, is particularly appealing for the fabrication of micrometer (μm)-sized fibers with relatively substantial surface areas, thereby enabling the anchoring of a significant quantity of photocatalysts with minimal disruption to the fabrication process.

Building upon prior research findings, this study seeks to address the limitations associated with ammonia removal by investigating the use of fibrous TiO₂ composite materials. Recognizing the inherent drawbacks of TiO₂ powder, the objective is to harness the advantages of composite materials incorporating polymers. Prior research has demonstrated the efficacy of incorporating zeolites into polymer matrices for various applications, including heavy metal removal [34]. Our earlier investigations have revealed that polymer composites containing zeolites exhibit superior performance in heavy metal removal and decontamination efforts when compared to powdered zeolite. In these investigations, a specific polymeric material, polyether-sulfone (PES), was employed due to its exceptional mechanical properties, chemical stability, high heat resistance, and ease of processing. This article is primarily focused on the fabrication of TiO₂-PES composite fibers and their application in the photooxidation of ammonia for decontamination under light exposure. The investigation entails varying the loading amounts of TiO₂ embedded within the fibrous PES scaffold, with the aim of characterizing their suitability as materials for ammonia removal.

2. Material and Methods

2.1. Materials

TiO₂ nano powder was procured from Fujifilm Wako Pure Chemical Co., Ltd., with the X-ray Fluorescence (XRF) analysis revealing the following chemical composition in percentage values: CO₂: 14.6%, TiO₂: 85.0%, Na₂O: 0.284%, and Fe₂O₃: 0.024%. Prior to its incorporation with PES, the TiO₂ powder underwent a crushing process and was subsequently sieved through a No. 230 sieve. N-Methyl-2-pyrrolidone (NMP) and various other chemicals were acquired

from Nacalai Tesque Inc. (Japan) and utilized in their as-received state without additional purification. The polyethersulfone (PES) employed, specifically Ultrason E2010, was sourced from BASF Co. Ltd. (Germany). To prepare the Ammonium-Nitrogen solutions, ammonium bicarbonate (NH_4HCO_3) obtained from Nacalai Tesque Inc., Japan, was dissolved in distilled water, resulting in a working solution with a concentration of 1000 mg/L. Before conducting the adsorption experiments, the ammonium solution was diluted accordingly. In cases where 0.1 M HCl and 0.1 M NaOH solutions were employed, the pH values of the solutions were adjusted as necessary.

2.2. Fabricating TiO_2 -PES Composite Fibers with Wet Spinning Process

In accordance with our previously established procedures [35] the wet-spinning process was employed to fabricate TiO_2 -PES composite fibers by utilizing the phase inversion of a PES solution into solid PES [36]. Here, PES was dissolved in NMP at a concentration of 30 wt%. Subsequently, varying amounts of TiO_2 powder (2, 5, 8, and 10 wt%) relative to the weight of PES were introduced. The resultant mixture was extruded through a cylindrical needle with a 0.6 cm-diameter, and an applied pressure of 0.42 MPa was utilized to extrude it into a water coagulation bath maintained at 25°C. Within this coagulation bath, the composite fibers took form and were subsequently rinsed in excess water at 60°C to eliminate any residual NMP. Finally, the composite fibers were subjected to drying under vacuum conditions at 60°C. The fibers produced at 30 wt% PES, with varying TiO_2 content of 0, 2, 5, 8, and 10 wt%, were denoted as PeTi0, PeTi2, PeTi5, PeTi8, and PeTi10, respectively.

2.3. Characterization of the Composite Fibers

To explore the alterations in fiber morphology, scanning electron microscopy (SEM) was conducted using a TM3030Plus HHTC instrument from Japan. The samples were sputter-coated with gold before examination, and imaging was carried out at an accelerating voltage of 15 kV. The surface area of both the TiO_2 and composite fibers was determined using the Brunauer-Emmer-Teller (BET) method, and the measurements were performed with a Tristar II 3020 apparatus (Micromeritics Inc., Tristar II, Shimizu, Japan). Prior to analysis, the samples were subjected to degassing under vacuum conditions overnight at 70°C. X-ray diffraction (XRD) spectra of limonite and the composite fibers were acquired using a SmartLab X-ray diffractometer (Rigaku Corporation) equipped with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The XRD patterns were recorded over a 2θ range spanning from 10° to 70°, employing parameters of 40 kV and 30 mA. For component analysis of TiO_2 and composite fibers, an X-ray fluorescence analyzer (ZSX Primus II, Rigaku Corporation, Japan) was utilized. Pellets with a 10 mm diameter were fabricated from TiO_2 , composite fibers, and an aluminum ring using a hydraulic press, applying a pressure of 450 kgf/cm² for the mea-

surements. The tensile strength of the TiO₂ composite fibers was determined with a load measurement device (LTTU500N, Minebea Co. Ltd., Japan) operating at 500 N and 23 °C with a relative humidity of 50%. The gauge length was set at 30 mm, and the crosshead speed was maintained at 2 mm/min. Five specimens were subjected to testing for each sample, and each specimen had a length of 50 mm. Initially, the diameter of each piece was measured using a micrometer (Mitutoyo 103 - 177, Japan) to calculate the cross-sectional surface area. The tensile strength and elongation were subsequently computed using the following equations: tensile strength (MPa) = maximum load/cross sectional area and elongation (%) = 100 × (elongation at rupture/initial gauge length). The density of the composite fibers was determined through the Archimedes method. A dry specimen with a known weight was immersed in excess water until equilibrium was reached with the specimen in the water. The density of the prepared specimens (ρ) was calculated using the formula:

$$\rho = \frac{W_s}{W_s - W_w} \times (\rho_0 - d) \quad (1)$$

where ρ is the density (g/cm³), W_s denotes the specimen weight in air (g), W_w represents the specimen mass in ethanol (g), ρ_0 is the density of ethanol (g/cm³), and d is the density of air (g/cm³).

Zeta potential measurements were conducted on both the TiO₂ powder and the composite fibers (after they were ground into powder form) within a pH range of 5 - 11. This analysis was carried out using a Zeta-potential analyzer (ELSE1NGK; Otsuka Electronics Co. Ltd., Japan), with distilled water employed as the dispersion medium. The medium's pH was adjusted through titration, utilizing 0.1 M HCl and 0.1 M NaOH solutions, to determine the zeta potential of the TiO₂ powder and the composite fibers.

2.4. Photocatalytic Adsorption Process of Ammonium Ion in the Batch Mode

The photocatalytic oxidation of ammonia in water, employing either TiO₂ composite fiber or TiO₂ powders, was carried out within a batch water medium. This reaction was conducted under exposure to light, specifically illuminated using a UV-A Hg lamp with a power rating of 25 W, positioned at a fixed distance of 10 cm above the central point of a pyrex glass reactor. The reactor possessed a 5 L capacity, and the average light intensity throughout the experiments approximated 300 μ W/cm². To ensure the accuracy of the experiments, the entire system was shielded by an aluminum foil sheet, effectively preventing any interference from external light sources. For the purpose of maintaining well-mixed solutions during the experiments, circulating water was employed. Additionally, an air diffuser was installed at the base of the reactor tube as part of the experimental setup.

To conduct the ammonium adsorption experiments, either 10 g of TiO₂ composite fiber or 1 g of TiO₂ nano powder was individually introduced into a 1 L

solution containing $\text{NH}_4\text{HCO}_3^-$. Subsequently, the mixtures were exposed to UV-A lamp irradiation at an intensity of $300 \mu\text{W}/\text{cm}^2$ for a duration of 12 hours at a temperature of 25°C . The adsorption kinetics of NH_4^+ were examined using the chosen adsorbents, namely TiO_2 , PeTi2 , PeTi5 , PeTi8 , and PeTi10 , across varying concentrations ranging from 0.27 to 2.7 mM (equivalent to 5 to 50 ppm). During the experiments, small sample solutions, each comprising less than 10 mL, were withdrawn and stored in opaque vials to minimize potential interference from indoor fluorescent lighting before subsequent analyses. The concentrations of NH_4^+ , NO_2^- , were determined using a UV-visible spectrophotometer (Jasco V-750). Specifically, NO_3^- concentrations were ascertained using the NO_3^- 11S LAQUATwin Kit designed for nitrate measurements. The concentrations of NH_4^+ , NO_2^- , and NO_3^- were calculated using five-point external standard calibration curves. Standard solutions were freshly prepared on a daily basis, and the analysis of standards was consistently repeated daily. The NH_4^+ ions in the samples were detected through a colorimetric method following the 4500-NH₃ F-Phenate method. The colored samples were assessed for absorbance at 640 nm. For the determination of NO_2^- content, a Griess assay was employed, utilizing N-(1-naphthyl)ethylenediamine (NED) as a coupling component in the reaction. The colored samples were analyzed for absorbance at 540 nm. The adsorption equilibrium isotherms were assessed using both the Langmuir and Freundlich models. In the Langmuir model, the equation took the form:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (2),$$

q_e is equilibrium adsorption amount (mmol/g), q_m is maximum adsorption capacity (mmol/g), and K_L is Langmuir constant.

Conversely, for the Freundlich model, the equation adopted was:

$$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e) \quad (3),$$

K_F , and n are Freundlich constant.

It is well-established that the degradation rate is associated with the formation of hydroxyl radicals ($\text{OH}\bullet$) on the catalyst surface. The quantity of hydroxyl radicals generated is contingent upon several factors, including the catalyst type, catalyst dosage, pH value, and light intensity. In this particular study, the impact of pH, catalyst dosage, and light intensity were also thoroughly investigated. In the context of photo exposure experiments, 10 g of the composite fibers were brought into contact with a 1 L aqueous ammonia solution containing 35 ppm concentration. Subsequently, the UV-A lamp was exposed to the solution for a duration of 96 hours.

3. Results and Discussion

3.1. TiO_2 Composite Fiber Characterization

Figure 1 provides an insight into the morphology of TiO_2 -PES composite fibers

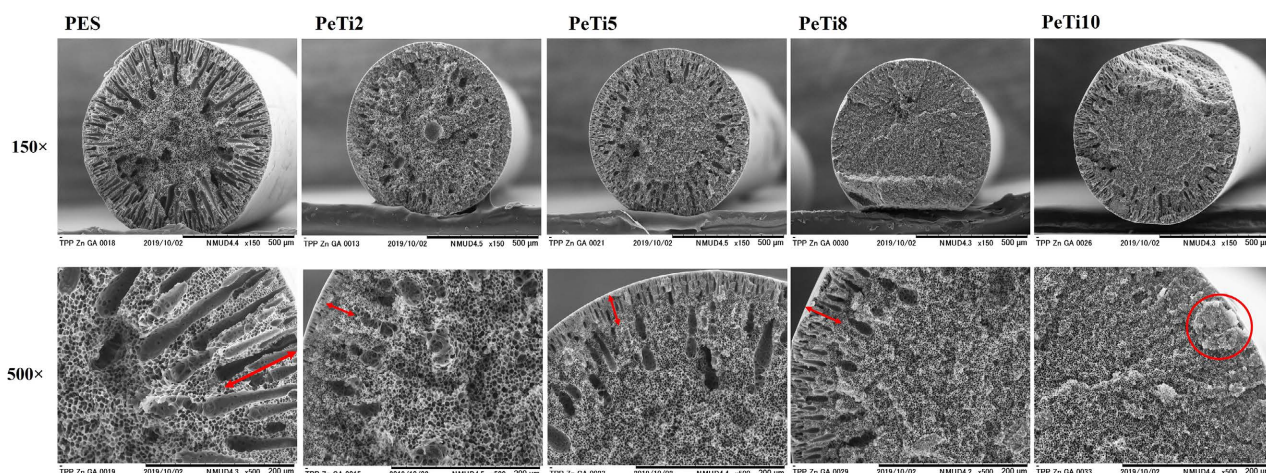


Figure 1. Cross-section of PES fiber and TiO_2 composite fibers at 150 and 500 magnifications.

loaded with varying amounts of TiO_2 within PES fibers. These resultant fibers exhibited an approximate diameter of 500 μm . Examination of their cross-section revealed a highly porous, sponge-like structure with pores smaller than 5 μm at the central region. This structure displayed a finger-like, elongated pore distribution extending from the fiber's core to its surface. However, it's noteworthy that the larger finger-like pores transitioned into much smaller structures when the TiO_2 content ranged from 2 to 8 wt%, and they were distributed at approximately 50 μm from the fiber surface. Remarkably, when the TiO_2 content reached 10 wt%, these larger pores nearly vanished, and the fiber cross-section exhibited a generally dense and spongy appearance. These observations suggest that, when the TiO_2 dispersion solution is added to the PES and coagulated in water, the coagulation rate slows down with increasing TiO_2 content, and the solvent exchange rate also becomes less rapid. Furthermore, the XRF elemental analysis presented in **Table 1** reveals that the TiO_2 content closely aligns with the quantity of added TiO_2 . As the TiO_2 content in the composite fiber increases, the density values exhibit a trend of 0.81, 0.83, 0.87, and 1.07 for 2, 5, 8, and 10 wt% respectively. The BET surface area values, determined through nitrogen adsorption, demonstrate a pattern where the surface area increases for PeTi2, PeTi5, and PeTi8, and then decreases in PeTi10. These findings indicate that the incremental addition of TiO_2 in the composite influences the surface area of the resulting fibers, with the highest surface area noted at 8 wt%. At a TiO_2 content of 10 wt% in the composite fibers, the surface area exhibited a slight decrease, suggesting the initiation of an aggregation process of TiO_2 nano powder. These results are further corroborated by the SEM cross-section images shown in **Figure 1**.

In **Figure 2**, N_2 adsorption is presented at various relative pressures for each composite fiber. The results clearly indicate that the N_2 adsorption amount exhibited an increase in proportion to the TiO_2 loading. Notably, the composite fibers displayed a substantial increase in N_2 adsorption, particularly under a relative pressure of 0.1. To provide a quantitative perspective, the BET surface areas

of PES and the composite fibers, including PeTi2, PeTi5, PeTi8, and PeTi10, were measured and found to be 18.09, 25.93, 48.19, and 37.76 m²/g, respectively. As shown in **Figure 3**, XRD patterns for both TiO₂ and the TiO₂ composite fibers are depicted. The main peaks, discerned at 25.3°, 37.9°, 48.3°, 53.9°, 54.9°, 62.7°, 68.84°, 70.1°, and 75.03°, correspond to the facets (101), (004), (200), (105), (211), (204), (113), (220), and (215), respectively. These peak positions align with the characteristic pattern of tetragonal anatase TiO₂ [37]. Importantly, no other diffraction peaks were observed in the XRD pattern, signifying the absence of any chemical reactions between TiO₂ and the PES polymer during the synthesis process.

Table 1. Properties of composites fibers, PES fiber, and TiO₂.

Sample	TiO ₂ content (%)	Density (g/cm ³)	BET surface area (m ² /g)	Pore size (nm)	Tensile strength (MPa)	Zeta potential at pH 9
PES	0	0.8	1.73	8.3	11.4	-6.7
PT2	2	0.81	18.1	7.9	10.1	-9.4
PT5	5	0.83	25.9	6.8	10.1	-8.6
PT8	8	0.87	48.2	6.5	9.7	-7.8
PT10	10	1.07	37.8	5.7	7.6	-10.4
TiO ₂	100	-	204.9	7.4	-	-18.3

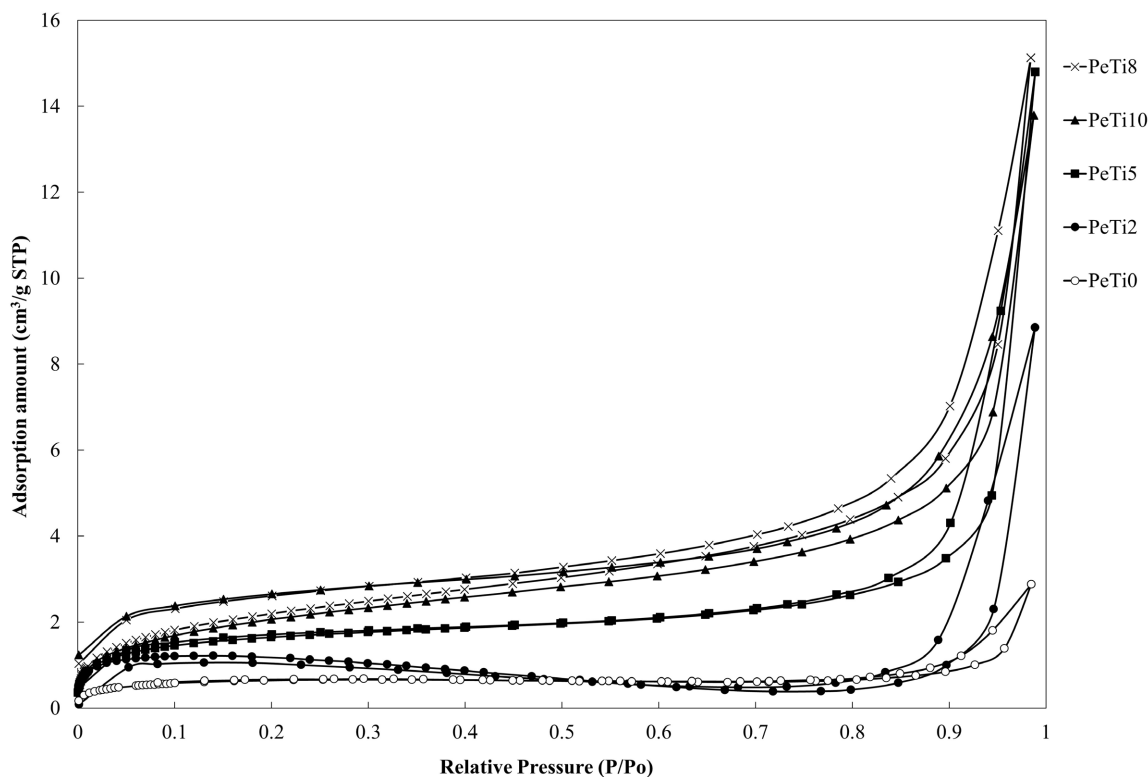


Figure 2. N₂ adsorption of PES and the TiO₂-PES composite fiber.

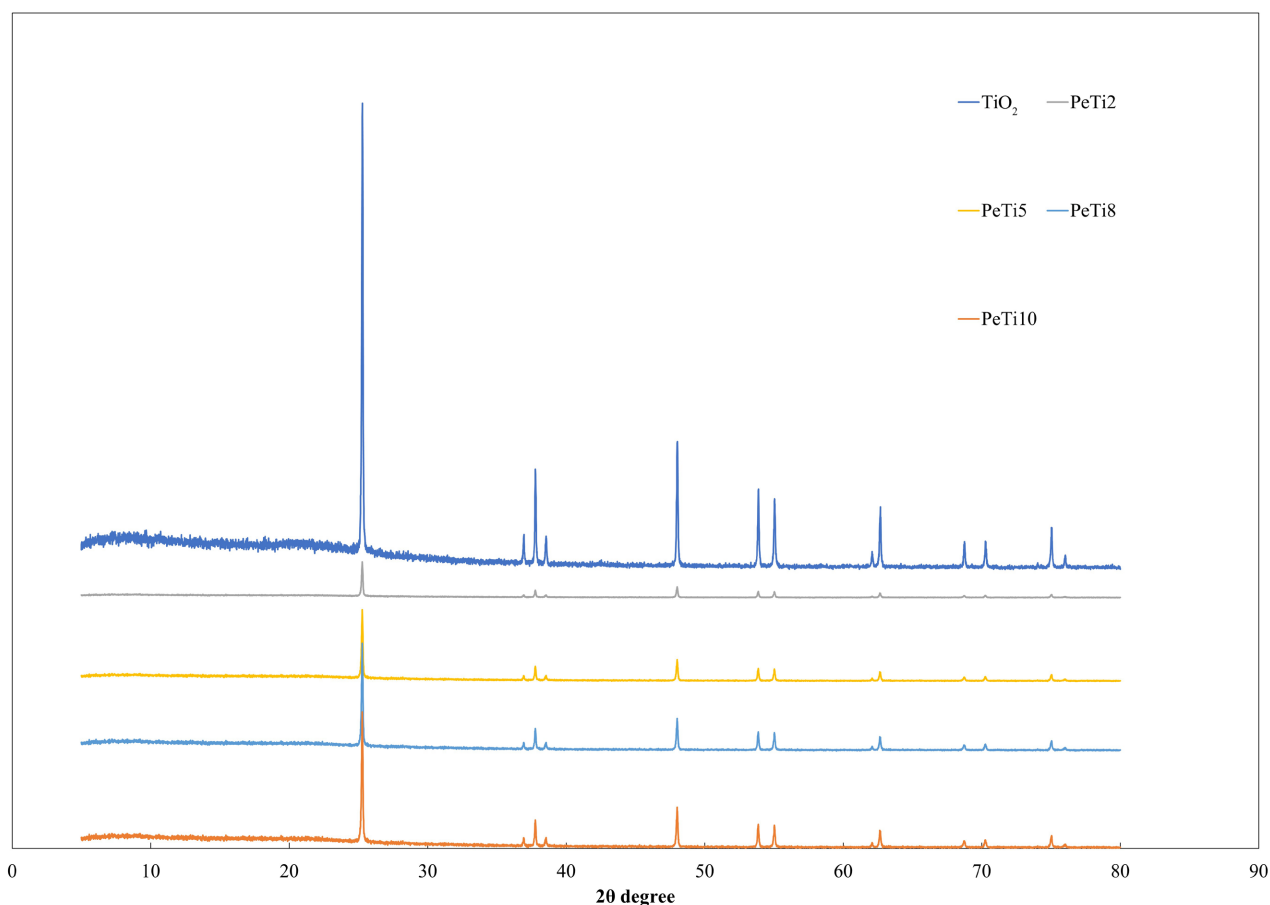


Figure 3. XRD spectra of the TiO₂-PES composite fiber.

3.2. Adsorbent Behavior of Composite Fiber to Ammonium under the UV-A Lamp Exposure

Figure 4. pH effect on the NH₄⁺ removal by using photocatalyst method with TiO₂ composite fibers. The ammonia photo-oxidation process was conducted across a range of pH values, spanning from 5 to 11. This pH variation was achieved by the addition of either 0.1 N NaOH or 0.1 N HCl solutions, and the results are depicted in the accompanying **Figure 4**. pH is a crucial parameter in the photocatalytic oxidation of ammonium, as it plays a role in adjusting the surface charge of the photocatalyst. The results clearly illustrate that ammonia removal efficiency was notably lower in acidic pH conditions. This phenomenon can be attributed to the inhibition of hydroxide group production necessary for the formation of hydroxyl radicals under acidic conditions. Moreover, the adsorption of ammonia molecules onto the photocatalyst surface decreased due to the positively charged nature of the photocatalyst surface, leading to repulsive forces. Consequently, the degradation efficiency of ammonia diminishes under acidic pH. Conversely, the removal efficiency of ammonia exhibited a substantial increase, rising from 18.5% to 60%, as the pH was raised from 5 to 11 during a 12-hour period under UV irradiation. This increase can be attributed to the higher concentration of hydroxide ions generated under alkaline pH conditions.

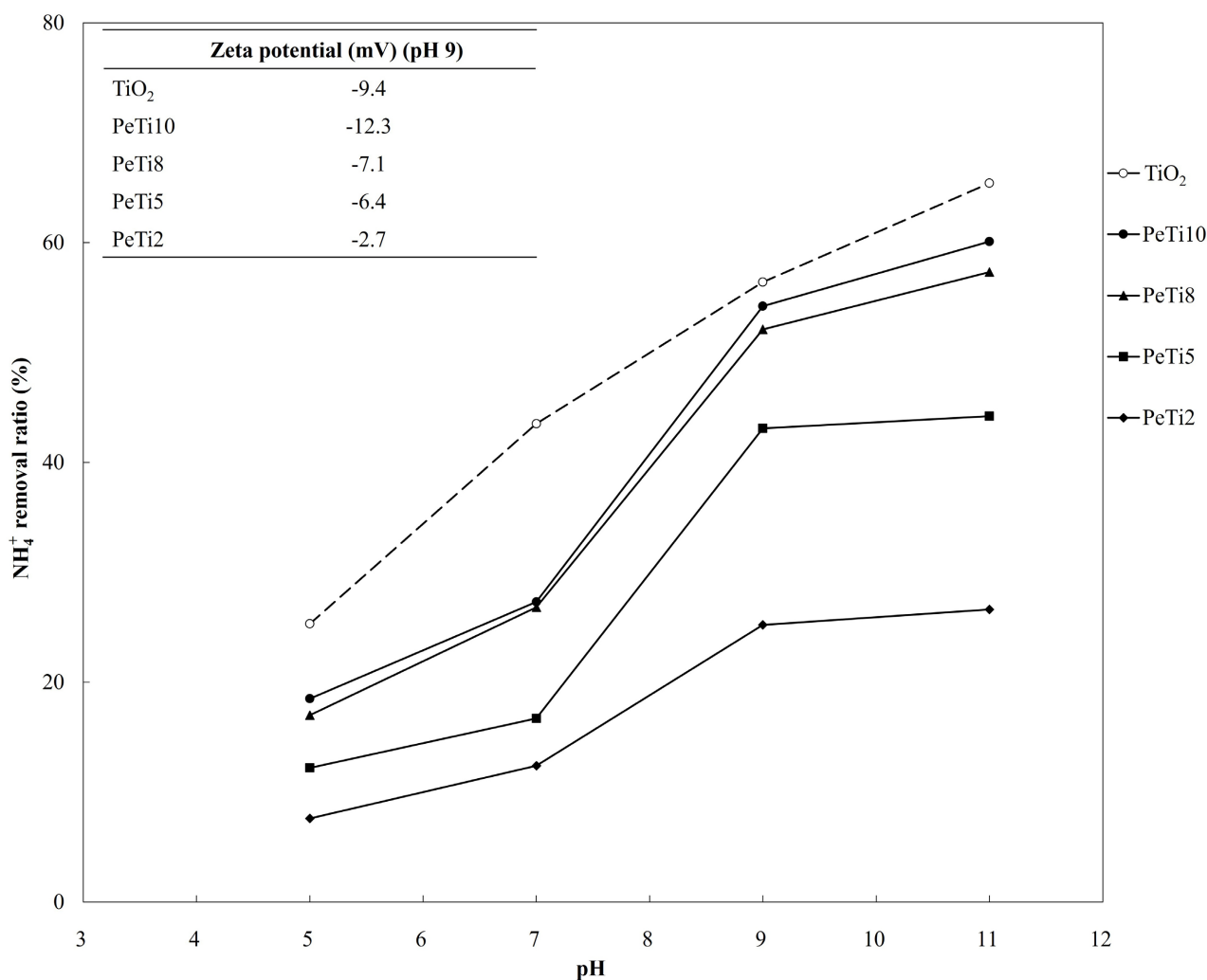


Figure 4. pH effect on the NH_4^+ removal by using photocatalyst method with TiO_2 composite fibers.

These hydroxide ions facilitate the reaction with the photo-generated holes, resulting in the formation of hydroxyl radicals. For practical and environmentally friendly considerations, this study chose to operate at pH 8, which demonstrated high removal efficiency, reaching approximately 50%.

Figure 5 illustrates the adsorption isotherms for ammonium on TiO_2 and the TiO_2 composite fibers. Equilibrium concentration data were analyzed using two isothermal models, Langmuir and Freundlich, and the results are presented in **Table 2**. In the adsorption isotherm, the data fit well to the Langmuir model, with correlation efficiency (R^2) values ranging from 0.9401 to 0.9936, while the Freundlich model yielded R^2 values in the range of 0.8345 to 0.9601. These results suggest that the saturation adsorption on TiO_2 sites within the fibers forms a monolayer. The maximum adsorption capacity (q_m) for ammonium ions on TiO_2 and composite fibers followed this order: PeTi10 > PeTi8 > PeTi5 > PeTi2. This indicates that q_m values are dependent on the porous structure of the adsorbents.

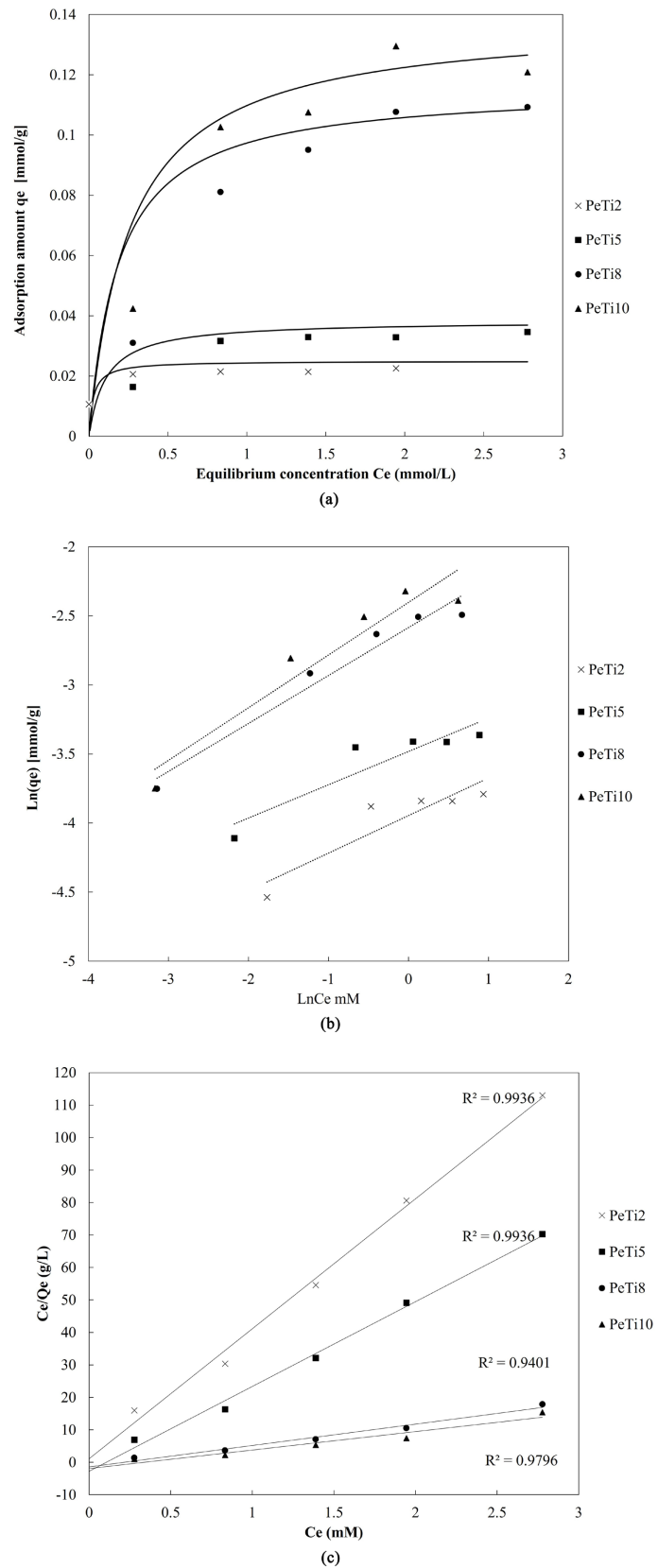


Figure 5. Adsorption isotherm of NH_4^+ by using the TiO_2 composite fibers (a), Freundlich adsorption plots (b), Langmuir adsorption isotherm plots (c).

Table 2. Parameters on Langmuir and Freundlich of ammonium adsorption by the composite fibers.

Isotherm models parameter			
PeTi2	Langmuir	q_m (mg/g)	0.43
		K_L (L/mmol)	37.54
		R^2	0.99
	Freundlich	K_F	66.2
		$1/n$	0.07
		R^2	0.83
PeTi5	Langmuir	q_m (mmol/g)	0.69
		K_L (L/mmol)	9.4
		R^2	0.99
	Freundlich	K_F	74.7
		$1/n$	0.07
		R^2	0.84
PeTi8	Langmuir	q_m (mmol/g)	2.09
		K_L (L/mmol)	5.3
		R^2	0.98
	Freundlich	K_F	50.1
		$1/n$	0.13
		R^2	0.92
PeTi10	Langmuir	q_m (mmol/g)	2.49
		K_L (L/mmol)	3.8
		R^2	0.94
	Freundlich	K_F	47.2
		$1/n$	0.16
		R^2	0.85

The photocatalytic performance of TiO₂ and the composite fibers was evaluated through the degradation of NH₄⁺ in an aqueous solution.

In **Figure 6**, the adsorption of NH₄⁺ on TiO₂ and PeTi8 was significantly enhanced compared to other samples, indicating that the PeTi8 sample possesses more active sites on its surface. To optimize reaction conditions, the effects of photocatalyst exposure time and illumination intensity on the photocatalytic removal of aqueous NH₄⁺ by TiO₂ and TiO₂ composite fibers under a UV-A lamp were further investigated. **Figure 6** demonstrates the decrease in aqueous NH₄⁺ concentration when treated with TiO₂ and TiO₂ composite fibers, starting with an initial solution pH of 8 and a light intensity of 300 μW/cm², while the

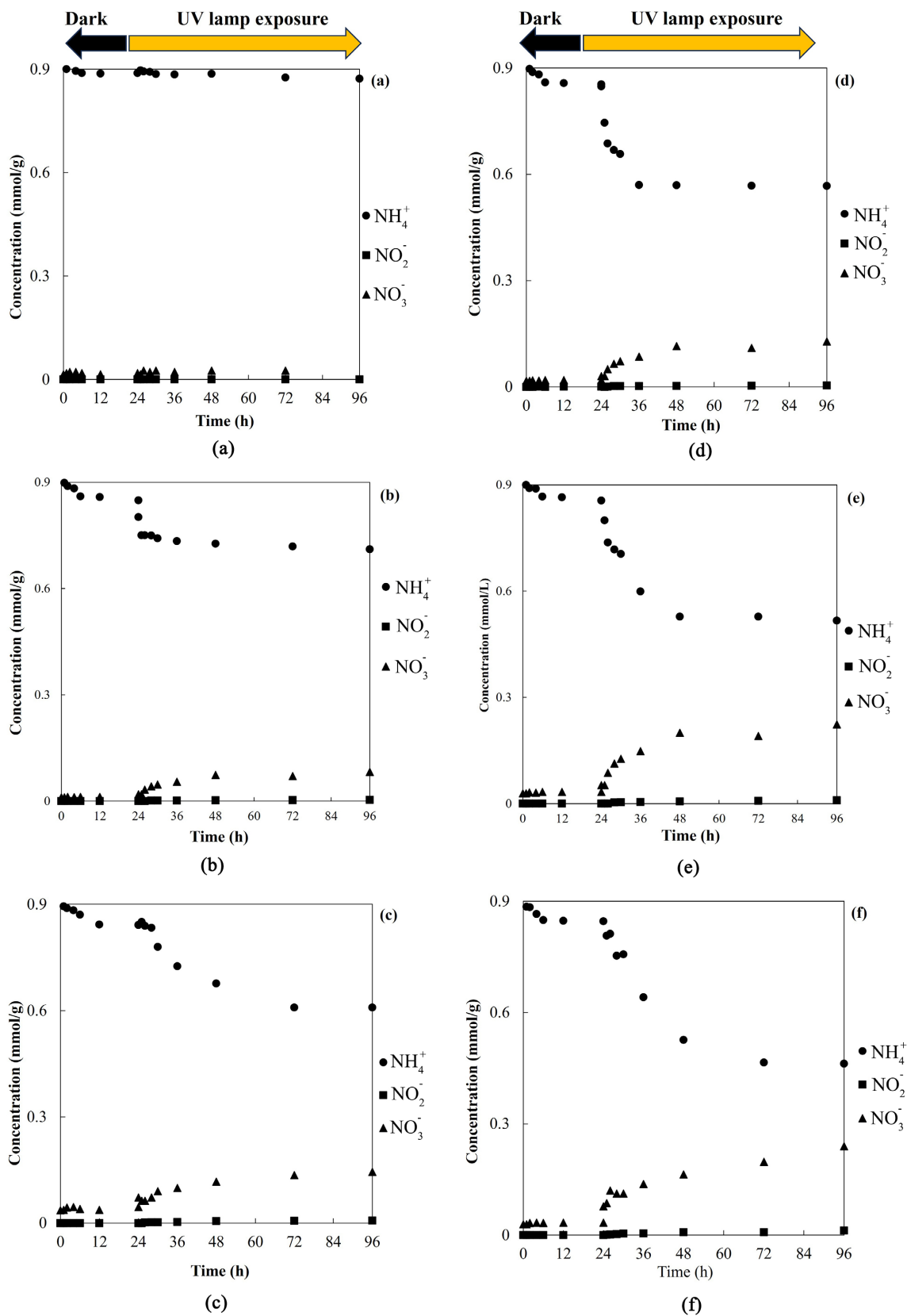


Figure 6. Conversion concentration between NH_4^+ , NO_2^- , and NO_3^- when exposed to UV-A lamp for 96 hours. Pe-Ti0 (a), Pe-Ti2 (b), Pe-Ti5 (c), Pe-Ti7 (d), TiO_2 (f).

photocatalyst dosage was fixed at 10 g for TiO₂ composite fibers and 1 g of TiO₂ nano powder. As the TiO₂ content in the composite fibers changed, the removal of aqueous NH₄⁺ initially decreased slowly in the absence of light. However, the removal dramatically decreased when the UV-A lamp was activated, observed between 25 to 36 hours. This phenomenon was consistent across all TiO₂ composite fibers. In cases of composite fibers with lower TiO₂ content, the production of reactive oxygen species was limited, affecting their photocatalytic performance. **Figure 6(b)** confirms this observation, as NH₄⁺ concentration stabilized after 24 hours of exposure under the UV-A lamp, reaching 0.7 mmol/g. In the case of the highest TiO₂ content in the composite fiber, PeTi10, the NH₄⁺ concentration was 0.5 mmol/g higher than the tank content of 10 g of PeTi8, which recorded 0.46 mmol/g, due to aggregation within the fiber structures. On the other hand, the results obtained from TiO₂ nano powder exhibited good adsorption ability in the first 6 hours when the UV-A lamp was turned on, but the removal ability gradually decreased and stabilized after 12 hours of exposure under irradiation. Compared to PeTi0, PES fiber showed no adsorption ability for NH₄⁺. Additionally, **Figure 6** also presents the concentrations of photoconversion products, NO₂⁻ and NO₃⁻, during the photocatalytic process. The high removal ratio of aqueous NH₄⁺ and the presence of oxidation byproducts (NO₃⁻ and NO₂⁻) could not be attributed to the weak volatilization of aqueous NH₄⁺ under illumination. The results clearly demonstrate that TiO₂ composite fibers can effectively photo-catalytically remove aqueous NH₄⁺ under the UV-A lamp. The higher NO₃⁻ yields in the tank content of 1 g of TiO₂ and 10 g of PeTi8 and PeTi10 compared to PeTi2 and PeTi5 are attributed to the appearance of TiO₂ in the photocatalyst process, as documented in previous research. These higher NO₃⁻ yields provide evidence that heterogeneous reactions dominate at higher TiO₂ concentrations.

Figure 7 depicts the variation in aqueous NH₄⁺ concentration when treated with TiO₂ and TiO₂ composite fibers under a UV-A lamp with different tank volumes. Altering the tank volume affects the interaction distance between the light source and the pollutant, providing insights into the impact of light intensity at varying distances. With the same initial concentration of NH₄⁺ in the aqueous solution and a consistent dosage of 10 g, the tank with a 0.25 L volume demonstrated effective NH₄⁺ removal. Conversely, in the 2 L volume tank, the larger volume limited the utilization of photons in the solution, resulting in a less effective photocatalytic performance. The rate at which photocatalysis activates and forms electron-hole pairs in photochemical reactions is significantly influenced by the intensity of light. The efficiency of pollutant degradation depends on the distribution of light intensity within the reactor.

To explore the impact of light intensity on photocatalytic efficiency at different distances (2 cm, 5 cm, 10 cm, 15 cm, and 20 cm), all experiments were conducted under identical conditions, and the results are presented in **Figure 8**. Clearly, as the distance between the photocatalyst (PeTi8) and the light source

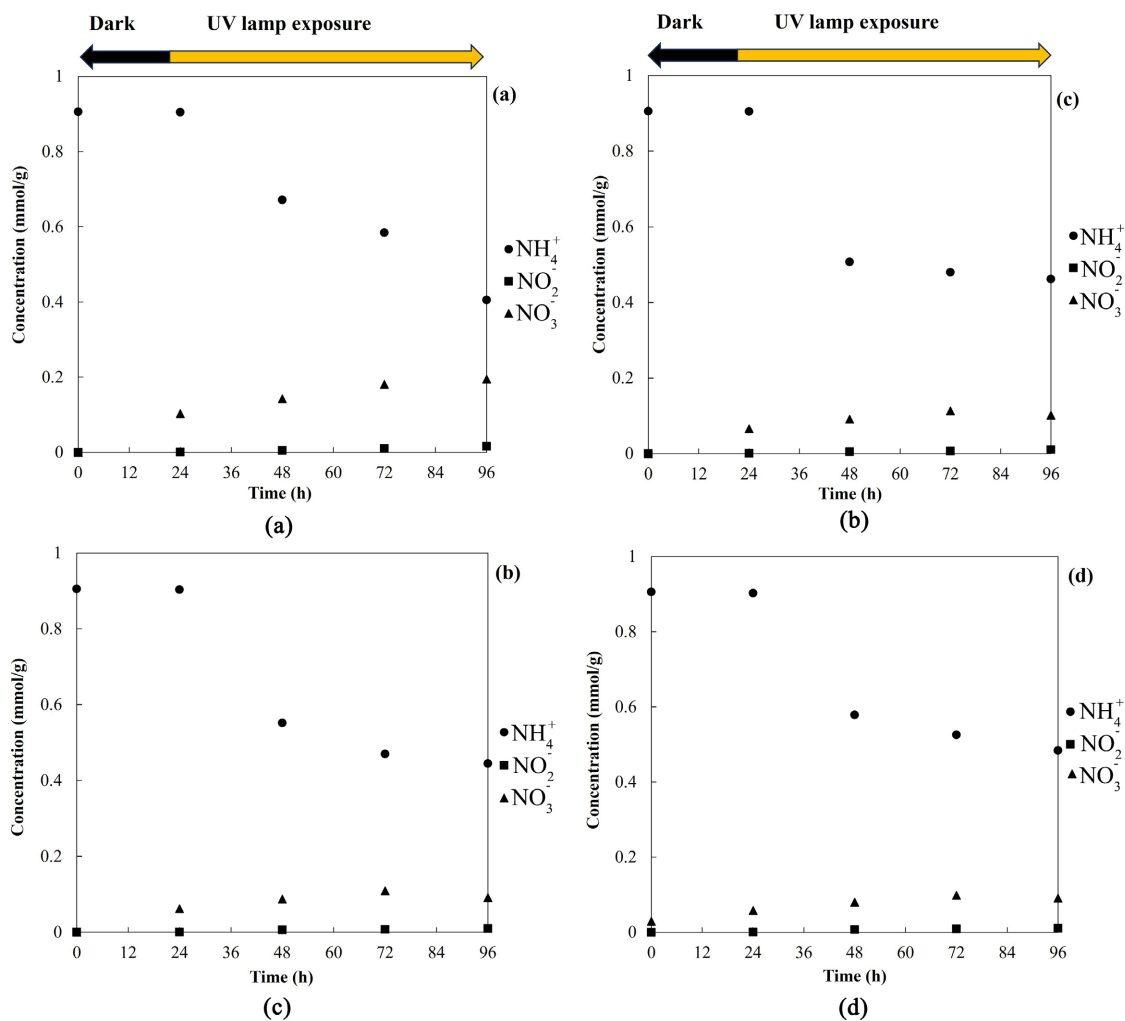


Figure 7. Conversion of concentration between NH_4^+ , NO_2^- , and NO_3^- exposed to UV-A lamp with changing the tank volume. The PeTi8 composite were used, 0.5 L (a), 1 L (b), 1.5 L (c), 2 L (d).

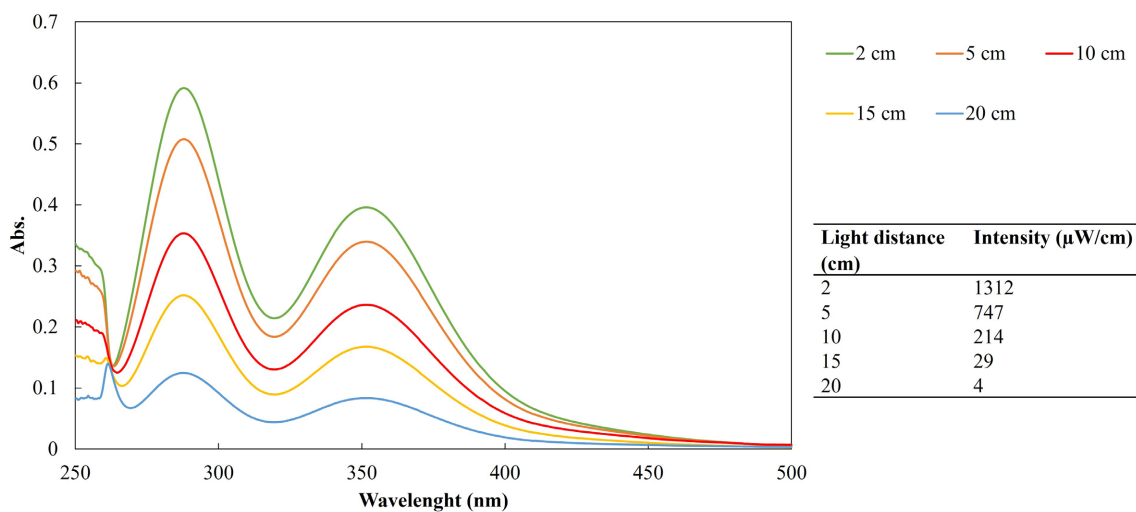


Figure 8. Distance dependent absorption spectra for the photocatalytic degradation of PeTi8 under UV-A light irradiation.

increases, the concentration of hydroxyl radicals ($\text{OH}\cdot$) decreases. Generally, the distance between the light source and the photocatalyst has a significant effect on the reaction kinetics. It was observed that an increased distance led to a reduction in the rate constant, resulting in decreased catalyst activation and diminished photocatalytic degradation of ammonia. **Figure 8** presents the $\text{OH}\cdot$ concentration at different distances and light intensities after 12 hours of initiating the reaction. Throughout the photocatalyst experiments, a certain quantity of hydroxyl radicals is produced. Changing the distance of the light source also impacts the ability to generate hydroxyl radicals in the aqueous environment. An experiment was conducted under the same conditions to assess the amount of hydroxyl radicals generated when altering the lamp distance from the catalyst. The results, as shown in **Figure 8**, indicate that as the distance of the lamp increases, the concentration of hydroxyl radicals decreases, with virtually no hydroxyl radicals being produced at a distance of 20 cm.

4. Conclusion

In conclusion, the TiO_2 -PES composite fibers containing different loading amounts of TiO_2 were prepared using phase inversion. The properties of the composite fibers and adsorption behavior were investigated to characterize them on porous adsorbents. These composite fibers had sponge-like structures and embedded TiO_2 nanoparticles on a polymer matrix. The photocatalytic performance of the TiO_2 composite fibers and TiO_2 nanoparticles was evaluated. The removal of ammonia from aqueous solutions under UV-A light exposure demonstrated that PeTi8 composite fibers had higher adsorption capacity compared to other samples. The study also explored the effects of pH, light intensity, and catalyst dosage on the photocatalytic degradation of ammonia. The adsorption equilibrium isotherms for ammonium were well-fitted to the Langmuir model, and the results indicated that the q_m values (maximum adsorption capacity) depended on the porous structure of the adsorbents. The research highlighted the ability of TiO_2 composite fibers to photocatalytically remove aqueous NH_4^+ under UV-A light. It was observed that increasing the distance between the photocatalyst and the light source led to a decrease in hydroxyl radical concentration, affecting the photocatalytic performance.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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