Synthesis of Nano-Composite Ag/TiO$_2$ for Polyethylene Microplastic Degradation Applications

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Abstract. The aim of this research is to synthesize Ag/TiO$_2$ nano-composites to study their ability to degrade microplastics in water, followed by varying size of microplastic particles as pollutants in drinking water. The method used for synthesizing Ag/TiO$_2$ is Photo Assisted Deposition (PAD). Characterizations done to determine the difference between TiO$_2$ and Ag/TiO$_2$ were SEM-EDX and UV-Vis DRS. Polyethylene microplastics were selected as samples in this study. The variation of microplastic size used is 100-125, 125-150, and 150-250 micrometers with initial concentrations of 100 ppm. Magnetic stirrers used at a rotational speed of 2000 rpm during the degradation process with a UV lamp irradiation. The addition of the Ag dopant has a good effect in microplastic degradation, where the percentage of degradation reaches 100% within 120 minutes of irradiation at an initial concentration of 100 ppm. An initial concentration of 100 ppm obtained the best percent degradation at particle size 125-150 micrometers, where 100% degradation achieved at 90 minutes irradiation.

1. Introduction
Bottled drinking water meets the standards of WHO (World Health Organization) regarding quality and eligibility for consumption. Therefore, consumers believe that consuming bottled water is safe for health. However, in 2018 a study from the State University of New York at Fredonia that tested 259 bottles of drinking water from 11 brands sold in eight countries found that 93 percent of the water in the bottles tested contain microplastics [1]. One sample taken from Indonesia on average contains 382 microplastic particles per liter with sizes ranging from 6.5 to more than 100 micrometers [1]. It is known that bottled drinking water samples taken from local products contain up to 4713 microplastic particles per liter. Whereas non-local drinking water samples contain up to 10390 particles per liter of microplastic with polypropylene, nylon, polystyrene, and polyethylene types [1]. The test is carried back to the bottled water products under the same brand in the laboratory of the faculty of Mathematics, University of Indonesia, and found a microplastic particle size of 11 to 247 micrometers [2]. Microplastic carcinogenicity of particles contain in drinking water are known to cause cancer [3]. Physically existence microplastic as pollutants can also trigger clotting in the digestive tract. It is thought that microplastics can also translocate in the human body if they are below 150 µm [4]. Therefore, it should underline that the drinking water purification technology not only separates base on the size of microplastic particle, but also can be decomposed into harmless compounds.

The most important component in a water purification unit is a technology that can be apply to disinfect pathogenic microorganisms and degrade other pollutants. Plasma ion technology has been widely apply with the main component of ion generators which can produce OH radicals for water
purification. However, purification units with plasma ion technology are still relatively expensive in terms of purchase costs and operating costs. In addition, plasma technology also has a high enough risk relate to work safety when apply. Therefore, purification technology using photocatalytic nanocomposite materials has become the choice and much develop. Various studies have combine several materials into composites to obtain an effective purification unit. Previous studies have shown that TiO$_2$ nanoparticles compile with plastic PE particles with a composition of 1% weight, showed microplastic degradation activity of 86% with UV irradiation, but the irradiation time required was quite long at 300 hours [5]. In increasing photocatalytic ability, a photocatalyst can be combine with a metal dopant. This increase is relate to the efficiency and ability of the core dopant to capture the charge carrier (electron trapping) and decrease the rate of recombination between e$^-$ and h$. Researcher chose silver metal as a dopant because it has been proven to reduce band-gap energy, so it can be active under visible light and act as an electron catcher that can limit the rate of recombination so that electrons are more easily excited and increase the photocatalytic activity of TiO$_2$ [6]. Besides being proven to be able to support the performance of TiO$_2$ in degrading organic compounds, silver metal also has advantages as an antibacterial agent. [7].

In this study, Ag/TiO$_2$ was synthesized by PAD method in which AgNO$_3$ precursor was added to TiO$_2$ P25 slurry where it was put under photoreactor for 6 hours. Characterizations such as SEM-EDX (Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy) and UV-Vis-DRS (UV-Vis Diffuse Reflectance Spectroscopy) were done to provide knowledge regarding differences between TiO$_2$ and Ag/TiO$_2$. Ag/TiO$_2$ was then tested for its ability to degrade polyethylene microplastics in water in the presence of a stirrer under UV irradiation. Polyethylene microplastics were selected as samples because of their wide application in a variety of needs both industrial and household [8].

2. Experimental

The purpose of this research is to synthesize Ag/TiO$_2$ nano-composites to test their ability to degrade polyethylene microplastics in liquid media. This study includes several stages of synthesis Ag/TiO$_2$, characterization, and testing of polyethylene degradation microplastics.

2.1. Tools and Materials

Polyethylene microplastic is derived from one of the raw materials for making facial wash (scrub) obtained from an online supplier with a size of 50-300 micrometers. The silver metal (Ag) used as a dopant for TiO$_2$ Evonik P25 is synthesized from AgNO$_3$ salt by the PAD method using a photoreactor equipped with a UV lamp and magnetic stirrer. Supporting materials such as anhydrous methanol (96%) and nitric acid (HNO$_3$) 65% are needed in synthesizing nano-composites. Distilled water (aquadex) was used in all experiments. During the synthesis process also used equipment such as analytical balance with an accuracy of 0.001 gram, hot plate, sonicator, centrifuge, oven, and furnace. The characterization equipment used in this study is the UV-Vis DRS Spectrophotometer to measure absorption and band-gap energy, as well as the Inspect F50 Scanning Electron Microscope (SEM-EDX device) to see the morphology on the surface of nano-composites.

2.2. Methods

This section will explain the Ag/TiO$_2$ synthesis method, composite characterization, and polyethylene microplastic degradation test methods.

2.2.1. Synthesis of Ag/TiO$_2$ nano-composite. Synthesis of Ag/TiO$_2$ nanocomposites was carried out using the Photo Assisted Deposition (PAD) method. The first step of this research is to make TiO$_2$ slurry by adding 3 grams of TiO$_2$ to 405 mL of distilled water and adding nitric acid to reduce the pH of the slurry to 3 before being put into the sonicator for 30 minutes. The next step is to add AgNO$_3$ to a slurry of 0.047 grams to get a 1% addition of dopant to Ag/TiO$_2$ based on the initial mass of TiO$_2$ used. Stirring was continued for 30 minutes and added 45 ml of methanol to the slurry. Next, insert the slurry into the photoreactor for irradiation for 6 hours in the presence of stirring. Then the slurry is centrifuged 2 times.
to separate and increase the pH of the composite at 4000 rpm for 30 minutes. Finally, the sample was dried at 150ºC then calcined at 300ºC for 1 hour.

2.2.2. Characterizations of Ag/TiO$_2$. The characterizations done include SEM-EDX (Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy) to analyse the final composition and surface morphology of the photocatalyst. UV-Vis-DRS (UV-Vis Diffuse Reflectance Spectroscopy) is also performed to determine the band-gap energy and light absorption power from the photocatalyst.

2.2.3. Microplastic degradation test. Polyethylene microplastic degradation test was carried out using the mass lose method. The performance of catalysts in microplastic degradation can be measured through measured microplastic mass reduction before and after UV irradiation treatment for 2 hours. Photoreactors used to activate photocatalysts in degrading microplastic pollutants are shown in Figure 1.

Figure 1. Front view of photoreactor with (A) beaker containing photocatalyst, microplastic and magnetic stirrer, (B) UV lamp, (C) aluminum reflector, and (D) hot plate as a base.

In this study, to determine the ability of Ag/TiO$_2$ in microplastic degradation testing, a variation in the size of the microplastic used are 100-125, 125-150, and 150-250 micrometers at a concentration of 100 ppm. Microplastic degradation analysis was carried out for 2 hours for each sample.

3. Results and Discussion

After synthesizing Ag/TiO$_2$ with the Photo Assisted Deposition method, the ability to degrade polyethylene microplastic will be tested. The researcher characterizes nano-composites to obtain relevant data that can support the results of the polyethylene degradation test. Characterization data that can be analyzed are the morphology and composition of nano-composites (SEM-EDX) and absorbance (UV-vis DRS).

3.1. Nano-composite characterizations

Data from SEM-EDX characterization and UV-vis-DRS used as a parameter of success in the manufacture of nano-composite Ag/TiO$_2$. 

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3.1.1. SEM-EDX characterization. The SEM-EDX characterization of the catalyst was carried out to see the surface morphology of the synthesized Ag/TiO$_2$ catalyst and to see the percentage loading of Ag elements in Ag/TiO$_2$ composites. The results of SEM characterization can be seen in Figure 2.

![SEM-EDX characterization of (a) TiO$_2$ P25 and (b) 1% Ag/TiO$_2$.](image)

Based on the results of the characterization in Figure 2, it can be explained that the treatment of Ag dopant loading on TiO$_2$ does not provide enough topological changes on the surface of the catalyst. It can be observed that samples from Ag/TiO$_2$ have fairly uniform morphology. The addition of dopants, in general, does not greatly affect the aggregate size of each catalyst sample. Therefore, the ability of Ag as a dopant can work optimally because the surface morphology of the catalyst has not changed significantly, where no other aggregates are found that can interfere with the photocatalytic performance of TiO$_2$. However, the addition of high Ag concentrations can increase the amount of Ag deposited on the surface of the TiO$_2$ photocatalyst [9]. This is causes the color of Ag/TiO$_2$ composite on SEM characterization changed gray. Besides that, the addition of large Ag loading can be a barrier on the active side of TiO$_2$ in absorbing photon energy for photocatalytic processes and can become a recombination center [10]. The advantage of the PAD method does not provide significant changes to
the structure, size, and uniformity of the photocatalyst because Ag metal is deposited by electron photo-excitation mechanism which reduces Ag on the TiO$_2$ surface [11]. It is different from the hydrothermal method which substitutes metal into the crystal lattice, so it is quite influential on the structure, size, and uniformity of the crystal which has an impact on optical absorption and energy gap [12]. The sol-gel method also requires heat treatment up to 800$^\circ$C, so it is quite dangerous during the synthesis process and has a significant effect on the photocatalyst crystal size [13]. Based on EDX results, it found that the mass of silver metal propelled on TiO$_2$ was sufficient by the desired percentage of 1.11% Ag/TiO$_2$. Therefore, the PAD method used for composite synthesis is appropriate and gives quite good results that is performed by very simple procedures.

3.1.2. UV-vis-DRS characterization. UV-Vis DRS characterization was performed to determine the band-gap value of a semiconductor. In this study, characterization was carried out on a 1% Ag / TiO$_2$ catalyst with the results shown in Figure 3.

![Figure 3. 1% Ag/TiO$_2$ absorbance.](image)

Figure 3 shows the ability of photocatalyst absorbance to light with a wavelength of 370-490 nm which belongs to the wavelength region of visible light as shown by the x-axis. The absorbance value of the catalyst to light at wavelengths >400 nm is increasing. This shows that Ag/TiO$_2$ photocatalyst has responsiveness to visible light. This capability makes Ag/TiO$_2$ photocatalysts can be active under sunlight. In contrast to pure TiO$_2$ P25 which only has maximum performance under UV irradiation with a wavelength of <380 [14]. It should be noted that this absorbance measurement focuses on the intensity of light or electromagnetic radiation that can be absorbed by the composite so that an electron gets the energy to be able to move from a low energy level to a higher energy level. In the case of photocatalysts especially semiconductors, the low energy level is in the valence band position while the high energy level is in the conduction band position. This relates to the band-gap energy of a semiconductor which shows the minimum energy required by electrons to be excited from the valence band to the conduction band.

Based on the calculation of the band-gap using the Kubelka-Munk equation of 1% Ag/TiO$_2$ composite, it can be proven that the addition of silver metal dopants can reduce the band-gap to 3.02 eV with an optimum wavelength of 411 nm. Meanwhile, the band-gap owned by pure TiO$_2$ P25 is 3.19 eV with an optimum wavelength of 381 nm [15]. This decrease in band-gap energy results in the composite being able to absorb light at wavelength regions above 380 nm. Therefore, synthesized Ag/TiO$_2$ nanocomposites can be active under UV irradiation and also visible light irradiation. This can be seen from the increased absorbance ability of Ag/TiO$_2$ in the visible light region, but no peaks were found showing plasmonic resonance activity of Ag. This may be due to the relatively wide size distribution of Ag nanoparticles in Ag/TiO$_2$ [13]. Therefore, the role of Ag as a dopant is more dominant in its ability to capture electrons with a lower fermi level energy and a higher energy work function than TiO$_2$. This electron trapping process significantly reduces the electron-hole recombination rate, which results in stronger photocatalytic reactions.
3.2. Microplastic degradation

3.2.1. Degradation performance based on variations in the size of microplastic particles. Research with variations in microplastic particle size was carried out using an initial microplastic concentration of 100 ppm. Concentrations of 100 ppm were obtained by dispersing 10 mg of microplastic polyethylene particles into 100 ml of distilled water. Meanwhile, the nano-composite mass used was 50 mg. The degradation performance of nano-composites can be seen from the decrease in microplastic mass for 2 hours with observations every 30 minutes. The decrease in microplastic mass and the percentage of degradation can be seen in Table 1 and Table 2.

| Particle size (μm) | 0 min | 30 min | 60 min | 90 min | 120 min |
|-------------------|-------|--------|--------|--------|---------|
| 100-125           | 10    | 6      | 4      | 2      | 0       |
| 125-150           | 10    | 6      | 2      | 0      | 0       |
| 150-250           | 10    | 8      | 6      | 2      | 0       |

Table 1. Microplastic mass reduction based on variations in particle size.

| Particle size (μm) | 0 min | 30 min | 60 min | 90 min | 120 min |
|-------------------|-------|--------|--------|--------|---------|
| 100-125           | 0     | 40     | 60     | 80     | 100     |
| 125-150           | 0     | 40     | 80     | 100    | 100     |
| 150-250           | 0     | 20     | 40     | 80     | 100     |

Table 2. Percent degradation base on variations in particle size.

The ratio of decreased microplastic concentration due to degradation activity by Ag/TiO$_2$ nano-composites is presented in graphical form in Figure 4.

![Figure 4](image_url)

Figure 4. Decreased microplastic concentration based on variations in the initial size of microplastic particles.

The graph in Figure 4 shows that the decrease in microplastic concentration reaches 0 at the 90 minute for microplastic samples with particle sizes of 125-150 micrometers. This event is related to the ability of the microplastic to mix evenly in a solution. The mixing of solid particles is affected by the stirring carried out. Where the stirring process is carried out to suspend microplastic and nano-composite solids in aquades. The type of stirrer influences the flow pattern produced in the beaker. In this study, the magnetic stirrer used has the same concept as the paddles type stirrer, where the resulting flow
pattern has a radial and tangential direction to cause the formation of a whirlpool. This whirlpool has an effect on microplastic particles in the solution.

The density of polyethylene microplastic is smaller than the density of aquades, so microplastic particles are more likely to be on the surface. Therefore, microplastic particles will experience centrifugal force. The centrifugal force is directly proportional to the mass of the particle and the speed of the particle, but inversely proportional to the radius of the path. Particle speed is influenced by the speed of stirring, where the stirring speed in this study is made constant at 2000 rpm. The radius of the track is also constant, because the diameter of the beaker used is the same. Therefore the main factor affecting the centrifugal force on microplastic particles is the mass of the particle.

The mass of a microplastic particle varies depending on the size of the particle. The particle size of 100-125 micrometers experiences a centrifugal force that is small enough that the particles cannot be mixed optimally. Meanwhile, particles with a size of 150-250 micrometers accept maximum centrifugal force, so they tend to be thrown to the outermost path which is limited by the wall of the beaker. Microplastic particle gives the optimum mass for one particle at a size of 125-150 micrometers. Therefore, the contact between the microplastic and radical species is optimal at that size. This research took 2 hours to degrade microplastics up to 100%. These results are better than previous studies by Zhao 2007, which were only able to degrade microplastics up to 86% for 300 hours of irradiation in the solid phase PE-TiO$_2$ (1% wt) under UV irradiations.

It should be underlined that this study uses mass reduction measurements to determine decreased microplastic concentrations after irradiation. Therefore, the accuracy of the measuring instrument will determine the quality of the data obtained. Measuring instruments that researchers use have accuracy of 0.001 grams or equivalent to 1 mg, so that the measurement error of each mass reduction data obtained is equal to 1 mg.

Some suggestions that can be given for the development of further research are conducting a microplastic degradation test with variations in stirring speed, using a measuring instrument with higher accuracy, at least four digits behind the comma so that the measurement results are more accurate, then after obtaining optimum degradation performance, it can be applied to drinking water treatment equipment to avoid health hazards due to microplastics.

4. Conclusion
The characterization of silver doped TiO$_2$ using SEM EDX technique revealed the dispersion of silver metal on the surface of TiO$_2$, while the UV-Vis DRS result show that the band-gap energy of TiO$_2$ decreased as a result of the presence of deposited silver metal. The silver doped TiO$_2$ composite catalysts show an adsorption threshold extended into the visible region. Under UV irradiation, Ag deposits exhibit the effect only as electron traps, thus leading to the enhancement in the Ag/TiO$_2$ photocatalytic activity. The synthesized material of Ag/TiO$_2$ has been tested in microplastic degradation and it and it was shown that microplastics with a size of 125-150 micrometers showed very good results. Where the degradation performance was obtained up to 100% under UV irradiation and the presence of stirring which affected the mixing of microplastic particles in the slurry.

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