

## OPTIMIZATION FOR COLOUR REMOVAL PROPERTY OF PREPARED GRAPHENE OXIDE (GO)

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### Abstract

In this research work, graphene oxide (GO) was prepared from graphite powder by Modified Hummer's method. Layers of graphene oxide consist of various oxidizing groups like hydroxyl, epoxides, carbonyl and carboxyl at the basal planes as well as at the edges. Prepared GO were characterized by XRD, FT IR, UV-visible, SEM and EDX techniques. To investigate the colour removal property of GO, malachite green (MG) was used as model dye contaminant. Firstly, wavelength of maximum absorption ( $\lambda_{\max}$ ) of malachite green was investigated at different dye concentrations in the wavelength range of 400-800 nm. Malachite green was found to have  $\lambda_{\max}$  of 617 nm. To investigate the optimum conditions for colour removal, effects of concentration, pH, contact time and dosage on removal of malachite green dye using prepared GO were carried out. The optimal conditions were found to be 10 ppm of MG concentration, pH 4, 60 min of contact time and 0.08 g of adsorbent dosage for colour removal of malachite green by using prepared GO.

**Keywords:** graphite, graphene oxide, Modified Hummer's Method, malachite green

### Introduction

Graphite, one of many allotropes of carbon, can provide great potential in many applications such as in electronic and functional nanocomposites (Hidayah *et al.*, 2017). Single atomic plane layer of graphite is called graphene. Graphene can produce from graphite using by chemical vapour deposition (CVD), mechanical or chemical methods (Zaaba *et al.*, 2017). Both graphite and graphene have unique properties (Hidayah *et al.*, 2017). Graphene Oxide (GO) is prepared from oxidation of graphite powder by Modified Hummer's Method (Mindivan, 2016). The oxidation of graphite in protonated solvents leads to graphite oxide, which consists of multiple stacked layers of graphene oxide. GO has a similar hexagonal carbon structure to graphene but also contains hydroxyl, alkoxy, carbonyl, carboxylic acid and other oxygen-containing functional groups (Smith *et al.*, 2019). GO was synthesized and characterized using various analytical techniques and exploited as adsorbent for rapid removal of malachite green dye from the aqueous solution (Mohamadi *et al.*, 2016).

### Materials and Methods

#### Sample Collections

In this research, graphite powder (extra pure purchased from China Aladdin Industry Corporation), sodium nitrate ( $\text{NaNO}_3$ ), sulphuric acid ( $\text{H}_2\text{SO}_4$ ), potassium permanganate ( $\text{KMnO}_4$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and hydrochloric acid ( $\text{HCl}$ ) were purchased from local chemical shop. All chemicals used were of analytical reagent grade.

#### Preparation of Graphene Oxide

Graphene oxide was prepared from graphite powder using Hummer's Method. Firstly, 5g of graphite and 5 g of  $\text{NaNO}_3$  were added to 120 mL of concentrated sulphuric acid ( $\text{H}_2\text{SO}_4$ ). The mixture was ultrasonicated for 1 h and maintained the temperature approximately 5 °C using ice bath. After that, 15 g of  $\text{KMnO}_4$  was added slowly. Then a mixture was stirred by ultrasonication

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using ultrasonic bath for 1 h for a homogeneous mixture. After that, 250 mL distilled water was added gradually to mixture followed by ultrasonication for 1 h. The brown colour of the mixture was observed. The colour of the mixture changed to light brown. Subsequently, another 100 mL deionized water was added to the mixture and the temperature was increased to 90 °C while stirring for 1 h. Finally, 50 mL of hydrogen peroxide and 100 mL of distilled water were added to obtain a light yellow suspension. When hydrogen peroxide was added, the residual  $\text{KMnO}_4$  and  $\text{MnO}_2$  formed in the solution was also reduced to colourless soluble salts and the colour changes from brown to light yellow.

### **Characterization of Graphene Oxide**

The prepared graphene oxide was characterized by using modern techniques. X-ray Diffraction (XRD, Rigaku, /max 2200, Japan) examined the crystalline phase present in the sample. Fourier Transform Infra-Red (FT IR, spectrometer) was used to investigate the presence of functional groups in the sample. For morphological analysis, Scanning Electron Microscopy (SEM, JOEL-JSM-5610, Japan, Ion Sputter-JEC-1600) was used. The relative abundance of element in graphene oxide was detected by Energy Dispersive X-Ray Fluorescence (EDXRF) method. The absorbance of sample solution was measured by UV-visible Spectrophotometer (Shimadzu: UV-1800).

### **Colour Removal of Malachite Green Dye Solution by the Prepared Graphene Oxide**

In this research, prepared graphene oxide was used for investigation of colour removal efficiency. The stock solution of malachite green (MG) (1000 mg/L) was prepared in distilled water. Series of standard MG solution were prepared by serial dilution. The absorbance values of standard solutions were measured at the wavelength range of 400-800 nm by means of a spectrophotometer. The standard calibration curve was constructed by plotting the absorbance versus concentration of the malachite green solution.

### **Determination of the Optimum Conditions for Colour Removal of MG Dye**

For the determination of the optimum conditions for colour removal of MG dye by using prepared GO, effects of initial dye concentration, pH, contact time, dosage of adsorbent were carried out.

#### **Effect of initial concentration of malachite green**

Accurately weighed samples (0.06 g each) were placed in separate conical flasks. Then 50 mL each of dye solution was added into each conical flask. The mixtures were shaken for 120 min and the sampling mixture was centrifuged immediately at 200 rpm for 20 min to obtain a clear solution. After sampling out 10 mL of clear solution the residual content of malachite green in the solution was determined by a spectrophotometer at 617 nm.

#### **Effect of pH on the colour removal of malachite green**

Accurately weighed samples (0.06 g each) were placed in separate conical flasks. Then, 50 mL each of dye solution was added into each conical flask. The initial pH value of the solution was previously adjusted with 0.1 M HCl or NaOH using a pH meter and shaken with electric shaker at room temperature for 1 h and the sampling mixture was centrifuged immediately at 200 rpm for 20 min to obtain a clear solution. After sampling out 10 mL of clear solution the residual content of malachite green in the solution was determined by a spectrophotometer at 617 nm.

### Effect of contact time on the colour removal of malachite green

Accurately weighed samples (0.06 g each) were placed in separate conical flasks. Then 50 mL each of dye solution was added into each conical flask and was shaken with electric shaker. The contact time was varied at interval of 30 min, 60 min, 90 min, 120 min and 150 min. The sample solution was centrifuged immediately at 200 rpm for 20 min to obtain a clear solution. The residual content of malachite green in the solution was determined by a spectrophotometer at 617 nm.

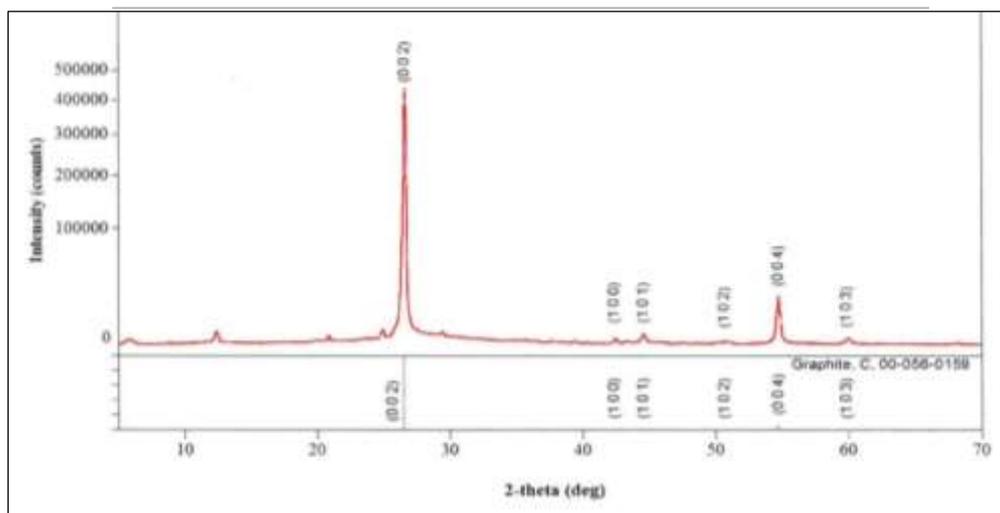
### Effect of dosage of graphene oxide for the colour removal of malachite green

The samples of various masses (0.02, 0.04, 0.06, 0.08 and 0.10) g were separately placed in the conical flask and 50 mL each of standard dye solutions was added into each conical flask. In order to attain complete equilibrium, the solutions were shaken with electric shaker for 1 h at room temperature. The sample solutions were removed from the sorbent by centrifugation at 200 rpm for 20 min. The residual content malachite green in the solution was determined by a spectrophotometer at 617 nm.

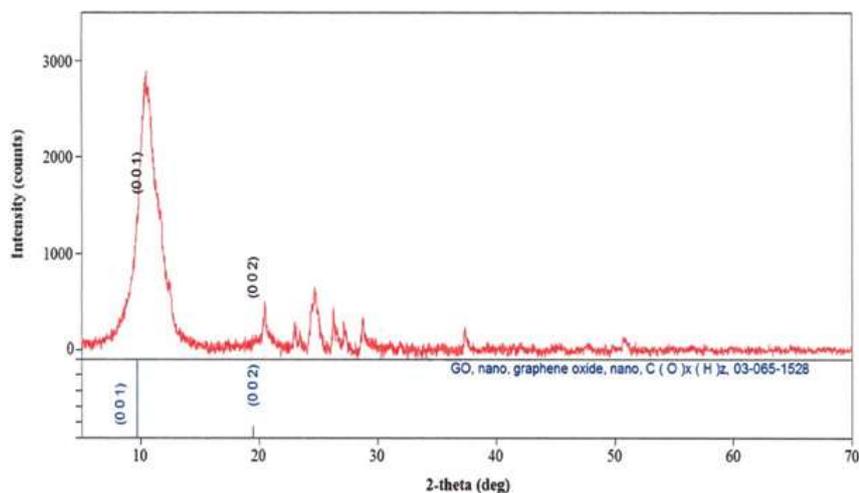
## Result and Discussions

### X-ray Diffraction (XRD) Analysis

A sharp diffraction peak of graphite powder was observed at  $2\theta$ ,  $26.609^\circ$  (002) and d-spacing (interplanar spacing) was 0.334 nm (Figure 1). For graphene oxide its diffraction peak appeared at  $2\theta$   $10.557^\circ$  with d-spacing of 0.850 nm (Figure 2). The characteristic (001) crystal plane of GO was evident. The increased distance in GO was due to the introduction of a number of oxygen-containing groups on the edge of each layer, which increased the distance between the layers. The crystallite size of graphite was calculated based on the (002) plane, using the Scherrer's equation and found to be 40.3 nm whereas that of the prepared GO was 4.1 nm.



**Figure 1** X-ray diffractogram of graphite powder

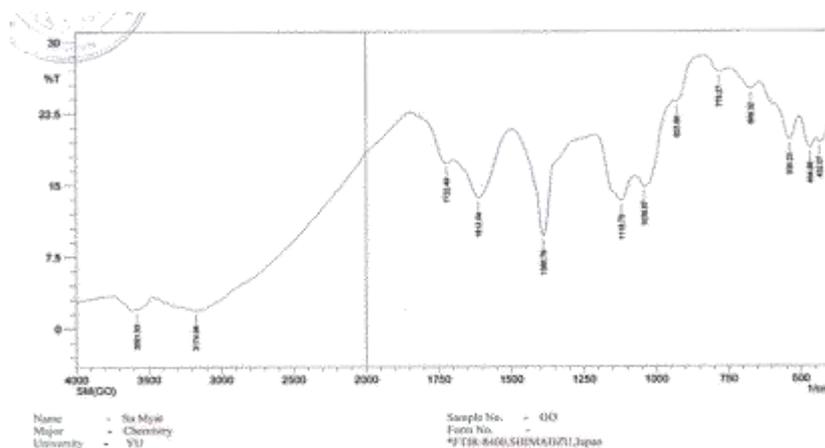


**Figure 2** X-ray diffractogram of prepared GO

## Characterization of Prepared GO

### FT IR analysis

The FT IR spectrum of GO (Figure 3) shows the intense and broad peak that appeared at  $3581\text{ cm}^{-1}$  due to the presence of (O-H) bond, the stretching vibration of hydroxyl group. Moreover, C=O carbonyl stretching (COOH) group at  $1722\text{ cm}^{-1}$  and the C-O epoxy group stretching at  $1039\text{ cm}^{-1}$ . With the presence of all these carboxylic, hydroxyl and epoxide groups oxygen molecules were confirmed to be highly occupied at the edge and the basal plane of GO which can be concluded that GO was synthesized successfully.



**Figure 3** FT IR spectrum of graphene oxide

### Optical property

The UV spectroscopic measurement was carried out in the range of 200-400 nm to monitor the optical property of graphene oxide (Figure 4). The  $\pi-\pi^*$  absorption peaks of graphene oxide appeared at  $\lambda_{\text{max}} = 238\text{ nm}$  which was in agreement with the reported value of Hidayah *et al.* (2017). The absorption peak at 238 nm in the UV spectrum of GO corresponds to  $\pi \rightarrow \pi^*$  transitions of the aromatic  $\text{sp}^2\text{ C} = \text{C}$  bonds.

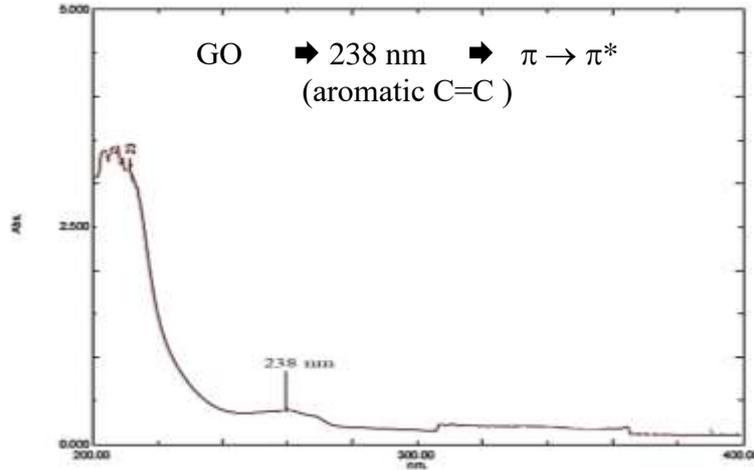


Figure 4 UV absorption spectrum of GO

**Scanning electron microscopic (SEM) analysis**

The SEM measurement was carried out to investigate the morphology of prepared GO (Figure 5). In SEM micrograph, platelet-like morphology was observed in GO crumpled morphology.

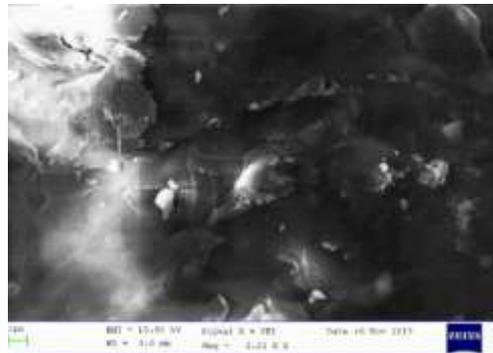


Figure 5 SEM micrograph of graphene oxide (GO)

**Energy Dispersive X-Ray (EDX) Analysis**

The elemental composition of prepared GO was analyzed by Energy Dispersive X-Ray (EDX) spectrometer (Figure 6 and Table 1). EDX analysis pointed out that elemental composition of carbon and oxygen in GO was found to be 53.82% and 41.84%. According to the literature (Mindivan, 2016) oxygen percent 41.84% in GO can be confirmed the formation of GO.

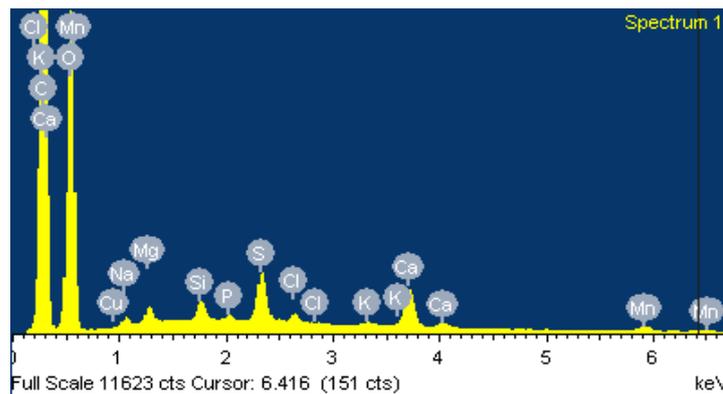


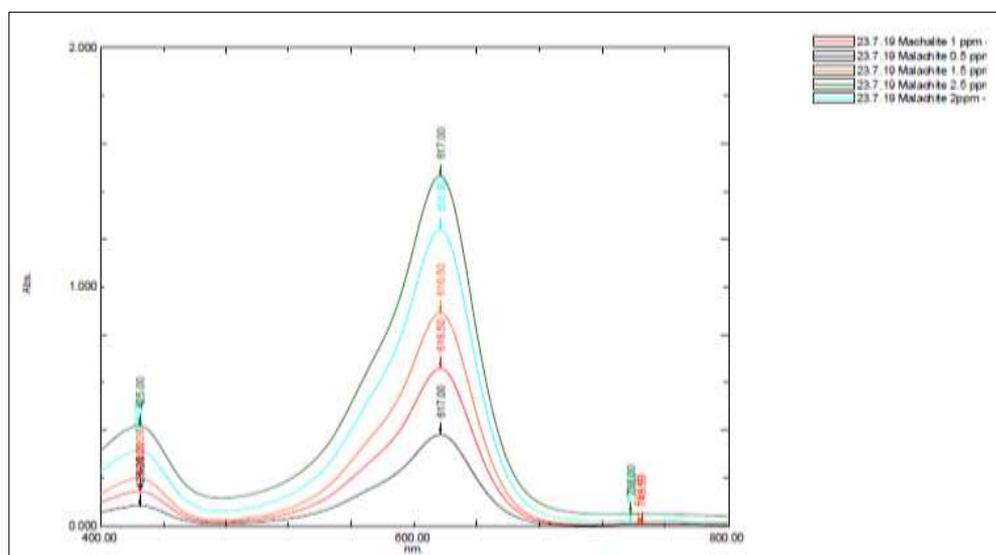
Figure 6 EDX spectrum of graphene oxide (GO)

**Table 1 Relative Abundance of Elements in Graphene Oxide**

No.	Elements	Weight (%)
1	C	53.82
2	O	41.84
3	Na	0.28
4	Mg	0.39
5	Si	0.36
6	P	0.12
7	S	1.11
8	Cl	0.21
9	K	0.10
10	Ca	1.23
11	Mn	0.38
12	Cu	0.16
13	Total	100.00

### The Wavelength of Maximum Absorption of Malachite Green

In this work, the absorption spectra of MG Dye with various concentrations were recorded in the wavelength range of 400-800 nm. It was observed that the wavelength of maximum absorption was 617 nm (Figure 7).



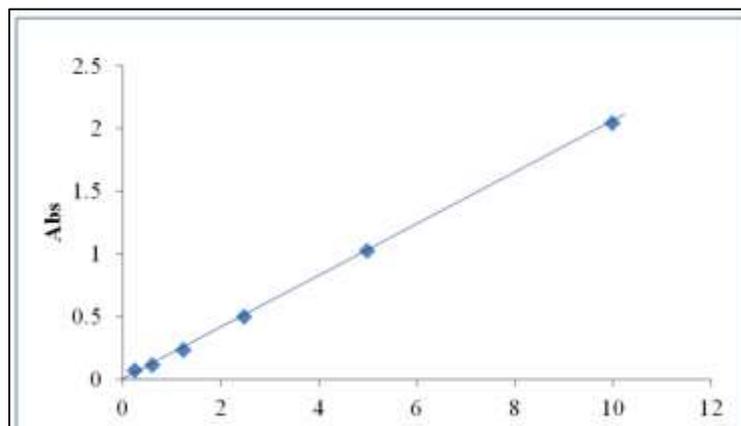
**Figure 7** Wavelength of Maximum Absorption of Malachite Green at Various Concentrations

### Construction of Standard Calibration Curve

Standard calibration curve for malachite green dye at various concentrations was constructed. At a wavelength of maximum absorption ( $\lambda_{\max}$ ) of 617 nm, a plot of absorbance vs. concentration was also drawn by plotting six different concentrations (0.312, 0.625, 1.250, 2.500, 5.00 and 10.000 ppm) of MG dye. The curve was straight line and passed through the origin indicating that Beer's Law was well obeyed (Table 2 and Figure 8).

**Table 2 Changes of Absorbance with Concentration of Malachite Green**

Concentration (ppm)	Absorbance at 617 nm
0.312	0.0052
0.625	0.0701
1.250	0.18884
2.500	0.4457
5.000	1.0176
10.000	2.0101



Concentration of malachite green (ppm)

**Figure 8** Calibration curve for malachite green

**The Optimum Conditions for Colour Removal of MG Dye using Prepared GO**

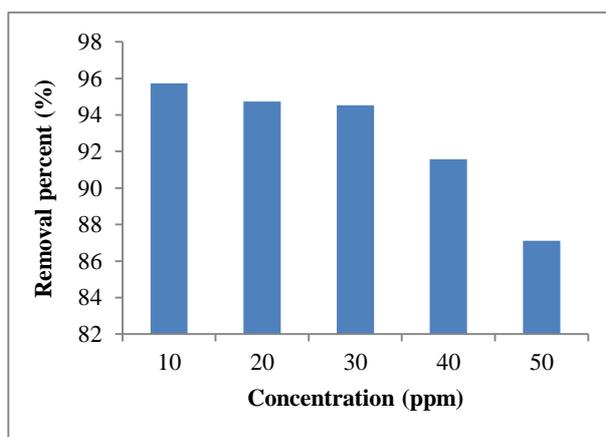
**Effect of initial concentration**

The effect of initial concentration of dye on adsorption capacity was well studied and elicited. The initial concentrations of MG dye in solution were varied as 10, 20, 30, 40 and 50 ppm at pH 7 by using 0.06 g of prepared GO. The maximum colour removal efficiency was obtained at initial concentration of MG dye (10 ppm). The highest colour removal percent was 95.73% as shown in Table 3 and Figure 9. With increase in initial dye concentration the available adsorption sites became saturated and insufficient to accommodate the increasing amount of dye molecules.

**Table 3 Effect of Initial Concentration of Malachite Green**

No.	Concentration (ppm)	Percent Removal (%)
1	10	95.73
2	20	94.73
3	30	94.52
4	40	91.57
5	50	87.12

Volume of dye solution = 50 mL  
 Weight of sample (GO) = 0.06 g  
 Contact Time = 60 min  
 Temperature = room temperature  
 pH = 7



**Figure 9** Effect of initial concentration of malachite green

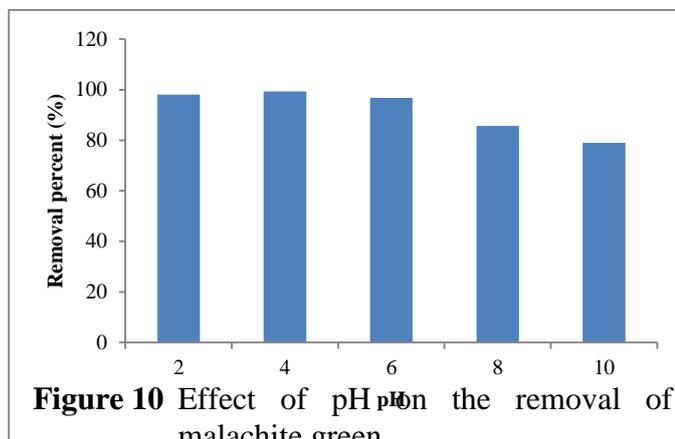
### Effect of pH

The effect of pH (2, 4, 6, 8 and 10) on removal of MG dye by using prepared GO was carried out for 60 min at room temperature. The maximum colour removal efficiency of 99.30 % was obtained at pH 4 by using 0.06 g of prepared GO (Table 4 and Figure 10).

**Table 4 Effect of pH on the Removal of Malachite Green**

No.	pH	Percent Removal (%)
1	2	98.08
2	4	99.30
3	6	96.83
4	8	85.71
5	10	79.02

Volume of dye solution	=	50 mL
Concentration	=	10 ppm
Weight of sample	=	0.06 g
Contact Time	=	60 mins
Temperature	=	room temperature



**Figure 10** Effect of pH on the removal of malachite green

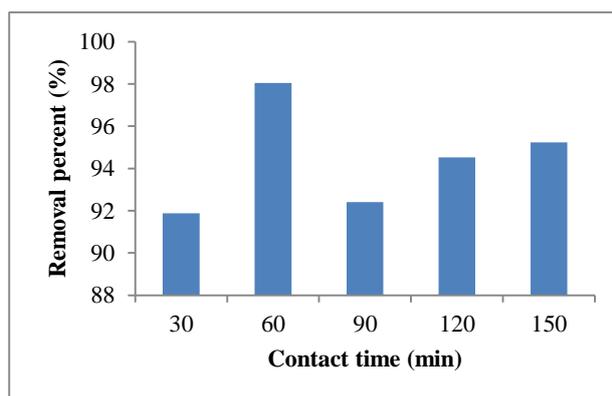
### Effect of Contact Time

The effect of contact time between the adsorbent and adsorbate was varied as (30, 60, 90, 120 and 150 min) on rotary shaker. After 60 min of contact time, the highest colour removal percent (98.05 %) was obtained using 0.06 g of prepared GO at RT and pH 7 (Figure 11 and Table 5).

**Table 5 Effect of Contact Time on the Removal of Malachite Green**

No.	Time (min)	Percent Removal (%)
1	30	91.88
2	60	98.05
3	90	92.41
4	120	94.53
5	150	95.23

Volume of dye solution	=	50 mL
Concentration of dye solution	=	10 ppm
Weight of sample	=	0.06 g
Temperature	=	room temperature
pH	=	7



**Figure 11** Effect of contact time on the removal of malachite green

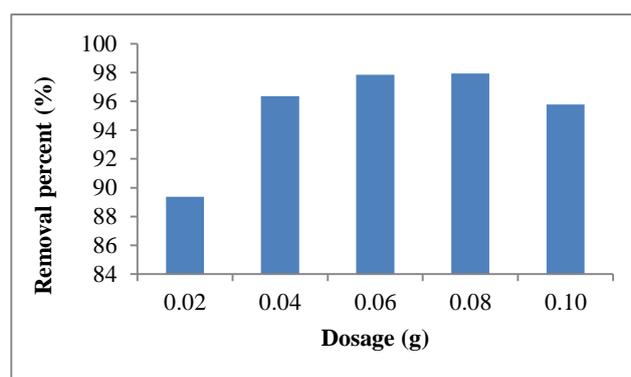
### Effect of Dosage

The dosage of adsorbent was varied in the range of 0.02 to 0.10 g (0.02, 0.04, 0.06, 0.08 and 1.00) g while keeping contact time and concentration of MG at 60 min and 10 ppm respectively. The maximum colour removal percent was observed at the dosage of 0.08 g of prepared GO (Figure 12 and Table 6). When the amount of dosage of GO was increased, the total surface area of the adsorbent became larger. Subsequently, the available adsorption sites also increased, which in turn improved the dye adsorption process. However, as the dosage amount further increased to 0.10 g the colour removal percent slightly decreased due to the desorption of dye molecules.

**Table 6 Effect of Dosage of Graphene Oxide for Removal of Malachite Green**

No.	Dosage (g)	Percent Removal (%)
1	0.02	89.38
2	0.04	96.35
3	0.06	97.84
4	0.08	97.92
5	0.10	95.78

Volume of dye solution	= 50 mL
Concentration of dye solution	= 10 ppm
Time	= 60 mins
Temperature	= room temperature
pH	= 7



**Figure 12** Effect of dosage of graphene oxide for removal of malachite green

### Conclusion

Graphene oxide was successfully prepared by oxidizing graphite by a Modified Hummer's Method. Chemical method results as an efficient method for the synthesis of GO as required for various applications. The prepared GO was confirmed by XRD, FT IR, SEM, UV-visible spectroscopy and EDX result. The optimized values of initial concentration of MG dye, pH, contact time and adsorbent dose were found to be 10 ppm, 4, 60 min and 0.08 g, respectively, for colour removal using prepared GO. These unique properties possessed by graphene oxide could open up possibilities to satisfy the needs in various applications.

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