

Photodegradation of Phenol using N-doped TiO₂ Catalyst

Safni Safni*, Mechy Rezita Wahyuni, Khoiriah Khoiriah, Yulizar Yusuf

Laboratory of Applied Analytical Chemistry, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Andalas University, Kampus Limau Manis, Padang, 25163, Indonesia

*Corresponding author email: safni@sci.unand.ac.id

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ABSTRACT. Phenol (C₆H₅OH) is a common contaminant in wastewater. In certain concentrations, phenol can inhibit the activity of microorganisms and give adverse effects to human health, such as liver and kidney damage, perfect heart rate, and lower blood pressure. In this study, phenol was degraded with and without N-doped TiO₂ under photolysis UV-light (10 Watts, λ = 365 nm) and visible-light (13 watt Philips, lux= 1400, λ = 465-640 nm) irradiation. The reduction of phenol concentration was measured by a UV-Vis spectrophotometer at a wavelength 200-400 nm. Some parameters such as catalyst dose, irradiation times and type of light sources were studied. The XRD and DRS UV-Vis characterization confirm that the nitrogen modified of titania catalyst potentially actives in visible-light. The N-doped TiO₂ is able to catalyze and improve the efficiency of phenol degradation in photocatalysis system. Phenol with initial concentration 8 mg/L was degraded by 30.51% and 33.89% without catalyst and increased to be 67.80% and 90.8% by addition of 15 mg N-doped TiO₂ catalyst under visible-light and UV-light for 210 minutes photolysis, respectively. From the results, irradiation using UV-light achieves higher efficiency than visible-light on phenol degradation.

Keywords: Degradation, Phenol, N-doped TiO₂, Photocatalysis

INTRODUCTION

Phenol is a toxic hydroxybenzene which is sourced from chemical process industries such as herbicides and fungicides production, coal gasification, paper mill, polymeric resin production coking plants, and oil refining (Pattersom, 1985). Exposure to humans may occur by absorption through the skin, swallowing, cutaneous adsorption, and inhalation (Meena, Band, & Sharma, 2015; Wiley & Sons, 2003). Phenol can cause caustic burns on the area of skin, the corrosive effect, paralysis of the central nervous system with collapse and a severe drop in body temperature, cause damage inner organs, namely kidneys, liver, spleen, lungs, and heart (Wiley & Sons, 2003). The concentration of phenol in wastewater must be less than 2 µg/L and in drinking water must be less than 0.1 µg/L (Nikeslat, Amin, Izanloo, Fatehizadeh, & Mousavi, 2013).

Treating wastewater containing phenol has been investigated by conventional methods such as physical methods (activated carbon adsorption, filtration, and reverse osmosis), chemical methods (ion exchange, solvent, and electrochemical extraction) and biological methods (aerobic and anaerobic processes) (Abdelwahab, Amin, & El-Ashtouky, 2009). However, the three methods require several stages of processing, high costs, low efficiency and producing secondary waste (Safni, Putri, Wellia, & Septiani, 2017).

One of the potential methods to degrade phenol is the advanced oxidation processes (AOPs). These techniques produce and use hydroxyl radical (•OH) as a highly reactive species for organic pollutant degradation. Phenol

is oxidized to be hydroquinone, benzoquinone, and catechol. Those products would be further oxidized by hydroxyl radical forming aliphatic carboxylic acids such as maleic acid and fumaric acid. The final compounds formed from phenol degradation process using this technique, are more environmentally friendly and biodegradable (Wu & Zhou, 2001).

Photocatalysis, one of the advanced oxidation process techniques (AOPs), is most widely developed in the degradation of organic pollutants. It has been reported effective in the degradation of dyes (Molla et al., 2017; Sacco et al., 2012; Safni, Wellia, Komala, Putri, & Deliza., 2016; Šima & Hasal, 2013) and pesticides (Khoiriah, Wellia, & Safni, 2019). This method combines the role of semiconductor catalysts and light as a photon source. The electrons of catalyst will be excited from the valence band to the conduction band by the presence of equal or greater energy photon than its band gap energy. This process produces hole and reactive species (•OH) which act as strong oxidant for the target compounds. The final products expected from this method are a simpler and more environmentally friendly compound such as CO₂ and H₂O (Safni et al., 2017).

Titania (TiO₂) is the most commonly used as a semiconductor catalyst in the photocatalytic process with several advantages that is non-toxic (poison), cheap, and high stability (Wellia, Fitria, & Safni, 2018). However, titania has a fairly large band gap (3.2 eV) and active under high energy rays such as UV light. Modifying the titania by doping is one option to activate it at lower energy (visible-light). The potential element that can be

used as a dopant is nitrogen. This element has small ionization energy, the size is not much different from the oxygen and also can narrow the band gap energy, as a result, it can be applied in solar-light (Safni., Wellia, Komala, & Putri, 2015; Teh & Mohamed, 2011).

The modified-titania with nitrogen (N-doped TiO₂) has been successfully synthesized by peroxo sol-gel method (free of organic solvents). The presence of nitrogen reduces titania band gap (Wellia et al., 2018). This catalyst has been applied on direct red-23 and direct violet dyes degradation under ozonolysis and photolysis process and reported effective as a catalyst (Safni, Anggraini, Wellia, & Khoiriah, 2015). So far, there have been no reports of the N-doped TiO₂ synthesized by the peroxo sol-gel method on phenol degradation. Therefore, the aim of this study is to modify titania with nitrogen using an environmentally friendly peroxo sol-gel method. The catalyst was applied to degrade phenol by photocatalysis. Some parameters studied are; the effect of the of catalyst dose, irradiation times, and the type of light source.

EXPERIMENTAL SECTION

A. Research Tools and materials

The tools used for experimental are UV Lamp 10 watt ($\lambda = 365$ nm Germicidal CEG13 Base BFC11004), visible lamp (Philips LED 13 watt 1400 Lux), centrifuge (NASCO with speed 3000 rpm), ultraviolet-visible Spectrophotometer (Thermo Scientific Evolution 201 UV-Vis Spectrophotometer), HPLC (Serial No L203047, SHIMADZU corporation, Kyoto), analytical balance (AA-200, Denver Instrument Company), and glasses equipments. X-Ray Diffraction (XRD, Philips X'pert powder PANanalytical) and Diffuse Reflectance Spectra UV-Vis (DRS UV-Vis, Shimadzu UV-Vis 2450 Spectrophotometer) instrument were used for catalyst characterization.

The materials used in this study are phenol (Merck), methanol HPLC grade (Merck), and double distilled from Dwipraga Chemical, Co (Indonesia). The powder N-doped TiO₂ catalyst was prepared by peroxo sol-gel method (Wellia et al., 2018; Xu et al., 2011) using titanium (IV) chloride (Merck) and ammonia solution 25% (Merck) as titania and nitrogen precursors consecutively.

B. Experimental

1. The effect of catalyst mass on phenol degradation by photocatalysis UV and visible-light using N-doped TiO₂.

The solution of 8 mg/L phenol with 20 mL volume was loaded into Petri dishes and added by (5, 10, 15, 20 mg) N-doped TiO₂ catalyst. The suspension solution was irradiated under UV and visible-light for 120 minutes. The degraded phenol solution was centrifuged for 30 minutes for separating catalyst with 3000 rpm. The reduction of phenol concentration was analyzed by UV-Vis spectrophotometer at wavelength 270 nm.

2. The effect of time irradiation on phenol degradation by photocatalysis UV and visible-light using N-doped TiO₂ as a catalyst.

The solution of 8 mg/L phenol with 20 mL volume was loaded into a Petri dish and added by 15 mg N-doped

TiO₂ catalyst. The suspension of phenol solution was degraded under UV and visible-light irradiation for (90, 120, 150, 180, and 210) minutes. N-doped TiO₂ catalyst was separated by centrifuging the solution for 30 minutes with 3000 rpm. The reduction of phenol concentration was analyzed by UV-Vis spectrophotometer at wavelength 270 nm. Direct photolysis without catalyst under the two source energy (UV and visible-light) was also carried out as a control.

RESULTS AND DISCUSSION

1. Characterization of Catalyst

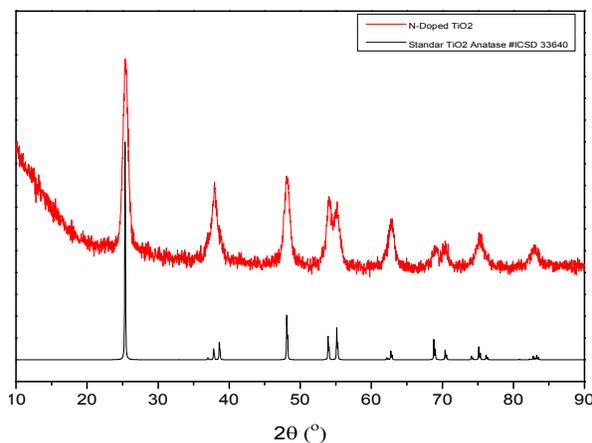


Figure 1. XRD pattern of N-doped TiO₂

Analysis of X-ray diffraction patterns was investigated to determine the structure and size of crystals from N-doped TiO₂ photocatalyst. **Figure 1** shows the XRD pattern, N-doped TiO₂ has peaks at 2θ values of 25.20, 37.70, 47.90, 53.80, 55.10, 62.70, 75.20, 82.50. Those peaks are corresponding to the anatase phase according to the TiO₂ standard (ICSD no. 9852). This crystal structure is expected on photocatalysis because anatase has a larger surface area than rutile or brookite. In addition, the anatase crystal has stability at relatively lower temperatures than rutile and brookite (Zhang, Zhou, Liu, & Yu, 2014). The UV-Vis diffuse reflectance spectra of synthesized N-doped TiO₂ by peroxo sol-gel is shown in **Figure 2**. The absorption of TiO₂ shifted to 428 nm. The band gap energy calculated using Plank formula with equation $E_g = 1239.8/\lambda$ is 2.89 eV, where E_g is the band-gap energy (eV) and λ is the wavelength of the absorption edges (nm) in the spectrum. The band gap decreases from 3.09 eV to be 2.89 eV as reported by Wellia (Wellia et al., 2018). This change is attributed to the presence of nitrogen in the crystal structure phase of titania (Sacco et al., 2012). This result confirms the ability of photocatalysts to be activated under visible-light.

2. The effect of catalyst dose on phenol degradation by photocatalysis UV and visible-light using N-doped TiO₂

The effect of N-doped TiO₂ catalyst dose on phenol degradation was conducted with variation 5, 10, 15, and 20 mg N-doped TiO₂ by photocatalysis under UV and visible-light for 120 minutes. **Figure 3** shows the degradation of phenol increases with increasing the

number of catalysts. This result was explained by the higher active site, the number of absorbed photons and the amount of produced hydroxyl radical ($\bullet\text{OH}$) (Tang, Huang, Yu, & Tang, 2012). The optimal N-doped TiO_2 catalyst mass obtained is 15 mg with percent degradation 50.85% under UV-light and visible-light by 30.51% for 120 minutes photocatalysis. While the solution becomes a saturation point (turbidity) in addition of N-doped TiO_2 catalyst up to 15 mg. Turbidity in the solution can block the UV-light penetration as a result the reduction on active species ($\bullet\text{OH}$) formation from N-doped TiO_2 catalyst, causing light scattering and the decreasing effectiveness of phenol degradation (Safni et al., 2016). The same result is also reported by Chiou and Juang degrading phenol under 400 W UV-light photocatalysis using Pr-doped TiO_2 as catalyst (Chiou & Juang, 2007).

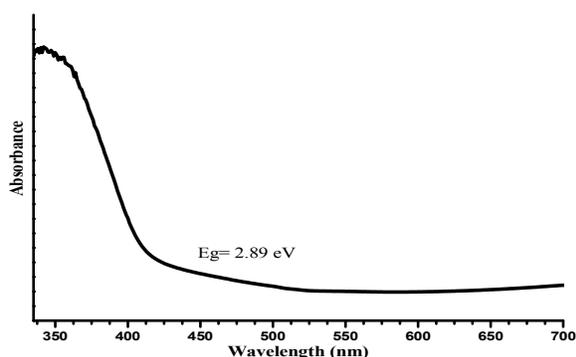


Figure 2. The optical pattern of N-doped TiO_2

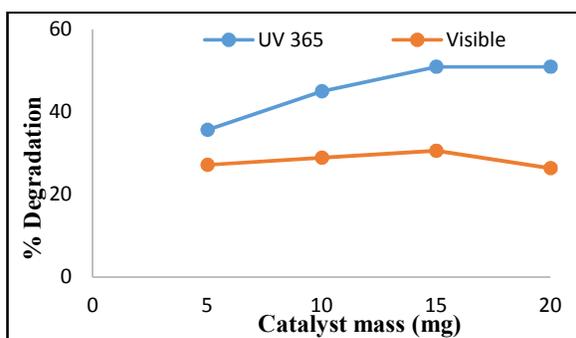


Figure 3. The effect of N-doped TiO_2 catalyst mass (5, 10, 15, 20 mg) on 8 mg/L phenol by under UV and visible light irradiation

3. The effect of N-doped TiO_2 catalyst presence on phenol degradation by photocatalysis UV and visible-light

The phenol degradation is higher in efficiency in presence of N-doped TiO_2 catalyst than without catalyst. The efficiency is found 8.47%, 11.86%, 16.10%, 21.18%, 24.57%, 28.81%, and 33.89% under direct UV photolysis for 30-210 minutes and increases significantly to be 36.44%, 48.31%, 53.39%, 62.71%, 73.72%, 82.20%, and 90.67% in presence of 15 mg N-doped TiO_2 catalyst shown in figure 4. The mechanism phenol reduction without a catalyst is degraded by direct photolysis under

higher energy photon from UV-light. While there are more $\bullet\text{OH}$ radicals formation in photocatalysis system. A photon from UV-light will excite electron of N-doped TiO_2 photocatalyst from the valence band to the conduction one. The generated-hole in valence band reacts with water and produces $\bullet\text{OH}$ radicals as strong oxidizing agents to oxidize phenols into simple compounds such as CO_2 and H_2O (Palmisano, Augugliaro, Pagliaro, & Palmisano, 2007; Shayegan, Lee, & Haghghat, 2018; Wardhani, Purwonugroho, Fitri, & Prananto, 2018).

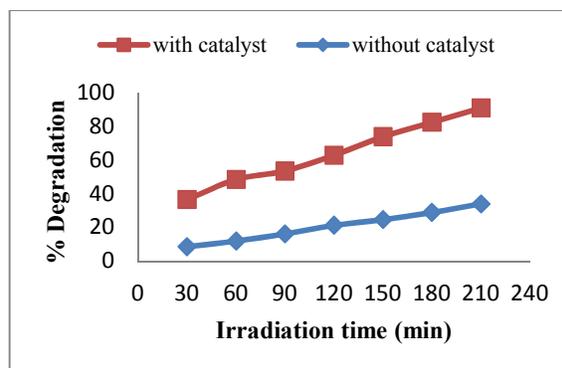


Figure 4. The effect of 15 mg N-doped TiO_2 catalyst presence on 8 mg/L phenol degradation by UV-light irradiation

The phenol was degraded by photolysis with and without catalyst and conducted under two kinds of lamps (UV-light and visible-light) to investigate the effect of energy sources. The largest degradation percentage of phenol under UV-light ($\lambda = 365$ nm) is 33.89% and 90.67% without and with the addition of catalyst for 210 minutes irradiation. This is due to the energy generated from UV-light higher compared to visible-light. The results agree with the Planck's law stating the photon energy and the wavelength are inversely proportional. Figure 5 also proves that N-doped TiO_2 catalyst can be activated under low energy source (visible-light) and can accelerate phenol degradation two folds. The efficiency achieves 67.79% in presence N-doped TiO_2 and only 30.50% without catalyst system (Darzi, Mahjoub, & Sarfi, 2012).

Time is one of the important parameters affecting the amount of organic pollutant degraded. The photocatalysis degradation was conducted over the range 30–210 with constant catalyst dose and initial phenol concentration. As seen in Figure 5, the efficiency of phenol steadily increases by increasing the time. Phenol concentration is reduced from 36.44% to 90.67% when the radiation times were from 30 to 210 minutes. This increase is due to the more effective contact between photon and N-doped TiO_2 catalyst, the more photons absorbed by the catalyst, and the higher production process of holes and $\bullet\text{OH}$ radicals (Safitri, Santoni, Wellia, Khoiriah, & Safni, 2017; Sari, Agustina, Melwita, & Aprianti, 2017). Also, the generated reactive species and phenol could react perfectly by increasing irradiation time (Jonidi-Jafari, Gholami, Farzadkia, Esrafil, & Shirzad-Siboni, 2017).

5. The effect of energy source on phenol degradation by photolysis and photocatalysis

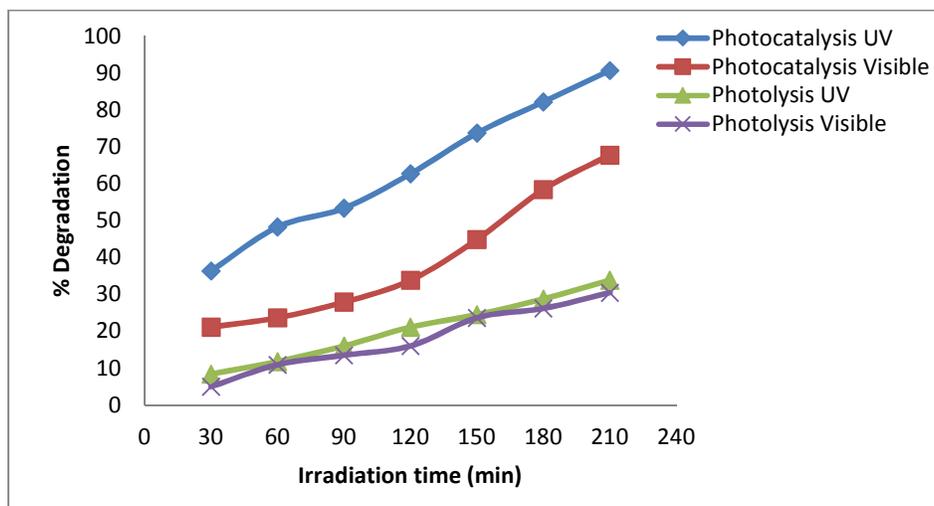


Figure 5. The effect of energy source on 8 mg/L phenol degradation by photolysis and photocatalysis under UV-light and visible-light irradiation

CONCLUSIONS

Phenol was degraded successfully by photocatalysis using N-doped TiO₂ under UV-light and visible-light irradiation. The degradation of phenol was significantly affected by catalyst mass, energy source and irradiation time. Phenol solution with 8 mg/L as initial concentration was degraded by 30.51% and 33.89% under visible-light and UV-light for 210 minutes irradiation respectively. In the same condition, the degradation efficiency increased significantly to be 67.80% and 90.68% in presence of 15 mg N-doped TiO₂. From the results, irradiation using UV-light achieves higher efficiency on phenol degradation than visible-light.

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