Photodegradation of Rhodamine B using Composite Andisol/TiO$_2$

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Abstract. This research aims to determine the ability of andisol which is composited with TiO$_2$ as a degrading agent of Rhodamine B dye. The composite was made by sonication and calcination. Each material was characterized by FTIR and XRD. Photodegradation was carried out under a UV lamp with variation of the degradation time for 1, 2, and 3 hours. While the pH variation was carried out at 3, 5, 7, and 9. The photodegradation results were tested using UV Vis spectrophotometer at wavelength of 552 nm. Based on these results, the optimum conditions for photodegradation at pH 5 with irradiation time of 2 hours was 39.55%.

1. Introduction
Rhodamine B (RhB) is one of synthetic cationic dye. The structure of RhB shows in Figure 1. RhB used in industrial production, such as textile, printing, and photographic industries[1]. It has red color when dissolved in water. It is highly soluble in water[2]. RhB is potentially toxic for environmental and human, if exposed for long periods of time may cause skin irritation.

![Figure 1. Structure of Rhodamine B.](image)

Photodegradation is one of method to decompose organic contaminant with photon energy. This method is required semiconductor photocatalysts, such as TiO$_2$. The study of removal dyes using photocatalytic TiO$_2$ has been confirmed. Titanium dioxide (TiO$_2$) is a semiconductor material and has redox properties, which are able to oxidize organic pollutants and reduce a number of metal ions in solution. The principle of the photocatalyst is when semiconductor is exposed to light with a certain
appropriate energy, there will occur transfer of electrons from the valence band to the conduction band and leaving the hole in valence band. These holes and electrons initiate the generation of free radicals on semiconductor[4]. Schematic diagram of photocatalyst principle showed in Figure 2. In the other study, TiO₂ and clay can be alternative method to remove synthetic dyes. Clay has several minerals, such as kaolinite, allophane, montmorillonite, and etc[5]. These minerals can be found in andisol soil. It has properties such as cation and anion exchange, high surface area, and good adsorbent for wastewater treatment[6]. Andisol soil can be found in Lawu Mount, Dieng, Merbabu Mount, and Willis Mount.

![Figure 2. Schematic diagram showing electron jumps in semiconductors.](image)

In previous research, clay supported TiO₂ for photocatalytic degradation of environmental pollutants[4], such as synthetic dyes[7], organic contaminants[8], etc. Jing et al (2016) was remove RhB use adsorbent/TiO₂, the schematic diagram for the photodegradation of RhB showed in Figure 3. In this research, andisol is added into the TiO₂ to degradation of RhB under UV light.

![Figure 3. Schematic diagram for the photodegradation of RhB use adsorbent/TiO₂.](image)

2. **Experimentals**

2.1 **Materials**

Andisol soil was obtained from Lawu Mount, Central Java. Titanium dioxide (TiO₂) used is a commercial anatase structure. Aquadest, RhB solution, NaOH (Merck), HCl 37%.
2.2 Methods

2.2.1 Preparation of Composite Andisol/TiO$_2$ (ATC)

Andisol soil (A) was activated by NaOH solution for 5 hours. Then 1 gram of activated andisol soil was dispersed in 30 ml aquadest. It was sonicated for 30 minutes. TiO$_2$ was added into andisol dispersed (1:1) wt%. Then, andisol and TiO$_2$ were sonicated for an hour. The composite was dried for 12 hours at 70 °C\textsuperscript{[10]}. Then, the composite was dried in furnace at 500 °C for 2 hours.

2.2.2 Photodegradation of RhB

2.2.2.1 Effect of Irradiation Times

Typically 0.1 g of ATC was added into 10 mg/L of RhB solution. RhB and the composite was stirred continuously for 15 min without UV-light. After that, the suspension was irradiated under UV-light for 1, 2, and 3 hours. After irradiated with UV-light, the solutions were centrifuged at 4000 rpm for 20 minutes. The initial and equilibrium concentrations of RhB were determined by UV-Visible Spectrophotometer at 552 nm.

2.2.2.2 Effect of pH

Firstly, 0.1 g of ATC was added into 10 mg/L RhB solution at optimum variation times. RhB and the composite was stirred continuously for 15 min without UV-light. RhB solution was varied at pH 3, 5, 7, 9. After photodegradation under UV light, the mixture were centrifuged at 4000 rpm for 20 minutes. The solutions were determined by UV-Visible Spectrophotometer at 552 nm.

3. Result and Discussion

3.1 FTIR Characterization

![FTIR Spectra](image)

Figure 4. Spectra FTIR of (a) ATC, (b) TiO$_2$, and (c) Activated Andisol.

Figure 4. Shows the FTIR spectra of TiO$_2$ and activated andisol. In spectra of TiO$_2$, broad band at 515-678 cm$^{-1}$ possibly due to the vibration of Ti-O bonds in the TiO$_2$ lattice\textsuperscript{[10]}. The FTIR spectra of activated andisol show a broadband at 3420,90 cm$^{-1}$, which can be attributed to the stretching vibrations of O-H bonds of surface adsorbed water molecules. Bending vibration of –OH bond form H-O-H is observed at broad peaks 1646,32 cm$^{-1}$\textsuperscript{[11]}. The peak at 1006,89 cm$^{-1}$ is stretching vibration of Si-O-Si or Al-O-Al and 400-500 cm$^{-1}$ is stretching vibration of Si-O or Al-O\textsuperscript{[12]}. 
3.2 XRD Characterization

The XRD characterization of ATC(a), TiO2(b), and activated andisol(c) show in Figure 5. Based on Figure 5, the peak intensity of TiO$_2$ (b) at 25.2116°, 37.6925°, 47.9216° and 48.0728° which is indicating TiO$_2$ in anatase phase. That diffraction pattern of TiO$_2$ anatase was compared with reference to JCPD database No. 84-1286 (TiO$_2$ anatase). The peak intensity of activated andisol (c) shows the peak of allophane (A) minerals are found at angles (2θ) 26.46° (JCPDS 02-0039). There are also other minerals such as montmorillonite (M) at 21.99°; 29.58° and 35.72° (JCPDS 02-0014), kaolinite (K) at 62.03°-63.82° (JCPDS 80-0886), gibbsite (G) at 27.79° (JCPDS 07-0324) and feldspar (F) at 23.92° and 34.15° (JCPDS 84-0710). The low intensity and broad pattern indicating the nanoparticles are amorphous. The peak intensity change after andisol and TiO$_2$ were composed.

![Figure 5. Diffractogram of (a) ATC, (b) TiO$_2$, and (c) activated andisol.](image)

3.3 Photodegradation of RhB

3.3.1 Effect of Irradiation Times

Interaction between ATC and UV-light produce OH radicals. The longer time irradiation with UV-light can produce more OH radicals. These OH radicals degrade Rhodamine B, so the concentration will decrease with the length of irradiation time. Based on Figure 6, degradation percentage increases from an hour to 2 hours, but after 3 hours percentage degradation decreases.

![Figure 6. Colerration between contact time irradiation and percentage of degradation](image)
The result of percentage degradation for 1, 2, and 3 hours are 17.61%; 29.55%, and 26.79%. The optimum irradiation time for composites to degrade RhB is at 2 hours of irradiation time. At this composition, RhB was degraded by 39.55% from the initial concentration of 10 mg/L.

3.3.2 Influence of pH at optimum irradiation time

Figure 8 presents the percentage degradation of RhB at different pH values. Based on Figure 8, at pH 5 is the optimum pH. It causes RhB in an acidic state, the H⁺ ion binds to the N atom, which has free electrons. It causes the substitution of the CH₃ group by H so that the N atom releases the CH₃ group\(^{[13]}\). The result showed that at pH 5 is the optimum pH. At pH 5, RhB was degraded by 39.55% from the initial concentration of 10 mg/L.

In this study, percentage at pH 3 is low because competition between more H⁺ ions and RhB to occupy the sorption sites and the surface of ATC is positive\(^{[14]}\). RhB in an alkaline state is zwitterionic. In this form, RhB can undergo increased aggregation to form larger molecules. It causes RhB can't enter the pore. The repulsion between the composite and deprotonated RhB caused a decrease in the degradation ability of RhB\(^{[14]}\).

![Figure 8. Correlation between variation pH and percentage of degradation](image)

4. Conclusion

Andisol/TiO₂ Composite (ATC) was prepared by ultrasonication and calcinacion. Based on the results of the study, the optimum conditions for photodegradation by ATC at pH 5 with 2 hours irradiation is 39.55%.

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