

# Comparison of Two Different Ultrasonic Devices (Ultrasonic Bath and Ultrasonication) Used in Synthesis of Reduced Graphene Oxide

Meryem Göktaş<sup>1</sup>, Ferda Mindivan<sup>2</sup>

<sup>1</sup>Biotechnology Application and Research Center, Bilecik Seyh Edebali University, Bilecik, Turkey  
Vocational College, Department of Metallurgy, Bilecik Seyh Edebali University, Bilecik, Turkey

<sup>2</sup>Biotechnology Application and Research Center, Bilecik Seyh Edebali University, Bilecik, Turkey  
Corresponding Author: Meryem Göktaş

## -----ABSTRACT-----

*The present work reported the comparison of the effectiveness of both ultrasonic bath and ultrasonication for synthesis of reduced graphene oxide and vitamin C was used as a reducing agent. Samples obtained from using ultrasonic bath and ultrasonication was coded as RGO and RGOS, respectively. Experimental results indicated that the RGO samples showed better thermal stability and had more dispersed layered structure than RGOS samples because ultrasonic bath generated better dissociation than ultrasonication.*

**KEYWORDS** - Reduced graphene oxide, thermal stability, ultrasonic bath, ultrasonication, vitamin C.

Date of Submission: 27-07-2018

Date of acceptance: 11-08-2018

## I. INTRODUCTION

Graphene and its derivatives, in particular graphene oxide (GO) and reduced graphene oxide are interest due to their extraordinary properties (thermal conductivity, mechanical, electronic properties and huge surface area), and various application areas in the composites [1, 2]. Natural graphite is abundantly available in nature and GO is produced by the oxidative treatment of graphite by Hummers method [2]. GO is an oxidized graphene sheet and has epoxy, hydroxyl, carbonyl and carboxyl groups [3]. The reduced graphene oxide sheets are usually considered as one kind of chemically derived graphene [2] and significant amounts of epoxy and carbonyl groups are removed by producing the reduced graphene oxide [1]. Hydrazine hydrate, dimethyl hydrazine, hydroquinone and sodium borohydride are the most commonly used hazardous or toxic reducing agents for graphene oxide (GO) reduction [1, 4]. Therefore, it was necessary to the reduction of GO by environment-friendly methods [5]. To this aim, vitamin C for synthesis of the reduced graphene oxide was used and effect of the ultrasonic devices on the structural and thermal properties of obtained samples was investigated. In this study, ultrasonic experiments were carried out in both ultrasonic bath and ultrasonication for the reason that the sonochemical power of the individual instruments affected differently into the reaction system [6].

## II. MATERIALS AND METHODS

The GO was synthesized using the modified Hummers method [7, 8] to which the details of the process were given previously [9]. To prepare the RGO, 0.5 g of GO was dispersed into 100 ml of distilled water with both ultrasonic bath and ultrasonication for comparison. The pH of the GO suspension was adjusted to ~9 by using NH<sub>3</sub>. The different weights of vitamin C (0.5, 0.75 and 1g) were added to the mixture and were kept at 97°C for 8 hours under constant stirring. By changing the weight ratios of the vitamin C and ultrasonic devices, a series of samples were prepared and Table 1 showed their codes. Fig. 1 presented digital images of the ultrasonic bath and ultrasonication used in the present study. The different ultrasonic devices used in the present study were procured from Bandelin electronic GmbH & Co. KG, Berlin. The ultrasonic bath (Model RK 106) has an operating frequency of 35 kHz and power dissipation as 120 W. The ultrasonication (Model MD2070) has an operating frequency of 20 kHz and rated power output of 70 W. The obtained RGO and RGOS samples were characterized using Fourier transformed infrared spectroscopy (FTIR, Spectrum 100, Perkin Elmer, in the range of 4000–400 cm<sup>-1</sup>), X-Ray Diffraction (XRD, PAN analytical, Empyrean in the range of 5–30°) and Thermogravimetric analysis (TGA). TGA was carried out under nitrogen atmosphere using a TGA instrument (STA 409, Netzsch) at a heating rate of 20°C min<sup>-1</sup> from 25°C to 600°C. The surface morphology was examined by a Scanning Electron Microscopy (SEM, Supra 40VP, Zeiss).

**Table 1:** Sample codes and experimental conditions used two different ultrasonic devices.

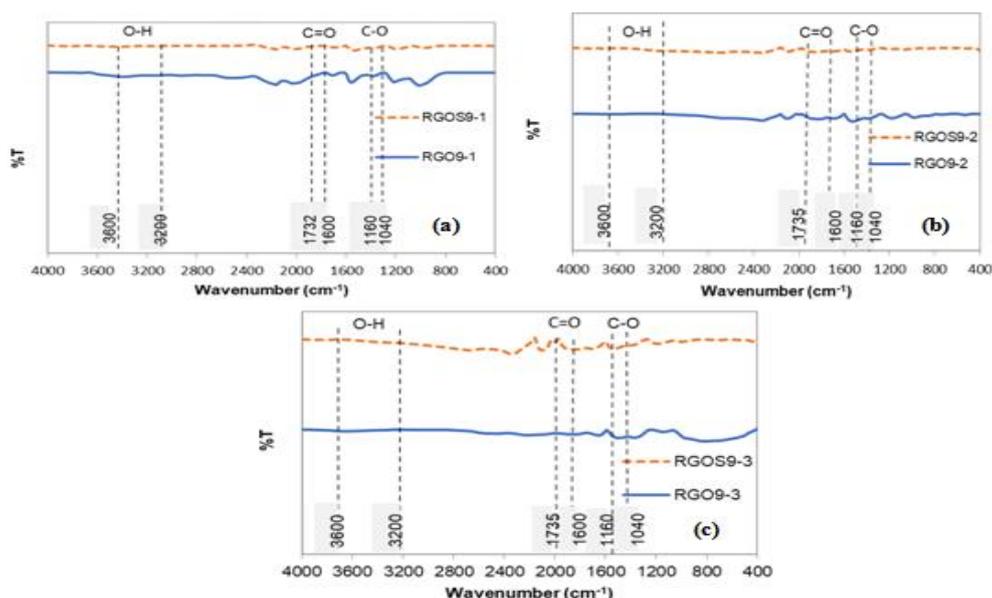
pH	Ultrasonic Devices	Samples codes	Vitamin C rate (g)	GO rate (g)
~ 9	Ultrasonic bath	RG09-1	0.5	0.5
		RG09-2	0.75	0.5
		RG09-3	1	0.5
	Ultrasonication	RGOS9-1	0.5	0.5
		RGOS9-2	0.75	0.5
		RGOS9-3	1	0.5



**Fig. 1:** Digital images of ultrasonic bath and ultrasonication

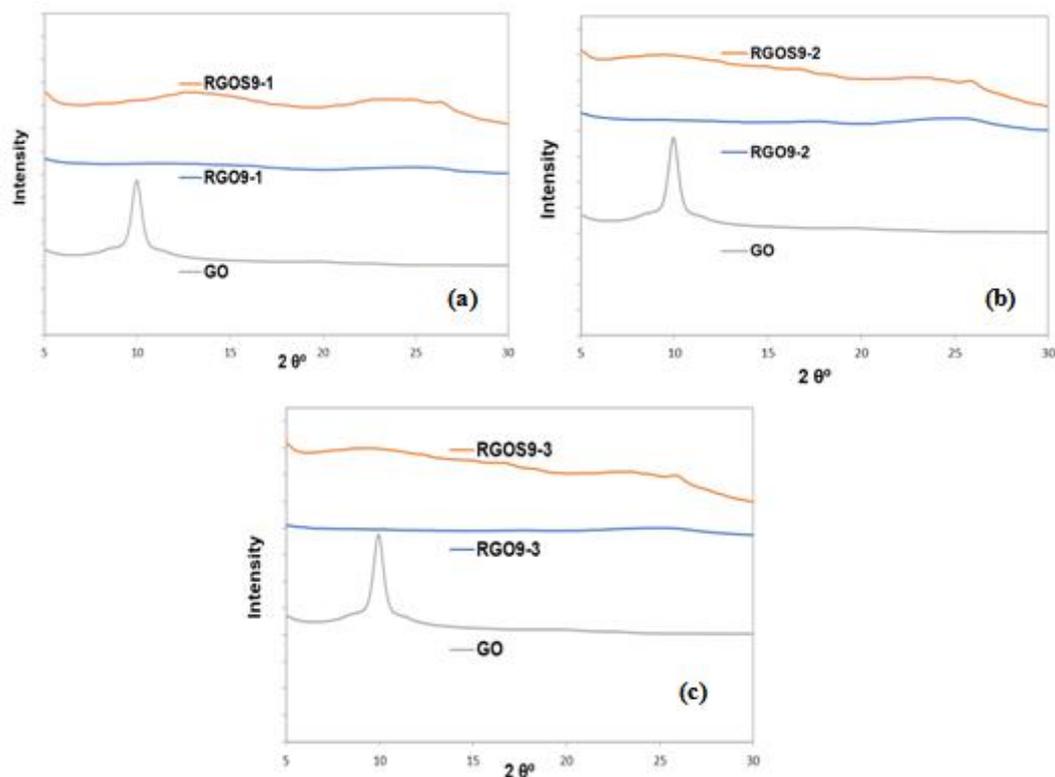
### III. THE RESULTS AND DISCUSSION

FTIR spectrums of RGO and RGOS samples were shown in Fig. 2(a-c). As shown in the FTIR spectrums, the characteristic peaks of the RGO and RGOS samples at around  $1160\text{ cm}^{-1}$  and  $1040\text{ cm}^{-1}$  were assigned to the C-O (epoxy groups) and COOH (carboxylic acid), respectively [10, 11]. For the RGO and RGOS samples, the C=O (carbonyl groups) peaks were observed at around  $1700\text{--}1600\text{ cm}^{-1}$  [11]. The broad peak in the range of  $3200\text{--}3600\text{ cm}^{-1}$  corresponded to O-H stretching vibrations of hydroxyl groups [10]. In comparison the FTIR spectrums of RGO and RGOS, for RGO samples, the peaks intensities of functional groups decreased along with an increase in the amount of vitamin C and for RGOS samples, the characteristic peaks of functional groups were almost disappeared along with an increase in the amount of vitamin C (Fig. 2(a-c)). This result can be attributed to the partial reduction of oxygen containing functional groups due to the ultrasonication which has lower frequency and power than those of ultrasonic bath. Moreover, FTIR results presented that the most intense characteristic peaks of oxygen containing functional groups were observed in RG09-1 and RGOS9-3 samples.

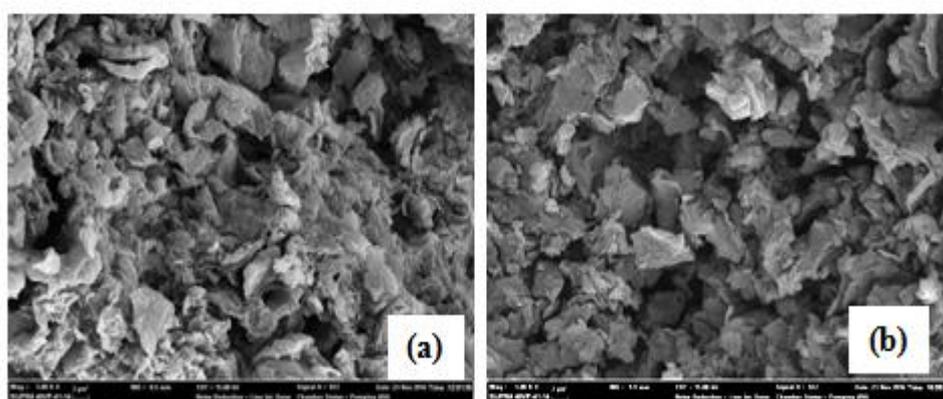


**Fig. 2:** FTIR spectrums for (a) RGOS9-1 and RGO9-1, (b) RGOS9-2 and RGO9-2, (c) RGOS9-3 and RGO9-3 samples

XRD patterns of GO, RGO and RGOS samples were depicted in Fig. 3(a-c). The XRD pattern of the GO showed a peak at  $2\theta = 9.95^\circ$ , which indicated that the graphite was fully oxidized into the GO [12]. RGOS samples exhibited a broader diffraction peaks centered at  $2\theta = 25^\circ$  which may be due to restacking of graphene layers as shown in Fig. 3(a-c) [8], but RGO samples had flatter tendency than RGOS samples. This result may be due to the fact that the ultrasonic bath prevented to restacking of graphene layers because of its higher frequency and power than those of ultrasonication. Thus, RGO samples had more dispersed layered structure than RGOS samples and SEM images supported the results of XRD analysis (Fig. 4(a-b)).



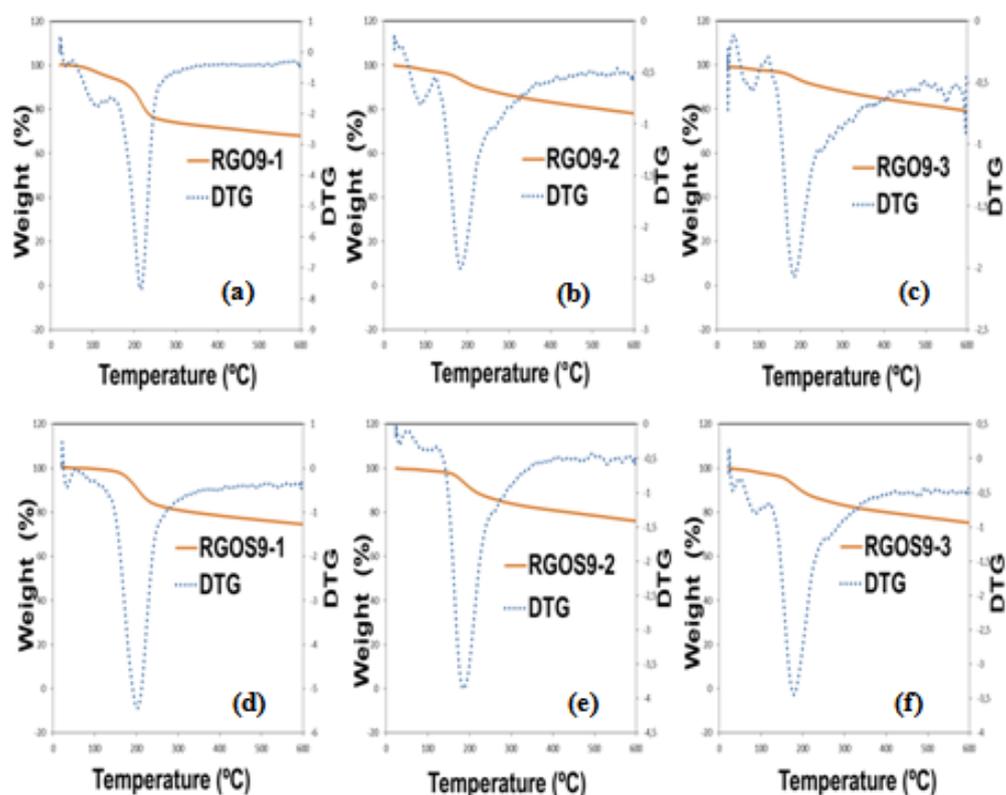
**Fig. 3:** XRD patterns for (a) RGOS9-1 and RGO9-1, (b) RGOS9-2 and RGO9-2, (c) RGOS9-3 and RGO9-3 samples



**Fig.4:** SEM images of (a) RGOS9-1 and (b) RGO9-1 (magnification 5000X).

The thermal stability of RGO and RGOS samples were investigated using TGA. Weight losses (%) and derivative thermograms (DTG) for the RGO and RGOS samples at two different dispersion types were given in Fig. 5(a-f) and their thermal parameters were summarized in Table 2. RGO and RGOS samples showed three stages of decomposition. For the RGO and RGOS samples, the first weight loss ( $T_1$ ) in the range of  $24.3\text{--}38.3^\circ\text{C}$  was attributed to the elimination of moisture due to nature of reduced graphene oxide [1] (Table 2). The second weight loss between  $33.9^\circ\text{C}$  and  $109.6^\circ\text{C}$  was resulted from decomposition of RGO to  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CO}$  gases.

The third weight loss at  $T_3$  temperature was assigned to the removal of the oxygen containing functional groups [11, 13]. As seen from Table 2, the RGO samples exhibited higher weight loss than RGOS samples, but RGO9-1 powder was lower weight loss than other RGO and RGOS samples. Additionally, for the RGO samples the weight losses increased and the residue amount decreased at the same temperature along with an increase in the amount of vitamin C. Therefore, the thermal stability of RGO9-3 was higher than those of other RGO and all RGOS samples.



**Fig. 5:** TGA and DTG curves for (a) RGO9-1, (b) RGO9-2, (c) RGO9-3, (d) RGOS9-1, (e) RGOS9-2, (f) RGOS9-3 samples

**Table 2:** Thermal parameters for the RGOS and RGO samples (20 °C/min heating rate, under nitrogen atmosphere)

Samples	T (°C) range			Weight loss at 600°C (%)	Residue at 600°C wt. (%)
	T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>		
RGOS9-1	25.1	33.9	201.6	74.6	25.4
RGOS9-2	31.6	93.3	186.8	76.1	23.9
RGOS9-3	33.9	85.9	179.4	75.3	24.7
RGO9-1	38.3	109.6	216.4	68.1	31.9
RGO9-2	24.3	90.4	183.8	78.1	21.9
RGO9-3	25.8	84.4	183.8	79.2	20.8

#### IV. CONCLUSIONS

In this work, the influence of the two different ultrasonic devices on the synthesis of reduced graphene oxide was investigated. The XRD results indicated that the ultrasonic bath prevented to restacking of graphene layers. The FTIR results presented that there are visible characteristic peaks of oxygen containing functional groups of samples obtained by the ultrasonic bath providing better dissociation than ultrasonication. Also, the RGO samples showed higher thermal stability than RGOS samples.

## ACKNOWLEDGEMENTS

The authors thank the financial support of the research foundation (Project no: 2017-02. BSEU.11-01) of Bilecik Seyh Edebali University.

## REFERENCES

- [1]. S. Park, J. An, J.R. Potts, A. Velamakanni, S. Murali, and R.S. Ruoff, Hydrazine-reduction of graphite- and graphene oxide, *Carbon*, 49, 2011, 3019-3023. DOI: 0.1016/j.carbon.2011.02.071
- [2]. S. Pei and H.-M. Cheng, The reduction of graphene oxide, *Carbon*, 50, 2012, 3210–3228. DOI:10.1016/j.carbon.2011.11.010
- [3]. D. Konios, M. M. Stylianakis, E. Stratakis, E. Kymakis, Dispersion behaviour of graphene oxide and reduced graphene oxide, *Journal of Colloid and Interface Science*, 430, 2014, 108–112. DOI:10.1016/j.jcis.2014.05.033.
- [4]. L. Stobinski, B. Lesiak, A. Malolepszy, M. Mazurkiewicz, B. Mierzwa, J. Zemek, P. Jiricek, and I. Bieloshapka, Graphene oxide and reduced graphene oxide studied by the XRD, TEM and electron spectroscopy methods, *Journal of Electron Spectroscopy and Related Phenomena*, 195, 2014, 145-154. DOI: 10.1016/j.elspec.2014.07.003
- [5]. J. Zhang, H. Yang, G. Shen, P. Cheng, J. Zhang, and S. Guo, Reduction of graphene oxide via L-ascorbic acid, *Chemical Communications*, 46(7), 2010, 1112-1114. DOI: 10.1039/b917705a
- [6]. T. Kimura, T. Sakamoto, J.-M. Leveque, H. Sohmiya, M. Fujita, S. Ikeda, T. Ando, Standardization of ultrasonic power for sonochemical reaction, *Ultrasonics Sonochemistry*, 3, 1996, 157-161. DOI: 10.1016/S1350-4177(96)00021-1
- [7]. W. S. Hummers, and R. E. Offeman, Preparation of graphitic oxide, *Journal of the American Chemical Society*, 80, 1958, 1339. DOI: 10.1021/ja01539a017
- [8]. S. Thakur, and N. Karak, Green reduction of graphene oxide by aqueous phytoextracts, *Carbon*, 50, 2012, 5331-5339. DOI: 10.1016/j.carbon.2012.07.023
- [9]. F. Mindivan, The synthesis, thermal and structural characterization of polyvinylchloride/graphene oxide (PVC/GO) composites, *Material Science Nonequilibrium Phase Transformations*, 3, 2015, 33-36.
- [10]. D. Kong, L.T. Le, Y. Li, J. L. Zunino, and W. Lee, Temperature-dependent electrical properties of graphene inkjet-printed on flexible materials, *Langmuir*, 28(37), 2012, 13467-13472. DOI: 10.1021/la301775d
- [11]. C. Zhu, S. Guo, Y. Fang, and S. Dong, Reducing sugar: new functional molecules for the green synthesis of graphene nanosheets, *ACS Nano*, 4(4), 2010, 2429-2437. DOI: 10.1021/nn1002387
- [12]. J. Hu, X. Jia, C. Li, Z. Ma, G. Zhang, W. Sheng, X. Zhang, and Z. Wei, Effect of interfacial interaction between graphene oxide derivatives and poly (vinylchloride) upon the mechanical properties of their nanocomposites, *Journal of Materials Science*, 49, 2014, 2943-2951. DOI:10.1007/s10853-013-8006-1-
- [13]. M. J. Ferná'ndez-Merino, L. Guardia, J. I. Paredes, S. Villar Rodil, P. Solis'-Ferná'ndez, A. Martí'nez-Alonso, and J. M. D. Tasco'n, Vitamin C is an ideal substitute for hydrazine in the reduction of graphene oxide suspensions, *Journal of Physical Chemistry C*, 114, 2010, 6426-6432. DOI: 10.1021/jp100603h

Meryem Göktaş was born in Malatya on May 24th 1982. She received the B.Sc. degree in Mining Engineering from İnönü University, Malatya, Turkey in 2003, and M.S. degree in Mining Engineering from Dokuz Eylül University, Izmir, Turkey in 2007, and Ph.D. degree in Mining Engineering from İnönü University, Malatya, Turkey in 2013. Since 2017, she has been working as an assistant professor of Metallurgy Department at Bilecik Seyh Edebali University, Bilecik, Turkey. Her main research interests include physicochemical operations and mechanochemical processes in mineral engineering, graphene derivatives, polymer matrix composites and their characterization.



Assistant Prof. Dr. Ferda Mindivan, born in 1983, graduated from Ataturk University, Erzurum, Turkey, Department of Chemistry, in 2005. After receiving her PhD degree from the same university in the field of Physical Chemistry in 2013, she is continuing her professional career as an assistant professor in the Biotechnology Application and Research Center, Bilecik Seyh Edebali University, Bilecik, Turkey. Also, she graduated from Bilecik Seyh Edebali University, Bilecik, Turkey, Department of Mechanical Engineering, in 2018.. Her main research interests include green synthesis of graphene derivatives, polymer matrix composites, biomaterials and their structural, thermal, mechanical characterization.



Meryem Göktaş "Comparison of Two Different Ultrasonic Devices (Ultrasonic Bath and Ultrasonication) Used in Synthesis of Reduced Graphene Oxide. "The International Journal of Engineering and Science (IJES) 7.8 (2018): 75-79