Effect of H$_2$O$_2$ Addition on the Photocatalyst Properties of Ag$_3$PO$_4$ for Methylene Blue Photodegradation

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Abstract

In this work, a facile enhanced property of Ag$_3$PO$_4$ photocatalyst using H$_2$O$_2$ for methylene blue photodegradation has been conducted. Ag$_3$PO$_4$ photocatalyst was synthesized using the co-precipitation method. Then, the photocatalytic activity and stability of Ag$_3$PO$_4$ were tested in the methylene blue degradation under the addition of an H$_2$O$_2$ 30% solution. According to the results, the prolonged photocatalysis reaction led to a decrease in the catalysis ability of the Ag$_3$PO$_4$ photocatalyst. Meanwhile, the addition of 5 mL of H$_2$O$_2$ (AH-10% sample) tends to enhance the stability of Ag$_3$PO$_4$ photocatalyst with the dye removal percentage and recycling test were up to 90.3% and three recycle runs, respectively. The low stability of Ag$_3$PO$_4$ might be due to the catalyst photo-corrosion through Ag$^+$ reduction. This research suggests that H$_2$O$_2$ is beneficial to inhibit the photo-corrosion of Ag$_3$PO$_4$ photocatalyst, even though released Ag ions that were caused by the excess addition of H$_2$O$_2$ oxidizing agent should be considered.

Keywords: Ag$_3$PO$_4$; H$_2$O$_2$ compound; methylene blue; photocatalysis; photocatalyst stability

Introduction

Recently, silver phosphate or Ag$_3$PO$_4$ has been intensively investigated for degrading organic and inorganic contaminants, and microorganism deactivations. This is caused by its high quantum yield (the amount of reactant consumed to the amount of photon absorbed using photocatalyst) of more than 90%. It can absorb visible light lower than 530 nm with band gap energy of 2.2-2.5 eV, and high photooxidation ability under visible light illumination (Joo, 2006; Yi et al., 2010; Bai et al., 2013; Hewer et al., 2014; Luo et al., 2014; Sulaeman et al., 2016).

Based on the previous literature, we summarize that there are three major studies or explorations in the development of Ag$_3$PO$_4$ photocatalyst for dye and wastewater treatments (Chen et al., 2014; Ji et al., 2015; Diao et al., 2019; Chen et al., 2020). First, photocatalysis ability enhancement. Second, material stability. The last is precursor’s usage efficiency by considering the use wisely of the costly silver compound during the Ag$_3$PO$_4$ synthesis. To fulfill the three studies mentioned above, researchers devote themselves to designing an efficient and effective pathway of Ag$_3$PO$_4$ fabrication. It is composite materials, morphology design, defect engineering, support material...
combinations, doping strategy, reaction system, and environment adjustments (Ma et al., 2014; Xie and Wang, 2014; Song et al., 2017; Zheng et al., 2019; Febiyanto and Sulaeman, 2020). For example, adding some sacrificial agents such as silver sources (AgNO₃) into suspension could significantly increase the stability and photocatalysis reaction of Ag₃PO₄ as well (Yi et al., 2010). This might be due to the Ag₃PO₄ structure destruction being much lower than that without a sacrificial agent. The structure destruction may be caused by the phase changing through Ag ions alteration to be its metal (Ag⁰) species so restricts their wide application in the dye and wastewater concern.

Given the photo-corrosion processes of Ag₃PO₄ photocatalyst; under visible light irradiation, electron (e⁻) excites to the conduction band (CB) level and a hole (h⁰) can be produced in the valence band (VB) energy level. In the system without a sacrificial agent, the electron can reduce the Ag ions from the Ag₃PO₄ structure to be Ag⁰ when exposed to the visible light (Ag₃PO₄ + 3e⁻ → 3Ag⁰ + PO₄³⁻, E° = 0.45 eV vs. NHE). Prolonging the catalysis reaction, the photo-corrosion proceeded continuously, and then it was given even worse. Thereby, structure destruction and/or phase changing are inevitable. Finally, the low-photocatalysis and stability of Ag₃PO₄ catalyst have resulted.

The addition of sacrificial agents is considered an effective way to enhance the stabilities as well as the photocatalytic performances. Nevertheless, a silver precursor is commonly known as an expensive material in inhibiting the photo-corrosion of Ag₃PO₄. Therefore, the other sacrificial agents are necessary to explore and research.

Hydrogen peroxide (H₂O₂) is one of the chemical compounds that can be used as an additive solvent. The potential redox (vs. NHE) of H₂O₂ is lower than CB of Ag₃PO₄ and may act as an electron acceptor. Jia et al., (2019) suggested that the photogenerated electron is easier to combine with H₂O₂ than Ag₃PO₄ due to more negative reduction potential of •OH/H₂O₂ than that Ag/Ag₃PO₄ (H₂O₂ + e⁻ → •OH + •OH⁻, E° = 0.87 eV vs. NHE). By this, the excited electron from CB of Ag₃PO₄ can be transferred to H₂O₂. Subsequently, it can hinder the severe Ag ions reduction well. Here, the photocatalytic and stability properties will be increased.

In the dye wastewater removal studies, a synergistic reaction named Fenton’s mechanism could have proceeded through a combination of Fe ions and H₂O₂ in enhancing the photocatalyst performances (Riyapanit et al., 2015; Tama et al., 2020). Wang et al., (2014²) use of the sacrificial agent of H₂O₂ 30% can slow down the oxidative destruction and thus extend the working life of Ag₃PO₄ photocatalyst on the methylene blue degradation. Agbe et al. (2017) synthesized H₂O₂-rejuvenated Ag₃PO₄. During synthesis, as-prepared Ag₃PO₄ containing Ag⁰ is rejuvenated by an appropriate H₂O₂ and shows a higher photocatalytic activity for methyl orange, methylene blue, and rhodamine B photodegradation than fresh Ag₃PO₄. Despite them, the use of H₂O₂ in the dye photodegradation using Ag₃PO₄ catalyst directly over various concentration additions on the photocatalytic and photostability properties of Ag₃PO₄ has been not explored, especially on the methylene blue dye. At least, the H₂O₂ is relatively cheap than the well-known electron acceptor of the AgNO₃ precursor. Therefore, in this work, we investigated a direct way for increasing Ag₃PO₄ properties using the H₂O₂ compound. Then, the results were discussed and presented in this paper.

Research Methodology

Materials

Materials that are used were silver nitrate (AgNO₃), disodium hydrogen phosphate dihydrate (Na₂HPO₄•2H₂O), hydrogen peroxide (H₂O₂) 30%, methylene blue (MB) dye that was purchased from MERCK, and commercial aquadest. Materials were used without further purification before. A visible light source that is used was LED Philips Daylight 12 W.
Photocatalyst synthesis

Photocatalyst synthesized by using co-precipitation method. Herein, the solutions were divided into two precursors that were solution-A and solution-B. Solution-A: 5 mmol of AgNO₃ was poured into 20 mL of aquadest and stirred until all powders were dissolved. Meanwhile, solution-B consisted of 20 mL of Na₃HPO₄·2H₂O (3 mmol). During stirring, solution-B was poured drop by drop into solution-A until a yellow light precipitate has resulted. Subsequently, the Ag₃PO₄ precipitate was stirred for 20 minutes. The precipitate was rinsed using aquadest to remove unreacted precursors and to adjust the pH at neutral (~7) conditions has been achieved. The as-synthesized sample was dried at 100 °C for 2 h and stored in a sealed bottle containing silica gel to restrict the water and contaminant adsorption from the atmosphere.

Photocatalysis test

Catalyst with 50 mg was dispersed into 50 mL of methylene blue (MB) 10 mg/L. Lamp and suspension were left for 10 minutes in the dark condition to reach an equilibrium state between catalyst and dye molecules. The distance of the suspension surface and lamp was set at 15 cm away. Then, the lamp was switched on and a sample was mixed for 50 minutes. To know the effect of H₂O₂ on the MB photodegradation, the experiment was carried out by adding 0, 1, 3, and 5 mL (0.2, 6, and 10% (v/v)) of H₂O₂ 30%. After degradation, samples were centrifuged and measured using a UV-Visible spectrophotometer. Samples were labeled as Ag₃PO₄, AH-2%, AH-6%, and AH-10% respectively.

Recycling ability of Ag₃PO₄ photocatalyst

To know the stability of the catalyst, the Ag₃PO₄ photocatalyst was recycled for degrading MB 10 mg/L under identical conditions three times. The photocatalysis system was set at the optimum or maximum condition of H₂O₂ addition.

Figure 1. Fourier Transform IR of Ag₃PO₄ sample.

Photocatalyst mechanism

The radical species test on the MB photodegradation can be determined by using radical trappers such as p-benzoquinone (BQ), isopropanol alcohol (IPA), and ammonium oxalate (AO) for superoxide (•O₂⁻), hydroxyl (•OH), and hole (h⁺) radicals (Febiyanto et al., 2016), respectively.

Characterizations

Photocatalyst was characterized using Fourier Transform IR Prestige-21 at a wavenumber range of 400-4000 cm⁻¹. Filtrate after photodegradation was measured using UV Vis Spectrophotometer Genesys 10S.

Results and Discussion

Functional group analysis of Ag₃PO₄ photocatalyst

Functional groups of Ag₃PO₄ were identified using FTIR and shown in Fig. 1. The Ag₃PO₄ characteristics were observed at a wavenumber of 930 and 550 cm⁻¹ that assigned as O–P–O bending vibration and Ag–O group (Qian et al., 2019; Wu et al., 2013; Piccirillo et al., 2015), respectively. Moreover, some previous reports confirmed O–P–O bending and P–O stretching vibrations could be found near 550 cm⁻¹ (Chai et al., 2014; Anwer and Park, 2019). The stretching and
bending vibrations of the O–H group may strictly be found at a broad spectrum of 3400 and 1650 cm⁻¹, respectively. Further, nitrogen impurity was not detected at 1384 cm⁻¹ (Ma et al., 2014), indicating that the Ag₃PO₄ was free of unreacted precursors and successfully synthesized using the facile co-precipitation method.

**Methylene blue (MB) characterization**

Methylene blue (MB) dye was characterized by the maximum wavelength absorption (λmax) over the visible region of 400 up to 800 nm. The λmax was presented in Fig. 2. It was concluded that MB has λmax at around 664 nm. Besides, the pH of the tested solution was 6 similar to previous research (Zhang et al., 2020).

**Photocatalysis experiment of Ag₃PO₄ photocatalyst**

The photodecomposition of MB was presented in Fig. 3 and Table 1. It could be seen from Fig. 3 that the addition of H₂O₂ generally restricts the photocatalysis reaction. In particular, although the activity was lower than pristine Ag₃PO₄, the addition of 5 mL (AH-10% sample) into the Ag₃PO₄-MB suspension system shows a higher catalysis activity than the other additions. Here, to know the effect of MB dissolution, photolysis, and H₂O₂-catalyzed MB degradation, the system was also tested for MB+H₂O₂+light, MB+H₂O₂ (dissolution effect), and photolysis reaction under identical conditions.

![](image1.png)

**Figure 2.** Wavelength scanning of MB maximum absorption. The inset picture was MB structure and solution.

**Table 1. Photocatalyst activities of samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photolysis</td>
<td>6.6</td>
</tr>
<tr>
<td>MB+H₂O₂ (5 mL) + light</td>
<td>15.6</td>
</tr>
<tr>
<td>MB+H₂O₂ (5 mL)</td>
<td>3.3</td>
</tr>
<tr>
<td>Ag₃PO₄</td>
<td>89.7</td>
</tr>
<tr>
<td>AH-2%</td>
<td>39.5</td>
</tr>
<tr>
<td>AH-6%</td>
<td>41.8</td>
</tr>
<tr>
<td>AH-10%</td>
<td>70.0</td>
</tr>
</tbody>
</table>

Based on Table 1, shows that the MB+H₂O₂+light system as a percentage of MB photodecomposition was about 15.6%. However, by considering other things, the high of this percentage could be also caused by the photolysis reaction of 6.6% and H₂O₂-activated catalysis reaction by following the reaction in Eq. 1 (Deng and Zhao, 2015).

$$\text{H}_2\text{O}_2 + \text{Vis} \rightarrow \text{•OH} + \text{•OH}$$

(1)

The H₂O₂ compound is one of the strong oxidizing agents with a reduction potential value is 1.776 V and is beneficial in degrading the dye pollutants (Setyaningtyas et al., 2019). Further, under visible light irradiation, the H₂O₂ compound can be
broken down into the highest reactive agent of hydroxyl radical (•OH) (Eq. 1) with redox potential 2.720 V (Jiang and Lloyd, 2002; Li et al, 2011). In addition, at least, the dissolution and H2O2-activated catalysis effects can be counted by ~9%. Thereby, we assumed the dissolution effect caused by the excessive H2O2 addition was negligible (~3%) and the catalysis percentage of the AH-10% sample was relatively comparable with single Ag3PO4 catalysis activity. Noted that the addition of 10% of H2O2 was further used in the following experiments.

Recycling test of Ag3PO4 photocatalyst

The stability of Ag3PO4 with and without the addition of H2O2 for the degradation of MB (10 mg/L) was observed through a recycling test under visible light illumination and the results were shown in Fig. 4 and Table 2. After four times running, the photocatalytic ability of the Ag3PO4 catalyst was significantly reduced from 89.7% to 29.6%, confirming the poor catalyst stability of single Ag3PO4 or without H2O2 addition. In contrast, the catalysis percentage of 50 up to 90% could be achieved by using the AH-10% sample, indicating an excellent stability performance of the sample. However, the slight reduction of catalysis ability on the 2nd recycle run of AH-10% sample might be caused by MB molecule deposition on the catalyst’s surface so which inhibits the dye and photocatalyst interactions. This caused a little photocatalysis reduction in their catalysis performance.

The stability test of the Ag3PO4 and AH-10% system was visually displayed in Fig. 5. For 1st run, Ag3PO4 powder becomes grey or dark attributing to the silver metallic generation as compared to yellow powder of the AH-10% system. Ag0 can be observed by the visual appearances of samples and was indicated through catalyst’s color from yellow to grey or dark brown (Khan et al., 2012; Trench et al., 2018), as shown in Fig. 5 (above). Moreover, the Ag3PO4 sample became even darker for long recycling up to the 4th run. In contrast, the AH-10% remained stable with the visual appearance of yellow powder. Interestingly, the quantity of powder is relatively low than the used Ag3PO4 (3rd and 4th runs). An excess of H2O2 may slightly increase the stability of Ag3PO4, through the electron acceptor mechanism of H2O2 owing to the more negative reduction potential of •OH/H2O2 than that Ag/Ag3PO4 (H2O2 + e− → •OH + •OH−, E0 = 0.87 eV vs. NHE). This process caused the yellow light Ag3PO4 powder to remain in the MB suspension.

Figure 4. Recycling test of Ag3PO4 with and without the addition of H2O2 solution.

At the same time, nevertheless, in a long catalysis reaction, the Ag0 metallic may be produced higher. In the presence of excess dissolved H2O2 and without the precipitate precursor addition like phosphate sources, the photoinduced Ag0 will be regenerated into Ag+ ions. Nonetheless, the release into solution and reduce the catalyst quantity of Ag3PO4 photocatalyst because of Ag+ dissolution. The regeneration mechanism can be followed by the reaction in Eq. 2 (Wang et al., 2014b). Although the photocatalytic stability was better than single Ag3PO4, the photocatalysis reaction was slightly reduced in the 2nd time and increased up to 4th recycling runs sacrificed the powdered Ag3PO4 led to dissolve rapidly. The dissolution of Ag3PO4 powder is shown in the 4th recycle run of the AH-10% sample. In this research, the AH-10% powder shows a little quantity, whereas the Ag3PO4 becomes darker over the long photocatalysis reactions.
Figure 5. Visual appearances of recycling test for Ag₃PO₄ (above) and AH-10% systems (below), respectively.

2 Ag + H₂O₂ + 2H⁺ → 2 Ag⁺ + 2H₂O  \hspace{1cm} (2)

Table 2. Recycle experiment of samples

<table>
<thead>
<tr>
<th>Recycle</th>
<th>Degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ag₃PO₄</td>
</tr>
<tr>
<td>1ˢᵗ</td>
<td>84.9</td>
</tr>
<tr>
<td>2ⁿᵈ</td>
<td>49.8</td>
</tr>
<tr>
<td>3ʳᵈ</td>
<td>30.5</td>
</tr>
<tr>
<td>4ᵗʰ</td>
<td>29.6</td>
</tr>
</tbody>
</table>

Role of reactive oxygen radical species

It is well known that the catalysis reaction of photocatalyst-based materials has occurred on their surface’s photocatalyst. Additionally, the photogenerated radical species of photocatalyst are useful for degrading the pollutant structures into harmless small molecules and minerals. Therefore, a series of trapping experiments have been carried out to determine the main active radical on the MB photodegradation in more detail. In this study, radical scavenger such as isopropyl alcohol (IPA), ammonium oxalate (AO), and p-benzoquinone (BQ) was employed as hydroxyl (•OH), hole (h⁺), and superoxide (•O₂⁻) quenchers, respectively. The results were shown in Fig. 6 and Table 3.

Without scavenger additions, Ag₃PO₄ has a photocatalytic activity was 89.7%. With the addition of IPA, the photocatalysis reaction was 92.6% and slightly similar to the Ag₃PO₄, confirming the •OH was not the main radical species in the MB photodegradation. Conversely, the addition of AO and BQ scavenger inhibited the catalyst’s ability with the percentage of 51.8 and 44.3%, respectively. This result concluded that the •O₂⁻ and h⁺ were the main and secondary photogenerated radicals in the MB removal than •OH species. Moreover, to observe the effect of H₂O₂ in the BQ system as main radical was also done and showed the percentage of 50.4% indicating H₂O₂ addition did not disturb the radical determination.

Figure 6. Photocatalytic mechanism of Ag₃PO₄ sample (without H₂O₂ addition).

Table 3. Mechanism test of Ag₃PO₄ sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>89.7</td>
</tr>
<tr>
<td>IPA</td>
<td>92.6</td>
</tr>
<tr>
<td>AO</td>
<td>51.8</td>
</tr>
<tr>
<td>BQ</td>
<td>44.3</td>
</tr>
<tr>
<td>BQ+H₂O₂</td>
<td>50.4</td>
</tr>
</tbody>
</table>

The •OH species was not observed based on the mechanical test results. Insufficient energy of Valence Band (VB) (+2.45 V vs. NHE) of Ag₃PO₄ to oxidize the H₂O to be •OH \( E^\circ(\text{•OH/H}_2\text{O}) = \text{+2.68 V vs. NHE} \) causing the •OH radical has been not produced in MB decomposition. On other hand, the •O₂⁻ radical could be the main radical species, even though the CB level of Ag₃PO₄ is more positive (+0.45 V vs. NHE) than a single-reduction reaction of O₂ \( E^\circ(O_2/O_2^-) = -0.33 \text{ V vs. NHE} \) (Katsumata et al., 2013). However, the •O₂⁻ and h⁺ as main and secondary radical species of Ag₃PO₄ for
degrading the dye wastewater have been reported before (Xu et al., 2017; Pavanello et al., 2020). We assumed the O2 reduction mechanism might be happened by the O2 dissolution that has been resulted under bubbling processes through stirring treatment.

Possible mechanism of Ag3PO4 photocatalyst

Based on the results above, the photocatalytic process of MB dye is proposed as follows. The possible mechanism illustration is shown in Fig. 7. When Ag3PO4 is irradiated using visible light, e- can be excited to the CB and left h+ in the VB. An excited e- can be transferred to the O2 producing the \( \cdot \text{O}_2^- \) radical species. Radicals of photogenerated \( \cdot \text{O}_2^- \) and h+ can break down the MB structures into small molecules and minerals, properly.

![Figure 7. Dye photodegradation and H2O2 inhibited Ag metal production of Ag3PO4 powder. Blue and red circles were hole (h+) and electron (e-), whereas VB and CB were Valence Band and Conduction Band levels, respectively.](image)

However, under simultaneous catalysis reaction, e- can also be easily captured by Ag+ and changed into Ag0 (Wang et al., 2014; Mu et al., 2019). As the prolonging reaction time, more silver was likely to undergo photoreduction. It was indicated by the yellow precipitate of Ag3PO4 photocatalyst became grey or dark color as illustrated in Fig. 5 for pristine Ag3PO4. It concluded that the photo-corrosion of Ag3PO4 had occurred and led to the decrease in the catalysis efficiency after every cycle (Fig. 4 and 5).

In contrast, the addition of H2O2 compound can inhibit directly the photocorrosion of Ag3PO4 into Ag0, due to the more negative reduction potential of \( \cdot \text{OH}/\text{H}_2\text{O}_2 \) compared to Ag/Ag3PO4 (\( \text{H}_2\text{O}_2 + \text{e}^- \rightarrow \cdot \text{OH} + \cdot \text{OH}^- \), \( E^\circ = 0.87 \text{ eV vs. NHE} \)). Notwithstanding, the excessive time reaction and more H2O2 solution will oxidize the Ag0 into Ag+ ions (Eq. 2). Besides, without the precipitation agents, Ag+ ions will release to the suspension, causing severe Ag3PO4 structure destruction. It can be seen in Fig. 5 for the AH-10% sample. Therefore, a proper consideration in the H2O2 quantity and principal aim to create the high photocatalytic and stability properties of Ag3PO4 should be selectively selected.

Conclusions

The direct addition of H2O2 into the Ag3PO4 suspension system has enhanced the stability property of its catalysis reaction for MB photodegradation under visible light. The maximum condition of H2O2 was 5 mL (AH-10% sample) with the percentage of MB removal being 70%. This study found that the excessive addition of H2O2 could enhance the stability of catalyst up to three-cycle runs, indicating that the photo-corrosion of Ag3PO4 photocatalyst had been restricted simultaneously. Although, the Ag0 oxidation into released-Ag+ ions caused by H2O2 addition, however, should be considered for an efficient and effective way of photocatalysis reaction system of Ag3PO4 photocatalyst in the future.

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