Performance of TiO$_2$/Graphene (cocoPAS) Composite as Photocatalyst for Removal of Phenols in Aqueous Solution

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Abstract. As one of the hazardous industrial wastes, an excessive amount of phenol in the environment can cause damage to the biological ecosystem and nutrient cycle. Phenol removal can be done by photocatalysis process using photocatalyst materials such as titanium dioxide (TiO$_2$). The photocatalysis activity of TiO$_2$ can be improved by making TiO$_2$-graphene (cocoPAS) composite. The obtained TiO$_2$-graphene (cocoPAS) composite was characterized by Scanning Electron Mircoscopy (SEM), X-ray Diffraction (XRD), Fourier Transform Infrared absorption spectroscopy (FTIR), and Breneur Emmet Teller (BET). The performance of the TiO$_2$-graphene (cocoPAS) composite in phenol degradation was tested in a photocatalysis process with variation are the concentration of phenol (10, 20, and 30 ppm, respectively) and photocatalysis temperature (30, 40, and 50 $^\circ$C, respectively). TiO$_2$ particle loaded on the graphene sheet and Ti-O-C bond was formed at 719 cm$^{-1}$. The size of anatase and rutile crystals are 26.39 nm and 27.39 nm with the fraction of anatase and rutile are 57% and 43%. The surface area of the TiO$_2$-graphene (cocoPAS) composite is 40.9 m$^2$/g. The highest efficiency of phenol degradation was achieved when the concentration of phenol is 10 ppm and photocatalysis temperature is 50 $^\circ$C which efficiency of phenol degradation is 96.9%. The higher concentration of phenol will decrease the efficiency of degradation but the degradation efficiency of phenol increases with an increase in photocatalysis temperature.

1. Introduction
Titanium dioxide (TiO$_2$) is a material that can be used for various purposes like photocatalysis, dye-sensitized solar cells, pigments, sensor devices, and protective coatings. TiO$_2$ is the most widely studied photocatalyst because of its high efficiency, chemical and biological stability, non-toxicity, and low cost [1]. Photocatalysis is a reaction carried out in the presence of a semiconductor and light [2]. The photocatalysis is a method that can be used for various applications such as degradation of various organic pollutants in wastewater, antibacterial activity, production of hydrogen, and purification of air. Recently, the photocatalytic process has recently received great attention for wastewater treatment [3]. As one of the hazardous industrial wastes, phenol can be degraded with photocatalysis process. Many kinds of research have studied about phenol degradation due to their carcinogenicity, toxicity, teratogenicity, and mutagenicity to humans, even at low concentrations [4].

The reaction of photocatalysis depends on energy (photons) and catalyst. When the energy (photons) that fall on the surface of the semiconductor is equivalent or more than the band gap energy of TiO$_2$, the electrons (e-) of the valence band are agitated and move to the conduction band while the hole would be left in the valence band. Hole (h$^+$) in the valence band can oxidize the donor molecule and react with the water molecules to produce hydroxyl radicals (OH$^+$). The hydroxyl radicals have a strong oxidizing power for degrading pollutants [3].

The problems that occur when using pure TiO$_2$ as a photocatalyst material is relatively fast recombination of the photogenerated electron–hole pairs. Therefore, various methods have been
developed to improve its photocatalytic activity. Carbon nanomaterials such as graphene, fullerenes, and carbon nanotubes have attracted considerable attention, especially graphene [5]. Graphene has a large Brunauer-Emmett-Teller (BET) specific surface area, high electron mobility, and excellent thermal conductivity. Graphene is an excellent tank to store the electrons from conduction band of TiO₂. Using graphene as an excellent electron tank is an effective method to separate the electron-hole pairs in TiO₂ and it can improve the performance of photocatalysis. Graphene should be a best solution to modifier photocatalysts compared with other carbon nanomaterials because of its highest electron mobility [6]. The excited electrons transfer from the conduction band of TiO₂ to graphene will increase the separation of the electron–hole pairs [5].

However, TiO₂-Graphene composite has an agglomerated morphology and less synergy effect between TiO₂ and graphene due to the severe aggregation of the graphene layers. A method that can be used to control their morphologies and structures is the modification of TiO₂-graphene composite with a surfactant. CocoPAS is fabricated from coconut oil so it is environmentally friendly. The simplified commercial PAS system behaves in a manner very similar to SDS, forming hexagonal, intermediate, and lamellar phases [7]. Modification TiO₂-graphene with cocoPAS makes the morphology of TiO₂ firmly grown on the surface of graphene which can effectively separate the photo-induced electrons and holes from TiO₂ to the graphene acceptor through interfacial interactions to prevent the electron-hole recombination [8].

2. Materials and Methods

There are two main processes for synthesize TiO₂-graphene (cocoPAS) composite, first modification the surface of graphene using cocoPAS surfactant and then making the composite of graphene (cocoPAS) with TiO₂.

2.1. Materials

Graphene was purchased from Hongwu International Group Ltd. TiO₂ (P25), coconut-oil based primary alkyl sulfate (cocoPAS), HNO₃, and aquades.

2.2. Modification graphene by adding cocoPAS (coconut oil-based primary alkyl sulfate) surfactant

Graphene (1 gram) and cocoPAS (0.5 gram) were mixed with 100 mL aquades. Then, the solution was sonicated for 1 hour. The solution was then dried.

2.3. Synthesis of TiO₂-graphene (cocoPAS) composite

0.015 gram graphene (cocoPAS) was mixed with 100 mL aquades and the solution was sonicated for 30 minutes. After that, 1 g TiO₂ P25 was added into the solution and then sonicated for 30 minutes. The solution was then stirred for 3 hours. Then, the solution was dried. Sample was then calcinated at 400°C for 2 hours in a nitrogen atmosphere.

2.4. Performance test of TiO₂-graphene (cocoPAS) composite for phenol degradation.

0.3 gram TiO₂-graphene (cocoPAS) composite was put into 300 ml of phenol solution 10, 20 and 30 ppm, respectively. The experiment was conducted for 4 hours using mercury lamp as photon source. The solution was continuously stirred during experiment in order to make photocatalyst particles and phenol distributed evenly in sample solution. The photocatalysis process temperatures were controlled at 30, 40 and 50°C, respectively. Photocatalyst used for the process was 0.3 gram 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. Characterization

Sample was characterized by using SEM, BET, FT-IR, XRD, and UV-vis spectroscopy.
3. Results and Discussion
The morphology of TiO$_2$-graphene (cocoPAS) composite was represented in Figure 1. It was observed that TiO$_2$ was successfully loaded on the graphene sheet and some of TiO$_2$ aggregated into larger particles. TiO$_2$ particles is more dominant than graphene because of the small amount of graphene. The graphene sheet is like a bridge that connects TiO$_2$ nanoparticles. Hence, it can increase the separation of photogenerated electron-hole pairs and also enhancing the performance of photocatalysis process [9].

![Figure 1. Morphology of TiO$_2$–graphene (cocoPAS) composite.](image1)

The crystal structures of TiO$_2$-graphene (cocoPAS) composite are shown in Figure 2. The peak at $2\theta = 25.351^\circ, 37.824^\circ, 48.082^\circ, 55.137^\circ, 62.778^\circ, 69.006^\circ, 70.405^\circ$ and $75.058^\circ$ correspond to crystal planes [101], [004], [200], [211], [204], [116], [220] and [215] respectively, indicate formation of anatase titanium dioxide [ICDD card No. 01-070-7348].

![Figure 2. XRD pattern of TiO$_2$-graphene (cocoPAS) composite.](image2)
Table 1. Size and crystalline fraction of TiO$_2$-graphene (cocoPAS).

| Crystal Phase | Crystal Size (nm) | Crystal Fraction (%) |
|---------------|------------------|---------------------|
| Anatase       | 26.39            | 57                  |
| Rutile        | 27.39            | 43                  |

The diffraction peaks of graphene were not shown in the composites due to the relatively low diffraction intensity and low content of the graphene [9]. The average crystal sizes were determined using Scherrer’s equation and the results are shown in Table 1. Average crystal sizes of anatase and rutile in TiO$_2$-graphene (cocoPAS) composite have optimum size for photocatalytic activity. The optimum crystal size for photocatalytic activity is 25 to 40 nm [10]. TiO$_2$-graphene (cocoPAS) composite have anatase and rutile crystal. In generally, anatase phase has a better photocatalytic activity compared to rutile phase, but recently the mixture of anatase and rutile phases have a magical effect on the charge transfer process and it can increase the performance of photocatalysis process compared to pure phases [11].

The surface area of TiO$_2$-graphene (cocoPAS) is 40.9 m$^2$/g. Tang et al. [6] reported that a large BET area not equals a good photocatalytic performance because the surface area is not the only one parameters for photocatalytic activity. The other parameters that can affect photocatalytic performance are crystal size, crystal phase, intensity of photon, etc. Figure 3 present FTIR spectra of TiO$_2$, graphene and TiO$_2$-graphene (cocoPAS) composite. Figure 3(a) shows the spectrum of graphene. FTIR spectrum of graphene has peaks at 1365 cm$^{-1}$ (C-OH), 1669 cm$^{-1}$ (C=O) and the peak located at the range of 3000-3500 cm$^{-1}$ arise from O-H group [12]. FTIR spectra of TiO$_2$ from Figure 3(b) is shown the peak at 400-700 cm$^{-1}$ corresponds to Ti-O-Ti bonding. The band at 1651 cm$^{-1}$ dan 3067 cm$^{-1}$ belongs to O-H [13]. The FTIR spectra of TiO$_2$-graphene (cocoPAS) composite (Figure 3(c)) is show the broad band below 800 cm$^{-1}$ is related to the Ti-O-Ti and Ti-O-C bonds [14]. Also the peak at 652 cm$^{-1}$ and 719 cm$^{-1}$ is corresponds to Ti-O-Ti and Ti-O-C bonds [5].

![Figure 3. FTIR spectra of TiO$_2$, TiO$_2$-graphene (cocoPAS) and graphene.](image)

Photodegradation of phenol was studied by using different concentration of phenol and photocatalysis temperature. Effects of photocatalysis temperature on degradation efficiency are shown in Figure 4. When the concentration of phenol is 10 ppm, degradation efficacy of phenol at 30, 40
and 50 °C are 80.2%, 93.3% and 96.9%, respectively. Efficiency of degradation is increase with an increase in photocatalysis temperature. When the photocatalysis temperature is increase, it can increase reaction rate between phenol molecules and OH radicals [4]. Increase the temperature is also makes the kinetic energy of the phenol molecules increase which modifies the collisions with the catalyst surface. If the photocatalyst surface is very active so numerous free radicals will be present, hence fast cracking reactions of the phenol molecules will take place, otherwise the molecules will escape without degradation [15].

Generally, an increase in photocatalysis temperature results in increased photocatalysis activity. However, when the photocatalysis temperature >80°C it can encourage the recombination of electron and hole of TiO₂ and dislike the adsorption of organic pollutant on the surface of TiO₂; hence the efficiency of degradation is decrease. Therefore, the effective temperature for photocatalysis process is between 20-80°C [16]. From the result of this experiment, the effectiveness photocatalytic activity of TiO₂-graphene (cocoPAS) composite was achieved when photocatalysis temperature was 50 °C.

Effects of concentration of phenol on degradation efficiency are also shown in Figure 4. When the photocatalysis temperature is 30°C, degradation efficiency of phenol at 10, 20 and 30 ppm are 80.2%, 68.5% and 63.4%, respectively. Efficiency of degradation is decrease with an increase in concentration of phenol. This may be because, when the concentrations of phenol increase, the number of active sites on the catalyst becomes insufficient [17]. The increases of the concentration of phenol lead to more molecules were adsorbed on the surface of the photocatalyst. Because of that unavailability of catalyst surface for the building of hydroxyl radicals, hence reduces the photocatalysis activity of the catalyst. Also, enhancing concentration of phenol decreases the number of photons or path length of photon that is arrived on the surface of photocatalyst which reduces the excitation of electron from valance band to conduction band. It results in the decrease in the performance of photocatalysis process [18]. The effectiveness photocatalytic activity of TiO₂-graphene (cocoPAS) composite was achieved when concentration of phenol is 10 ppm.

![Figure 4](image_url)

**Figure 4.** Effect of phenol concentration and photocatalysis temperature on the performance of composites to degrade phenols.

Figure 5 shown that TiO₂-graphene (cocoPAS) composite has a better performance than pure TiO₂ and graphene. The addition of graphene to be composited with TiO₂ can improve photocatalysis activity because graphene is a proper electron tank to promote the separation of the election-hole pairs in TiO₂ [6]. Moreover, from SEM and FTIR results it can be seen that there is a bonding between TiO₂ and graphene. Therefore, using composite is better than using pure material for photocatalysis process.
4. Conclusion

TiO₂-graphene (cocoPAS) composite has been successfully synthesized. Effectivity of performance of photocatalyst material composite was influenced by cristanility, morphology and function group. TiO₂ particle loaded on the graphene sheet and Ti-O-C bond was formed at 719 cm⁻¹. The size of anatase and rutile crystals are 26.39 nm and 27.39 nm with the fraction of anatase and rutile are 57% and 43%. The surface area of the TiO₂-graphene (cocoPAS) composite is 40.9 m²/g. The highest efficiency of phenol degradation was achieved when the concentration of phenol is 10 ppm and photocatalysis temperature is 50°C which efficiency of phenol degradation is 96.9%. The higher concentration of phenol will decrease the efficiency of degradation but the degradation efficiency of phenol increases with an increase in photocatalysis temperature.

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