Degradation of phenol in batik industry wastewater using thin layer TiO$_2$ photocatalyst

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Abstract. The synthesis of thin layer TiO$_2$ photocatalyst has been performed and its performance was tested to the degradation of phenol in wastewater of batik industry. The powder of anatase TiO$_2$ was impregnated in glass plate, so that thin layer TiO$_2$ photocatalyst was obtained. The performance test of thin-layer TiO$_2$ photocatalyst in the degradation of phenol was performed in a batch photoreactor equipped with six types of black light UV lamp (@10 watts) and a magnetic stirrer. This research has been performed at pH variation and UV radiation time. The result of this research showed that the initial concentration of phenol in batik wastewater was 3,3684 ppm. The optimum pH was obtained at pH 11 with percent degradation of 40.41%. The optimum UV radiation was obtained at 8 hours with percent degradation of 41.72%. The longer the irradiation time the more photon energy is absorbed by TiO$_2$ causes more positive holes to be formed. The positive holes will react with H$_2$O or hydroxyl ions to form OH radicals that further break down organic compounds in waste.

1. Introduction
The development of batik industry in Indonesia is quite rapid in line with the advancement of science and technology. This situation provides great benefits for the welfare of the community. Although it can have a positive impact on human life, industrial development can also cause environmental problems in the form of industrial waste [1]. Batik industrial liquid waste contains a lot of harmful organic compounds, one of the dangerous organic pollutants found in batik industrial waste is phenol [2].

Phenolic compounds are harmful substances to the body when inhaled, ingested, or in contact with skin or eyes. When heated, the vapor is very toxic (although only a few ppm) and explosive (at a concentration of 3% - 10% in air). Chronic poisoning causes gastric intestinal symptoms, difficulty swallowing, hypersalivation, kidney and liver damage, and can cause death. Phenol is also bad for the environment by killing bacteria or microorganisms. These dangers can occur from the manufacturing process to their use [3]. The phenol concentration in the batik industry wastewater is approximately 1 mg/L [4]. According to the Environmental Protection Agency, the threshold for phenolic compounds in industrial wastewater quality standards is valued in a range of 0.03 μg L$^{-1}$ to 4000 μg L$^{-1}$[5,6]. Phenol levels that exceed this quality standard need to be lowered before removing the waters to not endanger the environment and living things.
The reduction of phenol levels in batik wastewater can be accomplished by employing pyrolysis, absorption, ozonation and decomposition by microorganisms. These methods are less effective and less efficient such as pyrolysis can only use small amounts of samples and adsorption only localizes organic substances without degrading or simplifying these organic substances [7]. The use of microbiology requires a long period of time for complete mineralization and some organic substances can kill microorganisms [8]. Ozonation shows good results, but the cost used is expensive [9]. Therefore, it is necessary to have an alternative method that is simple, fast, efficient, and inexpensive. One of the alternatives is through the photooxidation process with the photocatalytic method [10].

Photocatalysis is a combination of photochemical and catalytic processes, in which UV light and a catalyst (semiconductor) are required to carry out a chemical transformation. The process of photoreduction and photooxidation begins when the photocatalyst adsorbs the photon energy with an energy equal to or greater than the semiconductor gap energy (TiO$_2$ has a band gap energy of 3.2 eV) then the electrons will be excited from the valence band to the conduction band which will produce a Hole (h$^+$) in the band valence. The hole (h$^+$) produced by TiO$_2$ is a strong oxidizing agent that will oxidize other chemical species that have an oxidation potential of +1.0 V to +3.5 V (relative to the hydrogen-Nernst electrode) [11], including water and/or hydroxyl groups which will produce hydroxyl radicals. This hydroxyl radical at pH = 1 has a potential of 2.8 V, and most organic substances have a smaller redox potential than this, so that most organic substances can be oxidized to CO$_2$ [12].

Meanwhile, the electrons in the conduction band are strong reducing agents that will reduce other chemical species that have a reduction potential of +0.5 V to -1.5 V (relative to the hydrogen-Nernst electrode) [13]. The photon energy used for the excitation of electrons from the TiO$_2$ photocatalyst is UV light and visible light [14,15]. Besides TiO$_2$, other semiconductors such as ZnO and WO$_3$ have a character comparable to TiO$_2$ in terms of their bandgap energy and redox potential. However, TiO$_2$ is mostly used as a photocatalyst because it is the most stable (resistant to corrosion) and relatively cheap. TiO$_2$ activity in degrading organic compounds is strongly influenced by the pH of the solution and irradiation time [16]. The purpose of this study was to study the effect of pH and irradiation time on TiO$_2$ photocatalyst activity in degrading phenol in batik industrial wastewater.

2. Materials and methods

2.1 Materials

The tools used in this research are photocatalytic reactors (Figure 1), magnetic stirrers, pH meters (Sentix 41 3210 set 2), glassware, UV-Vis spectrophotometers (Shimadzu UV-1601), plastic jerry cans, UV lamps (UV-C Phillips), glassware, filter paper, stopwatches, glass plates and porcelain cups, TiO$_2$ powder (Merck, 99%), aquades, phenol (Merck), 0.5 N NH$_4$OH (Merck), 4-aminoantipirin 2% (Merck), 8% potassium ferricyanide (Merck), ethanol (Merck), HCl (Merck) and NaOH (Merck). Batik liquid waste was collected from Sokaraja, Banyumas area, Indonesia.

![Figure 1. Photocatalytic reactor.](attachment:image.png)
2.2 Synthesis of thin films of TiO$_2$

The synthesis of TiO$_2$ thin films was modified from the report of Santos-Cruz [17]. The TiO$_2$ thin layer was prepared by dipping a glass plate measuring 7 x 15 cm$^2$ into the 15% TiO$_2$ suspension. Glass plate preparations are cleaned before use in TiO$_2$ thin layer preparations. The glass plate is cleaned with detergent, then washed with ethanol before being coated with TiO$_2$. A thin layer is prepared by dipping the glass in the suspension ± 10 times to obtain a sufficient thickness. Glass plate drying was carried out by heating at a temperature of 105 ºC for 1 hour. The white TiO$_2$ thin layer is ready to use.

2.3 Determination of phenol concentration [18]

A total of 10 mL of phenol waste was put into a 100 ml flask and added with NH$_4$OH solution, phosphate buffer, 2% 4-aminoantipirin, and 8% potassium ferricyanide. After that, the absorbance was measured with a UV-Vis spectrophotometer at the maximum wavelength. The same experiment was carried out for blanks and samples of batik industrial wastewater.

2.4 Effect of Wastewater pH on TiO$_2$ Activity for Phenol Degradation in Batik Waste.

A total of 5 @500 ml beakers containing 250 ml of batik waste, was each conditioned to a pH of 2; 5; 7; 9; and 11, by adding 1 N HCl and 1 N NaOH accordingly to adjust the wastewater sample. Samples that have been varied in pH are then analyzed for initial phenol levels. The TiO$_2$ thin layer was inserted into the wastewater sample and placed in a closed reactor while being exposed to ultraviolet light for 5 hours and analyzed for its phenol content after the addition of TiO$_2$ photocatalyst. The greatest decrease in phenol levels at a certain pH is the optimum pH.

2.5 Effect of UV irradiation time on TiO$_2$ activity for phenol degradation in batik waste.

A 250 mL of wastewater sample was put into a 500 mL beaker and then conditioned to the optimum pH and further analyzed for its phenol content at the beginning (time of 0 hours). Afterward, a thin layer of TiO$_2$ is inserted into the wastewater sample that has been conditioned to the optimum pH and placed in a closed reactor while being illuminated by an ultraviolet light. Determination of phenol levels was carried out after irradiating for 1, 2, 4, 6, 8, and 12 hours. The biggest decrease in phenol content at a certain exposure time is the optimum exposure time. The photocatalytic efficiency percentage was measured using the equation:

$$\text{photocatalytic efficiency} (\%) = \frac{(C_0 - C_1)}{C_0} \times 100 \#(1)$$

where $C_0$ is the initial concentration and $C_1$ is the concentration at the equilibrium condition [19].

3. Results and discussion

3.1 Characterization

The diffractogram of TiO$_2$ sample was shown in Figure 2 a). It can be seen that TiO$_2$ sample has anatase phase crystal. the highest peak at 2θ 25.37°. The crystallite size of TiO$_2$ has 31.29 nm size was calculated by Scherrer equation. A relatively semi-transparent and smooth film layer was characterized using SEM as presented in figure 1 b). Compared to the crystallize size measured by XRD analysis, the SEM image represents aggregation on the particle that happened during the heating process. The film surface was rough however the TiO$_2$ particle was shown to be attached well to the glass surface.
3.2 Effect of Wastewater pH on TiO$_2$ Activity for Phenol Degradation in Batik Waste

This research was conducted to determine the optimum pH of TiO$_2$ catalyst activity in reducing levels of phenol. The pH variations used were 3, 5, 6, 7, 9, 10 and 11. The phenol levels of each pH were analyzed before and after the addition of TiO$_2$ thin-layer photocatalysts by irradiating using a UV lamp for 5 hours. The results of the analysis of phenol levels at variations in the pH of wastewater can be seen in Figure 3.

Figure 3 shows that the highest reduction in phenol levels is at pH 11 (40.41%). In alkaline conditions (pH 9, 10 and 11) there are many hydroxyl ions that cause the higher formation of OH radicals resulting from the h$^+$ reaction with hydroxyl ions. The hydroxyl radicals, •OH, are used to degrade dissolved and suspended organic compounds in waste. The •OH is a strong oxidizer that can oxidize and degrade organic compounds. The pH of the solution will affect the charge on TiO$_2$ particles, the form of TiO$_2$ aggregates and the position of the conduction band and the valence band of TiO$_2$ [20].
Phenol is a weak acid, which in water will ionize to become a negatively charged phenoxide ion. The results showed that the charge on the TiO$_2$ surface had less effect on the phenol photodegradation activity. The number of hydroxyl ions causes the higher formation of OH radicals resulting from the reaction of h$^+$ with hydroxyl ions. The more OH radicals formed in the system will increase the photodegradation activity [21]. •OH radicals are used to degrade organic compounds including phenols in batik wastewater. In general, the photocatalytic mechanism of TiO$_2$ in an alkaline state can be explained as follows [22]:

\[
\text{TiOH} + H^+ \rightleftharpoons \text{TiOH}_2^+ \quad (2)
\]

\[
\text{TiOH} + OH^- \rightleftharpoons \text{TiO}^- \quad (3)
\]

The photocatalytic reaction mechanism for an acidic condition can be explained in the following reaction equation [22].

\[
\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2 (e^- + cb + h + vb) \quad (4)
\]

\[
h^+ + H_2O \rightarrow \cdot \text{OH} + H^+ \quad (5)
\]

\[
h^+ + OH^- \rightarrow \cdot \text{OH} \quad (6)
\]

\[
e^- + O_2 \rightarrow \cdot \text{OH}_2^- \quad (7)
\]

\[
CcHhOo + \cdot \text{OH} \rightarrow cCO_2 + \frac{h}{2} H_2O \quad (8)
\]

In this study, the factor of the increasing photooxidation activity is the number of hydroxyl radicals in the system. The more hydroxyl radicals produced, the less recombinant between holes and electrons, the less recombinant between holes and electrons, the more phenol is oxidized.

3.3 The Effect of Time of UV irradiation on Photocatalyst Activity of TiO$_2$

3.3.1 Photocatalyst activity is also influenced by exposure time. Determination of the effect of UV irradiation time on the photocatalyst activity of TiO$_2$ was carried out by conditioning the wastewater at optimum pH, then irradiating it with a UV lamp in the photocatalytic reactor and samples were taken every hour to analyze the phenol content. The results of the analysis of phenol levels at the variation of exposure time using UV lamps can be seen in Figure 4.
Figure 4. Percentage of degradation of phenol concentration in batik wastewater at a variation of illumination time under UV lamp. The dashed line indicated the degradation percentage of phenol without UV lamp irradiation.

Figure 4 shows that the largest percentage reduction in phenol content in the batik industry wastewater occurred at 8 hours of irradiation time. Without lamp there was only 2.95% degradation occurred due to the inexistence of photocatalytic activity. The adsorption of the catalyst was low at this level. The decrease in phenol levels is proportional to the irradiation time. The longer the irradiation time means that the more photon energy \( (h\nu) \) is absorbed by \( \text{TiO}_2 \) so that more electrons in the valence band are excited to the conduction band, this condition causes more \( h^+ \) or positive holes to be formed. The positive holes will react with \( \text{H}_2\text{O} \) or hydroxyl ions to form OH radicals. OH radicals are used to break down organic compounds in waste. In general, the phenol degradation equation is as follows:

\[
\text{C}_6\text{H}_5\text{OH} + h\nu \rightarrow \text{C}_6\text{H}_5\text{OH}^+ \rightarrow \text{photoproduction} \rightarrow a \text{ CO}_2 + b\text{H}_2\text{O} \tag{16}
\]

Phenol is initially oxidized to hydroquinone and catechol which are then oxidized again to maleic acid. This acid is eventually oxidized to \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) [23]. The decrease in phenol content at 8 hours irradiation time showed the greater value, namely 41.72%. The photocatalytic efficiency at this optimum condition is 58.43%. The irradiation time after 8 hours shows a fairly constant percentage decrease. This constant decrease percentage can be caused by the abundant supply of OH radicals during the process while the phenol concentration in the waste is reduced because it has been degraded, so that the OH radicals are difficult to degrade phenol because the amount of phenol is already small in the solution.

4. Conclusion

Based on the results of this study, it can be concluded that the pH of the waste affects the photooxidation activity of phenol. The optimum pH obtained to reduce phenol levels in the batik industrial wastewater was pH 11 with a reduction percentage of 40.41%. Time of exposure affects the photooxidation activity of phenol. The optimum irradiation time obtained to reduce the phenol content in the batik industry wastewater is at 8 hours with a reduction percentage of 41.72%.

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