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PHOTODEGRADATION OF BATIK DYE COLOUR INDIGOSOL YELLOW IRK USING ZNO-CHITOSAN COMPOSITE

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ABSTRAK

Penelitian bertujuan untuk mengetahui kondisi optimum degradasi *zat warna batik Indigosol Yellow IRK* menggunakan komposit ZnO-Kitosan, meliputi waktu radiasi, konsentrasi zat warna, pH dan penentuan efektifitas degradasi. Sintesis komposit ZnO-kitosan menggunakan metode impregnasi basah. Waktu radiasi dengan perbedaan waktu 10, 30, 60, 120, serta 180 menit, variasi konsentrasi zat warna 50, 100, 150, 200, dan 250 ppm, variasi pH zat warna 2,5,7,9 dan 11. Besarnya konsentrasi hasil degradasi zat warna diukur dengan Spektrofotometer UV-Vis, panjang gelombang 319 nm. Hasil menunjukkan komposit ZnO-kitosan dapat mendegradasi zat warna batik *Indigosol Yellow IRK* dengan waktu radiasi 180 menit (98,28%), konsentrasi optimum 150 ppm (98,06%), pH optimum 9 (98,98%). Uji efektifitas fotodegradasi komposit ZnO-kitosan menggunakan sinar UV efektif sebesar 5,60% dibandingkan ZnO-kitosan tanpa sinar UV. Disimpulkan bahwa komposit ZnO-kitosan dapat mendegradasi zat warna batik *Indigosol Yellow IRK* sehingga komposit ZnO-kitosan-UV lebih efektif digunakan sebagai pendegrasi zat warna yang ramah lingkunga

Kata Kunci: Fotodegradas*i, Indigosol Yellow IRK,* Komposit ZnO-kitosan.

ABSTRACT

This experiment research aims to determine the optimum conditions for degradation of Indigosol Yellow IRK batik dye using ZnO-Chitosan composite, including radiation time, dye concentration, pH and determining the effectiveness of degradation. Synthesis of ZnO-chitosan composite using wet impregnation method. Radiation time with variations in time of 10, 30, 60, 120, and 180 minutes, variation in dye concentration 50, 100, 150, 200, and 250 ppm, variation in pH of dye 2,5,7,9 and 11. Measurement of the resulting concentration dye degradation using a UV-Vis Spectrophotometer with a wavelength of 319 nm. A ZnO-chitosan composite was found to degrade Indigosol Yellow IRK batik dye at 180 minutes (98.28%), optimum concentration of 150 ppm (98.06%), optimum pH of 9 (98.98%). The photodegradation effectiveness test of the ZnO-chitosan composite using effective UV light was 5.60% compared to ZnO-chitosan without UV light. It was concluded that the ZnO-chitosan composite could degrade the Indigosol Yellow IRK batik dye so that the ZnO-chitosan-UV composite was more effectively used as an environmentally friendly dye degrader.

Keywords: Photodegradation, Indigosol Yellow IRK, ZnO-chitosan composite

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INTRODUCTION

The increasing interest in batik among users today is driving the batik industry to meet market demands. However, the growth in the number of batik industries is not matched with proper waste management, it can lead to environmental problems. The batik process involves dyeing and bleaching, which use chemicals soluble in water and are often discharged without prior treatment. Waste management in the batik industry is not yet optimal and efficient, hence a method for treating batik dye waste is currently being developed called the photodegradation method.

The use of batik dyes is divided into two categories based on their sources there are natural dyes and synthetic dyes. Plant extracts are used as natural dyes, which are generally unstable, fade easily, and have limited color variations. Conversely, synthetic dye is more durable, has better color stability, as well as produces a wider spectrum of colors. Therefore, the majority of batik dyeing processes nowadays utilize synthetic dyes (Nugroho et al., 2013). One widely used type of dye in the batik industry is Indigosol. This synthetic dye consists of a molecular structure comprising six to ten benzene rings, offering high stability, resistance to degradation, carcinogenic properties, potential environmental pollution from its waste, negative health impacts such as skin irritation and cancer, and disruption to river ecosystems (Agil et al., 2016; Nugroho et al., 2013; Sutanto, 2017). Consequently, efforts are needed to manage this waste.

A variety of methods can be used to manage batik dye waste, including biological, chemical, and physical methods. Biological management of batik waste can involve wood-degrading fungi (*Pleurotus flabellatus*), but their ability to degrade dyes is not yet optimal (Husna et al., 2017), making this method inefficient. Chemical and physical methods such as adsorption, ion exchange, electrochemistry, coagulation, and sedimentation can also be implemented. The adsorption method accumulates dye adsorbed in the adsorbent without breaking down the toxic and carcinogenic properties of the dye waste, similarly, ion exchange and electrochemistry methods require a significant amount of reagents and incur high costs leading to new challenges (Setyaningsih, 2007). Utilizing coagulation and sedimentation methods in waste treatment results in new waste in the form of coagulants that cannot be reused (Rahmah et al., 2015).

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Currently, a method for treating batik dye waste is being developed, known as the photodegradation method. Photodegradation is a process where organic compounds are broken down into simpler compounds with the assistance of photon energy from UV radiation. This method is effective as it can break down dye compounds into simpler and environmentally safe components while generating less secondary waste (Kabra et al, 2004). Photodegradation can be carried out using semiconductors as catalysts such as ZnO, TiO_2, CdS, and Fe_2O_3. ZnO stands out due to its wide band gap of 3.17 eV (Ali and Siew, 2006), cost-effectiveness, environmental friendliness, and high photocatalytic activity (Surono dan Sutanto, 2014). In the process of photodegradation, the low adsorption capacity of ZnO photocatalysts becomes one of their weaknesses. To enhance their photocatalytic activity, ZnO needs to be combined with an adsorbent material such as activated carbon, zeolite, silica, and chitosan (Panda, 2017).

Chitosan, as an excellent supporting material is beneficial due to its ability to reduce organic waste and heavy metals (Hasri, 2015), being non-toxic and antibacterial (Damayanti, 2016). Incorporating chitosan with ZnO produces a chitosan-ZnO composite, exhibiting high photocatalytic activity with up to 80% methylene blue degradation in 4 hours (Dhanavel, 2014). The degradation percentage of phenol using ZnO-Chitosan reaches 60-70% within a maximum exposure time of 120 minutes (Panda, 2017). The combination of chitosan and ZnO as a composite shows great potential for colorant degradation and, to the best of researchers' knowledge, the utilization of chitosan as a supporting material combined with ZnO remains limited. Therefore, research on the photo-degradation of the batik dye Indigosol Yellow IRK using ZnO-Chitosan is necessary.

METHOD

Tools and Material

The equipment and materials used include glassware, an oven, a hot plate, a magnetic stirrer UV reactor, Phillips lamp (TUV 15W/G15 T8), LC-200 TOMY centrifuge, pH meter, Scanning Electron Microscopy– Electron Dispersive X-Ray Analyzer (SEM-EDX), Shimadzu Prestige-21 FT-IR spectrophotometer, and UV-Vis 2600 Series spectrophotometer.

Materials such as ZnO crystals, 85% chitosan, 2% acetic acid (CH_3COOH), 0.5 M sodium hydroxide (NaOH),1 M hydrochloric acid (HCl), deionized water, distilled water, Indigosol Yellow IRK dye, filter paper, and aluminum foil were also used.

Procedure

Synthesis of ZnO-Chitosan Composite

10 grams of chitosan were dissolved in 500 mL of 2% CH_3COOH, and 5 grams of ZnO powder were dissolved in 500 mL of 2% CH_3COOH. Both solutions were mixed, and NaOH 0.5M was slowly added until a solid formed and then stored for 24 hours, followed by washing until neutral pH was reached. Subsequently, Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) were used to characterize the composite of ZnO-Chitosan (Preethi, 2017).

Optimization of Indigosol Yellow IRK Dye Degradation

Radiation time determination

A total of 20 mL of Indigosol Yellow IRK solution with a concentration of 150 ppm was added to each beaker and supplemented with 50 mg of ZnO-chitosan composite. The suspension was irradiated for varying times of 10, 30, 60, 120, 180, and 240 minutes with stirring. UV-Vis Spectrophotometer was used to measure the absorbance of the suspension after centrifugation. Subsequently, the percentage degradation value was calculated for each time variation**.**

Optimal concentration determination

The same procedure as in radiation time determination, but the varying factor was the concentration of Indigosol Yellow IRK dye solution, which was set at 50, 100, 150, 200, and 250 ppm using the optimal radiation time.

Optimal pH determination

Similar procedure as in radiation time determination, but the varying factor was the pH adjusted to pH levels of 2, 5, 7, 9, and 11 using the optimal radiation time and concentration.

Effectiveness of Degradation

A total of 20 mL of Indigosol Yellow IRK solution at optimal concentration, time, and pH. The same treatment was applied for degradation using Chitosan-UV, ZnO-Chitosan-UV, ZnO without UV, Chitosan UV, and ZnO-Chitosan without UV.

RESULT AND DISCUSSION

Synthesis of ZnO-chitosan composite

The ZnO-chitosan composite is synthesized using the wet impregnation method with NaOH as the precipitant. The basic principle of wet impregnation is forcibly inserting the metal catalyst into the pores of the support. ZnO and chitosan are dissolved in 2% acetic acid, in an acidic environment, allowing the amino group of chitosan -NH_2 to easily form NH_3^+ ions that can effectively bind to negative ions, similarly, zinc oxide will form Zn^{2+} ions (Abdelhady, 2012). The resulting catalyst comprises granules from the reaction solution of NaOH, NH_2, OH groups of chitosan that form bonds with Zn^{2+} ions. The composite of ZnO-chitosan is ripened for 24 hours to achieve a homogenous size after drying followed by grinding. Characterization of the ZnO-chitosan composite is conducted using FTIR to observe changes in functional groups (Figure 1).

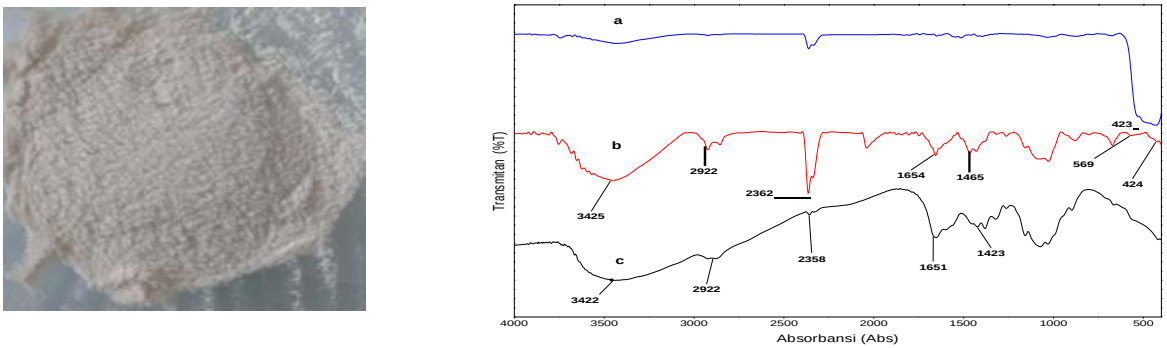

Figure 1. ZnO-Chitosan Synthesis Result (left), FTIR Functional Group Analysis (right)

Interpretation of functional groups in Figure 1 (right) shows absorptions in the region around (3000–3750) cm^{-1}, indicating the presence of hydroxyl (-OH) and NH_2 (primary amine) groups, which are active in chitosan. The absorption band at 2900–2930 cm^{-1} signifies the stretching vibration of -CH (methylene) groups. Absorption around 1375-1450 cm^{-1} indicates the presence of methyl (-CH_3) groups. There is a bending vibration present in the area of 1600–1655 cm^{-1}, which indicates the occurrence of the amide-NH bond. New peaks at wave numbers 569 cm^{-1} and 424 cm^{-1} indicate the vibrations of Zn-N and Zn-O groups (Tang, 2001), suggesting that impregnation has taken place based on the functional group information, particularly the appearance of new peaks. Morphological analysis and composition determination of the ZnO-chitosan composite using SEM-EDX can be seen in Figures 2 and 3 showing the atomic mass data presentation of the ZnO-chitosan composite. Figure 2 illustrates the irregularity of the ZnO-

Chitosan composite surface, with random particles of small sizes scattered over it. These aggregates are presumed to be ZnO materials distributed on the composite surface non-uniformly due to inhomogeneity during particle size reduction. EDX characterization results in Figure 3 reveal that the composition of the ZnO-chitosan composite consists of N, O, and C, as well as Zn atoms, as well as impurities such as Mg, Si, Ca, and Au.

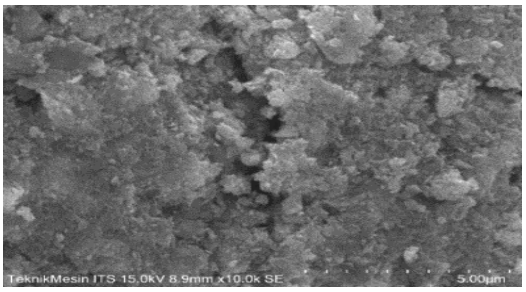

Figure 2. SEM analysis results of ZnO-Chitosan composite at 10,000x magnification.

Element	Weight %	Atomic %	Net Int.	Error %
C K	4.04	11.54	2.04	99.99
N K	3.52	8.62	2.48	23.09
O K	18.75	40.23	27.34	10.28
MgK	1.25	1.76	1.59	28.17
SiK	0.82	0.76	1.42	36.38
AuM	3.66	0.64	3.55	24.76
CaK	1.98	1.69	3.19	16.82
ZnK	66.18	34.75	17.61	7.02

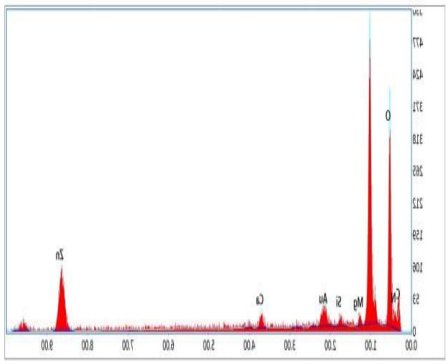

Figure 3. Analysis results of ZnO-chitosan composite from EDX.

Optimization of Indigosol Yellow IRK dye degradation

Time is one of the factors affecting the extent of degradation of Indigosol Yellow IRK. The determination of the optimum radiation time was carried out by reacting ZnO-chitosan composite into a solution of Indigosol Yellow IRK dye at a concentration of 150 ppm, adjusted to pH 7, and then irradiated with UV light for varying periods. The final concentration of Indigosol Yellow IRK dye was measured using a UV-Vis Spectrophotometer at a wavelength of 319 nm. Based on Figure 4, the degradation of Indigosol Yellow IRK dye showed the highest degradation percentage at 180 minutes, with a degradation percentage of 98.28%. Longer irradiation periods result in increased degradation percentage due to the greater absorption of photon energy by the photocatalyst, activating the catalyst to form •OH radicals, thereby

enhancing the degradation of Indigosol Yellow IRK dye (Saraswati, et al., 2015). However, at 180 and 240 minutes, no significant changes were observed as the ability of ZnO-chitosan to degrade Indigosol Yellow IRK had already reached its maximum point.

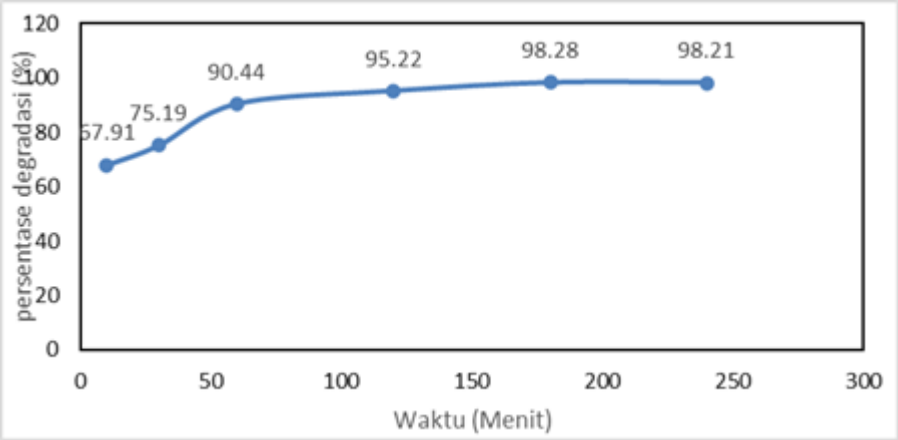

Figure 4. Degradation percentage of the dye Indigosol Yellow IRK over time.

Optimum concentration determination of Indigosol Yellow IRK dye degradation

Based on Figure 5, the highest degradation percentage of Indigosol Yellow IRK dye occurs at a concentration of 150 ppm, reaching 98.06%. As the dye solution concentration increases, the dye degradation capacity by the ZnO-chitosan catalyst decreases. This is due to catalyst saturation at high concentrations, leading to catalyst surface coverage, resulting in some of the catalysts not being exposed to UV light. Furthermore, with increasing dye concentrations, light penetration into the photocatalyst is hindered, reducing photon absorption by the catalyst and consequently decreasing the degradation rate (Dini and Wardani, 2014).

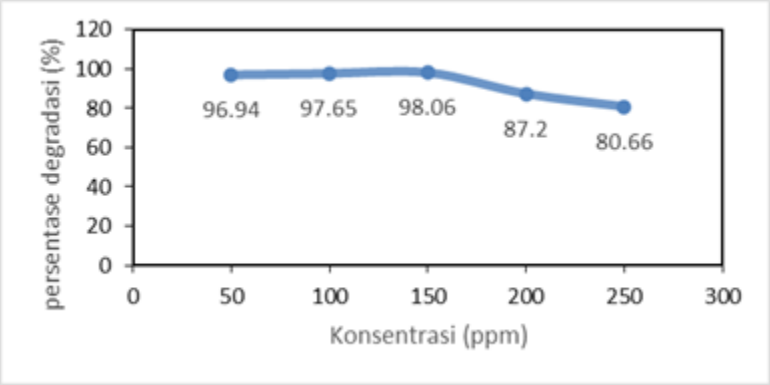

Figure 5. Percentage of degradation of Indigosol yellow IRK dye at various concentrations

Optimum pH Determination for Degradation

The degradation percentage increases with the rise in pH. This occurs because the increase in the pH value of the solution causes the concentration of OH- to increase, causing OH- to react with holes in the valence band in order to form hydroxyl radicals (•OH) in greater quantities. Hydroxyl radicals (•OH) are strong oxidants that oxidize Indigosol yellow IRK into CO_2 and H_2O compounds. The more hydroxyl radicals formed, the more Indigosol yellow IRK is degraded. The optimum pH is obtained in a basic pH of 9 with a degradation percentage of 98.98%. The decrease in degradation percentage at low pH is due to the saturated catalyst surface with an excess of H^+ ions in a low pH environment, hindering the absorption of Indigosol yellow IRK. When acidic conditions are present, this reduces the positive charge on catalyst surfaces, enabling hydroxyl radicals to be formed (Sapawe et al., 2013).

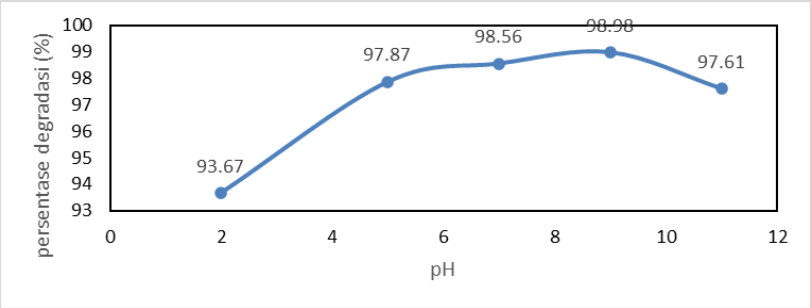

Figure 6. Percentage of degradation of Indigosol yellow IRK dye at pH variations

The effectiveness of Indigosol yellow IRK photodegradation

The purpose of this treatment is to understand the role of catalysts in photocatalysis. According to Figure 7, it is shown that the use of ZnO without UV light resulted in a degradation percentage of 12.50%. This is because ZnO is not effective in forming hydroxyl radicals, as there is no photon energy from UV light reaching the ZnO catalyst. Thus, the energy used to degrade the dye is only from the system. On the other hand, utilizing UV light led to a degradation percentage of 76.08%. This demonstrates the presence of a photodegradation reaction, where when the ZnO photocatalyst is irradiated with UV light, it generates a hole (h^+_{VB}) and an electron (e^-_{CB}). The hole reacts with H_2O to form hydroxyl radicals capable of degrading the dye (Vifta et al., 2016). Chitosan, whether exposed to UV light or not, showed a degradation percentage of 0.28%. This indicates that the use or absence of UV light has no impact as chitosan does not undergo photodegradation reactions but functions as an adsorbent (Hasri, 2015).

In the treatment of ZnO-chitosan under UV light, degradation results of 98.97% were obtained, while ZnO-chitosan without UV resulted in 93.39%. This indicates that UV irradiation can increase the degradation percentage due to additional energy from UV light. Research findings show that ZnO-chitosan under UV has the highest degradation percentage, suggesting that impregnating chitosan into ZnO enhances the degradation activity of ZnO photocatalysts. Chitosan prevents particle aggregation, assumed to increase specific surface area, leading to increased hydroxyl radical formation. The more hydroxyl radicals formed, the greater the photocatalytic ability to oxidize organic compounds. The effectiveness of the photodegradation process using photocatalysts compared to UV light alone shows that photocatalysts with UV light are more effective than those without photocatalysts under UV light (Sararwati et al, 2015).

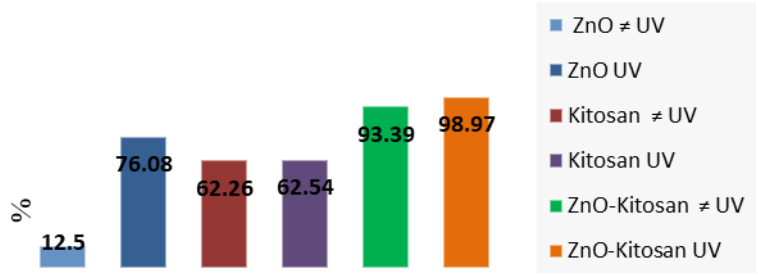

Figure 7. Percentage of degradation of Indigosol Yellow IRK dye

CONCLUSION

It is concluded that the optimum condition of ZnO-chitosan composite can degrade the Indigosol Yellow IRK batik dye including a radiation time of 180 minutes (98.28%), a concentration of 150 ppm (98.06%), and pH 9 (98.98%). The effectiveness test of ZnO-chitosan-UV composite photodegradation shows a higher degradation percentage compared to ZnO-chitosan without UV light, with a difference of 5.60% in degradation percentage. Therefore, ZnO-chitosan-UV composite is more effectively used as an environmentally friendly dye degrader.

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