Synthesis and characterization of photocatalyst TiO$_2$ doped with Ni for treatment of waste model from nuclear facility

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Abstract. Synthesis and characterization of photocatalyst TiO$_2$ doped with Ni for treatment of waste model from nuclear facility. Ni doped TiO$_2$ as photocatalyst material has been made. Addition of dopant Ni was carried out by impregnation technique. The Ni content was varied between 3, 5, 7 and 10 wt.%. The TiO$_2$-Ni samples obtained were then characterized by X-Ray Diffractometer and SEM-EDS. The catalyst test is carried out using UV-VIS. The anatase crystal structure appears at 2$\theta$ = 25.41º, 37.89º, 48.13º, 55.14º 62.78º. The NiO crystal structure was also found at X-Ray peak 2$\theta$ = 38.8º. It obvious that addition of Ni dopants decreased significantly the TiO$_2$ crystal main size. The anatase crystal structure formed on TiO$_2$-Ni (3 wt.%) is 84.21%. The results of SEM-EDS analysis showed the best success rate of 91.6% wt 3 wt.% Ni addition. The photocatalyst material TiO$_2$-Ni was then applied to treat the standard non-radioactive liquid waste material from BATAN nuclear facility modeled by a mixture based on methylene blue exposed with UV light with variation of time. The degradation rate during processing of methylene blue waste with TiO$_2$-Ni (3 wt.%) using UV light was measured 0.021/hour. The longer the UV irradiation time is the greater the degradation of methylene blue. The making of TiO$_2$ photocatalyst by adding variations of Ni dopant has been successfully carried out, with a fairly good success rate. The highest success rate is addition of Ni by 3% with a success rate of 91.6%.

1. Introduction

One of the BATAN nuclear facilities built to carry out nuclear science and technology R&D activities is the Serpong Nuclear Area. Serpong Nuclear Area is a nuclear science and technology central R&D area which was built with the aim is to supporting the development of the nuclear industry and preparing for the construction and operation of nuclear power plants in Indonesia. Radioisotope applications at this time have covered a very broad field, for example in the fields of medicine (diagnostics and therapy), pharmacy (as a tracer), and industry. From the nuclear facilities and laboratory activities, radioactive and non-radioactive waste is produced. BATAN has many facilities / installations and laboratories that produce non-radioactive waste that is waste originating from the use of hazardous and toxic chemicals. The B3 waste needs to be managed in accordance with applicable standards and regulations so that it does not cause danger to humans and the environment. Based on PP RI NO. 74 of 2001 concerning B3 management, each facility One of the management activities carried out is collecting hazardous chemical waste from each facility / laboratory and clarifying it according to its potential hazard. laboratory has an obligation to be able to manage B3 [1]. One of the management activities carried out is collecting hazardous chemical waste from each facility /
laboratory and clarifying it according to its potential hazard. B3 Chemical waste is then collected in a temporary storage room. Problems that occur in the field accumulate the amount of B3 chemical waste.

In this research, a simulation of methylene blue non-radioactive wastewater treatment will be carried out exposed to UV light. The purpose of this study is to reduce environmental pollution in the Serpong Nuclear Area due to non-radioactive liquid waste generated from research activities in laboratories that use chemicals.

This dye has the molecular formula C_{16}H_{18}ClN_{3}S. Non-radioactive wastewater treatment methods that are often used are adsorption, filtering, oxidation and photodegradation methods. These methods are quite effective in dealing with waste. The photodegradation method utilizes ultraviolet light and photocatalysts by using inorganic materials in the form of semiconductors which have photocatalyst activity to absorb photons and carry out transformational reactions of the material's surface simultaneously. Semiconductor materials commonly used are TiO_{2}, Fe_{2}O_{3}, ZnO, CdS and ZnS [2]. There are also many other methods commonly used, such as combination coagulation, electrochemical oxidation, flocculation, reverse osmosis, and adsorption using activated carbon. However, these methods also have many disadvantages, namely the emergence of new problems such as the generation of new phases that contain more concentrated pollutants.

The photocatalysis method using TiO_{2} has many advantages including being easy to obtain, relatively inexpensive, harmless, strong oxidizing power, high photochemical stability and corrosion resistance [3]. The disadvantage of TiO_{2} is that it is only active in the UV light region to initiate the photocatalytic process. Various efforts to increase the photocatalytic activity of TiO_{2} and shift the work area of TiO_{2} have been carried out, including the addition of metal dopants [4]. The addition of dopant will produce a more regular crystal structure so that it has better crystal properties [5]. In this research Ni metal doping will be carried out on TiO_{2} using the impregnation method.

On this basis spectrophotometry was designed to measure the concentration of an existing in a sample. Where the substances in the sample cell were irradiated with light that has a certain wavelength. When some of the samples light will be absorbed, part of it will be scattered and part of it will continue.

In spectrophotometry, incoming light that hits the surface of the substance and the light after passing through the substance cannot be measured, which can be measured is I_{0}/I, or I/I_{0} (the ratio of the incoming light to light after passing through the material (sample)). The process of absorption of light by a substance can be described as follows:

![Figure 1. Schematic of absorption process light by sample.](image)

The picture shows that the substance before passing through the sample cell is brighter light than after passing through the sample cell.

The absorbed light is measured as absorbance (A) while scattered light is measured as transmittance (T), expressed by the law of Lambert-Beer or Beer's Law, "The amount of visible light radiation (ultraviolet, infrared, etc.) absorbed or transmitted by a solution is an exponential function of the concentration of the substance and the thickness of the solution".

Based on Lambert-Beer law, the formula used to calculate the amount of light scattered:

\[
T = \frac{I}{I_0} \quad \text{atau} \quad \%T = \frac{I}{I_0} \times 100\%
\]

and absorbance expressed by the formula:
where $I_0$ is the intensity of the incident light and $I_t$ or $I_1$ is the intensity of the light after passing through the sample. The data released by UV-VIS can be absorbance or transmittance which is directly read on the spectrophotometer.

The graph of the absorbance relationship ($A$) with concentration ($C$), where $a$ is the slope is shown in the following figure:

![Graph of relationship between absorbance and concentration](image)

**Figure 2.** Graph of relationship between absorbance and concentration.

The concentration of an analyte can be determined by measuring absorbance. The main requirement for the analyte must be completely dissolved and the solution colored or made colored. UV-Vis spectrophotometry in this study was used to calculate the concentration of methylene blue in adsorption.

The UV-Vis spectrophotometry used is the Lambda 25 PERKIN ELMER brand type found in the UV-Vis lab BSBM-PSTBM.

2. Materials and methods (work procedures)

2.1 Tools and materials

The materials used in this study were anatase TiO$_2$ powder, NiSO$_4$.6H$_2$O and methylene blue (C$_{16}$H$_{18}$CIN$_3$S). The tools used include: photocatalyst reactor, glassware, mortar, porcelain cup, magnetic stirrer, analytical balance, SEM / EDS (Scanning Electron Microscopy / Energy Dispersive Spectroscopy), XRD (X-Ray Diffractometer) and UV-VIS Diffractometer.

2.1.1 Samples preparation

The steps are as follows:

a. Weigh TiO$_2$ by 50 grams
b. Considering 6.68 grams of NiSO$_4$.6H$_2$O, 11.14 grams, 15.59 grams and 22.27 grams
c. Prepare 300 ml of demin water.

2.1.2 Conducting synthesis activities of TiO$_2$:Ni waste processing materials 3%, 5%, 7% and 10%

a. Mix TiO$_2$ and NiSO$_4$ above in a measuring cup measuring 500 mL with 300 ml demin water added.
b. Stir in the magnetic stirrer by heating 90 C until all the water evaporates and a solid is obtained.
c. Smooth the solid sample by grinding using a mortar.
d. Warming the sample in the furnace fox temperature of 400 C for 1 hour.

2.2 Characterizing the TiO$_2$ waste processing material with the addition of Ni variations of 3%, 5%, 7% and 10%

X-RD characterization aims to identify the crystal structure of TiO$_2$ for variations of the addition of Ni. Crystal size is obtained by calculating from half the maximum width of FWHM with the Scherrer equation. Characterization with SEM aims to determine the surface structure (morphology), porosity, thickness and composition of a specimen.
2.3 Simulation of methylene blue waste
1. Weigh Methylene Blue as much as 0.5 gr then weigh TiO$_2$-Ni (3%, 5%, 7%, 10%) according to variables of 5, 10 and 15 grams using weigh paper as a container on the analytical balance.
2. Dissolve methylene blue powder with 500 mL of distilled water.
3. Dilute the 3 mL concentrated blue methylene into 300 mL aquadest.
4. Mix TiO$_2$-Ni powder (3%, 5%, 7%, 10%), into each methylene blue solution with a concentration of 10 ppm.
5. Stir with a magnetic stirrer in the photocatalyst reactor for 5 hours (at room temperature) away from the light source.
6. Take a sample of 10 mL using a goiter every 1 hour. Store in a container and place in a total dark place.

2.4 Photocatalis testing
The container to be used is a 500 ml beaker equipped with a magnetic stirrer and hotplate. The container is inside the test box which is equipped with a lamp fitting which is a lamp holder used as a UV light source. Catalyst performance testing was carried out in a photoreactor with a 300 ml methylene blue simulation waste. The catalyst that was prepared was put into place by varying the concentration of Ni. The test container is placed on a hot plate so that the temperature can be adjusted at 30$^\circ$C, as well as to be stirred with a magnetic stirrer to increase the reaction kinetics. After that, the UV light is turned on so that photocatalysis activity begins. The reaction time is 5 hours. Waste liquid samples are taken every 1 hour intervals and then the composition is analyzed by UV-VIS spectrometry equipment.

3. Results and discussion
3.1. Evaluation of the synthesis results as follows
Doping sample results obtained between Ni in TiO$_2$ with the appearance of the sample rather greenish. This is due to the NiSO$_4$ content which is purely green in color.

The grains in the sample are also quite homogeneous and with a uniform appearance of color. However, other tests still need to be done to determine the quality of the material produced, for example by XRD, SEM and UV-VIS performance.

3.2. XRD characterization results
XRD characterization aims is to identify the crystalline structure of the TiO$_2$-Ni catalyst with variations in Ni content of 3%, 5%, 7% and 10%, as well as to determine the crystal size, and determine the ratio of anatase and rutile phases. The percentage of anatase and rutile phases in the sample can be estimated from the peak intensity of the XRD results with the Debye equation [6]:

\[
X = \left( \frac{0.8 I_A}{1 + I_R} \right)^{-1}
\]

(3)

\(X\) = Anatase weight fraction in the catalyst powder
\(I_A\) = Intensitas X-ray with peak anatase
\(I_R\) = Intensitas X-ray with peak rutile

While the crystal size can be determined from the Scherrer equation [7]:

\[
L = \frac{0.9 \lambda}{(\beta \cos \theta)}
\]

(4)

\(L\) = Crystal size
\(\lambda\) = Wavelength of X-ray
\(\beta\) = Full width half maximum (FWHM)
\[ L = \text{Crystal size (nm)} \]
\[ \lambda = \text{wavelength of X-ray radiation used (nm)} \]
\[ \beta = \text{width of highest half of the wave crest (rad)} \]
\[ \theta = \text{peak angle (°)} \]

Figure 3 shows the diffraction peak with the highest intensity of 5209 at \( 2\theta = 25.41° \). The formed phase is the anatase phase. The diffraction pattern of the anatase phase is seen at \( 2\theta = 25.4°, 37.9°, 48.1°, 55.1°, 62.8°, 75.1° \), while the rutile phase is seen at the peak \( 2\theta = 27.54°, 36.18°, 41.3°, 56.7°, 68.9°, 70.3° \). Comparison of the formed phases of anatase 84.21% while the rutile phase formed only 15.79%. NiO's diffraction peaks have also been seen at \( 2\theta = 38.8° \) which is doping / impurity.

Table 1. XR-D characterization results.

| No. | Sample          | Peak (°) | L (nm) | X (%) anatase |
|-----|-----------------|----------|--------|---------------|
| 1.  | TiO\(_2\)-Ni (3 %) | 25.41    | 42.5937| 84.21         |
| 2.  | TiO\(_2\).Ni (5 %) | 25.39    | 42.5676| 92.25         |
| 3.  | TiO\(_2\).Ni (7 %) | 25.44    | 42.8439| 90.28         |
| 4.  | TiO\(_2\)-Ni (10 %) | 25.33    | 42.8439| 91.42         |

Table 1 shows the grain size on TiO\(_2\)-Ni (3%) of 42.5937 nm. The addition of variation of Ni 3% on TiO2 resulted in its grain size being relatively smaller than TiO\(_2\) (50.59 nm) [8]. While variations in the addition of Ni 3%, 5%, 7% and 10% relative do not affect grain size. According to Sayilkan et al that the addition of dopants will reduce grain size [9]. The grain size produced is still in the range of 1-100 nm, this indicates that the sample provides high catalyst activity [10].

3.3. SEM / EDS characterization results

SEM / EDS characterization aims is to determine the surface structure (morphology), porosity, thickness and composition of a specimen.
Figure 4. seen the shape of the grain of TiO$_2$-Ni, in the picture it looks like there is a relatively same Ni grain. In general, the addition of Ni dopants above 3% does not greatly affect the size of the grain. For more details the results of SEM EDS characterization are shown in table 2.

Table 2. Results of SEM EDS characterization

| No | Sample          | Ni content (%) | Level of success (%) |
|----|-----------------|----------------|----------------------|
| 1  | TiO$_2$ - Ni(3%)| 2.75           | 91.6                 |
| 2  | TiO$_2$ - Ni(5%)| 2.66           | 53.2                 |
| 3  | TiO$_2$ - Ni(7%)| 2.96           | 42.3                 |
| 4  | TiO$_2$ - Ni(10%)| 2.30          | 23                   |

From table 2 it can be seen that the success rate of adding Ni dopants to TiO$_2$ is quite high at more than 90%. The highest success rate was seen in Ni content (3%) of 91.6%. This is due to TiO$_2$-Ni 3% smaller crystalline size compared to TiO$_2$, so that more pores are formed that can absorb methylene blue waste. The lowest success rate is seen in dopants Ni 10%, which is 23%. This is due to the method of impregnation of the crystalline size of dopant Ni 5%, 7% and 10% tends not to change so that only a small portion is dispersed on the surface of TiO$_2$. As a result, Ni dopants 5%, 7%, 10% are not well bound to TiO$_2$ and will easily be released again.

3.4. Testing photocatalyst activity

The waste used is methylene blue waste. The initial methylene blue waste contains a concentration of 10 ppm. The catalyst reduction test for methyl blue was carried out for 1-5 hours by mixing TiO$_2$-Ni (3%, 5%, 7% and 10%) then stirred with a stirrer and irradiated with UV during the stirring process. Using the regression equation calibration results of standard waste solutions, table (3) can be obtained as follows:

Table 3. TiO$_2$-Ni catalyst test results (3%, 5%, 7%, 10%) against methylene blue.

| No | Stirring Time (Hours) | TiO$_2$-Ni (3%) Concentration (ppm) | TiO$_2$-Ni (5%) Concentration (ppm) | TiO$_2$-Ni (7%) Concentration (ppm) | TiO$_2$-Ni (10%) Concentration (ppm) |
|----|-----------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| 1  | 0                     | 10.000                              | 10                                  | 10                                  | 10                                  |
| 2  | 1                     | 4.1903                              | 4.5014                              | 4.1725                              | 4.1865                              |
| 3  | 2                     | 4.1581                              | 4.0988                              | 3.8252                              | 3.7889                              |
| 4  | 3                     | 4.1839                              | 3.7703                              | 3.4827                              | 3.3017                              |
| 5  | 4                     | 3.9612                              | 3.5668                              | 3.2347                              | 3.0915                              |
| 6  | 5                     | 3.8632                              | 3.3426                              | 3.0846                              | 2.9094                              |

The old mixing graph vs the concentration of methylene blue waste is obtained as follows:
Figure 5. Graph of the concentration of methylene Blue waste against stirring time.

From Table (3) and Figure (5) we can see that the highest concentration of waste decreases during the first hour, from 10 ppm to an average of 4 ppm. From this it can be seen that the TiO$_2$ catalyst with variations in the addition of Ni dopant is very well used to reduce methylene blue waste. It also shows that the more Ni increases the more the concentration of waste decreases[11].

Table (4) Relationship between stirring time and methylene blue Ln (Co / Ct) degradation as follows

| No. | Stirring time | TiO$_2$-Ni (3%) Ln (Co/Ct) | TiO$_2$-Ni (5%) Ln (Co/Ct) | TiO$_2$-Ni (7%) Ln (Co/Ct) | TiO$_2$-Ni (10%) Ln (Co/Ct) |
|-----|---------------|-----------------------------|-----------------------------|-----------------------------|----------------------------|
| 1   | 0             | 0.869813                    | 0.7981966                   | 0.8740697                   | 0.87072                    |
| 2   | 1             | 0.877527                    | 0.8918908                   | 0.9609743                   | 0.9705094                  |
| 3   | 2             | 0.871341                    | 0.9754305                   | 1.0547772                   | 1.1081476                  |
| 4   | 3             | 0.926038                    | 1.0309163                   | 1.1286489                   | 1.1739287                  |
| 5   | 4             | 0.951089                    | 1.0958361                   | 1.1761631                   | 1.2346382                  |
| 6   | 5             | 0.926038                    | 1.0309163                   | 1.1286489                   | 1.1739287                  |

From Table (4) the relationship curve between the exposure time of methyl blue degradation to ln Co / Ct from methylen blue degradation is given by the following graph.

Figure 6. Graph of the relationship between irradiation time and MB degradation.

From figure 6 we get the reaction rate constant (hour-1) as in the following table:

\[
\begin{align*}
Y &= 0.021X + 0.835 \\
Y &= 0.073X + 0.738 \\
Y &= 0.077X + 0.807 \\
Y &= 0.093X + 0.792
\end{align*}
\]
Table 5. Reaction rate constants / hour.

| No. | Sample          | Regression Equation | Reaction Rate Constant (hour⁻¹) |
|-----|-----------------|---------------------|----------------------------------|
| 1   | TiO₂-Ni 3%      | y = 0.021X + 0.835  | 0.021                            |
| 2   | TiO₂-Ni 5%      | y = 0.073X + 0.738  | 0.073                            |
| 3   | TiO₂-Ni 7%      | y = 0.077X + 0.807  | 0.077                            |
| 4   | TiO₂-Ni 10%     | y = 0.093X + 0.792  | 0.093                            |

The reaction rate constants obtained from TiO₂-Ni photocatalyst (3%, 5%, 7%, 10%) on methylene blue waste were 0.021 hour⁻¹, 0.073 hour⁻¹, 0.077 hour⁻¹, 0.093 hour⁻¹.

4. Coordinating the synthesis of TiO₂-Ni Waste Processing Materials 3%, 5%, 7% and 10% and catalyst test
The synthesis of TiO₂-Ni waste processing materials 3%, 5%, 7% and 10% is carried out with the coordination of Associate Expert Nuclear, Work Safety and Radiation Protection Sub-Bid - Field Work Safety and Engineering.

5. Conclusions
From the synthesis activities of TiO₂-Ni Waste Processing Materials 3%, 5%, 7% and 10% which have been completed, the following results are obtained:

Adding NiSO₄ to TiO₂ changes color to green. Physical appearance shows an even mixture with finer grain in all parts of the sample. TiO₂ photocatalyst making by adding variations of Ni dopants has been successfully carried out, with a fairly good success rate. The best addition of Ni dopant to TiO₂ catalyst is the addition of 3% Ni because it can produce crystalline sizes smaller than TiO₂ catalyst so that the success rate gets the highest that is 91.6%. TiO₂ catalysts with variations in the addition of Ni (3%, 5%, 7%, 10%) can be used to treat methylene blue waste by photocatalysis. Regression equation of TiO₂-Ni photocatalyst reaction (3%) to methylene blue waste is \( y = 0.021X + 0.835 \). The reaction rate of processing methylene blue waste with TiO₂-Ni (3%) is 0.021 hours⁻¹. The longer irradiation time of UV rays increases the degradation of methylene Blue.

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