Microplastic Pollutant Degradation in Water Using Modified TiO$_2$ Photocatalyst Under UV-Irradiation

Muhamad Haris Fadli$^{(a)}$, Muhammad Ibadurrohman$^{(b)}$ and Slamet Slamet$^{(a)}$

$^1$Department of Chemical Engineering, Universitas Indonesia, Depok, West Java, 16424, Indonesia

$^a$Corresponding Author: slamet@che.ui.ac.id
$^b$ibad@che.ui.ac.id
$^c$muhamad.haris@ui.ac.id

Abstract. Modified TiO$_2$ photocatalyst has been widely studied on its ability to degrade pollutants in water. Nowadays, one of the water pollutants that significantly polluted water is microplastic. Photocatalyst TiO$_2$ can create an oxidizing agent to degrade microplastic pollutants but have a very high recombination rate of electrons and holes. By modifying TiO$_2$ with silver dopant using Photo-assisted Deposition (PAD) and Reduced Graphene oxide (RGO) using the ultrasonic radiation method, can highly increase the ability of TiO$_2$ catalyst. The modified catalyst was characterized by SEM-EDX and UV-Vis DRS to analyze the properties change of the composite. The performance of composites in degrading microplastic (polyethylene) was tested under UV radiation for 4 hours. The Ag/TiO$_2$/RGO catalyst has a significantly high degradation percentage with 76% compared to pure TiO$_2$ and Ag/TiO$_2$ with degradation percentage of 56% and 68% respectively.

1. Introduction

Microplastic has recently become a major problem for the environment because of its nature which is difficult to degrade and small in size and its impact on the environment because it is widely spread in nature [1]. New problems caused by microplastics emerged in 2018 ago. According to the results of research from the State University of New York at Fredonia which tested 259 bottles of drinking water from 11 brands sold in eight countries, the results obtained are that 93 percent of the water in the bottled bottles tested contains microplastics. Samples taken from Indonesia on average contain 382 microplastic particles per liter with sizes ranging from 6.5 to more than 100 micrometers [2]. Clarifying the results of the study, a re-testing of bottled drinking water products was conducted at the University of Indonesia's Faculty of Mathematics and Natural Sciences laboratory. With the same brand, the test results obtained that the bottled water products contain microplastics measuring 11 to 247 micrometers [3]. The danger of the presence of microplastics in water is known to trigger cancer caused by the nature of the carcinogenic it has [4]. Physically, the presence of microplastics as pollutants can generally trigger clots in the digestive tract. Microplastics are also expected to translocate in the human body if they are below 150 µm [5].

The usage of photocatalyst has an opportunity to degrade microplastic in water. Research lately have been done to prove the ability of photocatalyst to degrade microplastic. Previous study revealed that the microplastic degradation mechanism using LDPE as the model of plastic, starts with the formation of hydroxyl radicals that will react with LDPE to form polyethylene alkyl radicals and water. The alkyl...
radical polyethylene will then be degraded to CO$_2$ and H$_2$O after undergoing several series of reactions [6]. However, the ability to reduce microplastic mass is still very low. A study by Ariza-Tarazona and team (2019) investigated the degradation of microplastics using N-TiO$_2$ modified photocatalyst. From the result, the degradation of microplastic is still not efficient using the N-TiO$_2$ modified photocatalyst shown by low mass degradation percentage [7]. According to Ahmed and team (2010), the photocatalytic activity of titania are reliant on the surface and structural properties of the semiconductor in which including the surface area, crystal composition, particle size distribution, band gap, and others. These factors have a huge impact on the adsorption behavior during degradation of pollutants [8]. Tavakoli and team (2018) conducted a research to examine the effect of the addition of Ag metals and graphene on TiO$_2$ on their photocatalyst performance by assessing the degradation efficiency of the organic acid Acid 7, modeled with Acid Orange (AO7). The addition of graphene and Ag increased the efficiency of degradation from 61% to increase to 99%.

From the study above, modifying TiO$_2$ with Ag metals or graphene proves to be effective in increases the photocatalyst performance of TiO$_2$. In this study, the effect of Ag metals and graphene derivatives, which is reduced graphene oxide (RGO) to the photocatalyst activity of TiO$_2$ on the degradation of microplastic modeled as polyethylene scrub was investigated. The modified photocatalyst was synthesized using photo-assisted deposition (PAD) and ultrasonic radiation mixing method. The catalyst was characterized with SEM-EDX and UV-Vis DRS and the degradation efficiency was tested under UV irradiation.

2. Experimental Method

2.1. Tools and materials

The material used in this study is polyethylene scrub with a size of 100-150 $\mu$m as the model of microplastic, aquades, photocatalyst TiO$_2$ P25 Evonik powder, AgNO$_3$ as the precursor of Ag metal, RGO, HNO$_3$ and methanol as the solvent. The degradation process of the microplastic was carried out in a photoreactor with eight 8watt UV lamps, reflector from aluminium plate, and a magnetic stirrer in the reactor.

2.2. Preparation of catalyst

The Ag/TiO$_2$ and Ag/TiO$_2$/RGO photocatalyst was prepared using TiO$_2$ P25 Evonik powder as the titania precursor, while AgNO$_3$ and RGO used as the source of silver (Ag) and RGO respectively. HNO$_3$ and methanol are used as a solvent in the PAD method. The catalyst was first synthesized with PAD to get Ag/TiO$_2$. The amount of AgNO$_3$ was weighed based on the dopant concentration which is 3% Ag. TiO$_2$ P25 was dissolved in distilled water that had been added with HNO$_3$ solution to a pH of 3 and stirred with a magnetic stirrer and sonicated with ultrasonication. AgNO$_3$ was added to TiO$_2$ soles with varying concentrations and stirred with magnetic stirrers. Then, add methanol while stirring. After that, irradiated with a UV lamp for 6 hours and centrifuged for 30 minutes at 4000 rpm. Dry the sample at 150 °C using a hotplate. The sample then calcined using a furnace at 300 °C for 1 hour. The Ag/TiO$_2$ catalyst was then synthesized with RGO to get Ag/TiO$_2$/RGO. The amount of RGO is 1% wt of Ag/TiO$_2$. Ag/TiO$_2$ and RGO were mixed in 10 ml distilled water. After that, the solution was sonicated for 4 hours and irradiate with UV for 4 hours. Then the solution dried at 60°C and the solid-state calcined at 500°C for 1 hour.

2.3. Characterization of catalyst

The catalyst was characterized by using SEM-EDX (Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy) and UV-Vis DRS (UV-Vis Diffuse Reflectance Spectroscopy). The SEM-EDX characterization of the catalyst was carried out to see the pattern or surface structure of the synthesized Ag/TiO$_2$ and Ag/ TiO$_2$/RGO catalysts and to see the percentage loading of Ag elements on Ag/TiO$_2$ and the percentage of carbon in Ag/TiO$_2$/RGO catalysts. The UV-Vis DRS characterization is
intended to determine the value of the energy gap band of the TiO₂ photocatalyst composite which has been supported by silver metal.

2.4. Microplastic degradation test
Microplastic degradation test is done by adding microplastics modeled with polyethylene scrub sized 100-150 μm into distilled water. For the test 100 ml distilled water and 50 mg microplastic were added to beaker glass and then 50 mg of catalysts were added to the solution. The solution was stirred continuously during the degradation test. The tests carried out at room temperature with the help of UV irradiation. Tests were conducted for 1, 2, 3 and 4 hours with the same initial amount of microplastic pollutant. The leftover of microplastic in the solution then filtered using Whatman Filter Paper 41. After that, the filter and the microplastic were dried using an oven with temperature 100 °C for 1 hour. The degradation reactor is modeled in Figure 1.

![Figure 1](image)

Figure 1. Design of microplastic degradation test reactor with (A) beaker containing photocatalyst, microplastic and magnetic bar, (B) magnetic stirrer, (C) UV lamp, and (D) reflector.

Determination of the performance of microplastic degradation is done by measuring the percentage of microplastic mass loss for every hour of UV irradiation. The equation for calculating the percentage using Equation (1).

\[
\% = \frac{m_0 - m_t}{m_0} \times 100\% 
\]

where:
\[
\%
\] : microplastic mass degradation percentage (%)
\[
m_0
\] : microplastic initial mass (mg)
\[
m_t
\] : microplastic mass at time t (mg)

3. Result and Discussion

3.1. Characterization of catalyst
The SEM characterization of the catalyst is shown in Figure 2. SEM characterization aims to see the surface pattern or structure of the synthesized Ag/TiO₂ and Ag/TiO₂/RGO catalysts. From the figure, it shows spherical particles, unevenly sized and a bit of agglomeration occur in certain areas. The agglomeration can occur due to the formation of a solid bridge between surface hydroxyl groups during the drying process or combination of the particle after being treated with a high temperature in the
calcination process [10,11]. It can be explained that the treatment of PAD and ultrasonic radiation does not greatly affect the aggregate size of each catalyst sample when compared to TiO$_2$ P25.

From the EDX results, it founded that the mass of silver metal-doped on TiO$_2$ was sufficient by the desired percentage of 2.71%wt Ag on Ag/TiO$_2$ and 3.94%wt on Ag/TiO$_2$/RGO. Therefore, the PAD method used for synthesis gives quite good results of silver dopant on photocatalyst. From the EDX, it also gives the carbon content in Ag/TiO$_2$/RGO with the amount of 1.56%wt which indicates that RGO was compiled with Ag/TiO$_2$ as a composite.

Figure 2 shown the absorbance of catalyst from UV-Vis DRS characterization result of 3%Ag/TiO$_2$ catalyst compared to TiO$_2$ P25. Based on 3, with the presence of silver dopant, the absorbance of light wavelength greater than 380 nm is increasing. Then by using the Kubelka-Munk equation the value of the band gap energy for TiO$_2$ and 3%Ag/TiO$_2$ catalyst was calculated as 3.1 eV and 2.85 eV respectively. The effect of loading silver metal dopants is quite significant in the value of the catalyst band gap energy. This can occur because the silver metal dopant acts as a good electron trapper and causes the band gap energy of the catalyst to decrease so that it can absorb light with a wavelength higher than 380 nm. Moreover, silver metal as a noble metal is highly absorbed UV and visible light and thus can be integrated into a semiconductor to improve photoactivity [12, 13, 14]. The higher absorbance for visible light and also has a plasmonic effect that can help to increase the electron-hole charge separation of photocatalyst [15, 16].
3.2. Microplastic Degradation Test

In this test, there are three variations of the sample and one blank test using no catalyst to test if the degradation of microplastic can happen only with UV irradiation. The catalyst that is used for testing is pure TiO$_2$ P25 catalyst, 3% Ag/TiO$_2$, and 3%Ag/TiO$_2$-1%RGO. The test is carried out using an initial microplastic mass of 50 mg in 100 mL of distilled water and a catalyst of 30 mg. The experiment time is 1 hour, 2 hours, 3 hours, and 4 hours with each experiment will have the same initial amount of microplastic. The results of the experiment can be seen in Table 1.

| Catalyst            | Mass of microplastic (mg) at time |
|---------------------|-----------------------------------|
|                     | 0 h      | 1 h      | 2 h      | 3 h      | 4 h      |
| Without catalyst    | 50       | 50       | 50       | 50       | 50       |
| TiO$_2$ P25         | 50       | 40       | 32       | 26       | 22       |
| 3% Ag/TiO$_2$       | 50       | 30       | 24       | 19       | 16       |
| 3% Ag/TiO$_2$-1%RGO | 50       | 28       | 18       | 14       | 12       |

Based on Table 1 the microplastic degradation performance of 3% Ag/TiO$_2$ and 3% Ag/TiO$_2$-1% RGO catalysts are greater than pure TiO$_2$. This is because silver metal and RGO has high electron mobility properties so that it will act as an efficient electron acceptor to increase the induced photon transfer thus inhibiting the rate of electron-hole recombination [9,12,13]. Also, silver metal is highly absorbed UV and visible light and because of the higher absorbance for visible light can help to increase the electron-hole charge separation of the photocatalyst [16]. Therefore, it will cause more active sites on the surface of the catalyst. Moreover, RGO has a large theoretical specific surface area which can help to increase the electron mobility to RGO so electron will be stored on the surface of RGO. Also because of the large surface area, it can increase the adsorption ability of catalysts so it will help the catalyst to get contact with the pollutant. Using Equation (1), the percentage of microplastic degradation of each catalyst can be calculated. The data of microplastic degradation percentage then plotted into graphic and shown in Figure 4 below.

![Figure 4](image-url)
4. Conclusion
From the study, it can be concluded that the addition of silver metal dopant and RGO to the TiO$_2$ photocatalyst significantly increases the degradation performance of microplastic in water. From the experiment that had been done, the best performance of microplastic degradation is 76% which is from the 3%Ag/TiO$_2$-1%RGO catalyst.

Acknowledgment
The study was funded by PUTI Proceedings of Universitas Indonesia 2020 Grant, No. Contract NKB-1107/UN2.RST/HKP.05.00/2020. The author also would thank all people and organizations that help and support the author during this research.

References
[1] Tofa T, Kunjali K, Paul S and Dutta J 2019 Environ. Chem. Lett. 17 1341-6
[2] Mason S, Welch V and Neratko J 2018 Front. Chem. 6 407
[3] Tyree C, Morrison D, Makitan G and Maulidar I 2018 Mikroplastik dalam Botol Air Mineraldmu. Investigasi Tempo
[4] Benno Meyer-Rochow V, Valérie Gross J, Steffany F, Zeuss D and Erren T 2015 Environ. Res. 142 575-8
[5] Lusher A, Hollman P and Mendoza-Hill J 2017 Microplastics in Fisheries and Aquaculture: Status of Knowledge on Their Occurrence and Implications for Aquatic Organisms and Food Safety
[6] Ali S, Qazi I, Arshad M, Khan Z, Voice T and Mehmood C 2016 Environ. Nanotechnol. Monit. Manag. 5 44-53
[7] Ariza-Tarazona M, Villarreal-Chiu J, Barbieri V, Siligardi C and Cedillo-González E 2019 Ceram. Int. 7 9618-24
[8] Ahmed S, Rasul M G, Martens W N, Brown R and Hashib M A 2010 Desalination 261 3–18
[9] Tavakoli F, Badiei A and Ghasemi J 2019 J. Water Environ. 4 31-9
[10] Sikirman A, Krishnan J, Jai J and Senusi F 2014 Adv. Mater. Res. 894 245–9
[11] Krishnan J, Mohamad E N and Hadi A 2014 Adv. Mater. Res. 661 63–7
[12] Rycenga M, Cobley C M, Zeng J, Li W, Moran CH, Zhang Q, Qin D and Xia Y 2011 Chem. Rev. 111 3669–712
[13] Mogensen K B and Kneipp K 2014 J. Phys. Chem. C. 118 28075–83
[14] Wen B, Liu C and Liu Y 2005 Inorg. Chem. 44 6503–5
[15] Zhang S, Ren F, Wu W, Zhou J, Sun L, Xiao X and Jiang C 2014 J. Colloid Interface Sci. 427 29–34
[16] Zaleska-Medinska A 2018 Metal oxide-based photocatalysis
[17] Tang B, Chen H, Peng H, Wang Z and Huang W 2018 J. Nanomater. 8 105