



PREPARATION OF VISIBLE PHOTOCATALYST N-TiO₂ AND ITS ACTIVITY ON CONGO RED DEGRADATION

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ABSTRACT

TiO₂ photocatalyst is a widely used catalyst because it is inert, non-toxic, and economical. However, the energy gap (bandgap) on TiO₂ is about 3.2 eV which is equivalent to ultraviolet (UV) light at $\lambda = 388$ nm, limiting the application of its photocatalyst only in the UV, but not in the visible region. Whereas, visible light is available in abundance as the sunlight reaching the earth. One approach to improve the efficiency of TiO₂ photocatalytic is by inserting dopants in the crystalline TiO₂ matrix, which has a smaller energy gap and equivalent to the energy of visible light. One of the most promising dopants is nitrogen. The results of material characterization showed that the N-TiO₂ has a smaller energy gap which was equal to 2.6580 eV compared with TiO₂ standard which was equal to 3.2949 eV. The success indication of nitrogen insertion was obtained by the UV-Vis spectrum, infrared absorption peaks, and XRD analysis. The testing of photocatalytic activity by using visible light revealed that the reaction rate constant of N-TiO₂ can degrade congo red dye faster than the TiO₂ standard.

Keywords: N-TiO₂, Photocatalytic, Congo red, UV light, Visible light.

INTRODUCTION

Today, Titanium dioxide (TiO₂) has been a lot of attention almost from all over the world due to its chemical stability properties, non-toxic, economical and many other advantages. TiO₂ is widely used for various applications such as photovoltaic cells, photocatalytic, wastewater treatment, photoinduction hydrophilicity and as a pigment in paint (Ibhadon and Fitzpatrick, 2013).

By regarding to its application in photocatalytic, it is very close relation to the TiO₂ photocatalyst because of its properties (Carp *et al.* 2004). In general, the crystal structure of TiO₂, i.e. anatase and rutile, is often used as a photocatalyst and some studies have put that anatase photoactivity is higher than the rutile (Asahi *et al.* 2000). There are also several other studies claiming that mixing between anatase and rutile phase produces higher efficiency than the original phase.

In a different result, photocatalyst must rely on the intervention effect of several factors such as surface area, crystal size, pore size and method of preparation (Nurdin and Maulidiyah, 2014). In the photocatalytic reaction, TiO₂ can degrade not only the organic components such as hydrocarbons, chlorine components and nitrogen- or sulfur-, but also inorganic components such as nitrogen oxides (NO_x) (Lachhep *et al.* 2002; Nurdin, 2014). Overall, the photocatalytic reactions can be summarized that at first e⁻ and h⁺ generated using photon energy ($h\nu$) which has an energy that is equal to or higher than the energy band gap of TiO₂ (3 to 3.2 eV). Some electrons (E_{cb}⁻) excited from the valence band into the conduction band, so the hole (h⁺) is formed in the valence band and then both of them will move to the surface of TiO₂ for oxidation reduction reaction. The hole in the valence band has a very strong oxidizing properties (+1.0 to +3.5 V relative to the hydrogen electrode Nernst), while the electrons in the conduction band has reducing properties (+0.5 to -1.5V relative to the hydrogen electrode Nernst) (Zhang *et al.* 2009).

On the other hand, e⁻ and h⁺ can recombine in the bulk and at the surface. The recombination process is usually regarded as the deactivation process in the photocatalytic reaction. In most studies of the photocatalytic, oxygen (O₂) has an important role in the primary electron acceptor. Furthermore, the electrons will move to oxygen and then produce H₂O₂ and •OH. Meanwhile, h⁺ reacts with water molecules adsorbed on the surface or surfaces of titanol group (>TiOH) and eventually forms hydroxyl radical (•OH). H₂O₂ contributes to the degradation of the part that acts as an electron acceptor or directly as a source of •OH for cutting homolytic. TiO₂ with anatase structure has the energy gap (bandgap) of about 3.2eV, which is equivalent to UV light with a wavelength of 388 nm so as to limit the catalytic activity that can occur only in the UV and cannot take place in the visible region (Muggli and Ding, 2001; Maulidiyah *et al.* 2015b).

The energy of sunlight that reaches the earth is one of the energy sources that are abundant in the earth's surface. This abundance will be of great benefit if the photocatalyst can be activated by the sunlight. Several research have done a matrix modifying TiO₂ photocatalyst that can be activated by visible light. One modification is by inserting other atoms (dopants) into the TiO₂ crystal matrix in order to make the new catalyst matrix that has small energy gap value equivalent to the energy of visible light. One promising technique is the use of dopant with nitrogen (N), N-TiO₂, showing a significant photocatalytic activity in various types of reaction under visible light region (Ruslan *et al.* 2013).

The use of sol-gel method can produce photocatalyst N-TiO₂ that has activity with visible light irradiation to degrade methylene blue (Gole and Stout, 2004). The same method successfully prepares the N-doped TiO₂ active in the emission of visible light by using dopants from peroxide (Jagadale *et al.* 2008) while conducting the synthesis of N-doped TiO₂ using Titanium



(IV) Chloride precursors NH_3 as a nitrogen sources (Sathish *et al.* 2005).

Various other studies have been conducted with various types of dopants such as C, N, B, and S (Tian-Hua *et al.* 2006; Chen *et al.* 2008). However, dopant with N atom is more interesting than other dopants. This is because the size of the atom is almost the same between N and O atoms, the energy of electro negativity which is almost the same between N and O atoms, the small ionization energy of O atoms and its good stability (Wang and Lewis, 2006).

There are various effective methods effective in the preparation of powders, thin films and membranes layer of TiO_2 or TiO_2 modifications, i.e.: deposition, solvo thermal, sol-gel, micro emulsion, electrochemical, MOCVD (Metal Organic Chemical Vapor Deposition), ion implantation and ball milling method (Jagadale *et al.* 2008). Focusing on the sol-gel method, most of the recent studies typically use this method because compared with other methods, there is a great number of advantages it offers, e.g. in terms of its purity, homogeneity, flexibility, easy stoichiometry controlled, ease of processing, fast, economical, simple, and accurate (Maulidiyah *et al.* 2015a). The synthesis of TiO_2 by using dopant N atom can be obtained by hydrolysis of titanium alk oxides and aliphatic amines (e.g: NH_4Cl , N_2H_4 , NH_4NO_3 , HNO_3^- , or NH_3 as source of N atoms). This paper reports the result of preparation of TiO_2 doped with nitrogen (N- TiO_2), characterization, and initial test of its photocatalyst performance.

MATERIALS AND METHODS

Materials

The materials used in this study were Titanium Tetra Isopropoxide (TTIP) 97% (Aldrich), aquabidest, 31% HCl (Merck), 98% acetone (Merck), 99% ethanol (Merck), acetylacetonate (Merck), sodium nitrate (Merck), acetic acid (Merck), NH_4Cl (Merck), triethylamine (Et_3N) (Merck).

Synthesis of TiO_2 and N- TiO_2 Sol-gel Method

In this research, there were two solutions used. The first solution was in the form of a colloidal solution of TiO_2 prepared by controlled hydrolysis of 4 mL TTIP, 0.5 mL acetylacetonate and 15 mL of 99% ethanol. The second solution was in the form of 15 mL of 99% ethanol and 2 mL aquabidest by adding 1 mL of 0.1 M acetic acid. The solution mixture was refluxed at 50 °C for 180 minutes.

To dope TiO_2 with nitrogen, the same sol was then stirred by the addition of 1 M, 3 M, 5 M NH_4Cl and triethylamine to produce TiO_2 sol containing nitrogen. The same sol solution is made and then heated in an oven at a temperature of 85 °C for 30 minutes and calcined at a temperature of 450 °C for 2 hours to produce powder TiO_2 and N- TiO_2 .

Preparation of Inner Wall Glass Tube (IWGT)

The glass tube which has been prepared then was immobilized with sol TiO_2 and N- TiO_2 by coating IWGT for 10 minutes with dip coating technique. Then, the tube was heated in an oven at a temperature of 80 °C for 30 minutes and calcined at a temperature of 450 °C for 2 hours to get anatase crystal. In order to get a whole thin coat on the tube wall surface, the process was repeated five times. This preparation was used for photocatalytic activity test.

Characterization of Catalyst TiO_2 and N- TiO_2

The energy gap of catalyst TiO_2 and N- TiO_2 were characterized using UV-V is spectrophotometer. The measurement with FTIR aimed to know the form of indication of Ti and nitrogen. The measurement with XRD aimed to know the structure and crystalline size of TiO_2 .

Photocatalytic Activity

The congo red solution of 4 mL with a concentration of 5 ppm was placed in a tube IWGT that has been coated with sol TiO_2 and N- TiO_2 with treatment:

- Using TiO_2 with UV irradiation
- Using N- TiO_2 with UV irradiation
- Using TiO_2 with visible light irradiation
- Using N- TiO_2 with visible light irradiation

The sample solution was measured by UV-V is spectrophotometer at 10, 20, 30, 40, 50, 60 minutes.

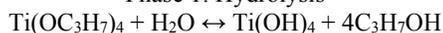
RESULTS AND DISCUSSIONS

Synthesis of TiO_2 and N- TiO_2

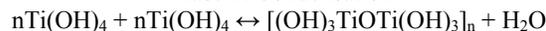
In this study, TiO_2 and N- TiO_2 were synthesized by using sol-gel method. The sol-gel process has several advantages compared with other techniques such as easily controlled by reaction conditions, pH, temperature and the rate of hydrolysis. The precursor compounds were dissolved in an organic solvent to form sol, then for the preparation of N-doped TiO_2 with addition of nitrogen sources were then hydrolysed slowly to obtain a gel, and calcined to remove the solvent. The gel was formed when the precursor molecules polymerized to form chains that were cross linked at some point and become a macromolecule to the solvent trapped.

The precursor compound used in this study was TTIP, which was proposed a series of reactions as follows:

Phase 1: Hydrolysis



Phase 2: Condensation



As the first step in this research, TTIP mixed with acetylacetonate (AcAc) was added with ethanol, water and acetic acid (CH_3COOH) slowly. In this study, sol given pH 3 was based on the previous research which states that the TiO_2 synthesis process by using a pH 3 has a small band gap that is 3.20 eV. AcAc acts as a chelating agent that would produce an exothermic reaction and become yellow



solution. In previous studies, using instrumentation ^1H and ^{13}C -NMR and IR spectrophotometer indicates that AcAc is not free but bound with titanium (Valentin *et al.* 2007). The structure is as follows.

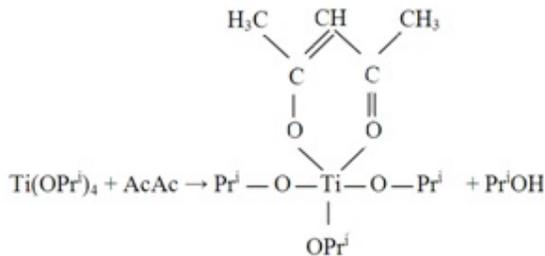


Figure-1. TTIP Structure modified of AcAc.

Whereas to dope with nitrogen, the sol formed was added NH_4Cl as a source of nitrogen atoms which aims to reduce the energy gap (bandgap), in which the nitrogen atom would replace some of the positions of oxygen atoms in these TiO_2 semiconductor.

The formed sol-gel was heated in an oven at a temperature of 85°C for 30 minutes. The heating process was applied to evaporate the water trapped in the gel. Furthermore, it was calcined at 450°C for 2 hours. Calcination is required to evaporate the trapped solvent in the gelopolymer. Calcination is also required to obtain crystals of anatase TiO_2 because the crystals photo degradation activity is better than the other types of crystals. To obtain anatase crystals, calcination can be done at a temperature of $300\text{--}500^\circ\text{C}$ (Shifu *et al.*, 2005).

The study provides the properties of the synthesized photocatalyst and the doping N influence on the photocatalytic activity on congo red degradation. This work will help for developing modified TiO_2 photocatalyst to operate efficiently under visible light.

Characterization of the UV-Vis Diffuse Reflectance Spectrometry

Diffuse Reflectance measurements with UV-Vis spectrometer aims to determine the character of absorption at long area of both UV and Visible wavelength (200-800nm). In Figure 2 it can be observed that for TiO_2 and N- TiO_2 with variations in dopant concentration addition has different reflectance spectrum profile. There reflectance spectrum profile clearly shows that the N- TiO_2 has the absorption of visible light region ($\lambda > 400\text{nm}$).

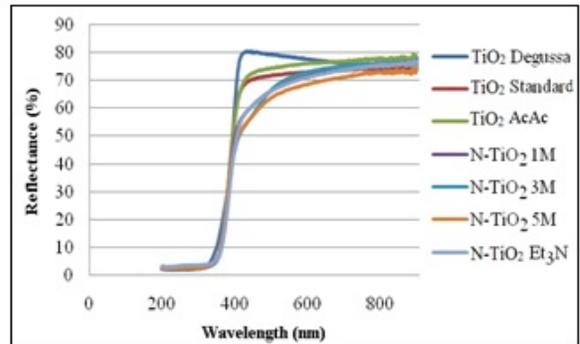


Figure-2. Spectrum Diffuse Reflectance TiO_2 and N- TiO_2 (% reflectance vs. wavelength).

Based on the obtained spectrum, the energy gap is determined by using the equation:

$$F(R) = \frac{K}{S} = \frac{(1-R)^2}{2R} \quad (1)$$

where is:

- F(R) = factor of Kubelka-Munk
- K = coefficient of absorption
- S = coefficient of scattering
- R = reflectance value measured

$$F(R) = A(h\nu - E_g)^{m/2} \quad (2)$$

Where is:

- A = constant proportional
- E_g = energy gap
- m = 1 for the direct transition

By plotting $F(R)$ against $h\nu$ and extra plotting the line a region it can be determined $h\nu$ value in $F(R) = 0$, which is none other than the value of the energy gap of the absorbing species. With this approach the energy gap of TiO_2 and N- TiO_2 thin layer was determined.

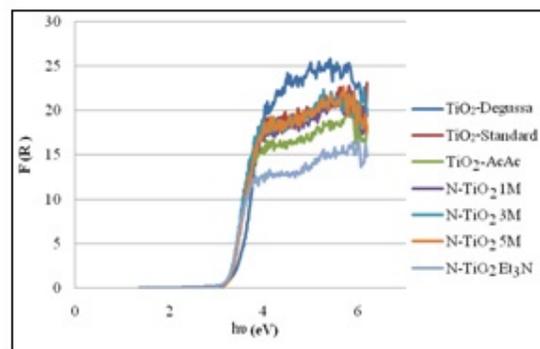


Figure-3. Spectrum of Diffuse Reflectance TiO_2 and N- TiO_2 (% reflectance vs. Wave length).

**Table-1.** Band Gap Value of TiO₂ and N-TiO₂.

Sample	Band Gap (eV)
TiO ₂ degussa	3.3177
TiO ₂ standard	3.2949
TiO ₂ -AcAc	3.2865
N-TiO ₂ 1M	3.2807
N-TiO ₂ 3M	3.2616
N-TiO ₂ 5M	3.2031
N-TiO ₂ Et ₃ N	2.6580

Table-1 shows that the value of the band gap of TiO₂ degussa, TiO₂ standard and TiO₂ doped with nitrogen dopant concentration variations have different values, where TiO₂ doped with nitrogen has smaller band gap energy value than the TiO₂ degussa and TiO₂ standard. With the decline in the value of the band gap, the high energy of light is needed for obtaining photo hole (conduction band) and photo electron (valence band) by using visible light source. Moreover, it can also be seen that the addition of Et₃N as a nitrogen source to prepare N-TiO₂ resulted the optimum value of the band gap which was obtained on N-TiO₂-Et₃N.

Characterization by Fourier Transform Infra Red (FTIR)

The measurements with FTIR aimed to identify the presence indication of bond formation between Ti with nitrogen as a resulted effect of adding nitrogen dopant on TiO₂.

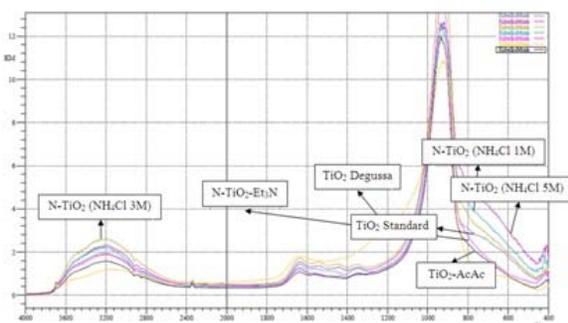
**Figure-4.** FTIR spectra of TiO₂ and N-TiO₂.

Figure-4 shows the absorption peaks in the area of the wave number 400-1250 cm⁻¹ which is the characteristic of the bond O-Ti-O (Shifu *et al.*, 2005) while the peak at wave number region 1625-1650 cm⁻¹ is the peak related to OH bending vibrations from the water that is still trapped in the crystal structure of TiO₂, or titanol group. Moreover, it can also be observed that the absorption peak profile resulting from the synthesis of TiO₂ is similar to the profile of the TiO₂ degussa, while the absorption peak profile of the N-TiO₂ showed similar absorption area but it was not the same with that profile.

To identify the presence of N-TiO₂ obtained by comparing the absorption peak profiles are formed, where

the measurement of N-TiO₂ variations with addition of dopant concentration changes the characteristic of peak absorption than TiO₂ standard and TiO₂ Degussa profiles. The analytical signal shift may indicate the formation of a bond other than O-Ti-O, which is expected because of the presence of N-TiO₂.

Characterization by X-Ray Diffraction (XRD)

The characterization by means of XRD was performed to obtain information crystal structure of TiO₂ and N-TiO₂ synthesis results. The materials of TiO₂ and N-TiO₂ that analyzed were the result of calcinations coated on glass substrates.

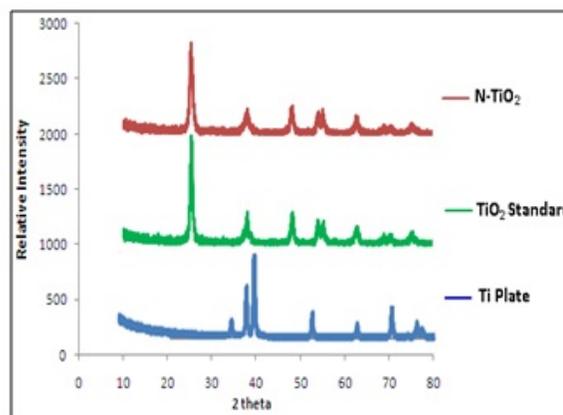
**Figure-5.** XRD diffractogram of TiO₂ photocatalyst and N-TiO₂.

Figure-5 is an XRD analysis of TiO₂ and N-TiO₂ synthesis. In the spectrum, it can be seen that the peaks can provide the identity of the crystalline form of TiO₂ and N-TiO₂. The crystal form can be determined by comparing the value of 2θ or d (Å) and the results of measurements with data interpretation card of TiO₂ crystal that can be seen in Table-2.

Table-2. The value of d(Å) measurement and interpretation of the data card TiO₂ crystal.

Interpretation of data card d(Å)		Measurement of d(Å) synthesis result		Note
Anatase	Rutile	TiO ₂	N-TiO ₂	
3.52	3.24	3.506	3.531	Anatase
2.378	2.487	2.375	2.375	Anatase
1.892	2.188	1.891	1.890	Anatase
1.699	2.054	1.700	1.704	Anatase
1.666	1.687	1.666	1.668	Anatase
1.481	1.623	1.478	1.481	Anatase
1.364	1.479	1.363		Anatase
1.338	1.359	1.336	1.337	Anatase
1.265	1.346	1.265	1.264	Anatase

The XRD measurement results for TiO₂ catalysts shows nine peaks while the N-TiO₂ only shows eight peaks, which when compared with the data card



interpretation, it shows that TiO₂ and N-TiO₂ synthesized an anatase crystal line structure. Through the obtained diffractogram peak and with the help of Scherrer equation, it can be calculated that the crystallite size of TiO₂ and N-TiO₂ were 13.5532 nm and 11.2267 nm, respectively.

Photocatalytic Activity

This study focused on comparing the activity of TiO₂ and N-TiO₂ in both UV and visible light on the timing and amount of the same catalyst. The test substance used is the congo red dye, while TiO₂ and N-TiO₂ catalyst were used for photocatalytic activity test on congo red solution.

In principle, the photocatalytic will degrade the organic matter to CO₂ and H₂O (Moon,2000; Khan *et al.*, 2002). The process of degradation of congo red dye can be observed from the decrease in the maximum absorbance value of congo red that can be seen in the Figure-6.

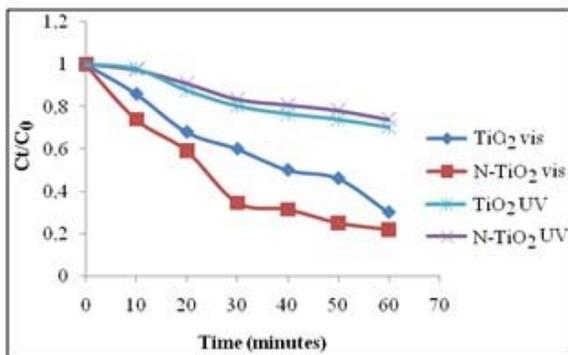


Figure-6. Degradation of 5 ppm congo red curve on TiO₂ and N-TiO₂ by using UV and visible light sources.

Table-3. Percent of congo red remaining.

Time (minutes)	The remaining% of congo red			
	TiO ₂ UV	N-TiO ₂ UV	TiO ₂ Visible	N-TiO ₂ Visible
0	100	100	100	100
10	86.00	73.94	97.34	97.87
20	68.00	59.04	90.96	87.77
30	59.99	34.57	83.51	80.32
40	50.00	31.38	80.85	76.60
50	46.00	25.00	78.19	73.93
60	30.00	21.81	73.94	70.21

From Figure-6 and Table-3, these can be observed that the decrease in the relative concentrations of the N-TiO₂ is greater than the TiO₂, which means that the N-TiO₂ can degrade congo red more than TiO₂ in the same time in the UV and visible light source. The data obtained, indicated that the N-TiO₂ catalysts are more active than TiO₂ catalyst to degrade congo red.

Reaction Kinetics of photo catalytic degradation of congo red

The congo red degradation rate constant can be determined by using the Langmuir-Hinshelwood kinetic equation.

$$r = \frac{dC}{dt} = kr\theta = \frac{krKCo}{(1 + KCo)} \tag{3}$$

Where:

dC / dt = rate of degradation of congo red

kr = reaction rate constant

θ = fraction of the catalyst by the reactants scoping

K = constant absorption of reactants

Co = initial concentration of congo red

If it is integrated with equation becomes:

$$\ln \frac{Co}{C} + \frac{k(Co - C)}{1 + KsCs} = \frac{krKt}{1 + KsCs} \tag{4}$$

$$\ln \frac{Co}{C} + k(Co - C) = kt \tag{5}$$

If the initial concentration (Co) has a very low value (Co <<1), the equation will follow the first-order rate equation:

$$\ln \frac{Co}{C} + k = k' t \tag{6}$$

The plot of Ln Co/Ct of impact irradiation time (t) yield curve is a straight line with slope k', as shown in Figure-7.

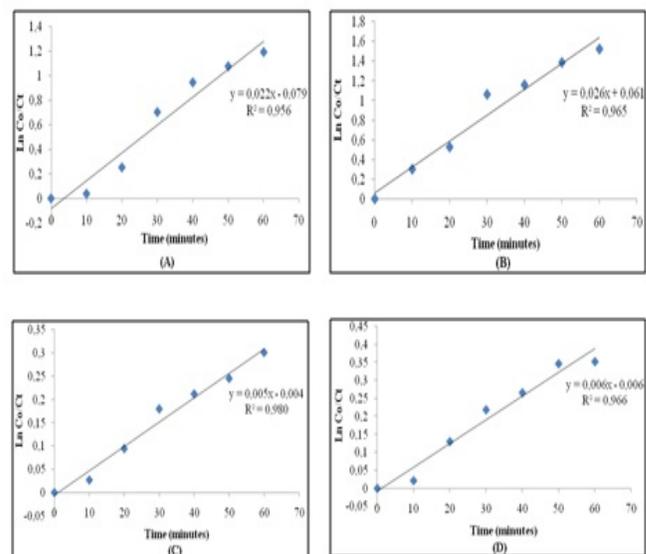


Figure-7. Kinetics of first order of 5 ppm congo red in (a) TiO₂UV, (b) N-TiO₂UV,(c) TiO₂Visible, and(d) N-TiO₂Visible.



Table-4 shows that the reaction rate constant for the N-TiO₂ is greater than the TiO₂ in the UV and visible source, which indicated that N-TiO₂ is more active than TiO₂ catalyst.

Table-4. Reaction rate constant for degradation of congo red.

Variable	k' (ppm/minute)
congo red + TiO ₂ + UV	0,018
congo red + N-TiO ₂ + UV	0,026
congo red + TiO ₂ + Visible	0.006
congo red + N-TiO ₂ + Visible	0.005

From the Table-4, it can also be seen that the reaction rate constant for congo red by using a UV light source is greater than that using a visible light source where the difference is very small. The rate constant comparison of TiO₂ and N-TiO₂ in the visible light are 0.006 ppm/minutes and 0.005 ppm/minutes, respectively.

CONCLUSIONS

The conclusions of this research are as follows: The synthesis of TiO₂ and N-TiO₂ were made by sol-gel method, in which the titaniumisopropoxide as the precursor of TiO₂ and Et₃N as the nitrogen source.

The measurement by UV-Vis spectrometer known that the lowest band gap of N-TiO₂ (2.6580eV) is smaller than the TiO₂ synthesis (3.2949 eV). The photocatalytic activity by using visible light indicated that the reaction rate constant of N-TiO₂ can degrade congo red dye faster than the TiO₂ standard.

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