

Tempe Waste Water Degradation Using TiO₂-N/Bentonite alginate Granule Photocatalyst with Ultraviolet Light Irradiation

Aldila Khoirun Nisaa¹,¹ Sri Wardhani,^{1*} Danar Purwonugroho,¹ Darjito¹

¹Chemistry Department, University of Brawijaya, Malang, Indonesia

Email: wardhani@ub.ac.id

Abstract. Tempe waste water stew has high ammonia concentration which causes odor due to polluting by anaerobic decay. Free ammonia in the waste has exceeded the limit, thus endangering the aquatic environment. This research aims to determine the activity of photocatalyst granule TiO₂-N/bentonite-alginate as decomposers of compounds in the photodegradation process. Photodegradation is the decomposition process of compounds by semiconductors with light. Results expected includes the photocatalyst activity of TiO₂-N/bentonite-alginate granule produced by ultraviolet rays is known based on the effect of dopant N concentration on the catalyst and the effect of photocatalytic ratio toward tempe waste water. Methods proposed in this research are activation of bentonite using H₂SO₄ 0.8 M, TiO₂-N synthesize by sonication method with urea as the source of N, then TiO₂-N impregnation into bentonite. Photocatalyst in granule form synthesized with alginate was then dripped with syringe pump into 3% (w/v) CaCl₂. The photocatalyst characterization will be performed using XRD. The optimum tempe waste water degradation at the concentration of TiO₂-N 0.4 (g/g) bentonite is 53.66%. The ratio of photocatalyst and tempe waste water, optimum at 150 mg of photocatalyst with 25 mL of waste equal to 53.66%.

Keyword: photodegradation, photocatalyst, tempe waste water, TiO₂-N/bentonite-alginate

1. Introduction

Soybean consumption in Indonesia is 50% for tempe production, 40% of tofu production, and 10% in other products such as tauco, soy sauce, and others. Currently, average tempe consumption every person per year in Indonesia is estimated to reach about 6.45 kg [1]. One potential alternative method for simultaneously processing organic wastes is photocatalytic photodegradation [2]. Photodegradation is the process of decomposing organic compounds into simpler compounds making them safer for the environment. The decomposition uses the aid of photon energy [3]. Photocatalytic reactions require active catalysts when exposed to light [4]. One of the catalysts that can be active under the sun is TiO₂. TiO₂ has a band gap energy (E_g = 3.2 eV) which can be activated by UV light from UV lamps [7].

The dopant element will form a new catalyst matrix with a smaller gap energy and the equivalent of visible light energy. TiO₂ has a weak adsorption power in degrading the target compound. The dispersed TiO₂ properties in each part of the solution cause the contact of TiO₂ with less than optimal pollutant. TiO₂ can be modified by expanding on a mineral having a high adsorption capacity so that the semiconductor adsorption power is increased [5]. The widely used carrier is bentonite because bentonite is a silica-alumina that has a large pore and surface area, can absorb both organic and inorganic substances, as a catalyst for various reactions, and as a cation exchange [6].



Photocatalyst TiO_2 can be made with a granular form to facilitate the photodegradation process. This is because when the photocatalyst is in the form of a spherical bead, the photocatalyst does not mix with the waste that causes the formation of suspension during the photodegradation process. Making granules is need and can be done with the addition of alginate.

Based on the above background, this study aims to determine the effect of TiO_2 -N concentration on TiO_2 -N/bentonite-alginate, the ratio of TiO_2 -N/bentonite-alginate granule to tempe waste water, and the effect of degradation on the long-exposure of TiO_2 -N/bentonite-alginate with ultraviolet light

2. Procedures

2.1. Preparation of Activated Bentonite

Bentonite was grinded with a porcelain mortar and sieved with a size of 200 mesh. The bentonite solid that passes on the 200 mesh sieve is used for further research. The resultant bentonite was weighed 50 g, soaked with 500 mL of H_2SO_4 0.8 M in erlenmeyer 1000 mL and covered with aluminum foil, then shook at 9 rpm for 3 h. The soaking samples were washed with distilled water until SO_4^{2-} free. This can be known by the universal pH that shows the pH according to the aquadest. The samples were dried in an oven at a temperature of 110 °C for 2 h and then the bentonite solution was calcined 5 h at a temperature of 500 °C.

2.2. Preparation of Photocatalyst TiO_2 -N

Preparation of TiO_2 -N was made with a mole ratio of (20:3) by mixing 2.4 g of TiO_2 , 0.27 g of urea and 5 mL of aquademineralization in erlenmeyer, then the mixture was sonificated for 30 minutes and heated over hot plate heaters until the evaporated. Subsequently the suspension was transferred in the oven at 110 °C and calcined at a temperature of 300 °C for 2 h.

2.3. Development of TiO_2 -N in Bentonite

Preparation of TiO_2 -N impregnated on bentonite was done by mixing TiO_2 -N variations 0.9; 1.2; 1.5; and 1.8 g with 3 g of activated bentonite and 10 mL of 96 % ethanol in 50 mL beaker, then stirred with magnetic stirrer for 5 h. The formed TiO_2 -N/bentonite was dried in an oven at 120 °C for 5 h. And then it was calcined at 500 °C for 5 h.

2.4. Synthesis of TiO_2 -N/bentonite-alginate granule

The TiO_2 -N/bentonite photocatalyst is impregnated with sodium alginate gel to prepare granular-shaped adsorbents in a calcium chloride solution. 5 g of sodium alginate was dissolved in 200 mL of distilled water, stirred using a magnetic stirrer while heated at 40 °C to form a gel phase. TiO_2 -N/ bentonite of 20 g is mashed using the mortar and then mixed into the alginate gel. The suspension then injected into 3% (w/v) calcium chloride solution with syringe 50 mL/h. Complex granules TiO_2 -N/bentonit-alginate that was formed, then separated and dried at 70 °C for 3 h.

2.5. Effect of TiO_2 -N Concentration on TiO_2 -N/bentonite-alginate Photocatalyst

A total of 25 mL of tempe waste water was prepared in 4 cups, each added a photocatalyst contained 3 g of bentonite and TiO_2 -N of 0.9; 1.2; 1.5; and 1.8 g. Then illuminated with sunlight and UV for 5 h. Measurement of COD value was done on tempe waste water before degradation for 5 h. The photodegradation process was conducted twice.

2.6. Effect of TiO_2 -N/bentonite-alginate Photocatalyst Ratios and Tempe Liquid Waste Industries Against Liquid Waste Degradation of Tempe Industry

The concentration of TiO_2 -N in the TiO_2 -N/bentonite-alginate photocatalyst provides the highest reduction in COD values used to degrade tempe waste water with the ratio between the mass of the photocatalyst and the volume of the liquid waste. Mass ratio photocatalyst with volume of tempe waste water is 4:1 (100 mg photocatalyst:25 mL tempe waste); 2:1 (100 mg photocatalyst:50 mL of tempe waste); 3:1 (150 mg photocatalyst:50 mL of tempe waste); and 6:1 (150 mg photocatalyst:25 mL of

tempe waste); as well as done twice. The COD degradation of the waste in a variety of ratio was measured.

2.7. Test of Chemical Oxygen Demand

The degraded tempe waste water was diluted 1 mL in 250 mL, then 25 mL plated was added to the Erlenmeyer, and added HgSO 40.5 g and 5 mL concentrated H₂SO₄ are also mixed. Next, the solution plus K₂Cr₂O₇ as much as 25 mL was added. Erlenmeyer containing the mixture of the solution is arranged in the reflux apparatus with the condenser using water flows. Then the solution in the erlenmeyer was added with concentrated H₂SO₄ of 32.5 mL through the condenser and rinsed with a small amount of distilled water. The solution was refluxed for an hour at a temperature of 265 °C. The reflux solution is awaited to cooldown and followed by adding 5 drops of Ferriin indicator. The solution was then subjected to a solution of FAS and recorded titration volume. Titration and reflux were performed twice. The COD test was carried out for the test results of the tempe wastewater activity of the tempe industry treated by the variation of the concentration of TiO₂-N on TiO₂-N/bentonite-alginate photocatalyst and the mass ratio of TiO₂-N/bentonite-alginate photocatalyst and the volume of tempe waste.

3. Result

3.1. Various types of photocatalyst activity

In the various types of photocatalyst activity three tempe waste water treated, the first without additional photocatalyst, the second tempe waste water with TiO₂-N/bentonite powder photocatalyst, and the third tempe waste water with TiO₂-N/bentonite-alginate granule photocatalyst.

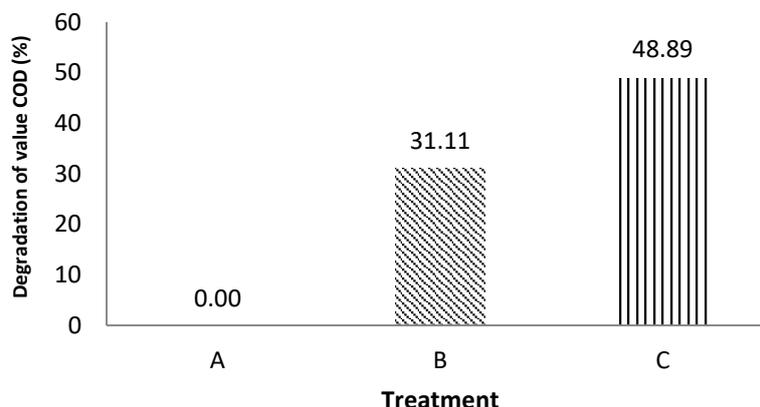


Figure 1. Relation of various type of photocatalyst with tempe waste water degradation

A: tempe waste water without photocatalyst

B: tempe waste water with TiO₂-N/bentonite powder photocatalyst

C : tempe waste water with TiO₂-N/bentonite-alginate granule

Activity test was conducted to determine the effectiveness of photocatalyst form in decreasing the COD value of tempe waste water. The volume of the tempe waste water has used 25 mL of filtered to reduce sediment and photocatalyst weighing 0.15 g. Irradiation did for 5 h. In the test results can be seen in Figure 1, the addition of photocatalysts gives the effect of the COD value of tempe waste water. Tempe waste water without the addition of photocatalyst did not decrease the COD value, the addition of TiO₂-N/bentonite powder photocatalyst gave a decrease of 31.11% the COD value, while the addition of TiO₂-N/bentonite-alginate granule photocatalyst showed a 48.89% decrease for the the COD value. The photocatalyst shape affects the photodegradation process. Photocatalyst in the form of granule works better than powder form. This is because ultraviolet light cannot affect the photocatalyst particles evenly so that the photodegradation process does not run optimally. In addition, photocatalyst in powder form can only photodegradation process.

Photocatalyst added to absorb the energies of photons from ultraviolet light. The addition of N dopant can decrease the energy of the TiO_2 catalyst band gap so that it can absorb more photon energy to produce hydroxyl radicals. The small band gap energy absorbs the energy of ultraviolet light photons larger [8]. TiO_2 when exposed to ultraviolet light will produce electrons (e^-) in the conduction band and hole (h^+) in the valence band. Hole when reacting with H_2O produces a radical $\cdot\text{OH}$ that can degrade organic substances. The inclusion of bentonite causes the photocatalyst to have multiple capabilities, in addition to being able to degrade also as an adsorbent.

3.2. Effect of TiO_2 -N Concentration on TiO_2 -N/bentonite-alginate Photocatalyst

The concentration of catalyst applied to the carrier was varied to four, ie 0.9; 1.2; 1.5; and 1.8 gr into 3 gr of bentonite.

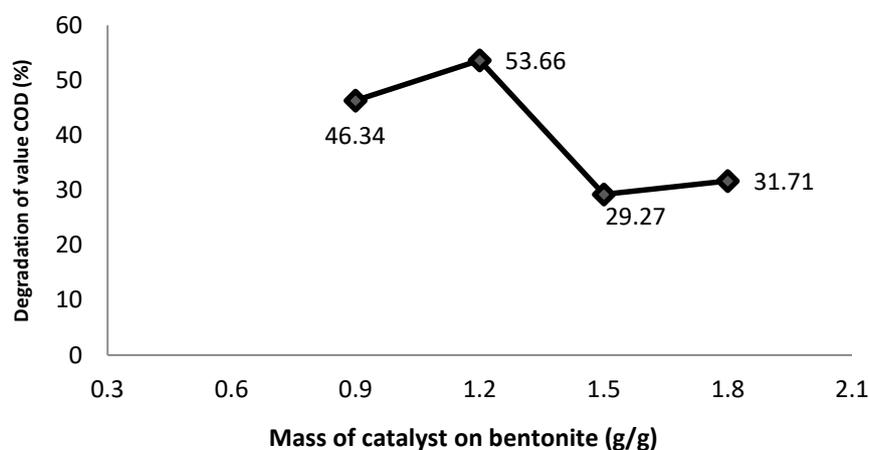


Figure 2. Relation of mass of photocatalyst with tempe waste water degradation

Based on Figure 2 shows the effect of TiO_2 -N concentration on the degradation of tempe waste water. The addition of TiO_2 -N in photocatalysts can increase the degradation of tempe waste water, with an optimum value of TiO_2 -N 1.2 g degrading to 53.66%. In addition, 0.9 g of degradation reached 46.34%, 1.2 g decreased by 29.27% degradation, while 1.8 g of degradation increased to 31.71%. The addition of TiO_2 -N as a catalyst affects tempe waste water degradation, since the number of catalysts will have an impact on photodegradation.

The optimum concentration of TiO_2 -N in per gram bentonite is 0.4 gr. This happen because the addition of excess TiO_2 -N will reduce the adsorption capacity of the photocatalyst, so the adsorption process will decrease. Photocatalysts that have a balanced adsorption and photocatalytic ability provide better degradation results than photocatalysts with only one process. The composition between the catalyst and the carrier shall be suitable for obtaining an optimum photocatalyst [9]. In addition, excess TiO_2 -N in the photocatalyst will cover the pores of the adsorbent so that the photocatalyst surface area will shrink and decrease the photocatalyst activity [10].

3.3. Effect of TiO_2 -N/bentonite-alginate Photocatalyst Ratios and Tempe Liquid Waste Industries Against Liquid Waste Degradation of Tempe Industry

The ratio of photocatalyst and tempe waste water was used two variations. The first variation of tempe waste water volume is 25 and 50 mL. Variations in both photocatalyst mass of 100 and 150 mg. Based on Figure 3 shows the ratio of the mass of photocatalyst and tempe waste water volume to degradation which gives the different result on the parameters of photocatalyst and tempe waste water volume. The tempe waste water volume parameters use 25 mL and 50 mL, while the photocatalyst mass parameters use 100 mg and 150 mg. At 25 mL volume, 100 mg photocatalysts degrade 39.02%, while the 150 mg mass was able to degrade up to 53.66%. Volume 50 mL, 100 mg photocatalyst mass degrades 43.90%, for 150 mg photocatalyst mass degrades 48.78%.

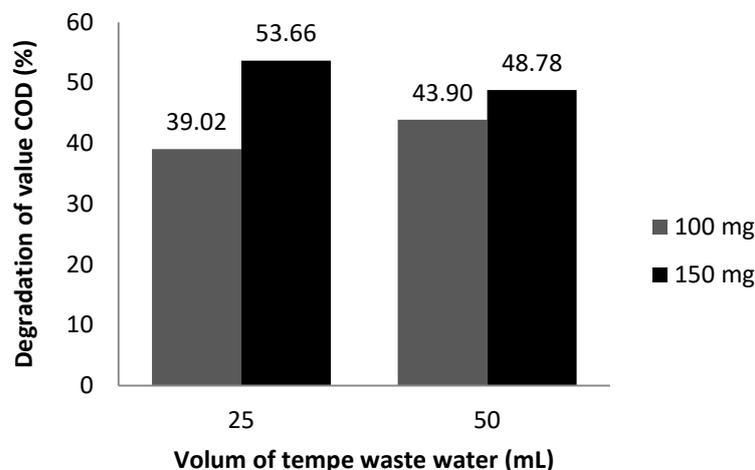


Figure 3. Relation of ratio of photocatalyst mass and with tempe waste water degradation

The optimum degradation of each volume at photocatalyst mass 150 mg, optimum degradation value 53.66% with ratio 150 mg photocatalyst and 25 mL tempe waste water volume. The addition of an increasingly high photocatalyst at low tempe waste water volume will provide the best degradation. This is because the higher number of photocatalysts will decompose and optimally adsorb the organic substances in tempe waste water volume. Ultraviolet light will affect and activate photocatalyst that are based glass at low volume so that photodegradation runs optimum. The amount of photocatalyst used is quite large, 150 mg per 25 mL. It is expected that more photocatalyst, degradation and adsorption process run better so that tempe waste water discharged into the waters will not pollute the environment.

3.4. X-Ray Diffraction Characterization

The photocatalyst characterization was performed using XRD spectrophotometer to determine the photocatalyst crystallinity. In addition, to find out the N dopant added to the photocatalyst. Characterization results were analyzed by comparison with JCPDS (Journal Committee of Powder Diffraction Standard) characterization for TiO_2 and bentonite. Characterization was performed on natural bentonite, activated bentonite, TiO_2 , $\text{TiO}_2\text{-N}$, and $\text{TiO}_2\text{-N/Bentonite}$.

Natural bentonite and activated bentonite were characterized to determine the effect of the activation process on the bentonite crystal structure. The characterization results shown in Figure 4, there is no change in the bentonite crystal structure, but there are changes in some peaks. Activated bentonite showed an increase in intensity at some peaks compared to natural bentonite. This is because the activation process has removed the free oxide impurities but did not alter the bentonite structure. Thus the crystal structure is more dominant and the adsorption capacity of bentonite increases.

Characterization of TiO_2 and $\text{TiO}_2\text{-N}$ was performed to determine the dominant phase in TiO_2 used and the effect of N dopant on $\text{TiO}_2\text{-N}$. Diffractogram showed different results for TiO_2 and $\text{TiO}_2\text{-N}$ at peak height and 2θ , as in Figure 5. Based on the comparison of 2θ samples of TiO_2 with JCPDS TiO_2 anatase in Table 1, there are several similarities of properties, so the TiO_2 crystals are anatase. Some peaks that have high intensity on the TiO_2 decrease and the 2θ per value shift becomes greater in $\text{TiO}_2\text{-N}$. This is due to the presence of an N dopant which replaces the position of the O atom on the TiO_2 bond.

$\text{TiO}_2\text{-N}$ is impregnated with activated bentonite, the success of impregnation can be known by XRD characterization. Figure 6 is a $\text{TiO}_2\text{-N}$ diffractogram, bentonite after activation, and $\text{TiO}_2\text{-N/bentonite}$. The $\text{TiO}_2\text{-N/bentonite}$ diffractogram is a combination of the diffraction patterns of $\text{TiO}_2\text{-N}$ and bentonite. Some of the peaks of $\text{TiO}_2\text{-N}$ and bentonite diffractogram were changed in the $\text{TiO}_2\text{-N/bentonite}$ diffractogram showing the lattice changes due to the impregnation process. The shift of the 2θ value and the peak change of the diffractogram are shown in Table 2.

Table 1. The 2 θ value of TiO₂ diffractogram

JCPDS of TiO ₂ rutil No. 00-021-1276		Sample of TiO ₂		JCPDS of TiO ₂ anastase No. 00-021-1272	
2 θ	Int (%)	2 θ	Int (%)	2 θ	Int (%)
		25.3143	35.25	25.281	100
27,477	100	27,4991	17.86	-	-
-	-	29,4360	100	-	-
36,086	50	36,1064	13.26	-	-
-	-	36,9502	1.64	36,947	10
-	-	37,8186	7.36	37,801	20
-	-	38,5818	2.04	38,576	10
41,226	25	41,2607	3.46	-	-
-	-	48,050	10.42	48,050	35
-	-	53,9306	6.01	53,891	20
54,323	60	54,3252	10.43	-	-
-	-	55,0573	5.11	55,062	20
56,642	20	56,6369	4.21	-	-
-	-	-	-	62,690	14
69,010	20	-	-	-	-
-	-	-	-	75,032	10

Table 2. The 2 θ value of photocatalyst diffractogram

TiO ₂		TiO ₂ -N		Bentonite		TiO ₂ -N/Bentonite		Phase
2 θ	Int (%)	2 θ	Int (%)	2 θ	Int (%)	2 θ	Int (%)	
-	-	-	-	22.2796	100	-	-	Montmorillonite
25.3143	35.25	25.4316	78.10	-	-	25.5434	70.11	Anatase
-	-	-	-	26.9632	61.70	-	-	Montmorillonite
27,4991	17.86	27,5839	23.33	-	-	27,6563	30.66	Anatase
29,4360	100	29,5833	100	-	-	29,6202	100	Anasase
36,1064	13.26	36,1405	18.45	36,3805	31.92	36,2187	31.23	Montmorillonite
37,8186	7.36	37,9470	18.84	-	-	37,9869	14.65	Anatase
48,050	10.42	48,1315	26.04	-	-	48,2130	15.03	Anatase
-	-	-	-	51,0653	16.75	-	-	Montmorillonite
54,3252	10.43	54,4227	17.22	-	-	54,5028	14.29	Anatase
55,0573	5.11	55,1444	15.76	-	-	55,2999	9.19	Anatase

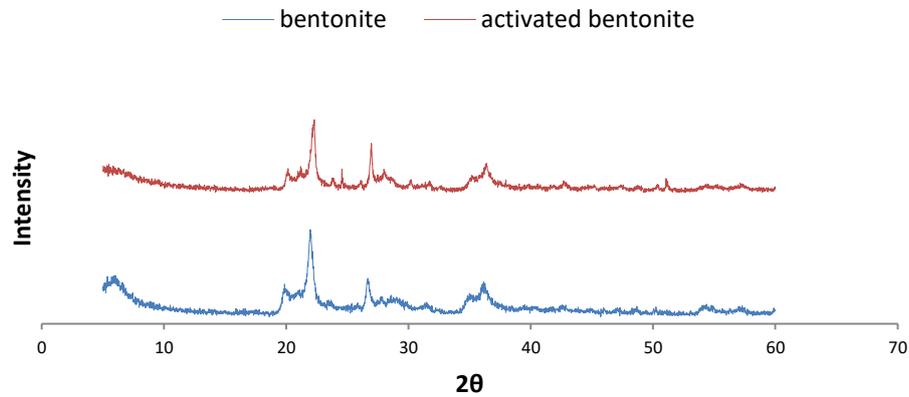


Figure 4. Diffractogram of Bentonite

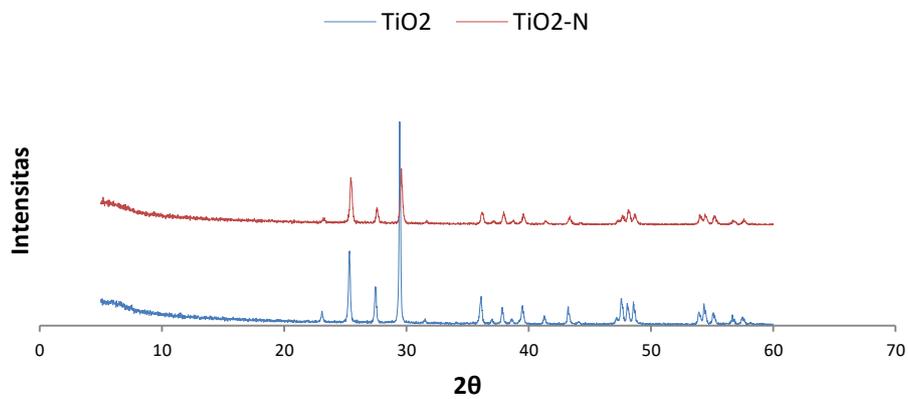


Figure 5. Diffractogram of TiO_2 and $\text{TiO}_2\text{-N}$

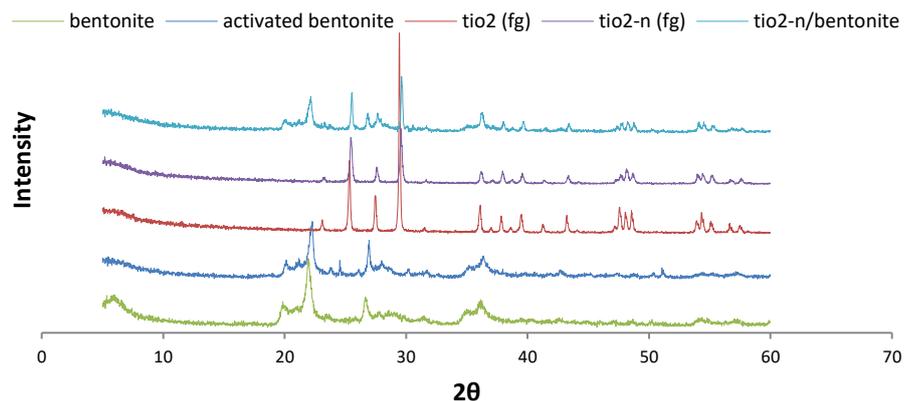


Figure 6. Diffractogram of Bentonite, TiO_2 , $\text{TiO}_2\text{-N}$, and $\text{TiO}_2\text{-N/bentonite}$

4. Conclusion

Based on the result of research, degradation of tempe waste water with the optimum result using photocatalyst in form of granule $\text{TiO}_2\text{-N/bentonite}$ -alginate. The optimum concentration of $\text{TiO}_2\text{-N}$ 0.4 g/g bentonite to degrade the tempe waste water with the ratio of photocatalyst and tempe waste water is 1:6 (150 mg:25 mL). The characterization results show that TiO_2 used has similarity properties with

TiO₂ anatase, it can also be seen from the comparison of JCPDS anatase. Addition of dopant N into the photocatalyst decreases the intensity of TiO₂ due to substitution of N atoms and is expected to decrease the band gap energy of TiO₂.

References

- [1] PUSIDO BSN, 2012, Tempe : Persembahan Indonesia untuk Dunia, Badan Standardisasi Nasional, Jakarta.
- [2] Fatimah, I., 2006, Titanium Oxide Dispersed on Natural Zeolite (TiO₂/Zeolite) and Its Application for Congo Red Photodegradation, *Indo. J. Chem.*, Vol. 6, No. 1, 38-42.
- [3] Septiana, R., 2014, Pengaruh Penambahan Ion Logam Cu(II) terhadap Dekolorisasi Zat Warna Methylene Blue dan Methyl Orange oleh Komposit TiO₂ Kitosan, Skripsi, Fakultas Sains dan Teknologi, Universitas Islam Negeri Sunan Kalijaga, Yogyakarta.
- [4] Abdullah, M. Arutanti, O. Isnaeni, V.A. Fitria, I. Amalia. Maturi. Aliah, H. dan Khairurrijal., 2011, *Pengolahan Air Limbah dengan Material Struktur Nanometer*, Jurnal Seminar Kontribusi Fisika, INV05
- [5] Naimah, S., 2014, Degradasi Zat Warna pada Limbah Cair Industri Tekstil dengan Metode Fotokatalitik Menggunakan Nanokomposit TiO₂-Zeolit, *J. Kimia dan Kemaasan*, Vol. 36, No. 2, 215-224.
- [6] W.T. Tsai, H.P. Chen, M.F. Hsieh, H.F. Sun, S.F. Chien, 2002, "Regeneration of Spent Bleaching Earth by Pyrolysis in a Rotary Furnace", *Journal of Analytical and Applied Pyrolysis*, 63, hal. 157-170.
- [7] Stamate, Marius and Gabriel Lazar, 2007, *Application Of Titanium Dioxide Photocatalysis To Create Self-Cleaning Materials*, MOCM 13 – Volume 3–ROMANIAN TECHNICAL SCIENCES ACADEMY – 2007.
- [8] Wismayanti, D.A., Diantariani, N.P., dan Santi, S.R., 2015, Pembuatan Komposit ZnO-Arang Aktif sebagai Fotokatalis Untuk Mendegradasi Zat Warna Metilen Biru, *Jurnal Kimia*, Vol. 9, No. 1, 109-116.
- [9] Zuhriah S, 2011, Degradasi Zat Warna Methyl Orange menggunakan Fotoakatalis ZnO-Zeolit dengan Sinar UV, Skripsi, Fakultas Matematika dan Ilmu Pengetahuan, Universitas Brawijaya, Malang
- [10] Riyani, K., Setyaningtyas, T., Andreas., R.(2008). Pengolahan Limbah Logam Berat Industri Tekstil Menggunakan Fotokatalis TiO₂/Arang Aktif. *Molekul*. 3.(1) : 40 – 47