DOI: https://doi.org/10.4038/sljp.v24i2.8134

INSTITUTE OF PHYSICS – SRI LANKA

Research Article

Mass scale production and purification of graphite oxide from Sri Lankan vein graphite and spectroscopic characterization

S. D. M. Lakshani[1,2], D. B. H. I. Bandara[1,2], R. C. L De Silva[1],
A. M. K. L. Abeykoon[*,1], M. H. T. Dulaj[1] and I. R. M Kottegoda[1]

[1]*Materials Technology Section of Industrial Technology Institute, No. 363, Bauddhaloka Mawatha, Colombo 07, Sri Lanka,00700*
[2]*Department of Chemistry, University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka.*

Abstract

Discovery of graphene has enhanced attention on industrial scale production of graphene using natural graphite which involves oxidation followed by reduction processes. Aiming for the first time, mass scale production of graphite oxide from Sri Lankan vein graphite of natural purity 99.5% carbon, following an improved Hummer's method was experimented at optimized conditions minimizing chemical, energy and time wastage. The present study further aimed at determination of pH and manganese ions on successive purification processes of graphite oxide. The X-ray diffraction spectroscopy (XRD), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) characterizations were followed for verification of products. The wastewater produced from graphite oxide preparation process was systematically tested for Mn^{2+} ion using Atomic Absorption Spectroscopy (AAS). XRD peaks verified the formation of graphite oxide successfully through a complete oxidation of graphite. FTIR spectrum exhibited characteristic peaks related to typical graphite oxide while SEM shows the typical morphological features. XPS analysis verified complete removal of Mn from graphite oxide after purification. AAS analysis reveals entire removal of Mn after several washing cycles using only water. The investigation concludes that even mass scale production of quality graphite oxide is possible from Sri Lankan pure vein graphite which can subsequently be used to produce precious graphene and derivatives for various high-end applications.

Keywords: Graphite oxide, graphene, manganese, vein graphite, XRD, FTIR, SEM

---

* Corresponding author: lahiru.kulanga@gmail.com

1. INTRODUCTION

Graphene is an atomic layer carbon material which has become one of the most intensively studied materials based on its excellent thermal conductivity, mechanical strength, current density, electron mobility and surface area. These extraordinary properties have become reasons to make graphene to be developed and applied in various fields such as electronics and photonics, biomedical applications, membrane developments, developing composites and coatings, catalysis and so on.[1,2] Graphene can be prepared by chemical and thermal reduction of graphite oxides prepared by diverse scientific communities including Brodie[3], Hofmaan, Hummers[4], Staudenmaier[5] and Tour (Improved Hummers)[6] method. The most popular methods for synthesizing graphite oxide are Hummer's method and its modified protocols. Tour method can be pointed as a popular modified form of Hummer's method. The Hummer's method uses concentrated sulfuric acid (H_2SO_4) as the intercalator and potassium permanganate ($KMnO_4$) as the oxidant for preparing graphite oxide. The main oxidation procedure of the method can be pointed as the oxidative exfoliation of graphite by dimanganese heptoxide (Mn_2O_7) and permanganyl cation (MnO_3^+), which are the reduction products formed between potassium permanganate and concentrated sulfuric acid.[7,8] There are three types of graphite called vein graphite, flake graphite and amorphous graphite. The properties and composition of those varieties are different from each other due to reasons such as weather conditions, origin etc. Among them vein graphite exhibits the highest carbon content in the range of 95-99% carbon. Among the countries with natural graphite resources, Sri Lanka is well renowned for its highly crystalline vein graphite with high natural purity which is suitable to synthesize high quality graphene-based derivatives.[9] It is important to conduct mass scale production of graphite oxide from Sri Lankan graphite utilizing time, energy and resources effectively. The present study mainly focuses on synthesis of graphite oxide from Sri Lankan vein graphite on laboratory scale as well as on mass scale

Furthermore, the study aimed at effective production of graphite oxide on mass scale by optimizing raw materials and wastewater treatment cost as well. Synthesis of graphite oxide involves centrifugation or filtration process to purify graphite oxide leaving a large amount of acidic wastewater containing Mn^{2+} ions. Therefore, it is necessary to determine the exact number of washing steps for removal of all manganese ions in graphite oxide as well as knowing the pH variation in every washing cycle for systematic purification of graphite oxide at industrial scale. Generally, the hydrochloric acid is used in the purification process of graphite oxide to remove Mn ions from the slurry more efficiently.[10] The usage of HCl is not only an additional cost but also makes the wastewater treatment harder. Because it produces acidic wastewater. Therefore, in the current study, usage of HCl to purify graphite oxide has been avoided, replacing it with additional washing cycles to achieve an eco-friendly approach to purify graphite oxide at industrial scale.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation and characterization of graphite oxide

Modification to Hummer's method was followed to synthesize graphite oxide.[11,12] 1 g of natural vein graphite (99.9% purified) obtained from Ragedara graphite mine was added to 23 cm^3 of Con.H_2SO_4 at 0 ^{0}C. Then 3 g of $KMnO_4$ was added gradually to the mixture while stirring. The mixture was then stirred at RT for 30 minutes. 45 g of ice was added slowly and heated at 90 ^{0}C for 15 minutes. 135 cm^3 of distilled water was added at room temperature. 30% H_2O_2 was added until the solution becomes characteristic yellow colour. The solid was separated by repeated centrifuged washing using distilled water until sulphate could not be detected with $BaCl_2$. Subsequently, purified graphite oxide was oven dried at 110 ^{0}C. Washing with 5% HCl is avoided in the present method since it involves additional cost and chloride contamination. A schematic illustration of the experimental process is shown in Figure 01. Mass scale synthesis of GO was also followed subsequently for verification using a double walled reactor (not shown).

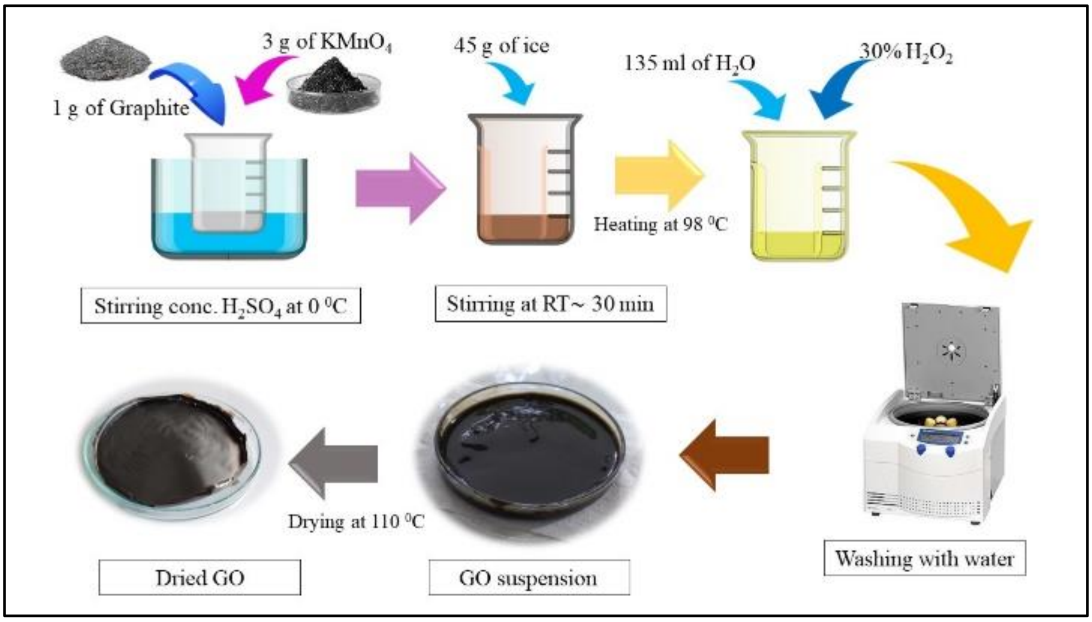

Figure 1: A schematic illustration of the experimental process

Samples were subjected to FTIR analysis using a Bruker Tensor 27 FTIR spectrometer in the mid-IR spectral range of 600 - 3000 cm^{-1} to identify the presence of functional groups on the surface and XRD analysis was done using a Bruker D8 Advanced Eco Powder XRD with Cu Kα ($\lambda = 0.154$ nm) radiation for verification of structural changes in graphite oxide. SEM analysis was conducted using ZEISS EVO SEM for the morphological analysis and XPS analysis was carried out using a Thermo Scientific, Nexsa spectrometer (England) equipped with a monochromatic, micro-focused, 72 W Al Ka X-ray source (photon energy 1486.6 eV).

2.2 Preparation of wastewater samples for AAS and pH analysis

The graphite oxide sample was centrifuged at 3000 rpm repeatedly with deionized water to purify graphite oxide. After every centrifuging turn, the supernatant of the sample was decanted carefully and collected separately as wastewater during the washing process. Wastewater samples were filtered using filter papers to remove suspension. After that, filtrates were filtered two times using nylon 0.2 μm syringe filters and followed AAS analysis to determine the Mn ion concentration. According to the convenience of detection, some of first few samples were diluted by a factor of 1000. The other samples were diluted by a factor of 100. The same dilution factors were considered when diluting samples for the pH analysis. The number of centrifuging turns required to remove Mn ions and acidity from the samples were determined here.

3. RESULTS AND DISCUSSION

Figure 2 shows images of graphite in powder form as well as graphite oxide in liquid and dried forms. Graphite powder is shiny gray in colour while oxidation of graphite resulted in dark brown colour suspension which converts to darker colour crumpled thin film after drying.

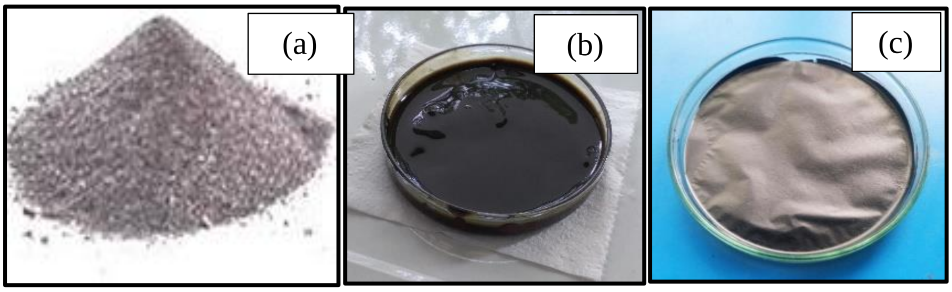

Figure 2: Images of graphite (a) graphite oxide in suspension form (b) and dried form (c)

Figure 3 shows structure of graphite and graphite oxide. Graphite is a 3D material consisting of layered hexagonal carbon atoms arranged in a honey comb structure in which each carbon atom is sp^2 hybridized. When graphite is oxidized to graphite oxide various oxygen containing functional groups are attached converting some sp^2 hybridized carbon atoms to sp^3 hybridization. The structural changes occur on conversion can be identified using XRD, FTIR and XPS etc.

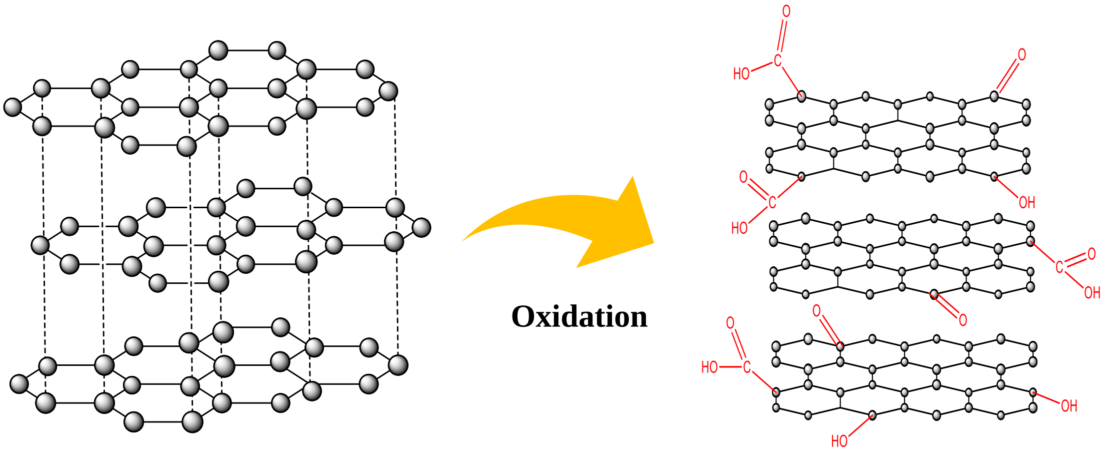

Figure 3: Structure of graphite and graphite oxide

3.1 SEM analysis

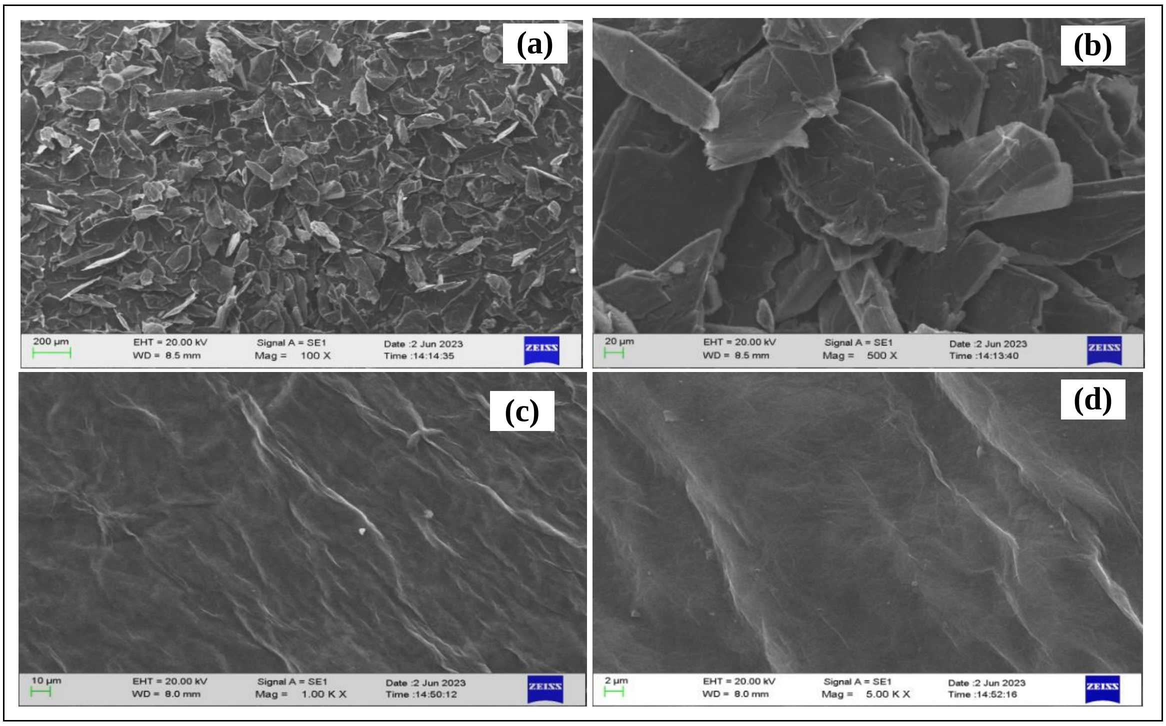

Figure 4: SEM images of graphite (a, b) and graphite oxide (c, d)

The SEM images of graphite and GO at different magnifications are shown in the Figure 4. Graphite appears as flaky type particles below 200 μm sized whereas GO exhibits a typical morphology of GO with a wrinkled and folded texture showing irregular edges and crumpling which can be pointed out as a reflection of its thin layered microstructure.

3.2 XRD Analysis

XRD is a primarily analytical technique used for phase identification of a crystalline material. In the present study an improved Hummer's method was followed to synthesize graphite oxide from graphite. According to prior art, the oxidation of graphite to graphite oxide can be verified using two characteristic peaks at about 2θ = 26° and at 2θ = 11° corresponding to graphite and graphite oxide respectively.[13]

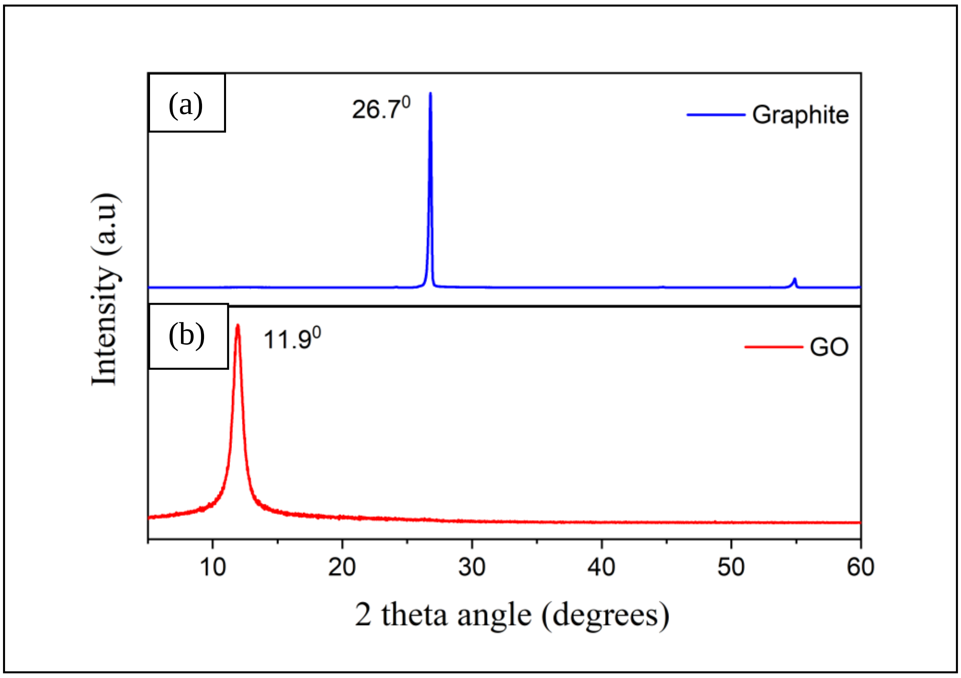

Figure 5: XRD of (a) graphite and (b) GO from graphite

Figure 5 shows the XRD spectra of naturally pure vein graphite (99.5% carbon) and GO synthesized using graphite. Natural graphite shows highly crystalline nature according to the XRD analysis. The highly intense characteristic peak appears at 2θ = 26.7° and small peak at 2θ = 54.9° was observed analogous to (002) and (004) planes related to graphite. Corresponding d-spacing values are 0.33 nm and 1.67 nm, respectively. A sharp peak can be observed at 2θ = 11.9° corresponding to GO exhibiting a *d*-spacing of 0.75 nm while the peak corresponding to graphite at 2θ ~ 26.7° is disappeared indicating complete conversion of graphite to GO. An increase in *d*-spacing from 0.33 to 0.75 nm is observed due to formation of graphite oxide.[14,15,16] The entire conversion of GO observed in this study is important for subsequent reduction to graphene for various high-end applications. The natural high purity of graphite eventually produces high quality graphene.

3.3 FTIR analysis

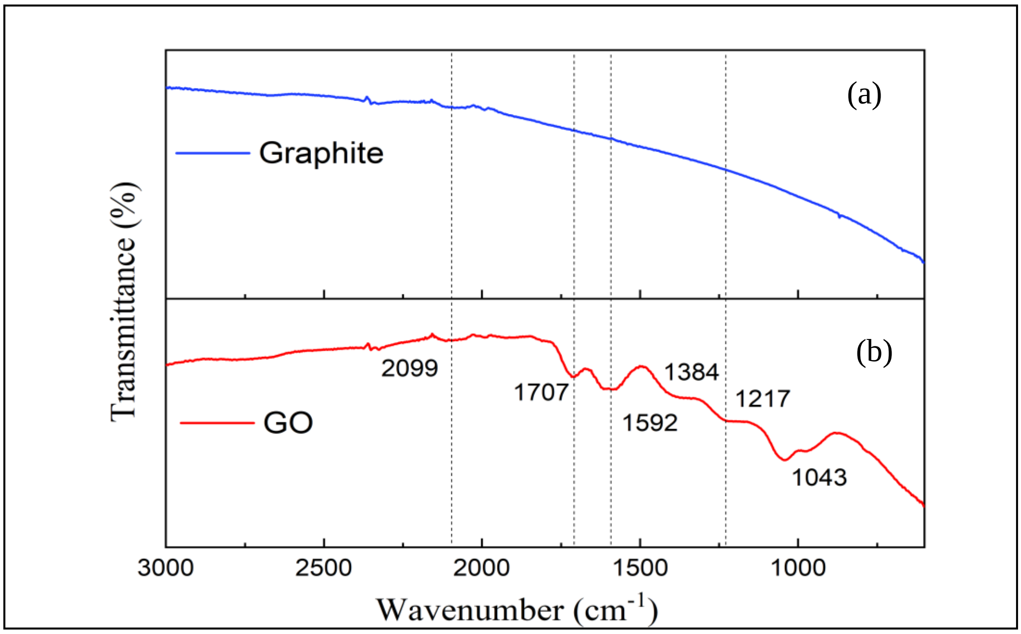

Figure 6: FTIR spectrum of graphite(a) and graphite oxide(b)

FTIR spectra of graphite and graphite oxide in Figure 6 shows characteristic bands corresponding to oxygenated functional groups appear in GO, indicating that the oxidation process has been successful. As shown in the spectrum, there is a fairly intense band near ~1707 cm^{-1} relevant to C=O stretching vibrations of carboxyl groups. Bands at 1384 cm^{-1} and 1217 cm^{-1} are from C-OH and C–O–C, stretching vibrations. The band at 1592 cm^{-1} is corresponding to the stretch vibration of the sp^2 carbon skeletal network (C=C). In addition, the peak ranging from 1040 cm^{-1} to 1170 cm^{-1} at 1043 cm^{-1} in the above spectrum signifies C-O (alkoxy) stretching vibrations[17,18, 19, 20]. It was also observed that the mass scale synthesis of GO also resulted similar characteristics for SEM, XRD and FTIR analysis and therefore was not shown here.

Table 01: Mn ion concentration, ion releasing percentage and cumulative releasing percentage respective to sample collected from GO washing process

Sample Number	Mn ion concentration (ppm)	Ion release (%)	Cumulative release (%)
1	5729	78.29%	78.29%
2	1129	15.43%	93.72%
3	420	5.74%	99.46%
4	14	0.19%	99.65%
5	14	0.19%	99.84%
6	9	0.12%	99.96%
7	2	0.03%	99.99%
8	Zero detection	0.00%	99.99%
9	Zero detection	0.00%	99.99%

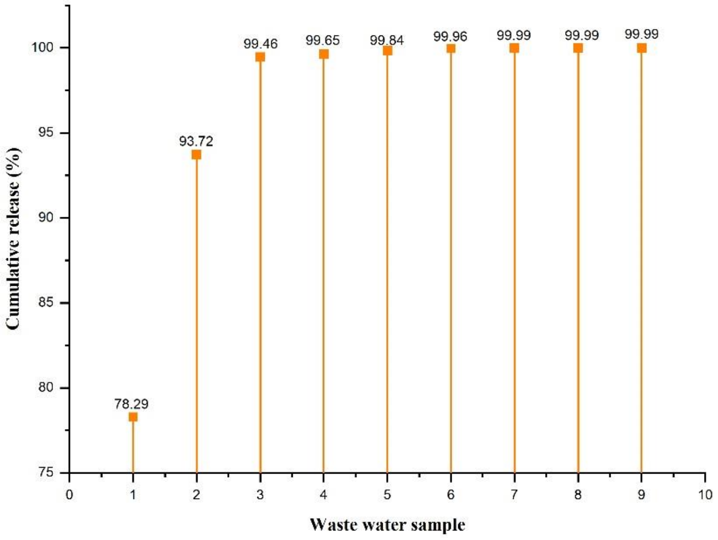

Figure 7: Cumulative ion releasing percentage over wastewater samples

According to the results on variation of Mn ion concentration over samples (Table 01), the first centrifuging turn itself has the potential to remove most of the Mn ions in the sample. It is approximately 5700 ppm in concentration and 78% as an ion releasing percentage. Second and third centrifuging turns also exhibit a kind of considerable release of ions from the graphite oxide samples. Interestingly, 99.5% removal of Mn ions was achieved by centrifuge washing for 3 times in accordance with the cumulative ion releasing percentage respective to the sample. The aim of this washing process is to remove almost all the heavy metals (Mn) from the sample to make it pure. Therefore, this process was carried out until zero detection of Mn ions is observed. After the third turn, there is a considerable reduction in Mn ion removal because most of them have been eliminated already. But the process needs to be carried out to remove the remaining Mn ions. The eighth centrifuging turn has achieved zero detection of manganese ions. Nineth also shows the same results. Therefore, it can be recommended to centrifuge at least eight times to obtain high-quality graphite oxide without manganese ions.

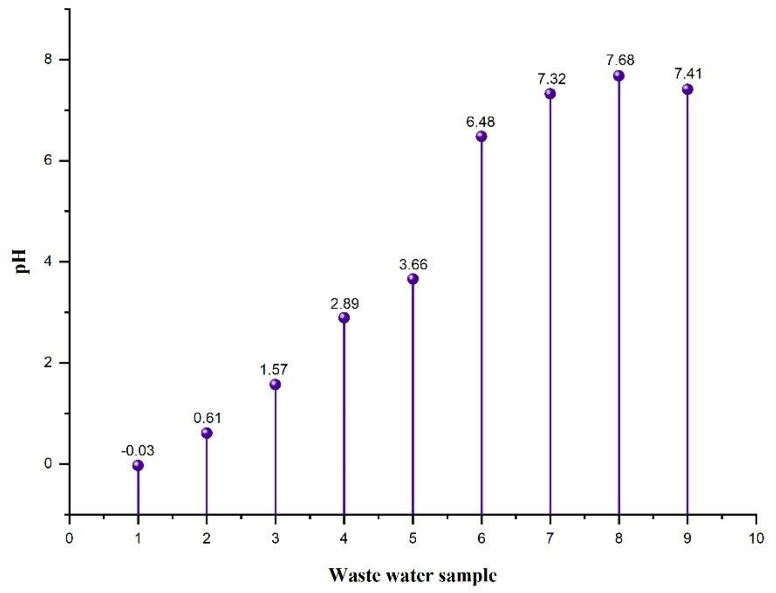

Figure 8: pH variation of collected wastewater samples from graphite oxide synthesis

The wastewater from the first washing turn of graphite oxide exhibits a highly acidic condition. It is a negative value which means H^+ concentration is even higher than 1 moldm^{-3}. It is because of the utilization of concentrated sulfuric acid for the synthesis of graphite oxide as the intercalator. The second and third turn also shows highly acidic conditions which is below 2. The next two samples also indicate the strong acidic effect of the intercalator, but it shows a regular reducing pattern of acidity. After the 5th sample, it seems to have a considerably reduced pH value, but it is still acidic. From 7th sample onwards, all the samples show neutral pH conditions (Figure 8).

3.4 XPS quantitative analysis

XPS is a spectroscopic technique that provides information such as elemental composition, chemical state, and electronic structure of materials on exposure to soft X-rays[21,22]. XPS quantification report revealed that the graphite was successfully oxidized to graphite oxide (Table 2).

Table 2: XPS quantification report of graphite oxide

Name	Peak BE	Atomic %	Title
C1s main	284.17	35.08	C1s Scan
C1s C1s C-Ox1	286.28	28.23	C1s Scan
C1s Scan C	288.04	6.36	C1s Scan
S2p	167.69	0.12	S2p Scan
O1s	532.07	30.22	O1s Scan

The C/O ratio of GO reflects that the oxide is twice as rich with oxygen compared to graphite. Report further demonstrates that manganese ions is completely removed from graphite oxide while a trace amount of sulphur is detected presumably from sulfate residue.

4. CONCLUSIONS

Sri Lankan high purity vein graphite can be effectively used for mass scale production of high-quality graphite oxide. XRD and XPS analysis verified complete conversion of graphite to graphite oxide without any remaining unoxidized graphite. FTIR characteristic peaks confirmed the quality of the oxidized material through typical characteristic peaks related to different oxygenous functional groups. SEM exhibits a layered microstructural morphology of resulting graphite oxide. The study on mass scale production of graphite oxide from graphite was useful for value addition to graphite. According to the AAS and pH analysis of wastewater produced from the sample, it is concluded that approximately 99.5% of Mn-ion removal can be achieved by centrifuge washing for 3 times. While 8 times were conducted to obtain graphite oxide entirely free from Mn ions. Neutral pH is achieved after washing 7 times. To reach both goals (pH neutralization and Mn ion removal) it is advisable to centrifuge at least 8 times. High initial purity of Sri Lankan vein graphite contributed to produce high quality graphite oxide which can be used to produce superior quality graphite oxide on industrial scale.

ACKNOWLEDGEMENT

The work is funded by National Research Council- 16/138 Grant. Authors are thankful to Yosef Gofer at Bar Ilan University, Israel for XPS analysis.

REFERENCES

1. Geim, A., Novoselov, K. (2007), The rise of graphene. *Nature Mater* **6**, 183–191 (2007).
2. Arshad, A.; Jabbal, M.; Yan, Y.; Reay, D. (2019), A Review on Graphene Based Nanofluids: Preparation, Characterization and Applications, ***279***, 444–484.
3. B. C. Brodie, On the atomic weight of graphite. Philos. Trans. R. Soc. London 14(1859) 249–259.
4. Hummers W, Offeman R, (1958), Preparation of graphitic oxide. *Journal of the American Chemical Society,* **80**:1339–1339.
5. Staudenmaier, L. (1898) 'VerfahrenzurDarstellung der Graphitsäure', *Berichte der deutschen chemischen Gesells chaft,* 31(2), pp. 1481–1487.
6. Marcano D.C., Kosynkin D.V., Berlin J.M., Sinitskii A., Sun Z., Slesarev A., Alemany L.B., Lu W., Tour J.M. (2010), Improved synthesis of graphene oxide. *ACS Nano,* **4**:4806–4814.
7. Sun, L.; Fugetsu, B. Mass Production of Graphene Oxide from Expanded Graphite. *Materials Letters* **2013**, *109*, 207–210.
8. Dimiev, A. M.; Tour, J. M. Mechanism of Graphene Oxide Formation. *ACS Nano* **2014**, *8* (3), 3060–3068.
9. Rathnayake, R. M. N. M.; Wijayasinghe, H. W. M. A. C.; Pitawala, H. M. T. G. A.; Yoshimura, M.; Huang, H.-H. (2017), Synthesis of Graphene Oxide and Reduced Graphene Oxide by Needle Platy Natural Vein Graphite, ***393***, 309–315.
10. Zhang, Q.; Yang, Y.; Fan, H.; Feng, L.; Wen, G.; Qin, L.-C. Roles of Water in the Formation and Preparation of Graphene Oxide. *RSC Advances* **2021**, *11* (26), 15808–15816.
11. Chen, J.; Li, Y.; Huang, L.; Li, C.; Shi, G. (2015), High-Yield Preparation of Graphene Oxide from Small Graphite Flakes via an Improved Hummers Method with a Simple Purification Process, ***81***, 826–834.
12. I. R. M. Kottegoda; Nurul Hazrina Idris; Lu, L.; Wang, J.; Zhang, L. (2011), Synthesis and Characterization of Graphene–Nickel Oxide Nanostructures for Fast Charge–Discharge Application, ***56* (16)**, 5815–5822.

13. Kartick, B.; Srivastava, S. K.; Srivastava, and I. (2013), Green Synthesis of Graphene. Journal of Nanoscience and Nanotechnology, ***13* (6)**, 4320–4324.
14. Cai, X., T. S., Xie, A., Lin, M., Liu, Y., Zhang, X. 2011. *Material Research Bulletin* 46: 2358.
15. Hou, J., S. Y., Ellis, M. W., Moore, R. B. and Yi, B. 2011. *Phys. Chem*. 13: 15384.
16. Mishra, A. K., Ramaprabhu, S. 2011. *Desalination*. 282: 39.
17. I.R.M. Kottegoda, X. Gao, L.D.C. Nayanajith, C.H. Manorathne, J. Wang, J.-Z. Wang, H.-K. Liu, Y. Gofer, (2015), Comparison of Few-layer Graphene Prepared from Natural Graphite through Fast Synthesis Approach, **31**, 907–912.
18. Ruiz, S.; Tamayo, J. A.; Ospina, J. D.; Navia Porras, D. P.; Valencia Zapata, M. E.; Hernandez, J. H. M.; Valencia, C. H.; Zuluaga, F.; Grande Tovar, C. D. (2019), Antimicrobial Films Based on Nanocomposites of Chitosan/Poly(Vinyl Alcohol)/Graphene Oxide for Biomedical Applications, ***9* (3)**, 109.
19. Song J, Wang X and Chang C-T 2014 Preparation and characterization of graphene oxide *J.Nanomater*. **2014** Article ID 276143
20. Ossonon B D and Bélanger D 2017 Synthesis and characterization of sulfophenyl-functionalized reduced graphene oxide sheets *RSC Adv.* **7** 44 27224-34
21. O.J. Guy, K.-A.D. Walker, Chapter 4 - Graphene Functionalization for Biosensor Applications, in: S.E.B.T.-S.C.B. (Second E. Saddow (Ed.), Elsevier, 2016: pp. 85–141. https://doi.org/https://doi.org/10.1016/B978-0-12-802993-0.00004-6.
22. D.R. Baer, S. Thevuthasan, Chapter 16 - Characterization of Thin Films and Coatings, in: P.M.B.T.-H. of D.T. for F. and C. (Third E. Martin (Ed.), William Andrew Publishing, Boston, 2010: pp. 749–864. https://doi.org/https://doi.org/10.1016/B978-0-8155-2031-3.00016-8.