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Photocatalitic Degradation of Naphthol Blue Black Using TiO_2-Chitosan Catalyst By Solar Energy

Degradasi Fotokatalisis *Naphthol Blue Black* Menggunakan Katalis TiO_2-Kitosan Dengan Bantuan Energi Sinar Matahari

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ABSTRACT

Naphthol blue black (NBB) is an aromatic azo compound that is potentially carcinogenic and mutagenic. An alternative method of dealing with dye waste is photocatalysis. Photocatalysis is a combination of photochemical processes with the use of catalysts. The purpose of this study is to obtain data on the ratio of TiO_2: Chitosan, which produces composites with the best ability, irradiation time and optimum dose of TiO_2, which is effective in the process of photodegradation of NBB. The process of NBB photodegradation by chitosan beads and composites and chitosan irradiated with the best irradiation time on reducing NBB levels is for 360 minutes with a decrease in concentration of NBB more than 80%. Beads composite TiO_2: Chitosan ratio of 5: 10 produces optimal ability. The optimum dose of composite beads in the NBB photodegradation process is 1 g composite / 100 mL solution.

Keywords: Naphthol blue black, TiO_2-chitosan beads, photocatalytic

ABSTRAK

Naftol blue black (NBB) merupakan senyawa aromatik azo yang berpotensi karsinogenik dan mutagenik, sehingga bersifat toksik. Salah satu metode alternatif penanganan limbah zat warna dengan fotokatalisis. Fotokatalisis merupakan suatu kombinasi proses fotokimia dengan penggunaan katalis. Tujuan dari penelitian ini untuk mendapatkan data rasio TiO_2:Kitosan yang menghasilkan komposit dengan kemampuan paling baik, waktu penyinaran dan dosis optimum TiO_2 yang efektif dalam proses fotodegradasi NBB. Proses fotodegradasi NBB oleh beads kitosan dan komposit dan kitosan diiradiasi dengan waktu penyinaran terbaik pada penurunan kadar NBB adalah selama 360 menit dengan penurunan konsentrasi dari NBB lebih dari 80 %. Beads komposit TiO_2 : Kitosan rasio perbandingan 5:10 menghasilkan kemampuan optimal. Dosis optimum beads komposit dalam proses fotodegradasi NBB adalah 1 gram komposit / 100 mL larutan.

Kata kunci : NBB, *beads* TiO_2-Kitosan, fotokalisis.

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1. INTRODUCTION

Naphthol blue black (NBB) is an aromatic azo compound that is potentially carcinogenic and mutagenic (Harsini et al., 2017), making it toxic to humans. This compound can cause skin irritation, gastrointestinal irritation if swallowed, cyanosis if inhaled, and reproductive effects. Naphthol is carcinogenic, and with a solubility of 1-5 grams in 100 grams of water, naphthol can be easily released into the environment (Fathoni, 2016). NBB is commonly used in the textile industry such as the synthesis of polyester, acrylic, rayon, wool, nylon, silk, and other industries such as paint, ink, plastics, soap coloring, aluminum anodes, wood coloring, and leather synthesis (Onder et al., 2011 & Garg et al., 2015).

In order to improve the efficiency and effectiveness of the environmental remediation process, various methods have been developed for the treatment of dye waste. One alternative method of dye waste treatment is photocatalysis. Photocatalysis is a combination of photochemical processes with the use of catalysts. In photocatalysis, light and catalysts are used to perform or accelerate chemical transformations, with light sources coming from the sun or UV lamps (Zhao et al., 2004). Photocatalysis using semiconductor TiO_2 is widely used as a photocatalyst because of its characteristics that have high photocatalytic efficiency, good physical and chemical stability, economic cost and low toxicity (Khataee & Kasiri, 2010). TiO_2 in suspended solution is a very effective and efficient catalyst for use in photocatalysis (Pataya, 2016). However, one of the obstacles in the use of TiO_2 is that TiO_2 cannot adsorb the target compound. As a result, the opportunity for TiO_2 to contact the pollutant is not optimal, and the photocatalytic degradation process does not work well (Wibowo et al., 2016). In addition, TiO_2 in powder form is difficult to separate, so other alternative forms of TiO_2 are needed, one of which is made into a composite (Agustin et al., 2013).

Several studies have used sunlight for photocatalytic processes, such as photocatalytic ozonation with sunlight can significantly reduce COD and TOC in wastewater (Gimeno et al., 2016), other studies can degrade methylene blue dye quite high up to 65% and Congo red by 75% (Pathania et al., 2016). Chekir et al. (2016), even managed to degrade methylene blue up to 98% in 0.75 g/L TiO2 by using sunlight.

In this study, TiO_2 is used as a photocatalyst in the degradation of NBB dye. In this research, the modification of TiO_2 by preparing a TiO_2-chitosan composite was investigated. The modification with chitosan increases the effectiveness of TiO_2 in degrading NBB. Some aspects observed include the effect of the ratio of TiO_2 and chitosan on the quality of the resulting composite, the effect of the dose of TiO_2-chitosan composite on the process of photocatalytic degradation of NBB using sunlight.

2. MATERIALS AND METHODS (Times New Roman 12 pts, bold, all capital letters)

2.1. Materials

The tools used are standard laboratory glassware, analytical balance (Pioneer), hot plate stirrer (Stuart), UV-Visible Spectrophotometer Genesys 10uv, pH meter, glass reactor, Oven (Memmert) and Rotary Flask Shaker (Stuart). The materials used were TiO_2 antase (Merck), naphthol blue black (Merck), chitosan powder, 2% acetic acid (Merck), epichlorohydrin (Merck), 0.1% EDTA (Ajax Chemical), NaOH (Merck), and distilled water.

2.2. Methods

2.2.1 Synthesis of TiO_2-chitosan composite

A total of 0.5 g of chitosan powder and 0.05 g of TiO_2 were dissolved in 20 mL of 2% acetic acid. The mixture was stirred continuously for 45 minutes and then 1 mL of epichlorohydrin was added. Stirring continued for 5 hours. The mixture was dropped into 0.25 M NaOH solution until beads were formed. The beads were left in the solution for 12 hours and rinsed with distilled water. TiO_2 kitosan beads were placed in an Erlenmeyer flask containing 100 mL of 0.1% EDTA and stirred for 4 hours. The beads were then washed again with distilled water. The beads were then placed in 0.05 M NaOH solution and stirred for 2 hours. The TiO_2-chitosan beads were washed with distilled water and dried at 60 °C (Zhao et al., 2012). The synthesis of TiO_2-chitosan composites was repeated by varying the ratio of TiO_2-chitosan to obtain optimal comparisons. Variations of the ratio of TiO_2-chitosan that will be done is 1:10, 2:10 and 5:10 (grams of TiO_2: grams of chitosan).

2.2.2 Determination of Time Effect on NBB Photodegradation

NBB solution was put into the reactor, then added 5 grams of TiO_2. Stirred continuously while irradiated in the reactor. At an interval of 20 minutes the solution was taken and measured the absorbance using a UV-Vis spectrophotometer at the maximum wavelength of NBB.

2.2.3 Determination of the Effect of the Optimum Dose of TiO_2-Chitosan on NBB Photodegradation

NBB solution was put into the reactor, then added TiO_2-chitosan composite. The amount of composite added varied 0.1 grams; 0.2 grams; 0.5 grams and 1 gram in 100 mL of solution. Stirred continuously during irradiation for the optimum time.

2.2.3 Data Analysis

Data analysis was carried out by displaying the data obtained from this study, namely numerical data of sample absorbance at wavelengths, Fourier Transform Infrared (FTIR) star spectra data. and in the form of photos of Scanning Electron Microscope (SEM) results. The effect of time and dose of TiO_2-chitosan composite on changes in NBB concentration is shown in tabulation.

3. RESULTS AND DISCUSSION

3.1 Synthesis of TiO_2-chitosan composite

The TiO_2-kitosan composite synthesized in this study is prepared in the form of granules (beads). The preparation of TiO_2-kitosan composite beads is done by dissolving TiO_2 and in 2% acetic acid solution. The mixture is added epichlorohydrin, which acts as a cross-linker, then into the solution dripped in NaOH solution so that it is shaped beads. The modification of this chitosan by adding epichlorohydrin as a crosslinker to the chitosan results in stretching the distance between the chitosan polymer chains, causing the chitosan to be large, thus increasing the pore size and increasing its adsorption capacity (Nisfayati et al., 2017). Thus, with the possibility of chitosan active groups easily interacting with TiO_2 and dyes in the photocatalytic process. Thus, the TiO_2-chitosan composite in the form of beads has a greater adsorption capacity to NBB, where then NBB will be degraded with TiO_2 as photocatalytic.

3.2 Characterization of TiO_2-Chitosan Composite

The synthesized TiO_2-Kitosan composite was characterized by functional groups using an infrared spectrophotometer. FTIR spectra generated on the analysis of TiO_2-Kitosan composites are shown in **Figure 1**.

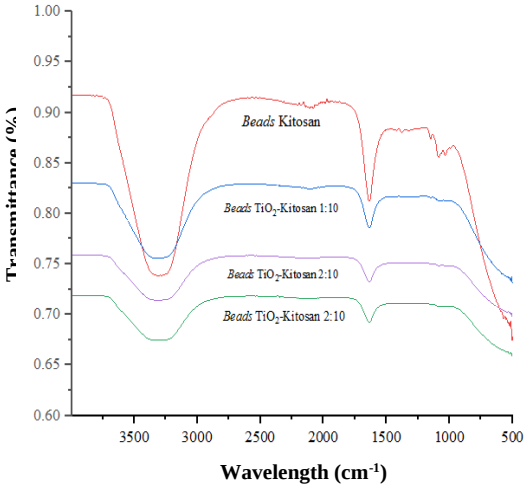

Figure 1. FTIR spectra of TiO_2-Chitosan Composite Beads and chitosan

Figure 1 clearly shows that the peak characteristic of chitosan spectra shows at 3290 cm^{-1} wave number shows the vibrations of −OH and −NH groups. 3000-3700 cm^{-1} area shows the −OH or −NH region. Peak shows that there are $-R_2NH$ and −OH bonds whose hydrogen bonds are extensive so that the peak widens and O−H bonded with hydrogen derived from −NH (Fessenden, 1986). The width of this absorption is also due to the peak of the −OH bond overlapping with the −NH bond of the amine (Dompeipen, 2017). While the peak at 1629 cm^{-1} shows a C=O bond derived from the protonation of secondary amines which are usually in the 1640-1820 cm^{-1} region. One of the characteristic absorptions for chitosan compounds is the weak stretching absorption region at 1650 cm^{-1} which identifies the presence of a C=O group derived from the $-NHCOCH_3$ bond (Dompeipen, 2017).

The peak that appears at 1472 cm^{-1} comes from the C−H bond that experiences vibrations derived from amines. The existence of a bond between C−O is seen from the peak that appears at 1151 cm^{-1}, while the peak at 1050 cm^{-1} comes from the C−O−C bond. In the spectra of the TiO_2-chitosan composite, the peak intensity at these wave numbers decreased. This is likely due to the bonding between TiO_2 and chitosan reducing the amount of cross-linking that occurs in chitosan beads, so that the number of C−O−C bonds that exist is reduced. While the peak at wave number 966 cm^{-1} is a bond that determines the C−H of the polysaccharide structure. The peak that appears at wave number 1373 cm^{-1} indicates the presence of aromatic nitro bonds ($-C-NO_2$) (Negrea et al., 2015).

The peaks showing OH and NH from chitosan beads are so strong that the peaks are sharply downward. While the TiO_2-chitosan composite beads with varying TiO_2 ratios make the peaks of −OH and −NH less sharp. The decrease in transitation intensity at wave numbers 3290 cm_{-1} and 1629 cm^{-1} occurs because the concentration of intermolecular −OH is getting weaker, this may be due to −OH or −NH bonds from chitosan interacting with TiO_2 (Dompeipen, 2017).

3.3 Morphological analysis of TiO_2-chitosan composite

The results of the analysis of TiO_2-chitosan composite in this study observed the morphology of the composite on a microscopic scale, analyzed the TiO_2-chitosan composite. The results of SEM analysis of composites with the three variations in the ratio of TiO_2 are shown in **Figure 2**.

Figure 2(a) shows the SEM of chitosan. **Figure 2(b)** shows a TiO_2-chitosan composite with a ratio of 1:10. The SEM analysis results show that there are white spots on the surface, which may come from TiO_2 binding to chitosan. TiO_2 can bind to chitosan with the addition of a cross-linking agent. The process of fusion between TiO_2 particles and chitosan through the process of unification (coalscene) until formed round (spherical). Agglomeration of TiO_2 and chitosan is also due to the

influence of interactions between particles of TiO_2 and chitosan (Charbonneu et al., 2009).

TiO_2-chitosan composite with a ratio of 2:10 in **Figure 2(c)** the distribution of TiO_2 looks evenly distributed on the surface of chitosan. As the amount of TiO_2 in the composite increases, more and more white spots appear on the surface of chitosan.

Figure 2(d) shows a ratio of 5:10, where the number and size of the white spots of TiO_2 are increasingly visible and large due to the increase in the amount of TiO_2 used in the composite synthesis. The distribution of TiO_2 becomes irregular, even visible large clumps due to the relatively large amount of TiO_2 used. At the time of composite synthesis process, the amount of TiO_2 added is most likely TiO_2 is not evenly dissolved in the solution. As a result, the TiO_2 suspended in the solution forms granules that clump together and cause its distribution on the chitosan surface to be uneven. It can be concluded that the higher the TiO_2 ratio used in the composite synthesis, the more the morphology of the resulting composite will be affected.

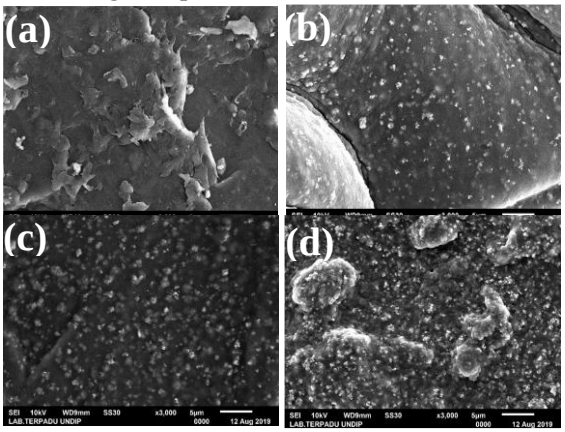

Figure 2. (a) chitosan, (b) 1:10 composite, (c) 2:10 composite and (d) 5:10 composite

3.4 Effect of irradiation time on photodegradation.

Changes in NBB concentration observed after irradiation with sunlight with TiO_2-chitosan composites 1:10; 2:10 and 5:10. The decrease in NBB reached more than 80% with an optimum time of 6 hours. Thus, it can be concluded that the TiO_2-chitosan composite beads are able to reduce the NBB level in solution. The longer the contact time between the sample and the composite and the time of irradiation of the sample with sunlight, the concentration of NBB in the sample will decrease because the photons from UV radiation will continue to increase on TiO_2 will also increase, allowing reduction and oxidation reactions to occur so as to produce hydroxyl radicals (Muslimah et al., 2019). In addition to the degradation of NBB catalyzed by TiO_2, the decrease in NBB concentration in solution is also caused by the degradation-absorption of NBB on TiO_2-chitosan composite beads. The decrease in NBB concentration from the solution for chitosan beads and the type of composite used is shown in **Table 1**.

Table 1 shows that after contact for 6 hours, chitosan beads can absorb NBB by 78.52%. While the mass of NBB lost in the composite treatment is greater than the adsorption of chitosan beads. Thus, it can be said that NBB is lost not only by adsorption but also by photodegradation process. The decrease in NBB levels is due to the adsorption-degradation process by TiO_2-chitosan composite beads using light energy. Chitosan has a large and fast adsorption capacity in absorbing anionic pollutants of dyes. The active groups $-NH_2$ and $-OH$ are protonated and bind anionically with the anion of the dye (Huang et al., 2013).

The adsorption of NBB molecules by chitosan also facilitates the contact between the NBB solution and TiO_2, where TiO_2 can be more effective in degrading NBB. The NBB degradation process in this study took place with the help of sunlight, with sunlight being the main source of UV light.

Table 1 Percentage of NBB degradation-adsorption on chitosan beads and TiO_2-chitosan composite

No	*Beads*	Initial concentration (mg)	Final mass (mg)	% Degradation and adsorption
1	Chitosan	24.45	5.25	78.52 %
2	Composite 1:10	25.18	2.83	88.76 %
3	Composite 2:10	25.76	1.80	93.00 %
4	Composite 5:10	25.12	0.36	98.56 %

According to Lestari & Khunur (2015), sunlight can be used as the main source for the photodegradation process because it has an intensity and wavelength between (310-2300 nm), which is larger than the wavelength of UV light (200-380 nm). UV light from sunlight produces photon energy to produce −OH radicals occurs because light energy from sunlight becomes chemical energy and thus produces hydroxyl radicals (−OH), which undergo redox reactions. According to Pataya (2016), TiO_2 does not absorb visible light, but is capable of absorbing UV radiation, resulting in the formation of hydroxyl radicals.

When TiO_2 is irradiated with energy greater than its band gap energy, an electron will move from the valence band to the conduction band, producing a hole (h + vb) in the valence band and electrons in the conduction band of the process that occurs.

Electrons are excited from the lower valence band (vb) to the higher conduction band (cb), producing positive holes and negative electrons in the TiO_2 layer. Oxygen and water are absorbed at the surface of the TiO_2 pore and react directly with the hole-electron pair to form the product $O_2^{-\bullet}$, $HO_2^{\bullet}$ or OH. $HO\bullet$ from the resulting TiO_2 radical directly oxidizes NBB. The mechanism of photocatalysis by TiO_2 in degrading dyes is shown in the following equation (Ajmal et al., 2014, Nasikhudin et al., 2018):

$$TiO_2 + h\upsilon \rightarrow TiO_2(e_{cb}^- + h_{vb}^+) \quad (1)$$

$$H_2O(ads) + h_{vb}^+ \rightarrow \bullet OH + H^+ \quad (2)$$

$$O_2 + e_{cb}^- \rightarrow O_2^{-*}(ads) \quad (3)$$

$$O_2^{-\bullet} + H^+ \rightarrow HO_2^{\bullet} \quad (4)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (5)$$

$$H_2O_2 + e_{cb}^- \rightarrow HO\bullet + HO^- \quad (6)$$

$$H_2O_2 + h\upsilon \rightarrow 2\,HO^{\bullet} \quad (7)$$

$$dye + h_{vb}^+ \rightarrow oxidation\ product \quad (8)$$

$$dye + e_{cb}^- \rightarrow reduction\ product \quad (9)$$

3.5 Effect of TiO_2-Chitosan Ratio in Photodegradation

The amount of TiO_2 in the TiO_2-chitosan composite also affects the NBB photodegradation process. The results of observations on the effect of the ratio of TiO_2-chitosan on the amount of NBB shown in **Figure 3**.

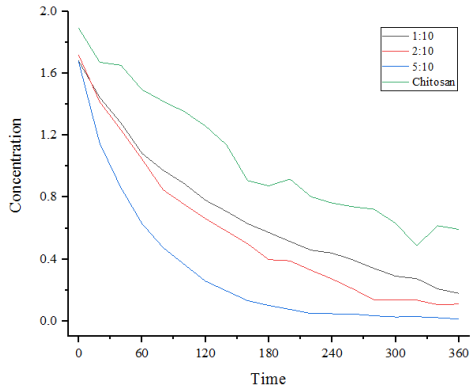

Figure 3. Effect of TiO_2-Chitosan Ratio

Figure 3 shows the reduced concentration of NBB from the solution by using each variation of the TiO_2-chitosan composite. The percentage reduction in NBB concentration using composites that provide better results in reducing NBB levels is a composite with a TiO_2-chitosan composition ratio of 5:10 which is more effective in degrading NBB solutions. The greater the ratio of TiO_2 in the composite,

the faster the decrease in NBB levels. Because the amount of catalyst increases so that the photodegradation process takes place faster. According to Muslimah et al., (2019), a lot of TiO_2 is added in the photocatalysis process, the percentage of degradation is also greater. This is because the amount of TiO_2 used forms more holes that are formed as well. Holes formed from the excitation process will react with surrounding water molecules to form hydroxyl radicals. These hydroxyl radicals are very reactive, so they are able to degrade organic compounds. So, it can be concluded that with the increasing ratio of TiO_2 in the composite, the number of hydroxyl radicals that play a role in the photocatalysis process will also increase. This also indicates that the most likely the process that occurs is photodegradation by sunlight is more dominant than the adsorption process by chitosan.

3.6 Dose variation in photodegradation.

In this study, the NBB photodegradation process was carried out by varying the dose to obtain the optimal dose in degrading NBB. The change in NBB concentration in the sample shown in **Figure 4** shows the results of the decrease in NBB concentration due to the treatment with composite beads and chitosan beads at different doses.

Figure 4 shows that the greater the ratio of TiO_2 and the dose of beads, the greater the decrease in NBB concentration. The amount of NBB absorbed by chitosan beads with different doses is shown in **Table 2** and the percentage decrease of NBB concentration in solution for treatment with chitosan and composite beads is shown in **Table 3**.

From **Tables 2 and 3**, after 6 hours of contact, the dose variation of chitosan beads and TiO_2-chitosan composite affects the reduction of NBB concentration in solution. In a few treatments with the TiO_2-chitosan composite, the reduction of NBB from the solution was lower than when treated with chitosan beads.

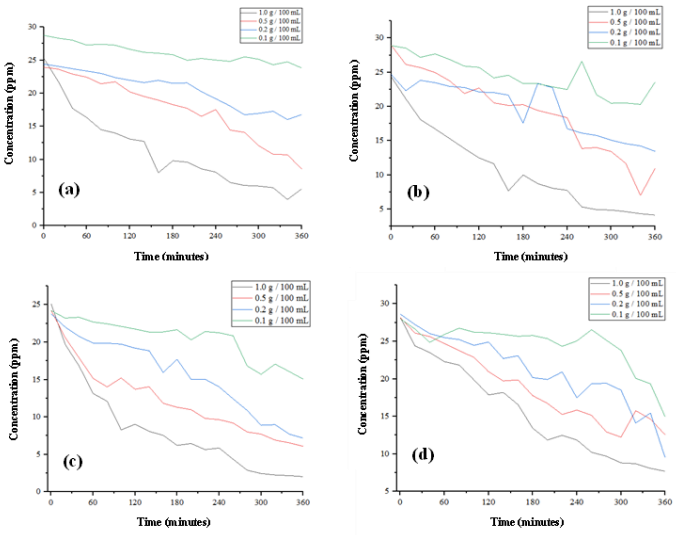

Figure 4. Decrease in NBB concentration with composite beads of (a) 1:10, (b) 2;10, (c) 5:10 and (d) chitosan.

However, the use of higher doses of TiO_2-chitosan composite generally resulted in a greater reduction in NBB concentration than the use of chitosan beads. This indicates that the loss of NBB from the solution is not only due to the adsorption process, but also to the photodegradation process catalyzed by TiO_2 in the composite.

Increasing the catalyst dosage before the optimum dosage will increase the photocatalysis efficiency, because the number of active sides of the catalyst surface increases. However, increasing the catalyst dosage above the optimum dosage will decrease the photocatalysis efficiency.

A high amount of catalyst will cause turbidity in the solution resulting in the penetration of UV light. In addition, too large an amount of catalyst in the solution causes particle agglomeration so that, there are parts of the catalyst surface that are not exposed to UV radiation to adsorb photons, so that the NBB photocatalysis process does not take place effectively.

Table 2. Elimination of NBB in chitosan beads

No	Sample	Dose (% g/mL)			
		0.1 g / 100 mL	0.2 g / 100 mL	0.5 g / 100 mL	1 g / 100 mL
1	Kitosan	21.01 %	62.29 %	55.45 %	72.71 %

Table 3. Adsorption-degradation of NBB

No	Composite	Dose (% g/mL)			
		0.1 g / 100 mL	0.2 g / 100 mL	0.5 g / 100 mL	1 g / 100 mL
1	1:10	17.20 %	31.27 %	64.26 %	78.08 %
2	2:10	18.36 %	45.53 %	62.07 %	83.02 %
3	5:10	37.78 %	72.78 %	86.17 %	91.94 %

Conversely, the amount of catalyst dose below the optimum dose can cause the efficiency of the photocatalysis process to decrease because with a decrease in the composite dose, there is also less catalyst that produces hydroxyl radicals (Sugiyana & Yulianti, 2014).

The addition of the composite dose can improve the photocatalysis process, where the percentage of adsorption-degradation is also increasing because the amount of TiO_2 that forms holes is also increasing. Holes formed from the excitation process will react with surrounding water molecules to form hydroxyl radicals. These hydroxyl radicals are very reactive, so they can degrade NBB. Increasing the dose of composite added encourages the photodegradation process by sunlight to be more dominant than the adsorption process by chitosan. The minimum dose to degrade NBB is 0.1gram composite/100 mL sample for ratio composite. And the optimum dose to degrade NBB is 1 gram of composite/100 mL.

4. CONCLUSIONS

The conclusion that can be drawn from this research is that the NBB photodegradation process by composite beads irradiated with UV light from sunlight obtained the best irradiation time on reducing NBB levels is for 360 minutes with a decrease in the concentration of NBB more than 80%. The ratio of the production of TiO_2 composite beads: Chitosan produces the optimum ability in the photodegradation process is a ratio of 5:10. The optimum dose of composite beads in the NBB photodegradation process is 1 gram of composite / 100 mL sample.

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