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Photocatalytic Degradation of Phenol Red Using Titanium Dioxide (TiO_2)–Chitosan Composite Catalyst Assisted By Solar Energy

Degradasi Fotokatalitik Fenol Merah Menggunakan Katalis Komposit Titanium Dioksida (TiO_2)-Kitosan Dengan Bantuan Energi Sinar Matahari

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ABSTRACT

Phenol Red is a very water-soluble textile dye that belongs to the triphenylmethane dye class. In this study, a photocatalyst composite was synthesized by combining TiO_2 as photocatalyst with chitosan as a solid support material. The aim of this research is to study what ratio of TiO_2: Chitosan would yield the best-performing composites in catalysing the photodegradation of phenol red. This research also studied, the optimum dose of TiO_2-chitosan for photodegradation of phenol red, and the effect of solar radiation time towards the photodegradation of phenol red. Into 100 mL of phenol red solution with an initial concentration of 25 ppm, chitosan beads and TiO_2-Chitosan composites were added with various doses, i.e: 0.5:100, 1:100, 2:100, and 5:100 gram/mL. The mixtures were put into solar radiaton exposure for 6 hours, where the concentration of phenol red in the solution was analysed every 20 minutes. The highest degradation level of phenol red (72.84%) was achieved by using TiO_2-Chitosan 5:10 composites, where the dose added was 5 grams of composite for in 100 mL sample along with a 6-hour of solar radiation exposure.

Keywords: *Phenol red, photochemistry, TiO_2-Chitosan composite, solar radiation*

ABSTRAK

Fenol merah adalah pewarna tekstil yang sangat larut dalam air yang termasuk dalam kelas pewarna triphenylmethane. Dalam penelitian ini, dilakukan pengolahan atas fenol merah menggunakan komposit kitosan. Tujuan dari penelitian ini adalah mendapatkan data rasio TiO_2: Kitosan yang menghasilkan komposit dengan kemampuan paling baik dalam proses fotodegradasi fenol merah, mendapatkan dosis optimum TiO_2-Kitosan yang efektif dalam proses fotodegradasi fenol merah, dan mendapatkan informasi mengenai pengaruh atas waktu penyinaran terhadap fotodegradasi fenol merah. Larutan fenol merah dengan konsentrasi 25 ppm sebanyak 100 mL ditambah dengan beads kitosan dan komposit TiO_2-kitosan sebanyak 0,5:100, 1:100, 2:100, dan 5:100 gram/mL. Larutan disinari dengan sinar matahari selama 6 jam, dimana konsentrasi fenol merah dalam larutan dianalisis setiap 20 menit. Degradasi fenol merah tertinggi (72,84 %) dicapai pada komposit TiO_2-Kitosan 5:10, dimana dosis yang ditambahkan adalah 5 gram komposit dalam 100 mL larutan dengan penyinaran selama 6 jam.

Kata Kunci : *Fenol merah, fotokimia, komposit TiO_2-kitosan, sinar matahari*.

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1. INTRODUCTION

The textile industry is one of the fastest-growing industries and plays an important role in Indonesia. During the production process, this industry generates solid and liquid waste containing various toxic compounds that can pollute the environment if not properly treated. The main pollutants in textile waste originate from the dyeing and finishing processes, which involve both synthetic and natural dyes to produce permanent colors. A key characteristic of textile industry effluents is their high content of synthetic dyes, which, when discharged into the environment, can harm aquatic ecosystems.

Phenol red is a highly water-soluble textile dye belonging to the triphenylmethane class of dyes. At room temperature, phenol red appears as red crystals, is stable in air, and has a solubility of 0.77 g/L in water. At 20°C, the compound has a pKa value of 8.00. Therefore, phenol red is often used as a reagent to measure water pH within the range of pH > 6.8. Its application as an indicator is widely practiced in cell biology laboratories and for water quality testing (Mittal et al., 2009).

The most common method for treating textile waste is adsorption. This process is simple and widely used for removing organic pollutants. However, adsorption has certain limitations, including the need for adsorbent regeneration once it becomes saturated with organic compounds. An effective alternative for treating dye waste, including phenol red, is photocatalysis. Photocatalysis combines photochemical and catalytic processes to enable chemical transformation reactions (Febriyani et al., 2012). Titanium dioxide (TiO_2) is one of the most widely used semiconductor materials that acts as a photocatalyst. Chiou et al. (2008) reported that TiO_2 can degrade phenol by up to 56%. The advantages of TiO_2 photocatalysts include high chemical stability, low cost, and non-toxicity (Hashimoto et al., 2005). Additionally, chitosan is often used alongside TiO_2 due to its excellent ability to adsorb both organic and inorganic pollutants (Aranas et al., 2010).

2. MATERIALS AND METHODS

2.1. Materials

The instrument that was used in this research include Pyrex glassware, a Genesys 10uv UV-Visible Spectrophotometer, SEM (Scanning Electron Microscope), FTIR (Fourier-transform Infrared Spectroscopy), pH meter, magnetic stirrer, irradiation box, glass reactor, Philips UV lamp (30 Watt), Recent RC-999 aerator, Recent RC-650 submersible pump, analytical balance (O'Hauss), and PMC stirrer. The materials used in this study are TiO_2 anatase powder (p.a Merck), phenol red (p.a Merck), food-grade chitosan powder, 2% acetic acid (p.a Merck), epichlorohydrin (p.a Merck), 0.1% EDTA (p.a Merck), HCl (p.a Merck), NaOH (p.a Merck), ethanol (p.a Merck), and distilled water.

2.2. Methods

2.2.1. Manufacture of photocatalytic reactors

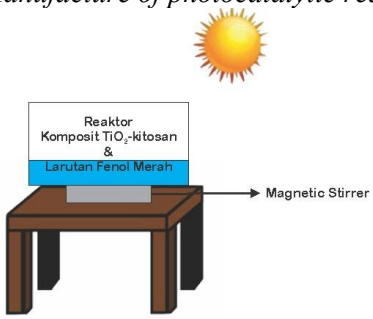

Figure 1. Arrangement of the Photocatalytic Reactor.

The reactor casing was built according to the dimensions of the waste reactor. The waste reactor was made of glass with a size of 25 cm × 10 cm. A glass tank was prepared to hold the dye wastewater. The tank was placed in an open area exposed to sunlight. A magnetic stirrer was placed inside the tank to prevent photocatalyst sedimentation. Figure 1 shows the arrangement of the photocatalysis reactor.

2.2.2. Synthesis of TiO_2–Chitosan Composite

The synthesis method of the TiO_2–chitosan composite used for degrading phenol red dye was adapted from the method proposed by Zhao et al. (2012). A total of 0.5 grams of chitosan powder and a specific amount of TiO_2

were dissolved in 20 mL of 2% acetic acid. The amount of TiO_2 was varied to observe the effect of the chitosan-to-TiO_2 ratio on the photocatalytic efficiency of the resulting TiO_2–chitosan composite. The mixture was continuously stirred for 45 minutes, followed by the addition of 1 mL of epichlorohydrin. Stirring continued for 5 hours at 30°C. The mixture was then dropped into a 0.25 M NaOH solution using a dropper to form beads.

The beads were left in the solution for 12 hours and then rinsed with distilled water. The TiO_2–chitosan beads were placed into an Erlenmeyer flask containing 100 mL of 0.1% EDTA solution and stirred at 30°C for 4 hours. The beads were then washed again with distilled water and subsequently stirred in 50 mL of 0.05 M NaOH solution at 30°C for 2 hours. Afterward, the TiO_2–chitosan beads were rinsed with distilled water and dried at 60°C. The resulting TiO_2–chitosan beads were characterized using SEM (Scanning Electron Microscope). The synthesis of the TiO_2–chitosan composite was repeated with varying TiO_2-to-chitosan ratios to determine the optimal composition. The TiO_2–chitosan ratios tested were 1:10, 2:10, and 5:10 (grams TiO_2: grams chitosan). The same procedure was also carried out using chitosan beads (without the addition of TiO_2).

2.2.3. Effect of Irradiation Time on the Reduction of Phenol Red Concentration

A total of 250 mL of 25 ppm phenol red solution was placed into the reactor, followed by the addition of 5 grams of beads. The mixture was continuously stirred at a speed of 400 rpm (Garg, 2015) while being irradiated in the reactor for 6 hours. At time intervals of 0, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 300, 320, 340, and 360 minutes, 5 mL samples of the solution were taken, and their absorbance was measured using a UV-Vis spectrophotometer at the maximum wavelength of phenol red.

2.2.4. Determination of the Optimum Dose of TiO_2–Chitosan

A total of 100 mL of 25 ppm phenol red solution was placed into the reactor, followed by the addition of varying amounts of TiO_2–chitosan composite. The composite-to-sample ratios used were 0.5:100, 1:100, 2:100, and 5:100 (grams of composite: volume of sample in mL). The mixture was continuously stirred at a speed of 400 rpm during irradiation (Garg, 2015). After reaching the optimum contact time, the remaining phenol red concentration in the sample was determined by measuring its absorbance at the maximum wavelength using a UV-Vis spectrophotometer. The same procedure was performed on 100 mL of the sample without TiO_2 addition as a negative control.

2.2.5. FTIR Analysis (Fourier Transform Infrared Spectrophotometer)

The obtained beads were analyzed using a Fourier Transform Infrared Spectrophotometer (FTIR). The beads were prepared using the KBr-press method, and spectra were recorded in the wavenumber range of 4000–400 cm^{-1}. This analysis aimed to identify the functional groups of both chitosan powder and chitosan beads by observing the absorption peaks of the functional groups (Kurniasih et al., 2016).

2.2.6. Data Analysis

The results of the TiO_2–chitosan study were obtained in the form of numerical data, including the optimum degradation time and the optimum dose of the TiO_2–chitosan composite in the degradation of phenol red. The data were organized using tabulation and graphs. The results were compared between irradiation using UV light and sunlight. The standard curve analysis and maximum wavelength determination of phenol red were performed using a UV-Vis spectrophotometer based on the Lambert-Beer law. FTIR spectroscopy was used to analyze the functional groups present in the TiO_2–chitosan composite based on the obtained spectra. The surface morphology of the TiO_2–chitosan composite was characterized using SEM.

3. RESULTS AND DISCUSSION

3.1. Synthesis of TiO_2–Chitosan Composite

The TiO_2–chitosan composite was prepared by dissolving TiO_2 and chitosan in 20 mL of 2% acetic acid, followed by stirring for 45 minutes. Then, 1 mL of epichlorohydrin was added, which acts as a crosslinking agent for chitosan. The mixture was stirred again for 5 hours until a thick, milky-white solution was obtained. This mixture was then converted into beads by dropping it into a 0.25 M NaOH solution. The formed beads were washed to remove residual NaOH and subsequently dried.

3.2 Functional Group Analysis of TiO_2–Chitosan Composite

To identify the functional groups, present in chitosan powder and the TiO_2–chitosan composite, Fourier Transform Infrared (FTIR) spectrophotometry analysis was conducted. The FTIR spectra of chitosan powder and TiO_2–chitosan composite is shown in Figure 2. The figure displays the transmittance values of the chitosan beads and TiO_2–chitosan composite as a function of the wavenumber.

A significant difference can be observed in the absorption patterns of the TiO_2–chitosan composite. Compared to the spectrum of unmodified chitosan, the TiO_2–chitosan composite exhibits a sharp absorption peak at around 3300 cm^{-1}, which indicates the stretching vibration of the –OH group. The broadening and shift of the –OH band are due to overlapping with the –NH group from amines. A sharp absorption peak is also observed at 1638 cm^{-1}, which is a characteristic peak of secondary amide (C=O) bonds. This absorption corresponds to the N–H stretching vibration of amides (Dompeipen, 2017). Another significant difference between the IR spectra of chitosan powder and the TiO_2–chitosan composite is the absorption observed in the wavenumber region around 650 cm^{-1}. As reported by Saravanan et al. (2018), the presence of absorption in this region indicates the incorporation of TiO_2 within the chitosan matrix.

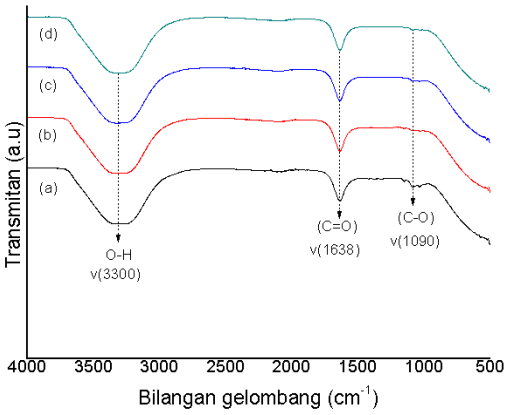

Figure 2. FTIR spectra of (a) Chitosan beads, (b) TiO_2–Chitosan composite 1:10, (c) TiO_2–Chitosan composite 2:10, and (d) TiO_2–Chitosan composite 5:10.

3.3. Morphological Analysis of TiO_2–Chitosan Composite

SEM analysis was conducted to observe the morphology of the composite on a microscopic scale. In this study, SEM analysis was performed on unmodified chitosan powder and TiO_2–chitosan composites. The SEM results of chitosan powder and TiO_2–chitosan composites with the three different TiO_2-to-chitosan ratios are shown in Figure 3.

Based on morphology at Figure 3(a), it can be observed that the surface of unmodified chitosan powder appears very rough. A different surface morphology is shown in Figure 3(b), which depicts the TiO_2–chitosan composite with a 1:10 ratio. In this image, the chitosan surface appears smoother, with white spots indicating TiO_2 particles attached to the chitosan surface. Figure 3(c) presents the SEM analysis of the TiO_2–chitosan composite with a 2:10 TiO_2-to-chitosan ratio, where a greater number of TiO_2 particles can be seen adhering

to the chitosan surface. The bright spots are more evenly distributed across the chitosan surface. Figure 3(d) shows the SEM result of the TiO_2–chitosan composite with a 5:10 ratio. A noticeable difference compared to other composites is observed, where TiO_2 particles on the chitosan surface tend to undergo agglomeration or clumping in certain areas.

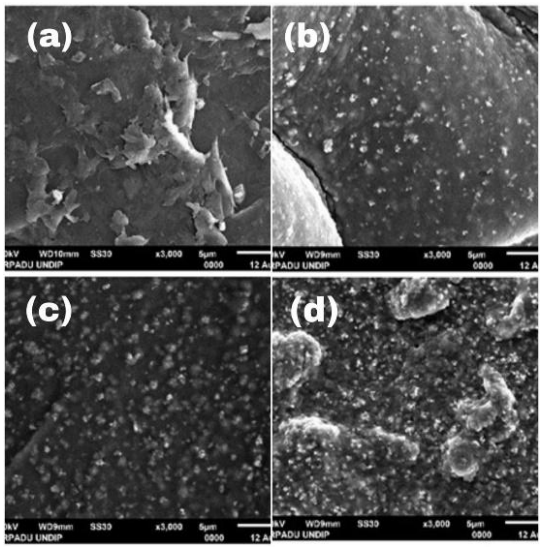

Figure 3. SEM analysis results (3000× magnification) of samples: (a) chitosan powder, (b) TiO_2–chitosan composite 1:10, (c) TiO_2–chitosan composite 2:10, and (d) TiO_2–chitosan composite 5:10.

3.4. Effect of Irradiation Time on the Reduction of Phenol Red Concentration

To study the effect of irradiation time on the reduction of phenol red concentration, TiO_2–chitosan composite was added to a phenol red solution with an initial concentration of 25 ppm at a ratio of 2:100 (g/mL). The solution and composite were exposed to sunlight for 6 hours, and the concentration of phenol red in the sample was analyzed every 20 minutes. The changes in phenol red concentration for each measurement over the observation period are presented in Figures 4, 5, 6, and 7.

Figure 4 shows that at the end of the observation period, after 6 hours of irradiation, the final concentration of phenol red was 16.386 ppm, corresponding to a reduction of 33.964% from the initial concentration. During the observation period, the concentration of phenol red fluctuated, indicating that the adsorption equilibrium of phenol red on chitosan had not yet been reached. Consequently, some of the phenol red that had been adsorbed was desorbed back into the solution.

Figure 5 shows that at the end of the observation period, after 6 hours of irradiation, the final concentration of phenol red was 18.207 ppm, representing a reduction of 23.775% from the initial concentration.

Figure 6 shows that at the end of the observation period, after 6 hours of irradiation, the final concentration of phenol red was 20.993 ppm, representing a reduction of 30.339% from the initial concentration.

Figure 7 shows that at the end of the observation period, after 6 hours of irradiation, the final concentration of phenol red was 21.707 ppm, representing a reduction of 10.988% from the initial concentration.

The effect of irradiation time was observed over a 6-hour period. Based on the pattern of phenol red concentration changes in the solution, the reduction of phenol red concentration occurred at an optimum rate during the first 20 minutes. This can be seen from the significant decrease in phenol red concentration within the initial 20 minutes. After the first 20 minutes and up to the end of the observation period, the phenol red concentration continued to decrease, but the reduction rate was no longer as high as that observed in the initial 20 minutes.

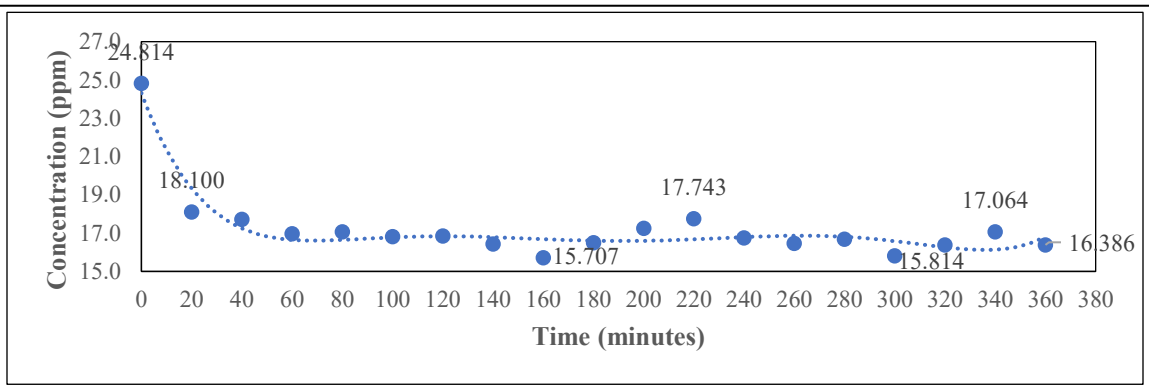

Figure 4. Effect of Irradiation Time (6 Hours) on the Reduction of Phenol Red Concentration in the Photocatalysis Process Using Chitosan Beads.

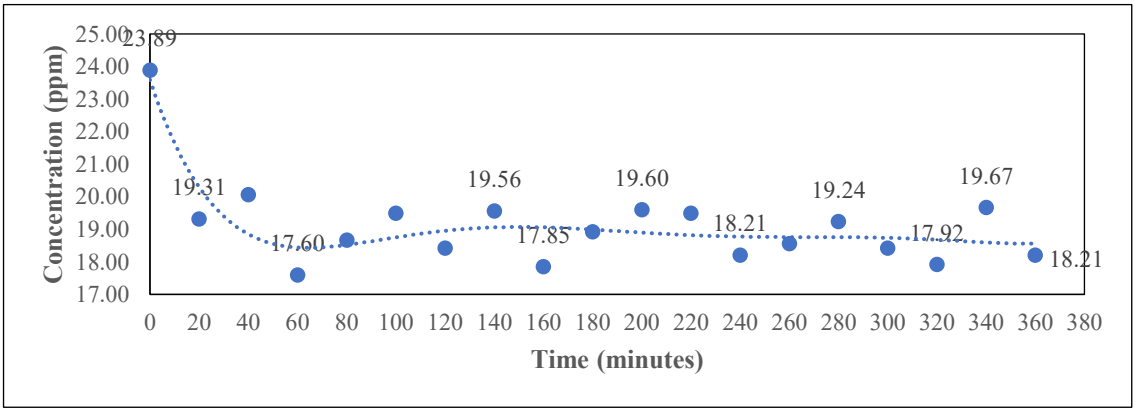

Figure 5. Effect of Irradiation Time (6 Hours) on the Reduction of Phenol Red Concentration in the Photocatalysis Process Using TiO_2–Chitosan Beads (1:10 Ratio)

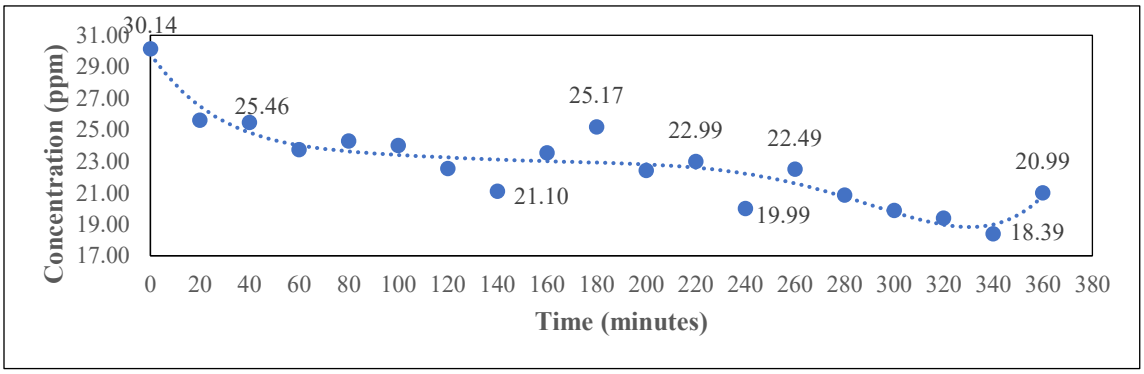

Figure 6. Effect of Irradiation Time (6 Hours) on the Reduction of Phenol Red Concentration in the Photocatalysis Process Using TiO_2–Chitosan Beads (2:10 Ratio)

When the sample was treated using TiO_2–chitosan composite beads, the reduction in phenol red concentration was estimated to occur through two processes: adsorption by chitosan and photocatalytic degradation catalyzed by TiO_2. However, the decrease in phenol red concentration observed with the TiO_2–chitosan composite was smaller compared to that with pure chitosan beads.

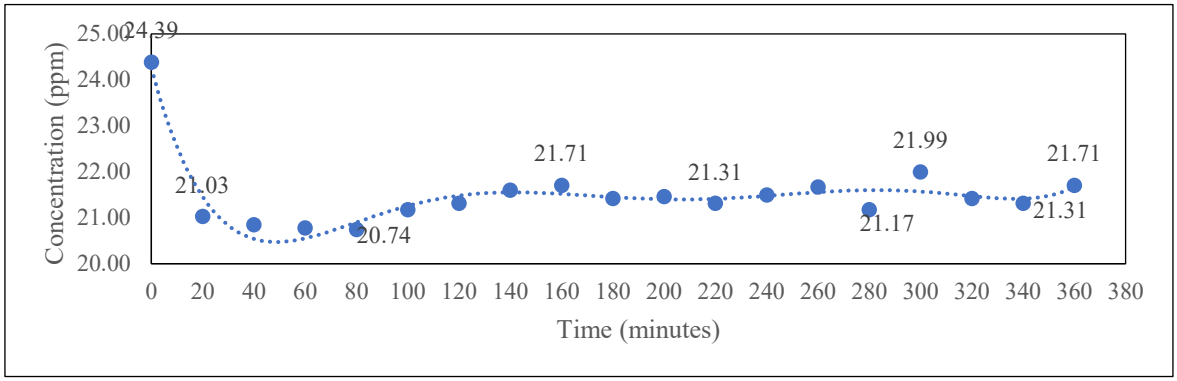

Figure 7. Effect of Irradiation Time (6 Hours) on the Reduction of Phenol Red Concentration in the Photocatalysis Process Using TiO_2–Chitosan Beads (5:10 Ratio)

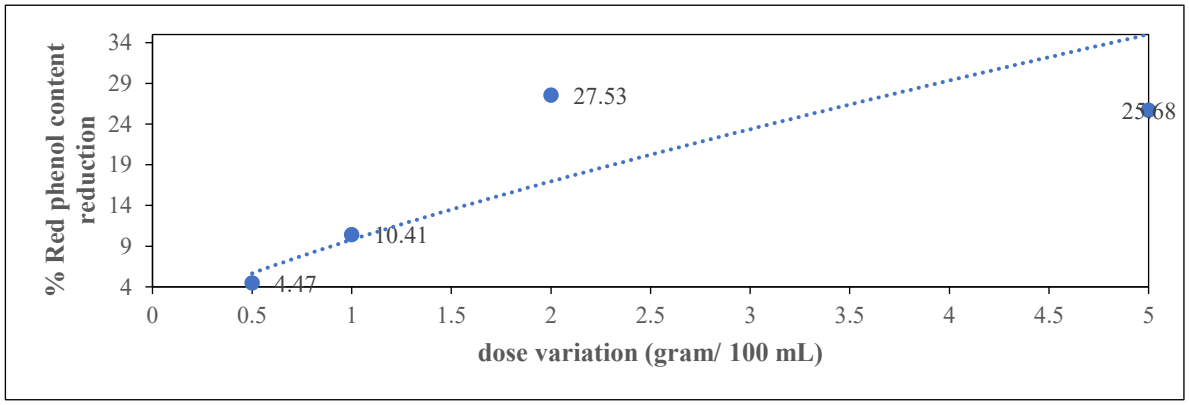

Figure 8. Results of Optimum Dose Determination using Chitosan Beads

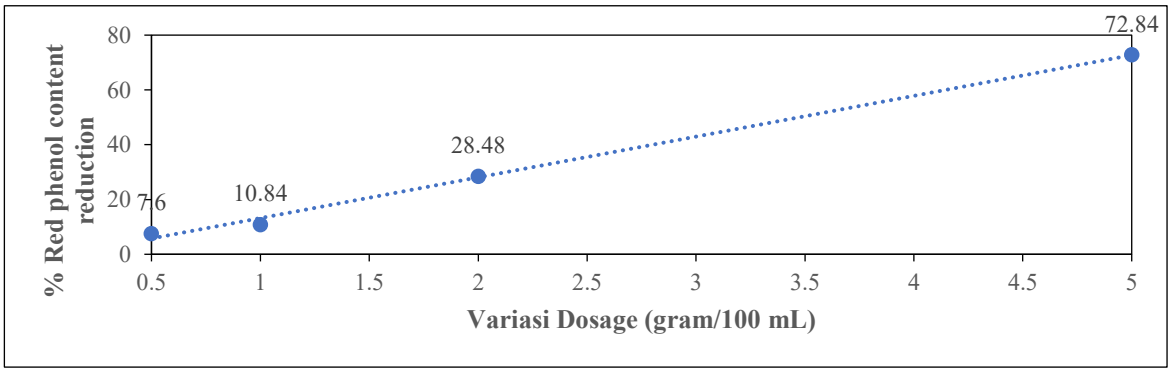

Figure 9. Optimum Dose Degtermination using TiO_2 Chitosan Beads with a 5:10 Ratio

This result indicates that the performance of chitosan in adsorbing phenol red, as well as the photocatalytic activity of TiO_2 in degrading phenol red, was not optimal. This is because the amine groups in chitosan, which play a crucial role in interacting with phenol red, are partially bonded to TiO_2 in the composite. TiO_2 bound to chitosan can also react with other TiO_2 particles dissolved in water (Saputro et al., 2016). Additionally, the decrease in the effectiveness of chitosan is also attributed to the use of epichlorohydrin, which forms covalent bonds with the –OH groups in chitosan (Gunawan et al., 2017).

3.5. Optimum Dose for Phenol Red Degradation

The purpose of determining the optimum dose of TiO_2–chitosan in the photochemical process of phenol red degradation is to identify the most effective amount of TiO_2–chitosan for achieving maximum degradation. In this study, the determination of the optimum TiO_2–chitosan dose was conducted by varying the ratio of TiO_2–chitosan to sample volume, namely 0.5:100, 1:100, 2:100, and 5:100 (grams/mL). In this degradation process, two types of beads were used: chitosan beads and composite beads with a TiO_2–chitosan ratio of 5:10 (grams:grams). Based on Figure 8, the optimum dose was obtained at a composition of 2:100 (g/mL), where the percentage reduction of phenol red concentration reached 27.53% from the initial concentration.

Based on Figure 9, the optimum dose was obtained at a 5:100 (g/mL) dosage variation, resulting in a 72.84% reduction of phenol red concentration. Figure 9 shows that the higher the TiO_2 ratio in the composite, the greater the percentage of phenol red degradation. This is because an increased amount of TiO_2 in the composite leads to the formation of more holes. These holes, formed during the excitation process, react with surrounding water molecules to produce highly reactive hydroxyl radicals. These hydroxyl radicals are extremely reactive and capable of degrading organic compounds effectively.

4. CONCLUSIONS

The conclusions of this study are as follows: The optimum TiO_2–chitosan ratio in the composite is 5:10. The optimum dose of the TiO_2–chitosan composite for photochemical degradation of 25 ppm phenol red is 5:100 (g/mL), achieving a reduction percentage of 72.84%. Furthermore, the longer the irradiation time (up to 6 hours) in the photocatalysis process using the TiO_2–chitosan composite, the greater the percentage of phenol red degraded through photochemical reactions.

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