

Photocatalytic Degradation of Phenol Using TiO₂-Fe Under H₂O₂ Presence by Visible and Sunlight Irradiation

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Abstract

Phenol is one of the essential organic pollutants released into the environment because of its high stability and toxicity. It is harmful to organisms, environment, and posing a serious threat to human health at low concentration. This research investigated the photocatalytic degradation process of phenol using a TiO₂-Fe catalyst under visible light irradiation and additional H₂O₂. The effect of various conditions process was applied, including different catalyst doses (0.2, 0.4, 0.6, and 0.8 g/L), pH (3, 6, 8, and 11), irradiation times (60, 90, 120, 150, and 210 minutes) and the presence of H₂O₂. The degradation process was studied at an initial concentration of phenol 5 mg/L. This study has been decreasing phenol content (90.51%) with catalyst doses 0.6 g/L sample solution, pH solution 11, reaction time 210 minutes and H₂O₂ concentration 30%. This final phenol concentration after photodegradation under halogen light was 0.18 mg/L, while sunlight irradiation was 0.11 mg/L. This result is below government regulation as per Permen LH RI No. 5/2014 i.e. 0.5 mg/L. Therefore, this process possible to remove phenol in aqueous such as industrial wastewater or other resources.

Keywords: Halogen-ray, hydrogen peroxide, phenol, sunlight, TiO₂-Fe.

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1. INTRODUCTION

Phenols are listed in the US EPA as dangerous substances abandoned in the aquatic environment. It is one of the essential organic pollutants released into the environment because of its high stability and toxicity. Phenol is harmful to the organism, environment, and posing a severe threat to human health at low concentration. According to Indonesia's government regulation, Permen LH RI No. 5/2014, minimum concentration of phenol compounds in wastewater must be below 0.5 mg/L (Menteri *et al.*, 2014). The pharmaceutical industry, petrochemical industry, pesticides, polymeric resin, mine sewage, coal conversion are the primary sources of phenolic pollution (Sufian, 2020). It is a substantial issue to remove them in order to minimize the risks to environments. Several treatments such as adsorption (Luo *et al.*, 2015), advanced oxidation (Bethi *et al.*, 2016), biodegradation and activated sludge, membrane filtration, and photocatalytic degradation have already been established

(Aryani, 2011 ; Zul *et al.*, 2020). However, photocatalytic degradation and adsorption are considered the most effective treatment techniques (Heydaripour *et al.*, 2018; Linda J Kusumawardani *et al.*, 2020). These are simple, high performance for the elimination of phenol, and available at low cost.

TiO₂ has the ability to oxidize large amounts of harmful organic pollutants into non-toxic products and promote as a potential photocatalyst. Because of its ability to oxidize large amounts of harmful organic pollutants into non-toxic products, TiO₂ has a relatively moderate to low bandgap energy between the valence and conduction bands. In addition, it has been promoted as a potential photocatalyst that can be used for the degradation of phenol compounds. However, TiO₂ works at the wavelength of UV light to activate photocatalysts. Gota *et al.*, 2014 reported 0.2 g TiO₂ in a 1-liter sample solution gives the optimum effect for phenol reduction (Sundaramurthy, 2014). Kusumawardani and Syahputri (2019) reported that the structural

and optical properties of TiO₂ differ from the addition of Fe(III) in the photocatalytic process under visible light (L J Kusumawardani & Syahputri, 2019). Kusumawardani and Syahputri (2020) have reported the high degradation for paraquat dichloride as an organic compound using TiO₂-Fe, which reached 98.4% by catalyst TiO₂-Fe from 30 mg/L to 0.2 mg/L only for 75 minutes (Linda J Kusumawardani *et al.*, 2020). Iron (III) is a promising dopant into TiO₂ crystal lattice due to ionic radius, where the Fe radius is 0.64 Å and Ti is 0.745 Å (Sood *et al.*, 2015).

The present work aims to develop conditions process for phenol removal using TiO₂-Fe catalyst and the presence of H₂O₂. The TiO₂-Fe catalyst, with the amount of Fe³⁺ dopant by 10% (w/w), was prepared by the sol-gel method, as a previous report by our group research (L J Kusumawardani & Syahputri, 2019). The various operating conditions including catalyst doses (0.2, 0.4, 0.6, and 0.8 g/L), pH (3, 6, 8, and 11), and reaction times (60, 90, 120, 150, and 210 minutes). Phenol removal will be evaluated under halogen light and measured by spectrodirect Lovibond. Then, the optimum operating process will be applied under sunlight irradiation.

2. MATERIALS AND METHODS

Materials and Instruments

Materials used are phenol GR for analysis and H₂O₂ 30% were purchased from Merck, NaOH and HCl for pH adjusting, Aquadest, and Halogen Lamps (Philips, 1000 watt) as a visible light source. Spectrodirect from Lovibond was used for determining the concentration of phenols.

Procedures

In this experiment, catalyst TiO₂-Fe was prepared by the sol-gel method, with the amount of Fe³⁺ dopant by 10% (w/w) as reported by our previous research (L J Kusumawardani & Syahputri, 2019). Photocatalytic degradation was carried out by adding TiO₂-Fe to the sample solution with a concentration of 5.00 mg/L phenol compound. The light sources used are halogen and sunlight. The reaction vessel is equipped with magnetic stirring. Photocatalytic degradation of phenol was evaluated with the presence of 2.5 ml H₂O₂ and measured by Spectrodirect Lovibond. The effect of various condition

process was applied i.e., different catalyst dosages (0.2, 0.4, 0.6, and 0.8 g/L), pH (3, 6, 8, and 11), reaction times (60, 90, 120, 150, and 210 minutes). The optimum condition for phenol removal under halogen light was selected as the optimum goal for photocatalytic degradation under sunlight exposure. Figure 1. shows a photocatalytic degradation reactor model. The percentage of photocatalytic activity was calculated using Eq. (1), where % D is the percentage of degradation, C_o is the initial concentration of the sample before halogen and sunlight irradiation and C_t is the final concentration after irradiation under halogen and sunlight at various condition process (Catalyst Dosages, pH, and time reaction) under H₂O₂ presence as an independent variable.

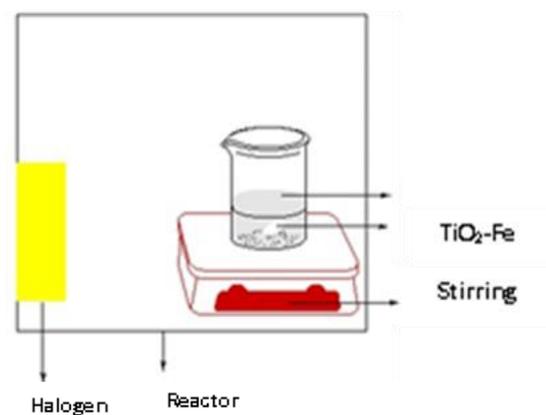


Figure 1. Reactor model for photocatalytic degradation processes, under halogen light

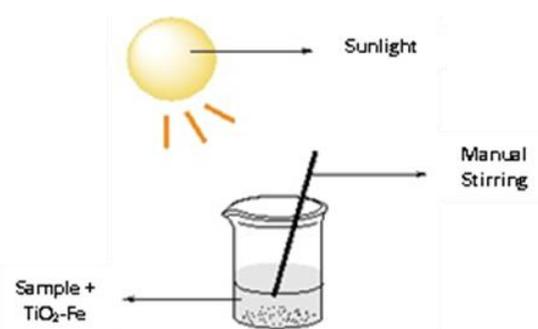


Figure 2. Photocatalytic degradation processes, under sunlight

$$\%D = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

3. RESULTS AND DISCUSSION

Prior to the photodegradation study at various operation conditions, the effect of 2.5 ml H₂O₂ addition on photocatalytic

degradation of phenol was investigated. This study was carried out at an initial phenol concentration of 5.00 mg/L, under halogen light for 60 minutes. The phenol removal is illustrated in Fig. 3. This study showed that higher degradation was demonstrated by H₂O₂ presence. According to Table 1. The phenol successfully degraded by 45.01 %, while the photodegradation without H₂O₂ was only 17.17 %. The result shows the faster photocatalytic degradation is caused by H₂O₂ which acts as accelerators in the degradation process. It leads to higher formation of •OH radicals. The OH• radicals are the most powerful and important oxidizing species, which effectively oxidized various organic compounds into CO₂ and H₂O during the photodegradation process. The oxidizing agent is highly responsible for the degradation of such organic compounds by producing OH• radicals, which leads to increase the quantum yield. The photocatalytic degradation in the presence of H₂O₂ using catalyst TiO₂-Fe have an advantage by the OH• radicals by H₂O₂ dissociation (Wicaksono *et al.*, 2020). Phenol degradation enhancement could be primarily credited to the speedily reduction of recombination of electrons hole pairs over the photocatalyst surface though the formation of more OH• (Zul *et al.*, 2020).

Table 1. Comparison on Photocatalytic Activity between with and without H₂O₂

Experiment	Co (mg/L)	Ct (mg/L)	% Degradation
With H ₂ O ₂	4.91	2.7	45.01
Without H ₂ O ₂	4.95	4.1	17.17

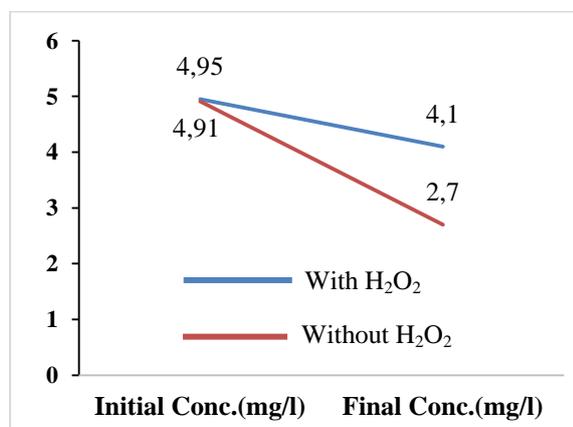


Figure 3. Phenol degradation in the presence of H₂O

The catalyst dose is one of the important factors affecting the photocatalytic degradation process (Mohamed *et al.*, 2019). In this study, the effect of catalyst dosages was carried out by using catalyst amounts 0.2, 0.4, 0.6, and 0.8 g/L at an initial concentration of 5 mg/L. The result was shown in Fig. 4. It shows the highest degradation efficiency at 0.6 g/L during 1-hour halogen lamp exposure. This catalyst dose demonstrated the sufficient number of active sites could be provided. We also reported that the maximum catalyst dose will increase the photocatalytic efficiency due to the increasing number of surface active sites of the catalyst. Meanwhile, the excessive amount of catalyst dose will cause turbidity in the solution and agglomeration between particles. Hence, it will reduce the light absorption on the catalyst surface, thus decreasing the light penetration and photo absorption efficiency. Hence, in the next operating conditions study, the addition of H₂O₂ was used as an independent variable.

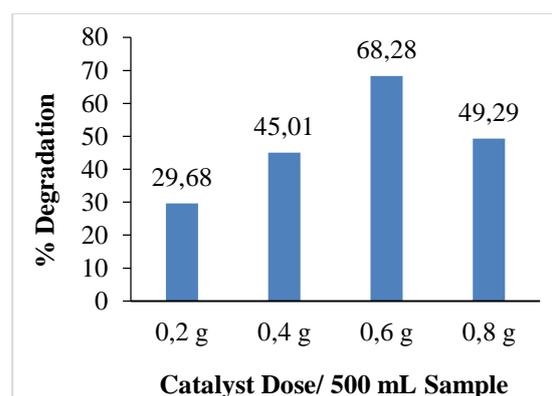


Figure 4. Effect of catalyst dosages, initial phenol conc = 5.00 mg/L

The effect of pH on reducing phenol concentrations was carried out at various pH (3, 6, 8, and 11). The results are shown in Fig. 5. It shows that the removal in phenol levels will increase with increasing pH due to the presence of OH⁻ ions. Degradation efficiency of phenol was improved during 1 hour, respectively at pH 3 < pH 6 < pH 8 < pH 11, which was 33.62; 39.08; 41.19; and 51.49%. pH alkaline causes more degradation of phenol oxides than phenol. Meanwhile, an acidic pH causes the phenol to break down slightly. This is consistent with Gota *et al.* (2014), who reported that increasing the pH value can increase the efficiency of removing phenol in

solution (Sundaramurthy, 2014). Phenol was converted to phenoxide ion that more degradable than phenol. A simple scheme is reported in Fig. 6 to represent phenol can lose a hydrogen ion because the phenoxide ion formed is stabilised to some extent. This seems contrary to (Borji *et al.*, 2014) which reported the highest degradation efficiency occurred at acidic condition. However, it also stated the higher phenol degradation occur at alkaline condition due to the presence of phenol molecules as negatively charged phenolate species which more reactive than phenol molecules and can be cause of more degradation of phenol. According to the result, this study showed the high concentration of OH⁻ in the solution was not prevent the penetration of visible light to reach the catalyst surface.

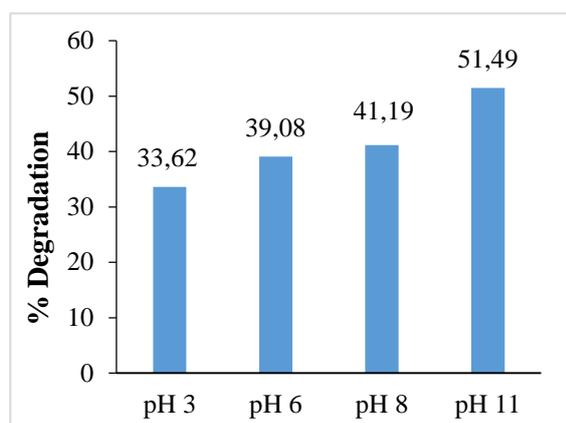


Figure 5. Effect of pH solution, initial phenol conc = 5.00 mg/L



Figure 6. Mechanism of Phenol Converted to Phenoxide Ion

Fig. 7 shows the relative changes in phenol removal with TiO₂-Fe with respect to time was monitored by increasing the reaction time under the same condition, i.e., catalyst dose 0.6 g/L, at pH 11 and the addition of H₂O₂ over 210 minutes period under a halogen lamp. The photolysis process achieves the degradation efficiency during 210 minutes' radiation time. The phenol compounds were successfully degraded 96.25%. This result

shows that radiation time has a significant effect and an important aspect of the overall photocatalytic process. It can be observed that the longer exposure time will degrade more phenol, and the efficiency degradation will increase. The final concentration of phenol after a degradation process for 210 minutes reached 0.18 mg / L. This is in accordance with the Permen LH RI No. 5/2014, which states that the maximum phenol levels in wastewater allowed is 0.5 mg / L.

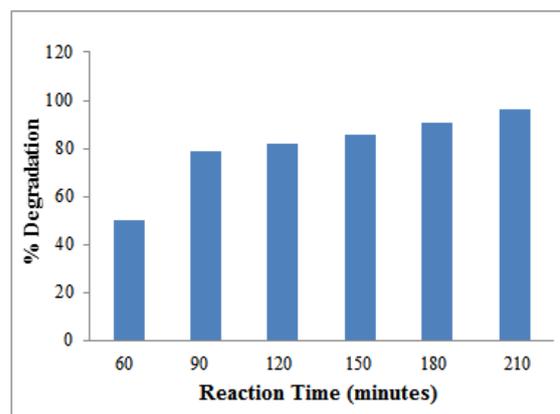


Figure 7. Effect of irradiation time, initial phenol conc = 5.00 mg/L

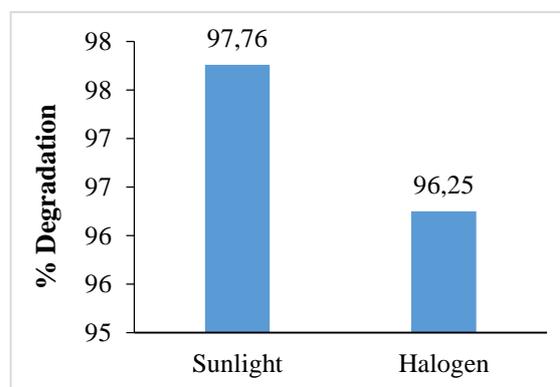


Figure 8. Photocatalytic degradation of phenol under halogen and sunlight irradiation, (initial phenol conc. = 5.00 mg/L; pH 11; catalyst dosage 0.6 g/L solution; and 210 minutes time reaction).

The optimum operating process, such as pH, catalyst dose and time reaction applied under sunlight irradiation as the final stage of this research. Fig.8. shows that degradation product with halogen and sunlight irradiation for 210 minutes has been degraded by 96-97% from 5 mg/L to 0.11 – 0.11 mg/L. It implies the photon energy generates a stronger oxidizing agent, •OH radical, which will assist in phenol compounds degradation. During the

photodegradation process, sunlight intensity gives a different phenol reduction level due to the amount of •OH radical. The sunlight intensity received plays a major role in the photodegradation process. This study was conducted in the late morning, 10.30 a.m to 02.00 p.m at wet season falls in Bogor, Indonesia in October-November. This result shows that 0.6 g/L of TiO₂-Fe under H₂O₂ presence was sufficient to degrade 500 ml of phenol at pH 11 for 210 minutes under sunlight. It shows the duration of irradiation improves the degradation efficiency of waste, the longer the irradiation time, the more the composition will be degraded.

4. CONCLUSION

The summary of the results of the phenol photodegradation test under halogen and sunlight irradiation reached 96-97% for 210 minutes using catalyst TiO₂-Fe at pH 11, catalyst dose 0.6 g/L and the presence of H₂O₂. This result implied the acceptable utilized photoreactor and an advantage from H₂O₂ dissociation. It is a promising and easy work in environmental water treatment from toxic molecule such as phenol.

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