Effect of Adding Fe$_3$O$_4$ in Graphene/TiO$_2$/Fe$_3$O$_4$ Composite for Phenol Photodegradation Application

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Abstract. In order to improve the performance of TiO$_2$, a material that can increase the adsorption ability of TiO$_2$ is needed, one of which is graphene. Graphene/TiO$_2$ composites can be used to degrade phenol. The addition of a magnet material to the graphene/TiO$_2$ composite, namely Fe$_3$O$_4$ is expected to facilitate the separation of the catalyst after being used in the phenol degradation process. This study aims to synthesize and characterize graphene/TiO$_2$/Fe$_3$O$_4$ composites. The composite obtained was used to degrade phenol. This research begins with the modification of graphene with the surfactant cocoPAS. Synthesis of graphene/TiO$_2$/Fe$_3$O$_4$ composite with various amount of Fe$_3$O$_4$ in composite (0.3, 0.5 and 0.7 g, respectively). Composites used for phenol degradation and separated after degradation. The composite materials were characterized by the scanning electron microscopy (SEM), X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) specific surface areas, Fourier transform infrared (FT-IR) and UV-vis absorption spectroscopy. Graphene/TiO$_2$/Fe$_3$O$_4$ composite with a mass of Fe$_3$O$_4$ in the composite of 0.3 g indicates the highest degradation, while the catalyst separation process after phenol degradation showed the fastest time in the separation of the Fe$_3$O$_4$ mass in the composite, which was 0.5 g. The faster the separation time required, but the performance of the composite in degrading phenol is decreasing.

1. Introduction
Phenol is one of the most toxic, and is used widely in petrochemical, chemical, and pharmaceutical industries [1]. The presence of phenol in aqueous environments presents serious problems due to its toxicity. In humans, excessive exposure to phenol can cause seizures, cyanosis, coma, and even death. Because of its toxicity, wastewater containing phenols must not be discharged in an environment without treatment [2]. Phenol waste treatment methods have been developed, one of which is by photocatalysis technology. Photocatalytic is widely applied for the degradation of liquid waste because it can degrade waste compounds into more environmentally friendly compounds namely CO$_2$ and H$_2$O [3 - 5]. Among semiconductor photocatalyst, titanium oxide (TiO$_2$) is the most widely used for wastewater treatment because of its chemical stability properties, strong degradation power, low cost, and non-toxic [6].

To enhance the adsorption ability and photocatalyst compatibility, TiO$_2$ is composed with carbon-based materials such as activated carbon, carbon nanotubes and graphene. Graphene, since its discovery in 2004 [7], has attracted extensive attention due to its excellent mechanical, thermal, optical, electronic properties, and high surface area [8 - 10]. The graphene is proposed to serve as an...
efficient acceptor for the photogenerated electrons in graphene/TiO₂ composites, thus will suppressing charge recombination and enhancing its photocatalytic activity of the composite as compared to that of pure TiO₂ nanoparticles [11].

Fabricated TiO₂/graphene nanocomposite showed an agglomerated morphology and the synergy effect between TiO₂ and graphene bonds is low. An effective method for controlling the morphology and structure of these composites is to modify the TiO₂/graphene composites with surfactants. cocoPAS or coconut oil-based primary alkyl sulphate is an anionic surfactant that is environmentally friendly because it is made from coconut oil so that it is easily degraded by nature [12 - 13].

However, in the application of photodegradation of organic compounds, TiO₂/graphene composites still considered difficult for separating the photocatalyst material from the solution. So it is necessary to develop composite that are easier to use during the separation process after the photodegradation process [14]. An effective and appropriate method to simplify the separation process is by combining the composite with magnetic materials, thus after photodegradation process was finish, the composite can be magnetically separated from waste water by using an external magnet [15]. One magnetic material that has been widely used for the photocatalytic process is magnetic nanoparticles Fe₃O₄ or magnetite, which is superparamagnetic [16]. Magnetite shows the strongest magnetism among other iron oxides materials [17].

Based on the explanation above, in this graphene/TiO₂ composites, graphene was modified by surfactants cocoPAS is expected to enhance the performance of photocatalysts in degrading phenol compounds. Also the addition of magnetic material, Fe₃O₄ is expected to facilitate catalyst separation and process simplification.

2. Methodology

Graphene for the research was purchased from Hongwu Int’l Group Ltd., cocoPAS (Coconut Oil-Based Primary Alkyl Sulphate), TiO₂ (P25), Nitric Acid (HNO₃), Iron (III) Chloride Hexahydrate (FeCl₃.6H₂O), Iron (II) Chloride Tetrahydrate (FeCl₂.4H₂O), Hydrochloric Acid (HCl), Ammonium Hydroxide (NH₄OH) and aquadest.

2.1 Modification of graphene with cocoPAS surfactant

Graphene with mass of 1 g and 0.5 g of cocoPAS were mixed into 100 ml aquadest. The mixture was sonicated for 1 h. After that, the mixture was filtered using a vacuum pump to obtain solid suspension. The solid suspension was dried in temperature 100 °C to obtain graphene (cocoPAS).

2.2 Synthesis of Fe₃O₄

Firstly, 2.6 g of FeCl₃.6H₂O and 1 g of FeCl₂.4H₂O were dissolved in 5.15 ml of HCl 0.1 N and stirred till all of the solid fully dissolved. After that, the iron salt solution was diluted by adding 7.5 mL of aquadest, followed by stirring using a magnetic stirrer 300 rpm for 15 minutes. 135 ml of NH₄OH 1.5 N were added into the solution. The black colour solution thus obtained was stirred using magnetic stirrer 300 rpm for 1 h. Then, it was washed using aquadest and magnetically separated using an external magnet until it reached pH 7. The obtained solid suspension was dried in temperature 100 °C. The dried product was crushed to obtain Fe₃O₄ in powder form.

2.3 Synthesis of graphene/TiO₂/Fe₃O₄ composite

The synthesized Fe₃O₄ was taken as 0.3, 0.5 and 0.7 grams to vary the composition of Fe₃O₄ in the composite graphene/TiO₂/Fe₃O₄. 1 g of TiO₂ and 0.015 g of graphene (cocoPAS) were mixed into 100 ml aquadest. HNO₃ was added into the mixture until it reached pH 3. Afterwards, the mixture was stirred by using magnetic stirrer 300 rpm for 30 minutes and then sonicated for 30 minutes. 0.3 g of Fe₃O₄ was added into the mixture to make graphene/TiO₂/Fe₃O₄ composites with mass variations of Fe₃O₄ in composites that is 0.3 gram. After that, stirring and sonication is done for 30 minutes. The mixture was dried in temperature 100 °C. Sample was then calcinated with in temperature of 400°C for 2. The dried product was crushed to obtain graphene/TiO₂/Fe₃O₄ in powder form. Furthermore, the
same procedure was performed to synthesize graphene/TiO$_2$/Fe$_3$O$_4$ composites with variations of Fe$_3$O$_4$ in composites, 0.5 and 0.7 grams.

2.4 Performance test of Graphene/TiO$_2$/Fe$_3$O$_4$ composites using phenol compound

0.3 g composite sample graphene/TiO$_2$/Fe$_3$O$_4$ was put into 300 ml of phenol liquid 10 ppm. The experiment was conducted for 3 h, in which first 30 minutes was conducted without light (light off) and next 150 minutes the photodegradation using mercury lamp 250 watt as photon source (light on) was conducted. Photocatalyst used for the process was 0.3 grams powder and continuously stirred during experiment in order to make photocatalyst particles and phenol distributed evenly in sample solution. Quantitative result of degrade phenol was acquired by using UV-Vis Spectrophotometer in accordance with procedure on SNI 06-6989.21-2004.

2.5 Magnetic separation test of Graphene/TiO$_2$/Fe$_3$O$_4$ composites

Magnetic separation test is carried out after the phodegradation process is complete. The vessel containing the mixture of phenol and graphene/TiO$_2$/Fe$_3$O$_4$ composite was placed on an external magnet. Images of the composite sol condition in the vessel were taken from time to time and the time until all composites particles were fully separated from the liquid phase.

2.6 Characteristic

Sample was characterized by using SEM, XRD, FT-IR, BET and UV-vis absorption spectroscopy

3. Result and Discussion

3.1 SEM Characterization

Based on the Figure 1 the morphology of graphene, TiO$_2$ P25 and graphene/TiO$_2$/Fe$_3$O$_4$ composite was characterized using SEM. The SEM image clearly shows that TiO$_2$ and Fe$_3$O$_4$ were attached on the sheets of graphene. In composite, it seen that TiO$_2$ forms are small granules and the magnetic material, Fe$_3$O$_4$ is seen in the form of small clustered. Fe$_3$O$_4$ in the form of clusters can provide advantages in the magnetic separation process of separating magnetic composites from solution, because the volume is relatively large so that the composite magnetic response will be stronger and the superparamagnetic characteristics which are properties of Fe$_3$O$_4$ can be maintained [18]. In the figure, it appears that Fe$_3$O$_4$ is spread on the composite surface. The spread of Fe$_3$O$_4$ on the composite surface is caused by the ultrasonication process in the manufacture of graphene/TiO$_2$/Fe$_3$O$_4$. It can also help make the separation process easier. However, on the other hand, Fe$_3$O$_4$ can cover TiO$_2$ particles which cause TiO$_2$ to not get enough light so that it can reduce photodegradation activity.

3.2 FT-IR Characterization

Figure 2 shows the FT-IR spectra of graphene, TiO$_2$, and graphene/TiO$_2$/Fe$_3$O$_4$ composite. In the wavelength spectrum of 1651 cm$^{-1}$, C-C bonds appear from graphene [20]. At a wavelength of 3185 cm$^{-1}$ there is a peak indicating O-H bonds [21]. At wavelength of 510 cm$^{-1}$, Ti-O-Ti bonds emerge from TiO$_2$ and at 1557 cm$^{-1}$, Ti-O-C bonds appear which are bonds between graphene and TiO$_2$ [22]. Fe-O bonds appear in the spectrum at wavelengths of 615 cm$^{-1}$ originating from Fe$_3$O$_4$ [23]. It shows that this combination is composed of graphene, TiO$_2$ and Fe$_3$O$_4$.

3.3 XRD Characterization

Figure 3 showed the X-ray powder diffraction patterns of graphene/TiO$_2$/Fe$_3$O$_4$. As can be seen, the dominant peaks appeared at 2θ values of 25.3088°; 48.0362°; 37.8106°; 54.0188°; 55.0699° could be indexed to the anatase TiO$_2$ (101); (200); (004); (105); (211) planes (ICDD, No. 01-072-7058). The peaks appeared at about 2θ values of 27.4287°; 68.8803°; 56.6337°; 40.8278°; 70.2697° could be indexed to the rutile TiO$_2$ (110); (301); (220); (111); (112) planes (ICDD, No. 01-089-6975). The
peaks appeared at $2\theta = 34.829^\circ; 48.0362^\circ; 35.7755^\circ; 37.8106^\circ; 42.47^\circ$ correspond to (230); (321); (111); (400); (301) crystal planes of magnetite (ICDD, No. 01-074-4121). Furthermore, no graphene peaks can be observed from XRD diffraction patterns. Similar results were also obtained by Liu, Sun, Liu, and Wang [24] in their research. This is probably due to low graphene content in the composites and the relatively low diffraction intensity of graphene.

**Figure 1.** SEM image of (a) Graphene (b) TiO$_2$ (P25) [19] (c) Graphene/TiO$_2$/Fe$_3$O$_4$ composites

**Figure 2.** FT-IR spectra of (a) graphene, (b) TiO$_2$, (c) graphene/TiO$_2$/Fe$_3$O$_4$
Figure 3. XRD pattern of graphene/TiO$_2$/Fe$_3$O$_4$

Average crystallite size was estimated according to Scherrer’s equation (1) below [25].

$$d = \frac{k\lambda}{\beta \cos \theta}$$

where $d$ is the average crystallite size (nm), $k$ is the wavelength of the Cu Kα applied ($\lambda = 0.15406$ nm), $\beta$ is the peak width at half-maximum and $k$ is the constant usually applied as 0.89. Table 1 shown the average crystallite size of anatase, rutile and magnetite in graphene/TiO$_2$/Fe$_3$O$_4$ were calculated to be 22.5, 25.9, and 22.4 nm, respectively.

Table 1. Average crystallite size

| Crystal         | Size (nm) |
|-----------------|-----------|
| Anatase         | 22.5      |
| Rutile          | 25.9      |
| Magnetite       | 22.4      |

3.4 BET Characterization

The surface area can affect the performance of composites in the process photocatalytic. The higher specific surface area can offer more surface active sites and photocatalytic reaction centers and thus is beneficial to the enhancement of photocatalytic performance [21]. The BET surface area of graphene/TiO$_2$ and graphene/TiO$_2$/Fe$_3$O$_4$ composites are 40 and 38 m$^2$/g, respectively (Table 4.2). The surface area of graphene/TiO$_2$/Fe$_3$O$_4$ is lower than surface area of graphene/TiO$_2$. It is caused by the addition of Fe$_3$O$_4$ in composites that can reduce the surface area of composite. Taufik, Muzaki, and Saleh [26] obtain similar result, where the surface area of TiO$_2$/CuO/graphene composite is smaller when compared to the surface area of TiO$_2$/CuO/graphene/Fe$_3$O$_4$.

Table 2. Specific surface area of samples

| Composite                  | Surface Area (m$^2$/g) |
|----------------------------|-------------------------|
| Graphene/TiO$_2$           | 40                      |
| Graphene/TiO$_2$/Fe$_3$O$_4$| 38                      |
3.5 Photodegradation Application
The percentage of phenol degradation was calculated using equation (2) below [23].

\[
\% \text{ Degradation} = \frac{C_0 - C_t}{C_0} \times 100 \%
\]

Phenol concentrations were obtained from UV-Vis spectrophotometer characterization. Phenol concentration decreases with increasing photodegradation time. Figure 4 below shows the performance of graphene/TiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} composite in degrading phenols with mass variations of Fe\textsubscript{3}O\textsubscript{4} in composites are 0.3, 0.5 and 0.7 grams with phenol degradation percentage of 45.3%, 43.3% and 36.2%, respectively. Performance graphene/TiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} composite with mass variation of Fe\textsubscript{3}O\textsubscript{4} is 0.3 g has a higher performance than graphene/TiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} composite with mass variation of Fe\textsubscript{3}O\textsubscript{4} are 0.5 and 0.7 g. It shows that the higher Fe\textsubscript{3}O\textsubscript{4} mass in the composite, the lower the composite performance in degrading phenol. This is because the surface of TiO\textsubscript{2} was covered by Fe\textsubscript{3}O\textsubscript{4} particles scattered on the composite surface (as seen in the SEM analysis, Figure 1c) so that TiO\textsubscript{2} does not get enough light to activate the photocatalyst. The reduced quantity of light that hits the active site of the photocatalyst causes a small amount of hydroxyl radicals to be formed, so that the performance of the composite to degrade phenol compounds is reduced.

![Figure 4](image)

**Figure 4.** Performance test of graphene/TiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} composites in degrading phenol

3.6 Magnetic Separation Test
The effect of magnetic particle (Fe\textsubscript{3}O\textsubscript{4}) loading on separation efficiency of the composite was clearly shown by the Figure 5 which demonstrates that easy separation of the catalyst through external magnet. The separation time until the composite separated from the solution and the solution became clear for graphene/TiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} composites with mass variations of Fe\textsubscript{3}O\textsubscript{4} in composites were 0.3, 0.5 and 0.7 g are 60, 45 and 23 minutes, respectively. The magnetic separation time is inversely proportional to the amount of mass of Fe\textsubscript{3}O\textsubscript{4} in the composite. The higher the mass of Fe\textsubscript{3}O\textsubscript{4} in graphene/TiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} composites, the faster the separation time needed. The separation time of a composite was determined not only by magnetic response but also the density of the composite. The density of the composite which would also increase as the amount of Fe\textsubscript{3}O\textsubscript{4} increased. High density of composite would make the composite to sink faster in water [18].
4. Conclusion
Graphene/TiO$_2$/Fe$_3$O$_4$ composite photocatalysts have been successfully synthesized and characterized by SEM, XRD, FT-IR, and BET. Based on the experimental results, the higher photocatalytic activity of graphene/TiO$_2$/Fe$_3$O$_4$ composite in degrading phenol is 45.29% with the addition of Fe$_3$O$_4$ mass in the composite which is 0.3 g. The addition of magnetic material, Fe$_3$O$_4$ in composite could the separation process easier using an external magnet. Magnetic separation test show that the higher the mass of Fe$_3$O$_4$ in graphene/TiO$_2$/Fe$_3$O$_4$ composites, the faster the separation time needed.

Acknowledgment
The authors would like to thank DRPM Universitas Riau and Directorate General of Higher Education (DGHE) Indonesian Ministry of National Education for the financial support of this research (Hibah) Penelitian Dasar, no. 482/UN.19.5.1.3/PT.01.03/2021.

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