ISSN-1996-918X

Pak. J. Anal. Environ. Chem. Vol. 24, No. 2 (2023) 167 – 175

http://doi.org/10.21743/pjaec/2023.12.05

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Photocatalytic Activity of Ag/TiO_2 Composite Synthesized Using Aqueous Plant Extract from *Mirabilis jalapa* for Degradation of Rhodamine B Under Visible Light

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Received 15 September 2022, Revised 16 August 2023, Accepted 17 December 2023

Abstract

In this study, aqueous plant extract from *Mirabilis jalapa* has been used for the synthesis of Ag/TiO_2 utilizing a green synthesis method. UV-Vis analysis revealed a Surface Plasmon Resonance (SPR) band at 461 nm, indicating that silver nanoparticles had formed. The anatase phase of TiO_2 and the presence of silver could be seen in the X-ray diffraction (XRD) patterns. Scanning Electron Microscope (SEM) images for Ag and TiO_2 show cuboid and irregular shapes, respectively. The photocatalytic activity of material (Ag/TiO_2) was analyzed in the degradation of Rhodamine B under visible light irradiation with various concentrations of silver that were labelled as PT (pure TiO_2), Ag1T, Ag2T, Ag3T, and Ag4T. The photocatalytic activity indicated that Ag2T has the highest catalytic activity among all catalysts after 240 minutes of reaction time. Furthermore, this study provides Ag/TiO_2 composite act as a promising candidate to resolve environmental problems.

Keyword: Ag/TiO_2, Green synthesis; *Mirabilis jalapa*, Photocatalytic activity, Rhodamine B

Introduction

Rhodamine B is a green or reddish-purple dye used in textiles, cosmetics, and industrial paper [1]. This compound is included in the toxic and hazardous compounds if consumed by people or animals which can irritate the skin, eyes, and respiratory systems [2]. In addition, it is dangerous to the environment due to difficult to reduce [3]. To solve this environment problem, some reports have mentioned that Rhodamine B could be degraded using a variety of methods, including photocatalytic, electrochemical, and ozonization [4-5].

Some materials could be used as catalysts to reduce Rhodamin B, such as TiO_2 due to its high surface area, ease of production, and less toxic. This material is also renowned as a semiconductor material and has been utilized in gas sensors, batteries, and mostly in photocatalyst activities [6]. However, as photocatalyst, TiO_2 was constrained by its high bandgap, which causes a narrow range of light absorption, particularly in visible light, a quick recombination rate which impacts low quantum yield, and its tiny surface area [7]. Furthermore, many researchers combined TiO_2 with other metals or non-metals materials to solve these problems, such as utilizing noble metals (Au, Ag) [8]. Silver is a prospective candidate to be used as a dopant to increase catalytic activity due to its ease of modification, high conductivity, and strong absorption capacity, [9-10].

There are several synthesis methods that have been used for the synthesis of nanoparticles or composites. Biosynthesis of materials by using plant extract has several advantages such as low temperature and toxicity. One of the plants which can be used is *Mirabilis jalapa* which is a plant that has been used as an herbal remedy and is native to tropical regions [11]. In earlier research, leaf extract from the *Mirabilis jalapa* plant was used to synthesise monometallic and bimetallic nanoparticles [12]. Our research also showed that a plant extract from the *Mirabilis jalapa* plant could be utilized as a reducing agent to create silver nanoparticles and that it also had potent antibacterial properties and a sizable surface area [13]. To the best of our knowledge, there is no report about the synthesis Ag/TiO_2 using *Mirabilis jalapa* plant extract and their photocatalytic activity against Rhodamine B. The objective of this work was to synthesis the composite of Ag/TiO_2 by an environmentally friendly method utilizing the green synthesis and aqueous plant extract from *Mirabilis jalapa*. Assessment of Ag/TiO_2 photocatalytic activity for the degradation of Rhodamine B was conducted under visible light irradiation. A schematic representation of the photocatalytic activity of Ag/TiO_2 composite synthesized using aqueous plant extract from *Mirabilis jalapa* for degradation of Rhodamine B under visible light irradiation is described in Fig. 1.

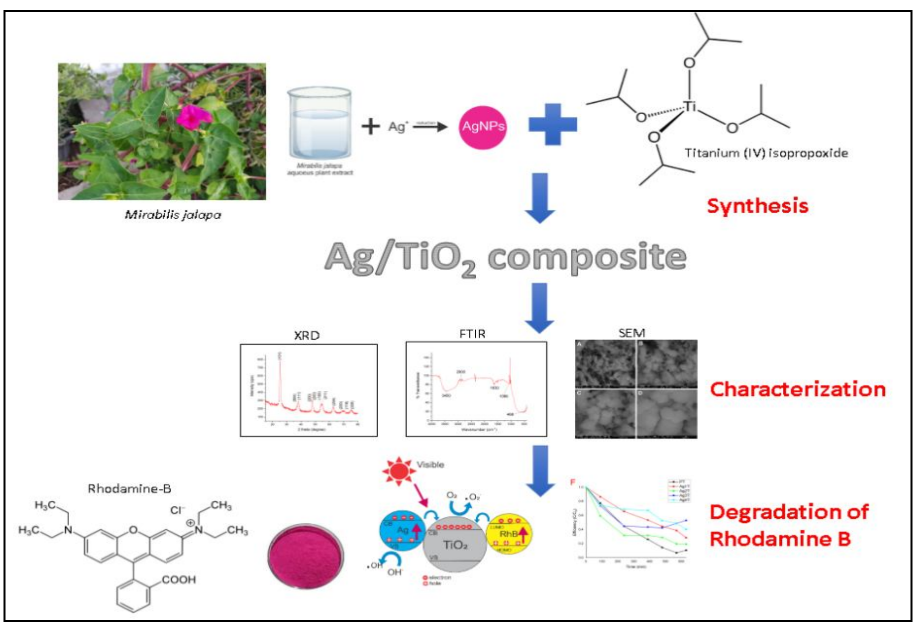

Figure 1. **Schematic representation of photocatalytic activity of Ag/TiO_2 composite synthesized using aqueous plant extract from Mirabilis jalapa for degradation of rhodamine B under visible light**

Experimental Section

Collection of Mirabilis jalapa Aqueous Plant Extract

Fresh plants were procured at Depok, Jawa Barat, Indonesia (Fig. 2). Samples were brought in, cleaned with distilled water to remove dust, and then allowed to air dry for 10 days. The dried plant was then ground into a fine powder after drying, and 20 g of the powder was extracted using 100 mL of distilled water. Then, the crude extract was filtered using Whatman No. 41 filter paper.

Figure 2. **Typical of *Mirabilis jalapa* plant (snapped in Depok, West Java)**

Green Synthesis and Characterization Ag/TiO₂ using Mirabilis jalapa Plant Extract

The precursor solution in this procedure was made by combining 5 mL titanium (IV) isopropoxide (TTIP) with 50 mL of ethanol over the course of an hour. Under constant stirring for one hour, 0.5 mL of $AgNO_3$ at four different concentrations (1 mM (Ag1T), 5 mM (Ag2T), 10 mM (Ag3T), and 20 mM (Ag4T)) was added to this solution with 30 mL of *Mirabilis jalapa* plant extract. The mixture was first calcined at 110 ^oC for 1 h, and then at 200 ^oC for the same time. The obtained materials (white powder) were characterized using XRD (Shimadzu X-ray Diffractometer 7000), FTIR (Shimadzu IRTracer-100), and SEM (Model JSM 6390LV).

Photocatalytic Measurements

Percent Degradation of Rhodamine B using Ag/TiO_2 visible light irradiation (150 W) was calculated. Rhodamine B (8 mg/L) in 250 mL aqueous solution and catalyst powder were combined. Then the mixture was irradiated using a visible light lamp for 90, 240, 390, 480, 570, and 630 min, respectively. UV-Vis spectrophotometer was used to analyze the absorption of Rhodamin B (PG Instrument T80+). Using the equation below, the photodegradation efficiency was calculated:

$$\text{Photocatalytic efficiency} = C/ C_o \ [14]$$

where, C_o for rhodamine B absorbance without exposure to visible light, and C for rhodamine B absorbance with exposure to visible light over a given period of time.

Results and Discussion

Characterization of Ag/TiO_2 Composite

For the synthesis process of Ag/TiO_2, plant extract from *Mirabilis jalapa* served as a reducing and stabilizing agent. Using UV-Vis spectrometer, the growth of silver nanoparticles (AgNPs) was shown in Fig. 3. AgNPs were generated and it was confirmed the SPR band at 461 nm which showed that there was no absorption prior to the addition of the extract plant. A typical AgNPs SPR band was seen around 390-530 nm [15]. An illustration of AgNPs mechanism can be seen in Fig. 4 where the color of the $AgNO_3$

solution changed from colorless to green-brownish after the addition of *Mirabilis jalapa* extract plant. This color shift indicated the reduction of Ag^{+} to Ag°.

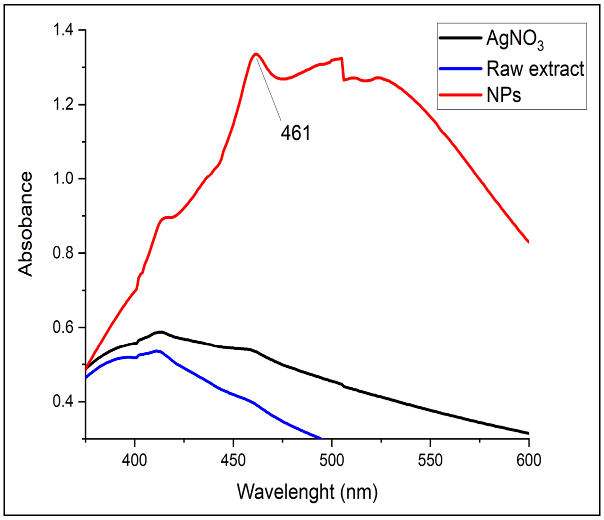

Figure 3. **UV-Vis spectra of AgNPs with SPR band at 460 nm**

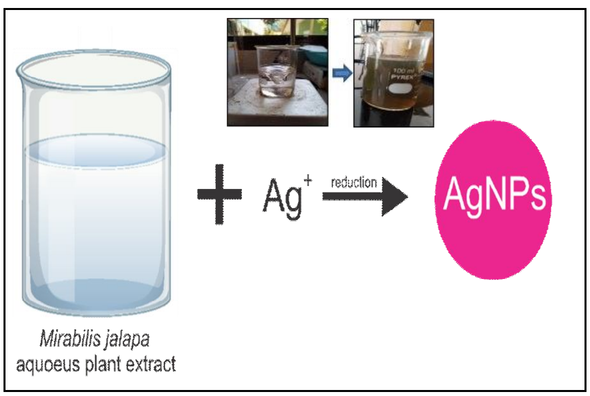

Figure 4. **Illustration picture for the AgNPs formation using *Mirabilis jalapa* aqueous plant extract**

Figure 5 exhibited an Ag/TiO_2 XRD pattern with diffraction peaks. The XRD pattern shows the anatase phase of TiO_2 with 2 theta values of 25.50°, 37.8°, 48.1°, and 62.8° (JCPDS No. 211272). The presence of silver was indicated by the 2 theta of 38.1°, 44.3°, 64.1°, and 77.4° (JCPDS No. 040783) [16]. Furthermore, Fig. 6 displays FTIR spectra which analyzed functional groups of material. The peaks at 2900 cm^{-1} and 3450 cm^{-1} corresponded to the vibration of the -CH and -OH, respectively while the peak at 1630 cm^{-1} is the typical vibration of alkenes. The Ti-O-Ti stretching bond was identified in the 468 cm^{-1} band. Fig. 7 shows the Ag/TiO_2 SEM images. According to the images, there were irregular shapes and cuboid shapes for TiO_2 and silver, respectively, and the distribution of titanium and silver was also not uniform. To determine the size of Ag/TiO_2, SEM images from the randomly chosen area were analyzed by using ImageJ software with up to 100 particles and analyzed. From that analysis, the size of Ag/TiO_2 particles had a majority between 400 to 500 nm (Fig. 8).

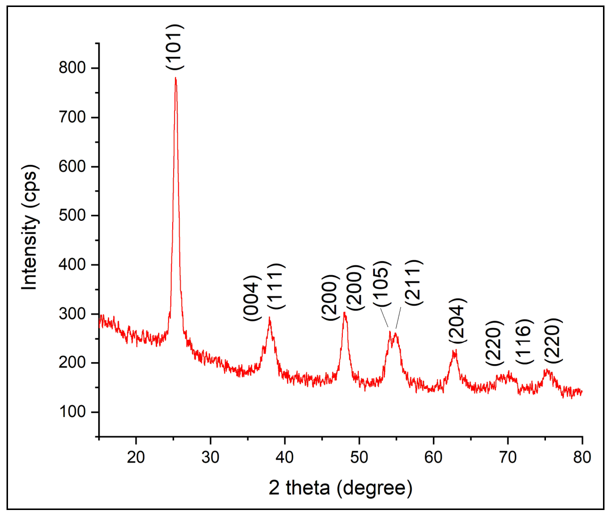

Figure 5. **XRD patterns of Ag/TiO_2**

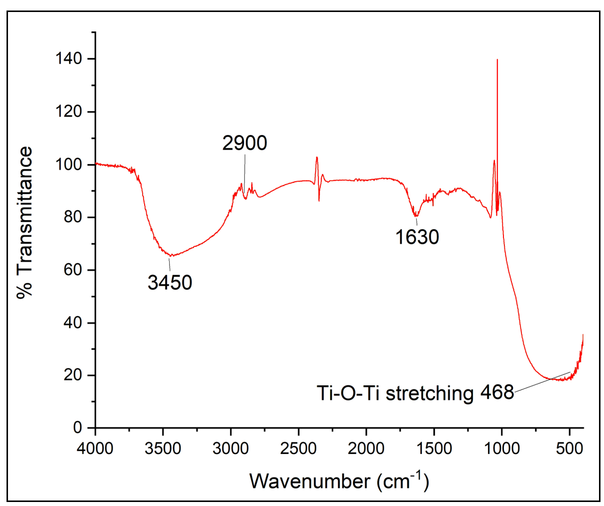

Figure 6. **FTIR spectra of Ag/TiO_2**

(a)

(b)

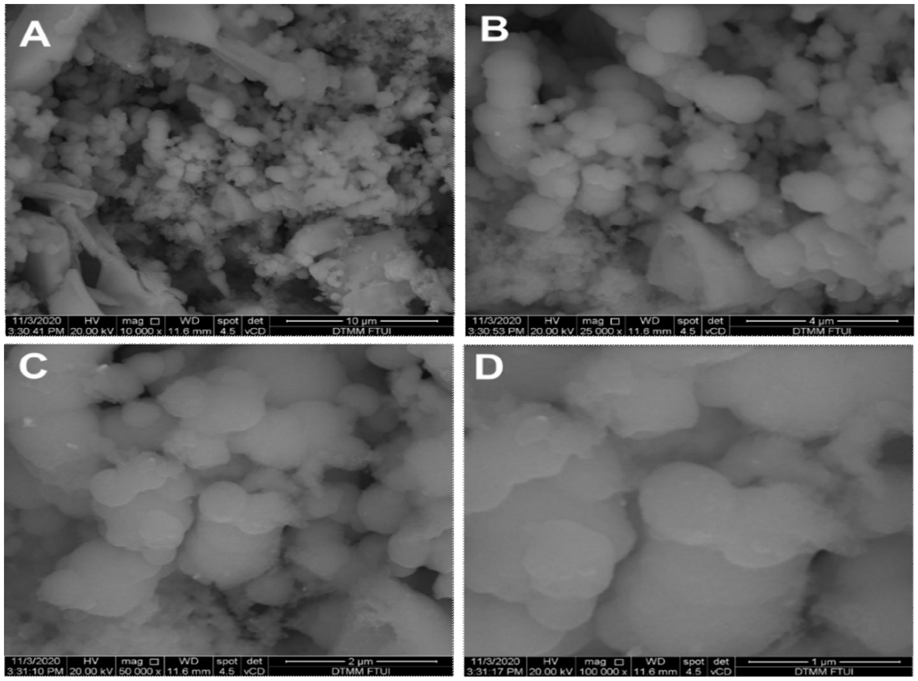

Figure 7. **SEM images of Ag/TiO_2**

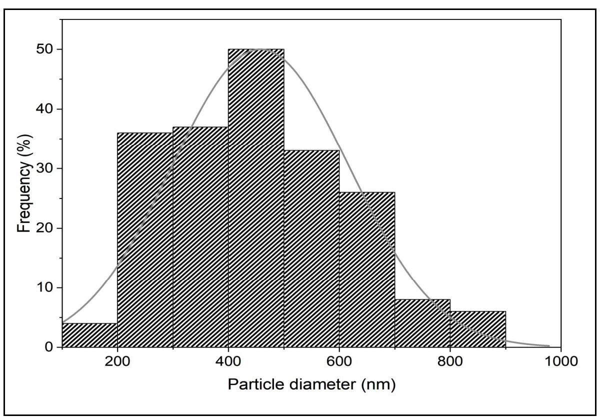

Figure 8. **Particle size distribution of Ag/TiO_2**

Application of Ag/TiO_2 for Photodegradation Rhodamine-B

Rhodamine B is a common organic dye in the paper and cosmetics industries. Rhodamine B could be degraded using some photocatalyst materials, such as Ag/TiO_2 composite. Fig. 9 shows a mechanism of Rhodamine B photodegradation utilizing an Ag/TiO_2 composite. Silver can influence the photodegradation, operate as a $(e^- + h^+)$ trap, and change the pace at which $(e^- + h^+)$ pair recombination occurs in response:

$$RhB + hv \rightarrow RhB^*$$
$$Ag\text{-}TiO_2 + RhB^* \rightarrow Ag\text{-}TiO_2\ (e^-) + \cdot RhB^+$$
$$TiO_2\text{-}Ag\ (e^-) + O_2 \rightarrow TiO_2\text{-}Ag + \cdot O_2^- [17]$$
$$\cdot O_2^- + H_2O \rightarrow OH^- + H_2O\cdot [18]$$
$$OH^- + h^+ \rightarrow \cdot OH\ [19]$$
$$\cdot OH + \text{organic pollutant} \rightarrow \text{photodegradation products}\ [20]$$

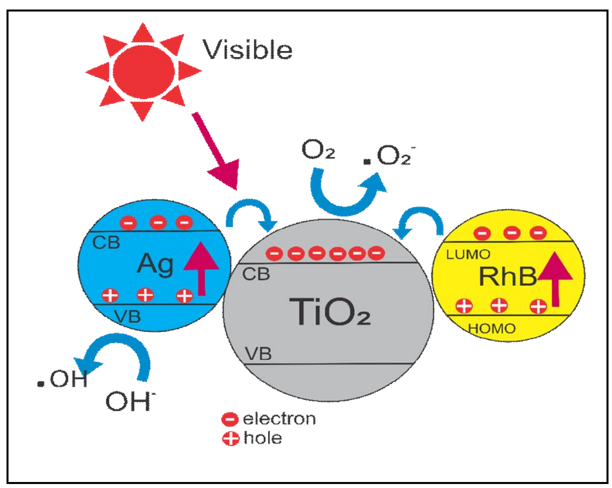

Figure 9. **Schematic diagram mechanism for rhodamine-B using Ag/TiO_2 under visible light radiation**

Under visible light irradiation, the photocatalytic activities of Ag/TiO_2 and pure

TiO_2 (PT) were compared. Rhodamine B solution was added with a certain amount of TiO_2 and various concentrations of silver, and the photocatalytic activities were determined. By examining the degradation of Rhodamine B, the catalytic activity of PT, Ag1T, Ag2T, Ag3T, and Ag4T was investigated. A specific amount of the solution was collected during the reaction to determine the reduced concentration of Rhodamine B. Fig. 10 shows characteristic peak of Rhodamine B at 550 nm was utilized to demonstrate how the sample's absorbance decreased with increasing exposure time. Except for the PT photocatalyst, the major absorption peak clearly shifts to the blue from 550 to 498 nm with increasing reaction time. Rhodamine B self-degradation's data, demonstrate low degradation in the absence of a photocatalyst, confirming that the degradation process may have been caused by the photocatalyst material.

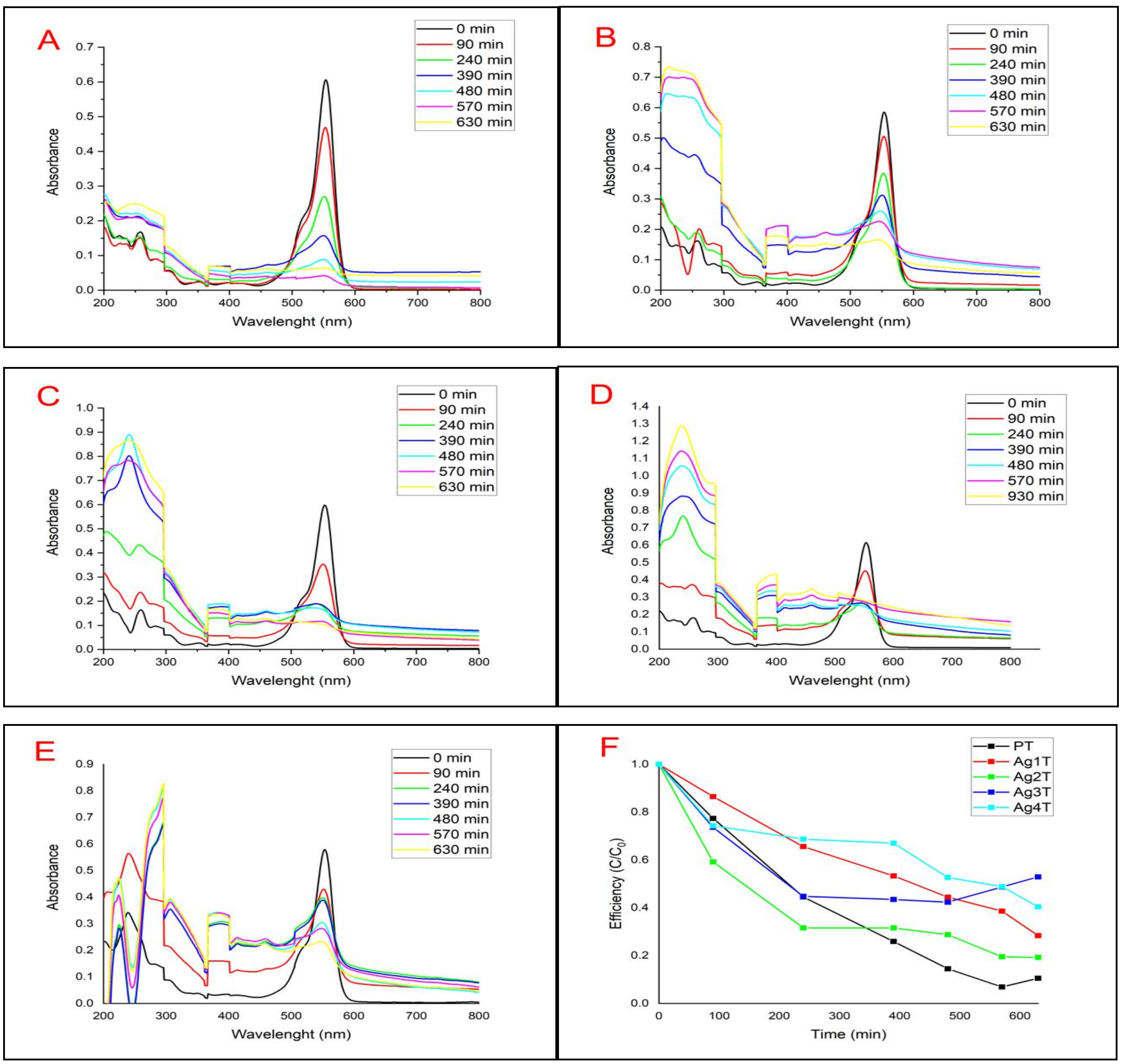

Figure 10. **UV–vis spectrum changes and photocatalytic degradation efficiency curves of RhB under visible light (A); PT; (B) Ag1T; (C) Ag2T; (D) Ag3T; (E) Ag4T; (F) photocatalytic degradation efficiency of RhB corresponding to (A), (B), (C), (D) and (E), respectively**

Table 1. **Related samples and catalysts with their performance.**

Catalyst	Dosage	Time (min)	Light source	Degradation (%)	Reference
Ag/TiO_2	250 mL (8 ppm)	240	Visible light (150 W)	67	This work
$C/F\text{-}Ag/TiO_2$	100 mL (10 ppm)	240	Visible light (150 W)	84.2	[21]
Ag/TiO_2	100 mL (0.02 mM)	90	Sunlight	98.63	[22]
Ag/TiO_2	400 mL (0.025 mM)	30	Visible light (300 W)	-	[23]
Ag/TiO_2	100 mL (not mentioned)	-	UV light (not mentioned)	99	[24]
Ag/TiO_2	20 mL (10 ppm)	180	Visible light (350 W)	91.4	[25]
$g\text{-}C_3N_4\text{-}Ag/TiO_2$	120 mL (10 ppm)	30	Visible light (300 W)	92.82	[26]
Ag/TiO_2	100 mL (10 ppm)	150	Visible light (150 W)	96.8	[27]
Ag/TiO_2	150 mL (4 ppm)	330	Visible light (500 W)	95	[28]
Ag/TiO_2	120 mL (10 ppm)	60	UV light (18 W)	-	[29]
Ag/TiO_2	50 mL (not mentioned)	120	UV light (not mentioned)	More than 90	[30]
Ag/TiO_2 nanofiber	25 mL (10 ppm)	180	Visible light (40 W)	-	[31]

The photodegradation efficiency was demonstrated in Figure 9 (F) which utilized Ag/TiO_2 as a photocatalyst. The results show that Ag2T, which was synthesized with a 5 mM concentration of silver, had the maximum catalytic activity compared to the other catalysts for the first 240 min. However, as the amount of Ag increased, the catalytic activity gradually reduced, particularly for Ag3T and Ag4T. This was due to much $AgNO_3$ would interfere with the light absorbance. For further evaluation, we have compared rhodamine-B degradation with relevant photocatalysts (Table 1).

Conclusion

In conclusion, using the aqueous plant extract from *Mirabilis jalapa*, we were able to successfully synthesize the Ag/TiO_2 composite using a green synthesis method. Rhodamine B degradation under visible light irradiation was used to examine the photocatalytic activity of Ag/TiO_2. Rhodamine B photodegradation has shown that the activity of each catalyst may be changed by altering the amount of Ag. In addition, Ag2T had superior photocatalytic performance compared to other catalysts for 240 min with up to 67% efficiency.

Conflict of Interest

The authors declare no conflicts of interest.

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