Research Article

Comparison of Photocatalytic Degradation Performance of TiO_2-Polymer Based Composites in Wastewater Treatment

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Abstract

The composites of titanium dioxide (TiO_2) particles loaded on polystyrene (PS), acrylonitrile-butadiene-styrene (ABS), and low-density polyethylene (LDPE) were prepared using an internal mixer process, followed by compression molding to form sheets for photocatalytic applications. These composite sheets were evaluated for their effectiveness in degrading methylene blue and treating wastewater from a natural source. The morphology of the composite sheets was analyzed using scanning electron microscopy (SEM), and their water absorption properties were evaluated according to the ASTM D570 standards. It was found that the TiO_2/ABS exhibited the highest photodegradation efficiency, achieving a 31.38% degradation rate within 6 h under UV irradiation. This result highlights the potential of TiO_2/ABS for effective and sustainable wastewater treatment applications.

***Keywords**:* Photocatalyst; Composite material; Titanium dioxide; Wastewater treatment

1. Introduction

Rapid industrial development has led to persistent environmental challenges, with the textile and pharmaceutical industries being major contributors. These industries discharge large quantities of dyes and organic chemicals into natural water sources, many of which are resistant to degradation by light, temperature, and other natural processes. As a result, these pollutants accumulate in ecosystems, posing serious threats to aquatic life and human health [1, 2]. The increasing volume of contaminated wastewater has raised global concerns, prompting scientific efforts to develop effective and sustainable treatment methods to mitigate these environmental risks.

Among various treatment techniques, photocatalysis has gained attention as one of the most efficient methods for wastewater treatment due to its high efficiency in removing organic pollutants and harmful bacteria [3]. Common semiconductor photocatalysts include tin(IV) oxide (SnO_2) [4], zinc oxide (ZnO) [5], and ferrous oxide (Fe_2O_3) [6]. In the photocatalytic process, these semiconductors are excited by light with energy exceeding their band gap (E_g), generating electron-hole pairs—holes in the valence band and electrons in the conduction band. The holes react with water or hydroxide ions to produce hydroxyl radicals ($HO^{\bullet}$), while photo-generated electrons react with adsorbed oxygen molecules to form active superoxide radicals ($O_2^{\bullet}$). These active radical species play an important role in degrading organic pollutants and hydrocarbon bonds, as well as suppressing bacterial biochemistry [7] as shown in Fig. 1.

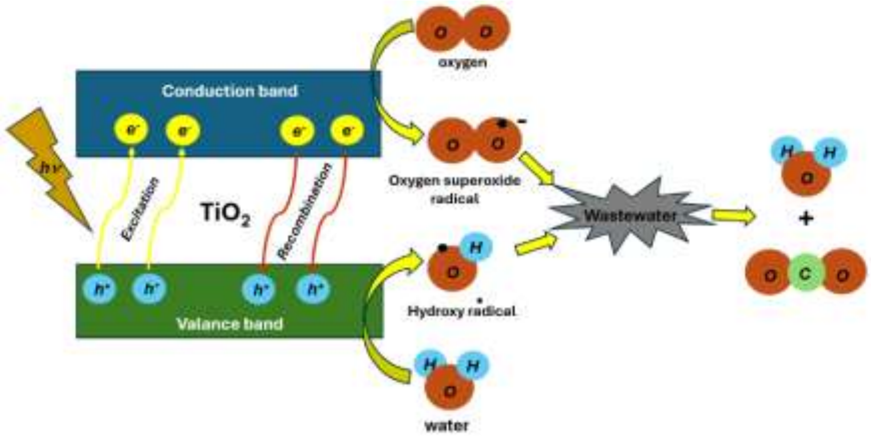

Fig. 1 Schematic illustration of TiO_2 photocatalytic.

Among these materials, titanium dioxide (TiO_2) is widely regarded as the most promising semiconductor photocatalyst due to its non-toxicity, high photodegradation efficiency, and exceptional thermal and chemical stability [8]. TiO_2 is extensively used in environmental applications such as air and water purification because of its ability to decompose organic compounds and harmful microorganisms under UV light. This photocatalytic activity is primarily attributed to its wide bandgap energy, approximately 3.20 eV for the anatase phase and 3 eV for the rutile phase, which allows excitation under UV irradiation [9]. However, using TiO_2 in powder form for water treatment presents several challenges. The fine particles tend to disperse in water, making recovery difficult and increasing the risk of secondary pollution due to residue accumulation, particularly when large amounts are used.

To address these issues, researchers have explored the incorporation of TiO_2 into films or composite materials. This approach not only facilitates the separation of TiO_2 from water, making it easier to recover, but also enhances its mechanical stability and reusability. Previous studies, such as the preparation of floating photocatalysts using TiO_2-Au and polymeric layer films by Gao et al. [10] and the development of electrospun polymer nanofiber membranes with a TiO_2 photocatalyst by Benuto et al. [11], have demonstrated TiO_2 can be effectively integrated into composite structures to improve pollutant removal, particularly for contaminants like methylene blue. These composite materials also allow for easier retrieval and recycling of the photocatalyst, making them more practical for wastewater treatment applications.

Despite these advancements, existing TiO_2-based composites still face challenges in durability and efficiency. For instance, Benuto et al. [11] observed that TiO_2 particles embedded in electrospun polymer nanofiber membranes could effectively degrade methylene blue under UV irradiation. However, the TiO_2 particles tended to detach from the membranes during use, leading to reduced efficiency and limited recyclability. This issue underscores the need for a more robust and durable composite design. Therefore, developing composite sheet photocatalysts using a more stable and uniform fabrication method could significantly enhance both performance and longevity in wastewater treatment applications.

In this study, TiO_2 was incorporated into polystyrene (PS), acrylonitrile-butadiene-styrene (ABS), and low-density polyethylene (LDPE) to create composite sheets using internal mixing and compression molding. These composite sheets were then tested for their photocatalytic efficiency in degrading methylene blue and treating wastewater. By integrating TiO_2 into polymeric sheets, this study aims to provide a more efficient, durable, and scalable solution for water purification, addressing key limitations of existing TiO_2-based photocatalysts.

2. Materials and Methods

2.1 Preparation of Composite Sheets

The composite materials were prepared using an internal mixer process. In a typical procedure, 0.50 g of titanium dioxide (TiO_2, 547 TITANIUM DIOXIDE, UNILAB, Ajax Finechem) was mixed with 200 g of polymers: polystyrene (PS, GPPS, GP110, IRPC Public Co., Ltd., melt flow index, 5 kg/200°C: 1.7 g/10 min), acrylonitrile-butadiene-styrene (ABS, SR101, IRPC Public Co., Ltd., melt flow index, 10 kg/220°C: 7 g/10 min), and low-density polyethylene (LDPE, JJ4324, TPI Polene Public Co., Ltd., melt flow index, 2.16 kg/190°C: 5.50 g/10 min) in an internal mixer (MX500-D75L90, Chareon Tut Co., Ltd., Thailand) at a rotation speed of 50 rpm. Mixing temperatures were set to 240°C for PS, 250°C for ABS, and 140°C for LDPE, with a mixing duration of 20 min. Subsequently, composite sheets were prepared using compression molding (PR2D-W300L350 PM-WCL-HMI, Chareon Tut Co., Ltd., Thailand) at the same temperatures (240°C for PS, 250°C for ABS, and 140°C for LDPE), resulting in the composite sheets designated as TiO_2/PS, TiO_2/ABS and TiO_2/LDPE, as shown in Fig. 2. The morphology of the composite sheets was examined using a scanning electron microscope (SEM, Hitachi, TM3030 tabletop microscope).

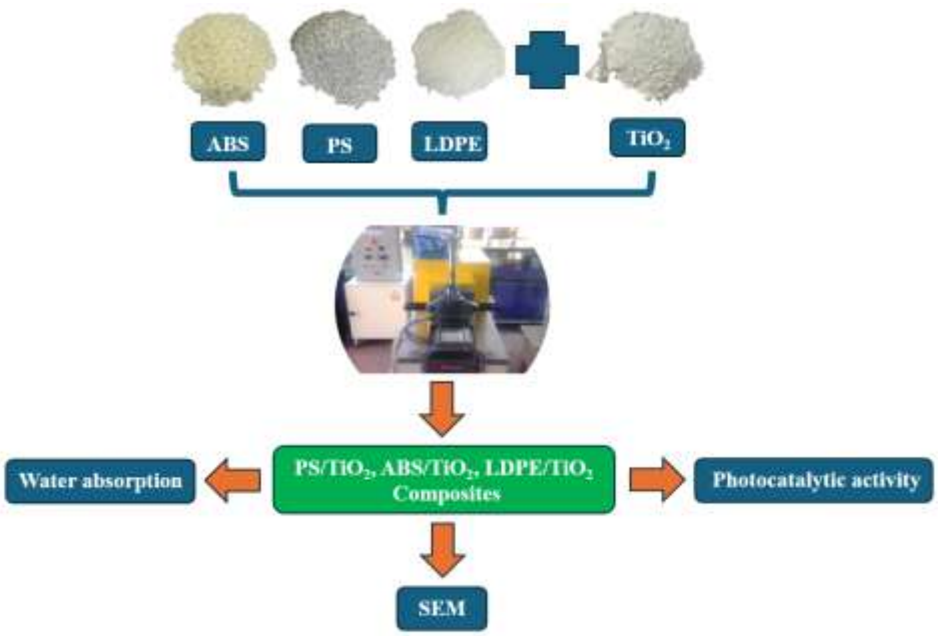

Fig. 2 Schematic of the composite process.

2.2 Water Absorption Testing

The percentage of water absorption of the composite sheets was estimated according to ASTM D570. Composite sheets measuring 60 × 60 × 1 mm³ were dried in an oven at 50°C for 24 h, weighed, and then submerged in distilled water at room temperature for 24 h. Afterward, the sheets were removed from the water and their wet weight was measured. The water absorption was calculated using equation (1):

$$\text{Water absorption (\%)} = \left(\frac{\text{Wet weight - Dry weight}}{\text{Dry weight}}\right)\times 100 \quad (1)$$

2.3 Photocatalytic Activity Testing

The photocatalytic activity of the composite sheets was evaluated by the degradation of methylene blue (MB; Nice Chemical Pvt. Ltd.) under UV irradiation (UV lamp, 50 W). Composite sheets measuring 1 × 1 cm² were added to 5 mL of methylene blue solution (1×10^{-5} M). After irradiation, samples of the methylene blue solution were collected hourly. The concentration of methylene blue was measured using a UV-Vis spectrophotometer (Jasco V530) at 664 nm. The removal percentage was calculated using equation (2) [12]:

$$\eta = \left(\frac{C_0\text{-}C}{C_0}\right)\times 100 \quad (2)$$

Where C_0 is the initial concentration and C is the remaining concentration.

The efficiency of wastewater treatment from a natural water source was determined by measuring the level of dissolved oxygen (DO) in the water after UV irradiation (UV lamp, 10W). Composite sheets measuring 1 × 1 cm² were submerged in 60 mL of wastewater. After irradiation, samples were collected every 8 h from the wastewater, and the dissolved oxygen level was measured using a dissolved oxygen meter (Extech, DO600).

3. Results and Discussions

3.1 Composite Sheets Characterization.

The surface of the composite sheets prepared by compression molding was relatively smooth and uniform. Fig. 3 displays the SEM microstructures of the fractured surface of the composite sheets, revealing an even distribution of TiO_2 particles (indicated by white arrows) within the polymer matrix. Fig. 3(a) shows that the fractured surface of TiO_2/PS exhibited a smooth and brittle fracture, reflecting the inherent properties of the PS matrix [13]. This brittle nature aligns with the typical behavior of PS, which lacks significant flexibility or ductility. In contrast, Fig. 3(b) shows that the fracture surface of the TiO_2/ABS had a coarse texture with visible cavities, indicating the ductile properties of the ABS matrix. Even with the inclusion of a small amount of titanium dioxide particles, the TiO_2/ABS maintained its ductile fracture behavior and morphology, consistent with the characteristics of the ABS matrix [14]. Lastly, Fig. 3(c) illustrates the TiO_2/LDPE, where the fractured surface appeared coarse with the upper part displaying wrinkles. This wrinkled appearance is indicative of the ductile and elastic properties of low-density polyethylene (LDPE), showing its ability to deform and recover under stress [15].

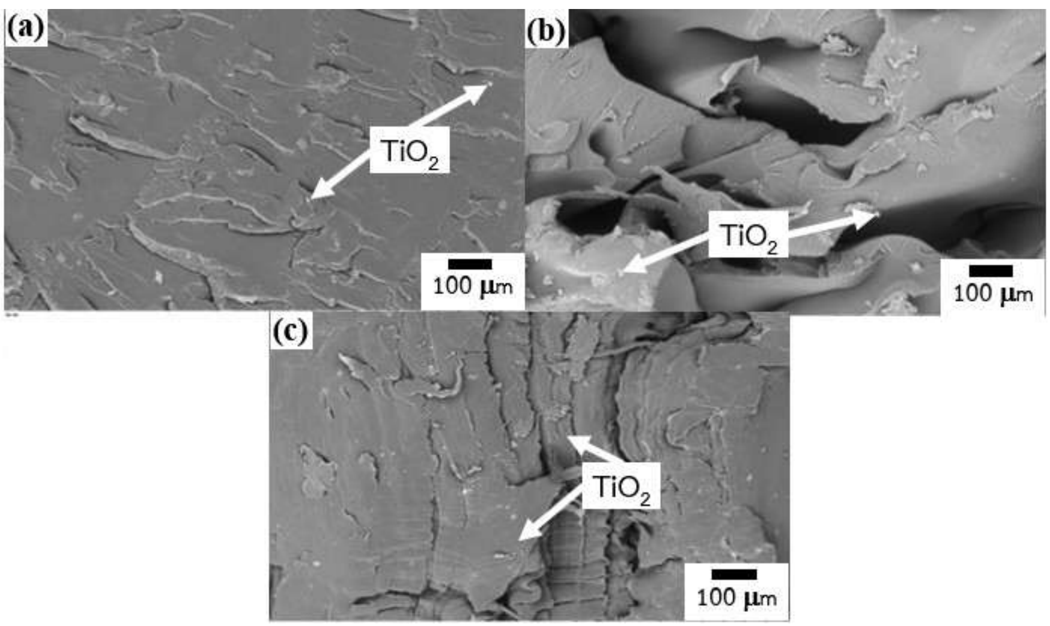

Fig. 3 SEM of fractured surface of composite sheets: (a) TiO_2/PS, (b) TiO_2/ABS and (c) TiO_2/LDPE.

3.2 Water Absorption.

Table 1 presents the percentage of water absorption for the prepared composite sheets. Among the samples, TiO_2/ABS exhibited the highest water absorption, followed by TiO_2/PS and TiO_2/LDPE. The higher water absorption of TiO_2/ABS can be attributed to the density and polarity of the ABS matrix. Although all composite sheets have densities greater than that of water, only the TiO_2/ABS was observed to fully sink upon immersion, maximizing its surface area in contact with water. In contrast, TiO_2/PS and TiO_2/LDPE floated partially, which limited their surface area in contact with water and may have contributed to their lower water absorption, as illustrated in Fig. 4.

Furthermore, ABS is recognized as a polar polymer due to its molecular structure, which contains acrylonitrile groups (−C≡N) that exhibit hydrophilic behavior [16, 17]. This polarity facilitates the absorption of water molecules, leading to a higher water uptake in TiO_2/ABS compared to the nonpolar and less hydrophilic nature of PS and LDPE [18]. The study of Han et al. [19] reported a significant increase in the hydrophilicity of TiO_2-ABS composite, demonstrating that the incorporation of TiO_2 into the ABS matrix enhances its water absorption capacity. These differences in polarity and molecular structure contribute significantly to the observed variations in water absorption among the composites.

Table 1 Density and water absorption of composite sheets.

Sample	Density (g cm^{-3})	Water absorption (%)
TiO_2/PS	1.91	1.23
TiO_2/ABS	2.00	12.08
TiO_2/LDPE	1.63	1.02

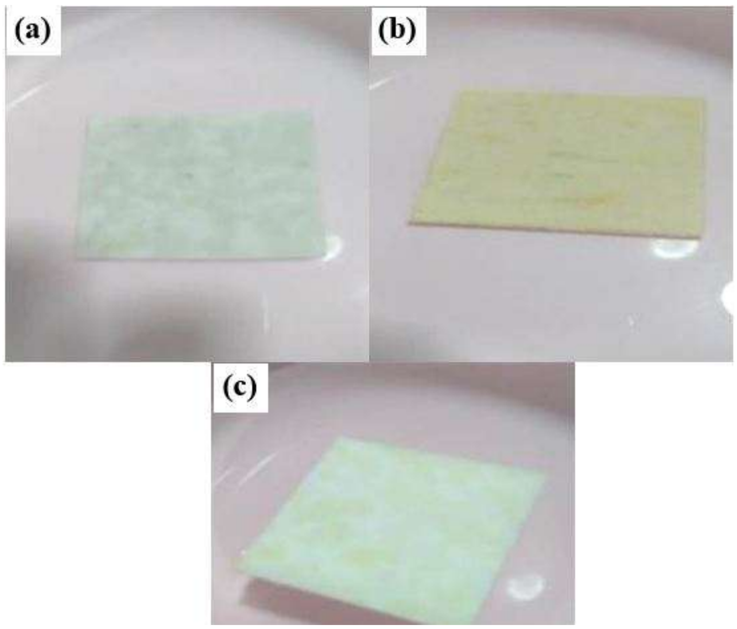

Fig. 4 Water absorption test of composite sheets: (a) TiO_2/LDPE, (b) TiO_2/PS and (c) TiO_2/ABS.

3.3 Photocatalytic Activity.

The photocatalytic degradation of methylene blue under UV irradiation using the composite sheets is shown in Fig. 5. The removal percentage of the photocatalysts for TiO_2/ABS, TiO_2/PS and TiO_2/LDPE were 31.38%, 30.97%, and 18.55%, respectively. The higher efficiencies observed with TiO_2/ABS and TiO_2/PS can be attributed to their larger surface area in contact with water, enabled by their densities, which allow them to sink and maximize exposure. The larger surface area is essential for effective photocatalytic activity, as it increases the interaction between the photocatalyst and the methylene blue solution, thus enhancing the generation of reactive species (e.g., hydroxyl radicals) under UV light [20, 21]. In contrast, TiO_2/LDPE floats due to its lower density, which limits its contact with the water and, consequently, its photocatalytic efficiency. This difference highlights the importance of surface area availability for achieving optimal photochemical performance. The photocatalytic activity of TiO_2 in polymer matrices depends not only on the dispersion and surface exposure of TiO_2 particles but also on the interfacial interaction between TiO_2 and the polymer. The polymer matrix can influence the electron transfer dynamics by either facilitating or hindering the migration of photogenerated charge carriers. In relatively polar matrices such as ABS, better interaction with TiO_2 may lead to more efficient separation of electron-hole pairs, enhancing photocatalytic performance. In contrast, more hydrophobic matrices like LDPE may create a barrier around TiO_2 particles, limiting their interaction with water or pollutants, and reducing photocatalytic efficiency [22, 23].

The experimental results indicated that the efficiency of the composite sheet as a photocatalyst was relatively low. This limitation is due to the fact that the photochemical reaction occurs only where the TiO_2 particles are directly exposed to UV irradiation and in contact with the methylene blue solution. The inner areas of the composite sheet, where the TiO_2 particles are embedded and not exposed to the solution, remain inactive. Additionally, the composite sheet may have absorbed the methylene blue solution at a slower rate, reducing the interaction between the pollutant and the photocatalyst. This suggests that to enhance the efficiency further, a more porous structure or a thinner composite sheet could be beneficial, as it would increase the surface area of the TiO_2 particles in contact with the solution and maximize their exposure to UV light. For instance, a study by Ishchenko et al. [24] found that mesoporous TiO_2 anatase films exhibited higher photocatalytic activity compared to dense TiO_2 anatase films. The increased porosity of these films resulted in a higher surface area, which allowed for more active photocatalytic processes and improved light absorption. In addition, the study by Sun et al. [25] demonstrated that the combination of TiO_2 and polyvinylidene fluoride (PVDF), prepared via tape casting and solvent replacement method, effectively addressed the issue of photocatalyst recovery. The resulting composite films could be reused for up to 10 cycles while maintaining stable photocatalytic performance. These findings highlight the potential of film or sheet-based photocatalysts as recyclable, sustainable, and efficient materials for environmental applications.

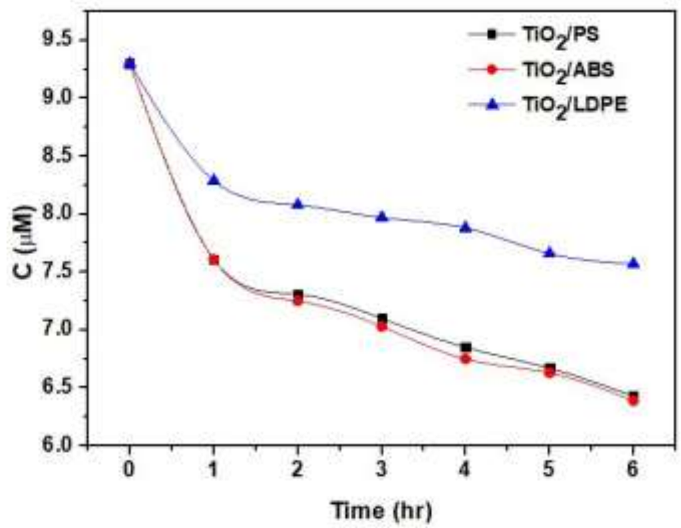

Fig. 5 Photocatalytic degradation of methylene blue using prepared composites under UV irradiation.

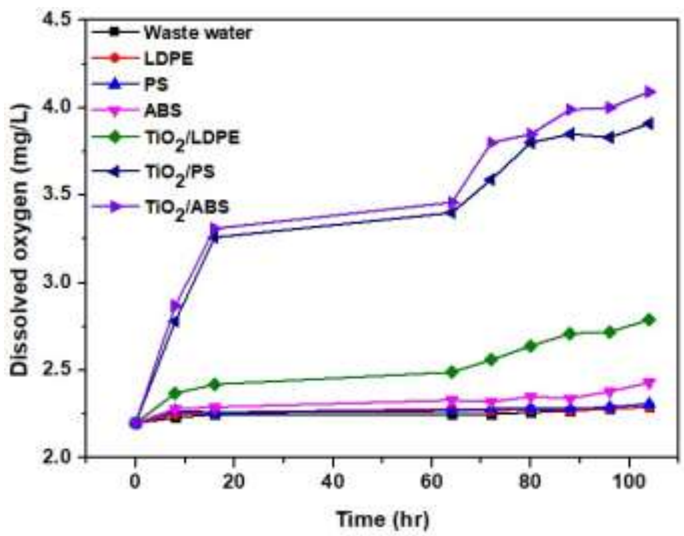

Fig. 6 Levels of dissolved oxygen in water after photocatalytic process under UV irradiation.

Fig. 6 shows the dissolved oxygen levels in wastewater after the photocatalytic process under UV irradiation using composite sheets, compared to the polymer matrix alone. The composite sheets demonstrated effectiveness in wastewater treatment, as indicated by the increase in dissolved oxygen levels from 2.20, 4.09, 3.91, and 2.79 mg L^{-1} when using TiO_2/ABS, TiO_2/PS, and TiO_2/LDPE as photocatalysts, respectively. In contrast, the polymer matrices without TiO_2 were not effective in treating wastewater. The photocatalytic process facilitated the treatment when titanium dioxide, evenly distributed within the matrix polymer, was activated by UV irradiation. This activation generated electron-hole pairs, leading to oxidation and reduction reactions that suppressed bacterial activity and broke down organic substances, ultimately increasing dissolved oxygen levels [26].

TiO_2/ABS was found to have the highest efficiency in wastewater treatment due to its large surface area in contact with water and its high water absorption capacity. This aligns with the results of the water absorption test, as the water-absorbing capability of ABS enhances the concentration of organic molecules near the TiO_2 surface, where they are effectively decomposed [27]. This observation is consistent with the study by Dalto et al. [28], which found that using activated carbon as a support material enhances photodegradation efficiency. In their study, organic molecules in water were adsorbed by activated carbon, increasing their concentration near the TiO_2 surface and leading to greater degradation of these molecules.

4. Conclusion

The composite sheet photocatalysts were successfully prepared using an internal mixer and compression molding. The degradation capabilities of TiO_2/PS, TiO_2/ABS, and TiO_2/LDPE were investigated using methylene blue as a model pollutant, along with wastewater from a natural water source. Among the composites, TiO_2/ABS demonstrated the highest photocatalytic activity, successfully removing methylene blue by up to 31.38% and increasing the dissolved oxygen level in wastewater from 2.20 – 4.09 mg L^{-1}. This enhanced performance can be attributed to the polar nature of ABS, which allows for greater water absorption compared to polystyrene (PS) and low-density polyethylene (LDPE). The increased absorption capacity of ABS leads to a higher concentration of organic compounds near the TiO_2, promoting effective degradation through photocatalytic processes. These findings highlight the potential of TiO_2/ABS as efficient photocatalysts for wastewater treatment applications, underscoring the importance of material selection in optimizing photocatalytic performance. Future research should explore the scalability of these composites in real-world wastewater treatment scenarios and investigate the incorporation of other polar materials to further enhance photocatalytic efficiency.

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