Effect of Ag and Mn doping for methylene blue photodegradation performance

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Abstract. Currently, wastewater management is ineffective, operationally expensive, and difficult to be implemented in Indonesia. The photocatalyst is a technology that may answer this problem. Titania (TiO2) is a high-activity, inexpensive, stable, and non-toxic photocatalyst material. However, TiO2 has large band-gap energy and rapid recombination. In this research, TiO2 was doped by Ag (a noble metal) and Mn (a transition metal) to compare the performance of photocatalysts in organic pollutant degradation, using methylene blue. Ag/TiO2 catalyst was synthesized by Photo Assisted Deposition (PAD) method, while Mn/TiO2 was synthesized by impregnation method. The physicochemical properties of both catalysts were assessed by SEM-EDX and UV-Vis DRS. SEM-EDX indicated that both methods successfully doped Ag and Mn into TiO2. Besides, UV-Vis DRS confirmed the presence of metal dopants that caused the narrowing of the bandgap. Ag/TiO2 catalyst increased the degradation of methylene blue by up to 97% in 30 minutes. Meanwhile, the Mn/TiO2 catalyst inhibited the degradation of methylene blue. The increased activity by Ag dopants is due to the Localized Electromagnetic Field (LEMF) and Schottky barrier phenomena which increase charge separation. Meanwhile, decreased activity by Mn dopants is due to the shading effect and Mn electronic structure that can facilitate recombination at high loading. Ag/TiO2 catalyst also improved photodegradation performance of TiO2 when irradiated by visible light.

1. Introduction
 Clean water is a human’s basic need. However, clean water provision is still problematic in Indonesia. It is estimated that 25.1% of Indonesia's rivers are heavily polluted [1]. The main sources of pollution come from industrial waste and household waste, which dispose of dangerous pollutants like synthetic dyes. Methylene blue is a commonly used synthetic dye which is difficult to degrade because it has a stable heterocyclic aromatic structure. Photocatalyst, one of the Advanced Oxidation Process (AOP) technologies, is a possible solution to degrade stable organic compounds like methylene blue. Titania (TiO2) is a high-activity, inexpensive, stable, and non-toxic photocatalyst material. However, compared to other AOP technologies such as Fenton and FeGAC/ H2O2, the operational cost of photocatalyst is more expensive because TiO2 has large bandgap and slow kinetics [2]. Moreover, WWTPs generally store large amounts of waste in outdoor ponds, so it is preferable if the catalyst can be activated by solar light. Solar radiation contains only 5% of UV, while the rest is an electromagnetic wave with lower frequency. Therefore, current efforts are directed to increase catalyst ability to capture photons with lower energy and reduce the rate of recombination.

Based on previous studies, it was found that the performance of TiO2 under solar radiation can be increased by doping metal. Different metal dopants serve this purpose in different ways. TiO2 that is
doped by noble metals such as Ag (silver) improve TiO$_2$ activity through plasmonic resonance that allows metal dopant to be activated by absorbing visible light [3]. While transition metal dopant allows catalyst activation under lower frequency radiation by introducing new energy levels below the conduction band and narrowing the bandgap. Previous studies that synthesized Ag/TiO$_2$ to degrade organic pollutants under visible light were prepared using the sol-gel and impregnation method [4-5]. Meanwhile, in current research, Ag/TiO$_2$ was prepared using Photo Assisted Deposition (PAD). This method was selected due to its better dispersion and performance compared to Ag/TiO$_2$ that was prepared with other methods [6]. As the price of noble metals is quite expensive, a comparative study with other cheaper metal dopants, such as Mn (manganese) is needed. Several studies found that the addition of Mn metal can increase photocatalyst activity under visible light [7-8]. When compared to transition metals with similar electronic configurations, such as Fe$^{2+}$, Ru$^{3+}$, and Os$^{3+}$, the Mn$^{2+}$ exhibited the best activity as well [9]. However, previous studies have not done comparative studies between the transition metal and noble metal directly.

This study aims to compare the performance of Mn metal dopants with Ag noble metal dopants to obtain a cheaper yet effective catalyst. The photocatalyst performance of various metal dopants on TiO$_2$ was tested by comparing the degradation of methylene blue. Ag/TiO$_2$ catalyst was synthesized by Photo Assisted Deposition (PAD) method, while Mn/TiO$_2$ was synthesized by impregnation method. The purpose of using different methods of synthesis was to obtain metal-doped-TiO$_2$ by using the most suitable method that yields optimal results.

2. Material and Method

All materials were of analytical grade and used without any further preparation. TiO$_2$ Evonik P25, anhydrous methanol (CH$_3$OH) 96%, nitric acid (HNO$_3$) 65%, silver nitrate solution (AgNO$_3$), methylene blue 1000 ppm, and Mangan acetate tetrahydrate (Mn(CH$_3$COOH)$_2$4H$_2$O) from Sigma Aldrich were purchased from local supplier. Distilled water was used in all experiments.

2.1. Synthesis of Ag/TiO$_2$

Ag/TiO$_2$ was synthesized with Photo Assisted Deposition (PAD) method inside a photoreactor. The first step was to make TiO$_2$ slurry by mixing 1 grams TiO$_2$ P25 with 100 mL distilled water and add nitric acid until the pH reached 3. The sol was stirred for 15 minutes and sonicated for 30 minutes. Then, AgNO$_3$ solution was made by mixing 0.016 gram (1% Ag) of AgNO$_3$ crystal with 100 mL distilled water until it dissolved. The solution was then stirred with TiO$_2$ slurry for 30 minutes. After that, 45 mL anhydrous methanol was added to the slurry while being stirred. Then, the mixture was put inside a photoreactor for 6 hours of continuous irradiation and stirring. The slurry was then separated using a centrifuge with rotation speed of 3000 rpm for 30 minutes. Then, the solid obtained was dried on hot plate with temperature of 150$^0$C and calcinated inside a furnace with temperature of 300$^0$C for 1 hour.

2.2. Synthesis of Mn/TiO$_2$

Mn/TiO$_2$ was synthesized with impregnation method. The first step was to make Mangan acetate solution by dissolving 0.0446 gram (1% Mn) of Mangan acetate tetrahydrate crystal in 50 mL distilled water. Then, 1 gram of TiO$_2$ P25 was added to the solution. It was sonicated for 1 hour at 60$^0$C. The catalyst was then dried on hot plate with temperature of 110$^0$C. Lastly, it was calcinated inside a furnace at 350$^0$C for 4 hours.

2.3. Structural and Optical Characterization

Structural and optical characterization was carried out to the catalyst. UV-Vis DRS characterization was done to obtain the band gap value of the catalyst. While, the SEM-EDX (Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy) characterization was to analyze the final composition, distribution of constituent material, and surface morphology of the photocatalyst.
2.4. Methylene Blue Degradation Test
Photocatalytic degradation of MB (C₁₆H₁₈ClN₃S) in aqueous solution (10 ppm) was carried out inside a reactor with 20-watt UV lamps and visible-light (Gold star, 20 watt) irradiation. The set-up of the reactor can be seen at Fig.1 that depicts the lamps arrangement with solution and reflector. About 50 mg of photocatalyst was added into a 100 ml of aqueous MB (10 ppm) solution. Prior to irradiation, the suspensions were stirred in the dark for 30 min to ensure establishment of an adsorption–desorption equilibrium among the photocatalyst and MB. Every 30 minutes, 5 mL of sample was taken. The test was carried out for 2 hours. After recovering the catalyst by centrifuging, subsequent variations in the MB concentration were analyzed by an ultraviolet–visible spectrophotometer and the absorbance at 664 nm (λmax for MB) was recorded.

Figure 1. Photoreactor set up with (a) lamp (b) magnetic stirrer and (c) reflector

3. Result and Discussion

3.1. Catalyst Characterization
The SEM results can be observed at Figure 2, that show undoped and doped TiO₂. It can be seen that doped TiO₂ did not change the morphology significantly. All of them looked like small aggregates resembling cotton.

Figure 2. Morphology of catalyst (a)TiO₂ P25 (b)1 % Ag/TiO₂ (c)1% Mn/TiO₂

Figure 3 demonstrated that the physical appearance of Mn/TiO₂ was considerably different from Ag/TiO₂ and TiO₂. The color changed and became darker. Even though Ag/TiO₂ and Mn/TiO₂ were synthesized with different methods, the EDX result indicated that both have successfully doped metal with the desired content, which is 1% wt. Besides, UV-Vis DRS confirmed the presence of metal dopants that caused the narrowing of the bandgap. Even though the metal was loaded to TiO₂ with the same amount, the absorbance shift observed is different. The TiO₂ catalyst that was loaded with Mn caused a greater shift compared to Ag.
Figure 3. Physical appearance of catalyst (a)TiO$_2$ P25 (b)1% Ag/TiO$_2$ (c)1% Mn/TiO$_2$

Table 1. EDX Result of Ag/TiO$_2$ and Mn/TiO$_2$

| Elements   | Ag/TiO$_2$ content (%) | Elements       | Mn/TiO$_2$ content (%) |
|------------|------------------------|----------------|------------------------|
| Ti         | 60.81                  | Ti             | 57.05                  |
| O          | 38.08                  | O              | 41.99                  |
| Ag         | 1.11                   | Mn             | 0.96                   |

Bandgap was calculated using the Kubelka-Munk equation. The result is presented in fig.4. The bandgap of TiO$_2$ was shifted from 3.05 eV to 3.01 eV for Ag/TiO$_2$ and 2.87 eV for Mn/TiO$_2$. This shift was also observed in previous study when doping TiO$_2$ with 3% mol Mn and with 5% mol Ag [10-11]. It is consistently observed that at the same loading, Mn will give greater shift than Ag.

Figure 4. Band gap energy.

3.2. Methylene Blue Degradation

Metal doping caused alteration in photocatalyst activity. In this research, Mn and Ag were used to dope TiO$_2$. Their photocatalytic activity was measured by observing methylene blue degradation under UV light for 2 hours. The result is presented in figure 4. Doping of Ag (1% wt) increased photocatalytic activity, while the doping of Mn (1% wt) caused an adverse effect. In 30 minutes, Ag/TiO$_2$ had managed to degrade 97% of methylene blue. This increase indicated the increase in hydroxyl radical production.
In methylene blue degradation, hydroxyl radicals are the most predominant active species \[11\]. Ag metal doping helped this process in several ways, which all of them are related to its characteristic as a noble metal. Ag metal doping can effectively create the Schottky barrier that prolongs separation between electron and holes \[3\]. It can also increase the amounts of excited electrons through the electromagnetic field. This process is called localized electromagnetic field (LEMF) which was already observed in Ag/TiO\(_2\) \[12\].

While in this study Mn/TiO\(_2\) produced inhibition effect to photocatalyst, this is not always the case. It has been observed that, in a small amount of doping, Mn/TiO\(_2\) increased photocatalytic activity under UV and visible light \[13-14\]. It is suggested that the result might come from the fact that the loading amount exceeded its optimum result. It is also possible than Mn metal caused significant shading effect that prevented photon reaching semiconductor effectively, as can be seen from the color of the catalyst. Mn metal has a unique orbital, which can trap both holes and electrons \[15\]. Therefore, it is hypothesized that: when Mn doping is small, the orbitals tend to act as electron trappers. While the amount increase, Mn orbital can trap both hole and electron simultaneously that increase the chance of recombination.

![Figure 5. Effect of Dopant to MB degradation.](image)

Proceeding further, Ag/TiO\(_2\) which exhibited increased performance was tested to degrade MB under visible light irradiation. Table 2 presents the result of the degradation of 2 hours. In comparison to performance under UV light, the MB degradation under visible light was much slower. In 2 hours, both doped and Ag-doped TiO\(_2\) has degraded>99% MB under UV light, while the result under visible light was less than 70%. However, Ag/TiO\(_2\) has significantly higher activity under visible light, which might come from its plasmonic activity.

| Catalyst     | % MB Degradation after 2 hours |
|--------------|--------------------------------|
| TiO\(_2\)    | 48.65                         |
| Ag/TiO\(_2\) | 69.89                         |

Table 2. Percent of MB degradation under visible light after 2 hours.
4. Conclusion
The purpose of this study is to compare the effect of metal doping for methylene blue photodegradation. The direction of this research is to obtain cheaper metal doping that can be activated under solar light. However, the present work is not successful to prove that a cheaper transition metal like Mn can substitute noble metal doping like Ag. From this study, Ag/TiO\(_2\) catalyst increased activity for the degradation of methylene blue by up to 97% in 30 minutes. Meanwhile, Mn/TiO\(_2\) catalyst inhibited activity for the degradation of methylene blue. The increased activity by Ag doping is due to the Localized Electromagnetic Field (LEMF) and Schottky barrier phenomena which increase the amount and time of charge separation. Meanwhile, decreased activity by Mn doping is due to the shading effect and Mn electronic structure that can facilitate recombination at high loading. Ag/TiO\(_2\) catalyst also improved photodegradation performance of TiO\(_2\) when irradiated by visible light.

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