



Original Article

# Synthesis of Fe<sub>3</sub>O<sub>4</sub>-Reduced Graphene Oxide Modified Tissue-Paper and Application in the Treatment of Methylene Blue

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**Abstract:** Graphene-based composites have received a great deal of attention in recent year because the presence of graphene can enhance the conductivity, strength of bulk materials and help create composites with superior qualities. Moreover, the incorporation of metal oxide nanoparticles such as Fe<sub>3</sub>O<sub>4</sub> can improve the catalytic efficiency of composite material. In this work, we have synthesized a composite material with the combination of reduced graphene oxide (rGO), and Fe<sub>3</sub>O<sub>4</sub> modified tissue-paper (mGO-PP) via a simple hydrothermal method, which improved the removal efficiency of the of methylene blue (MB) in water. MB blue is used as the model of contaminant to evaluate the catalytic efficiency of synthesized material by using a Fenton-like reaction. The obtained materials were characterized by SEM, XRD. The removal of materials with methylene blue is investigated by UV-VIS spectroscopy, and the result shows that mGO-PP composite is the potential composite for the color removed which has the removal efficiency reaching 65 % in acetate buffer pH = 3 with the optimal time is 7 h.

**Keywords:** Graphene-based composite, methylene blue, Fenton-like reaction

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## 1. Introduction

Wastewater treatment has received great attention because of its negative impacts on human life and health. There are various types of wastewater, however, colored organic wastewater is one of the most consideration because it does affect not only human health but also aquatic life. Therefore, the proper treatment of wastewater is necessary [1, 2].

In this report, methylene blue (MB) is employed as a model of the contaminant to evaluate the color processing ability of the synthesized material. MB is a basic dye which has the molecular formula  $C_{16}H_{18}N_3ClS$  (MW: 319.85 g/mol), and the structure is shown below [3].

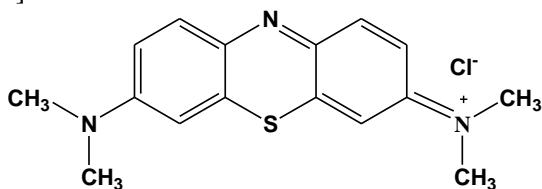


Fig. 1. Structure of methylene blue.

A variety of colored removal technologies is approached for wastewater treatment [1] such as biological degradation, physical or physico-chemical techniques, chemical techniques, and electrochemical techniques. Each of those showed the ability in the removal of colorants and has both advantages and disadvantages. For instance, biological degradation is considered to be low-cost, environmentally friendly [4]. However, it is difficult to apply on a large-scale and not effective with the high concentration of pollutants. Physical or physico-chemical techniques can cause sludge formation, using a large amount of chemicals [5].

To overcome the disadvantages of the above techniques, it is necessary to develop a new method which meets the requirements: high efficiency, applicable for large-scale, active for the wide range of organic pollutants, etc. Among these techniques, advanced oxidation processes (AOPs) is the most effective method which has

met the above requirements [6]. Moreover, to increase the efficiency of dye treatment, many researchers combined some AOPs such as UV/ $H_2O_2$ , UV/Fenton or synthesized new composite materials for good results [5].

The combination of reduced graphene oxide (rGO),  $Fe_3O_4$  and tissue paper form a new material that combines the advantage of all three components [7, 8]. rGO with large surface area is coated onto tissue paper which not only increases the stability of tissue paper but also improves the ability in removing of MB via presenting of functional groups on the surface of rGO [9, 10]. Moreover, the presence of tissue paper will provide a platform which helps the attachment of nanoparticles become easier and tightly keep it in the structure [11].

In this work,  $Fe_3O_4$ -reduced graphene oxide composite was synthesized by hydrothermal method and studied its catalytic ability in removing of MB from aqueous solution. This composite material is considered to be high removal efficiency, good catalytic properties, and it is a precursor to the production of graphene-based materials in the future.

## 2. Experimental

### 2.1. Chemicals

Graphite powder 100% (China),  $H_3PO_4$  85% (China),  $H_2SO_4$  98% (China), HCl 35% (China), Ethanol (BDH Prolabo),  $H_2O_2$  30% (China),  $KMnO_4$  (China), KOH (Merck),  $FeCl_3$  dehydrate (Fisher),  $FeSO_4 \cdot 7H_2O$  (Merck), L-ascorbic acid (BDH Prolabo), methylene blue trihydrate ( $C_{16}H_{18}ClN_3S \cdot 3H_2O$ ) (China). 3-ply tissue paper (Fairy-Vietnam), and double-distilled water.

### 2.2. Procedures

#### 2.2.1. Synthesis of graphene oxide (GO)

Pre-oxidized graphite: Graphite powder was dispersed in 1 M  $HNO_3$  solution at a ratio of 50 g:500 mL and stirred for 30 minutes at 50 °C. Next, the mixture was settled for 30 minutes, then the liquid was decanted. The solid part was

washed by pure water on a funnel with a filter paper. Finally, the cake of pre-oxidized graphite was dried at 110°C for 24 h [12].

A mixture of concentrated H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> was prepared with ratio 9:1 v/v (180 mL:20 mL) into a round-bottom flask and placed in an ice water pot to ensure that the temperature does not exceed 10°C. After that, 2 g of pre-oxidized graphite was added gradually to the mixture of acids under stirring slightly. Then, 12 g of KMnO<sub>4</sub> was slowly added to the obtained mixture and stirred until the mixture become homogeneous (fig 2a). Finally, the blend was kept at 60°C for 3 hours followed by cooling to room temperature and diluting with distilled water (fig 2b). Next, 7 mL of H<sub>2</sub>O<sub>2</sub> was added to the mixture to reduce KMnO<sub>4</sub> excess into Mn<sup>2+</sup> salts (fig 2c). The obtained GO solution was sonicated, ionic removed by dialysis method with 200 nm nitrocellulose membrane (fig 2d) [13].

#### 2.2.2. Synthesis of reduced graphene oxide modified tissue-paper (rGO-PP) composite.

##### a) Fabrication of GO-PP composite

A piece of three-ply tissues paper (PP) was immersed in a GO solution with an initial concentration of 2 mg.mL<sup>-1</sup>. GO allowed to be absorbed by tissues paper until saturated. Then, GO/PP was left in the drying cabinet after being separated from the GO dispersion. This process was repeated for three times.

##### b) Fabrication of reduced graphene oxide modified tissue-paper (rGO-PP) composite

GO-PP was reduced by two reducing agents: ascorbic acid and dimethylformamide (DMF) which was followed by the procedure as below:

**Ascorbic acid:** GO-PP was put into a Teflon-lined autoclave containing 0.1 M ascorbic acid. Then it was heated at 100°C for 6 h to reduce GO. After cooling down to room temperature naturally, the product was washed with double-distilled water (DDW) and ethanol, respectively [14].

**DMF:** GO-PP was put into a Teflon-lined autoclave containing 1:1 v/v DMF: H<sub>2</sub>O. Next, it

was heated at 160°C for 5 h to reduce GO. Then, it was cooled down to room temperature naturally followed by washing with DDW and ethanol, respectively [15].

##### c) Fabrication of magnetic-reduced graphene oxide modified tissue-paper (mGO-PP) composite

GO-PP was put into a Teflon-lined autoclave containing the mixture of 0.1 M Fe<sup>2+</sup>, 0.1 M Fe<sup>3+</sup> with the mole ratio of 1:1. After that, KOH 6 M is added to the mixture such that the pH value reaches 10. Next, it was heated at 100 °C for 6 h. Then, it was washed in turn with DDW and ethanol after cooling down to room temperature naturally [16].

### 2.3. Characterization

The morphology of obtained materials was observed by SEM using Hitachi S-4800 with an accelerating voltage of 15 kV. XRD pattern was acquired with a Bruker D8 diffractometer using Cu K $\alpha$  radiation (1.5418 Å). The size distribution of GO using in this study was carried out on Laser diffraction particle size analyzer (SHIMADZU SALD-2101). The conductivity of the composite was conducted on a two-probe electric-multimeter (HIOKI 3801-Digital HiTESTER - Japan).

The color of the solution changed from dark-green to dark-brown which is the evidence for the successfully oxidized from graphite to GO.

Fig. 3. shows an XRD pattern of graphite and graphene oxide and size distribution of obtained GO. The XRD pattern of graphite has a peak with high intensity at  $2\theta = 26^\circ$  [17]. After oxidized by strong oxidation agents such as H<sub>2</sub>SO<sub>4</sub>, and KMnO<sub>4</sub>, the XRD pattern of GO appear high-intensity peak at  $2\theta$  of  $11^\circ$  [17]. This phenomenon shows that the distance between layers in the structure is amplified by the presence of polar groups such as -OH, -COC-, -COO<sup>-</sup> on the surface. It can be seen clearly that the size distribution of synthesized GO material is quite evenly and centrally in the range of 1÷4  $\mu\text{m}$  (fig 3b).

### 3. Results and discussions

#### 3.1. Synthesis of GO and characteristics

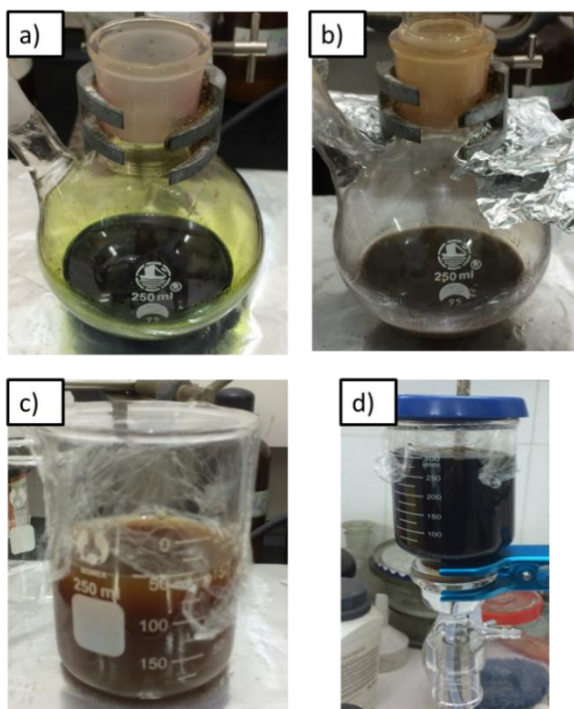


Fig. 2. Synthesis of GO from graphite by modified Hummer's method, a) the mixture of acids and graphite after  $\text{KMnO}_4$  added; b) the reaction mixture after continuously stirring at  $60^\circ\text{C}$  for 3 hours; c) the reaction mixture after cooled and reacted with  $\text{H}_2\text{O}_2$ ; d) GO solution obtained after sonication, ionic removal by dialysis method with 200 nm nitrocellulose membrane.

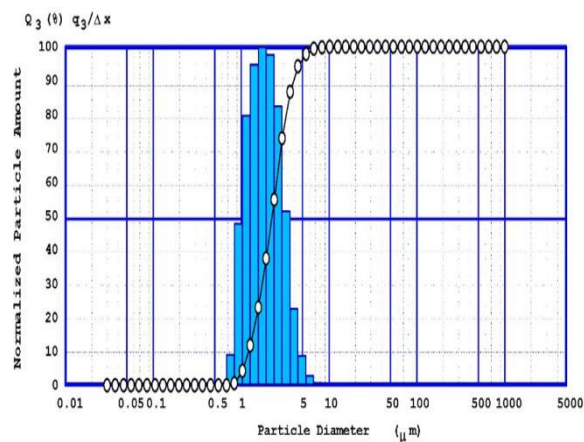
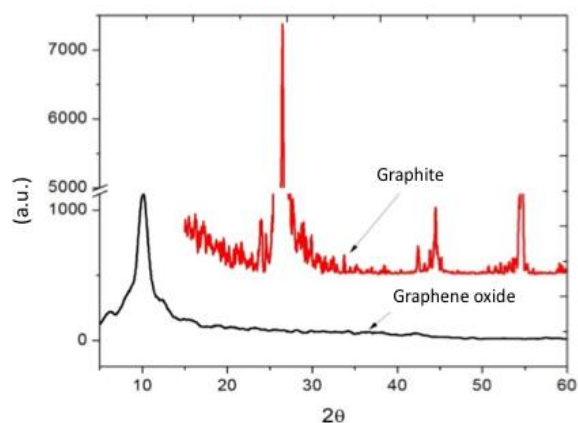


Fig. 3. XRD patterns of graphite and graphene oxide and particle size distribution diagram of GO.

#### 3.2. rGO-PP composite and characteristics

The photographs of synthesized composites are shown in Fig. 4.. They all show black and uniform distribution of color on the tissue paper substrate.

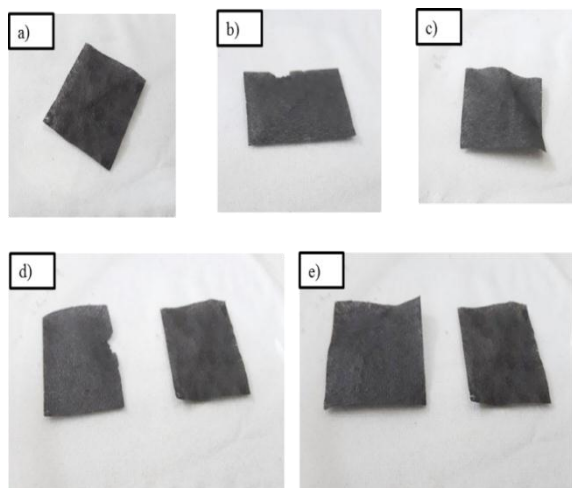


Fig. 4. Photographs of synthesized composites: a) GO; b) rGO-Asc (using ascorbic acid as reducing agent); c) rGO-DMF (using DMF as reducing agent); d) comparison between rGO-Asc (left) and GO (right); e) comparison between rGO-Asc (left) and GO (right).

Table 1. Electrical conductivity of GO-PP and rGO-PP composite

Materials	GO-PP	rGO-Asc	rGO-DMF
Conductivity (mS.cm <sup>-1</sup> )	0	$3.24 \times 10^{-2}$	$1.28 \times 10^{-2}$

As seen from the Fig. 4., rGO has a brighter color than GO, and the data in Table 1 show that GO-PP is a non-conductive material while rGO-PP is a conductive material and the reduction by Asc is more effective than DMF which is shown in the higher electrical conductivity of rGO-Asc in comparison with rGO-DMF. This is the evidence for the successfully reduced GO to rGO.

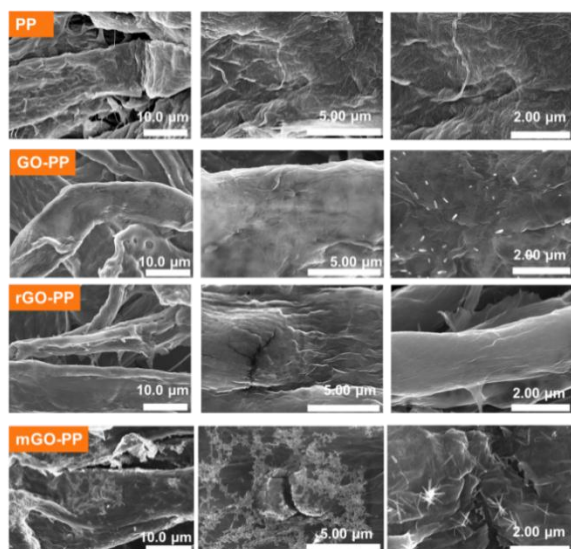


Fig. 5. SEM images of tissue paper (PP), GO-PP, rGO-PP, and mGO-PP.

SEM images were observed at the various magnification, showing the surface morphology of the materials. It is obvious to see from Fig. 5. that the surfaces of composite become less roughness than tissue paper after graphene oxide is coated on the surface. Besides, the SEM images of mGO-PP sample show a dense distribution of Fe<sub>3</sub>O<sub>4</sub> nano-rods on the material surface. This is the evidence for the successful synthesis of the magnetic material on the GO-PP platform becoming a potential candidate for high treatment efficiency to colored organic substances.

### 3.3. Catalytic ability of the composite materials to MB

MB solutions were prepared in the range of 1 - 10 ppm with a buffer solution pH = 3. A baseline of the buffer was measured, then the maximum absorption (UV-vis spectroscopy) wavelength ( $\lambda_{\max}$ ) of the MB solution at 6 ppm was determined with the value of  $\lambda_{\max} = 664$  nm. The optical absorption of the MB solution at  $\lambda_{\max}$  with the different concentrations from 1 ppm to 8 ppm was conducted. The calibration curve was constructed, and the plot is shown in Fig. 6. from the obtained data.

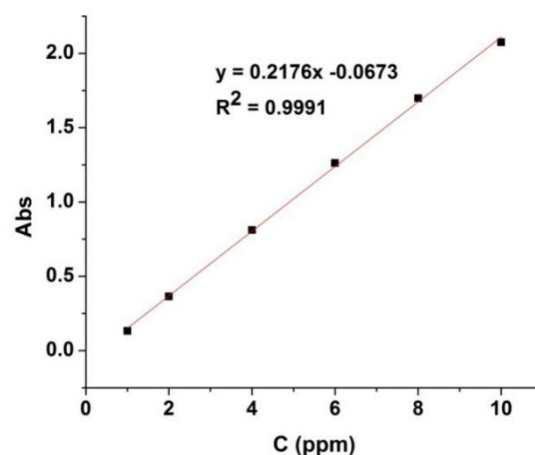


Fig. 6. Calibration curve of MB solution in a buffer solution pH=3.

The GO-PP was transferred into a beaker containing 7 mL of 8 ppm MB in the buffer solution at pH = 3. The solution was measured the value of optical absorption by UV-Vis equipment after 1.5 h, 3 h, 5 h, 7 h. The results are shown in Table 2:

Table 2. Effect of adsorption time on the removal efficiency of MB

Time (h)	1.5	3	5	7
Abs	0.927	0.831	0.606	0.318
C <sub>MB treated</sub> (ppm)	3.43	3.87	4.90	6.23
H (%)	42.88	48.37	61.30	77.86

In which, C<sub>MB treated</sub> and H (%) are calculated by the formula:



$$C_{MB\ treated} = C_{MB\ initial} - C_{MB\ measured\ time}$$

$$= C_{MB\ initial} - \frac{Abs+0.0673}{0.2176}$$

By using the calibration curve, we can calculate the removal efficiency of MB by the equation:

$$H\% = \frac{C_{MB\ treated}}{C_{MB\ initial}} \times 100\%$$

The obtained results are shown as follow:

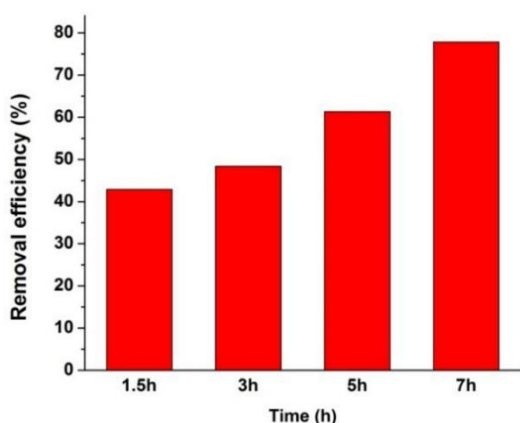


Fig. 7. Effect of adsorption time on the removal efficiency of MB.

The MB removal efficiency of materials at time longer than 7 h did not show the increase. Therefore, the optimal time is 7 h.

### 3.3.1. Effect of H<sub>2</sub>O<sub>2</sub> on the remove of MB

The effect of H<sub>2</sub>O<sub>2</sub> to removing of MB was conducted as below: the same amount of MB was poured into two conical flasks after that one is added H<sub>2</sub>O<sub>2</sub> solution such that its concentration is 20 mM, the other condition is kept unchanged. After 7 h, measure the absorbance of MB in two conical flasks and compare them to conclude the effect of H<sub>2</sub>O<sub>2</sub>. The result is shown in Table 3.

Table 3. The effect of H<sub>2</sub>O<sub>2</sub> on the MB solution

Sample	MB	MB + H <sub>2</sub> O <sub>2</sub>
Abs	1.675	1.521

After 7 hours, the absorbance value of the MB solution in the presence of H<sub>2</sub>O<sub>2</sub> is smaller

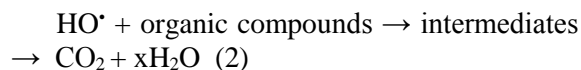
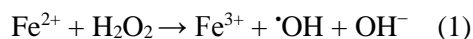
than that of MB with the absence of H<sub>2</sub>O<sub>2</sub>. Because H<sub>2</sub>O<sub>2</sub> can be decomposed to generate free radical which is very active, so it can increase the degradation rate of MB and cause a decrease in MB absorbance.

### 3.3.2. Efficiency of composite materials on the treatment of MB

The procedure is conducted as similar to the above description, but H<sub>2</sub>O<sub>2</sub> solution is absent or present in the mixture and its concentration is 20 mM. The results are shown in Fig. 8. . It can be seen that the presence of rGO in GO-PP, rGO-PP, and mGO-PP enhanced the removal efficiency largely compared with that on PP only. The results could be explained by the high surface area and remain function groups (hydroxide, carbonyl, carboxylic, etc.) on the surface of the rGO, which have electrostatic interaction with MB in aqueous solution [10].

Among these materials, mGO-PP composite shows its potential with the load of 2.433 mg.g<sup>-1</sup> and the efficiency reaches 65 %.

When H<sub>2</sub>O<sub>2</sub> is added, the main reaction is occurred as below [6, 18]:



Because  $\cdot OH$  radicals are very active, it can increase the decomposition of MB leading the increase in removal efficiency of MB.

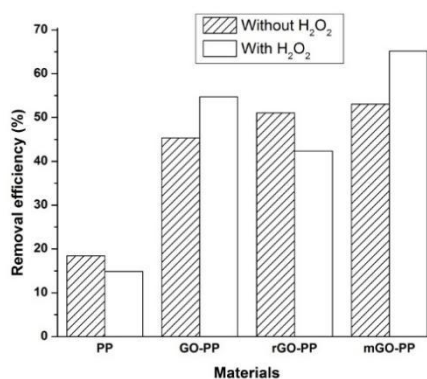


Fig. 8. Comparison of the removal efficiency of the composites in the case with/without the presence of H<sub>2</sub>O<sub>2</sub>.

It can be seen that the removal efficiency is higher in the presence of H<sub>2</sub>O<sub>2</sub>. Because in the presence of H<sub>2</sub>O<sub>2</sub>, it is not only the adsorption process but also the oxidation process occurring in the reaction time, while only the adsorption process occurs if H<sub>2</sub>O<sub>2</sub> is not added.

#### 4. Conclusions

GO has been successfully synthesized from graphite by the modified Hummer's method with uniform size distribution ranging from 1 to 4 μm. rGO-PP and mGO-PP composite have been also synthesized by the simple hydrothermal method. The composites were applied to remove MB from aqueous solution. At the optimal condition, the MB removal efficiency on mGO-PP composite reached 65 % and was higher than that of PP, GO-PP and rGO-PP composite materials. The ability of mGO-PP composite in color removal broaden the choice of materials in the field of water treatment.

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