

Synthesis of Chitosan–Al₂O₃ Composite using the Sol-Gel Method and Its Application in Photodegradation of Methylene Blue

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Abstract

The research on synthesis of composites Kitosan-Al₂O₃ by the sol-gel method for photodegradation of methylene blue has been carried out. Chitosan-Al₂O₃ varied by mass ratios (1:1), (1:2) and (1:3). The product was characterized using XRD and UV-DRS. Chitosan-Al₂O₃ ratio (1:1) were characterized by SEM-EDS. The best material will be used to degrade the methylene blue by various condition, i.e., effect of pH, contact time and initial concentration of methylene blue. The Chitosan-Al₂O₃ (1:1) composite was chosen as a material for degrading methylene blue. The result of characterization using XRD showed crystal size the Chitosan- Al₂O₃ (1:1) composites result were 3.17 nm. UV-DRS characterization, the band gap energy is 1.35 eV. The morphological condition by SEM of Chitosan-Al₂O₃ ratio (1:1) showed a spherical shape with a small size, and a porous surface the constituent elements C (4.93%), O (33.31%), Na (13.92%), Al (45.59%) dan Zn (2.24%). The degradation process showed the effective condition were pH 10 and contact time of 200 minutes. The optimum concentration of methylene blue at 20 ppm with percent effectivity of concentration reduction methylene blue i.e. 79.35% and the result of TOC analysis i.e. 22.36%. The Chitosan-Al₂O₃ can be used to degraded the Methylene blue.

Keywords: Composites, Chitosan-Al₂O₃, Photodegradation, methylene blue, H₂O₂

Abstrak (Indonesian)

Penelitian tentang sintesis komposit kitosan-Al₂O₃ menggunakan metode sol-gel dan aplikasinya pada degradasi metilen biru telah dilakukan. Kitosan-Al₂O₃ divariasikan dengan perbandingan massa (1:1), (1:2) dan (1:3). Produk dikarakterisasi menggunakan XRD dan UV-DRS. Material dengan perbandingan (1:1) dipilih untuk dikarakterisasi menggunakan SEM-EDS. Berdasarkan hasil karakterisasi maka akan dipilih material terbaik untuk diaplikasikan pada degradasi zat warna metilen biru terhadap pengaruh pH, waktu kontak dan konsentrasi awal zat warna metilen biru. Komposit Kitosan-Al₂O₃ (1:1) dipilih sebagai material untuk mendegradasi zat warna metilen biru. Hasil karakterisasi XRD menunjukkan ukurankristal komposit Kitosan-Al₂O₃ (1:1) sebesar 3,17 nm. Hasil karakterisasi UV-DRS menunjukkan nilai energi celah pita komposit kitosan-Al₂O₃ (1:1) sebesar 1,35 eV. Morfologi komposit kitosan-Al₂O₃ (1:1) menunjukkan bentuk bulat dengan ukuran yang kecil, serta permukaan yang berpori dengan komposisi unsur penyusun C (4,93%), O (33,31%), Na (13,92%), Al (45,59%) dan Zn (2,24%). Hasil degradasi menunjukkan bahwa kondisi optimum degradasi terjadi pada pH 10 dan waktu kontak 200 menit. Konsentrasi optimum metilen biru yang dapat didegradasi pada penelitian ini adalah sebesar 20 ppm dengan persentase degradasi sebesar 79,35% dan hasil uji TOC sebesar 22,36%. Komposit kitosan-Al₂O₃ dapat digunakan untuk mendegradasi zat warna metilen biru.

Kata Kunci: Komposit, Kitosan-Al₂O₃, Fotodegradasi, Metilen biru, H₂O₂

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INTRODUCTION

The textile industry is one of the contributors to synthetic dye waste in the waters. About 15% of the total use of dyes will be disposed of in the form of waste, because synthetic dyes are carcinogenic and

have high toxicity [1]. This has the potential to endanger the environment so that it can disrupt the sustainability of ecosystems in the waters [2]. In addition, water that has been contaminated with

synthetic dyes can cause health problems such as skin irritation, eye irritation to cause cancer. One of the most widely used synthetic dyes in the textile industry is Methylene Blue (MB). Methylene blue dye belongs to the group of organic compounds with a heterocyclic aromatic structure as its constituent [3], and is included in the positively charged basic dye [4]. In the research of Ozer and Dursun [5], methylene blue dye waste will be difficult to decompose because it is composed of aromatic groups, is resistant to aerobic processing, contains organic compounds, is stable to light and heat [6].

Various methods have been used to overcome synthetic dye contaminants such as adsorption, biodegradation, photodegradation and AOPs methods. The AOPs method is a water treatment method that utilizes chemical oxidation processes to neutralize organic contaminants in waters [7]. This AOPs method has the advantage of being able to degrade hazardous compounds that are not biodegradable in waste through an oxidation process [8]. The AOPs method shows efficiency in degrading synthetic dyes by utilizing semiconductors accompanied by the addition of strong oxidizing agents such as UV light and H_2O_2 [9].

The addition of H_2O_2 serves to increase the production of hydroxyl radicals through reduction, the more the number of hydroxyl radicals produced, the more the amount of dye degraded [10]. One of the semiconductors that has the potential to remove or degrade liquid dye pollutants is Al_2O_3 [11]. The photon energy is Ultraviolet (UV) light irradiated to metal oxides will stimulate electrons from the valence band to the conduction band so that electron holes are formed. When water interacts with holes it will form highly reactive ions. These ions will interact with organic compounds and decompose them into compounds with smaller molecular weights and are non-toxic (Nguyen et al., 2018). Pathania et al [12] have successfully utilized alumina oxide nanoparticles as a catalyst in the photocatalytic process to degrade malachite green dye by 45% for 6 hours.

Chitosan is one of the most studied biopolymers in composite studies because it has good adsorption ability, is biodegradable, and is non-toxic [13]. Semiconductor photocatalysts reactions treated by adding non-metallic elements can provide advantages such as expanding the light-responsive zone to increase the utilization of sunlight or UV rays, inhibiting electron-hole recombination and increasing the quantitative efficiency of semiconductor photocatalysts and having an absorption capacity that plays an important role in the reaction physics and

chemistry [14]. Zainal et al. [15] have succeeded in utilizing TiO_2 -Chitosan photocatalysts to remove monoazo dyes through the photodegradation-adsorption process with a success percentage of 47.9-87.0% in various mass ratio ratios.

In this research, the synthesis of Chitosan- Al_2O_3 composite using the sol-gel method will be applied to the photodegradation process of methylene blue on the effect of pH, contact time and concentration with the addition of H_2O_2 . The synthesized composites will be characterized using XRD, UV-DRS and SEM-EDS. Test for methylene blue after quantitative degradation using UV-Visible Spectrophotometer and Total Organic Carbon (TOC).

MATERIALS AND METHODS

Materials

Distilled water, aluminum nitrate, acetic acid anhydride 2%, hydrochloric acid, ammonium hydroxide 25%, ethanol 96%, hydrogen peroxide 30%, sodium hydroxide all of were purchased from Merck-millipore, methylene blue, chitosan.

Al_2O_3 Preparation

A total of 7 g of aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) was dissolved in 100 mL of 0.5 M HCl. Then NH_4OH was added until the solution reached pH 9. The solution was stirred using a stirrer for 4 hours at 70 °C, then filtered and the residue was washed with 96% ethanol and distilled water, then baked at 75 °C for 24 hours. The solid was calcined for 6 hours at a temperature of 600 °C, the result of the synthesis of Al_2O_3 will be characterized using XRD and UV-DRS analysis.

Synthesis of Chitosan- Al_2O_3 Composite

A total of 3.2538 g of chitosan was dissolved in 100 mL of 2% acetic acid, then stirred using a magnetic stirrer for 1 hour without heating. Then add $Al(NO_3)_3 \cdot 9H_2O$ which has been mixed with 10 mL of distilled water and 40 mL of ethanol, the mass of $Al(NO_3)_3 \cdot 9H_2O$ added can be seen in **Table 1**.

Table 1. Mass of materials in the synthesis of Chitosan Al_2O_3 composites

Materials	Mass ratio (g)		
	(1:1)	(1:2)	(1:3)
Chitosan	3.2538	3.2538	3.2538
$Al(NO_3)_3 \cdot 9H_2O$	10	20	30

The mixture is stirred for 1 hour, after that adjust the pH of the mixture at pH 6 using NH_4OH . The solution was stirred at high speed accompanied by heating at 120 °C until it dries. The dry mixture was

calcined at 800 °C for 2 hours, then the composite was ground to form a powder. The composites were characterized using XRD, SEM-EDS and UV-DRS analysis. The best results will be applied to degrade methylene blue.

Determination of the Best Conditions for Photodegradation of Methylene Blue Dyes

Effect of pH Variation

A total of 30 mL of methylene blue solution with a concentration of 15 ppm was put into a beaker. Adjusted the pH of the solution at 4, 6, 8, 10 by adding 0.1 M HCl for acid and 0.1 M NaOH for base. A total of 1 mL of 30% H₂O₂ solution was added to the mixture, then 0.05 g of composite was added. The mixture is stirred and irradiated with UV light for 150 minutes. The suspension was centrifuged at 3500 rpm for 10 minutes, the filtrate was measured for absorbance at the maximum wavelength and tested for TOC. For comparison, UV lamp irradiation was carried out with the addition of chitosan-Al₂O₃ composite, and UV lamp irradiation with the addition of H₂O₂.

Effect of Variation in Contact Time

30 mL of methylene blue solution with a concentration of 25 ppm was taken, then put into a beaker and adjusted to the optimum pH. A total of 1 mL of 30% H₂O₂ solution was added to the solution, then 0.05 g of composite was added. The mixture was stirred and irradiated with UV light for 40, 80, 120, 160, 200 minutes. The suspension was centrifuged at 3500 rpm for 5 minutes, the absorbance value of the filtrate was measured at the maximum wavelength and the TOC test was performed. For comparison, UV lamp irradiation was carried out with the addition of chitosan-Al₂O₃ composite and UV lamp irradiation with the addition of H₂O₂.

Effect of Variation in Initial Concentration of Methylene Blue Dye

Methylene blue solution with concentrations of 5, 10, 15, 20, 25 ppm was taken as much as 30 mL and then put into different beakers. Then the solution was adjusted to the optimum pH and 1 mL of 30% H₂O₂ solution was added, and 0.05 g of composite was added. The mixture was stirred and irradiated with UV light at the optimum contact time. The mixture was centrifuged at 3500 rpm for 10 minutes, the filtrate was measured for absorbance at the maximum wavelength and tested for TOC. For comparison, UV lamp irradiation was controlled with the addition of chitosan-Al₂O₃ composite and UV lamp irradiated with H₂O₂ addition.

Data Analysis

The results of each characterization will obtain data and spectral patterns. Analysis XRD instrument serves to determine the type of phase and structure as well as crystal size, UV-DRS is used to determine the energy band gap and SEM-EDS serves to provide information about the morphology and constituent elements as well as TOC analysis to see the success of the methylene blue photodegradation process based on the total organic carbon value. The crystal size is calculated using the Debye Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \dots\dots\dots (1)$$

Description:

- D : Crystallite size (nm)
- K : Constanta (0.9)
- λ : X-ray wavelength used (0.0175)
- β : FWHM of the diffraction peak
- θ : Bragg diffraction angle

The determination of the energy band gap is calculated using the Wood Tauc equation based on the results of UV-Vis DRS. The Wood Tauc equation is:

$$(\alpha h\nu)^2 = A (h\nu - E_g) \dots\dots\dots (2)$$

Description:

- $h\nu$: Photon energy
- α : Adsorption coefficient
- A : Constanta
- E_g : Band gap energy

Data obtained from UV-Vis spectrophotometer in the form of changes in the absorbance value of methylene blue dye before and after the degradation process. The calculation of the percent decrease in the concentration of methylene blue can be calculated using the equation:

$$P = \frac{C_0 - C_t}{C_0} \times 100\% \dots\dots\dots (3)$$

Description:

- P : Percentage of decrease in dye concentration
- C₀ : Initial concentration of solution (ppm)
- C_t : concentration of solution at time t (ppm)

The data obtained from the TOC analyzer is the change in the ppm C value of the initial and final dyestuffs. The ppm C is the amount of carbon (C) present in methylene blue dye. Percent degradation can be calculated using the formula:

$$\%D = \frac{\text{ppm C initial} - \text{ppm C final}}{\text{ppm C initial}} \times 100\% \dots\dots\dots (4)$$

Description:

%D : Percentage of Degradation

ppm C : Total carbon (C) in ppm

RESULTS AND DISCUSSION

XRD Characterization Result Material Characterization

The synthesized chitosan-Al₂O₃ composite based on variations in mass ratio (1:1), (1:2), and (1:3) were characterized using XRD to see that chitosan and Al₂O₃ have mixed based on the 2 θ diffraction angle and peak intensity. The intensity of the peak that appears will be compared with the JCPDS data. The results of XRD characterization can be seen in **Figure 1**. Based on the XRD characterization results of chitosan in **Figure 1(a)**, the chitosan diffractogram shows peak characteristics at an angle of 2 θ = 19.95°. Peak from chitosan which are characterized show similarity at the peak of chitosan characterization results in the study of Zavareh et. al [16] where the peak of chitosan is around 2 θ = 7.8; 10.9; and 19.9°. In addition, according to the research of Kumar and Koh [17], chitosan also shows typical peaks at angles of 2 θ = 10 and 20°.

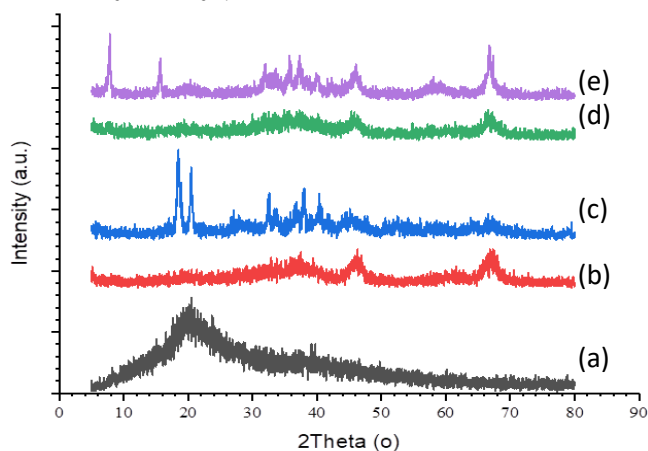


Figure 1. XRD spectra (a) Chitosan, (b) Al₂O₃, (c) Chitosan-Al₂O₃ (1:1), (d) Chitosan-Al₂O₃ (1:2), (e) Chitosan-Al₂O₃ (1:3)

Figure 1(b) is the result of the Al₂O₃ diffractogram. From the figure, the peak of Al₂O₃ is obtained at an angle of 2 θ = 38.0; 45.75 and 66.97°, when compared with JCPDS data no. 00-010-0425. The characteristic peaks at 2 θ angle of Al₂O₃ are 45.6 and 66.9°. Based on JCPDS data no. 00-010-0425 Al₂O₃ produced in this study has similar peaks at angles of 2 θ = 45.75 and 66.97°. The similarity of peaks is also in accordance with research from Rozita, et. al [18], namely at an angle of 2 θ = 38.5; 44.5; 65.0 and 78.0°.

Figure 1(c) is the result of a diffractogram of chitosan-Al₂O₃ composite with a ratio (1:1) which shows a peak at an angle of 2 θ = 20.376; 45.2 and 66.8°. **Figure 1(d)** is the result of the diffractogram of the chitosan-Al₂O₃ composite with a ratio (1:2) which shows a peak at an angle of 2 θ = 45.61 and 66.34°. **Figure 1(e)** is the result of a diffractogram of chitosan-Al₂O₃ composite with a ratio (1:3) which shows a peak at an angle of 2 θ = 7.82; 45.91; and 66.80°. So it can be concluded that the chitosan-Al₂O₃ composite was successfully made.

These data can be used to determine the size of the crystal using the Debye Scherrer equation, it was found that the crystal sizes of the Chitosan-Al₂O₃ composites in the ratio (1:1), (1:2), (1:3) were 3.17 nm, 4, respectively. 36 nm and 4.53 nm. The addition of Al₂O₃ mass to chitosan will affect the resulting crystal size.

UV-DRS Characterization Results

The synthesized Chitosan-Al₂O₃ composite was characterized by UV-DRS in order to see the band gap energy of the synthesized composite. Characterization using UV-DRS spectrophotometer was carried out by providing a certain amount of energy at a wavelength of 200-800 nm. Bandgap values of Al₂O₃ and Chitosan-AlO composites can be seen in **Table 2**.

Based on **Table 2**, it can be seen that the band gap energy of the synthesized Al₂O₃ in this study is 3.1 eV. This value is similar to Pathania's [12] study which succeeded in synthesizing Al₂O₃ with a band gap energy of 3.02 eV. After adding chitosan, the band gap energy decreased.

Table 2. Sample band gap value

Materials	Eg (eV)
Al ₂ O ₃	3.1
Chitosan-Al ₂ O ₃ (1:1)	1.35
Chitosan-Al ₂ O ₃ (1:2)	1.1
Chitosan -Al ₂ O ₃ (1:3)	1.55

According to Fauzi et al. [19] the decrease in band gap energy that occurs can be caused by a decrease in crystal size, where the increase in orbitals that form the valence band to the conduction band causes an overlap between the valence band and conduction band as a result the band gap distance decreases. In addition, the addition of different Al₂O₃ masses affects the bandgap value. Based on the results of XRD and UV-DRS characterization, chitosan-Al₂O₃ composite with a ratio of (1:1) was chosen as the composite to be applied to degrade methylene blue.

Morphology by SEM-EDS

SEM-EDS characterization aims to determine the surface morphology and determine the constituent elements in the sample. The samples used were Chitosan powder and Chitosan- Al_2O_3 (1:1) composite. The results of SEM characterization can be seen in **Figure 2**.

Based on **Figure 2(a)** it can be seen that chitosan is in the form of chips or sheets with a wavy surface and has a large particle size and chitosan also has a fairly large inter-particle cavity, while in **Figure 2(b)** it can be seen that the Chitosan- Al_2O_3 composite is homogeneous, has a spherical shape with a smaller particle size when compared to chitosan particles and the composite surface forms pores, and the distance between the particles is slightly tight.

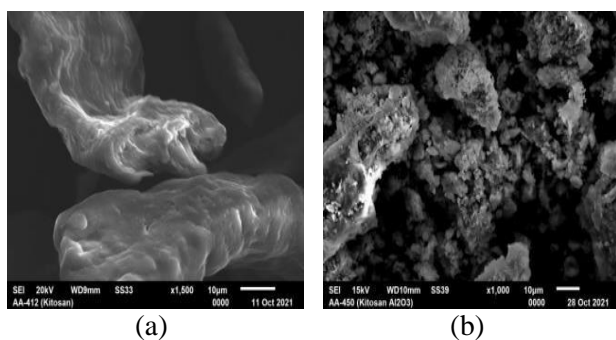


Figure 2. SEM morphology (a) Chitosan surface at 1500 \times magnification (b) Chitosan- Al_2O_3 composite surface at 1000 \times magnification

EDS results show that Chitosan has constituent elements in the form of C, O and Na with a percentage of 42.88; 48.68 and 8.44%. The Chitosan- Al_2O_3 (1:1) composite has the constituent elements in the form of C, O, Na, Al and Zn with a percentage of 4.93 each; 33.31; 13.92; 45.59 and 2.24%. The EDS results of Chitosan- Al_2O_3 composite showed that the addition of Al_2O_3 to Chitosan had been successfully carried out based on the percentage of its constituent elements, but there was an impurity in the form of Zn.

Determination of the Best Conditions for Photodegradation of Methylene Blue Dyes

Chitosan- Al_2O_3 composite with a ratio of 1:1 was applied to the photodegradation process of methylene blue by utilizing light from a 352 nm 10 watt UV lamp. The maximum absorption wavelength of methylene blue is 665 nm. Photodegradation was carried out by varying the effect of pH, the effect of contact time and the effect of the concentration of methylene blue.

Effect of pH Variation on Photodegradation of Methylene Blue Dye

The photodegradation process was carried out by varying the pH of the methylene blue solution in order to determine the optimum pH of the photodegradation process using chitosan- Al_2O_3 composite. Chitosan- Al_2O_3 composite with mass ratio (1:1) was used to degrade methylene blue with composites and UV light irradiation, as well as composites, addition of H_2O_2 and UV light irradiation. The percentage of effectiveness in reducing the concentration of the solution indicates the amount of methylene blue that has been successfully degraded.

The curve of percent decrease in the concentration of methylene blue on the effect of the pH of the solution can be seen in **Figure 3**. Based on the curve in **Figure 3**, it can be seen that under acidic conditions the effectiveness of reducing the concentration of methylene blue on both curves is quite small. This is because a small part of the Al_2O_3 surface is negatively charged Al-O^- so that only a small part can interact with methylene blue.

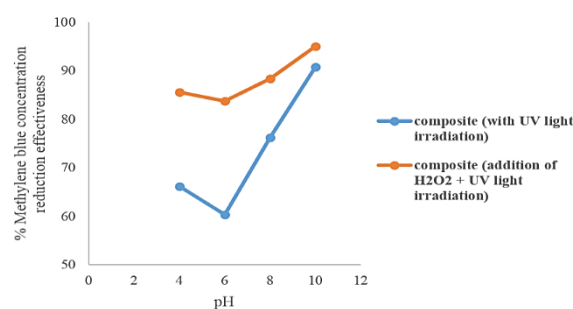


Figure 3. Curve of the effectiveness of reducing the concentration of methylene blue on the effect of variations in pH

The degradation of methylene blue using composites with irradiation and composites with the addition of H_2O_2 and UV light irradiation at pH 6 showed a decrease in the effectiveness of methylene blue degradation. This is because the surface of chitosan- Al_2O_3 is in a neutral state so that the interaction between the composite and methylene blue is small. At pH 8 and pH 10 the degradation of methylene blue using composites with UV light irradiation and composites with the addition of H_2O_2 and UV light irradiation increased. According to Nurbaiti [20], at a pH above 7 the hydroxyl group will experience deprotonation to form Al-O^- compounds so that it is easier to absorb cations because the surface of the chitosan- Al_2O_3 composite is negatively charged.

Based on **Figure 3**, pH 10 was chosen as the optimum pH because the highest percentage of

degradation effectiveness occurred at pH 10, which is 90.8% for methylene blue degradation using composites with UV light irradiation and 95% for methylene blue degradation using composites with the addition of H₂O₂ and UV light irradiation.

Effect of Variation in Contact Time on Photodegradation of Methylene Blue Dye

The effect of the contact time of methylene blue photodegradation by Chitosan-Al₂O₃ aims to determine the optimum time of the photodegradation process which can be seen in **Figure 4**. Based on the curve obtained, it can be seen that the Chitosan-Al₂O₃ composite has the ability to degrade methylene blue dye. In the degradation of methylene blue using a composite with UV light irradiation, the highest percentage of methylene blue reduction effectiveness was 66.44% with an irradiation time of 200 minutes. In the degradation of methylene blue using a composite with the addition of H₂O₂ and UV light irradiation, the effectiveness of methylene blue degradation with an irradiation time of 200 minutes is 85.4%. This can occur because of the excitation of electrons from the valence band to the conduction band, causing electron vacancies in the valence band. These electron vacancies will interact with water molecules and produce *OH radicals which function as oxidizing agents, while electrons will interact with oxygen to produce *O₂ radicals which function as reducing agents, which will degrade methylene blue dye [12]. Based on the curve, a contact time of 200 minutes was chosen as the optimum time to degrade methylene blue dye

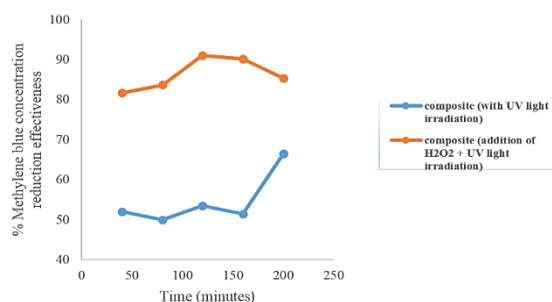


Figure 4. Effectiveness curve for reducing the concentration of methylene blue dye on the effect of contact time

Effect of Variation in Initial Concentration of Methylene Blue Dye

The effect of the initial concentration of methylene blue dye on the degradation process aims to see the optimum concentration of dye that can be degraded by the composite which can be seen in **Figure 5**.

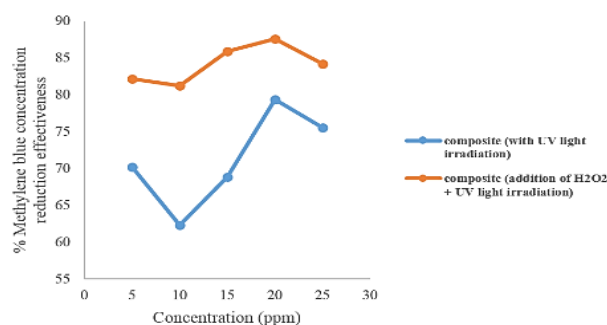


Figure 5. Effectiveness curve of reducing dye concentration on the effect of initial concentration of methylene blue dye

Based on **Figure 5**, it can be seen that in the degradation of methylene blue using a composite with UV light irradiation, the highest concentration of methylene blue decreased at a concentration of 20 ppm, which was 79.35%. Meanwhile, in the degradation of methylene blue using a composite with the addition of H₂O₂ and UV light irradiation, the highest concentration decreased at a concentration of 20 ppm at 87.55%. From the figure, it can be seen that there is a decrease in the percentage of effectiveness at a concentration of 25 ppm. This can happen because a greater concentration of dye will have a greater number of molecules as a result the molecules will cover the surface of the composite. The closed surface of the composite can lead to less formation of electron hole pairs, so that more composites are needed [21]. Based on the curve, the concentration of 20 ppm was chosen as the optimum concentration in this study.

TOC Test Results

The TOC test on methylene blue dye both after photodegradation and before photodegradation aims to see the amount of organic compounds in quantitative degradation. In TOC test, chitosan-Al₂O₃ composite with mass ratio (1:1) was used to degrade 20 ppm methylene blue. Based on the data obtained, the equation of the linear regression line is $y = 1.212(x) + 26.292$, with a value of $R^2 = 0.99846$.

The results of the measurement of methylene blue dye samples using a TOC analyzer found that the C concentration of methylene blue dye before (initial) degradation was 14.4878 ppm, while the C concentration of methylene blue after (final) degradation was 11.2599 ppm, this indicates that the % degradation of the sample of methylene blue dye is 22.36%. These data indicate a decrease in ppm before and after degradation, so that in this study it can be stated that the process of photodegradation or absorption of organic compounds in methylene blue dye by the Chitosan-Al₂O₃ (1:1) composite was

successfully carried out based on quantitative testing using a TOC analyzer.

CONCLUSION

Chitosan-Al₂O₃ composite with a ratio of (1:1), (1:2) and (1:3) has been successfully synthesized. The results of XRD characterization showed that the chitosan-Al₂O₃ composite with a ratio of (1:1) was similar to the JCPDS data No. 00-010-0425 at 45.2 and 66.8° angles. The results of UV-DRS characterization showed that the band gap energy of chitosan-Al₂O₃ in a ratio (1:1) was 1.35 eV. The morphological condition of the composite showed a small round shape and a porous surface with the composition of the constituent elements of C (4.93%), O (33.31%), Na (13.92%), Al (45.59%) and Zn (2.24%). The ability of Chitosan-Al₂O₃ composite in degrading methylene blue dye was best at pH 10 and a contact time of 200 minutes. The maximum concentration of methylene blue that can be degraded by the Chitosan-Al₂O₃ composite is 20 ppm with the percent effectiveness of reducing the concentration of 79.35%.

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