Tempe Waste Water Degradation Using TiO\textsubscript{2}-N/Bentonite alginate Granule Photocatalyst with Ultraviolet Light Irradiation

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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 TiO\textsubscript{2}-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 TiO\textsubscript{2}-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 H\textsubscript{2}SO\textsubscript{4} 0.8 M, TiO\textsubscript{2}-N synthesize by sonication method with urea as the source of N, then TiO\textsubscript{2}-N impregnation into bentonite. Photocatalyst in granule form synthesized with alginate was then dripped with syringe pump into 3\% (w/v) CaCl\textsubscript{2}. The photocatalyst characterization will be performed using XRD. The optimum tempe waste water degradation at the concentration of TiO\textsubscript{2}-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, TiO\textsubscript{2}-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 TiO\textsubscript{2}. TiO\textsubscript{2} has a band gap energy (E\textsubscript{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. TiO\textsubscript{2} has a weak adsorption power in degrading the target compound. The dispersed TiO\textsubscript{2} properties in each part of the solution cause the contact of TiO\textsubscript{2} with less than optimal pollutant. TiO\textsubscript{2} 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$_2$SO$_4$ 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 aquades. 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\textsubscript{4} 40.5 g and 5 mL concentrated H\textsubscript{2}SO\textsubscript{4} are also mixed. Next, the solution plus K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} 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 H\textsubscript{2}SO\textsubscript{4} 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 cool down and followed by adding 5 drops of Ferroin 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 TiO\textsubscript{2}-N on TiO\textsubscript{2}-N/bentonite-alginate photocatalyst and the mass ratio of TiO\textsubscript{2}-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 TiO\textsubscript{2}-N/bentonite powder photocatalyst, and the third tempe waste water with TiO\textsubscript{2}-N/bentonite-alginate granule photocatalyst.

![Figure 1. Relation of various type of photocatalyst with tempe waste water degradation](image)

| Treatment          | Degradation of value COD (%) |
|--------------------|-----------------------------|
| A: tempe waste water without photocatalyst | 0.00 |
| B: tempe waste water with TiO\textsubscript{2}-N/bentonite powder photocatalyst | 31.11 |
| C: tempe waste water with TiO\textsubscript{2}-N/bentonite-alginate granule | 48.89 |

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 TiO\textsubscript{2}-N/bentonite powder photocatalyst gave a decrease of 31.1% the COD value, while the addition of TiO\textsubscript{2}-N/bentonite-alginate granule photocatalyst showed a 48.89% decrease for 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$_2$O produces a radical -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](image-url)  
**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%.
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 absorb 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$_2$, TiO$_2$-N, and TiO$_2$-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 TiO$_2$-N was performed to determine the dominant phase in TiO$_2$ used and the effect of N dopant on TiO$_2$-N. Diffractogram showed different results for TiO$_2$ and TiO$_2$-N at peak height and 2θ, as in Figure 5. Based on the comparison of 20 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 TiO$_2$-N. This is due to the presence of an N dopant which replaces the position of the O atom on the TiO$_2$ bond.

TiO$_2$-N is impregnated with activated bentonite, the success of impregnation can be known by XRD characterization. Figure 6 is a TiO$_2$-N diffractogram, bentonite after activation, and TiO$_2$-N/bentonite. The TiO$_2$-N/bentonite diffractogram is a combination of the diffraction patterns of TiO$_2$-N and bentonite. Some of the peaks of TiO$_2$-N and bentonite diffractogram were changed in the TiO$_2$-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 2θ value of TiO$_2$ diffractogram

| Sample of TiO$_2$ JCPDS No. 00-021-1276 | JCPDS of TiO$_2$ rutile No. 00-021-1276 | JCPDS of TiO$_2$ anatase No. 00-021-1272 |
|-----------------------------------------|------------------------------------------|------------------------------------------|
| 2θ | Int (%) | 2θ | Int (%) | 2θ | 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 | - | - |
| 69.010 | 20 | - | - | 62.690 | 14 |
| - | - | - | - | - | - |
| - | - | - | - | 75.032 | 10 |

Table 2. The 2θ value of photocatalyst diffractogram

| TiO$_2$ | TiO$_2$-N | Bentonite | TiO$_2$-N/Bentonite | Phase |
|---------|-----------|-----------|---------------------|-------|
| 2θ | Int (%) | 2θ | Int (%) | 2θ | Int (%) | 2θ | Int (%) |
|-----------------------------------------|------------------------------------------|------------------------------------------|
| 25.3143 | 35.25 | 25.4316 | 78.10 | - | - | 22.2796 | 100 | - | - |
| - | - | - | - | 26.9632 | 61.70 | - | - | Montmorillonite |
| 27.4991 | 17.86 | 27.5839 | 23.33 | - | - | 26.9632 | 61.70 | - | - |
| 29.4360 | 100 | 29.5833 | 100 | - | - | 27.6563 | 30.66 | - | - |
| 36.1064 | 13.26 | 36.1405 | 18.45 | 36.3805 | 31.92 | 36.2187 | 31.23 | - | - |
| 37.8186 | 7.36 | 37.9470 | 18.84 | - | - | 37.9470 | 18.84 | - | - |
| 48.050 | 10.42 | 48.1315 | 26.04 | - | - | 48.1315 | 26.04 | - | - |
| - | - | - | - | 51.0653 | 16.75 | - | - | Montmorillonite |
| 54.3252 | 10.43 | 54.4227 | 17.22 | - | - | 54.5028 | 14.29 | - | - |
| 55.0573 | 5.11 | 55.1444 | 15.76 | - | - | 55.2999 | 9.19 | - | - |

Anatase |
Montmorillonite |
Anatase |
Anatase |
Anatase |
Montmorillonite |
Anatase |
Montmorillonite |
Anatase |
Anatase
4. Conclusion
Based on the result of research, degradation of tempe waste water with the optimum result using photocatalyst in form of granule TiO$_2$-N/bentonite-alginate. The optimum concentration of TiO$_2$-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
TiO$_2$ anatase, it can also be seen from the comparison of JCPDS anatase. Addition of dopant N into the photocatalyst decreases the intensity of TiO$_2$ due to substitution of N atoms and is expected to decrease the band gap energy of TiO$_2$.

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