Degradation of Paracetamol by Photolysis Using C-N-codoped TiO_2

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ABSTRACT

Paracetamol is generally used as analgesic and antipyretic drugs. Contamination paracetamol in the environment can occur because of waste material disposal from production site and immediate disposal of household that cause water pollution. Paracetamol is degraded by photolysis method under irradiation 10 watt UV-light (λ=365 nm), visible-light (Philips LED 13 watt 1400 lux) and solar-light with and without addition C-N-codoped TiO_2 catalyst. The solution is analyzed by UV-Vis spectrophotometer at λ 200-400 nm. Optimum weight of C-N-codoped TiO_2 catalyst obtained is 20 mg under UV-light photolysis. Paracetamol 4 mg/L is degraded 45.48% after 120 minutes under UV-light irradiation without catalyst, and increases to be 69.31% by using 20 mg catalyst. While degradation percentage of paracetamol is 16.96 % without catalyst, the percentage increases to be 34.29% after using 20 mg catalyst for 120 minutes photolysis under visible-light. Degradation of paracetamol by solar light achieves only 12.27% in absance of catalyst for 120 minutes irradiation, but it increases significantly until 70.39% in presence of 20 mg catalyst.

Keywords : C-N-codoped TiO_2, Paracetamol, Photolysis

INTRODUCTION

Paracetamol is an extremely popular analgesic pharmaceutical product which is purchased freely. It is produced in large quantities. The amount of paracetamol produced annually is about 145,000 tons per year (Sebastine and Wakeman, 2003). The larger number of paracetamol produced each year the more waste generated, and the higher paracetamol residue in the water. Paracetamol has been found up to 6 μg/L, and up to 10 μg/L in European STP effluents and in natural waters in USA respectively (Jallouli, Elghniji, Trabelsi, and Ksibi, 2017). Generally it is detected about 0.01–0.3 mg/L in the aquatic environment (Desale, Kamble, and Deosarkar, 2013). The residues of paracetamol in environment are from household sewer systems, hospital effluents, agricultural run-offs, manufacturing process, livestock, and disposal of unused and expired products are sources of paracetamol (Mameri, Debbache, Benacherine, Seraghni, and Sehili, 2016). Its continuous input may pollute water environment, decline water quality, contaminate the aquatic organisms and also can be a potential risk for aquatic and terrestrial organisms in the long term.

Advanced oxidation processes (AOPs) including heterogeneous photocatalysis is an effective technique reported for degrading drug waste in waters because semiconductors are inexpensive and capable of mineralizing various refractory compounds. The main goal of this waste treatment is to produce harmless, environmentally friendly products such as CO_2 and H_2O (Anggraini, Safni, Wellia, and Khoiriah, 2016; Morikawa, Asahi, Ohwaki, Aoki, Taga, 2001).

Titania (TiO_2), a heterogeneous photocatalyst, is efficient to degrade organic pollutants. This semiconductor catalyst has a band gap value about 3.2 eV that only can be activated in higher energy like ultraviolet irradiation. One of the steps to decrease its bad gap is by doping Titania with other elements. Nitrogen and carbon are the good dopant for minimizing the band gap of TiO_2 and this modification able to be activated in low energy like visible-light (Xu et al, 2011; Safni et al, 2016).

Several studies have reported using a C-N-codoped TiO_2 catalyst on dyes degradation. The study included Direct Red 23 and Direct Violet (Safni et al, 2016), Yellow GCN (Safni, Wellia, Komala, and Reza, 2015) by photolysis under UV-light, visible-light and

solar-light. In our previous research, paracetamol was degraded by photolysis under solar-light, UV-light and ozonolysis using N-doped TiO_2 catalyst. In this study, the degradation of paracetamol is by photolysis under UV-light (λ = 365 nm), visible-light and solar-light by using C-N-codoped TiO_2 catalyst. The effect of catalyst mass, irradiation time and energy source are investigated.

EXPERIMENTAL SECTION

Research Tools and materials

The tools used include ultraviolet-visible Spectrophotometer (Thermo Scientific Evolution 201 UV-Vis Spectrophotometer), HPLC (Shim-pack, SHIMADZU corparation, Kyoto) packed with CLC-ODS(M) 15CM column and UV detector, analytical balance (AA-200, Denver Instrument Company), UV Lamp 10 watt (λ = 365 nm), Visible lamp (Philips LED 13 watt 1400 Lux), centrifuge (NASCO with speed 3000 rpm), and glasses equipments.

The materials used in this study are generic paracetamol 500 mg tablets (indofarma production, Bekasi-Indonesia), titanium (III) chloride (purity > 99%) and ammonia solution (25%) were purchased from Merck. Sodium hydroxide and hydrogen peroxide (30%) were purchased from Sigma. Black carbon (10 mesh) was from coconut shell. The powder C-N-codoped TiO_2 catalyst was prapared Peroxo-gel method (Xu, 2011) using titanium (III) chloride, ammonia solution, and black carbon as precursor of titania, nitrogen and carbon precursors consecutively.

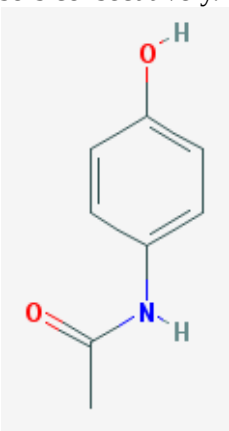

Figure 1. Stucture of paracetamol

Research Methods

Preparation and measurement of paracetamol solution by UV-Vis spectrophotometer

Stock solution 100 mg/L of paracetamol is prepared by dissolving 0.012 grams of paracetamol tablet with NaOH 0.1 N up to 100 mL volume. The solution is further diluted by sodium hydroxide to get working solution with concentration 2, 4, 6, 8, 10 mg/L. The absorbance of solution is measured by UV-Vis spectrophotometer at wavelength 200-400 nm. The data is taken at the wavelength that gives maximum absorbance.

Effect of catalyst mass on paracetamol degradation

20 mL solution of paracetamol 4 mg/L is loaded into the petridish. Each solution is added 5-25 mg C-N-codoped TiO_2 catalyst and irradiated under UV lamp for 120 minutes. The degraded solution is centrifuged for 15 minutes to separate the catalyst from the solution. The absorbance of each solution is measured by a UV-Vis spectrophotometer at a wavelength of 257 nm.

Effect of irradiation time on paracetamol degradation

20 mL solution of 4 mg/L paracetamol is degraded by photolysis with the addition of catalyst and without catalyst under radiation of UV light source (λ = 365 nm), visible-light, and solar-light for 30-120 minutes. The C-N-codoped TiO_2 catalyst is separated from solution by centrifuging for 15 minutes at 3000 rpm. The differences between initial and final absorbance of solution are detected by a UV-Vis spectrophotometer and indicated the percentage of paracetamol.

Analysis of paracetamol solution by HPLC

A paracetamol solution 4 mg/L is loaded into petridish and added 20 mg of C-N-codoped TiO_2 catalyst. The solution is irradiated under UV lamp (λ = 365 nm) for 120 minutes. Irradiated solution and non- irradiated solution are analyzed by HPLC.

RESULTS AND DISCUSSION

Preparation and measurement of paracetamol solution by UV-Vis spectrophotometer

The measurement of paracetamol absorption spectrum is performed at wavelengths 200-400 nm. The maximum wavelength is obtained at 257 nm. Figure 2 shows that the absorbance value of paracetamol solution with concentration 2, 4, 6, 8, 10 mg/L increases by increasing paracetamol concentration.

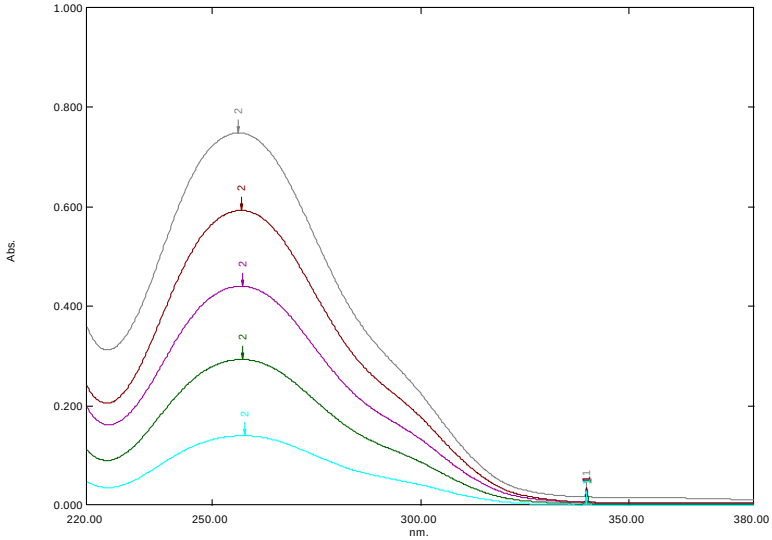

Figure 2. The absorbance spectra of paracetamol with variation concentration 2, 4, 6, 8, 10 mg/L

Based on Lambert Beer's law, a good absorbance value for measuring sample solution with UV-Vis spectrophotometer is in range from 0.2-0.8. Therefore for the next research used 4 mg/L paracetamol solution which gives the absorbance value 0.277.

Effect of catalyst mass on paracetamol degradation

The effect of catalyst mass on paracetamol degradation is investigated by varying the weight of the C-N-codoped TiO_2 catalyst 5, 10, 15, 20 and 25 mg. **Figure 3** shows the relationship between percent degradation and the weight of the C-N-codoped TiO_2 catalyst. The degradation percentage of paracetamol increases with increasing the number of catalysts from 10 mg to 20 mg with efficiency removal 46.2-67.87%. But the removal paracetamol decreases slightly by using 25 mg catalyst. Based on the results, the optimum C-N-codoped TiO_2 mass for degradation of paracetamol in aqueous solution is 20 mg.The increase of catalyst mass can accelerate the paracetamol decay mainly because the higher number of catalysts, the higher surface active side is in photolysis system so that the number of photons absorbed on catalyst surface hinger as well and lead to produce more reactive species like hydroxyl radicals. While large quantities of catalyst will cause agglomeration, sedimentation, declining light scattering, and decreasing penetration of light into the solution thereby decreasing the degradation efficiency (Desale et al, 2013; Yang, Yu, and Ray, 2008). Therefore for the next research uses 20 mg C-N-codoped TiO_2 catalyst on paracetamol degradation by photolysis.

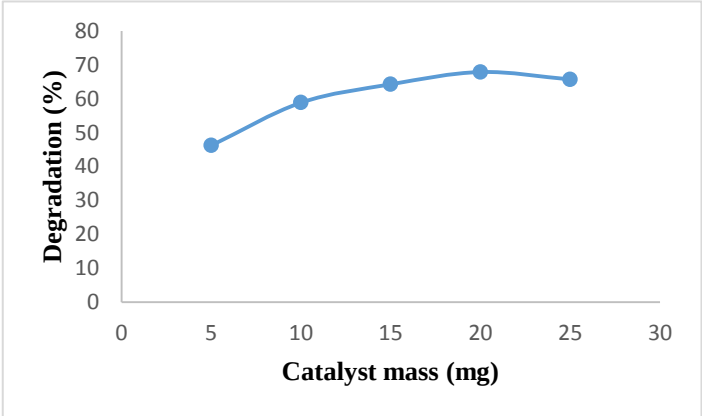

Figure 3. Effect of catalyst mass (5, 10, 15, 20 and 25 mg) C-N-codoped TiO_2 on paracetamol degradation for 120 minutes under UV photolysis

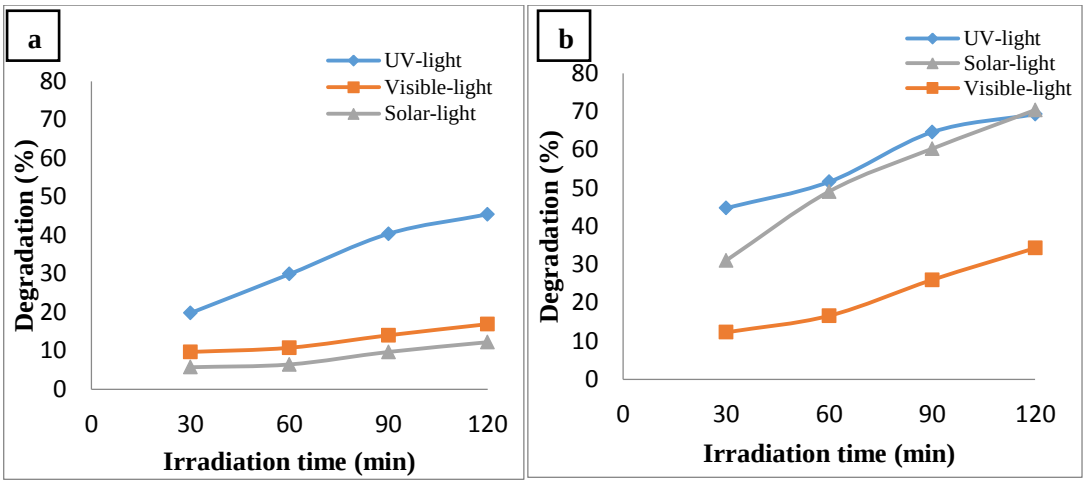

Figure 4. The effect of irradiation time (30, 60, 90, and 120 minutes) on paracetamol degradation (a) without (b) with addition 20 mg C-N-codoped TiO_2 catalyst by photolysis

Effect of irradiation time on paracetamol degradation

The main factor effecting organic pollutant degradation is irradiation time on photolysis. In this study, the effect of irradiation time (30-120 minutes) with and without adding C-N-codoped TiO_2 catalyst. The degradation percentage of paracetamol generally increases by increasing irradiation time.

The results describe photolysis by adding C-N-codoped TiO_2 catalyst giving better in efficiency than without catalyst. The degraded paracetamol is found 5.77%, 6.49%, 9.74%, and 12.27% under direct solar photolysis for 30-120 minutes shown in **Figure 4(a)**. While the paracetamol efficiency significantly rises to be 31.04%, 49.09%, 60.28% and 70.39% in presence of 20 mg C-N-codoped TiO_2 catalyst on the same condition of photolysis shown in **Figure 4(b)**. This results indicate that the C-N-codoped TiO_2 catalyst had a considerable role in the photocatalysis process. The contact between C-N-codoped TiO_2 catalyst and photon from energy sources (UV, visible and solar) increases in longer irradiation time, consequently the amount of OH• radical produced as paracetamol oxidant also increases. When the catalyst is exposed to light, the electron in the photocatalyst will excite from the valence band in to the conduction band which will produce holes in valence band. The hole will react with hydroxides to form OH•, a powerful oxidizing agent to oxidize paracetamol into simple compounds such as CO_2 and H_2O (Safni et al, 2015; Attia, Kadhim, and Hussein, 2008). Within 120 minutes without the addition of catalysts under UV-light (λ = 365 nm), visible-light and solar-light irradiation, the percentage degradation is obtained respectively 45.48%, 16.96%, 12.27% whereas with the addition of degradation percentage catalyst increases to be 69.31%, 34.295% and 70.39%.

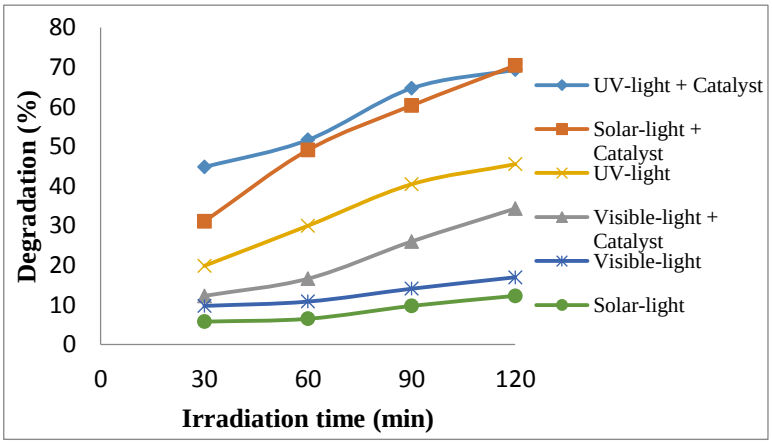

Figure 5. Effect of energy source on paracetamol degradation by photolysis for 120 minutes under UV, visible and solar irradiation with and without catalyst C-N-codoped TiO_2

Effect of energy source on paracetamol degradation

The type of light source also affects on paracetamol degradation by photolysis with and without using C-N-codoped TiO_2 catalyst. Paracetamol 4 mg/L is degraded by 3 types of light sources, UV-light (λ = 365 nm), visible-light and solar-light photolysis. The largest degradation percentage of paracetamol under UV-light (λ = 365 nm) is 45.48% and 69.31% without and with the addition of catalyst for 120 minutes of photolysis. This is due to the intensity generated from UV-light higher and more constant compared to two other energy sources (visible-light and solar-light).

In accordance with the planck's law which says the photon energy is inversely proportional to the wavelength. However, when the photolysis process is added with 20 mg of C-N-codoped TiO_2 catalyst, the largest percentage of degradation is reaching 70.39% under solar-light photocatalysis depicted in **Figure 5**. These results indicate that the energy provided by the sun can activate the C-N-codoped TiO_2 catalyst well so that the photodegradation process of paracetamol becomes more effective. In addition, those titania modification not only can active in higher energy like UV and solar-light but it also can accelerate paracetamol degradation two folds under low energy source (visible-light) with the efficiency 34.29% in presence C-N-codoped TiO_2 compared to absence catalyst on system only 16.96%.

HPLC analysis of paracetamol solution

Analysis of 4 mg/L paracetamol solution before and after degradation by photolysis UV using 20 mg C-N-codoped TiO_2 for 120 minutes is analyzed using a high performance liquid chromatography (HPLC) with UV detector at 257 nm.

The HPLC was packed by C18 column (250 x 4.6 mm). The mobile phase used is acetonitrile and phosphate buffer pH 7 (40: 60 v/v) and injection volume of paracetamol was 100 µm with a flow rate of 1.0 mL/min. Comparison of the chromatogram peaks between paracetamol solution before and after degradation under UV radiation (λ = 365 nm) by photolysis can be shown in **Figure 6**. Paracetamol peak appears in chromatogram at retention time t_R = 3.050 min with absorbance 0.277. Hence the chromatogram peak decreases with absorbance 0.085 after degradation under UV light (λ = 365 nm) photocatalysis for 120 minutes with the addition of the catalyst C-N-codoped TiO_2 indicating that paracetamol has been degraded. The existence of a new peak at retention time t_R = 6 min in chromatogram signifies the possible formation of new compounds as the paracetamol degradation products that need to be analyzed further. Some researchers have reported some paracetamol intermediates such as hydroquinone, benzoquinone, p-nitrophenol, and 1,2,4-trihydroxybenzene and p-aminophenol detected after treatment by photocatalysis using TiO_2 catalyst under UV-C light irradiation (Moctezuma, Leyva, Aguilar, Luna, Montalvo, 2012; Jallouli et al, 2014). Paracetamol products found by Yang are formic acid, acetamide, oxamic acid, hydroxy-acetic acid, malonic acid, butenedioic acid, succinic acid, malic acid, hydroquinone, acetamide, N-(2,4-ihydroxyphenyl), acetamide, N-(3,4-ihydroxyphenyl) (Yang et al, 2008). While degradation of paracetamol by direct photolysis under UV (254 nm) light irradiation produces 4-aminophenol (4-AP) as a product (Martignac et al, 2013).

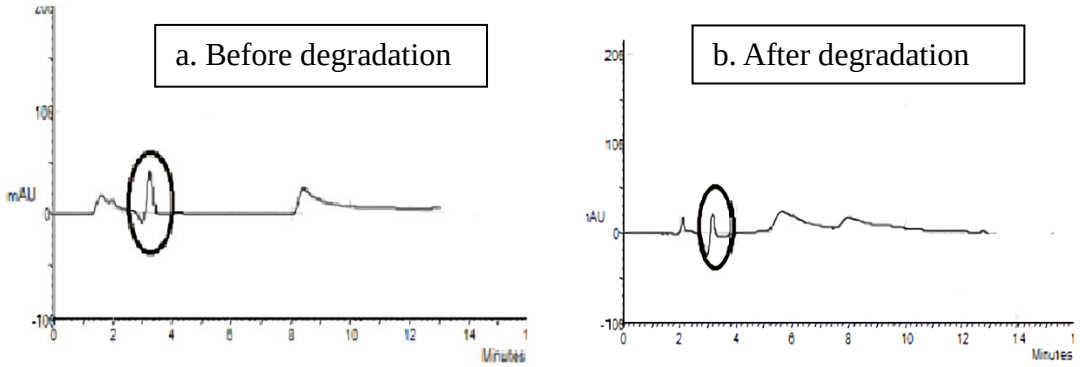

Figure 6. Chromatogram of paracetamol solution (a) before (b) after photocatalysis under UV radiation using 20 mg C-N-codoped TiO_2 catalyst for 120 minutes

CONCLUSION

A modification titania, C-N-codoped TiO_2, successfully accelerate on paracetamol degradation by photolysis method. The process was effected by catalyst mass, irradiation time and energy sources. The catalyst can active both in high (UV-light) and low energy sources (visible-light). Addition 20 mg C-N-codoped TiO_2 catalyst able to increase paracetamol degradation percentage from 45.48%, 16.96%, 12.27% without using catalyst to be 69.31%, 34.29%, 70.39% by using catalyst under UV-light (λ = 365 nm), visible-light and solar-light for 120 minutes respectively.

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