Influence of carbon-based material incorporation on Ag/Fe$_3$O$_4$/ZrO$_2$ composite as highly efficient catalyst for photo- and sonodegradation of organic pollutant

Y Kristianto$^{1,2}$ and R Saleh$^{1,2}$

$^1$Department of Physics, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Depok 16424, Indonesia
$^2$Integrated Laboratory of Energy and Environment, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Depok 16424, Indonesia

Corresponding author’s email: rosari.saleh@ui.ac.id

Abstract. In this work, a novel quaternary composite, Ag/Fe$_3$O$_4$/ZrO$_2$/NGP and Ag/Fe$_3$O$_4$/ZrO$_2$/graphene, as highly efficient catalysts were prepared through ultrasonic-assisted and co-precipitation methods. The prepared composite was characterized by X-ray diffraction (XRD), thermal gravimetric analysis (TGA) and vibrating sample magnetometer (VSM). The photo- and sonocatalytic activity of prepared composite were studied through the degradation of methylene blue (MB) as a model of organic pollutant under UV light and ultrasonic irradiation, separately. The experimental results showed that the composite contained a combination of the desired nanoparticles. In the catalytic activity, Ag/Fe$_3$O$_4$/ZrO$_2$/graphene exhibited much higher efficiency than Ag/Fe$_3$O$_4$/ZrO$_2$/NGP and Ag/Fe$_3$O$_4$/ZrO$_2$ composite. Furthermore, the influence catalyst dosage was studied. To understand the role of reactive species in the sonocatalytic activity, several scavengers were tested. The reusability study suggested that the prepared composite remain stable even after four cycles reused.

Keywords: Photodegradation, sonodegradation, methylene blue

1. Introduction
In last decades, significant attention has been focused by semiconductor metal oxide (SMO) for their applications in many energy and environmental issues [1, 2]. In environmental field, mostly, SMO has been used as catalyst for wastewater treatment using advanced oxidation process (AOPs), including photo- and sonocatalytic. The main purpose of AOPs is to produce hydroxyl radicals as reactive agent that could degrade organic pollutants from aqueous solution. Among various of SMO that could acts as catalyst, zirconium dioxide nanoparticles (NPs) have been studied to be promising candidates for decontamination of contaminated wastewater system because of their high specific surface are, high stability, environmental friendly and relatively inexpensive [3]. Several studies in the catalytic field revealed that combining ZrO$_2$ NPs with other material such as magnetic nanomaterial, noble metal and carbon based-material to form heterogeneous semiconductor is the best choice to modify the properties of ZrO$_2$ NPs [4–6].
The combination of ZrO$_2$ NPs with magnetic nanomaterial has been done in order to providing magnetism in ZrO$_2$ NPs so that magnetically separation could be done for separating the ZrO$_2$ from contaminated wastewater system. This method is so important when using it in practical application at large scale. Combining ZrO$_2$ NPs with noble metal could make Schottky junction between them, which inhibiting the recombination of generated electron-hole pairs and it also enhance the charge separation [7]. Carbon based-material, such as graphene, has been expected as the material that can support effectively the catalytic performance of ZrO$_2$ NPs by increasing the specific surface area and minimize electron-hole pair recombination [6, 8]. Therefore, the combination of magnetic nanomaterial, noble metal and graphene to produce highly efficient quaternary composite should be promising method to design ZrO$_2$ NPs for degradation of organic pollutant.

Based on these issues, herein, we proposed quaternary Ag/Fe$_3$O$_4$/ZrO$_2$/NGP and Ag/Fe$_3$O$_4$/ZrO$_2$/graphene composite as highly efficient catalyst, which successfully synthesized using ultrasonic-assisted and co-precipitation methods. The catalytic activity of prepared composite was tested toward the degradation of methylene blue (MB) from aqueous solution under UV light and ultrasonic irradiation, separately. Several studies such as catalyst dosages, reactive species and reusability were investigated and the results are discussed.

2. Experimental

2.1. Materials and reagents

Iron(II) sulfate heptahydrate (FeSO$_4$.7H$_2$O), silver nitrate (AgNO$_3$), sodium lauryl sulfate (SLS), disodium carbonate (Na$_2$CO$_3$), ethylene glycol (EG), zirconium(IV) chloride (ZrCl$_4$), and sodium hydroxide (NaOH) are products from Merck. While nano graphene platelet (NGP) and graphene are the products of Angstron Materials with S.A. of 30 m$^2$/g and 400 m$^2$/g, respectively. The analytical grade reagents are used in this study so no further purification is done against these reagents.

2.2. Preparation of samples

The ZrO$_2$ and Fe$_3$O$_4$ nanoparticle were prepared according to our previous articles [9, 10]. In Ag nanoparticles’ preparation, the EG solution is used as a solvent for SLS and silver nitrate, carried out separately and continuously stirred. The solvent used for disodium nitrate is distilled water. A disodium nitrate solution was then poured into the SLS solution, then a silver nitrate solution is added to the mixture of the two solutions. Stirring the mix of the three solutions was carried out for 10 min. After that, the mixture was put into a microwave oven (800 W) for 1 min and continued with 30 min of stirring using a magnetic stirrer. Separation by centrifugation is carried out to separate the mixture. To eliminate impurities from the separation results, washing several times using ethanol and distilled water is carried out. The Ag nanoparticles were obtained from the rinsed separation results heated for 5 h at 120 °C. The Fe$_3$O$_4$/ZrO$_2$ composites were synthesized using ultrasonic-assisted method. Briefly, deionized water and ethanol were used to mix the prepared ZrO$_2$ with Fe$_3$O$_4$ nanoparticle under ultrasonic irradiation exposure for 2 h. The precipitation results are obtained from separating the mixture from the solvent using a centrifuge. The resulting precipitation is then heated under vacuum for 12 h at a temperature of 80 °C. The dried precipitation is composite Fe$_3$O$_4$/ZrO$_2$ labeled FZ. In this synthesis process, molar ratio of Fe$_3$O$_4$ to ZrO$_2$ was adjusted, which is 0.5:1. The Ag/FZ composites were synthesized using same method as described above with 15 wt.% of Ag to the FZ composite. And then, quaternary Ag/Fe$_3$O$_4$/ZrO$_2$/NGP and Ag/Fe$_3$O$_4$/ZrO$_2$/graphene composite were prepared using co-precipitation method with similar procedures as our previous report with various mass ratio 10 wt.% of graphene NGP to the Ag/FZ composites, respectively [11].

2.3. Characterization

The crystal structures of the prepared composite were obtained by Rigaku Miniflex 600 diffractometer with $\lambda$ =1.5406 Å of Cu K-α radiation. Lattice parameters and crystal structure were obtained from
processing XRD pattern data using the Rietveld method and MAUD software. The Oxford Type 1.2 T vibrating sample magnetometer was used to obtain the magnetic characteristics of the prepared composites. The change in mass of the composites as a function of temperature is measured by thermal gravimetric analysis.

2.4. Photo- and sonocatalytic activity
A model of organic pollutant used in this study was 20-mg/L methylene blue (MB) solution. In photo- and sonocatalytic processes, certain amounts of the prepared composites were dispersed with vigorous magnetic stirring in 100 mL of MB solution for 30 min under dark conditions. Then the suspensions were irradiated with UV and ultrasonic irradiation for 2 h. UV-Vis spectrophotometer is used to measure the absorbance of MB every 15 min. MB degradation is presented as $C_t/C_0$ versus irradiation time, $t$, where $C_0$ is the initial concentration of MB and $C_t$ is the concentration of MB at time $t$. The experimental data were obtained by observing characteristic peak of MB absorption at 663 nm.

In photocatalytic, two UV-C lamps with power 40 W was used as sources. While sonocatalytic take place in ultrasonic bath that operated at 40 kHz and 150 W. The similar method as the previous publication was used for scavenger test [11].

3. Results and discussion
Phase structure and crystallinity of prepared samples are given in figure 1a. As we can see in figure 1a, all the main diffraction peaks of Ag, Fe$_3$O$_4$ and ZrO$_2$ nanoparticles occurred in both Ag/FZ/NGP and Ag/FZ/graphene composite, suggesting the crystal phase of those nanoparticles were not destroyed during reaction process. However, there is no diffraction peaks could be found on the incorporation of graphene, which may be due to the low content and weak diffraction intensity of graphene.

In contrast, NGP characteristic peak was detected at 26.49° as graphitic-like structure of NGP with (002) plane. The cubic phase of Ag nanoparticle showed reflection characteristics of the (111) and (200) crystal planes at 2θ = 38.14° and 44.26°, respectively. The diffraction reflections at 30.14°, 35.49°, 43.28°, 53.76°, 57.20° and 62.83° were identified as (220), (311), (400), (422), (511) and (440) planes of cubic spinel Fe$_3$O$_4$, respectively. The reflections at 30.18°, 35.03°, 50.36°, and 59.94° were assigned to the (111), (200), (220), and (311) plane of tetragonal ZrO$_2$, respectively.

The lattice parameters and grain size of the prepared composite shown in table 1 are the results of analyzing using the Debye-Scherrer equation [12] and Rietveld refinement method. As seen in table 1,

![Figure 1](https://example.com/figure1.png)

**Figure 1.** (a) The XRD curve of all prepared samples and (b) VSM measurement of Fe$_3$O$_4$, Ag/FZ and Ag/FZ/10 wt.% graphene.
Table 1. Lattice parameters and grain sizes of all prepared samples.

| Samples       | Ag\(a=b=c\) | Fe\(_2\)O\(_4\)\(a=b\) | ZrO\(_2\)\(c\) | NGP\(a=b=c\) | Ag | Fe\(_2\)O\(_4\) | ZrO\(_2\) |
|---------------|--------------|-----------------|---------------|--------------|----|----------------|----------|
| Ag            | 4.085        | -               | -             | -            | 13 | -              | -        |
| Fe\(_3\)O\(_4\) | -            | 8.375           | -             | -            | -  | 42             | -        |
| ZrO\(_2\)    | -            | 3.605           | 5.146         | -            | -  | -              | 13       |
| Ag/FZ         | 4.085        | 8.388           | 3.605         | 5.145        | -  | 13             | 40       |
| Ag/FZ/NGP     | 4.088        | 8.389           | 3.607         | 5.146        | 3.642 | 12             | 39       |
| Ag/FZ/graphene| 4.092        | 8.393           | 3.608         | 5.149        | -  | 12             | 37       |

The lattice parameter values of Ag, Fe\(_2\)O\(_4\), and ZrO\(_2\) did not change significantly, indicating that the crystallinity of each nanoparticles remain stable after the formation both of Ag/FZ/NGP and Ag/FZ/graphene. Furthermore, Absence of other peaks in the patterns indicated that there were no impurities in any of the prepared samples.

Figure 1b shows VSM measurement for Ag/FZ and Ag/FZ/10 wt.% graphene composite. As a comparison purpose, VSM measurement of Fe\(_3\)O\(_4\) was also plotted. The results show that magnetization of Ag/FZ and Ag/FZ/10 wt.% graphene composite is lower than Fe\(_3\)O\(_4\) nanoparticle. This is due to the presence of Ag and ZrO\(_2\) as non-magnetic material. However, the incorporation of graphene on Ag/FZ composite could increase the magnetization. The presence of graphene on Ag/FZ caused defects such as oxygen vacancy on the Fe\(_3\)O\(_4\) clusters that make occurrence of spin-flipping and thus enhance the magnetization of composite [13]. The inset in figure 1b shows the separation process of Ag/FZ/10 wt.% graphene composite from treated solution using magnetic bar, showing that composite can be easily separated by an external magnetic.

Figure 2a shows TGA plot for Ag/FZ, Ag/FZ/NGP and Ag/FZ/graphene. As can be seen, all TGA plot clearly shows the thermal degradation occurred around 50–200 °C. This degradation is attributed to removal of water molecules that are structurally bound on surface of ZrO\(_2\) nanoparticle [14]. The thermal degradation is also observed on Ag/FZ/NGP and Ag/FZ/graphene at 340 °C and 670 °C, respectively, which indicates combustion process of carbon-based material [15]. The total weight loss due to combustion process may be associated with the amount of NGP and graphene on the Ag/FZ composite.

The photo- and sonocatalytic activity of Ag/FZ/graphene composite was used to degrade MB as model organic pollutant under UV light and ultrasonic irradiation, separately. Figure 2b shows the photo- and sonocatalytic activity of Ag/FZ/NGP and Ag/FZ/graphene composite. For comparison, the photo- and sonocatalytic activity of Ag/FZ composite is also shown. The results demonstrate that the incorporation of NGP and graphene could enhance the catalytic activities of Ag/FZ composite. The highest degradation was obtained using graphene as an additional material. This might be due to the much larger specific surface area of graphene compared to NGP.

In order to obtain the optimum catalyst dosages, photo- and sonocatalytic experiment were carried out by varying the dosage of Ag/FZ/graphene from 0.1 to 0.4 g/L. As shown in figure 3, the percentage of decolorization increased with increasing the catalyst from 0.1 to 0.3 g/L, but the opposite results occurred for a further increase in the catalyst dosages. The increased in catalyst dosages related to increases in the number of active sites so that increasing in the number of photons and dye molecules adsorbed [16]. However, the further increases in dosages leading to increases the turbidity of the suspension, which reduce light penetration and inhibited photo-degradation [16].
To study the main active species that involved in photo- and sonocatalytic process, the experiment was repeated with the addition of di-ammonium oxalate, sodium sulfate and tert-butyl alcohol as hole, electron and hydroxyl radical scavengers, respectively. The influence of these scavengers on the photo- and sonocatalytic activity of Ag/FZ/graphene composite is shown in figure 3b. The presence of scavengers decreased photo- and sonocatalytic performance of Ag/FZ/graphene. The furthest decrease was achieved with the addition of di-ammonium oxalate, which indicate that the holes paid the most important role both in the photo- and sonocatalytic activity.

It is necessary to investigate the stability and reusability of the photo- and sonocatalyst for practical industrial application. Therefore, the catalyst Ag/FZ/graphene was reused by performing recycling reactions for four times. At the end of each cycle, the catalyst was separated from treated solution for reuse in the fresh condition; the results are shown in figure 4. As illustrated in figure 4,
Figure 4. Reusability of Ag/FZ/graphene composite in photo- (left) and sonocatalytic (right) activity.

the Ag/FZ/graphene composite show good reusability, the photo- and sonocatalytic activity still showed good performance after four times uses. However, the performance for the fourth run photo- and sonocatalytic activity is decreased by 5 % and 4 %, respectively compared to the first run.

4. Conclusion
In summary, the quaternary Ag/FZ/graphene composite were successfully prepared through ultrasonic-assisted and co-precipitation methods. As magnetic composite, Ag/FZ/graphene can be easily separated from aqueous solution under the external magnetic bar. The as-prepared composite display highly efficient in photo- and sonocatalytic activity for degrading MB under UV light and ultrasonic irradiation, separately. The incorporation of NGP and graphene could enhance catalytic activities of Ag/FZ composite. The incorporation of graphene exhibited the highest catalytic performances. Optimum catalyst dosage of Ag/FZ/graphene was achieved at 0.3 g/L. In addition, it was found that holes are the main active species both in photo- and sonocatalytic activity. At last, the designed quaternary Ag/FZ/graphene composite exhibited excellent stability and reusability.

References
[1] Huang Y, Yan C F, Guo C Q, Lu Z X, Shi Y and Wang Z D 2017 Int. J. Hydrogen Energ. 42 4007-16
[2] Ji Q, Yu X, Zhang J, Liu Y, Shang X and Qi X 2017 J. Environ. Chem. Eng. 5 1423-8
[3] Renuka L, Anantharaju K S, Sharma S C, Nagabhushana H, Vidya Y S, Nagaswarupa H P and Prashantha S C 2017 J. Alloys Compd. 695 382-95
[4] Fang L, Wu B and Lo I M C 2017 Chem. Eng. J. 319 258-67
[5] Ma J, Guo S, Guo X and Ge H 2015 Ceram. Int. 41 12453-8
[6] Yasin A S, Mohamed H O, Mohamed I M A, Mousa H M and Barakat N A M 2016 Sep. Purif. Technol. 171 34-43
[7] Zhang Y, Wu J, Deng Y, Xin Y, Liu H, Ma D and Bao N 2017 Mater. Sci. Eng. B Solid State Mater Adv. 221 1-9
[8] Hu X S, Shen Y, Zhang Y T and Nie J J 2017 J. Phys. Chem. Solids 103 201-8
[9] Taufik A, Susanto I K and Saleh R 2015 Mater. Sci. Forum 827 37-42
[10] Kristianto Y, Taufik A and Saleh R 2016 J. Phys. Conf. Ser. 776 012040
[11] Kristianto Y, Taufik A, Munisa L and Saleh R 2017 AIP: Conf. Proc 1788 030126
[12] Liu J S, Zhang S, Li Z Q, Zhu K J, Chen J K, Qiu J H, Wang C H, Gao X Q and Wang L P 2012 *Trans. Nonferrous. Met. Soc. China* **22** 2459-64

[13] Majidi M A, Wicaksono Y, Fauzi A D, Taufik A, Saleh R and Rusydi A 2017 *IOP Conf. Ser.: Mater. Sci. Eng.* **188** 012033

[14] Rahulan K M, Vinitha G, Stephen L D and Kanakam C C 2013 *Ceram. Int.* **39** 5281-6

[15] Lin C C and Ho J M 2014 *Ceram. Int.* **40** 10275-82

[16] Sapawe N, Jalil A A and Triwahyono S 2013 *Chem. Eng. J.* **225** 254-65