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Chitosan-ZnO Composite for Removal of Methylene Blue

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Abstract

This study aims to determine the effectiveness and increase in absorption of the chitosan-ZnO composite in the process of removing methylene blue when using the photodegradation method with the help of a UV lamp. Chitosan was synthesized from shrimp shell waste composite with metal oxide ZnO. The results of the characterization using XRD obtained the diffraction peak for chitosan at an angle of 2θ, namely 19.85°; 29.43°; 34.76° and chitosan-ZnO composite at an angle of 20.18°; 28.93°; 33.57°. The SEM-EDX characterization shows that chitosan-ZnO has small, light-colored grains and more gaps and contains elements of chitosan and Zn. In the FTIR characterization, there was a decrease in intensity at a peak of around 3360 cm^{-1} which was caused by the chitosan-ZnO composite producing OH groups which reacted with methylene blue dye. In testing the effect of contact time using a UV lamp, there was an increase in the percentage of degraded methylene blue compared to without using a UV lamp. The maximum contact time is obtained at 60 minutes. While testing the effect of methylene blue dye concentration, the maximum absorption concentration was 45 ppm at 60 minutes of contact time. The adsorption capacity of the composite against methylene blue dye without UV light was 18.91 mg/g while using a UV lamp it increased to 20.145 mg/g. Based on this research, the chitosan/ZnO composite can be used quite well as a methylene blue dye remover.

Keywords: Chitosan, Chitosan-ZnO, Photodegradation, Methylene blue

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Penelitian ini bertujuan untuk mengetahui efektivitas dan peningkatan serapan komposit kitosan-ZnO pada proses penghilangan metilen biru bila menggunakan metode fotodegradasi dengan bantuan lampu UV. Kitosan disintesis dari limbah cangkang udang yang dikomposit dengan bahan oksida logam ZnO. Hasil karakterisasi menggunakan XRD diperoleh puncak difraksi untuk kitosan pada sudut 2θ yaitu 19,85°; 29,43°; 34,76° dan komposit kitosan-ZnO pada sudut 20,18°; 28,93°; 33,57° Karakterisasi SEM-EDX menunjukkan kitosan-ZnO memiliki butiran kecil berwarna terang dan lebih banyak celah dan adanya kandungan unsur kitosan dan Zn. Pada karakterisasi FTIR terjadi penurunan intensitas pada puncak sekitar 3360 cm^{-1} yang disebabkan oleh komposit kitosan-ZnO menghasilkan gugus OH yang bereaksi dengan pewarna metilen biru. Pada pengujian pengaruh waktu kontak dengan menggunakan lampu UV terjadi peningkatan persentase metilen biru yang terdegradasi dibandingkan tanpa menggunakan lampu UV. Waktu kontak maksimum diperoleh pada waktu 60 menit. Sedangkan pada pengujian pengaruh konsentrasi zat warna metilen biru diperoleh serapan maksimum konsentrasi 45 ppm pada waktu kontak 60 menit. Kapasitas adsorpsi komposit terhahadap zat warna metilen biru tanpa lampu UV adalah sebesar 18,91 mg/g sedangkan jika menggunakan lampu UV meningkat menjadi 20,145 mg/g. Berdasarkan penelitian ini, komposit kitosan/ZnO dapat digunakan sebagai penghilang zat warna metilen biru dengan cukup baik.

Kata Kunci: Kitosan, Kitosan-ZnO, Fotodegradasi, Metilen biru

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INTRODUCTION

The value of Indonesian shrimp exports reached 142,000 tons with a total of 60,000 tons of unused shell and head waste. The abundant wastes are potentially used for raw materials and industrial products because they contain high economic value chitosan compounds and the processed products can be used for various purposes [1]. Chitosan is a long-chain polymer with the molecular formula $(C_8H_{11}NO_4)_n$ produced from chitin through a deacetylation process by removing the acetyl group into an amine group [2].

Chitosan was isolated from shrimp shell waste through four reaction stages of deproteination, demineralization, decolorization, and deacetylation [1]. Its chemical structure is possibly adjusted by physical methods such as larger surface area, active adsorption sites, and decreased crystallinity, and chemical impregnation. This chemical structure modification increases the effectiveness value in decomposing a substance not only as an absorbent [3].

Chitosan has a weakness as an adsorbent, namely its low adsorption capacity and poor mechanical properties. To overcome the weaknesses of chitosan, composites are usually made with other substances such as hydroxyapatite, TiO_2, ZnO, and Fe_3O_4 [4,5]. Researchers have recognized that the combination of chitosan with metal oxides is useful for adsorption, catalysis, degradation, and biomedicine [6,7]. In recent years, chitosan-based metal particle composites have been increasingly studied as alternative adsorbents in water treatment, and it is often combined with metal oxides known as ZnO with a total bandgap with a width of less than 3.37 eV [8]. The large surface area and high surface energy cause zinc oxide nanoparticles to aggregate. To increase the distribution area, the synthesis product was impregnated with chitosan to reduce the occurrence of agglomeration between zinc oxide particles Composite of chitosan with zinc oxide (nano-ZnO) in different amounts to improve the mechanical properties of chitosan [9]. Meanwhile, ZnO with a higher surface distribution can increase the decomposition of substances with the help of light, and as a photocatalyst, it can interact with UV light to produce more OH radicals. According to research conducted by Xu et.al. [10], the photodegradation process of organic waste in seawater using a TiO_2 catalyst exposed to visible light produces holes and free radicals. The photogeneration pits formed by the catalyst play an important role in the degradation of organic wastes, regardless of whether photodegradation occurs in seawater or fresh water.

Dhanavel stated that photodegraded methylene blue from water using ZnO chitosan composite with a ZnO ratio of 40% of chitosan weight (w/w) can result in an effective separation of about 80% within 4 hours [11]. In this research, a chitosan-ZnO composite was synthesized with a weight ratio between chitosan and ZnO, namely 1:1; 1:2 and 1: 3. The resulting composite was used to degrade methylene blue dye. The photodegradation process was carried out by varying the irradiation time. The results of photodegradation were measured using a UV-vis spectrophotometer. The resulting composites were characterized using XRD, FTIR, SEM-EDS and UV-vis and UV-DRS instruments.

MATERIALS AND METHODS

Materials

Material used in this research is shrimp sell was collected in Palembang city, natrium hydroxide (Merck), hydrochloric acid 37% (Merck), sodium hypochlorite technically, zinc acetate dihydrate (Merck), Methylene blue dye technically.

Methods

Chitosan Preparation

The dried shrimp shells were ground and sieved (60 mesh), and 50 g of the waste was added with 3.5% NaOH solution in a ratio of 1:10 (w/v). It was stirred at a temperature of 65°C for 2 hours and then filtered as well as neutralized with distilled water. The solid obtained was then dried in an oven at 100°C for 2 hours. Meanwhile, 25 g of deproteinized shrimp shells were added with 1 N HCl in a ratio of 1:15 (w/v) and mixed at a temperature of 60°C for 30 minutes. The precipitate was filtered, washed, and dried, and the deproteinized shrimp shell was dissolved in a solution of sodium hypochlorite (NaOCl) with a concentration of 0.315%. The deacetylation process in the form of 1.25 g of decolorized chitin was added with 60% NaOH in a ratio of 1:20 (w/v) and stirred for 1 hour. Furthermore, the precipitate was filtered and washed using distilled water, and the chitosan obtained was then dried in an oven at 100°C for 2 hours before the analysis. It was characterized by an FT-IR spectrophotometer at a frequency of 4000-400 cm^{-1} and SEM-EDX [1].

ZnO Material Preparation.

100 mL of zinc acetate dihydrate solution with a concentration of 0.01 M is added to 100 mL of 0.05 M NaOH and stirred. The precipitate obtained was washed using distilled water, filtered, and dried at 100°C, and pure ZnO was acquired through a calcination process using a furnace at a temperature of 450°C for 30 minutes. The obtained ZnO was characterized using XRD and UV-Vis DRS [1].

Chitosan-ZnO Synthesis

The obtained ZnO was dispersed in 100 mL of 2% acetic acid and 0.75 g of chitosan was added. Furthermore, chitosan and ZnO were prepared with 3 different mass ratios with that of chitosan-ZnO = 1:1, 1:2, and 1:3 (w/w). This mixture was stirred until obtaining a clear solution. NaOH 1 M solution was then injected dropwise until it reached pH 10, and the precipitate formed was washed and dried. The obtained chitosan-ZnO was characterized using XRD, SEM, and Uv-DRS spectrophotometer [11].

RESULTS AND DISCUSSION

Characterization of Chitosan and Chitosan-ZnO with XRD

Characterization of chitosan and chitosan-ZnO using XRD was conducted to observe that chitosan was mixed with ZnO based on the diffraction peaks formed as seen in Figure 1. Based on the diffractogram in **Figure** 1, it can be seen that there are differences in the crystallinity and density of chitosan-ZnO and chitosan composite structures. The distribution of ZnO nanoparticles in chitosan resulted in an increase in crystallinity in chitosan-ZnO composites compared to chitosan.

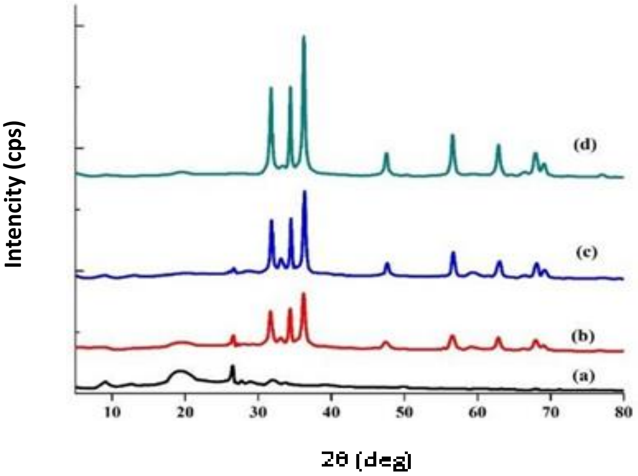


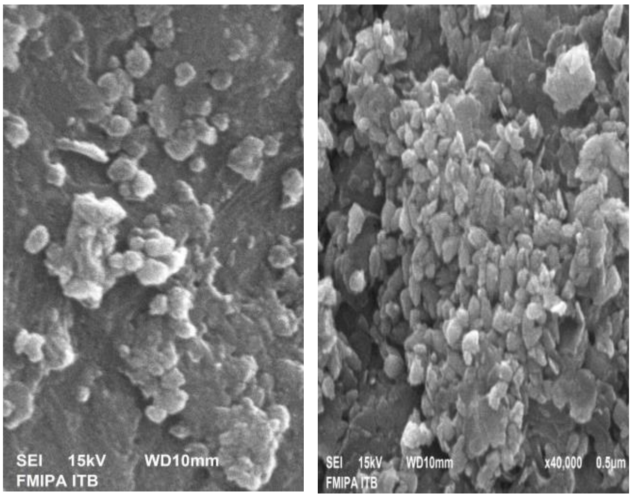
Figure 1. Diffractogram of (a) Chitosan; (b) Chitosan-ZnO 1:1; (c) Chitosan-ZnO 1:2; (d) Chitosan-ZnO 1: 3

This also indicates the presence of ZnO particles and those integrated with chitosan giving rise to a shift in peak angle at 2θ 19.85°; 29,43°; 34.76° in chitosan to 2θ 20.18°; 28,93°; 33.57° on Chitosan ZnO composites. The occurrence of a decrease in the peak intensity typical of chitosan in the regions of 2θ, 10° and 19° in chitosan-ZnO composites indicates that there is a change in the density of chitosan crystalline structure due to ZnO particles integrated with chitosan. ZnO particles integrated in chitosan-ZnO composites still produce characteristic peaks of ZnO materials. Typical peaks of crystalline ZnO occur in regions 2θ 30°, 34°, 36°, 48° and 68° where ZnO material dominates ZnO crystalline peaks in the chitosan-ZnO composite diffractogram [12].

In chitosan-ZnO composites with variations of 1:1, 1:2, and 1:3 there is an increase in the crystallinity of ZnO proportional to the increase in the ratio between chitosan and ZnO. Typical peaks of chitosan at 2θ, 19° and 28° decreased crystallinity. This is because ZnO particles experience maximum crystal growth as the mass of ZnO increases, it can be concluded that chitosan can inhibit or decrease the level of crystallinity of ZnO.

Characterization of Chitosan and Chitosan-ZnO Using SEM EDX

Chitosan and chitosan-ZnO were characterized using SEM EDX to determine the morphology of the surface before and after ZnO was added. **Figure** 2 showed the surface of chitosan and chitosan-ZnO.



(a) (b)

Figure 2. SEM Results of (a) Chitosan and (b) Chitosan-ZnO

The surface of chitosan in **Figure** 3a tends to be flat with few granules, while in Figure 3b chitosan-ZnO has small, light-colored granules and more crevices. This showed that there is a difference between before and after the addition of ZnO, where lighter particles appear on the surface of the chitosan. **Table** 2 showed the data characterization using EDX (Energy Dispersive X-ray) which is the percentage of elements contained in chitosan and chitosan-ZnO. From the results of the EDX characterization, as shown in **Table** 2, there was no Zn element found in pure chitosan and chitosan-ZnO. However, 29.98% Zn was found which indicated that ZnO had been composited with chitosan.

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Table 2. Composition of element

Element	Mass Ratio	
	Chitosan (%)	Chitosan-ZnO (%)
C	53.00	24.10
O	38.64	31.67
Na	2.64	2.09
Al	0.91	0.77
Si	1.59	0.85
Cl	0.73	-
Ca	2.49	8.03

Characterization of Chitosan and Chitosan-ZnO Using FTIR

Chitosan obtained from shrimp shells was characterized using an FTIR spectrophotometer to determine the functional groups. The comparison chart of chitosan-ZnO before and after the application is shown in **Figure** 5. Based on the results of the FTIR characterization of chitosan-ZnO, the absorption wavelength was 3,365.62 cm^{-1} before the application. Dhanavel reported the presence of -NH and -OH groups [11]. However, after chitosan-ZnO was applied as a methylene blue photocatalyst, a slight shift was experienced in the peak of 3,376.59 cm^{-1}, and the intensity after the application was reduced. Photocatalyst produces •OH radicals which react with dyes (methylene blue) therefore after the photodegradation process there is a decrease in intensity at 3,376.59 cm^{-1}.

Effect of time for removal of Methylene Blue

Figure 3 showed a comparison of the effect of light on the decomposition process of methylene blue by chitosan-ZnO. Graph (b) is lower than (a) where chitosan-ZnO decomposes more methylene blue. In graph (a) the percentage of adsorbed and photodegraded is 4.26; 10.32; 17.44; 25.48; and 32.95%. Meanwhile, the percentage of methylene blue without irradiation in a graph (b) is 1.73; 4.67; 4.57; 13.91 and 18.82%.

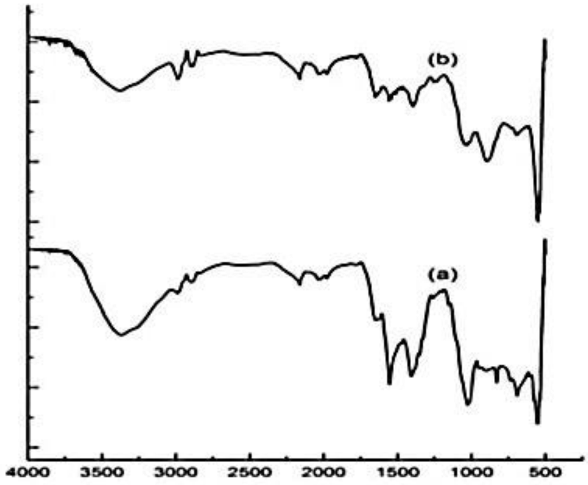

Figure 5. FTIR Spectra of (a) Chitosan-ZnO before and (b) Chitosan-ZnO after photodegradation

The percentage reduction of methylene blue in UV-irradiated chitosan-ZnO was greater than non-UV irradiated chitosan-ZnO. This is because the chitosan-ZnO received treatment in the form of UV light undergoing a photodegradation process, which decomposes the dye with the help of light. Meanwhile, chitosan-ZnO which was not treated with light only adsorbed methylene blue, and the photodegradation reaction of methylene blue using ZnO [13]

The rate of degradation is related to the formation of OH radicals (•OH), and when irradiated, it interacts with methylene blue resulting in the degradation of dyes. The chitosan-ZnO photocatalyst is dark when compared under the conditions of without and with light [14]. The photocatalyst cannot induce the formation of hydroxyl radicals with strong oxidation to achieve degradation due to the lack of ultraviolet light excitation in the semiconductor band. Therefore, hydroxyl radicals are not formed and methylene blue is not photodegraded, and under conditions with direct UV light, photodegradation efficiency can continue to increase. The hydroxyl radicals generated by the photocatalyst are directly exposed to UV light and when the photocatalyst is added to the methylene blue solution, the groups are formed and adhere to the surface of the photocatalyst. Similarly, the valence band site of the ZnO semiconductor is lower than the oxidation potential of the hydroxyl group, and the positively charged holes on the semiconductor surface will initially be trapped by the surface to produce hydroxyl radicals with strong oxidation by UV light.

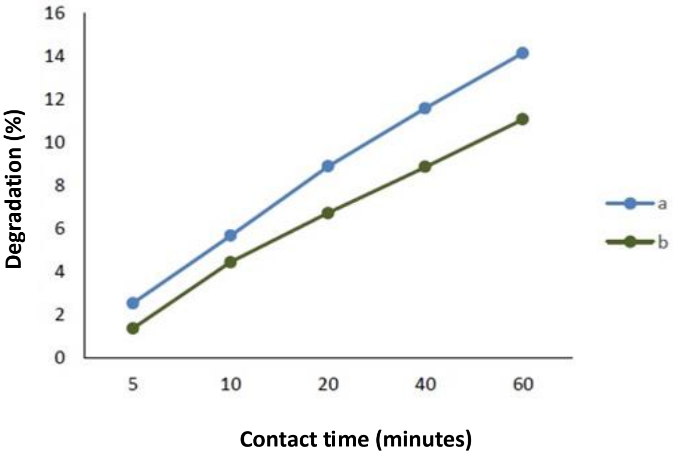

Figure 3. Effect of Time by (a) with UV light, (b) without UV light.

Therefore, it can be concluded that the longer the irradiation, the more OH radicals formed and the more photodegraded methylene blue. With increasing time, the adsorption capacity increases, possibly due to the migration of dye molecules into the inner pores of the adsorbent [15]. This study showed that chitosan-ZnO was effectively used as a photocatalyst for the degradation process of methylene blue.

Effect of Concentration for removal of Methylene Blue

Figure 4 shows that each treatment has a maximum absorption of methylene blue dye at a concentration of 45 ppm. In Figure 4 at a concentration of 45 ppm still shows an increase with the maximum absorption along with the addition of a UV lamp with a Q_e value of 20.145 mg/g. As for the treatment without using UV lamps, the absorption capacity is only 18.91 mg/g. The difference in treatment shows that in the chitosan-ZnO composite there is a photodegradation process caused by ZnO compounds which are metal oxides that can degrade dyes well.

In the treatment using UV lamps, there is the largest difference between the two methods at a concentration of 20 ppm with a Q_e difference of 1.685 mg/g, this occurs because at smaller concentrations methylene blue has a smaller number of particles and this results in the possibility of these particles being degraded by UV light will be even greater. Light from UV light will also be affected as the concentration of methylene blue increases, the greater the concentration, the light that reaches the chitosan/ZnO composite will be less, so that the energy of the photons that arrive is also small and causes the smaller the electron excitation process from the valence band to the conduction band, the less hydroxyl radical (•OH) is produced, so that only a small part of methylene blue can be oxidized.

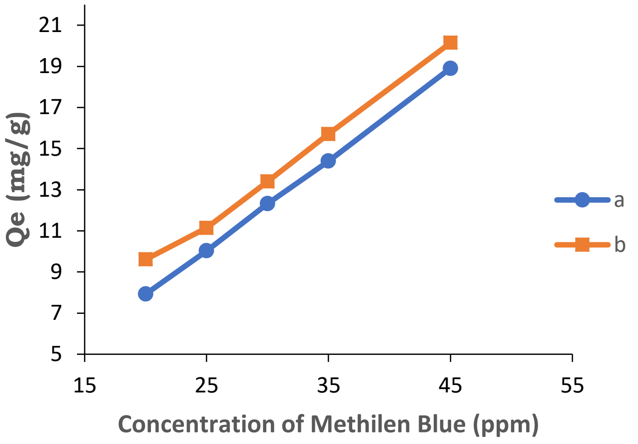

Figure 4. Effect of Concentration (a) without UV light, (b) with UV light

CONCLUSION

Based on the results of XRD characterization, it can be concluded that the decrease in peak intensity typical of chitosan in the regions of 2θ i.e. 10° and 19° in chitosan-ZnO composites shows that there is a change in the density of chitosan crystal structure due to ZnO particles integrated with chitosan. The SEM characterization shows that the surface of chitosan contains ZnO material in the form of small light-colored grains and is evidenced by the results of EDX there are Zn compounds in chitosan-ZnO composites. In FT-IR characterization, there is a peak in the range of about 3360 cm^{-1} which indicates the presence of OH and NH function groups. However, in the FT-IR results after the photocatalyst test, there was a decrease in peak intensity at 3365 cm^{-1} which indicates that the OH group in ZnO reacts with dyes. This is also evidenced by contact time trials and the effect of dye concentration that when using UV lamps there is an increase in absorption and efficiency of methylene blue dye removal.

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