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Synthesis Of Carbon Nanoparticles Decorated By Sno$_2$ Using Laser Ablation With Variation In Medium Concentration For The Photodegradation Of Methylene Blue

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Abstract— Carbon nanoparticles decorated by SnO$_2$ nanoparticles have been successfully synthesized by using the pulse laser ablation method in a carboxymethyl cellulose (CMC) solution. In this study, carbon nanoparticles were first synthesized in the CMC solution to produce colloidal carbon nanoparticles. Subsequently, the colloidal carbon nanoparticles were used as a solution medium in the production of colloidal SnO$_2$ nanoparticles decorating on the carbon nanoparticles. The results certified that the nanoparticles have been successfully produced with an average size of ten nanometers. The carbon nanoparticles decorated by SnO$_2$ nanoparticles have been employed as a catalyst to reduce methylene blue as an impurity. The produced nanoparticles can effectively be used as a catalyst in water purification.

Keywords— Carbon nanoparticles; SnO$_2$ nanoparticles; pulse laser ablation method; Nd:YAG laser; CMC

I. INTRODUCTION

Chemically-based synthetic dyes have infiltrated various aspects of human life, including the clothing, food, and cosmetic sectors. Despite research highlighting potential dangers associated with synthetic dyes, their use remains widespread, driven by practicality, the ability to produce a variety of colors, and economic factors[1]. In the context of the textile industry, for example, substances like methylene blue, a synthetic dye, are often employed. Unfortunately, this dye possesses carcinogenic properties and non-biodegradable characteristics, which prevent microorganisms from breaking it down, posing a threat to human health and the integrity of aquatic ecosystems[7]. In certain concentrations, methylene blue can disrupt aquatic ecosystems, hinder photosynthesis in aquatic organisms, and induce harmful effects such as digestive disorders, increased heart rate, and even death[6].

Several water treatment technologies and methods have been developed to mitigate the presence of methylene blue in wastewater and maintain its safety, including chlorination, ozonation, membrane filtration, and others. However, these methods often face challenges such as generating additional toxic waste, high maintenance costs, and limited effectiveness in removing pollutants from wastewater. Therefore, there is an urgent need to design efficient, cost-effective methods capable of converting wastewater pollutants into harmless byproducts[4]. One intriguing alternative is through Advanced Oxidation Processes, particularly photodegradation, which has the capability to transform hazardous compounds into safe ones, such as H_2O and CO_2[5].

Carbon, as a chemical element found in various forms and structures, has garnered significant attention in various scientific disciplines and applications. While much of the carbon used in industry and research is still at the macroscopic scale with large sizes, understanding the structural differences and intermolecular behaviors, including molecular assembly, stacking of molecules, and intermolecular relationships, offers significant potential for creating a wide range of properties and applications. Therefore, the ability to control carbon aggregation at the nanometer scale opens opportunities to create unique and innovative carbon characteristics[17]. Although several methods for synthesizing carbon nanoparticles (CNPs) have been developed, such as spray pyrolysis and chemical vapor deposition[3], many of these methods still face challenges related to low purity.

One solution to obtain high-purity CNPs is through laser ablation. This method has been proven to produce CNPs with purity levels exceeding 90% and an average nano diameter size of approximately 1.4nm[8]. Research shows that CNPs produced through laser ablation can be used as highly effective photocatalysts in the degradation of methylene blue[2]. One of the main challenges in using CNPs is maintaining their stability, which can be addressed by using stabilizing agents such as carboxymethyl cellulose (CMC). CMC has several advantages, including good biodegradability, non-toxic properties, water solubility, and the ability to form excellent films[11].

Therefore, this research proposes an innovative synthesis of CNPs using the laser ablation method, with CMC as a stabilizing agent. This approach has significant potential in the development of photodegradation materials for methylene blue, projecting to be a more efficient and environmentally friendly alternative. From this research, it is expected to gain deep insights into the effectiveness of the laser ablation method in synthesizing CNPs as materials for methylene blue photodegradation.

II. MATERIAL AND METHODS

2.1. Experimental Materials and Reagents

This research was conducted in less than a 5-month timeframe and took place at two primary locations: the Laser and Optics Laboratory and the Materials Physics Laboratory within the Department of Physics, Faculty of Science and Mathematics, at Diponegoro University. The equipment used in this study included a digital balance, Nd:YAG pulse laser, tweezers, chemical glassware, spatula, measuring glassware, pipettes, SEM-EDX, UV-Vis, XRD, and various other chemical instruments. The materials under investigation encompassed graphite plates (with a purity level of 99.5%), tin plates (with a purity level of 99.95%), deionized water, 70% alcohol, methylene blue, CMC (carboxymethyl cellulose) powder, and silicon plates. Despite the tight time constraints, this research was conducted with the appropriate equipment and materials to achieve the desired research objectives.

2.2. Preparation of Sample

Graphite and tin plates measuring 1.5 cm x 1.5 cm were cleaned with 70% alcohol to remove impurities from the surfaces. To ensure that no residual alcohol remained on the plates, both the graphite and tin plates were rinsed with deionized water (aquades) three times. After cleaning, the plates were dried using a clean cloth. Once dry, the carbon plate was placed into a previously cleaned petri dish with a solution of 70% alcohol and deionized water. Then, 20 ml of the CMC solution was poured into a beaker containing the graphite plate.

Synthesis of Carbon Nanoparticles

The synthesis of CNPs was carried out by irradiating a 99.5% pure graphite plate submerged in a 20 mL CMC solution with a Nd:YAG laser (1064 nm). In this research, the Nd:YAG laser had an energy output of 100 mJ and a pulse width of 7 ns. The laser irradiation process was conducted for 30 minutes with variations in the concentration of the CMC solution medium at 0.1%, 0.3%, and 0.5%. These concentration variations were performed to investigate the influence of different CMC solution concentrations on the size of the carbon nanoparticles.

Synthesis of Carbon Nanoparticles Doped with Tin

The synthesis of CNPs doped with tin was achieved by irradiating a 99.5% pure tin plate submerged in a 20 mL CMC medium containing CNPs with a Nd:YAG laser (1064 nm). In this research, the Nd:YAG laser had an energy output of 100 mJ and a pulse width of 7 ns. The laser irradiation process was carried out for 30 minutes with different concentrations of the CMC solution medium, specifically 0.1%, 0.3%, and 0.5%. During the synthesis, the laser beam was directed using a mirror towards a convex focus lens with a focal distance of 10 cm to ensure precise irradiation of the sample. Throughout the irradiation process, the beaker containing the carbon plate was gently moved to obtain homogeneous nanoparticles. The equipment setup for carbon synthesis using laser ablation is described below.

Degradation of Methylene Blue

The degradation process involved mixing CNPs doped with tin with a methylene blue solution. The ratio of CNPs doped with tin to methylene blue was 10:50 ml, with the 50 ml of methylene blue having a concentration of 20 ppm. Subsequently, the solution was placed in a lightbox and stirred with a stirrer under UV and fluorescent light radiation. At intervals ranging from 10 minutes to 1 hour, the methylene blue solution was sampled and characterized. The remaining amount of methylene blue was measured using a UV-Vis spectrophotometer at a wavelength of 664 nm.

Characterization and Testing

Some spectroscopic methods were used to characterize the produced nanoparticles. XRD (X-Ray Diffraction) was used to identify the phases formed during synthesis and determine the degree of crystallinity by analyzing diffraction patterns. SEM-EDX (Scanning Electron Microscopy Energy Dispersive X-Ray) was employed to study the morphology and detect compounds in the synthesized CNPs. FTIR (Fourier Transform Infrared) was utilized to identify functional groups and compounds present in the carbon nanoparticles. UV-Vis was conducted to evaluate the effectiveness of methylene blue degradation.

III. RESULT AND DISCUSSION

3.1. Synthesis of Carbon-SnO_2 Nanoparticle Colloids Using the Pulse Laser Ablation Method

The synthesis of carbon-SnO_2 nanoparticles was carried out using the pulsed laser ablation (PLA) method. The laser used is an Nd: YAG pulse laser with a wavelength of 1064 nm and a pulse width of 7 ns. To produce colloidal carbon-SnO_2 nanoparticles using the PLA method, a liquid medium is needed which is used as a medium for forming the nanoparticles. Different concentrations of liquid medium produce carbon-SnO_2 nanoparticles with different characteristics. In this research, the synthesis of carbon-SnO2 nanoparticles has been carried out using liquid carboxymethyl cellulose (CMC) medium with different concentrations in order to determine the level of stability of the colloidal nanoparticles produced, so that more stable colloidal nanoparticles can be applied as photocatalysts.

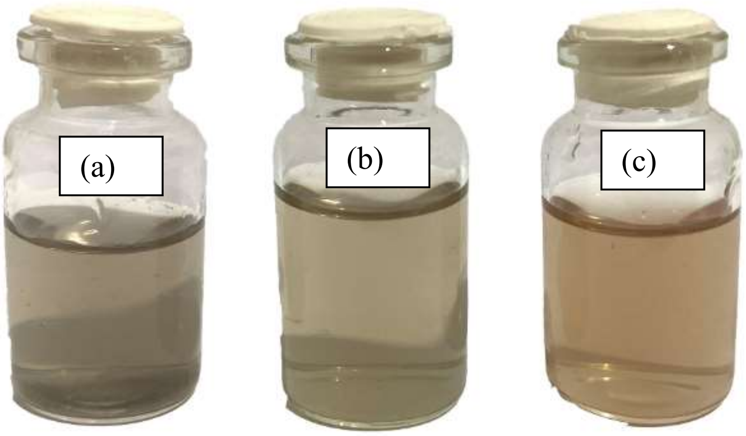

Figure 1. Synthesis Results of Carbon Nanoparticles Decorated by SnO2 for Variations (a) CMC 0.1% (b) CMC 0.3% and (c) CMC 0.5%

Fig. 1. shows a photo of carbon-SnO_2 nanoparticles produced using varying concentrations of 0.1% CMC medium; 0.3% and 0.5%. These three colloids produce different colors. In Figure 1. (a) the resulting nanoparticle colloid looks slightly turbid, in Fig. 1. (b), the resulting nanoparticle colloid looks more turbid than colloid 4.1 (a), and in Figure 1. (c) the resulting nanoparticle colloid looks more turbid and brownish color when compared to the two previous colloids. This is because the concentration of the solution media has a higher level of viscosity when compared to the CMC concentration of 0.1% and 0.3%. So the viscosity of this liquid media can reduce the effect of Brownian motion between particles and can make the carbon-SnO_2 nanoparticle colloid more stable and more nanoparticles are formed.

3.2. Structure and Morphology of Carbon-SnO_2

X-Ray Diffraction (XRD) aims to identify the crystalline phase in carbon and SnO_2 nanoparticle colloids at each CMC medium concentration. Figure 2 is the XRD spectrum of carbon and SnO_2 nanoparticles. This image shows that the resulting crystals are still amorphous, characterized by the irregularity of the peaks produced. The high and low peaks resulting from XRD characterization are influenced by heating the carbon-SnO_2 nanoparticle sample on the glass preparation for too long so that the solution sample is oxidized[9,10].

The aim of Scanning Electron Microscope EDX (SEM-EDX) analysis is to determine the surface morphology of carbon nanoparticles and determine the size of the resulting nanoparticles. Figure 3 is the result of the morphology of carbon-SnO2 nanoparticles (a) CMC concentration 0.1%, (b) CMC concentration 0.3% and (c) CMC concentration 0.5%. The image shows that the carbon-SnO2 nanoparticles have a round (spherical) shape. These results are in accordance with various studies[16] where carbon nanoparticles synthesized using the pulse laser ablation method are round in shape.

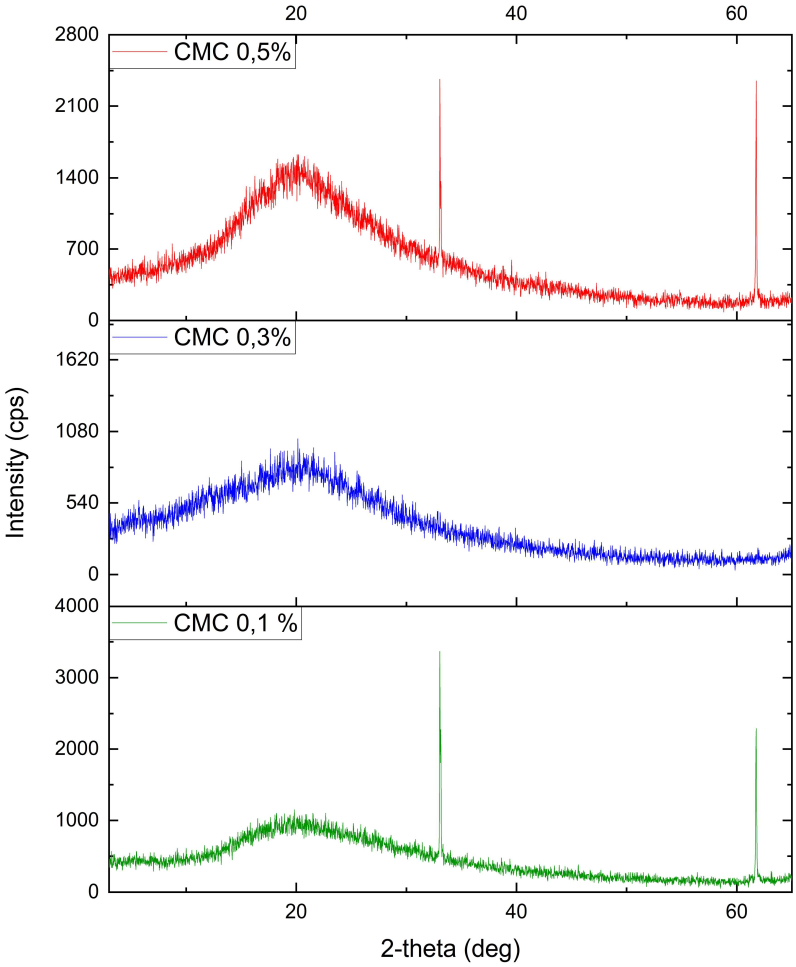

Figure 2. XRD spectrum of carbon-SnO2 nanoparticles at medium concentrations of (a) 0.1% CMC (b) 0.3% CMC and (c) 0.5% CMC

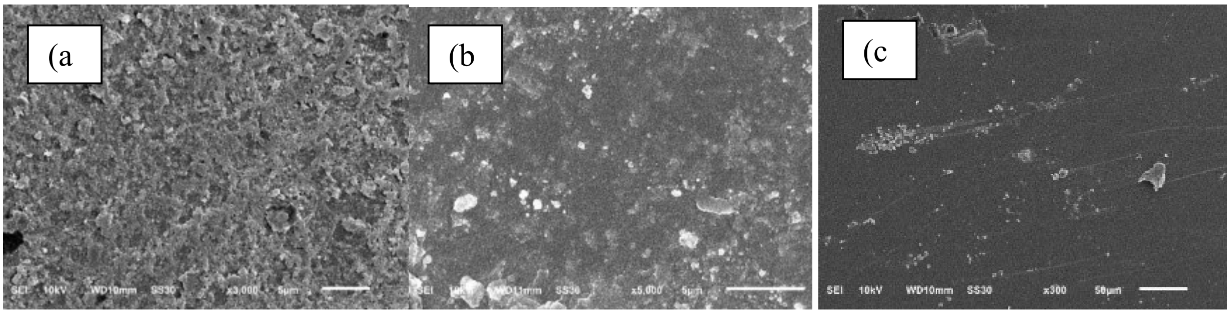

Figure 3. Morphology of carbon nanoparticles decorated by SnO2 at medium concentrations (a) CMC 0.1% (b) CMC 0.3% and (c) CMC 0.5%

3.3. Surface Chemistry Composition Analysis

Fourier Transform Infra-Red (FTIR) aims to qualitatively analyze the functional groups of chemical compounds in carbon-SnO_2 nanoparticle colloids. The functional groups of compounds contained in the carbon-SnO_2 nanoparticle colloids at each CMC medium concentration can be seen in Figure 4.

Fig. 4. is the FTIR spectrum of colloidal carbon nanoparticles and SnO_2 in 0.1% CMC medium; 0.3%; and 0.5%. In each image, a wide absorption peak can be seen at the wave number 3328.53 cm-1, which is the stretching frequency of the hydroxyl (-OH) molecule, which is caused by water molecules being absorbed at the wave number 2354 cm-1, the compound C= is detected. C which shows the functional group of carbon which is in accordance with the research[12]. A peak of 1643.06 cm-1 was detected from the carboxyl compound (COO-) in CMC and there was a peak around 675 cm-1 in the sample related to O-Sn-O stretching vibrations, this indicates the functional group of tin oxide is in accordance with the research[13,14]. The FTIR spectrum shows the functional groups bonding carbon nanoparticles and tin oxide. In the three sample spectra there is a carboxyl bond (COO-) which is the basic bond in the CMC medium. The presence of these bonds can prevent or reduce nanoparticle aggregation, so that the colloidal carbon nanoparticles decorated by SnO_2 become more stable.

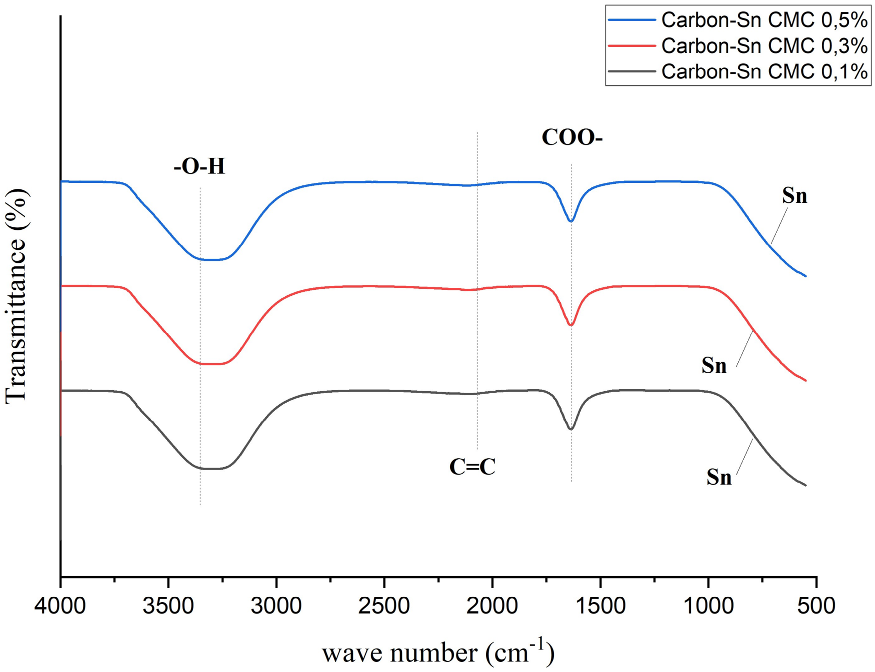

Figure 4. Functional groups of colloidal carbon nanoparticles decorated by SnO2 CMC concentration 0.1%, 0.3% and 0.5%.

3.4. Optical Properties of Carbon-SnO_2 Nanoparticles

In general, metal nanoparticles have unique characteristics when they are under electromagnetic radiation. To determine the optical properties of the obtained nanoparticles, the absorption of each sample was measured in the range of 200-800 nm by UV-Vis spectroscopy. Figure 5 shows the absorption spectrum of colloidal carbon-SnO_2 nanoparticles at a CMC concentration of 0.1%; 0.3% and 0.5%.

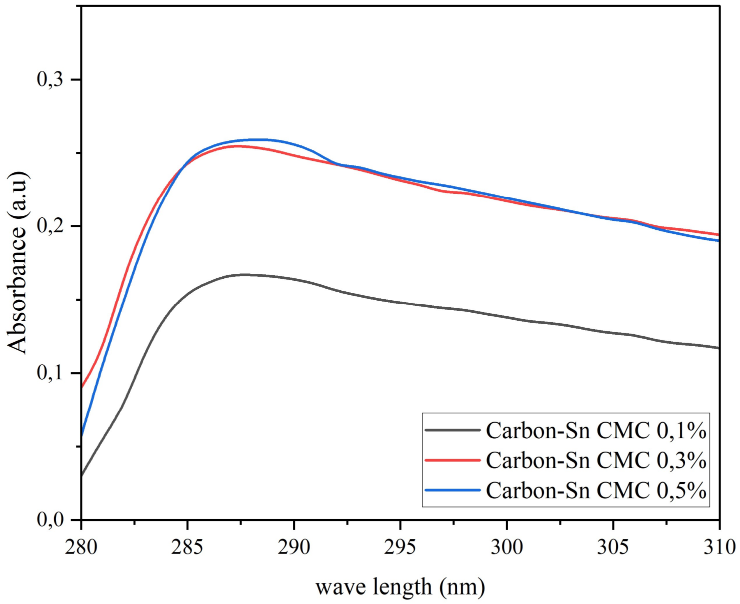

Figure 5. UV-Vis absorption spectrum of colloidal Carbon nanoparticles decorated by SnO_2 at medium concentrations of 0.1% CMC, 0.3% CMC and 0.5% CMC

The absorption spectrum of Carbon and SnO_2 can be seen in Figure 5 At a CMC concentration of 0.1%, an absorption peak of 0.172 was obtained with a wavelength of 287 nm, in 0.3% CMC media the peak absorption value was 0.255 at wavelength 287, while in 0.5% CMC media the peak absorption value was 0.259 at wavelength 288 nm. Various literature studies show that carbon nanoparticles have absorption at a wavelength of 280 nm.

3.5. Degradation of Methylene Blue

After knowing the absorption peak and absorption value at each medium concentration, the next step is to calculate the calibration curve for the methylene blue standard solution. The calibration curve is a curve of the relationship between absorption and the concentration of a standard solution. A standard solution calibration curve was created by measuring the absorption value of the methylene blue standard solution with varying concentrations of the methylene blue solution, namely 0; 2; 4; 6; 8; and 10 ppm at a wavelength of 664 nm. The calibration curve for the methylene blue solution can be seen in Figure 6.

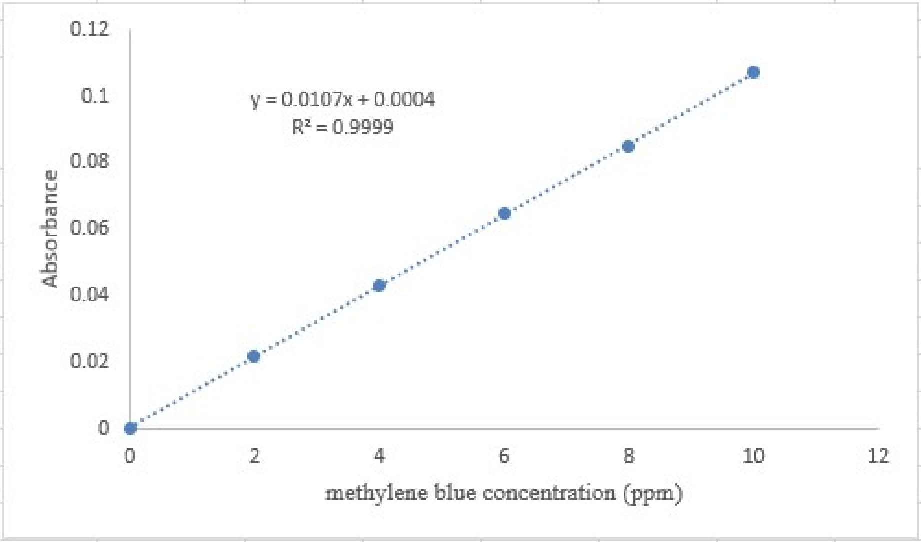

Figure 6. Methylene blue calibration curve

Determination of the optimum time for methylene blue degradation was carried out by UV radiation treatment using time variations of 10, 20, 30, 40, 50 and 60 minutes. The optimum time can be known by making a curve of the relationship between time and the percentage reduction in methylene blue which can be seen in Figure 7.

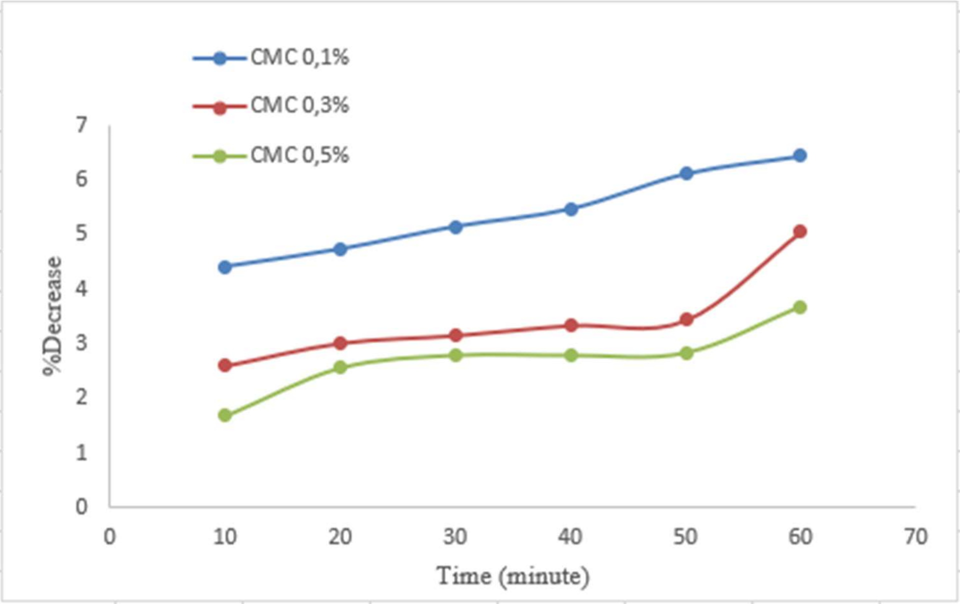

Figure 7. The relationship curve between radiation time and reduction percentage

Based on the image, it is known that carbon nanoparticles decorated by SnO_2 with each concentration are able to degrade methylene blue. Based on this treatment, it can be seen that the optimum radiation time obtained was 60 minutes. This proves that UV radiation and greater concentrations influence the methylene blue degradation process. The methylene blue degradation efficiency value can be obtained using equation 1 as follows.

$$C_0 - C / C_0 \qquad (1)$$

where Co is the initial absorbance and C is the final absorbance obtained from Figure 7 Calculations were carried out using the absorbance value at a wavelength of 664 nm. Based on the calculation results, it shows that the most optimal degradation results are produced from samples with a CMC concentration of 0.5% with a degradation value reaching 70%, while the degradation results of a CMC concentration of 0.3% are 65% and a CMC concentration of 0.1% is 60.25%.

IV. CONCLUSION

Based on the conducted research, it can be concluded that carbon nanoparticles decorated by SnO_2 can be synthesized using the laser ablation method. The results from UV-Vis and SEM EDX characterizations indicate that the colloidal carbon nanoparticles decorated by SnO_2 synthesized at a CMC medium concentration of 0.5% exhibit greater stability compared to other concentrations. FTIR and XRD analyses reveal the formation of colloidal carbon nanoparticles and SnO_2, along with the presence of functional groups and diffraction patterns. Based on UV-Vis data processing, the carbon nanoparticles decorated by SnO_2 synthesized in all three media were capable of degrading methylene blue. The most effective photocatalytic characteristics were observed in the nanoparticles synthesized at a CMC concentration of 0.5%. This is evident from the optimal methylene blue degradation rate, which reached 70% in the CMC 0.5% medium.

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