OPTIMAL CONDITION FOR THE REMOVAL OF METHYLENE BLUE BY USING GRAPHENE OXIDE (LGO, CGO) AND THEIR PROPERTIES

Nwe Nwe Win[1], Thazin Nyo[2], Ohn Ohn Soe[3]

Abstract

Environmental pollution as a result of rapid development of technologies is one of the serious global concerns. Dyes are usually used in textile manufacturing and are one of the major contaminations in water. Thus, from an environmental point of view, the removal of dyes is of great concern, and recent applications using graphene oxides showed high adsorption ability. Graphene oxide (GO) is a highly effective absorbent of methylene blue (MB) and can be used to remove from aqueous solution. Two different graphene oxides (LGO and CGO) were synthesized from two different graphite sources by using modified Hummer method. Local graphite sample (LGP) was collected from Lin-yaung-chi mine and commercial graphite powder (CGP) was purchased from local chemical shop. The crystalline structures of different graphite varieties and prepared graphene oxides were also characterized by XRD. The optical properties of each graphite and prepared graphene oxides were characterized by UV-Vis spectrometer. The analysis of FT IR spectra was performed to investigate functional groups of graphite and the prepared GO. The surface morphologies of each graphite and prepared graphene oxides were characterized by scanning electron microscope (SEM). Graphene oxide is a material containing functional groups such as carboxyl, carbonyl, epoxy and hydroxyl, that can adsorb cationic dyes. Factors such as initial concentration of dye (MB), the dosage, temperature, contact time, rpm and pH were evaluated. The adsorption capacities of methylene blue on CGO and LGO were nearly 99% under the optimal conditions (dosage = 0.1 g, MB concentration 30 ppm, contact time = 60 min, temperature 35 ºC, rpm = 150 and pH=8). Results show that the adsorption equilibrium, the removal efficiencies were higher than 99 % and the solution can be decolorized to nearly colourless. Results show that GO is an effective adsorbent being used to treat effluents contaminated with dyes.

Keywords: Graphite, graphene oxide, modified Hummer's method, dye and adsorption capacity

Introduction

Environmental pollution is one of the main problems nowadays. The rapid development of industries and the drastic increase of population are responsible for the destruction and damaging of the environment and adversely affecting the health of the people (Atkovska *et al*, 2018). Dyes are widely used in the textile, food, cosmetics, pharmaceutical, tanneries, electroplating factories and host other industries (Sayan, 2006). The methods of colour removal from industrial effluents include biological treatment, chemical coagulation followed by sedimentation, flotation, adsorption, oxidation and photocatalytic discoloration (Ozkan and Gokcay, 2010). Among these methods sorption processes appear to be preferable techniques. Graphene oxide has proven to be a promising adsorbent for removal of pollutants from water. There are some publications which report that the synthetic GO can be used directly for water treatment and exhibit high adsorption capacities toward dyes and heavy metal ions (Long *et al.*, 2016).Graphene oxide (GO) could be used for heavy metal removal. GO can be directly used as an effective absorbent for the decoloration of methylene blue which is widely applied to dye, cotton, wood, and silk. GO has a huge absorption capacity for MB, which is competitive with other high performance absorbents. The fast absorption process of MB onto GO is one

[1] 3PhD Chem-8, Department of Chemistry, University of Yangon
[2] Dr, Lecturer, Department of Chemistry, Dagon University
[3] Dr, Associate Professor, Department of Chemistry, Loikaw University

advantage. The absorption capacity of GO is regulated by many influencing factors such as dosage, concentration, temperature, contact time, stirring speed and pH (Sheng *et al.*, 2011).

The present work is concerned with the synthesis of graphene oxide as adsorbent for removal of dye.

Materials and Methods

Materials

In this research, local graphite was collected from Lin-yaung-chi mine, Mogok Township. Commercial graphite was purchased from local chemical shop. They were used without further purification. All chemicals used were of analytical reagent grade.

Preparation of Graphene Oxides

Each graphene oxide was prepared according to the modified Hummer method (Song *et al*., 2014). 5 g of graphite and 2.5 g of $NaNO_3$ were mixed with 108 mL H_2SO_4 and 12 mL H_3PO_4, and stirred in an ice bath for 10 min. Next, 15 g of $KMnO_4$ was slowly added so that the temperature of the mixture remained below 5 °C. The suspension was then reacted for 2 h in an ice bath and stirred for 60 min before again being stirred in a 40 °C water bath for 60 min. The temperature of the mixture was adjusted to a constant 98 °C for 60 min while water was added continuously. Deionized water was further added so that the volume of the suspension was 400 mL. After 5 min, 15 mL of H_2O_2 was added to stop oxidation reaction and to reduce excess $KMnO_4$ and the colour of mixture changed to brilliant yellow.The reaction product was washed with deionized water to remove the acid and with 5% HCl solution repeatedly to remove metal ions. The GO gel-like layer starts appearing when the pH of the supernatant is neutralized, after several centrifugation rounds. All GO samples were well-dispersed as a brownish aqueous colloidal suspension of physiological pH and stable at room temperature. Finally, the product was dried at 60 ºC.

Characterization of Different Graphites and the Prepared Graphene Oxides by XRD, UV-Vis, FT IR and SEM

The different graphite varieties (LGP and CGP) and prepared graphene oxides (LGO and CGO) were characterized by XRD, UV-Vis, FT IR and SEM.

Colour Removal Efficiency of Methylene Blue Model Dye Solution by the Prepared Graphene Oxides

In this research, the prepared graphene oxides (LGO and CGO) were used for investigation of colour removal efficiency. The stock solution of methylene blue MB (1000 mg/ L) was prepared in distilled water. All working solutions were prepared by dilution of the stock solution with distilled water to get the required concentrations. Adsorption experiments were carried out in a rotary shaker at different speeds and ambient temperature, using 250 mL shaking flasks containing 50 mL different concentrations of dye solutions (5-35 mg/L). The initial pH values of the solutions were previously adjusted with 0.1 M HCl or 0.1 M NaOH using a pH meter (pH 2011).

Different doses (0.02 g-0.1 4 g) of sorbents were added to each flask. After shaking the flasks for predetermined time intervals, the samples were withdrawn from the flask and the dye solutions were separated from the sorbent by filtration. Dye concentrations in the supernatant solution were estimated by measuring absorbance at wavelength of maximum absorption of dye

with a UV-Visible (1240) spectrophotometer (Shimadzu, Japan). The removal percent was calculated by the following equation:

$$R\ \% = A_0 - A_e / A_0 \times 100$$

where, A_0 and A_e (ppm) are the liquid-phase concentrations of dye at initial and at any time t, respectively (Ahmad *et al*., 2014).

Results and Discussion

XRD Analysis

The crystalline structures of different graphite varieties and prepared graphene oxides were characterized by XRD. XRD patterns of LGP and prepared LGO are shown in Figures 1 (a) and (c). The XRD spectra of LGO shows a sharp diffraction peak at $2\theta = 10.104^{\circ}$ with an interlayer distance of 0.8747 nm. The increase in interlayer spacing from 0.3248 nm in the case of LGP to about 0.8747 nm for LGO is due to the introduction of the various functional groups that have been introduced by the oxidation of the LGP. This spacing is slightly larger than that of the d spacing of local graphite (LGP).

The XRD patterns of commercial graphite (CGP) exhibited a strong and sharp peak at 26.609º in Figure 1(b), indicating a higher ordered structure, that corresponds to a basal spacing d_{002} = 0.33473 nm. Figure 1(d) shows the pattern of prepared graphene oxide (CGO), exhibited a (001) reflection at 10.557º corresponding to a basal spacing of d_{001} = 0.8373 nm. According to Figures 1 (a, b) the crystallite sizes were found to be 56.0 nm and 40.3 nm. LGP and CGP were found to have hexagonal structure. The prepared LGO and CGO were also found to have hexagonal structure. The smallest crystallite sizes were found to be 5.13 nm and 4.05 nm (Figures 1 (c, d)).The intensity and position of the GO peak in the XRD pattern can be used as an indication of the oxidation degree. The intensities of GO peaks increase with increasing the oxidation process while the GP peak disappears in the case of the complete oxidation. The peak intensity of GO has increased by increasing the oxidation time. The interlayer distance increased clearly from GP to GO due to the presence of oxygenated functional groups and intercalated water molecules (Table 1).

UV-Visible Analysis

UV-visible spectra of GO (LGO and CGO) were measured by an UV mini-1240 Shimadzu spectrophotometer in aqueous solution. The UV-vis spectroscopic measurement was carried out in the range of (200 – 400) nm to monitor the graphite samples and the degree of oxidation for the graphene oxide samples. The maximum π -π* transition of C = C, C - C peaks of LGP and CGP were found (λ = 258.0 nm and λ = 267.3 nm).Upon oxidation of graphite, the maximum n-π* transition of C = O peaks of LGO and CGO were found (λ = 311.6 nm and λ = 307.6 nm) (Table 2 and Figure 2).

FT IR Analysis

The FT IR spectra of different graphite varieties and prepared graphene oxides were studied in the range of 400-4000 cm^{-1} using (FT IR-8400 Shimadzu, Japan) (Figure 3). FT IR spectral data showed the presence of ionizable groups such as carboxyl, carbonyl, epoxy and hydroxyl which can involve in the major absorption sites of dye removal (Sun *et al*., 2011). The peak at 3700 cm^{-1} occurs due to the infrared absorption peak of adsorbent water molecules (Table 3).

SEM Analysis

Scanning electron microscope (SEM) was used for understanding changes of morphology from graphite to graphene oxide. The scanning electron microscopy (SEM) images of the different graphites as shown in Figures 4 (a, b) are platelet like crystalline form of carbon. Figure 4 (c) showed the SEM image of LGO which resembled randomly aggregated, thin crumpled sheets. Figure 4 (d) shows that CGO image revealed the crumpled and ripple structure.

Colour removal efficiencies of LGO and CGO (Batch adsorption study)

The batch experiments were done by studying different parameters.

Effect of dosage of adsorbent

The dosage of adsorbent was varied in the range of 0.02 g to 0.14 g while keeping contact time and concentration of methylene blue at 60 min and 20 ppm, respectively. Lower amount of dosage of adsorbent removed lower percentage of colour. As the dosage of adsorbent increased the colour removal by LGO and CGO also increased. The maximum colour removal percents were observed at the dosage of 0.1 g as 95.85 % for LGO and 96.18 % for CGO (Table 4 and Figure 5).

Effect of concentration

In this study, the initial concentration of methylene blue solution was varied such as 5, 10, 15, 20, 25, 30 and 35 ppm while other factors kept constant. As the concentration increased the colour removal percent also increased (Table 5 and Figure 6). The maximum colour removal efficiency was obtained at initial concentration of 30 ppm for both LGO and CGO.

Effect of contact time

To study the effect of contact time, the contact time between the adsorbent and adsorbate was varied as 10, 20, 30, 40, 50, 60 and 70 min on rotary shaker. At 60 min contact time, the colour removal percent by LGO and CGO were found to be 98.11 % and 97.58 %. The optimal contact times of both LGO and CGO were 60 min (Table 6 and Figure 7).

Effect of temperature

To study the effect of temperature, the temperature was varied as 25, 30, 35, 40, 45, 50 and 55 °C while keeping the other parameters constant to their optimum values. The optimum temperature for colour removal efficiency was found to be 50 °C for LGO and 35 °C for CGO (Table 7 and Figure 8).

Effect of stirring speed

To study the effect of stirring speed, the stirring speeds were varied as 25, 50, 75, 100, 150, 200 and 250 rpm for each sample. The other parameters such as contact time, concentration and adsorbent dosage were set to their optimum value. The optimum stirring speeds for all samples were found to be 150 rpm (Table 8 and Figure 9).

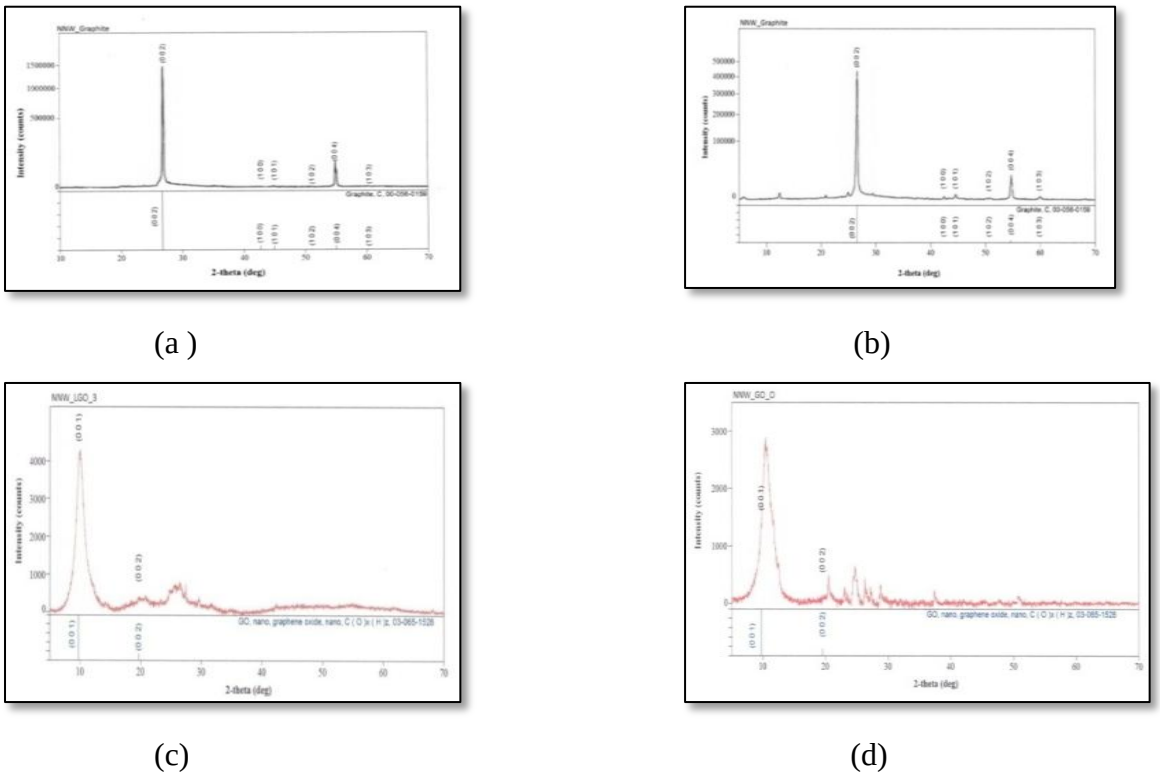
Effect of pH

The colour removal of methylene blue solution having initial concentration of their optimal values by optimal adsorbent dosages were tested for different pH values of 2, 4, 6, 7, 8 , 10 and 12. The stirring speeds were set at 150 rpm for optimal contact time 60 min on rotary shaker. Basic condition at pH 8, LGO and CGO could remove MB (99.62 % and 99.72 %) (Table 9 and Figure 10).

The optimum parameters (dosage, concentration, contact time, stirring speed and pH) for both LGO and CGO were found to be observed the same except temperature. The optimum temperature for LGO and CGO were observed at 50 °C and 35 °C. The removal efficiencies (%) of GO from LGO and CGO were found to be observed nearly 100 %. The aqueous solution of methylene blue can be completely decolorized. Therefore GO from different sources is an excellent adsorbent which can be used to treat effluents contaminated with dye (Table 10 and Figure 11).

Table 1 Phase Identification of LGP, CGP, LGO and CGO

Samples	Miller Indies (h k l)	Bragg angle (2θ) degree	Interplannar spacing d (nm)	Phase Identification	Crystallite size (nm)
LGP	0 0 2	27.44	0.3248	Graphite	56.0
CGP	0 0 2	26.609	0.33473	Graphite	40.3
LGO	0 0 1	10.104	0.8747	Graphene oxide	5.13
CGO	0 0 1	10.557	0.8373	Graphene oxide	4.05



(a) (b)

(c) (d)

Figure 1 XRD diffractograms of (a) local mine graphite (LGP) (b) commercial graphite (CGP) (c) prepared graphene oxide (LGO) and (d) prepared graphene oxide (CGO)

Table 2 UV-vis Analysis of LGP, CGP, LGO and CGO

Samples	Wavelength (nm)	Band Assignment
LGP	258.0	π-π* transition of C = C , C - C
CGP	267.3	π-π* transition of C = C , C - C
LGO	311.6	n-π* transition of C = O
CGO	307.6	n-π* transition of C = O

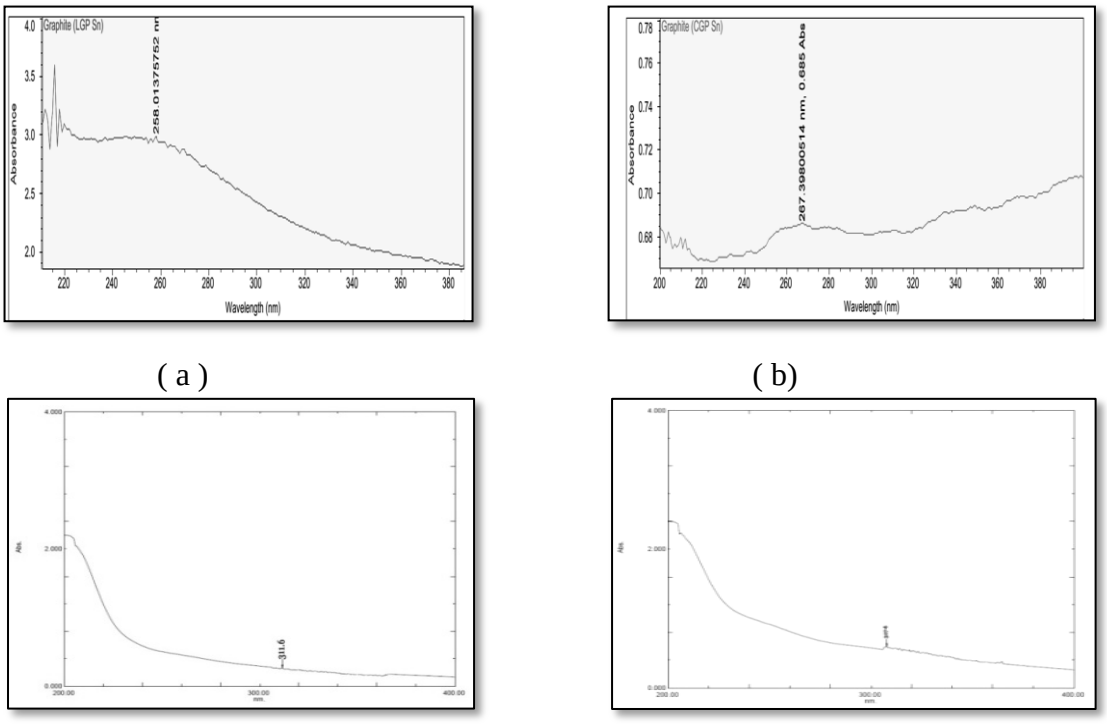
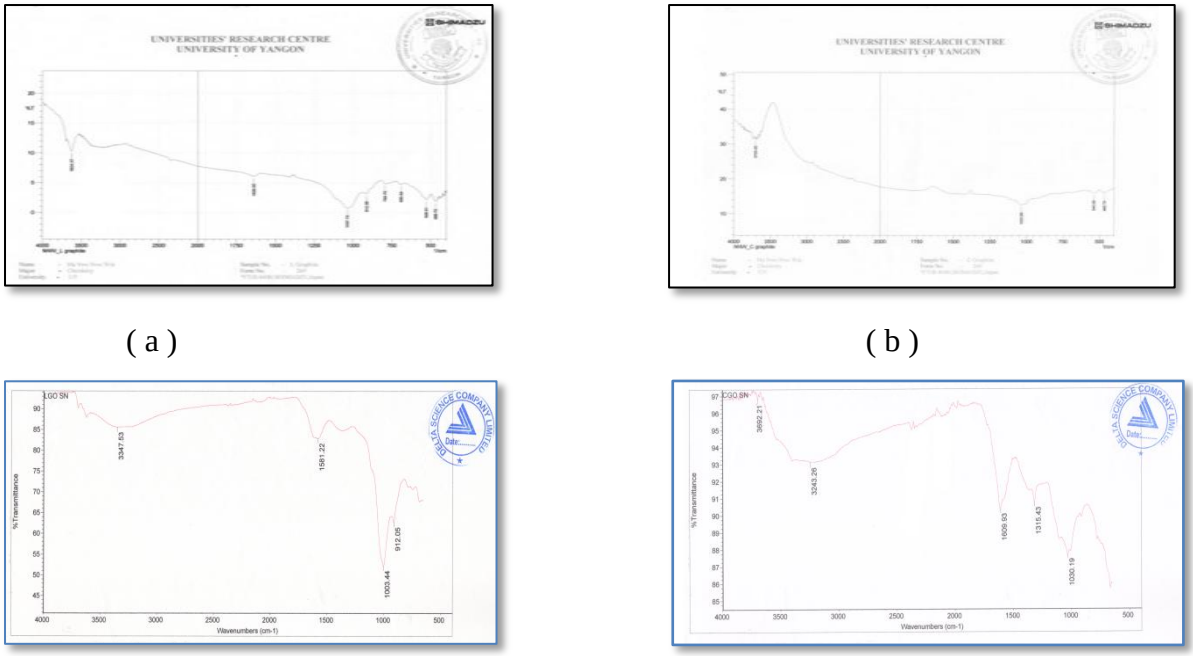


Figure 2 UV-vis spectra of (a) LGP (b) CGP (c) LGO (d) CGO

Table 3 Assignment of FT IR Spectra Data of LGP, CGP, LGO and CGO

No.	Observed value (cm^{-1})				Literature values* (cm^{-1})	Band Assignment
	LGP	CGP	LGO	CGO		
1	3624	3703	3347	3692	3200-3600	OH stretching vibration
2				3243		
3	1639	-	-	-	1600-1750	C=C stretching vibration
4	-	-	1581	1609	1540-1870	C=O stretching in carbonyl
5	-	-	-	1315	1230-1320	C-O-C stretching vibration of epoxide
6	1037	1033	1003	1030	990-1790	C-H in plane bending
7	912		912			
8	794					
9	690					C-H out of plane deformation
10	528	540	-	-	450-750	(benzene)
11	468	466				

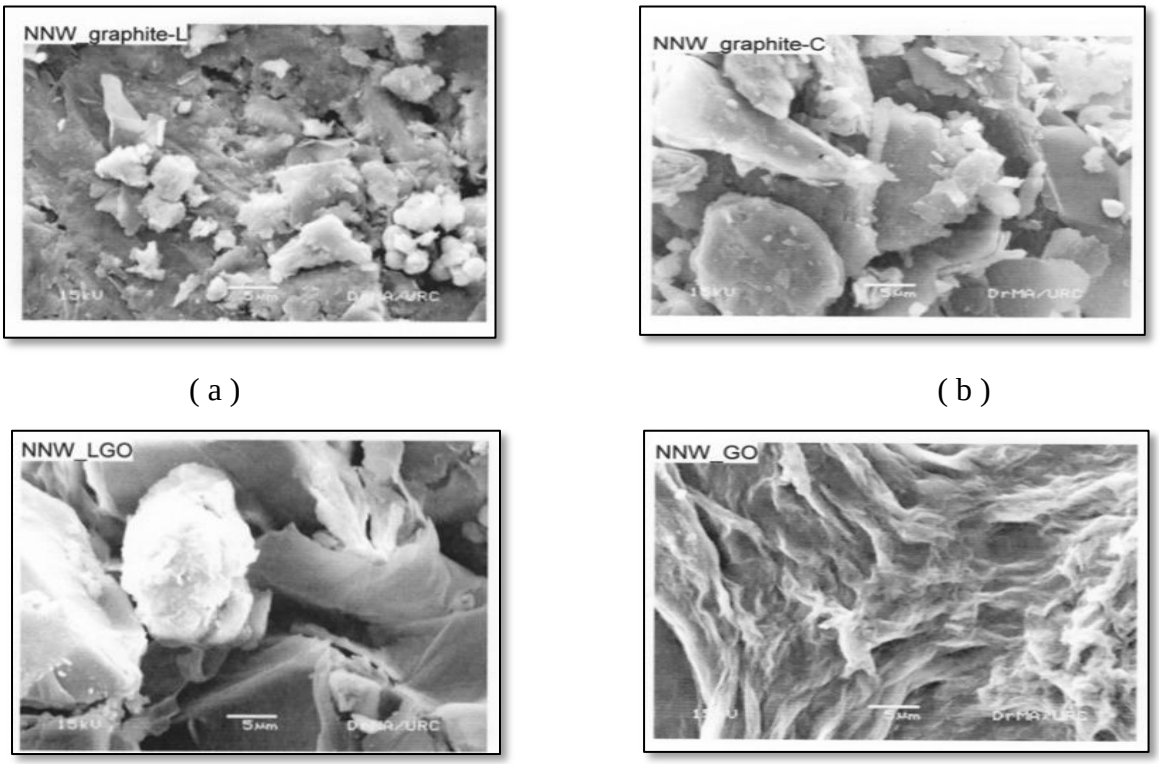
*Sun *et al*., 2011



(a) (b)

(c) (d)

Figure 3 FT IR spectra of (a) LGP (b) CGP (c) LGO (d) CGO



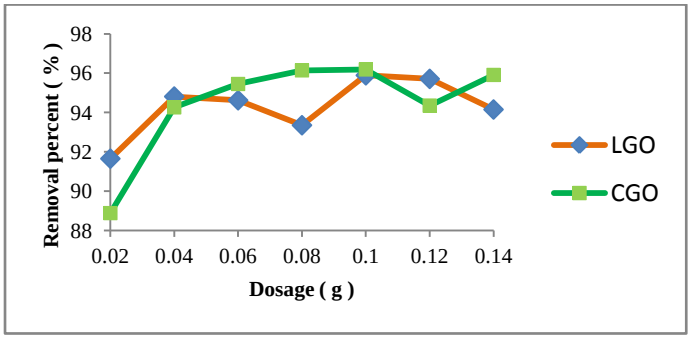
(a) (b)

(c) (d)

Figure 4 SEM micrograms of (a) LGP (b) CGP (c) LGO (d) CGO

Table 4 Removal Percent of Methylene Blue by Using Different Graphene Oxides (LGO, CGO) as a Function of Dosages

No.	Weight of Dosage (g)	Removal %	
		LGO	CGO
1	0.02	91.65 ± 0.66	88.88 ± 0.38
2	0.04	94.81 ± 0.13	94.26 ± 0.03
3	0.06	94.62 ± 0.26	95.45 ± 0.07
4	0.08	93.35 ± 0.16	96.14 ± 0.14
5	0.10	95.89 ± 0.03	96.18 ± 0.28
6	0.12	95.709 ± 0.53	94.35 ± 0.61
7	0.14	94.15 ± 0.26	95.91 ± 0.19

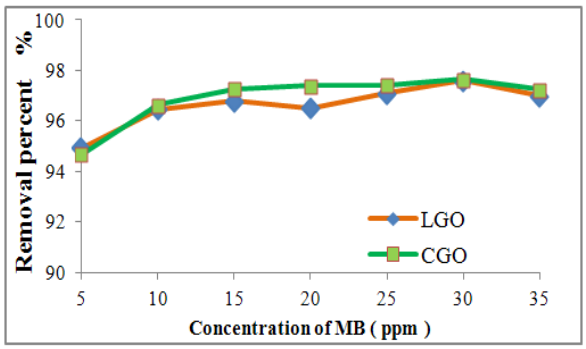


Experimental condition
Contact time = 60 min
Temperature = RT
Concentration of dye = 20 ppm
pH = 7.4
Stirring rate = 115 rpm
Volume of solution = 50 mL

Figure 5 Removal percent of methylene blue model solution by different graphene oxides as a function of dosages

Table 5 Removal Percent of Methylene Blue Model Solution by Using Different Graphene Oxides (LGO, CGO) as a Function of Concentrations

No.	Concentration of MB solution (ppm)	Removal %	
		LGO	CGO
1	5	94.93 ± 0.16	94.68 ± 0.87
2	10	96.46 ± 0.14	96.63 ± 0.34
3	15	96.78 ± 0.38	97.27 ± 0.68
4	20	96.51 ± 0.26	97.39 ± 0.08
5	25	97.09 ± 0.09	97.42 ± 0.25
6	30	97.61 ± 0.12	97.67 ± 0.46
7	35	97.00 ± 0.14	97.25 ± 0.43

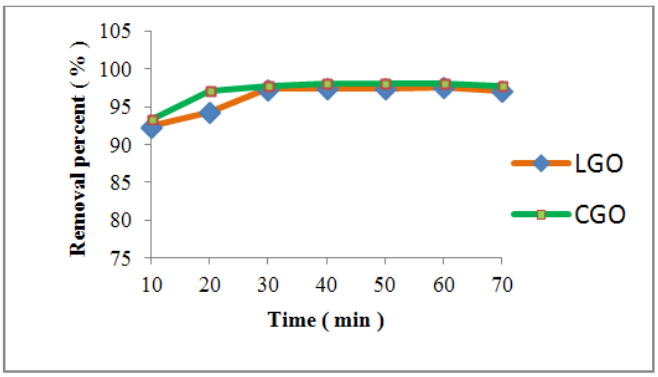


Experimental condition
Weight of dosage (LGO/CGO) = 0.1/0.1g
Contact time = 60 min
Temperature = RT
pH = 7.4
Stirring rate = 115 rpm
Volume of solution = 50 mL

Figure 6 Removal percent of methylene blue model solution by different graphene oxides as a function of concentrations of MB

Table 6 Removal Percents of Methylene Blue by Using Different Graphene Oxides (LGO, CGO) as a Function of Contact Times

No.	Contact Time (min)	Removal %	
		LGO	CGO
1	10	92.38 ± 0.06	93.27 ± 0.09
2	20	94.26 ± 0.02	97.08 ± 0.06
3	30	97.31 ± 0.09	97.71 ± 0.06
4	40	97.37 ± 0.03	98.02 ± 0.03
5	50	97.41 ± 0.04	98.03 ± 0.06
6	60	97.58 ± 0.09	98.11 ± 0.06
7	70	97.08 ± 0.02	97.67 ± 0.02

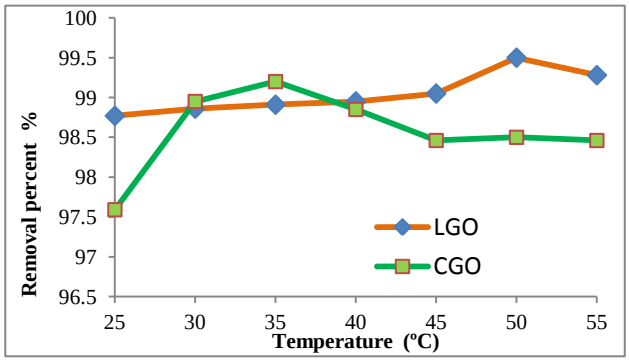


Experimental condition
Weight of dosage (LGO/CGO) = 0.1/0.1g
Concentration of dye (LGO/CGO) = 30 ppm
Temperature = RT
pH = 7.4
Stirring rate = 115 rpm
Volume of solution = 50 mL

Figure 7 Removal percent of methylene blue model solution by graphene oxides (LGO, CGO) as a function of contact times

Table 7 Removal Percents of Methylene Blue by Using Graphene Oxides (LGO, CGO) as a Function of Temperatures

No.	Temperature (ºC)	Removal %	
		LGO	CGO
1	25	98.77 ± 0.09	97.59 ± 0.06
2	30	98.86 ± 0.02	98.95 ± 0.06
3	35	98.91 ± 0.07	99.2 ± 0.04
4	40	98.95 ± 0.06	98.85 ± 0.02
5	45	99.05 ± 0.07	98.46 ± 0.12
6	50	99.50 ± 0.06	98.50 ± 0.07
7	55	99.28 ± 0.02	98.43 ± 0.06

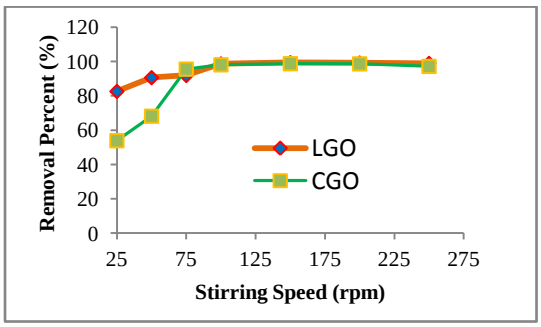


Experimental condition
Weight of dosage = 0.1 g
Stirring speed = 115 rpm
Concentration of dye = 30 ppm
Contact time = 60 min
pH = 7.4
Volume of solution = 50 mL

Figure 8 Removal percent of methylene blue model solution by graphene oxide (LGO, CGO) as a function of temperatures

Table 8 Removal Percent of Methylene Blue by Using different Graphene Oxides (LGO, CGO) as a Function of Stirring Speeds

No.	Stirring speed (rpm)	Removal %	
		LGO	CGO
1	25	82.64 ± 0.11	53.93 ± 0.29
2	50	90.64 ± 0.18	68.19 ± 0.25
3	75	91.91 ± 0.10	95.63 ± 0.05
4	100	98.69 ± 0.06	98.15 ± 0.31
5	150	99.37 ± 0.06	98.78 ± 0.06
6	200	99.19 ± 0.09	98.69 ± 0.02
7	250	98.96 ± 0.06	97.21 ± 0.19

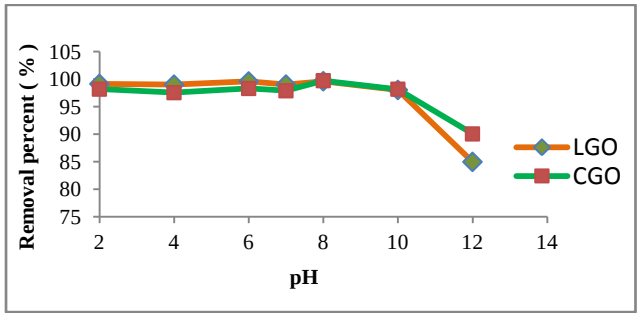


Experimental condition
Weight of dosage = 0.1 g
Concentration of dye = 30 ppm
Temperature =35ºC (CGO)/50 ºC (LGO)
pH = 7.4
Contact time = 60 min
Volume of solution = 50 mL

Figure 9 *Removal percent of methylene blue model solution by graphene oxides (LGO, CGO) as a function of stirring speeds*

Table 9 Removal Percent of Methylene Blue by Using Different Graphene Oxides (LGO, CGO) as a Function of pH

No.	pH	Removal %	
		LGO	CGO
1	2	99.13 ± 0.16	98.18 ± 0.35
2	4	98.99 ± 0.98	97.54 ± 0.02
3	6	99.57 ± 0.02	98.30 ± 0.16
4	7	99.01 ± 0.48	97.88 ± 0.71
5	8	99.62 ± 0.25	99.72 ± 0.13
6	10	98.03 ± 0.25	98.17 ± 0.32
7	12	84.96 ± 0.26	90.04 ± 0.39



Experimental condition

Weight of dosage = 0.1 g
Concentration of dye = 30 ppm
Temperature = 35 ºC (CGO)/50 ºC (LGO)
Stirring speed = 150 rpm
Contact time = 60 min
Volume of solution = 50 mL

Figure 10 Removal percent of methylene blue model solution by prepared graphene oxides (LGO, CGO) as a function of pH

Table 10 The Optimal Parameters of Prepared Graphene Oxides (LGO, CGO) for Removal of Methylene Blue

No.	Dosage (g)	MB (ppm)	Time (min)	Temp (ºC)	rpm	pH	Removal %
LGO	0.1	30	60	50	150	8	99.67 ± 0.03
CGO	0.1	30	60	35	150	8	99.69 ± 0.03

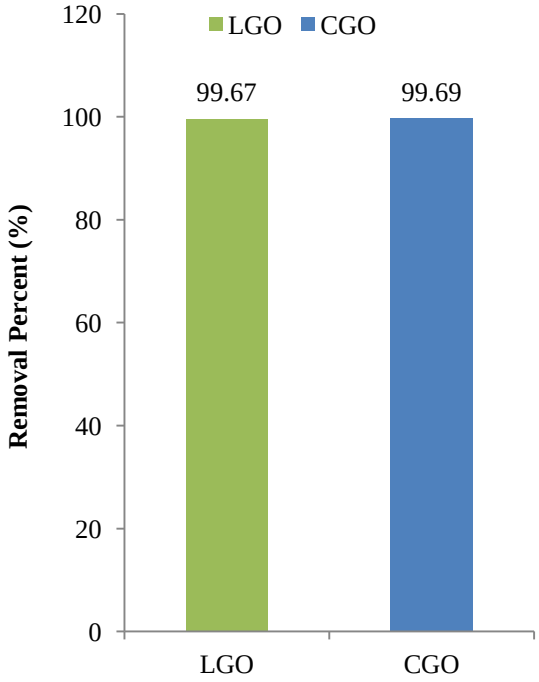


Figure 11 Comparison of removal percent of methylene blue solution under optimal condition

Conclusion

In this research, synthetic graphene oxides (LGO and CGO) were used as materials to remove the dyes from wastewaters. Removals of methylene blue by the prepared graphene oxides (LGO and CGO) were studied using model solutions of methylene blue.

In this work, the graphene oxides (LGO and CGO) produced from different graphite sources by using modified Hummer's method, were used as adsorbent to remove methylene blue (MB) from aqueous solution. Characterization of the prepared graphene oxides were carried out by XRD, UV-Vis, FT IR and SEM techniques. FT IR spectra showed the presence of ionizable groups such as carboxyl, carbonyl and hydroxyl in the graphene oxides (LGO and CGO). SEM micrographs indicated the changes of morphology from graphite to graphene oxide. Adsorption experiments were carried out at different parameters, such as dosage of GO, concentration of MB, temperature, time, stirring speed and pH. Adsorption capacity increase with increasing solution pH, MB concentration, dosage, temperature, contact time and rpm. Results show that the adsorption equilibrium, the removal efficiencies of all samples were higher than 99 % and the solution can be decolorized to almost colorless. Our results show that GO is an excellent adsorbent and can be used to treat effluents contaminated with dyes (MB concentrations).

Acknowledgements

The authors would like to thank the Myanmar Academy of Art and Science for allowing to present this paper and Professor and Head Dr Ni Ni Than , Department of Chemistry, University of Yangon, for her kind encouragement.

References

Ahmad, S., Supwatul, H. and Yuli, R. (2014). " The Effect of Contact Time and pH on Methylene Blue Removal by Volcanic Ash". *Int'l Conference on Chemical, Biological and Environmental Sciences (ICCBES)* vol. 14, pp. 11-13.

Atkovska, K., Kiril, L., Gordana, R., Aleksandar, T. D. and Anita, G. (2018). "Removal of Heavy Metal Ions from Wastewater Using Conventional and Nanosorbents : A Review". *Journal of Chemical Technology and Metallurgy,* vol. 53 (2), pp. 202-219.

Long, C., Yanhui, L., Jiankun, S., Qiuju, D., Xiaoxia, Y., Quan, J., Zonghua, W., Dechang, W. and Yanzhi, X. (2016). "Removal of Methylene Blue from Water by Cellulose/Graphene Oxide Fibers". *Journal of Experimental Nanoscience*, vol. 11(14), pp. 1156 – 1170.

Ozkan-Yucel, U.G. and Gokcayk, C.F. (2010). "Effect of Initial Azo Dye Concentration and Biomass Acclamation on Sludge Digestion and Dye Co-treatment". *Clean-Soil Air Water*, vol. 38, pp. 387–393.

Sayan, E. (2006). "Optimization and Modeling of Decolorization and COD Reduction of Reactive Dye Solutions by Ultrasound-Assisted Adsorption". *Chem. Eng. J.*, vol. 119, pp. 175–181.

Sheng, T. Y., Chen, S., Yanli, C., Aoneng, C., Yuanfang, L. and Haifang, W. (2011)." Removal of Methylene Blue from Aqueous Solution by Graphene Oxide". *Journal of Colloid and Interface Science,* vol. 359, pp. 24 – 29.

Song, J., Wang, X. and Chang, C. T. (2014). " Preparation and Characterization of Graphene Oxide". *Journal of Materials,* vol. 2014, pp. 1-6.

Sun, H., Yang, Y. and Huang, Q. (2011). " Preparation and Structural Variation of Graphite Oxide and Graphene Oxide". *Integrated Ferroelectrics an International Journal*, vol. 128, pp. 163-170.