Preparation Of ZnO/SiO_2 Composite From Battery Waste And Rice Husk Ash For Decolorization Of Methylene Blue

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Abstract. The composite of ZnO/SiO_2 has been synthesized from battery waste as a source of ZnO and rice husk ash as a source of SiO_2. The composite was used to decolorize of methylene blue by the photocatalytic method under visible light. The ZnO/SiO_2 composites were synthesized by the sol-gel method. The Zinc metal from the waste battery is separated, cleaned, and reacted with acid which then produces a solution of Zn^{2+}. While rice husk ash was reacted with a strong base to produce Na_2SiO_3 solution. Then the two solutions are mixed with the mole ratios of $ZnO:SiO_2$ are 1:4, 1:1, 4:1, 8:1 and 16:1. Composite characterization was carried out using XRD for all composites and SEM for composites with the best photocatalytic performance. The photocatalytic performance of composites was tested against methylene blue solution. The best performance of composites can decolorize methylene blue as much as 96.91% by using composite 4:1 as much as 150 mg with the exposure time of visible light for 180 minutes and using methylene blue 20 ppm as much as 25 mL.

Keywords: ZnO/SiO_2 composites, methylene blue, photocatalysts, battery waste, rice husk ash.

1 Introduction

ZnO is one semiconductor that the application is extensive [1] [2] [3] [4]. One of them is as a photocatalyst for handling organic dye [5]. Photocatalytic treatment is preferred because it has high efficiency [6], economical [7], and environmentally friendly [8]. Photocatalyst performance is influenced by particle size distribution [9], morphology [10], crystalline phase [11], porosity [3], and accessibility of active sites [12]. To increase the porosity of the material, it can be done by combining ZnO with another material that is not photocatalyst and has high porosity [13]. So it is expected that accessibility to active sites can be improved.

In this study, the synthesis of ZnO/SiO_2 composites was derived from waste batteries and rice husk ash. SiO_2 is chosen as a matrix because the amorphous state has a high porosity [14]. Besides that, the source of silica is quite easy to find from nature. ZnO is obtained from the treatment of Zn-C primary battery waste [15]. This battery is a type of disposable battery that usually after using it, Indonesian people disposed it into the environment without further handling. The metal mass of Zn found in battery size AA (R6) is around 20%. ZnO synthesis from battery waste was carried out using the precipitation method, this method was chosen because it produced ZnO with high purity [16].

The SiO_2 content in rice husk ash can reach above 90% [17], for this reason, rice husk ash is chosen as a source of SiO_2. Amorphous silica gel was obtained from rice husk ash by the sol-gel method. By this method, SiO_2 from rice husk ash is extracted using a strong base solution and condensed by lowering the pH to 7.

The synthesis of ZnO/SiO_2 composites was carried out by the sol-gel method. Where a solution of Zn^{2+} derived from battery waste is mixed at a certain ratio with sodium silicate solution from rice husk ash. After ripening, a ZnO/SiO_2 composite will be obtained. The composites obtained were used for photocatalyst treatment of methylene blue.

2 Experimental Procedure

2.1 The ZnO/SiO_2 composite preparation

The ZnO/SiO_2 composites were prepared by the sol-gel method. First, Zn^{2+} solution was prepared from battery waste and sodium silicate solution from rice husk ash.

Preparation of Zn^{2+} solution. The zinc metal was separated from the battery waste and cleaned from the impurities. To speed up the dissolution of Zn in hydrochloric acid, the size of the zinc metal was reduced. A total of 32.7 g of zinc metal from battery waste were dissolved in 225 mL of concentrated hydrochloric acid in a beaker glass. The mixture is left for 5 hours to dissolve all zinc metal. The mixture was stirred at 700 rpm and heated for a while. Then filtered to obtain a Zn^{2+} solution.

Preparation of sodium silicate solution. A total of 22.8 g of rice husk ash were dissolved in 125 mL of distilled water. Then add concentrated hydrochloric acid slowly until the mixture is obtained with pH 1 while stirred using a magnetic stirrer. The mixture obtained is then filtered. The residue was re-dissolved with 250 mL of 1 M NaOH while stirring with a magnetic stirrer at 80 °C. The mixture is then filtered to obtain a sodium silicate solution.

Composite was prepared by mixing Zn^{2+} solution and sodium silicate solution (mole ratio of $ZnO:SiO_2$ are 1:4, 1:1, 4:1, 8:1 and 16:1) using a magnetic stirrer until homogeneous. After that, 1 M hydrochloric acid was added to pH around 7 and left for 2 days. The precipitate was filtered then washed with demineralized water and heated. After that, it calcined at 400 °C for 3 hours [18].

Characterization of all composites was carried out using XRD (PANalytical-X'Pert High Score) to determine the crystal structure, and SEM (JEOL JCM 6000) to find out the morphology.

2.2 The photocatalytic properties of ZnO/SiO_2 composite

Photocatalytic properties of ZnO/SiO_2 composites for decolorization of methylene blue solution were carried out by batch method.

Composite variation. Composites (1:4, 1:1, 4:1, 8:1 and 16:1) were weighed as much as 0.15 g and then put into vial bottles and added 25 mL of 10 ppm methylene blue solution. After being sonicated for 4 minutes, the mixture is illuminated by UV light for 3 hours. The composite is separated from the filtrate. The filtrate obtained was determined by the spectrophotometry concentration of the residual methylene blue.

Composite mass variation. The best performance composites in the previous stage are used at this stage. The composite mass variations used were 50, 75, 100, 125, and 150 mg then put into vial bottles and added 25 mL of 10 ppm methylene blue solution. After being sonicated for 4 minutes, the mixture is illuminated by UV light for 3 hours. The composite is separated from the filtrate. The filtrate obtained was determined by the spectrophotometry concentration of the residual blue methylene blue.

Variation in radiation time. In this experiment, variations in irradiation time were carried out, namely 30, 60, 90, 120, 150 and 180 minutes. The composites used were composites with the best performance and the best experimental conditions in the previous stage. The filtrate is then separated from the mixture and determine the concentration of the residual methylene blue in the visible light spectrophotometry.

Variation in concentration of methylene blue solution. The methylene blue used is a concentration of 5, 10, 15, 20, 25 and 30 ppm. Experiments were carried out using composites with the best performance and experimental conditions in the previous stage. The filtrate is then separated from the mixture and determine the concentration of the residual methylene blue in the visible light spectrophotometry.

3 Result and Discussion

3.1 The ZnO/SiO_2 composite preparation

Zn^{2+} Solution Preparation

The zinc metal contained in the battery waste was separated from other battery components. Then sanded until shiny and cut into pieces to obtain a smaller size (size reducing). If the surface area becomes wider, the more collisions occur between the reactant particles, so that more products are produced. This causes the reaction rate to increase. The preparation of zinc metal was weighed 32,7 g and dissolved in 225 mL concentrated hydrochloric acid gradually. The chemical equation for the reaction that occurs when dissolving zinc is:

$$Zn\ (s) + 2HCl\ (aq) \rightarrow ZnCl_2\ (aq) + H_2\ (g) \quad (1)$$

To speed up the reaction rate, the solution is heated at 80 °C while stirring using a magnetic stirrer at a speed of 700 rpm. After all zinc metals was dissolve, a colorless solution is produced which is a Zn^{2+} solution.

Preparation of Sodium Silicate Solution

Rice husk ash was weighed as much as 22.8 g and added 125 mL demineralized water while stirring. After that, washing with acid through adding drop wise of concentrated hydrochloric acid until the mixture is obtained with pH 1 while stirring with a magnetic stirrer for 2 hours without heating. In pH 1 HCl solution, the impurities of oxide compounds in rice husk ash such as MgO, K_2O, Na_2O, CaO, Fe_2O_3, and P_2O_5 will dissolve and leave SiO_2 [19]. The residue containing SiO_2 was reacted with 3 M NaOH solution then at 700 rpm using a magnetic stirrer and heating at 80 °C for 90 minutes. As is known, that SiO_2 is an acid oxide, so it will react with alkaline, the reaction that occurs is:

$$SiO_2\ (s) + 2NaOH\ (aq) \rightarrow Na_2SiO_3\ (aq) + H_2O\ (aq) \quad (2)$$

The sodium silicate solution must be stored in a plastic container to avoid the reaction between silica in a glass container because of the base used.

ZnO/SiO₂ Composite Synthesis

In this study, composites were prepared by varying the mole ratio of $ZnO:SiO_2$ are 1:4, 1:1, 4:1, 8:1 and 16:1. The two solutions are then mixed and homogenized using a magnetic stirrer. Then neutralized through the addition of 1 M HCl or NaOH 1 M. The reaction that occurs after the addition of 1 M HCl solution or NaOH 1 M, the reaction that occurs is:

$ZnCl_2$ (aq) + 2NaOH (aq) → $Zn(OH)_2$ (s) + 2NaCl (aq) (4)

Na_2SiO_3 (aq) + 2HCl (aq) → SiO_2 (s) + 2NaCl (aq) + H_2O (aq) (5)

After aging for two days, a white gel was obtained. The gel was dried at 110 °C for 3 hours to remove the water content in it and continued with calcination at 400 °C for 3 hours. In this calcination stage there will be a change in $Zn(OH)_2$ to ZnO according to the following reaction equation:

$Zn(OH)_2$ (aq) → ZnO (s) + H_2O (aq) (6)

3.2 Characterization of Composite

To determine the crystal structure of the synthesized ZnO/SiO_2 composite, characterization using X-Ray Diffraction (XRD) in the range 2θ at 10-80° was done. The analysis of XRD measurements is done by comparing the intensity of the peaks in the diffractogram data measured by the database (reference code: 01-079-2070) for ZnO and the database (reference code: 01-075-0923) for SiO_2. Figure 1 shows the XRD results of the ZnO/SiO_2 composite. The resulting peak pattern is diffraction peaks with relatively varied intensities.

Based on the XRD results it can be concluded that the synthesis carried out has succeeded in forming a ZnO/SiO_2 composite made from battery waste and rice husk ash, where the composite diffractograms of ZnO/SiO_2 have a value of 2θ which are almost the same ZnO and SiO_2 standard diffractograms. ZnO crystalline phase formed in the form of zincite and SiO2 crystals formed cristobalite. In composites 1:4 and 1:1 a new compound is formed, namely Zn_2SiO_4 (willmite). This is possible due to the amphoteric nature of Zn, where Zn will dissolve in a very acidic or very alkaline environment but settles in an alkaline environment. Whereas in other composites no new compounds are formed. In addition, it is known that the formed silica is amorphous for composites 1:4, 1:1, and 4:1 but in composites 8:1 and 16:1 the formation of crystalline silica occurs.

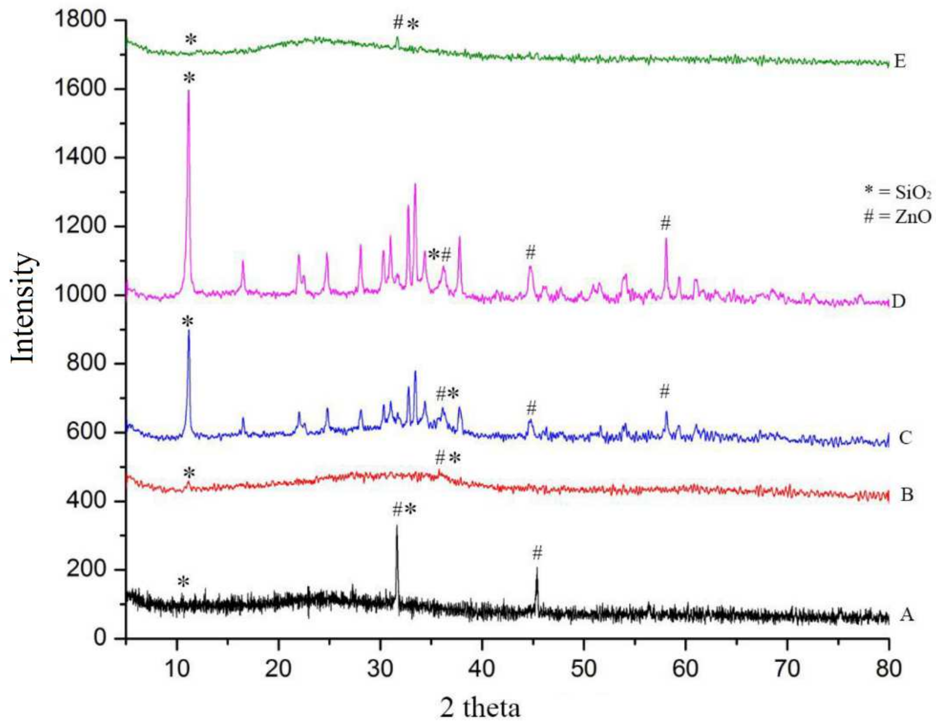

Figure 1. Difractograms of ZnO/SiO_2 Composite with mol ratios $ZnO:SiO_2$ A) 1:1, B) 4:1, C) 8:1, D) 16:1, and E) 1:4

To determine the morphology of the crystalline composite, the SEM characterization was carried out. The results of SEM characterization for ZnO/SiO_2 composites with two different magnifications 2000x and 5000x magnification can be seen in Figure 2. Composite particles show bulk and non-uniform sizes [10]. ZnO surface morphology shows agglomeration with a non-uniform size, where ZnO particles will be trapped in the SiO_2 matrix polymer. The factors of non-uniform shape and size of particles can be affected by stirring. The homogeneity of particle size is very important in catalyst applications because it can increase the selectivity of substrate adsorption. The increased selectivity of substrate adsorption will also increase the possibility of forming the desired reaction product.

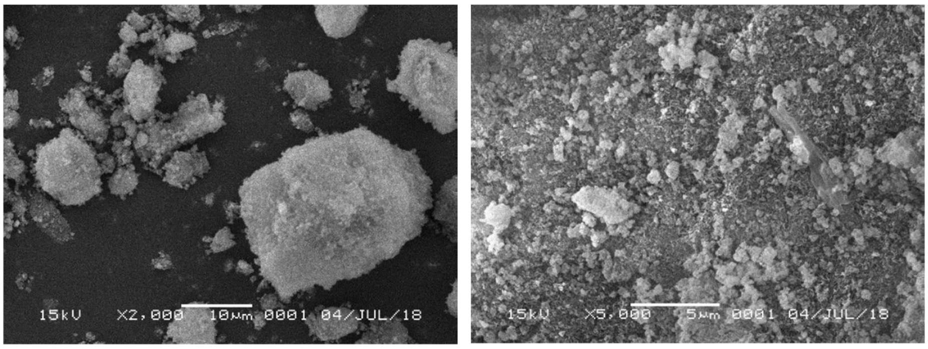

Figure 2. SEM Image of ZnO/SiO_2 Composite 4:1

3.3 The photocatalytic properties

Decreasing the intensity of dyes or commonly known as decolorization using ZnO/SiO_2 composites occurs through two mechanisms, namely adsorption and photodegradation using visible light. To find out the difference in composite activity in reducing the intensity of dyes, several variations were carried out during irradiation; a) variation of composite composition, b) variation of composite mass, c) variation of radiation time, and d) variation in concentration of dye solution.

The methylene blue solution was measured for its absorbance at the maximum wavelength, which is 644 nm. The decolorization process using ZnO/SiO_2 composites occurs in two ways at the same time, that is adsorption and photocatalysis. In the adsorption process, SiO_2 works in binding to blue methylene particles. While in the photocatalytic process, ZnO works to degrade methylene blue particles into simpler compounds.

The adsorption process occurs because the adsorbate attaches to the surface of the adsorbent, in this case the molecule of methylene blue acts as an adsorbate and SiO_2 in a ZnO/SiO_2 composite as an adsorbent. So that the methylene blue particles will stick to the surface of SiO_2. The adsorption process occurs physically because of the Van der Waals interaction between the positive charge of quaternary ammonium in methylene blue and the negative charge SiO_2 [20].

The photocatalytic process occurs when ZnO (in a ZnO/SiO_2 composite) as a photocatalyst obtains energy due to absorption of light from a UV lamp. The energy obtained will be used for the excitation of electrons from the valence band to the conduction band. This excitation process results in the formation of holes in the valence band which can break down water to form a radical hydroxy. This radical hydroxy can break down organic compounds into simpler compounds. In addition, excited electrons will form super oxide species when reacting with oxygen. This super oxide anion is able to react with compounds from the breakdown of organic molecules.

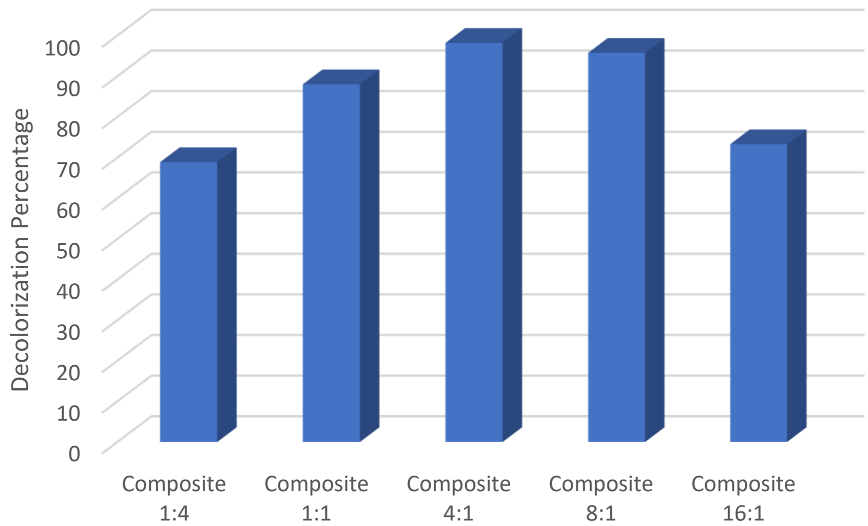

Figure 3. Decolorization percentage of some ZnO/SiO_2 composite with various composition

Figure 3 shows the performance of composite photocatalysts that were successfully synthesized. Based on these data, the 4:1 are composites with the best photocatalyst performance. From the experiments it is also known that the less amount of ZnO in the composite, the photocatalyst performance tends to get worse. This is understandable because ZnO is the component responsible for the photocatalytic process. The less amount of ZnO the worse the photocatalyst performance. But not vice versa. As it turns out, the more amount of ZnO in the composite, does not make the performance increase. Even more ZnO in the composite, the performance of the photocatalyst tends to decrease. A lot of ZnO in the composite, then more and more the ZnO agglomeration event will be more likely, so that ZnO accumulation in the composite, even though there are many, it will not improve the performance of the photocatalyst.

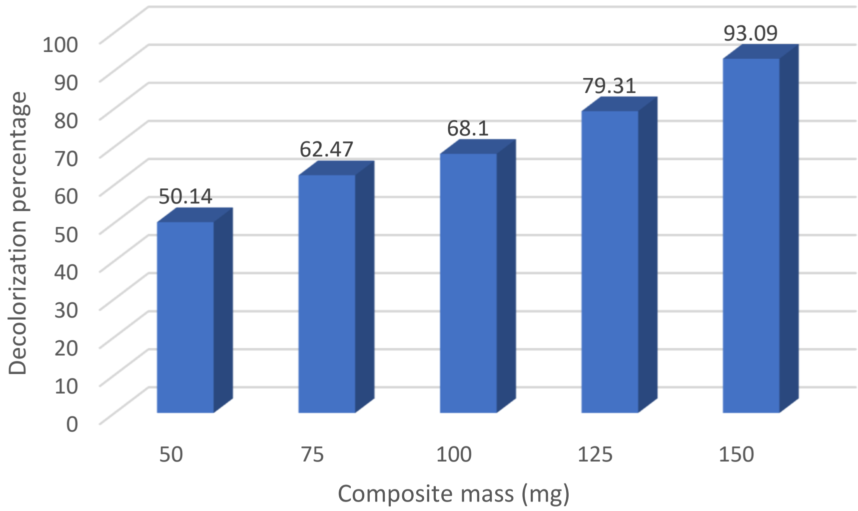

Figure 4. Decolorization percentage of ZnO/SiO_2 composite with various composite mass

Figure 4 shows the variation of composite mass used in the photocatalyst process. The experimental results show that the more composite mass used, the greater the percent decolorization. The optimum results were seen in the composite mass of 150 mg with percent decolorization of 93.09%. This is because the more composites used, the more composite particles that work to adsorb methylene blue or break the bonds of methylene blue. The breakdown of the bond can cause a loss of blue in the solution, so that it will reduce the intensity of the methylene blue color.

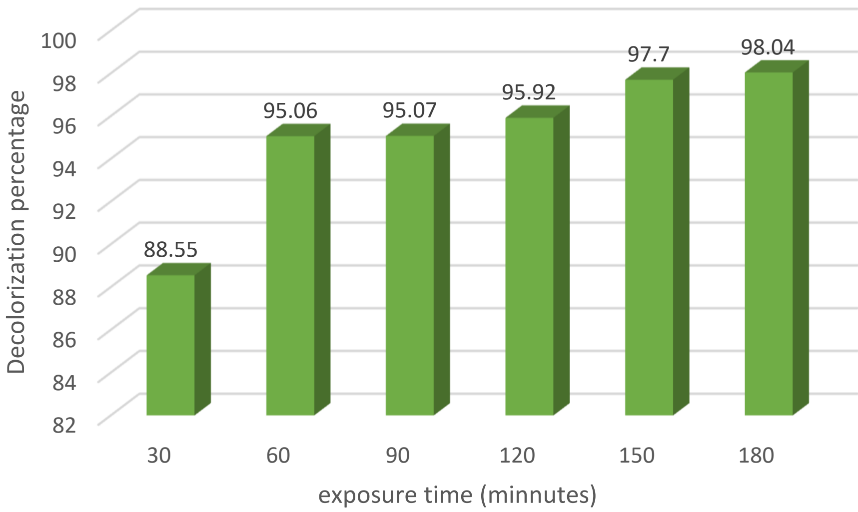

Figure 5. Decolorization percentage of ZnO/SiO_2 composite with various exposure time

Experiments show that the longer the irradiation process takes place the greater the percent decolorization, this is shown in Figure 5. The optimum results can be seen at 180 minutes of irradiation with a percentage of decolorization of 98.04%. This is because the longer the irradiation causes the more energy that electrons gain for excitation, the more the amount of radical hydroxy formed. The greater the amount of radical hydroxy in the solution can increase the process of breaking bonds in methylene blue.

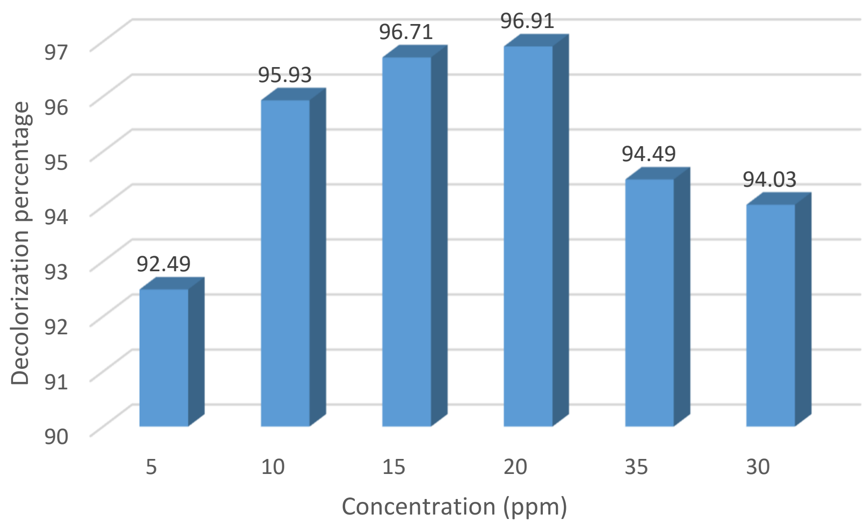

Figure 6. Decolorization percentage of ZnO/SiO_2 composite with various concentration of methylene blue solution

Based on the experimental results, % decolorization of methylene blue is not too influenced by the concentration of the solution used. Figure 6 shows that the results are not much different, ranging from 92-96%, the percent decolorization data shows that the ability of the composite to reduce the intensity of methylene blue dyes in concentrations of 5-30 ppm is above 90%. This shows that the decolorization process continues to occur in solution, where the higher the concentration of methylene blue in the solution, the more decolorized blue methylene particles also become. This shows that the composite continues to work in adsorbing and degrading methylene blue.

4 Conclusion

ZnO/SiO_2 composites from battery waste as a source of ZnO and rice husk ash as a source of SiO_2 was successfully synthesized by sol-gel method. The results of characterization using XRD showed that ZnO/SiO_2 composites had been formed and SEM images showed ZnO agglomeration in the composite. Composite obtained can be used to reduce the intensity of methylene blue solution by photocatalyst method with the help of visible light. 4:1 composite is the best performance composite which can reduce the intensity of methylene blue solution up to 96.91% when used as much as 150 mg when the exposure to visible light for 180 minutes and using methylene blue 20 ppm as much as 25 mL.

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