Photodegradation of remazol brilliant blue using Fe$_2$O$_3$ intercalated bentonite

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Abstract. This paper reports the use of Fe$_2$O$_3$ intercalated bentonite as a photocatalyst to degrade remazol brilliant blue. The photodegradation was conducted by irradiating aqueous solution of the coloring agent and Fe$_2$O$_3$ intercalated bentonite with UV ray at 259 nm. The degradation percentages were observed at various pH, photocatalyst mass, and irradiation duration to obtain the optimum condition of the photodegradation. The observation showed that the optimal photodegradation occurred at pH 4, using 100 mg bentonite-Fe$_2$O$_3$, irradiated for 2 hours. The process can degrade effectively 200 ppm remazol brilliant blue with a percentage of 98.20 ± 0.07%.

1. Introduction

Dyeing agent used by textile industries is one of the sources of pollution that contaminate the aquatic environment. Azo dyes such as remazol brilliant blue are widely used dyes. The dyes are usually organometallic compounds consisting of chromophore as the color carrier and auxochromes as the color binder [1]. Such structures are not easily degraded biologically. Once entering the river, the dye compounds become even more difficult to breakdown because of the complex chemical structure [2]. Physical treatment such as adsorption process cannot break down the complex compounds into simpler molecules, but only immobilizing them from the liquid phase into solid. Photodegradation method can be used to solve this pollution problem [3-7]. Through photodegradation, the organometallic compound will be broken down into simpler molecules, and the heavy metals will be reduced [8]; thus the dye waste is removed from the water.

In the process, dyeing compound is adsorbed on the surface of the photocatalyst and then degraded by UV light. Photocatalysts such as iron oxide can be used because its magnetic nature ensures efficient separation and it is reusable [9]. However, the limited adsorption capacity of the photocatalyst reduces its catalytic ability. Modification of the iron oxide by intercalating it on an adsorbent is one way to enhance the adsorption capacity, and bentonite is a natural adsorbent which is useful for several reasons. Bentonite has a layered structure with the ability to expand (swell) and contains cations that can be exchanged [3,6]. Bentonite is abundantly available in Indonesia and is relatively cheap [8]. Intercalation of bentonite using metal oxides can produce a photocatalyst that has high photocatalytic ability [3,6,8].

2. Experimental section

2.1. Materials

The materials used in this study included bentonite, Remazol brilliant blue dye, FeCl$_3$.6H$_2$O, AgNO$_3$, NaOH, HCl, demineralized water, and distilled water.

2.2. Apparatus.

Equipment used apart from the usual laboratory glasswares and equipment, were black plastic sheets, irradiation boxes with UV lamp (259 nm), 100 and 250 μm sieves. The instruments were UV-Vis spectrophotometer, FT-IR, and XRD.
2.3. Procedure

Ten grams of clean bentonite was added into 500 mL demineralized water and stirred with a magnetic stirrer for 5 hours. Then a solution containing 0.2 M FeCl₃ in NaOH was slowly poured into the suspension, and the mixture was stirred for 24 hours. The product was washed until free of chloride ions. Then it was oven-dried at 110-120°C. Once dried, it was crushed into powder and sieved using a 100 μm siever.

Fe₂O₃ -bentonite photocatalyst and bentonite were characterized by using XRD to determine their basal spacing D₀₀₁ and FTIR to determine their functional groups. Methylene blue method was used to measure the surface area. The determination of the optimum concentration of the photocatalyst was accomplished by varying the amount of catalyst by 50, 100, 150, 200, 250, and 300 mg in 25 ppm aqueous dye solution. The optimum pH was determined by varying the pH at pH 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10. The optimum irradiation time was determined by irradiating 25 ppm of dye solution with UV light at optimum pH, the optimum amount of catalyst, and stirring for 1, 2, 3, 4, 5, and 6 hours.

Photodegradation effectiveness was investigated by comparing the degradation percentages under UV radiation and under the dark condition of 25 mL of 200 ppm remazol brilliant blue under the optimum conditions using bentonite, Fe₂O₃, and bentonite- Fe₂O₃ composite. The percentage of degradation was obtained using the equation:

\[ D(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \]

where \( C_0 \) = the initial Remazol brilliant blue concentration
\( C_t \) = the concentration of Remazol brilliant blue concentration after irradiation

3. Results and discussion

3.1. The characteristics of the photocatalyst

There is an increase in the interlayer distance or basal spacing of Fe₂O₃-bentonite (4.63 Å) due to specific diffraction at 2θ = 19.13, compared to bentonite (4.59 Å) due to specific diffraction at 2θ = 19.31 (Figure 1).

The infrared spectra shown in Figure 2 confirm the difference between bentonite and the Fe₂O₃-bentonite. Absorption band at 3693.68 - 3624.25 cm⁻¹ in bentonite shifts to 3695.61 - 3624.25 in Fe₂O₃-bentonite, indicating the reduction of water trapped in Fe₂O₃-bentonite interlayer, resulting in the change in the OH stretching frequency. Si-O-Si stretch also shifts to 1112.93 (Fe₂O₃-bentonite) from 1111.0 cm⁻¹ (bentonite) and bend shifts to 690 from 696 cm⁻¹. In addition, the absorption at 796.6 (Fe₂O₃-bentonite) and 794.67 cm⁻¹ (bentonite) show the OH-Fe³⁺ vibration and OH-Al³⁺, respectively.

The surface area of Fe₂O₃-bentonite was slightly larger (47.8140 m²/g) than that of bentonite, which was 47.6473 m²/g, indicating that the intercalated bentonite was slightly smaller in particle size.

3.2. Optimum Photocatalyst concentration

Photocatalyst concentration was used to describe the mass of the catalyst used divided by the volume of the dye solution reacted; hence, 25 dm³. In the graph the mass is shown instead of concentration.

Figure 3 shows that the more the photocatalyst, the higher the percentage. This is caused by the increasing number of hydroxyl radicals and superoxide ions formed. The highest percentage is reached by 200 mg, meaning the optimum photocatalyst concentration is 200 mg/25 mL or 8 grams/L.

3.3. Optimum pH for the photodegradation

Figure 4 shows that the optimum photodegradation occurs at pH 4. This is because under the acidic condition, H₂O presents as H⁺ and OH⁻ which react to form hydroxyl radicals (OH •) which can degrade the dye. Degradation percentage tends to decrease with increasing pH. The percentage decrease in alkaline degradation may be due to the alkaline OH⁻, which, although can form hydroxyl radicals, the
excessive number of the OH− react with hydroxyl radicals (OH •) or the hydroxyl radical recombine into new compounds [3, 10].

3.4. Optimum irradiation time
From Figure 5 it can be seen the effect of irradiation time on the percentage of degradation, where the percentage of degradation increases with increasing UV irradiation time. The longer the time of UV light irradiation, the more photons are given on the surface of the photocatalyst, thus the greater photocatalysis activity, resulting in greater degradation percentage. The optimum irradiation time is reached at 2 hours.

3.5. The effectiveness of photodegradation of remazol brilliant blue
Photodegradation were conducted under optimum conditions namely pH 4, irradiation time of 2 hours, with 100 mg photocatalyst, on Remazol brilliant blue solution concentrations ranged from about 52 to 501 ppm. The experiment was conducted under UV radiation and under dark condition for three different catalysts, i.e. bentonite, Fe2O3, and Fe2O3-bentonite. The results are shown in Table 1
Figure 3. The photodegradation percentages at various photocatalyst masses.

Figure 4. The pH dependence of photodegradation percentage.

Figure 5. The change in degradation percentage with irradiation time.
Table 1. The degradation percentages of remazol brilliant blue by UV light in the presence of Fe$_2$O$_3$-bentonite, bentonite, and Fe$_2$O$_3$

| Catalyst            | Degradation % under UV | Degradation % under dark |
|---------------------|-------------------------|---------------------------|
| Bentonite           | 46.52 ± 0.06            | 45.37 ± 0.10              |
| Fe$_2$O$_3$         | 63.40 ± 0.69            | 1.04 ± 0.03               |
| Bentonite- Fe$_2$O$_3$ | 98.20 ± 0.07        | 47.81 ± 0.01              |

The highest percentage obtained by the Fe$_2$O$_3$-bentonite photocatalyst is 98.20 ± 0.07% (Table 1) of the initial concentration of 200 ppm of Remazol brilliant blue aqueous solution. Compared to the unmodified bentonite or Fe$_2$O$_3$, the Fe$_2$O$_3$-bentonite is far more effective to photodegrade the dyeing agent investigated. This is due to the ability of the bentonite in adsorbing the dye to increase contact between the photocatalyst and the dye molecules. The iron oxide, not having the adsorption capacity, cannot perform its photocatalytic activity optimally because of lack in contact with the dye molecules. The bentonite, on the other hand, can only adsorb the dye molecules without degrading them.

4. Conclusion
The Fe$_2$O$_3$-bentonite composite has shown its photocatalytic capability in degrading Remazol brilliant blue molecules. Under the optimum pH of 2, 100 mg composite can degrade 98.20% of 25 mL of 200 ppm Remazol brilliant blue during 2-hour irradiation. This finding suggests that this photodegradation procedure is potential to be improved for treating waste containing dye agents.

5. Suggestion/future work
Applying sunlight is preferable in the upscaled degradation process, thus experiment using sunlight in place of UV for the photodegradation should be conducted.

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