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Nickel Slag Coated by Titanium Dioxide for Degradation of Methylene Blue

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Abstract. The utilization of nickel slag waste coated titanium dioxide (TiO\textsubscript{2}) as material for organic contaminant degradation was carried out. The aim of this study is to influence of degradation time and nickel slag mass for contaminant degradation in photolysis and photocatalysis system. TiO\textsubscript{2} was synthesized by using sol-gel method. Material characterizations were performed using X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), and Optical Microscope. XRD Analysis of slag coated TiO\textsubscript{2} (Slag-TiO\textsubscript{2}) showed that TiO\textsubscript{2} in anatase phase at $2\theta = 68.30^\circ$ (230). XRF analysis showed that dominant compound in nickel slag was silicon. Furthermore, optical microscope analysis showed that surface morphology of nickel slag was porous and solid. The result of research reveals that degradation test of methylene blue was conducted in photolysis and photocatalysis system for 4 hours irradiation with time interval for 30 minutes. The percentage degradation of photolysis and photocatalysis were 48% and 87.50%, respectively. Meanwhile, a mass variety of slag used in methylene blue degradation were 5.46 gram; 7.43 gram, and 9.32 gram for photolysis and 5.49 gram; 8.02 gram, and 10.02 gram for photocatalysis. Degradation percentage was increased along with the increase of nickel slag mass.

Keywords: Nickel slag, TiO\textsubscript{2}, photocatalysis, photolysis, methylene blue

1. Introduction

Nickel can be produced either by reduction-smelting process from laterite ores [1] or roasting-smelting process from sulfide ores [2]. Both of these processes produce nickel slag, which will take up a lot of space and pollution to the environment. The nickel slag has a porous structure and a solid form. In addition the nickel slag can be utilized as the medium for overcoming the dye pollution by coating method that should be addressed [3].

Meanwhile, Methylene Blue (methylthionine chloride) is a heterocyclic aromatic chemical compound with the chemical name [3,7-bis (Dimethylamino)-phenazathionium chloride Tetramethylthionine chloride] under the molecular formula (C\textsubscript{16}H\textsubscript{18}ClN\textsubscript{3}S.3H\textsubscript{2}O) [4]. It is cationic and considered a significant threat to human and biota, as carcinogenic and mutagenic. Methylene blue is used for coloring paper, wool, and cotton staining [5]. In addition, the aromatic structure of methylene blue provides the stability of the chemical and physical attacks, so it needs serious treatment as a water pollution in environment.

Photocatalyst can be used to reduce and damage the organic or inorganic compounds through a photocatalytic process [6]. Titanium (IV) oxide (TiO\textsubscript{2}) is a heterogeneous photocatalyst most effective to degrade the organic compound pollutant. This is due to the photocatalytic activity of TiO\textsubscript{2} has a stable and high-photoactivity [7]. Photocatalyst with TiO\textsubscript{2} heterogeneous underultraviolet (UV) light is
an emerging technology to be applied in the removal or changing of waste through the mechanism of reduction and oxidation (redox) [8]. The addition of the metal surface of TiO$_2$ is the object of research that is important to examine the photocatalytic activity of TiO$_2$.

The addition of the metal widely increases the area of the spectral response of TiO$_2$ to the UV band gap changes effects [9]. In TiO$_2$ photoexcitation process, electrons can be transferred from the conduction band to metal particles on the TiO$_2$ surface. Dopant ions can create trap electrons which will minimize the recombinant process of electron and hole. Metals such as Ni and Zn have been reported to increase the catalytic activity of the photocatalyst [10]. Porous materials are frequently adopted as an adsorbent and still investigated in the design of adsorption assisted photocatalytic reaction systems [11].

Nickel slag porous structure and containing a metal oxide when coated with TiO$_2$ semiconductor was potentially helping the performance of TiO$_2$ in degrading organic pollutants. This study performs the coating with TiO$_2$ slag through a dip-coating method, which is expected to oxidize pollutants organic substances such as methylene blue and turn it into simpler compounds and does not harm the environment. The purpose of this study is to obtain the effect of TiO$_2$-nickel slag as material to degrade organic pollutants in photolysis and photocatalytic process.

2. Material and Methods

2.1 Materials

The materials used in this study were nickel slag, methylene blue, Titanium tetra-isopropoxide (TTIP) 97% (Aldrich), Nitric acid (HNO$_3$ 65% E. Merck), Ethanol (C$_2$H$_5$OH E. Merck) and distilled water.

2.2 Preparation of Sol-Gel TiO$_2$

Synthesis of TiO$_2$ sol-gel was adopted according to the method described by Kim et al. [12] TiO$_2$ sol-gel made using two solutions, namely solution I (250 mL of distilled water is added by nitric acid to a pH of 1.5 and then stored at cold temperatures) and solution II (Titanium tetra-isopropoxide (TTIP) 1.25 mL, then added with 25 mL of ethanol). The solution I and solution II were mixed using a magnetic stirrer for 30 minutes. Subsequently, it was stirred gently at 4°C for 12 hours and stored in the refrigerator.

2.3 Coating Process of Slag Nickel with TiO$_2$

Nickel slag with mass variation were coated with TiO$_2$ sol-gel by dip-coating technique based on the modified method described by Li et al. [13]. The dip-coating was performed for 10 minutes and calcined for 120 minutes at a temperature of 500°C, thus producing of slag coated TiO$_2$ (slag-TiO$_2$).

2.4 Preparation of Reactor

Reactor of wood was coated by aluminum foil on the inside cube with dimension of 30cm×30cm×30cm. Lights were placed in the form of two UV LEDs mounted on the top surface of the cube wall. The reactor equipped with a switch to turn off and turn on the UV light that can be seen in Figure 1.

![Figure 1. Illustration of photodegradation reactor](image_url)

2.5 Characterization of Slag and Slag-TiO$_2$

Morphology and diffraction pattern analysis. Morphology of TiO$_2$ slag and slag-known were observed by optical microscopy imaging tools. This analysis is done at 35 times magnification. Meanwhile, analysis of the diffraction pattern-TiO$_2$ slag and slag was carried out using X-Ray Diffraction (XRD) Shimadzu 6000.
Analysis of element compositions. Analysis of the elemental composition of TiO$_2$ slag and slag were performed using Portable X-Ray Fluorescence (XRF) with the type of Niton XL3t GOLDD. All samples were analyzed in the form of press powder. Measured data in the form of intensity (I) and elemental energy which is then converted in the form of numbers so that the data generated in the form of a percentage elemental composition of a sample.

2.6 Degradation Process of Methylene Blue

Variations in exposure time. Methylene blue dye degradation was carried out in a glass reactor with a volume of 50 mL, with a concentration of 4 mg.L$^{-1}$. Then put the catalyst that had been made previously, namely nickel slag coated TiO$_2$. The reactor was irradiated by UV light time variation of 30, 60, 90, 120, 150, 180, 210 and 240 minutes. After irradiation for 4 hours, the absorbance of degradation was analyzed by UV-Vis spectrophotometer at a maximum wavelength of 664 nm. The analysis results were compared to the concentration of methylene blue in photolysis and photocatalytic degradation. The percentage degradation has determined by equation (1) [14]:

$$
\text{(%D)} = \frac{C_0 - C_t}{C_0} \times 100\%
$$

Where $C_0$ is the initial concentration of the dye before irradiation, $C_t$ is the concentration of the dye on t.

Nickel slag mass variation. Degradation of methylene blue is carried out by using a mass variation. Mass variations were 5.49, 8.02, 10.02 grams. Then each beaker was put 50 mL of methylene blue and inserted nickel slag coated TiO$_2$. The reactor was irradiated with UV light with time variation of 30, 60, 90, 120, 150, 180, 210 and 240 minutes. After UV irradiation for 4 hours, degradation results absorbance were analyzed by spectrophotometer at a maximum wavelength of 664 nm. The results of the analysis were compared to the concentration of dye in photocatalytic degradation results determined the percentage of degradation of dyes by equation (1). Furthermore, the same treatments were performed in the photolysis of the slag mass variation of 5.46 gram, 7.43 gram, and 9.32 gram.

3. Results and Discussion

3.1. Process of Nickel Slag coated TiO$_2$

Nickel slag has been successfully coated TiO$_2$ as indicated by the white appearance on the surface of the slag. Slag mass after being coated successively were 5.49, 8.02, and 10.2 grams based on the slag mass original sample, so that the mass of TiO$_2$ deposited were 0.03; 0.59 and 0.88 grams. The TiO$_2$ synthesis are expected to have a crystal structure of anatase for calcined at 500°C for 2 hours. Anatase crystals have a large band gap energy (3.2 eV), so that it has also larger surface area that makes the high-performance for photoactivity [15].

3.2. Characterization of Nickel Slag

Analysis of optical microscope. Slag surface morphology are shown in Figure 2. Before coating the entire slag with different masses has pores and dark gray as the color of iron in general. It is certainly not out of the composition of the slag, but it is mostly in the form of iron.
**Figure 2.** Slag surfaces original samples (a) before TiO$_2$ coated 5.46 gram (b) after TiO$_2$ coated of 5.46 gram (c) 7.43 grams (d) after TiO$_2$ coated of 7.43 gram (e) 9.32 gram mass (f) after TiO$_2$ coated of 9.32 gram

**X-Ray Diffraction Analysis (XRD).** XRD analysis aims to interpret the dominant presence of the compounds contained in nickel slag and determine the crystal phase of TiO2 that has been synthesized by sol-gel method. Figure 3 shows the results of XRD spectrum on Pomalaa nickel slag and slag-TiO2. Slag diffractogram shows the pure slag where there are peaks at the position of \(2\theta = 28.57^\circ; 62.98^\circ; \) and \(63.16^\circ\) which indicate the presence of a compound CaMg(Si$_2$O$_6$). The analysis showed that the compound is a dominant compound in the slag with a composition of 50%. Other minerals with relatively large amounts of the Ni$_2$(SiO$_4$) and Fe$_2$(SiO$_4$) were detected at \(2\theta = 42.4^\circ\) and \(2\theta = 25.57^\circ\) with the composition of their respective 24% and 19%. These results demonstrate conformity with the research report by Tangahu et al. [16].

**Figure 3.** Diffractograms of (a) Slag, b) TiO$_2$, and (c) Slag-TiO$_2$

In addition to these three minerals, there is also diffraction at \(2\theta = 25.31^\circ\). Peaks are formed in very small or in other words have a very low intensity due to the minimal amount of slag-TiO$_2$. This confirms the validity of the research by Rusmini showed a small amount of TiO$_2$ in slag through XRD analysis [17].

Slag-TiO$_2$ diffraction spectrum show that the peaks are formed in common with pure slag where there are peaks of CaMg(Si$_2$O$_6$), Ni$_2$(SiO$_4$), and Fe$_2$(SiO$_4$) minerals with similar intensity. However, the coating of slag-TiO$_2$ indicate a very high peak intensity at the position of \(2\theta = 25.30^\circ\) and moderate intensity at \(2\theta = 53.98^\circ\). The existence of this second peak indicates the presence of TiO$_2$ anatase phase corresponding by JCPDS No.21-1272. In previous studies, Salmin and Al-Shamali [18] have reported that the structure of TiO$_2$ can be obtained by calcination at a temperature of 500 $^\circ$C so that the results of this study indicate suitability. Compounds of TiO$_2$ anatase has been successfully coated on the nickel slag surface of Pomalaa expected to provide efficiency degradation of organic pollutants.
**X-Ray Fluorescence (XRF).** The result of XRF as an elemental analysis technique can be seen in Table 1.

| No. | Elements/compounds | Composition | No. | Elements/compounds | Composition |
|-----|--------------------|-------------|-----|--------------------|-------------|
| 1   | Si                 | 29.50 %     | 9   | Zr                 | 0.02 %      |
| 2   | Fe                 | 8.75 %      | 10  | Zn                 | 10 %        |
| 3   | Ni                 | 0.13%       | 11  | Ca                 | 42.3 %      |
| 4   | Zn                 | 0.11 %      | 12  | Mg                 | 5.40 %      |
| 5   | Cu                 | 0.8 %       | 13  | Nb                 | 1.02 %      |
| 6   | Co                 | 0.6 %       | 14  | C                  | 0.1 %       |
| 7   | Mn                 | 0.2 %       | 15  | F                  | 0.3 %       |
| 8   | Cr                 | 0.4 %       | 16  | S                  | 0.16 %      |
|     | Total Composition  | 100%        |     |                     |             |

3.3. Degradation of Methylene Blue Dye

**Photolysis Degradation.** Methylene blue degradation by photolysis was performed on two conditions, namely degradation by using nickel slag with a mass variation of 5.46 gram, 7.43 gram, and 9.32 gram, without the use of TiO$_2$ catalyst, under UV light irradiation and degradation without using nickel slag (only UV light) for 4 hours. The relationship between the irradiation time by photolysis, and only with UV light, is shown in Figure 4 a, and the relationship between the irradiation time and slag variation mass is shown in Figure 4 b.

![Figure 4](image)

Figure 4. (a) Graph of time related to the concentration of methylene blue in the photolysis (Only Assistance UV rays). (b) Graph of irradiation time relationship and slag mass variation toward the concentration of methylene blue in the photolysis.

Figure 4 (a) shows the degradation of methylene blue under UV light without nickel slag for 4 hours in intervals of 30 minutes. The results showed that in intervals of 30 minutes the methylene blue dye has decreased of concentration. But a decrease in the concentration likely to be small. Decreasing the concentration of methylene blue to the irradiation time of 240 minutes was 2.7 mg.L$^{-1}$, with the percent degradation reaches 31%. Figure 4 (b) shows the results of degradation of methylene blue for
mg L\(^{-1}\) by using nickel slag mass 5.46 gram, 7.43 gram, and 9.32 gram and the time of irradiation for 4 hours in intervals of 30 minutes. The optimum time degradation is determined by observing at the most significant decrease in concentration, so the optimum degradation time is 60 minutes.

Based on Figure 4 (b) shows that the irradiation was greatly affects the decreasing of the concentration of methylene blue, the longer of exposure time was obtained the greater decrease in the concentration of methylene blue. In the higher percent degradation increases, the energy of photons produced by UV rays to generate OH radicals. OH radicals will be formed exponentially with time. Decreasing the concentration of methylene blue which tends to stay constant because in the longer OH radicals are formed H\(_2\)O\(_2\) [19]. Slag mass difference in the degradation of methylene blue also affects the efficiency of degradation. The greater the mass of slag is used, the greater the decrease in the concentration of methylene blue. Figure 4 (b) shows that the mass of slag 9.32 gram, can degrade methylene blue, it is quite large compared to the mass of 5.46 gram and 7.43 gram.

**Photocatalytic degradation.** The photocatalytic process is one of the degradation processes that use catalyst and photons. Photocatalytic degradation of methylene blue is done in two conditions, namely the degradation of methylene blue only with a catalyst of TiO\(_2\) and UV light, as well as the degradation of methylene blue with nickel catalyst coated by TiO\(_2\) slag and UV light irradiation time of 240 minutes as can be seen in Figure 5.

![Figure 5](image)

**Figure 5.** (a) Graph of irradiation time relationship toward the final concentration and (b) graph of irradiation time relationship and mass variation toward the final concentration of methylene blue in photocatalytic

Based on the data obtained can be seen that the degradation of methylene blue using a nickel slag coated TiO\(_2\) is much more effective than using TiO\(_2\) suspension, this is due to the nickel slag has a large surface, and the metal oxide is a semiconductor that helps the process of photodegradation.

3.4. **The Degradation Efficiency**

Based on Figure 6 the photocatalytic processes was provided better results than the photolysis process because the presence of radical species reproduce TiO\(_2\) catalyst to degrade the methylene blue which would accelerate the degradation reaction. Methods of using photon photolysis only produce radical species that tend to be a bit because it does not happen generating pairs of electron/hole by semiconductor TiO\(_2\).
Figure 6. Comparison of degradation results of methylene blue

4. Conclusion
Based on the results of research and discussion that has been described, it can be concluded that the percentage of degradation of methylene blue dye solution using nickel coated slag as photolysis and photocatalytic TiO$_2$ under UV light irradiation for 4 hours by 48% and 87.50%, respectively. The increase in mass of slag used is directly proportional to the increase in the percentage of degradation of methylene blue dye both photolysis and photocatalytic. Meanwhile, the optimum time of degradation is determined by observing at the most significant decrease in concentration so that the optimum time of degradation on the photolysis and photocatalytic process is 60 minutes.

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