PHOTOLYSIS OF NAPHTHOL BLUE-BLACK FROM KUBANG WEAVING WASTE USING TiO₂/ZEOLITE AS A CATALYST

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ABSTRACT

This research investigated the degradation of Naphthol Blue-Black dye, an azo compound used in dying weaving in Kubang using Clinoptilolite-Ca TiO₂ / Zeolite as a catalyst. Waste from this compound is harmful to humans, animals, and plants. Degradation was carried out using a UV lamp at a wavelength of 365 nm. To improve the degradation yield, TiO₂ is supported by the natural zeolite of Clinoptilolite-Ca. TiO₂ is the best semiconductor catalyst, while zeolite Clinoptilolite-Ca is a natural zeolite that can expand the surface of TiO₂. It was found that maximum absorption of Naphthol Blue-Black was at 235 nm and after 120 minutes of irradiation the degradation yields were: without catalyst 20.58% after 120 minutes, with 0.4 g of Clinoptilolite-Ca TiO₂ / Zeolite 71.68%, with 0.02 g of TiO₂ alone 51.92%, and with 0.38 g of zeolite alone 32.21%. When the was used without time limitations in a simulated treatment situation, the degradation of *Naphthol Blue-Black* dye achieved with the TiO₂ / zeolite catalyst was 94.20% in the laboratory and 90.30% when used on weaving wastewater. FTIR analysis of Naphthol Blue-Black before and after degradation showed a shift in wavenumbers, indicating a change in functional groups. However, FTIR and XRD characterization of the TiO₂ zeolite catalysts indicated no change in structure.

Keywords: Degradation, Photolysis, Naphthol Blue-Black, TiO₂ / Zeolite, Weaving Waste.

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INTRODUCTION

The growing textile industry in Indonesia produces industrial waste that can damage the environment so requires processing. Weaving, a source of livelihood for the local community in Kubang, West Sumatera, is one such textile industry that uses reactive dyes.¹ There is a lack of traditional knowledge about the processing of dye in the wastewater resulting from the dyeing process. This waste results in environmental pollution as it is discharged into waterways untreated² resulting in the water becoming colored and toxic to aquatic life^{3,4} due to high levels of dyes, COD, BOD, TSS, and organic C. Reactive dyes are generally made from azo compounds and derivatives, which contain a benzene group⁵ and include Naphthol Blue-Black, Meltlen Blue, Rhodamin-B, and Congo Red. These dyes cannot be degraded biologically and are very soluble in water. If they are left in the environment azo compounds become hazardous because they are carcinogenic and mutagenic. The Kubang weaving industry uses the azo containing Naphthol Blue-Black¹. Therefore, an effective method is needed to decompose this dye.⁶ Photolysis is one possible method that TiO₂ / zeolite and ZnO / zeolite are effective catalysts of the related azo dye congo red^{4,7}. Zeolite is a naturally occurring, an underutilized mineral found in Java and Sumatra in Indonesia. For this research the zeolite clinoptilolite-Ca found in the Lubuk Salasiah area of West Sumatra was used⁴. This zeolite can use to absorb metals and support the catalysts TiO₂, CuO, ZnO, and CaO increasing the percent degradation of organic waste materials in the photolysis of textile dyes⁷. It has been found to reduce color and improve the quality of dye wastewater reducing COD, BOD, TSS, and carbon in organic compound⁸.

EXPERIMENTAL

Material

The material used was wastewater from the weaving industry in Kubang Lima Puluh Kota Indonesia, CaO/TiO₂, West Sumatran Zeolite Clinoptilolite-Ca, Naphthol Blue-Black, HCl, NaCl, AgNO₃, NaOH, aluminum foil.

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Tools

UV-Vis spectrophotometer, 10 watt UV light with $\lambda = 365$ nm, magnetic stirrer, furnace.

Activation of Zeolite

250 μm zeolite particles were activated using 0.2 M HCl and then left for 30 minutes, the pH was measured, then the mixture was rinsed with distilled water until the pH was neutral. Then the mixture was filtered, the residue discarded and the filtrate tested with AgNO_3 .

TiO₂ / Zeolite Catalyst Preparation

400 grams of saturated zeolite were mixed with distilled water for 5 hours, then 16 grams of TiO_2 was added gradually while stirring. The product was separated by vacuum filtering and dried in an oven at 100 °C, then cooled. It was then ground until smooth and then sieved using a 100 mesh filter. The portion that passed through the sieve was calcined at 400 °C for 24 hours.

Determination of Optimum Degradation Conditions**Determination of Light Absorption for Different Concentrations of Dye**

Naphthol Blue-Black solutions with concentrations of 3, 6, 9, 12, 15 mg / L were made then the absorbance at 365 nm measured using a UV-Vis spectrophotometer.

Influence of Photolysis Time without Catalyst

20 mL of 6 mg / L *Naphthol Blue-Black* solution was put into five tubes, and then each tube was placed in a flask under a UV lamp for 5, 15, 30, 45, 60, and 75 minutes. The degradation yield was measured by a UV-Vis spectrophotometer.

Influence of Amount of TiO₂ / Zeolite Catalyst on Degradation

20 mL of 6 mg / L *Naphthol Blue-Black* was put into five tubes with 0.2; 0.4; 0.6; 0.8; or 1.0g TiO_2 / zeolite. It was then irradiated in a flask for 120 minutes and centrifuged for 15 minutes. The dye concentration in the filtrate was measured with a UV-VIS spectrometer.

Influence of Photolysis Time when using a TiO₂ / Zeolite Catalyst

20 mL of 6 mg / L *Naphthol Blue-Black* was put into five tubes with 0.4 g of TiO_2 / zeolite catalyst then irradiated for 5, 15, 30, 45, 60, 75, 90, 105, and 120 minutes. After 15 minutes of centrifuging the dye concentration in the filtrate was measured with a UV-VIS spectrometer.

Influence of Photolysis Time when using a TiO₂ Catalyst

A mixture containing 0.02 g TiO_2 catalyst and 20 mL of 6 mg / L *Naphthol Blue-Black* compound was put into 5 tubes then irradiated with time variations of 5, 15, 30, 45, 60, 75, 90, 105, and 120 minutes. After 15 minutes of centrifuging the dye concentration in the filtrate was measured with a UV-VIS spectrometer.

Influence of Photolysis Time when using a Zeolite Catalyst

0.38 g Zeolite catalyst was put into five tubes of 20 mL of 6 mg / L *Naphthol Blue-Black* compound and then irradiated for 5, 15, 30, 45, 60, 75, 90, 105, and 120 minutes. After 15 minutes of centrifuging the dye concentration in the filtrate was measured with a UV-VIS spectrometer. FT-IR and XRD were used to analyze the *Naphthol Blue-Black* solution before and after degradation.

RESULTS AND DISCUSSION**The Absorption Spectrum of Naphthol Blue-Black Compounds**

Figure-1 shows the absorption of *Naphthol Blue-Black* at wavelength 618 nm. For concentrations from 0.1-0.5 mg / L absorbance varied continuously from 0.2-0.8.

Influence of Photolysis Time without Catalyst

Degradation of 20 ml *Naphthol Blue-Black* 30 mg / L degraded using 10 watts for 30, 60, 90, and 120 (minutes) can be seen in Fig.-2.

Fig.-1: Absorption of Naphthol Blue-Black

Fig.-2: Percent Degradation of Naphthol Blue-Black for Various Photolysis times with no Catalyst

Figure-2 shows the longer irradiation time the higher the percent degradation to a maximum of 20.58% after 120 minutes. Further irradiation did not result in a substantial increase in degradation.

The degradation process uses UV light to produce OH radicals which attack the functional groups of the dye compounds breaking them down into simple parts. The formation of OH radicals decreases after the optimal time so that the percentage of degradation does not increase after that.^{7,9}

Influence of Amount of TiO_2 / Zeolite Catalyst on the Degradation of Naphthol Blue-Black Compounds

20 ml of 6 mg / L Naphthol Blue-Black was degraded using 10 watts of radiation using 0.2; 0.4; 0.6; 0.8 and 1 gram of catalyst. Results can be seen in Fig.-3.

The greater the amount of TiO_2 / zeolite the higher the percent degradation up to 71.68%, with 0.4 grams of TiO_2 / zeolite and 120 minutes of irradiation time. The percentage of degradation was low if less than 0.4 gram of TiO_2 / zeolite was used as the formation of OH radicals was not optimal. The addition of more than 0.4 grams over-saturated the solution reducing OH radical formation and increasing absorbance. In this degradation process, there is a synergy of adsorption and degradation where TiO_2 is a degrading agent and zeolite is an adsorbent.^{10,11}

Determination of Percent Degradation of Naphthol Blue-Black after Addition of TiO_2 / Zeolite

20 ml of 6 mg/L Naphthol Blue-Black was degraded for 30, 60, 90 and 120 minutes after the addition of 0.4 grams of TiO_2 / zeolite as shown in Fig.-4.

Figure-4 shows the formation of OH radicals was influenced by the presence of the catalyst and increased with irradiation time. OH, radical formation increased with time resulting in more Naphthol Blue-Black

compound being degraded up to 72.70% after 120 minutes. Catalysts resulted in the formation of more OH radicals facilitating the decomposition of Naphthol Blue-Black to CO_2 and H_2O .⁴

Fig.-3: Percent Degradation of Naphthol Blue-Black with Variations in Mass

Fig.-4: Effect of Time on Percent Degradation after the Addition of 0.4 grams of TiO_2 / Zeolite

Influence of Photolysis Time when using TiO_2 Alone

The TiO_2 / zeolite catalyst consisted of TiO_2 and zeolite in the ratio of 1: 25 i.e. 0.4 grams of TiO_2 / zeolite contained 0.02 grams of TiO_2 and 0.38 grams of zeolite. The degradation when using 0.02 grams of TiO_2 alone for 30, 60, 90, and 120 minutes can see in Fig.-5.

Figure 5 shows the percent degradation increases with the longer irradiation time up to 51.92% after 120 minutes. In the presence of the TiO_2 catalyst many OH radicals are formed and the longer the irradiation time the more OH radicals and the faster the decomposition of Naphthol Blue-Black due to those radicals⁷.

Influence of Photolysis Time when using Zeolite Alone

The percentage degradation occurring with the addition of 0.38 grams of zeolite after 30, 60, 90, and 120 minutes can be seen in Fig.-6.

In this case, longer irradiation increased percent degradation up to 32.21% after 120 minutes of irradiation. Not only did photolysis occur but the adsorbent properties of zeolite reduced the amount of dye in the solution.^{7, 12}

Comparison of Percent Degradation Rates using TiO_2 / Zeolite, TiO_2 , and Zeolite Catalysts

The degradation yields of Naphthol Blue-Black using each catalyst; 0.4 grams of TiO_2 / zeolite, 0.02 grams of TiO_2 , and 0.38 grams of zeolite are compared in Fig.-7.

Figure 6 shows the optimum time at 120 minutes resulted in the greatest degradation for all catalysts. The percentage degradation was highest for 0.4 g TiO_2 / zeolite at 72.70% followed by 51.92% for 0.02 g of TiO_2 and 32.21% using zeolite 0.38 g. The TiO_2 / zeolite gave superior results due to the synergy of adsorption and degradation. Supporting TiO_2 on zeolite is shown to increase the decomposition of this hazardous compound into harmless ones. Besides that, it reduces the mass of TiO_2 needed. TiO_2 is rarely

found in a natural state and so must be synthesized while zeolite, as is a mineral that is commonly found in nature, is cheaper to obtain.^{7, 11}

Fig.-5: Effect of Time on Percent Degradation with 0.02 grams of TiO_2

Fig.-6: Effects of Time on Percent Degradation after Addition of 0.38 grams of Zeolite

Fig.-7: Comparison of Percent Degradation Rates for TiO_2 / Zeolite, TiO_2 , and Zeolite Catalysts

Comparison of Percent Degradation Rate with UV Light and without UV Light when using the TiO_2 /Zeolite Catalyst

The degradation of the Naphthol Blue-Black compound catalyzed with 0.4 grams of TiO_2 / zeolite without light and with UV light is shown in Fig.-8. Figure-8 shows that in the presence of UV light, the percent degradation is greater. After 120 minutes, with percent of degradation using UV light was 72.70%, almost 5 times higher than without light at 14.97%.¹¹

FTIR Analysis of Naphthol Blue-Black

FTIR analysis of Naphthol Blue-Black solution and in dye waste before and after degradation is shown in Fig.-9. The FTIR spectra show that Naphthol Blue-Black degrades as evidenced by shifting wavenumbers in 2000 to 2500 cm^{-1} band. In the FTIR spectrum of waste containing Naphthol Blue-Black, regions around wavenumbers 1500 - 2000 and 2000- 2500 indicate the amount of organic matter and dyes in the water. This shift in wavenumber is due to the change of functional groups in OH^4 .

Fig.-8: Comparison of Percent Degradation using TiO_2 / Zeolite Catalyst without Light and with UV Light

Fig.-9a: FTIR of Naphthol Blue-Black Solution (a) before degradation, (b) after degradation

Fig.-9b: FTIR of Naphthol Blue-Black in Wastewater (a) before degradation, (b) after degradation

FTIR Analysis of TiO_2 / Zeolite before and after the Degradation Reaction

These FTIR spectra can see in Fig.-10. The results shown in Fig.-9a demonstrate that the TiO_2 / zeolite catalysts do not experience FTIR wavelength shifts either in Naphthol Blue-Black solution or wastewater containing the dye. This indicates that the catalyst structure was not changed so can be reused as a degradation agent.⁴

Fig.-10a: FTIR TiO_2 / Zeolite Catalyst in Naphthol Blue-Black Solution (a) before degradation, (b) after degradation

Fig.-10b: FTIR TiO_2 / Zeolite Catalyst in Naphthol Blue-Black in Wastewater (a) before degradation, (b) after degradation

XRD Characterization of the TiO_2 / Zeolite Catalyst before and after Degradation

The results of XRD of TiO_2 / zeolite catalyst used in the degradation of Naphthol Blue-Black can be seen in Fig.-11. Figure-11 shows the XRD characterization of Zeolite, TiO_2 and TiO_2 / zeolite catalysts before and after Naphthol Blue-Black degradation. The similarity in XRD results in terms of diffraction angle and intensity indicates that the structure of TiO_2 / zeolite is unchanged by the degradation reaction of the Naphthol Blue-Black solution but a slight shift in diffraction angle when the catalyst is used with industrial waste containing the dye. This is because of the additional organic material from the weaving material

contained in the weaving waste. This suggests that these catalysts are not only able to break down the dye but also absorb some of the organic components of the waste⁸. The interaction between some organic materials present in the waste; BOD, COD, TOC and TSS are shown below.

Fig.-11a: XRD Catalyst TiO_2 Zeolite
(a) before degradation, (b) after degradation

Fig.-11b: XRD Catalyst for TiO_2 Zeolite Waste
(a) before degradation, (b) after degradation

Analysis of BOD, COD, TOC, TSS and Waste Degradation

In the laboratory, Naphthol Blue-Black waste dye material degradation was 94.20%, while on the field using weaving waste it was 90.30%. BOD concentration before degradation was 33.5 mg / L while after degradation this dropped to 2.71 mg / L. COD concentration dropped from 2760 mg / L to 16.9 mg / L, TOC from 41.7 mg / L to 42.1 mg / L and TSS from 164 mg / L to 4.0 mg / L.

Table-1: BOD, COD, TOC, TSS, and Waste Content before and after Degradation of Dye

Types of Simulated Waste	Types of Industrial Waste	% Degradation	mg/L (before degradation)	mg/L (after degradation)	Quality Standards	Method Specifications
Naphthol blue black		94.20				
	Naphthol blue black	90.30				
	BOD		33.5	2.71	150	SNI.06.6989.72:2009
	COD		2760	16.9	300	SNI 6989.2:2009
	TOC		41.7	42.1	-	APHA 5310
	TSS		164	4.0	400	SNI 06-6989.3-2004

These reduced levels are within Indonesian environmental quality standards. These results suggest that this method could be successfully used for the treatment of the weaving waste.¹³⁻¹⁷

CONCLUSION

Implications for the Kubang Weaving Industry. Without the use of a catalyst, an irradiation time of 120 minutes only reduced the Naphthol Blue-Black dye by 20.58%. The use of zeolite to catalyze the reaction increased this to 32.21% and a TiO_2 catalyst resulted in 51.92% degradation. The best result was from using 0.4 grams of TiO_2 / zeolite as a catalyst where 72.70% of the dye was degraded. UV light was still necessary for this process as without it degradation was only 14.97%. When the TiO_2 / zeolite catalyst was trialed in a simulated treatment situation without time limitations, the degradation of Naphthol Blue-Black dye reached 94.20% in the laboratory situation and 90.30% when used on weaving wastewater. The FTIR results confirmed degradation of Naphthol Blue-Black as a shift in the spectrum was evident. Characterization of TiO_2 / zeolite catalysts with FTIR and XRD before and after degradation confirmed that the catalyst structure was unchanged.

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