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TiO_2-N/Polystyrene photocatalyst-combined Corona Plasma Treatment for Methylene Blue Degradation

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ABSTRACT. This study employed the corona plasma method combined with TiO_2-N/PS photocatalyst to degrade dye pollutants. The plasma reactor consisted of two needle-shaped stainless steel electrodes connected to a voltage of 8 kV. Methylene blue (MB) solution was used as a model pollutant with varied initial concentrations of 10, 50, and 100 ppm. The degradation efficiency was evaluated based on the absorbance of the degraded MB solution measured using a UV-Vis spectrophotometer. The results exhibited that the longer plasma treatment duration caused the absorbance value of the degraded MB to decrease, and then the MB degradation efficiency increased. MB-10 demonstrated a maximum degradation efficiency of 99.40% after plasma treatment for 30 minutes. Meanwhile, MB-50 and MB-100 reached maximum degradation efficiencies of 95.29 and 86.55% efficiency after plasma treatment for 60 minutes. The greater initial MB concentration caused the longer degradation process. Furthermore, the results revealed no increase in degradation efficiency due to the addition of TiO_2-N/PS photocatalyst into the plasma treatment. The degradation efficiencies of MB-10, MB-50, and MB-100 under TiO_2-N/PS-combined plasma treatment for 30 min were 94.48, 81.57, and 5.22%, respectively. This suggests the possibility that the UV light generated during the plasma process cannot activate the TiO_2-N/PS photocatalyst.

INTRODUCTION

Langmuir and Tonks define plasma as a combination of electrons, positive ions, negative ions, and free radicals. The combination of negative electrons and positive ions causes different properties from gases, so this phase is usually called plasma. Plasma includes the fourth phase after solid, liquid, and gas. It is formed due to the presence of high electrical voltage from two electrodes placed facing each other. Normally, air does not conduct electricity or is usually called an insulator. However, if the two electrodes are given a high voltage of 10 kV, it will show conductor properties in the air. This leads to the phenomenon of electrical breakdown, where electrical voltage begins to flow along with the air conductor's properties, called an electrical discharge. If the electric voltage applied to the electrode is greater, the free electrons and ions formed will be greater. Thus, it can be concluded that plasma is a collection of free ions, free electrons, and free atoms (Nur, 2011).

Plasma technology can be employed to treat organic pollutants in wastewater. It involves several electrical discharge processes with specific chemical and physical characteristics (Chen *et al.*, 2002). The electrical discharge processes will produce active species that can remove pollutants in wastewater (Harhausen *et al.*, 2011). The reaction between active species and the compounds in wastewater induces a chemical response that can degrade the harmful pollutants (Hadiwidodo *et al.*, 2009). Active species that play a role in degrading compounds in liquid waste include hydroxyl radicals (•OH) and hydrogen peroxide (H_2O_2). Nevertheless, waste degradation efficiency is influenced by several factors, including the reactor system, voltage, electrodes, solution pH, temperature, input gas, and conductivity (Anggraini *et al.*, 2018; Chanan *et al.*, 2018; Kusumandari *et al.*,

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2022; Kusumandari *et al*., 2022; Rasyidah *et al*., 2018; Wulandari *et al*., 2019).

Besides plasma technology, one alternative method currently being developed to remove pollutants in waste is the photocatalysis method. The principle of this method is the degradation of pollutants using semiconductor material activated with the help of light rays (Aditya *et al*., 2012). Photocatalysis using TiO_2 material is an efficient method for degrading organic compounds contained in liquid waste (Riyani *et al*., 2012). However, the wide bandgap energy of TiO_2 limits the light spectrum that can activate it. Modifying TiO_2 by adding dopant ions such as Nitrogen (N) can reduce its band gap energy so the absorption spectrum becomes wider (Pratama *et al*., 2012). Generally, TiO_2 doped N uses Polystyrene (PS) polymer supporting material, aiming to maintain the density of the photocatalyst so that it remains floating on the water surface, which eases the use of the photocatalyst and does not create new secondary pollutants (Ata *et al*., 2017).

The application of the plasma method combined with TiO_2 photocatalyst for the degradation of methylene blue (MB) dye has been carried out using a reactor in the form of a Cu wire electrode and stainless steel mesh with a 5 kV AC voltage source. 25 mL of 100 ppm MB was treated under plasma for 0, 2, 4, 6, and 8 minutes. The results showed that the formation of active species from plasma and the role of the TiO_2 catalyst effectively increased the efficiency of MB degradation, indicated by the color of the solution becoming clearer (Zuhaela *et al*., 2021). Meanwhile, other research using TiO_2-N/PS photocatalyst at 10 ppm MB showed % degradation efficiency of 82.94% (Ayuningtyas, 2022). Unlike prior research, this study reported the application of a single electrode-corona plasma and TiO_2-N/PS photocatalysts-combined plasma treatment for MB degradation. Further, this study also investigated the effects of varied initial MB concentrations and plasma treatment durations on MB degradation efficiency.

RESEARCH METHODS

Figure 1 shows a schematic of the plasma reactor circuit and the MB degradation process under a single plasma and TiO_2-N/PS photocatalyst-combined plasma treatments. The plasma reactor in this study used two needle-shaped stainless steel electrodes with a diameter of 2 mm. The electrodes were placed parallel, 3 cm apart, and 2 mm above the solution's surface, connected to an 8 kV AC high-voltage source.

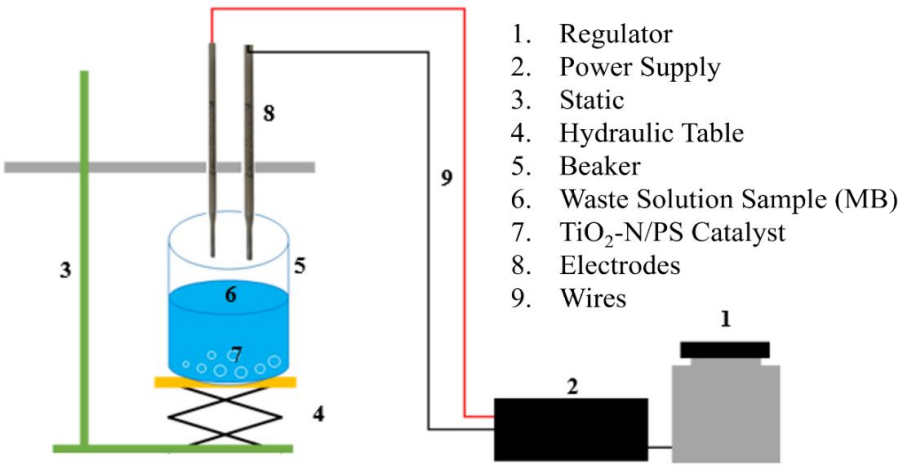

Figure 1. Schematic diagram of a plasma reactor for the MB degradation process.

As much as 50 ml of MB solution was used for the testing with various initial concentrations of 10, 50, and 100 ppm (later called MB-10, MB-50, and MB-100 for each sample). Approximately 0.7 grams of TiO_2-N/PS photocatalyst was added to each sample. Here, the duration of plasma treatment was varied: 0, 10, 20, and 30 minutes for MB-10 and 0, 15, 30, 45, and 60 minutes for MB-50 and MB-100. The absorbance of the degraded MB solution before and after plasma treatment was measured using a UV-Vis spectrophotometer. Then, the degradation efficiency (*%Eff*) value was calculated using Equation 1.

$$\%Eff = \frac{(A_0 - A)}{A_0} \times 100\ \% \quad (1)$$

A_0 and A are the absorbances of methylene blue before and after plasma treatment, respectively.

RESULTS AND DISCUSSION

Effects of Plasma Treatment Durations on Absorbance of the Degraded MB without TiO_2-N/PS Nanoparticle Photocatalyst

The effects of plasma treatment durations on the absorbance of the degraded MB solutions are shown in Figure 2. Figure 2 (a) displays the absorbance curves of the degraded MB-10 without and with plasma treatment for 10, 20, and 30 minutes. The maximum absorbance peak is at a wavelength of about 663.5 nm. This graph demonstrates that the absorbance declined sharply after plasma treatment for 10 min. The minimum absorbance value was reached after plasma treatment for 30 min.

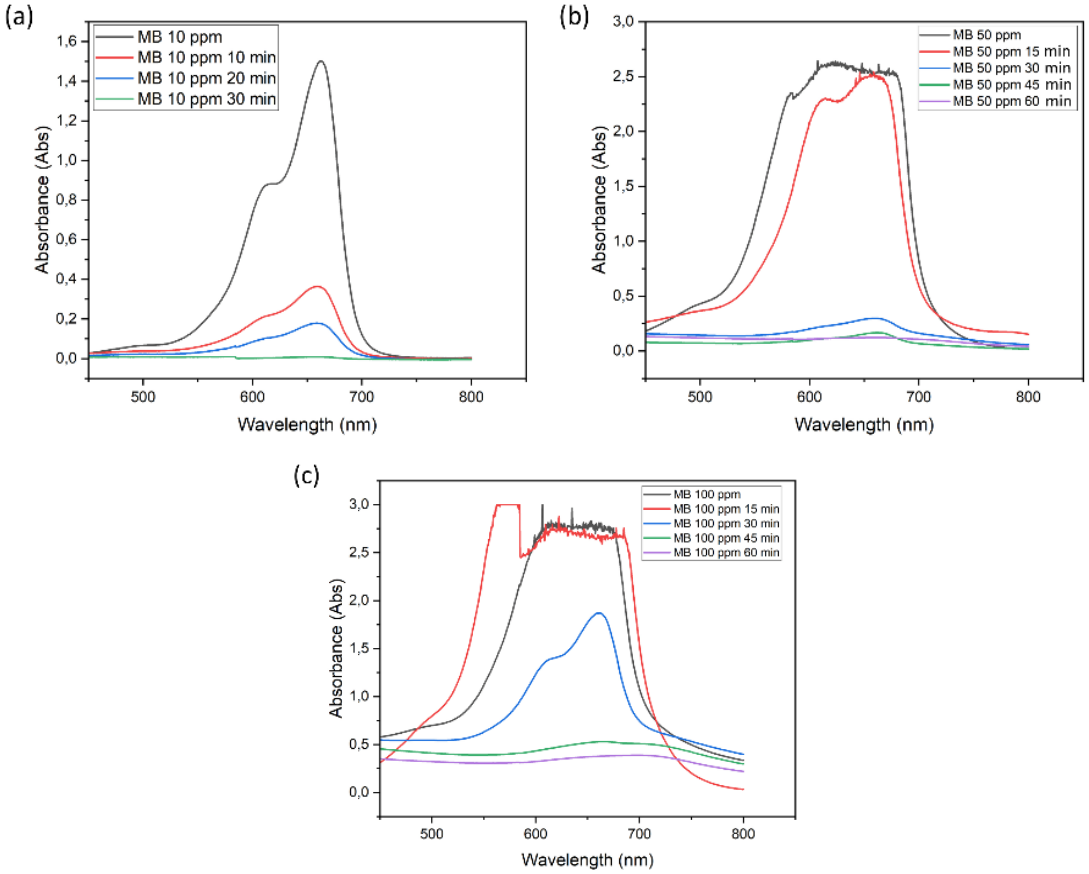

Figure 2. Absorbance curves of MB-10 (a), MB-50 (b), and MB-100 (c) under plasma treatment for various durations.

Figures 2 (b) and 2 (c) show graphs of absorbance values for MB-50 and MB-100 with plasma treatment for 15, 20, 45, and 60 minutes. The duration was longer than that used at MB-10 because it was applied to determine changes in absorbance at greater initial concentrations of the solutions. These graphs demonstrate that MB-50 and MB-100 reached the minimum absorbance value at 60 min of plasma treatment.

Effects of Plasma Treatment Durations on Degraded MB Absorbance with the Addition of TiO_2-N/PS Nanoparticle Photocatalyst

Figure 3 exhibits the absorbance curves of MB-10, MB-50, and MB-100 with TiO_2-N/PS-combined plasma treatment for various durations. Figure 3(a) shows the absorbance values of the degraded MB-10 with TiO_2-N/PS-combined plasma treatment for 10, 20, and 30 minutes. The results show that MB-10 has a minimum absorbance value after treatment for 30 minutes. Meanwhile, Figures 3 (b) and 3 (c) show graphs of the absorbance of degraded MB-50 and MB-100 with TiO_2-N/PS-combined plasma treatment for 15, 30, 45, and 60 minutes. It exhibits that MB-50 and MB-100 reached the minimum absorbance value at the treatment of 60 min.

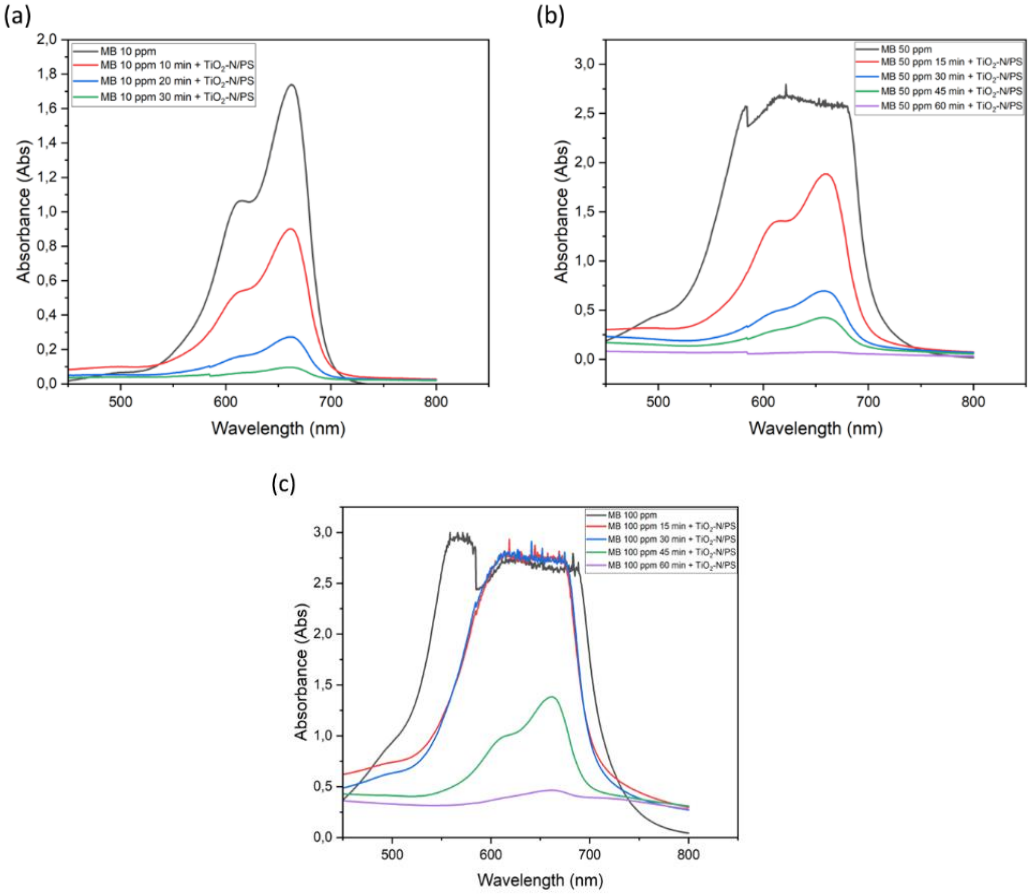

Figure 3. Absorbance curves of MB-10 (a), MB-50 (b), and MB-100 (c) with TiO_2-N/PS-combined plasma treatment for various durations.

MB Degradation Efficiency

MB degradation is characterized by decreased absorbance values due to the reaction of active species from plasma degrading harmful species. From the absorbance value, the degradation efficiency of each sample can be calculated using Equation 1. The effect of initial MB concentrations on the degradation efficiency values using only plasma and TiO_2-N/PS-combined plasma treatment can be seen in Figure 4. It shows that the longer plasma durations induce a higher degradation efficiency. This is due to the increasing number of active species produced by plasma reacting with MB. MB solutions with higher concentrations require a longer time for degradation. The MB-10 achieved a maximum degradation efficiency of 99.40% after plasma treatment for 30 minutes. Meanwhile, MB-50 and MB-100 solutions reached maximum efficiencies of 95.29% and 86.55%, respectively, after 60 minutes of plasma treatment. Besides inducing active species such as OH radicals and ozone, plasma generates UV light discharges. These charges are hoped to activate the TiO_2-N/PS photocatalyst, thereby accelerating the degradation process. However, based on Figure 4, it is known that with the addition of TiO_2-N/PS, the degradation efficiency of MB did not change significantly when compared with a single plasma treatment. This indicates that the UV light from the plasma was ineffective in exciting the electrons in TiO_2 and helping the catalyst process.

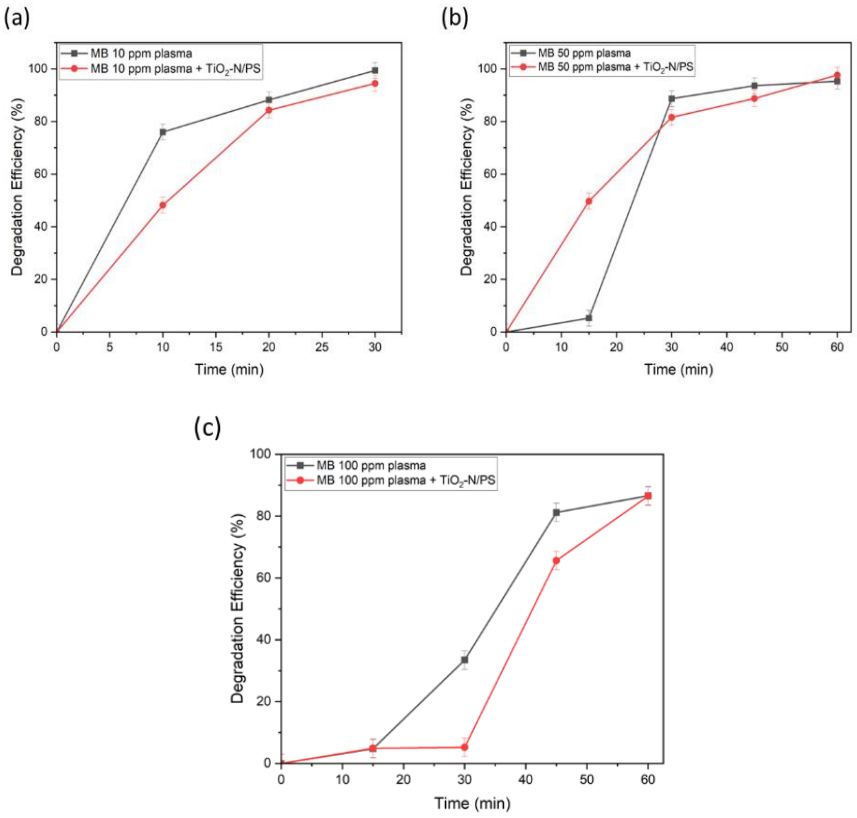

Figure 4. Degradation efficiencies of (a) MB-10, (b) MB-50, and (c) MB-100 with TiO_2-N/PS-combined plasma treatment for various durations.

Figure 5 presents the degradation efficiencies of MB-10, MB-50, and MB-100 with a single plasma and TiO_2-N/PS-combined plasma treatment for 30 min. The results showed that at 30 minutes of single plasma treatment, the degradation efficiency of MB-10, MB-50, and MB-100 was 99.40%, 88.67%, and 33.44%, respectively. It revealed that the greater initial MB concentration causes a lower degradation efficiency for the same plasma treatment duration. This is because the higher initial MB concentration causes the active species to require a long path and a long time to degrade dye pollutants completely, meaning the degradation rate becomes smaller.

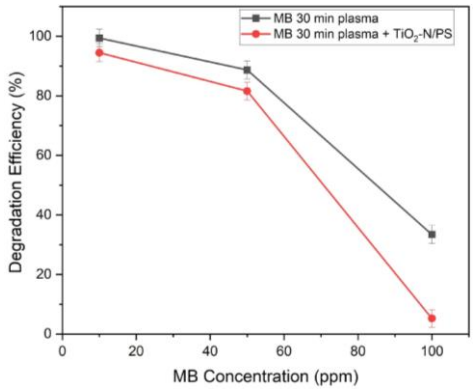

Figure 5. The degradation efficiency of MB-10, MB-50, and MB-100 with a single plasma and TiO_2-N/PS-combined plasma treatment for 30 min.

Meanwhile, at 30 minutes of TiO_2-N/PS photocatalyst-combined plasma treatment, the degradation efficiencies of MB-10, MB-50, and MB-100 were 94.48%, 81.57%, and 5.22%, respectively. It can be said that combining TiO_2-N/PS photocatalyst into the plasma method was ineffective in improving the efficiency of dye degradation. It might be because the UV light produced from the plasma is not yet effective in activating the

TiO_2-N/PS photocatalyst ultimately. Plasma discharge hitting TiO_2-N/PS on the surface may also cause some of the PS to be released, causing new pollutants and hindering the degradation process. In this research, corona discharge was produced using free air as a gas source. High voltage in the system creates a high electric field and accelerates the electrons so that collisions occur, causing the ionization of neutral molecules. Various plasma species, including electrons, ions, and high-energy radicals, are generated during this process. This study investigated the species produced in the gas phase during plasma processing using an optical electron spectrometer (OES), as previously reported (Qusnudin *et al.*, 2021). The main species detected were hydroxyl radicals (•OH), Nitrogen (N_2), nitric oxide (NO), and oxygen radicals at wavelengths of 306.068–315.874, 330.796–337.317, 380.1, and 780–790 nm, respectively. The reaction between oxygen radicals and O_2 produces O_3. Derived species, such as •OH, are produced through the reaction between O_3 and H_2O. Furthermore, these active species oxidize wastewater and cause degradation. Equations (2) – (7) present the formation and degradation processes by the species (Bansode *et al.*, 2017; Huang *et al.*, 2010).

$$e + O_2 \rightarrow e + 2\,O^* \quad (2)$$

$$O^* + O_2 \rightarrow O_3 \quad (3)$$

$$NO_2 + H_2O \rightarrow NO_3^- + 2H^+ \quad (4)$$

$$3\,O_3 + H_2O \rightarrow 2\,\bullet OH + 4O_2 \quad (5)$$

$$O_3 + M\ (\text{organic molecules}) \rightarrow O_3^- + M^+ \rightarrow \text{decomposed products} \quad (6)$$

$$\bullet OH + M \rightarrow \text{decomposed products} \quad (7)$$

Furthermore, UV radiation and shock waves are also generated during the plasma process. Therefore, the reaction between O_3 and H_2O supported by UV light (emitted during plasma discharge) induces the formation of H_2O_2. It can then be separated further by UV light, producing •OH, $\bullet HO_2$, O^{2-}, and O_2, as stated in Equations (8) – (13) (Reddy *et al.*, 2013; Jiang *et al.*, 2014).

$$O_3 + h\upsilon \rightarrow O_2 + O \quad (8)$$

$$O_3 + H_2O^+ \rightarrow H_2O_2 + O_2 \quad (9)$$

$$2O_3 + H_2O_2^+ \rightarrow 2\,\bullet OH + 3O_2 \quad (10)$$

$$\bullet OH + H_2O_2 \rightarrow H_2O + \bullet HO_2 \quad (11)$$

$$H_2O_2 + O_3 \rightarrow \bullet OH + \bullet HO_2 \quad (12)$$

$$O_3 + \bullet HO_2 \rightarrow \bullet OH + O_2 + O_2^- \quad (13)$$

Moreover, these species can mineralize pollutants, resulting in less decomposition, producing decomposed small molecules and minerals such as O_2 and $(NO_3)^-$. The UV light produced during the plasma process is also expected to activate the TiO_2-N/PS photocatalyst, producing free electrons that trigger the oxidation and reduction processes to produce active species such as •OH, O^{2-}, and others. As a result of the degradation process, the solution would appear more transparent visually, as shown in Figure 6. The figure presents the color changes in MB-50 degraded using a single plasma and TiO_2-N/PS-combined plasma treatments for the same duration. It can be seen that the solution color became clearer with more prolonged plasma treatment. However, for TiO_2-N/PS-combined plasma treatment, the color change was slower, meaning the degradation rate was lower.

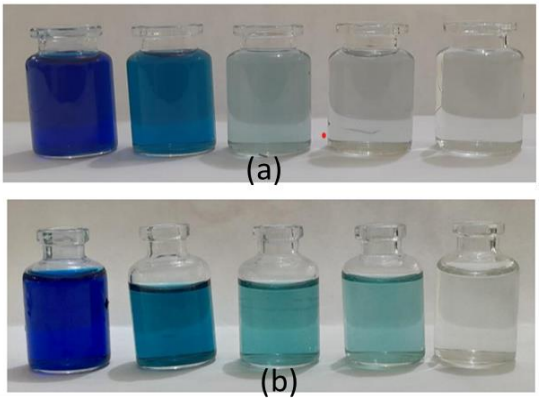

Figure 6. The color change of MB-50 during the degradation process using (a) a single plasma and (b) TiO_2-N/PS photocatalyst-combined plasma treatments.

CONCLUSION

The corona plasma method was successfully used in the MB dye degradation process. The longer plasma treatment duration induced the greater MB degradation efficiency. MB-10 (initial MB concentration of 10 ppm) obtained the maximum degradation efficiency of 99.40% after plasma treatment for 30 minutes. The greater initial MB concentration lowered the degradation rate for the same plasma treatment duration. Adding the TiO_2-N/PS photocatalyst material into the plasma treatment did not significantly affect the degradation efficiency. It could be possible that the UV light resulting from the plasma process could not activate the photocatalyst material. Therefore, further research needs to be conducted so that the use of photocatalysts combined with the plasma treatment can improve the effectiveness of the degradation process.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTION

AQ: Data curation and Wrote the Manuscript. KK: Conceptualization, Methodology. TES: Supervised the experiment and reviewed the manuscript. DD: review the manuscript. All authors agreed to the final version of this manuscript.

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