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The Effect of pH on the Eliminition of Dye Waste Using Combination of Photocatalytic and Electrocoagulation Methods

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ARTICLE INFO

Received 22/10/2022
revision 23/11/2023
accepted 27/11/2023
Available online 29/11/2023

ABSTRACT

The textile industry is proliferating, and the dye waste produced directly disposed into the environment can damage the environment. The dye waste can be degraded by an electrocoagulation process or using a photocatalyst. Electrocoagulation is a process of destabilizing a suspension so that it forms or flocs that are easily separated with the help of an electric current. Titania nanotube arrays are a commonly used photocatalyst. This catalyst is activated when exposed to light. The present study has investigated the impact of pH on integrating electrocoagulation and photocatalysis processes. From the research conducted, it was found that the best waste degradation electrocoagulation process was at pH 10 with a decrease in dye reduction of 67,72%; for the photocatalyst degradation process, the best results were at pH 10 with a decrease in dye reduction of 30,76%. The optimal conditions for combining photocatalysis and electrocoagulation were obtained at pH 10 with a reduction in dye waste of 71,6%.

Keywords: *Electrocoagulation, photocatalysts, TiO_2 Nanotobes, Dye*

1. INTRODUCTION

The current demand for textiles has caused the textile industry in Indonesia to grow quite rapidly. Textiles are something that is very closely related to everyday life [1]. The textile industry that operates produces waste that contains dyes. Suppose this dye is directly disposed into the environment into the environment, such as a river. In that case, the dye contained in it will make the color of the air turn cloudy so that sunlight cannot enter the riverbed, causing the essential ecosystem of the air that requires sunlight to be damaged [1,2]. In addition, this dye can poison living things in the river so that the existing plants and animals will die. As a result, the ecosystem in the river is disturbed. There are many ways to treat textile waste, including the Electrocoagulation method.

Electrocoagulation is collecting and collecting fine particles in the air using electrical energy. The basic principle of Electrocoagulation is to use reduction and oxidation (redox) reactions. In an electrocoagulation cell, oxidation occurs at the positive (+) electrode, namely the anode, and reduction occurs at the negative (-) cathode electrode. The components involved in Electrocoagulation are waste to be processed [3,4].

The Electrocoagulation process consists of three main processes: electrochemical, coagulation, and hydrodynamic, which aim to remove contaminants. In the electrocoagulation method, this solution's colloidal particles are electrically neutralized by producing a positive electric charge. Thus, the flocculation process occurs in solution by producing Fe^{3+}, Al^{3+}, or other metal cations (depending on the electrode material and the cathode anode). The

reduction in contamination during this process is due to the removal of suspended solids and molecular organic molecules in organic metal compounds. The Electrocoagulation process was chosen because it is environmentally friendly, energy-efficient, economical, and more suitable for automation. The Electrocoagulation method also makes it easier to deal with pollutants [4].

The application of Titanium dioxide (TiO_2) for the photodegradation of organic contaminants has attracted significant attention due to its unique and environmentally friendly characteristics. In addition, this option is attractive considering that TiO_2 has low cost, simple preparation, high capacity, and remarkable ability to degrade various volatile organic compounds (VOCs) pollutants [5]. In order to enhance the surface area of titanium dioxide (TiO2), many methods have been employed, such as morphological modifications resulting in the formation of nanorods [6,7] nanowires [8–10], and nanotubes [8,11–13]. Nanotubes are the most preferred TiO_2 morphology because their surface area is more significant than other morphologies and has better photocatalysis effectiveness [8,14,15]. The photocatalysis technique has the potential to be integrated with several additional methodologies, including ozone [16–18], zeolite incorporation [19–21], and Electrocoagulation [22–24].

Integrating the Electrocoagulation technique with photocatalysis has enhanced the efficiency of organic waste degradation. In order to achieve optimal qualification, it is necessary to conduct pH testing to assess the impact of its influence on the integration of the methods above. Therefore, this study tested the effect of pH on the combined process of photocatalysis and Electrocoagulation to eliminate methyl orange dye waste.

2. METHODOLOGY

Making TiO_2 nanotubes photocatalyst uses the anodization method using a 99.6% Ti plate measuring 4cm x 8cm with a thickness of 0.3 mm sanded until the surface is shiny. Then, wash the Ti plate with soapy water after using the chemical polishing/etching process with a solution containing 40% HF, 65% HNO_3, and aquadest in a 1: 3: 6 ratio for 2 minutes. Then, the Ti plate was dried at room temperature. In the anodization process, the solution is an electrolyte solution of 74.5% glycerol, 25% aquadest, and 0.5% NH_4F. The process is carried out at a voltage of 50V for 2 hours. After the anodization process is complete, the film formed on the surface of the plate is rinsed using aquadest. Then, stir the plate and calcinate the plate in a furnace at a temperature of 400° C for 3 hours.

After making the TiO_2 catalyst, an optimization was carried out to get the best results under operating conditions. In this stage, 10 ppm of methyl orange is inserted into the reactor sleeve. After that, illuminate it with a safe lamp for 2 hours. Sampling was conducted at 0, 15, 30, 45, 60, 90, and 120 minutes. This process was carried out at pH 5, 7, and 10. Before the optimization process:

- Photocatalyst/sensitizer is made by dipping the optimized TiO_2 catalyst into 0.1M $AgNO_3$ solution for 5 minutes.
- The plate then rinses with distilled water and dipping the plate into the In_2S_3 solution for 5 minutes.
- Dry the plate.

This dyeing process is done with one loop of silk. The variations of the sensitizer made are 5, 7, and 9 loops. After the TiO_2 nanotubes/$AgInS_2$ catalyst, an optimization process was formed to get the best results under operating conditions. In this stage, 10 ppm of methyl orange is first introduced into the reactor. Then, the catalyst was put into the old track and in the reactor. After that, illuminate it with a safe lamp for 2 hours. Sampling was conducted at 0, 15, 30, 45, 60, 90, and 120 minutes.

3. RESULTS AND DISCUSSION

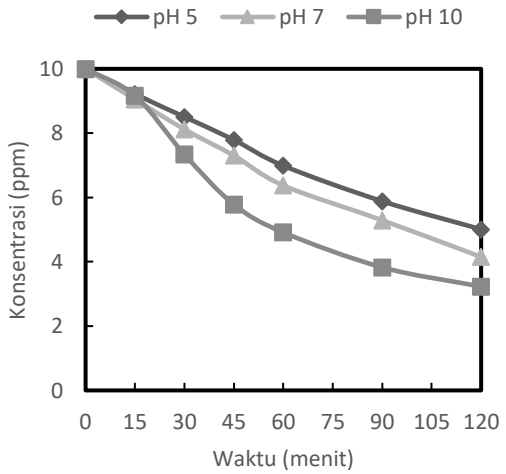
3.1. Effect of pH on Waste Decolorization in Electrocoagulation

The Electrocoagulation process is one of the waste treatment processes that combines electrochemical and coagulation processes. In this process, the anode acts as a releaser of active coagulants in the form of metal ions, while the cathode acts as a releaser of hydrogen gas due to the electrolysis reaction. The results obtained from the experiments that have been carried out are shown in Figure 1.

The pH level of the solution is a highly influential factor that significantly affects the outcomes of Electrocoagulation [25] The amount of pH will affect the results of the reactions that occur in the Electrocoagulation process. At acidic pH conditions, the reaction in Al ions with air will produce $Al(OH)_2$, H_2, and O2. At pH 7, conditions will produce $Al(OH)_3$, $Al(OH)_2$, and H_2. $Al(OH_3)$, H_2 and H_2O are formed at alkaline pH conditions.

The result of decolorization of methyl orange is smaller at acidic pH because $Al(OH)_3$ has not formed a coagulant. So, the decolorization process that occurs for methyl orange is not

good. When the coagulant $Al(OH)_3$ is formed at pH 10, the coagulant will form a methyl orange to form flocs. The floc that is formed will bind to each other; the larger floc will then be lifted to the surface with the help of the formed H_2 gas.



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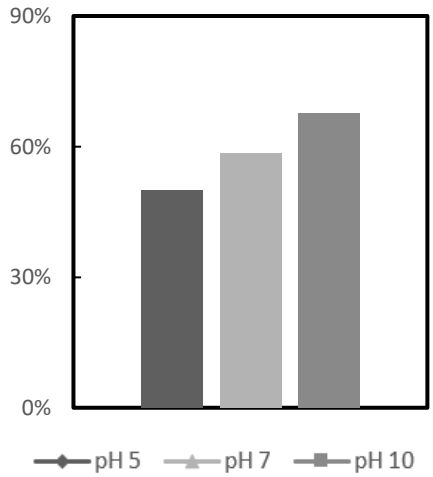

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Figure 1. Effect of pH on Decolorization of Methyl Orange Waste on Electrocoagulation. (1) Decrease in Methyl Orange Concentration, (2) Percent Decolorization of Methyl Orange.

The precipitate obtained from the Electrocoagulation process was separated and filtered using filter paper; at pH 5, a storage weight of 0,22 grams was obtained; at pH 7, a storage weight of 0,36 grams was obtained; and at pH 10, a storage weight of 0,49 grams was obtained.

3.2. Catalyst Characterization

The TiO_2 nanotube photocatalyst was formed by anodizing for 2 hours, where the Ti plate was the anode and Pt was the cathode. The electrolyte solution used is glycerol, which consists of 74,5% glycerol, 25% aquadest, and 0,5% NH_4F.

The viscosity of organic-based electrolyte solutions (such as glycerol and ethylene glycol) will affect the characteristics of the TiO_2 nanotubes formed. A thick electrolyte solution will form long and smooth TiO_2 nanotubes, while in an electrolyte solution that is not, uneven TiO_2 nanotubes will form [26].

The presence of fluorine ions also affects the anodization process. The concentration of fluorine ions will be directly proportional to the length of the nanotubes. When the concentration of fluorine ions in the solution is small (< 0,05% by weight), only an oxide layer is formed, and when the concentration of fluorine ions in the solution is high (>1% by weight) the oxide layer is not formed because when Ti^{4+} is formed, all react with fluorine ions then form $(TiF_6)^{2-}$ which is soluble. When there is sufficient fluoride ion, an oxide layer is formed, and the chemical dissolution occurs so that the formation of nanotubes can be observed. The morphology of TiO_2 nanotubes can be seen in Figure 3.

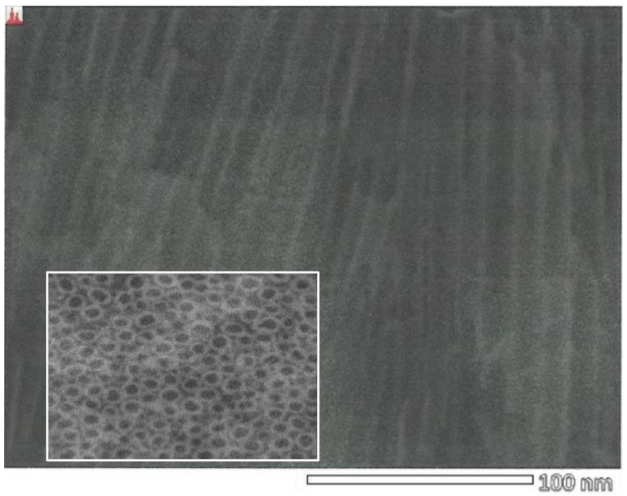


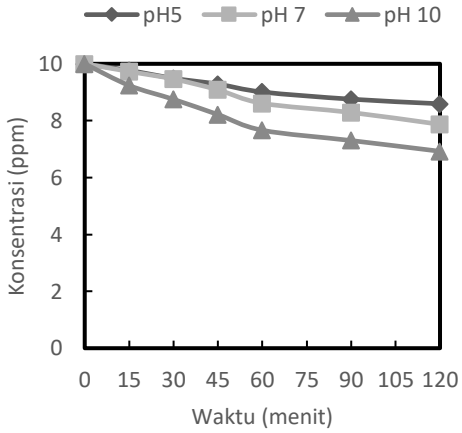
Figure 3. Photocatalyst morphology of TiO_2 nanotubes.

3.3. Effect of pH on Waste Degradation in Photocatalyst

When the TiO_2 catalyst is exposed to light, electrons will move from the valence band to the conduction band. In the conduction band, electrons are excited to produce e^-, leaving a hole (h^+) in the valence band. Then, the h^+ reacts with OH^-, which comes from the solvent and is a hydroxy radical ($\bullet OH$) with reactive properties to decompose the dye. The electrons in the conduction band will react with dissolved oxygen to form a superoxide (O^2)

which will then form hydroxyl radicals. This hydroxyl radical with a high oxidation potential value will degrade methyl orange dye [27,28].

The initiation by the hydroxyl radicals on the leading group of the methyl orange compound then produces phenyl and phenoxy radicals. Then, the presence of dissolved oxygen causes the abstraction of hydrogen ions and their radicals, namely the phenyl radicals. The next step produces nitrogen gas, followed by reducing the benzene ring radicals to simpler aromatic compounds. On the other hand, phenoxy radical groups are oxidized by hydroxy radicals to benzene groups [29]. The results of the degradation of methyl orange with this photocatalyst process can be seen in Figure 4.



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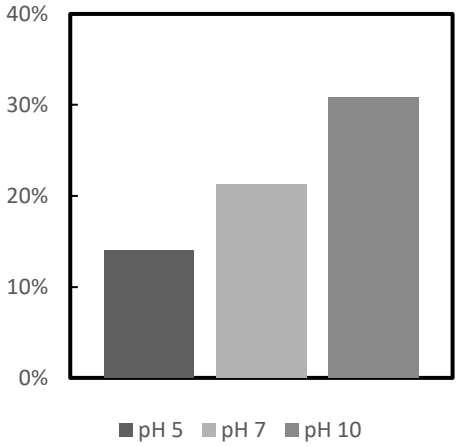

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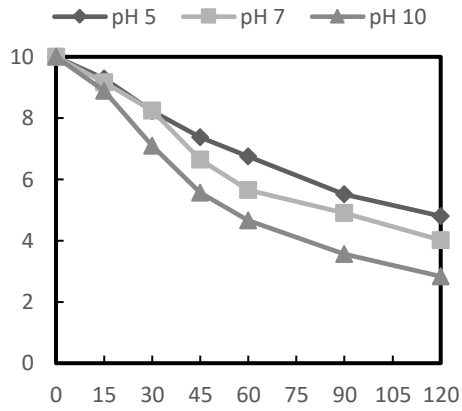
Figure 4. Effect of pH on Methyl Orange Waste Degradation with Photocatalyst. (1) Decrease in Methyl Orange Concentration, (2) Percent Degradation of Methyl Orange.

In the photocatalyst degradation process. Initially, there was an adsorption process for methyl orange dye on the surface of the TiO_2 catalyst, which was influenced by the pH value [30]. As in Figure 4.7, it can be seen that there is a decrease in the concentration of waste over time. The best decrease in concentration was at pH 10, with a concentration value at minute 120 with a percent decrease in concentration of 30,76%.

3.4. Effect of pH on the Combination Process

The best degradation in the combination process is at pH 10 with a concentration value at the 120 minute of 2,8 ppm with a percentage decrease in concentration of 71,6%, as shown in Figure 5.



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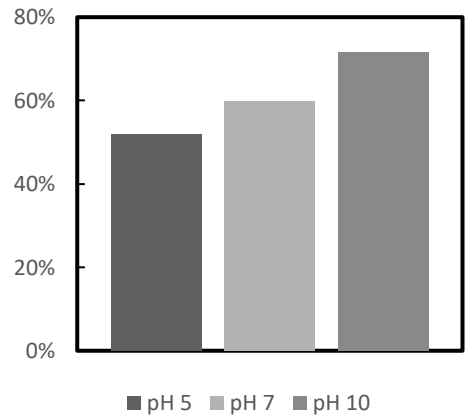

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Figure 5. Effect of pH on Waste Degradation in the Combination Process. (1) Decrease in Methyl Orange Concentration, (2) Percent Degradation of Methyl Orange.

TiO_2 at pH 10 forms $Al(OH)_3$ and H_2, which act as coagulants that bind contaminants and lift them to the surface. When the pH is >7, the $Al(OH)_3$ coagulant begins to form. In addition, at this pH, OH^- ions will accumulate, increasing the number of OH^- ions. This causes the energy needed for hydrogen and oxygen gas formation to be lower, and the air bubbles produced will increase. The existence of a

photocatalyst process also helps in the process of waste degradation.

4. CONCLUSION

Based on the research that has been done, the combination of the Electrocoagulation process with a photocatalyst can reduce the concentration of methyl orange waste. The best methyl orange elimination using Electrocoagulation and photo-catalytic processes was obtained at pH 10. At this pH, the % elimination of methyl orange was 71,6%.

ACKNOWLEDGMENTS

The authors thank the Ministry of Education, Culture, Research, and Technology of the Republic of Indonesia for the world-class research grant 2021.

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