

## The Treatment of Phenol in Batik Wastewater by TiO<sub>2</sub>-Copper Oxide (CuO And Cu<sub>2</sub>O) Photocatalyst

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### Abstract

Phenol is an organic material in batik waste that must be processed before disposal because it is carcinogenic and can reduce dissolved oxygen levels. The method used to treat phenol is Advanced Oxidation Process (AOPs). The AOPs method is a waste treatment technology with free radicals to degrade pollutants into CO<sub>2</sub> and H<sub>2</sub>O. Oxidizing agents are hydroxyl radicals ( $\bullet$ OH) produced by certain materials, one of which is TiO<sub>2</sub>. Although proven capable of degrading organic pollutants, the use of TiO<sub>2</sub> still encounters a reasonably significant band gap energy constraint for TiO<sub>2</sub> (3.2 eV). The modifications carried out in this study were the addition of copper (Cu) dopants to reduce the TiO<sub>2</sub> band gap and electron trapping to prevent electron and hole recombination. The synthesis of TiO<sub>2</sub>-Cu oxide was carried out by deposition method using TiO<sub>2</sub> and CuCl<sub>2</sub>·5H<sub>2</sub>O as Cu precursors. The results showed that the addition of Cu to TiO<sub>2</sub> reduced the band gap energy up to 2.25 eV. The data showed that phenol treatment using TiO<sub>2</sub>:Cu (98:2) for 6 hours at pH 2, under the influence of a tungsten lamp, could reduce phenol up to 98.03%. The photodegradation process with TiO<sub>2</sub>:Cu ratio and the same pH can occur more quickly with a UV lamp for 2 hours. The amount of phenol that can be degraded under these conditions is 98.23%.

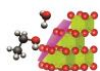
**Keywords:** Phenol, TiO<sub>2</sub>, TiO<sub>2</sub> doped Cu Oxide

### 1 Introduction

Batik is the ancestral heritage of Indonesia nation that UNESCO has recognized. This international recognition is considered to have a positive impact on the growth of the creative industry. The research results by Subekti et al. [1] stated at least 6120 units of UMKM Batik with a total production of 4.89 trillion rupiahs per year. Although considered to have a positive impact on economic growth, the development of the batik industry still faces several challenges, one of which is environmental pollution. The batik production process uses clean water up to 25-50 m<sup>2</sup> per meter of fabric, and 85% of the total clean water becomes liquid waste during the batik process [2]. In general, the pollutants in batik wastewater consist of dyes and dissolved organic substances [3]. One of the organic pollutants that focus in this research is phenol. The phenol content in batik wastewater comes from wax

dissolution at the 'pelodoran' step. In this step, the wax will be dissolved in water and dissolve the phenolic compounds with their derivatives. Phenol dissolved in water bodies then causes a decrease in dissolved oxygen levels, which causes the death of aquatic biota. Tests on waste liquid batik conducted by Ayuningtyas et al. [2] showed that the phenol content in batik wastewater from one of UMKM in Yogyakarta could reach 0.009 mg/L. This value certainly exceeds the environmental quality standard threshold required in the Decree of the Minister of Environment No. 5 of 2014. The potential for pollution and its impact makes the development of phenol waste treatment techniques interesting to study.

The phenol waste treatment technique studied in this research is Advanced Oxidation Processes (AOPs). AOPs is a waste treatment technology with free radicals to degrade organic and inorganic pollutants into CO<sub>2</sub> and H<sub>2</sub>O [2,3]. The free



radicals used as oxidizing agents are hydroxyl radicals ( $\bullet\text{OH}$ ) produced through photocatalytic reactions involving semiconductor materials,  $\text{TiO}_2$ . Dong et al. [4] stated that  $\text{TiO}_2$  irradiated by UV light would transfer electrons from the valence band to the conduction band. Electron excitation causes the formation of *holes* ( $h^+$ ) in valence band, while the conduction band will be filled with electrons. The oxidation potential of  $h^+$  in valence band is enormous so that it can oxidize water into hydroxyl radicals ( $\bullet\text{OH}$ ). This hydroxyl radical ( $\bullet\text{OH}$ ) acts as strong oxidizing agent that will oxidize organic substances into water, mineral acids, and carbon dioxide.

Although capable of degrading organic pollutants [5–7],  $\text{TiO}_2$  in wastewater treatment techniques still encounters obstacles. One of them is the band gap energy of  $\text{TiO}_2$ , which is quite large (3.2eV), causing the use of sunlight which only contains a small portion of UV light  $\pm$  5% become less efficient. Furthermore, the use of UV lamps during the catalytic process is considered inefficient because it provides high energy consumption, thereby increasing the operating costs of the  $\text{TiO}_2$  photocatalytic system. To increase catalytic activity,  $\text{TiO}_2$  used in this study was modified with the addition of copper (Cu) as the dopant. Cu metal was chosen as the dopant because Cu is not easily oxidized and has a high reduction potential (0.34 volts). It is estimated that Cu metal can effectively trap electrons and minimize the possibility of electron-hole recombination.

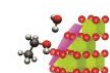
The results of Zhou et al. [8] showed that 1% Cu dopants in  $\text{TiO}_2$  used in Dye-Sensitized Solar Cells (DSSC) reduced the band gap energy of  $\text{TiO}_2$ , which had an impact on increasing the electric current density of solar cells up to 19.45%. Pongwan et al. [9] conducted a study on the effectiveness of Cu dopants on the demineralization ability of organic compounds by  $\text{TiO}_2$ . The results showed that  $\text{TiO}_2$  doped with 2% mol Cu was able to increase the performance of  $\text{TiO}_2$  in the demineralization of oxalic acid and formic acid under visible light. Slamet has also conducted phenol demineralization [10]. In this study,  $\text{TiO}_2$ -Cu was synthesized by the wet impregnation method using  $\text{TiO}_2$  P25 and Cu precursors (copper acetate, copper chloride, copper nitrate, and copper sulfate). The result is that the effectiveness of  $\text{TiO}_2/\text{CuO}$  synthesized from copper acetate precursor has the highest activity, with 100% Cr(VI) metal reduction conversion and phenol degradation conversion reaching 93.81%.

In this research,  $\text{TiO}_2$ -Cu photocatalyst was synthesized by the photodeposition method. The principle of the deposition method is photoreduction of metal ions which the metal occupies on the  $\text{TiO}_2$  surface. This deposition method is expected to strengthen the interaction between the dopants and  $\text{TiO}_2$  surface so that the distribution of dopant particles is more scattered than the catalyst synthesized using wet impregnation method. The source of  $\text{TiO}_2$  in this study used  $\text{TiO}_2$  (Merck), while the source of Cu dopant came from copper chloride salt ( $\text{CuCl}_2 \cdot 5\text{H}_2\text{O}$ ).

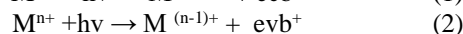
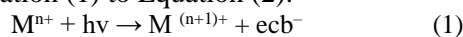
Chemical analysis to determine the characteristics of the  $\text{TiO}_2$  photocatalyst modified by photodeposition method in this study has been carried out. Diffuse Reflectance Spectroscopy (DRS) analysis of  $\text{TiO}_2$  modified with Cu showed that adding Cu increased the absorption at 400-500 nm and 600-800 nm regions. The absorption wavelengths for  $\text{TiO}_2$ -Cu (100:0), (99:1), (98:2), (97:3), and (96:4) are 356.55 nm, 492.40 nm, 551, 47 nm, 523.55 nm, and 528.01 nm [9]. The absorption at 400-500 nm is the absorption of  $\text{Cu}^{2+}$  clusters from CuO compounds [11]. Furthermore, 600-800 nm absorption appears due to the  $2\text{E}_g\text{-T}_{2g}$   $\text{Cu}^{2+}$  transition in the  $\text{TiO}_2$  octahedral configuration [12]. Based on the wavelength value, it is known that the Cu dopant changes the optical absorption properties of  $\text{TiO}_2$  caused by crystal defects due to the substitution of  $\text{Ti}^{4+}$  by  $\text{Cu}^{2+}$  on the  $\text{TiO}_2$  crystal lattice.

$\text{Cu}^{2+}$  ions present in bulk  $\text{TiO}_2$  caused rearrangement of atomic positions in the  $\text{TiO}_2$  lattice due to differences in the radii of  $\text{Ti}^{4+}$  and  $\text{Cu}^{2+}$ . The rearrangement of the  $\text{TiO}_2$  molecule will eventually cause lattice deformation, which can affect the electronic structure of  $\text{TiO}_2$  and reduce the band gap energy [13]. The band gap energy obtained from  $\text{TiO}_2$  analysis (Merck),  $\text{TiO}_2$ -Cu (100:0), (99:1), (98:2), (97:3), and (96:4) is 3, 48eV: 2.52eV: 2.25eV: 2.37eV: 2.35eV. Research data have also shown that the band gap energy from photocatalyst synthesized by photodeposition method is smaller than band gap energy from photocatalyst synthesized using wet impregnation method [8].

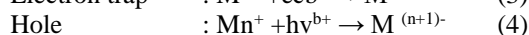
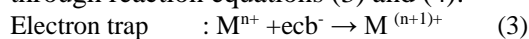
X-Ray Diffraction (XRD) analysis showed that the Cu dopant synthesized by the deposition method appeared as an oxide, CuO and  $\text{Cu}_2\text{O}$  [7,14,15]. CuO and  $\text{Cu}_2\text{O}$  have narrow band gaps, 1.2 and 2 eV [16]. The metal dopants will interact with  $\text{TiO}_2$  in the lattice structure to form new energy levels that reduce  $\text{TiO}_2$  band gap. The



reaction mechanism that may occur is shown in Equation (1) to Equation (2).



M and  $Mn^+$  in Equations (1) and (2) represent metals and dopant metal ions. The transfer of electrons or holes between metal ions and  $TiO_2$  can modify the electron-hole recombination through reaction equations (3) and (4).



Based on these conditions, the charge separation between holes and electrons is effective, and electron-hole recombination in  $TiO_2$  can be prevented. In the end, the photocatalytic activity of  $TiO_2$  can be increased [16]. To prove this hypothesis, the performance of  $TiO_2$ -Cu was tested in degrading phenol in batik waste. The focus of the study in this research is study the mole ratio of  $TiO_2$ :Cu, contact time, and pH on the effectiveness of  $TiO_2$ -Cu in degrading phenol from batik waste.

## 2 Research Method

### Material

$TiO_2$  (Merck, pa),  $CuCl_2 \cdot 5H_2O$  (Merck, pa), aqua DM (Bratachem), aquadest, phenol (Merck, pa),  $NH_4OH$  (Merck, pa), 4-aminoantipyrine (Merck, pa), phosphate buffer pH 8,  $K_3Fe(CN)_6$  (Merck),  $NaOH$  (Merck, pa),  $HCl$  (Merck, pa),  $NaOH$  (Merck, pa), perchloric acid (Merck, pa). Batik liquid waste is obtained from a batik center in Sokaraja, Banyumas, Central Java. The pre-treatment process is carried out using Whatman filter paper to separate liquid waste from solids and mucus.

### $TiO_2$ -Cu photocatalyst preparation [7]

$TiO_2$ -CuO photocatalyst was synthesized by the photodeposition method. The doping process was carried out by 3 grams of  $TiO_2$  and 100 mL of aquademine to form a suspension. The pH of the suspension was adjusted to 3 by adding 10% perchloric acid. After the pH of the suspension was matched, the solution was added with  $CuCl_2 \cdot 5H_2O$  in mole ratios 1, 2, 3, and 4 to  $TiO_2$ . The mixture was irradiated with a UV lamp for 3 hours and dried on a hot plate or oven. The dry solids were ground with a mortar and calcined at  $400^\circ C$  for 6 hours in a furnace.

### Photodegradation of Phenol

Testing the effectiveness of phenol photodegradation by  $TiO_2$  (Merck) and  $TiO_2$ -Cu was carried out with photon sources from UV lamps and tungsten lamps. A 250 mL beaker (Pyrex) was filled with 200 mL of batik waste, filtered and added with 0.2 g  $TiO_2$ -Cu with a  $TiO_2$ :Cu mole ratio of 99:1; 98:2; 97:3; and 96:4. The solution mixture was allowed to stand for 30 minutes in dark condition. After that, the solution was irradiated with a UV lamp while stirring. The photooxidation reaction used in this study is displayed in photocatalytic reactor as shown in Figure 1. The photocatalytic reactor is made from wood material with dimensions of 50x50cm. Radiation sources using of ultraviolet lamps and eight tungsten lamps are placed on the left, top, and bottom sides (2 lamps on each side). Tests for the phenol adsorption process by  $TiO_2$  and  $TiO_2$ -Cu were carried out by placing a system consisting of a mixture of  $TiO_2$  and batik liquid waste in a dark room.

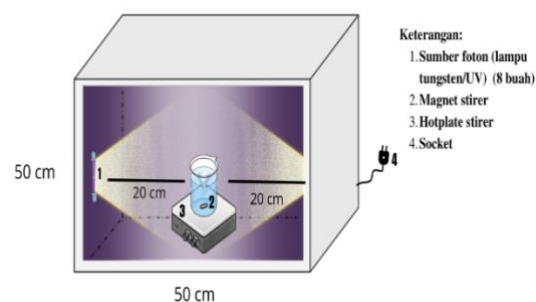
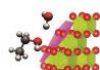


Figure 1. Photocatalytic Reactor

### Phenol Analysis

Phenol analysis was performed using spectrophotometry with the addition of 4-aminoantipyrine reagent. The principle of determining phenol using this method is the formation of quinoneimine by phenol and 4-aminoantipyrine to form a reddish-brown color with the addition of potassium ferricyanide  $K_3Fe(CN)_6$  under alkaline conditions. The maximum wavelength of phenol used in this study was 506.2, according to the wavelength scanning results shown in Figure 2.



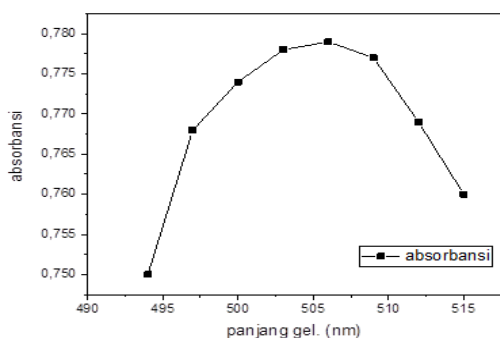


Figure 2. Phenol Wavelength Scanning

The percentage decrease in phenol content in wastewater is calculated by equation (5)

$$\%FD (\%) = \frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \times 100\% \quad (5)$$

%FD is the percentage decrease in phenol content,  $C_{\text{initial}}$  is the initial phenol concentration (30 minutes after settling), while the  $C_{\text{final}}$  is the phenol concentration after the photodegradation process.

### 3 Result and Discussion

The effect of  $\text{TiO}_2$ :Cu mole ratio on  $\text{TiO}_2$ -Cu effectivity in degrading phenol was carried out by varying the mole ratio of  $\text{TiO}_2$  and Cu to (99:1); (98:2); (97:3); and (96:4). Data on the percentage decrease in phenol content after 5 hours of reaction is shown in Figure 3.

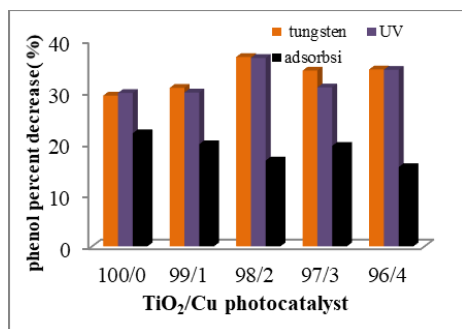


Figure 3. Decrease in Phenol Levels in Various  $\text{TiO}_2$ :Cu variations with UV Lamps and Tungsten lamps as photon sources.

Figure 3 shows an increase in the photocatalytic activity of  $\text{TiO}_2$  in visible light region after modification with the addition of Cu. Percentage of decrease in phenol content by  $\text{TiO}_2$ -Cu (99:1), (98:2), (97:3), and (96:4), which are: 30,79; 36,79; 34,15; and 34,37% under tungsten lamp, while the percentage decrease in phenol content under UV lamp (29,89%; 36,60%; 30,88%; and 34,30%). The research data showed

that increasing the mole ratio of  $\text{TiO}_2$ :Cu from 99:1 to 98:2 increased  $\text{TiO}_2$  effectivity in degrading phenol. Increasing the number of Cu moles generally affects the amount of metal oxide formed on  $\text{TiO}_2$  surface. It affects the decrease in  $\text{TiO}_2$ -Cu band gap energy and then impacts the photocatalytic activity of  $\text{TiO}_2$  in visible light.

The analysis of  $\text{TiO}_2$  Cu-modified described previously stated that Cu added to  $\text{TiO}_2$  appears as copper oxide,  $\text{CuO}$  and  $\text{Cu}_2\text{O}$ , which have a narrower band gap energy than  $\text{TiO}_2$  (Merck). Due to the small band gap value, it is estimated that the location of the  $\text{CuO}$  valence band is above the  $\text{TiO}_2$  valence band, while the  $\text{CuO}$  conduction band is below the  $\text{TiO}_2$  conduction band (see Figure 4).

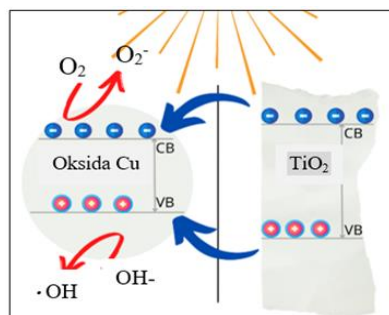
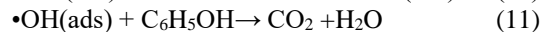
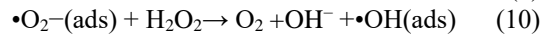
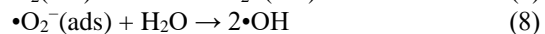
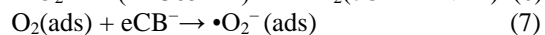
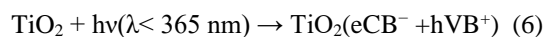
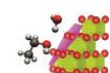


Figure 4. Modification of  $\text{TiO}_2$  Band Gap Energy Levels due to Metal Dopants [17]

The hole from the valence band of  $\text{TiO}_2$  will be transferred to the  $\text{CuO}$  valence band. That is used to oxidize water adsorbed on  $\text{TiO}_2$  surface to form hydroxyl radicals ( $\cdot\text{OH}$ ). In addition, electrons from the conduction band of  $\text{TiO}_2$  will be transferred to the conduction band of  $\text{CuO}$ . These electrons are used to reduce oxygen adsorbed on  $\text{TiO}_2$  surface to superoxide anion ( $\cdot\text{O}_2^-$ ). The hydroxyl radicals ( $\cdot\text{OH}$ ) and superoxide anions ( $\cdot\text{O}_2^-$ ) that have been formed will be used to oxidize phenol according to Equations 6 to 11 [18].



However, the amount of dopant exceeding the optimum condition can decrease the photocatalytic activity, as occurs when adding Cu moles to  $\text{TiO}_2$  up to 4:96. It can be due to localized



d-electron conditions in the TiO<sub>2</sub> band gap, which is the center of recombinant electrons and holes [19].

### Optimum Contact Time

The second parameter studied in this research is contact time. Phenol photodegradation test was carried out with TiO<sub>2</sub>-Cu (98:2) photocatalyst. The phenol percentage photodegradation data on the effect of contact time is shown in Figure 5. Based on the graph, it can be seen that the optimum contact time for the phenol photodegradation process using a TiO<sub>2</sub>-Cu (98:2) photocatalyst with a tungsten lamp is 6 hours. The optimum contact time for Phenol degradation by UV lamp is 2 hours.

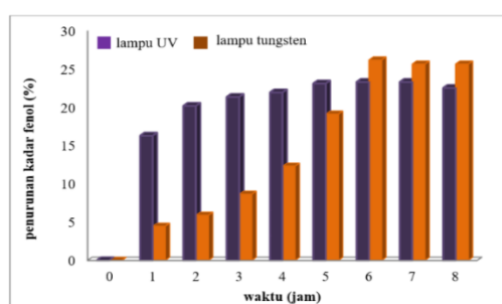


Figure 5. Graph of Percent Decrease in Phenol Levels by TiO<sub>2</sub>-Cu (98:2) at Various Times

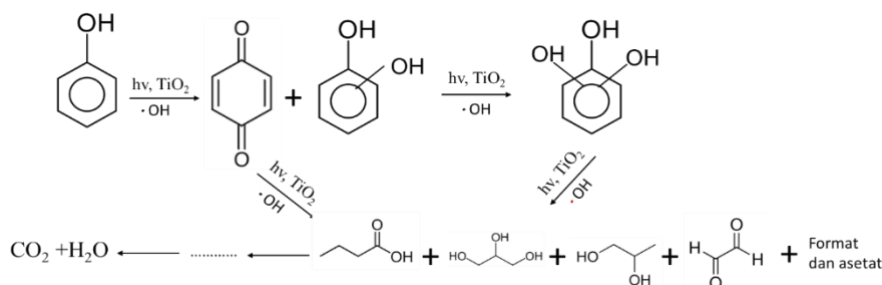


Figure 6. Phenol Oxidation Reaction by Hydroxyl Radicals [20]

### Determination of maximum pH on medium

The medium pH value is a key in photocatalytic reactions because it will affect the penetration ability of a compound on the photocatalyst surface. Determination to obtain the maximum pH in the photodegradation of phenol with TiO<sub>2</sub>-Cu was carried out by varying the pH of the sample solution to 2; 4; 7; 11; and 13 by adding HCl 1M or NaOH 1M. After the pH of the solution was matched, the sample solution was added with TiO<sub>2</sub>-Cu (98:2) photocatalyst, and the photocatalytic reaction was carried out during the optimum contact time. The phenol degradation

In general, if the irradiation time is longer, then the photocatalyst absorbs more photon energy so that the hole formation process that plays a role in forming •OH radicals on the photocatalyst surface is more optimal. The greater number of •OH radicals will increase the percentage of phenol that can be degraded into hydroquinone and p-benzoquinone. After a certain period, the rate of phenol degradation decreases. It is because •OH is also used to oxidize further intermediate compounds whose amount increases with increasing reaction time. Hydroquinone is oxidized to benzanetriol (1,2,4-Benzenetriol and 1,3,5-Benzenetriol). These compounds then undergo further oxidation into aliphatic compounds, such as glycerol, glycol, ethanediol, and butanoic acid, which undergo continuous oxidation reactions to produce CO<sub>2</sub> and H<sub>2</sub>O molecules as final products. Moreover, the compound and p-benzoquinone were oxidized directly to aliphatic compounds, CO<sub>2</sub>, and H<sub>2</sub>O. Phenol degradation pathways that may occur in photocatalytic reactions using TiO<sub>2</sub> are shown in Figure 6 [20].

results with a photon source of tungsten light and UV light are shown in Figure 7.

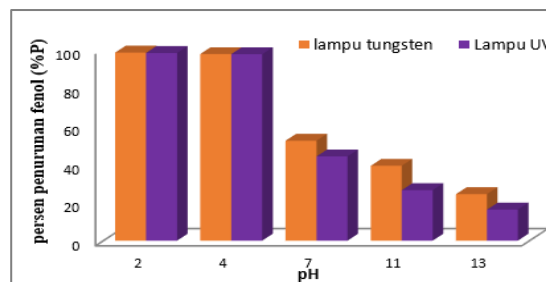


Figure 7. Graph of Percent Decrease in Phenol Levels by TiO<sub>2</sub>-Cu (98:2) at Various pH

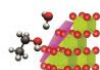
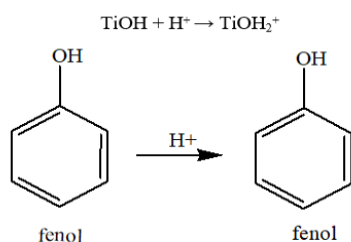


Figure 7 shows that a solution of pH 2 gave the maximum percent reduction in phenol compared to a solution with pH of 4; 7; 11; and 13. The decrease in phenol content at pH 2 reached 98.23% with a photon source from a tungsten lamp and 98.03% under UV light. Percent decrease in phenol content at pH 4; 7; 11; and 13 using a tungsten lamp is 97.50%; 52.20%; 39.10% and 24.30%, while with UV lamp it is 97.40%; 44,00%; 26.40%; and 16.20%.

TiO<sub>2</sub> will be negatively charged in alkaline conditions. When the degradation is carried out in alkaline medium, there will be repulsion between the TiO<sub>2</sub> surface and phenolic ions. It resulted in the phenol binding process on the surface of TiO<sub>2</sub> being inhibited. When the phenol binding on the catalyst's surface is inhibited, the degradation process will be slow. Otherwise, when the degradation process is carried out under acidic conditions, phenol tends to be found as a neutral compound while the surface of TiO<sub>2</sub> is positively charged (Figure 8). It will facilitate the occurrence of electrostatic forces compared to the alkaline state. If more phenol is bound to the TiO<sub>2</sub> surface, the phenol degradation process will be more effective.



**Figure 8.** The chemical structure of TiO<sub>2</sub> and phenol in acidic pH

#### 4 Conclusion

TiO<sub>2</sub>-Cu modified activity result showed that phenol photodegradation with TiO<sub>2</sub>: Cu (98:2) for 6 hours at pH 2 under tungsten lamp rays could reduce phenols up to 98.03%. The photodegradation process with the same TiO<sub>2</sub>:Cu ratio and pH can take place faster for 2 hours. The amount of phenols that can be degraded under these conditions is 98.23%.

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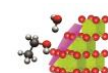
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