Synthesis, Characterization and Photocatalytic Activity of N-Doped TiO2/Zeolite-NaY for Methylene Blue Removal

Rendy Muhamad Iqbal1*, Indri Susanti2, Rahadian Abdul Rachman3, Tri Agusta Pradana3, Erwin Prasetya Toepak1

1Department of Chemistry, Faculty of Mathematic and Natural Sciences, Universitas Palangka Raya, Kampus UPR Tunjung Nyaho, Palangka Raya 73111, Indonesia
2Department of Science Education, Faculty of Teacher Training and Education, Universitas Islam Lamongan, Kampus UNISLA, Lamongan 62213, Indonesia
3Department of Chemistry, Faculty of Science and Analytical Data, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya 60111, Indonesia

*Corresponding email: iqbal.rm@mipa.upr.ac.id

Received 12 October 2020; Accepted 30 August 2021

ABSTRACT

Dye is an important compound in textile industry. The famous dye for coloring of textile is methylene blue. Methylene blue degradation has been difficult when carried out naturally by microorganisms. The advanced oxidative process is a promising method to degrade methylene blue using semiconductor material TiO2 and its modification. The modification catalyst of TiO2 such as TiO2-N, TiO2/zeolite-NaY and TiO2-N/zeolite-NaY. These materials were synthesized by mixing TiO2 and urea, then followed by impregnation of the mixture to zeolite-NaY as support material. The materials have been synthesized then characterized by XRD, and FTIR. Degradation of methylene blue on the synthesized materials was tested under UV light for 5, 20, 30, 40, and 50 minutes. The results showed that the diffractogram of TiO-N/zeolite-NaY and TiO2/zeolite-Y has a similar specific peak with TiO2 and zeolite-NaY. It indicates that the impregnation process was successfully. TiO2/zeolite-NaY and TiO2-N/zeolite-NaY also showed the excellent activity for degrading methylene blue, which reached up to 99% for 3 hours of reaction.

Keywords: TiO2-N, zeolite-NaY, photocatalyst, advanced oxidative process

INTRODUCTION

Textile waste from industries contain dyes compound with high concentration around 20-30 mg/L. The high concentration of dye has been difficult when carried out naturally by microorganism. It causes many problems in environment and lead to contaminate in water ecosystem [1]. Methylene blue is widely dye which used in textile industries. It is one type of aromatic heterocyclic compound that has positive charge (cation). The limitation of methylene blue in water is 5-10 mg/L [2]. The higher amount of methylene blue in water ecosystem could affect to human activities.

Some methods have been developed to reduce the dye such as physical, biological, and chemical treatment. The example of physical treatment is adsorption process, while biological treatment is utilization of bacteria, fungi as well as biomass, and the chemical treatment is the method using catalyst materials. Konwar et al [3] reported that promising method for dye removal is adsorption by porous materials. However, adsorption has disadvantages such as limited of adsorption capacity, unrepeatable adsorbent, and could release new waste to
environment. Another promising method to reduce of methylene blue as dye is Advanced Oxidative Process (AOP) which known as photocatalytic degradation. Photocatalytic degradation is a process uses semiconductor material to produce OH radical and superoxide anion, then gradually degrade the dye compounds. The advantages of AOP are reusable catalyst, low energy, low cost and possibly to apply using the sun light at low band gap energy catalyst as source of irradiation.

TiO$_2$ is tremendous semiconductor material widely used for photocatalytic degradation. TiO$_2$ of rutile and anatase structure have band gap energy up to 3.0 and 3.2 eV, respectively. Some efforts were conducted by many researchers to improve photocatalytic activity of TiO$_2$ such as supporting TiO$_2$ with porous materials such as zeolite, bentonite, diatomite, etc. The aims of using porous material as support material was to increase surface area of catalyst material. The higher surface area causes the higher catalytic activity. Zeolite was known as excellent porous material which has been many applications such as for adsorbent, ion exchanger, catalyst and raw material for membrane separation. Zeolite has many types which depend on their frameworks. International Zeolite Association (IZA) reported that zeolite have 218 framework [4]. One type of zeolites as a porous material which easily to synthesized is zeolite-NaY. It has 3D dimension structure with pore size of 7.4 Å [5]. In the previous research, zeolite-NaY was modified with MnO$_2$ to be MnO$_2$/Zeolite-NaY composite in order to improve the catalytic performance [6].

One of promising combination material to increase photocatalytic system are TiO$_2$ as semiconductor material and Zeolite-NaY as porous material to be TiO$_2$/Zeolite-NaY composite. This material was synthesized by simply method that is wet impregnation method. However, it causes the material has high band gap energy (3.2 eV) and it could be applied under UV radiation [7]. An alternative method to decrease band gap energy is doping process. Ansari et al [8] was synthesized of N-doped TiO$_2$ (TiO$_2$-N) and the result showed that band gap energy decreased from 3.2 eV to 2.46 eV by the N doping. N-doped TiO$_2$ material was also possibly to apply with sun light. Moreover, Kalantari et al [7] reported that particle size of TiO$_2$ also affected the performance for degradation of dye compound. This research aims to investigate the effect N-doped and zeolite-NaY as support porous material in synthesized TiO$_2$/Zeolite-NaY composite. Photocatalytic degradation of methylene blue with these materials also investigated in this research.

**EXPERIMENT**

**Chemicals and instrumentation**

The materials used in this research for synthesis of zeolite-NaY were sodium aluminate (Sigma-Aldrich), sodium silicate solution, NaOH and DM water. For synthesis TiO$_2$-N using TiO$_2$ anatase, ethanol 98%, and urea.

**Procedure reaction**

**Synthesis of Zeolite-NaY**

Zeolite-NaY was synthesized by refers to Susanti and Widiastuti [9], which includes preparation of:

a. Seed Gel Preparation

Seed gel was prepared by mixing 3.469 NaOH, 1.924 g sodium aluminate, 23.991 g DM water, and 17.518 g sodium silicate. Then, the mixture being closed at ambient temperature for 24 hours.
b. Feedstock Gel Preparation
Feedstock gel was prepared by mixing 0.1 g NaOH, 13.851 g sodium aluminate, 157.518 DM water, and 107.212 g sodium silicate.

c. Overall Gel Preparation
Overall gel was prepared by mixing 16.500 g seed gel with feedstock gel at room temperature for 24 hours. Then hydrothermal reaction at 100°C for 7 hours. Residual and filtrate separated by filtration method and residual washed by DM water until pH < 9. Then zeolite was dried at 100°C for 12 hours.

Synthesis of N-doped TiO\(_2\) (TiO\(_2\)-N)
TiO\(_2\)-N was synthesized by wet impregnation method. 4 g urea as the source of nitrogen dilutes into DM water. Then, 2 g TiO\(_2\) added into urea solution and stirred for 1 hour. The suspension was sonicated for 30 minutes and dried at 100°C for 24 hours. Then the suspension calcined at 400°C for 1 hour with heating rate is 5°C/minutes.

Impregnation TiO\(_2\) or TiO\(_2\)-N into Zeolite-NaY
Both of 1.2 g of TiO\(_2\) and 1.2 g of TiO\(_2\)-N was mixed with zeolite-NaY by added 10 mL ethanol 96% as a dispersant and stirred for 5 hours. TiO\(_2\)/zeolite-NaY and TiO\(_2\)-N/zeolite-NaY then dried at 120°C for 5 hours and calcined at 500°C for 5 hours.

Materials Characterization
The synthesized materials were characterized by XRD to identify of crystal structure, then crystal size was determined by Debye Scherer equation. Rietveld refinement method using to observe microstructure of crystal such as cell parameter, crystal volume, and crystal system. Then, materials was characterized by FTIR to determine of the functional group.

Photocatalytic Activity Test
50 mg variation of catalyst materials (TiO\(_2\), TiO\(_2\)-N, TiO\(_2\)/zeolite-NaY, TiO\(_2\)-N/zeolite-NaY) was added to methylene blue solution in 4 beaker glasses. Then, the methylene blue and catalyst gave UV radiation (UV lamp 8 W) for 3 hours. The concentration of methylene blue measured by spectrophotometer UV-Vis and equation (1) used to determine photodegradation efficiency of methylene blue.

\[
\text{Photodegradation efficiency (%)} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\%
\]  

RESULT AND DISCUSSION

Characterization of catalyst materials
N-doped TiO\(_2\) made by TiO\(_2\) as raw material, nitrogen as doping into TiO\(_2\) has the function to reduce band gap energy and it is possibly to active at visible light [8]. TiO\(_2\) was reacted with urea as a source of nitrogen that has lone pair electron and it formed covalent coordination bonding with the d orbital of titanium. Then, oxygen from TiO\(_2\) made a new bonding with hydrogen from urea to form H\(_2\)O. Then, the calcined process has function to evaporate H\(_2\)O to form TiO\(_2\)-N as the final product [7].

Each materials were characterized by XRD and the result is shown in Fig 1. Zeolite-NaY synthetic has the similar peak with JCPDS of Zeolite-NaY. It exhibits that Zeolite-NaY was successfully synthesized. TiO\(_2\)/zeolite-NaY and TiO\(_2\)-N/zeolite-NaY has the similar peak with TiO\(_2\) (at 2θ = 24.8, 37.3, 47.6, 53.5, 55.1, and 62.2°) and some peaks of zeolite-NaY also appear...
on diffractogram of TiO$_2$/zeolite NaY and TiO$_2$-N/zeolite-NaY. It indicates impregnation of TiO$_2$ or TiO$_2$-N into zeolite-NaY were successfully. Based on diffractogram, N-doping also can not destroy anatase structure due to the diffractogram of TiO$_2$-N represents similar specific peak with TiO$_2$, it only causes the increasing cell parameter due to the presence of nitrogen into interstitial lattice of TiO$_2$ as shown in Table 1. Nevertheless, based on previous research explain that doping process could defected into crystal lattice and N-doped TiO$_2$ expected have greater photocatalytic activity due to smaller distance between valence band and conduction band [7].

**Figure 1.** XRD pattern of catalyst material.

**Table 1.** Crystal structure analysis using Rietveld Refinement.

| Materials          | Cell length a=b (Å) | Cell length c (Å) | Crystal volume (Å$^3$) | α = β = γ (°) | Crystal System |
|--------------------|---------------------|-------------------|------------------------|--------------|---------------|
| TiO$_2$ (AMCSD 0017663) | 3.73                | 9.37              | 130.363                | 90           | Tetragonal    |
| TiO$_2$-N          | 3.78                | 9.51              | 135.88                 | 90           | Tetragonal    |

Rietveld refinement method uses for determine cell parameter, doping process was changed cell parameter of TiO$_2$ lattice, where adding N into TiO$_2$ lattice was increased cell parameter from 3.73 Å (for a=b) to 3.78 Å. The increasing of the cell parameter due to doping process didn't change crystal system of TiO$_2$ (tetragonal). In addition, cell length of c also increases as well as crystal volume of them. It indicates the changing of lattice parameter might to improving performance of photocatalytic activity and promoted to reduce band gap energy due to the presence of N into TiO$_2$ lattice. On other hand, the crystal size of all materials were successfully determine use Debye Scherer equation and the result is shown in Table 2.
Impregnation TiO₂-N (24.31 nm) into zeolite-NaY (48.51 nm) increase crystal size of those material.

**Table 2. Crystal Size of Materials.**

| Materials          | Crystalite Size (nm) |
|--------------------|----------------------|
| Zeolite-NaY        | 48.51                |
| TiO₂-N             | 24.31                |
| TiO₂/Zeolite-NaY   | 48.49                |
| TiO₂-N/Zeolite-NaY | 51.98                |

FTIR spectrum of TiO₂ and TiO₂-N are shown in Fig 2. The broad peak appears around 500-800 cm⁻¹ which exhibit Ti-O and Ti-O-Ti bonding. Another peak appears at 1160, 1274, 1430, 1340, and 1490 cm⁻¹ represent interstitial substitute into TiO₂ lattice, where it can be concluded that N successfully doped into lattice TiO₂ and formed TiO₂-N. It also made N-Ti-O bonding due to substitution oxygen and Ti-O-N obligation by interstitial inclusion [10,11,12,13,14].

FTIR spectrum of zeolite-NaY, TiO₂/zeolite-NaY and TiO₂-N/zeolite-NaY shown in Fig 3. At 3436.91 – 3631.71 cm⁻¹ appear broad peak that represents O-H stretching, besides that it also appears O-H bending at 1637.45 cm⁻¹ [15]. The wavenumbers around 505.31-680.83 cm⁻¹ actually represents characteristic vibration of Ti-N bonding. Stretching asymmetric of T-O-T (T is Al or Si) appear at 1066.56 cm⁻¹. The wavenumber at 680.83 cm⁻¹ exhibit Ti-O stretching vibration and Si-O bending appear at 462.88 cm⁻¹.

![Figure 2. IR spectra of TiO₂ (-), and TiO₂-N (·)](image-url)
Figure 3. IR spectra of zeolite-NaY (-), TiO$_2$/zeolite-NaY (-), and TiO$_2$-N/zeolite-NaY (-)

Evaluation of photocatalytic activity for methylene blue removal

TiO$_2$, TiO$_2$-N, TiO$_2$/zeolite-NaY, and TiO$_2$-N/zeolite-NaY have evaluated their activity to degradation of methylene blue. Fig 4 shows photocatalyst performance for methylene blue degradation.

Figure 4. Photodegradation efficiency of methylene blue with different catalysts.
As shown in Fig 4, the most excellent performance for MB degradation is TiO\textsubscript{2}-N/zeolite-NaY and its followed by TiO\textsubscript{2}/zeolite-NaY, TiO\textsubscript{2}-N, and TiO\textsubscript{2}. TiO\textsubscript{2}-N/zeolite-NaY has high photodegradation efficiency and its value was 99.9947\% during 3 hours of reaction. It causes catalyst material produced the higher amount of hydroxyl radical (•OH) and the larger surface area due to the presence of zeolite-NaY as porous support material which has the greater ability to adsorp and degrade methylene blue\textsuperscript{1}. The illustration of methylene blue degradation is shown in Fig 5. While, TiO\textsubscript{2}/zeolite-NaY and TiO\textsubscript{2}-N/zeolite NaY have a similar photodegradation efficiency, it causes the presence of zeolite NaY which leads to improve the integrated process of adsorption and phocatalytic degradation of methylene blue.

For TiO\textsubscript{2} material, it works under UV radiation due to TiO\textsubscript{2} has higher band gap energy. N doped TiO\textsubscript{2} might reduce band gap energy and improve the performance of their activity. If TiO\textsubscript{2}-N material contacted with photon, it was promote electron movement from valence band to conduction band. Hole in valence band appears due to electron movement, as a consequence neighbor electron move to filled the hole. The movement in valency band was known as vacancy electron. The presence of hole in valence band on catalyst surface lead to form hydroxyl radical (•OH). Meanwhile, the electron in conduction band adsorb to oxygen on catalyst surface and it leads to superoxide anion (O\textsubscript{2}\textsuperscript{-}) formation. Increasing •OH and O\textsubscript{2}\textsuperscript{-} production would increased photodegradation efficiency of MB \textsuperscript{[14],[16],[17].}

CONCLUSION
Modification process was successfully to improve the performance of TiO\textsubscript{2} in advanced oxidation process (AOP). TiO\textsubscript{2}-N/zeolite-NaY has the similar peak with XRD pattern of TiO\textsubscript{2} and zeolite-NaY, then IR spectrum of Ti-N appear at 505.31-680.83 cm\textsuperscript{-1} which can be concluded N doped TiO\textsubscript{2} was successfully synthesized. Based data from photodegradation efficiency shows that TiO\textsubscript{2}-N/zeolite-NaY was excellent material to degradation of methylene blue until 99\% for 3 hours of irradiation.

Figure 5. Illustration of methylene blue degradation.
ACKNOWLEDGMENT
We thank to Ministry Research and Technology-BRIN Republic of Indonesia for research grant under PDP scheme with contract No: 059/SP2H/LT/DRPM/2020 and 189/UN24.13/PL/2020.

REFERENCES
[1] Damayanti, C.A., Wardhani, S. and Purwonugroho, D, Jurnal Ilmu Kimia Universitas Brawijaya, 2014, 1 (1), 8.
[2] Hidayat, W, Teknologi Pengolahan Air Limbah, 2008, Majari Magazine, Jakarta.
[3] Konwar, R.J. and De, M, Int. J. Energy Res, 2015, 39 (2), 223-233.
[4] Fansuri, H., Iryani, A., Shahbihi, W.E., Santoso, E., Hartanto, D. and Iqbal, R.M, MJIAS, 2017, 13 (4), 817-20.
[5] Susanti, I, Science Education and Application Journal, 2019, 1 (1), 10-16.
[6] Endang, P.S., Rahadian, A.R., Ulva, T.I.M., Alvin, R.W., Rendy, M.I. and Nurul, W, Materials Science Forum, 2019, 964, 199-208, Trans Tech Publications Ltd.
[7] Kalantari, K., Kalbasi, M., Sohrabi, M. and Royaee, S.J, Ceram, 2016, 42 (13), 14834-14842.
[8] Ansari, S.A., Khan, M.M., Ansari, M.O. and Cho, M.H, New J Chem, 2016, 40 (4), 3000-3009.
[9] Susanti, I. and Widiastuti, N., MJFAS, 2019, 15 (2), 240-253.
[10] Bao, N., Niu, J.J., Li, Y., Wu, G.L. and Yu, X.H, Environ. Technol, 2013, 34 (21), 2939-2949.
[11] Sakhthivel, S., Janczarek, M. and Kisch, H, J. Phys. Chem. B, 2004, 108 (50), 19384-19387.
[12] Li, H., Hao, Y., Lu, H., Liang, L., Wang, Y., Qiu, J., Shi, X., Wang, Y. and Yao, J, Appl. Surf. Sci, 2015, 344, 112-118.
[13] Yang, G., Jiang, Z., Shi, H., Xiao, T. and Yan, Z, J. Mater. Chem, 2010, 20 (25), 5301-5309.
[14] Wang, H., Gao, X., Duan, G., Yang, X. and Liu, X, J. Environ. Chem. Eng, 2015, 3 (2), 603-608.
[15] Utubira, Y., Wijaya, K., Triyono, T. and Sugiharto, E, Indones. J. Chem, 2006, 6 (3), 231-237.
[16] Zarrabi, M., Entezari, M.H. and Goharshadi, E.K, Rsc Advances, 2015, 5 (44), 34652-34662.
[17] Khalil, M., Iqbal, R.M., Kadja, G.T. and Djuhana, D., Indones. J. Chem., 2020, 3 (3), 117-117.