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Research Article

Effect of Reduction Temperature and Time on The Reduction of Graphene Oxide with White Cabbage Extract

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Abstract
Graphene is an important material that has attracted attention in recent years due to its large surface area, mechanical strength, thermal, electrical and magnetic properties. In this work, reduced graphene oxide (RGO) was obtained by reducing the graphene oxide (GO) with green synthesis. For this purpose, white cabbage aqueous extract was selected to reduce GO. The total phenolic acids, which are the reducing agent in the extract, were determined according to the Folin-Cioceltau method. It was determined that there is 0.064 grams of polyphenols in 1 mL of white cabbage extract. In order to determine the reduction experimental conditions, a reduction temperature of 25, 50 and 100 ºC and 1, 2, 4 and 6 hours of reduction time were studied. Structural characterization of synthesized RGOs was performed with XRD, FTIR and SEM techniques. The results showed that GO was reduced at a reduction reaction temperature of 100 °C and a reduction reaction time of 6 hours. The peak seen at 22.08º in the XRD data is evidence of reduction of GO.

Keywords: Reduced graphene oxide, Green synthesis, White cabbage, Polyphenol

Beyaz Lahana Özütü ile Grafen Oksitin İndirgenmesi Üzerinde İndirgeme Sıcaklığı ve Süresinin Etkisi

Öz
Grafen, geniş yüzey alanı, mekanik dayanımı, ısıl, elektriksel ve manyetik özellikleri nedeniyle son yıllarda dikkatleri üzerine çeken önemli bir malzemedir. Bu çalışmada grafen oksitin (GO) yeşil sentezle indirgenmesi ile indirgenmiş grafen oksit (RGO) elde edilmiştir. Bu amaçla, GO'yu indirgemek için beyaz lahana sulu özütü seçildi. Özütteki indirgeyici ajan olan toplam fenolik asitler Folin-Cioceltau yöntemine göre belirlendi. 1 mL beyaz lahana özütünde 0.064 gram polifenol olduğu tespit edildi. İndirgeme deney koşullarını belirlemek için 25, 50 ve 100 ºC indirgeme sıcaklığı ve 1, 2, 4 ve 6 saatlik indirgeme sürelerinde çalışılmıştır. Sentezlenen RGO'ların yapısal karakterizasyonu XRD, FTIR ve SEM teknikleri ile yapıldı. Sonuçlar 100 ºC indirgeme reaksiyonu sıcaklığında ve 6 saat indirgeme reaksiyonu süresinde GO'nun indirgendiğini göstermiştir. XRD verilerinde 22.08º'de görülen pik GO'nun indirgendiğinin kanıtıdır.

Anahtar kelimeler: İndirgenmiş grafen oksit, Yeşil sentez, Beyaz lahana, Polifenol

1. Introduction

Graphite, which is formed by the overlapping of graphene sheets with strong π-π interaction, is a common and inexpensive source [1]. Graphene is a material that attracts science and industry due to its many unique properties such as strength, large surface area, high thermal conductivity, hydrophobic structure and electronic, catalytic, magnetic properties [2, 3]. Thanks to these properties, graphene is used in many different sectors such as medicine and energy [3]. The unique properties of graphene are due to the π electrons in the C=C bond [1]. It has a two-dimensional (2D) sheet of sp^2 carbon atoms and very thin structure [4–7]. It is thought that graphene has an electron mobility of more than 15000 cm^2V^-

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$^1S^{-1}$ at room temperature and a thermal conductivity of around 5000 $Wm^{-1}K^{-1}$ and surface area is 2630 m^2/g [8]. Some of the graphene synthesis methods are the top-down approach, micromechanical cleavage, solvothermal reduction, chemical reduction, laser irradation, liquid phase exfoliation, and the reduction of graphene oxide with chemical or vegetable agents [9, 10]. Graphene oxide is a graphene allotrope similar to graphene with its hexagonal carbon structure. However, it has many oxygen-containing (hydroxy, carbonyl, carboxylic acid, alkoxy) functional groups. If functional groups containing oxygen are formed on the graphite surface, graphite oxide is formed. Graphene oxide is obtained by the expansion of graphite oxide layers [7, 11]. Both graphene and GO have large surface areas. However, GO can dissolve in water due to its oxygenated functional groups. In addition, it has an amphiphic structure [12]. There are many synthesis methods of GO such as Hummers, Brodie, Hofmann, Staundenmaier [13].

In recent years, RGO is known as one of the graphene production methods, which has been prominent in many fields such as nanotechnology [14]. Reduced graphene oxide (RGO) is similar in structure and properties to graphene [4]. It has been reported that the measure of reduction of GO or the extent of oxidation of graphene affects some properties of electrical conductivity, catalysis activity. The degree of reduction of graphene oxide is controlled by temperature and time [10]. Reduced graphene oxide (RGO) is a biocompatible material with superior mechanical strength and electrical conductivity [15]. Reducing chemicals such as hydrazine (N_2H_4), hydrazine hydrate and sodium borohydride ($NaBH_4$) are frequently used to reduce GO. However, these chemicals are both toxic and harmful to the environment. Plant extracts (Lycium barbarum, Ginkgo biloba, Kombucha tea, carrot root, green tea, cinnamon, Chrysanthemum), cafffeic acid, organic acids, glucose, melatonin, vitamin C and some bacteria (Escherichia coli, E. fergusoni) have been used in recent years to reduce GO [3, 15-21]. White cabbage is an important vegetable that can be grown almost anywhere in the world. It belongs to the Cruciferae family. It has been reported that white cabbage is an important source of polyphenols [22, 23]. No studies of GO reduction with white cabbage extract have been reported to date.

In this study, it was aimed to obtain reduced GO by using white cabbage extract. Total phenolic content of white cabbage was determined by Folin-Cioceltau method. The effect of reaction temperature and reaction time on reduction was investigated by XRD, FTIR and SEM techniques.

2. Material and Method

2.1 Materials

The materials used in our experiments were gallic acid ($C_7H_6O_5$, Sigma-Aldrich) and sodium carbonate (Na_2CO_3, 99%, Sigma-Aldrich), Folin-Cioceltau reagent (Carlo-Erba). White cabbage was obtained from local markets.

2.2 Preparation of White Cabbage Extract

About 100 grams of white cabbage cut into long strips. It was extracted by brewing by soaking in 500 mL distilled water (at 70 ºC) for 30 minutes. The extract was obtained by filtration. The extract obtained was used fresh.

2.2 Folin-Cioceltau Method

The total amount of phenolic matter in white cabbage was determined according to the Folin-Cioceltau method. In the alkaline medium provided with 10 mL of supersaturated sodium carbonate, 1 mL of extract and 5 mL of Folin reagent and a blue solution of distilled water were prepared. It was kept in the dark for 1 hour. Then, absorbance was measured at 720 nm wavelength in UV-vis spectroscopy. With this method, the amount of reducing agent in white cabbage extract was determined.

2.3 Synthesis of Reduced Graphene Oxide

We used GO, which we reported in our previous article and synthesized by the Hummers method [19]. 50 mg of GO was added (concentration 1 mg/mL) into 50 mL of white cabbage extract and kept in an ultrasonic water bath at room temperature for 1 hour until it became homogeneous. Then, 50 mL more white cabbage extract was added onto this sonicated mixture. In this way, the concentration of the suspension was brought to the level of 0.5 mg/mL. The reaction vessel connected to the spiral refluxer was stirred at 400 rpm at different reaction temperatures (25, 50, 100 ºC) and times (1, 2, 4 an 6 h), and the black solution obtained was precipitated by centrifugation and dried at 60 ºC for 24 hours. The visual version of the method we use to reduce GO is given in Figure 1.

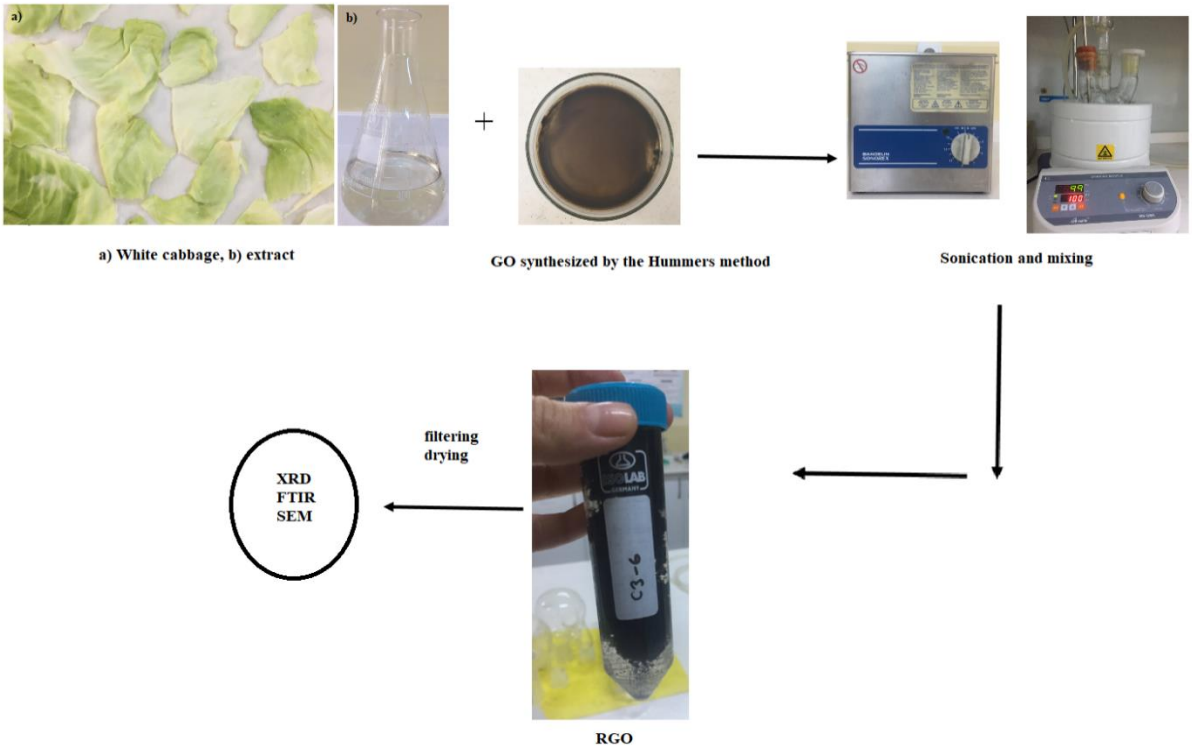

Figure 1. Schematic view of the reduction of GO with white cabbage extract

3. Results and Discussion

Gallic acid (GA) solution with ethanol was used to determine the total phenolic content. Because gallic acid is the equivalent of polyphenol. For this purpose, GA solution at different concentrations (1, 10, 20, 100, 250, 375 mg/L) was prepared and the calibration graph was prepared in Figure 2 by measuring the absorbance values at 720 nm. The total amount of phenolic matter in the white cabbage extract was determined from the equation (y=0.0049x+0.0945) obtained from the graph. It has been calculated that there is 0.064 grams of total phenolic substance in 1 mL of white cabbage extract.

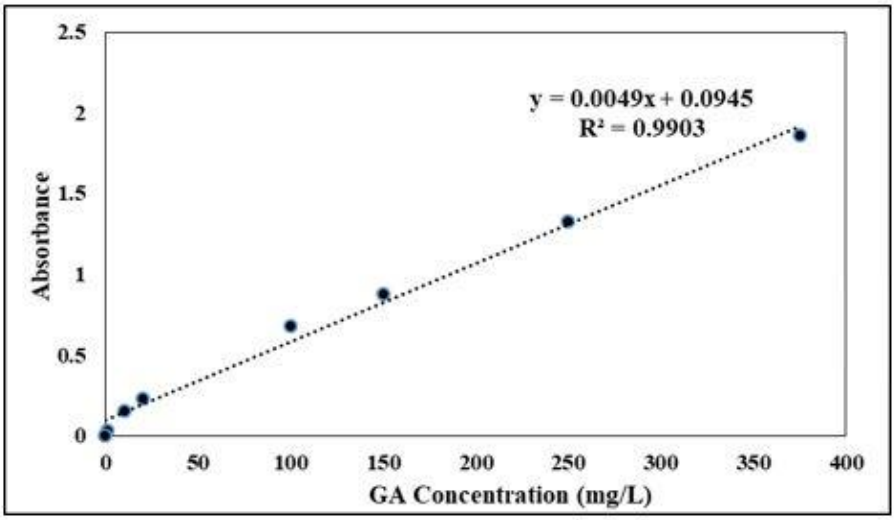

Figure 2. Gallic acid calibration graph

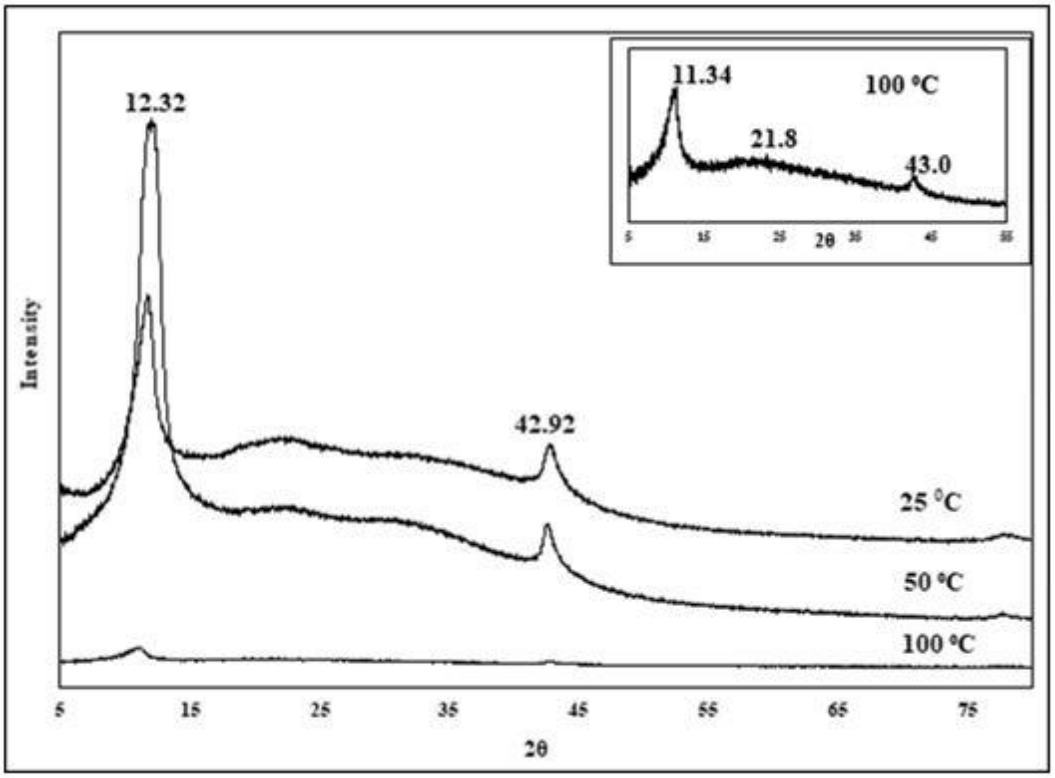

Figure 3. XRD spectra of RGO samples prepared at different reaction temperatures using white cabbage extract (Reaction time 1 hour).

Using white cabbage extract, RGO samples were prepared at reaction temperatures of 25, 50 and 100 ºC, with a constant reaction time of 1 hour. The properties of the prepared RGO samples were examined using XRD and FTIR techniques. According to XRD data in the literature, graphite gives a peak in the range of 25-26º, while GO gives a peak between 11-13º [19]. XRD spectra of RGO samples prepared with white cabbage extract at different reaction temperatures are given in Figure 3. In the RGO samples synthesized at 25 and 50 ºC, characteristic peaks of GO at 2θ = 12.32º and 42.92º were clearly observed. It is seen that the peak intensity of GO at 2θ= 12.32º decreases significantly when the temperature rises to 100 ºC. In addition, in this sample, it was observed that the peak of GO at 2θ=12.32º shifted to the left to 2θ=11.34º. The low intensity peak at 2θ=42.92º indicates the graphene crystal plane structure [18]. The inter-layer distance for RGO was calculated by Bragg's law (Eq. 1) [24]. RGO peak

seen at 2θ = 21.8º for the reaction temperature of 100 ºC, the interlayer distance was calculated as 0.41 nm.

$$\lambda = 2dsin\theta \quad (1)$$

In the formula, d is the distance between the layers and theta is the angle of diffraction. λ is 0.154056 nm wavelength value. The average crystal size (Dp) of the RGO samples was calculated with the Debye-Scherer equation (Eq. 2) using the Full Width at Half Maximum (FWHM) values obtained from the XRD graph.

$$Dp = K\lambda/\beta cos\theta \quad (2)$$

Where Dp is the average crystallite size, K is the Scherrer constant (0.94). λ is the wavelength, β is the full width at half the maximum intensity (FWHM) and θ is the diffraction angle in degrees [25].

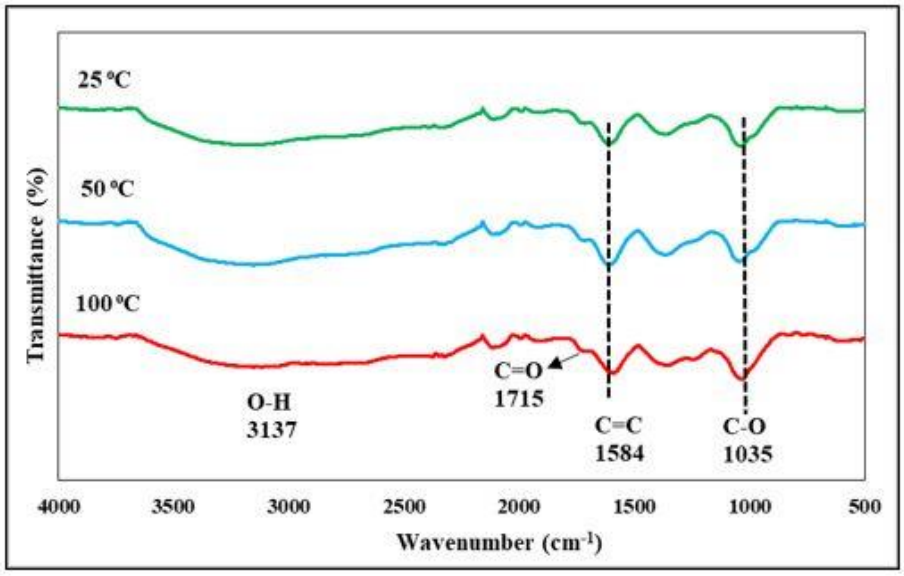

Figure 4. FTIR spectrum of RGO samples prepared at different reaction temperatures using white cabbage extract (Reaction time 1 hour).

The FTIR spectrum of the RGO samples prepared by using white cabbage extract at 25, 50 and 100 ºC reaction temperature with by 1 hour reaction time are shown in Figure 4. There are many functional groups on the GO surface. IR absorption peak values of functional groups on the GO surface in the literature are given in Table 1. In Figure 4, the peaks seen at 1035, 1584, 1715 and 3137 cm^{-1} on RGO surfaces show C-O (alkoxy) stretch, C=C aromatic stretch vibration, C=O stretch and O-H (hydroxyl) vibration respectively. The intensity of the peak corresponding to the C=O vibration band at 1715 cm^{-1} decreased with the increase in temperature [14, 26]. The permeability intensity of the hydroxyl group (3137 cm^{-1}) decreased as the temperature increased from 25 ºC to 100 ºC. The reason for this is that the absorbed water molecules evaporate by intercalation as the temperature increases. In addition, GO is reduced by losing the presence of oxygen-containing functional groups and its hydrophilic properties [14].

Table 1. Functional groups on GO surface and IR absorption peak values in the literature [19, 27]

Peak position (cm^{-1})	Functional group
3000-3500	O-H
1700-1750	C=O
1550-1650	C=C
1000-1100	C-O

The reduction temperature was chosen as 100 °C because of the peak attributed to the graphene structure in the XRD data at 2θ=21.8º and the functional peak intensities of oxygen-containing groups decreased slightly. XRD data of RGO samples prepared for 1, 2, 4 and 6 hours at a reduction temperature of 100 °C are shown in Figure 5. The characteristic peak of GO has emerged in the range of 2θ = 11.4-11.62º, shifted to the left for RGO samples prepared in 1, 2 and 4 hours reduction times. The characteristic wide and small peak of RGO prepared in 4 hours mixing period was seen at 2θ = 23.3º, and this peak is not seen in RGO samples prepared at 1 and 2 hours mixing times. When the reaction time reached 6 hours, a wide and distinct characteristic peak of RGO was observed at 2θ = 22.08º. For this peak, the distance between the layers can be calculated as 0.40 nm. According to literature, it can be concluded that this value is smaller than the distance between the layers (0.7-0.98 nm) of GO [17]. For this example, GO's peak was observed at 2θ = 13.2º. From the results, it can be said that the peak of RGO appears and peak of GO is reduced in direct proportion to the increase in reaction time [28]. According to Eq. 2, the average crystal size in the sample prepared with 100 °C reaction temperature and 6 hours reduction time was determined as 0.51 nm.

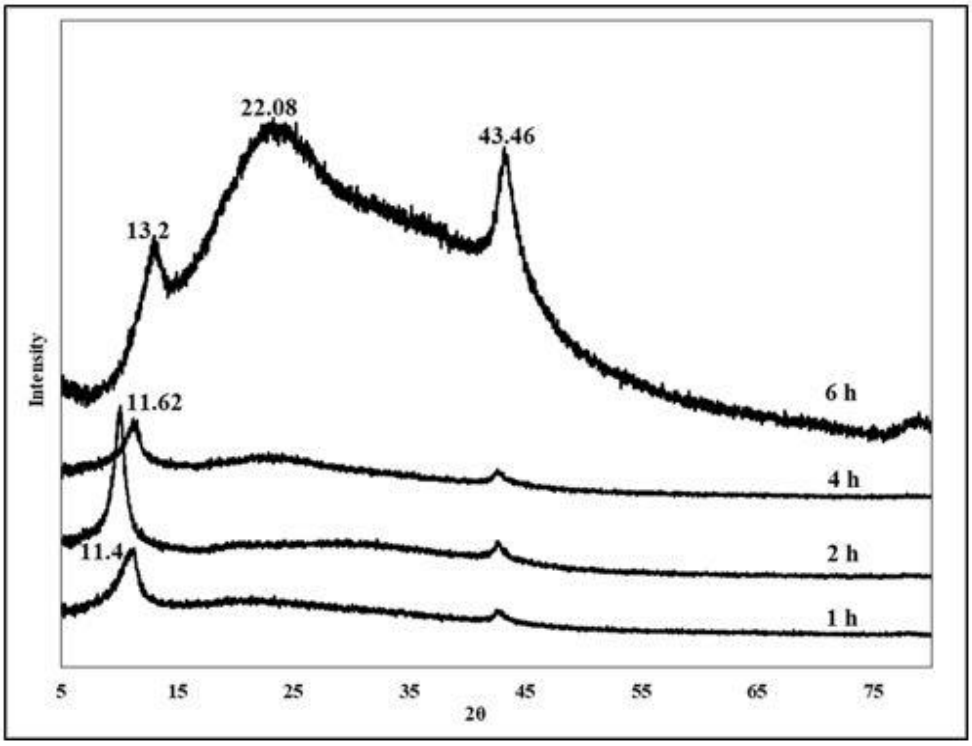

Figure 5. XRD spectrum of RGO samples prepared at different reaction times using white cabbage extract (Reaction temperature 100 ºC).

From the FTIR spectra where the effect of the reaction time for RGO obtained using white cabbage extract was investigated, reduction appears to be more effective after 2 hours (Figure 6). For RGOs prepared at the 4th and 6th hour, the peak intensity (O-H) at 3137 cm^{-1} and the intensity of the alkoxy (C-O) peak at 1045 cm^{-1} decreased significantly. Because the reducing temperature was chosen as 100 ºC, free water molecules intercalated in GO evaporated, weakening the peak intensity of the O-H functional groups [26, 28]. When the results obtained from FTIR and XRD are evaluated together, it is concluded that suitable conditions for the reduction of GO can be achieved using white cabbage extract at a reduction temperature of 100 ºC and a reduction time of 6 hours.

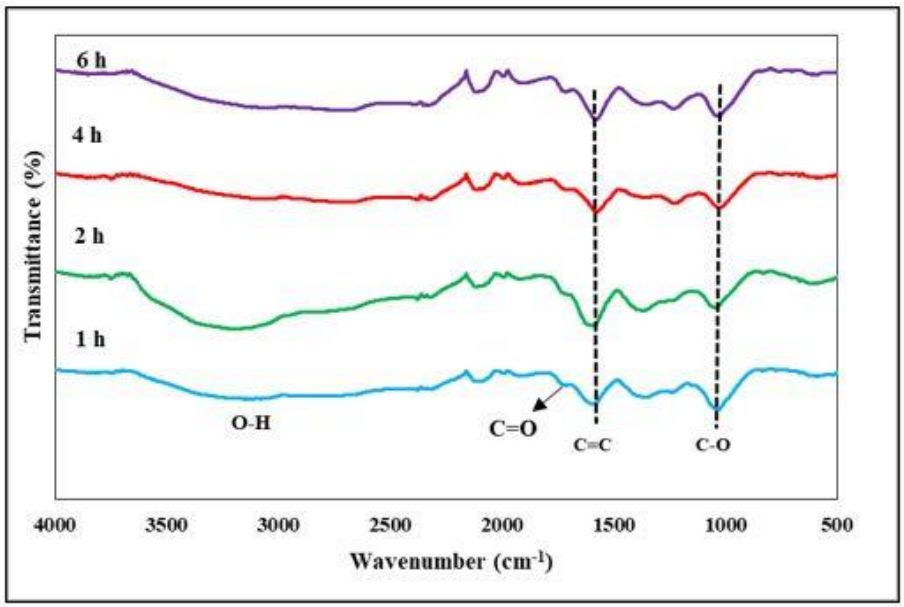

Figure 6. FTIR spectrum of RGO samples prepared at various reaction times using white cabbage extract (Reaction temperature 100 ºC).

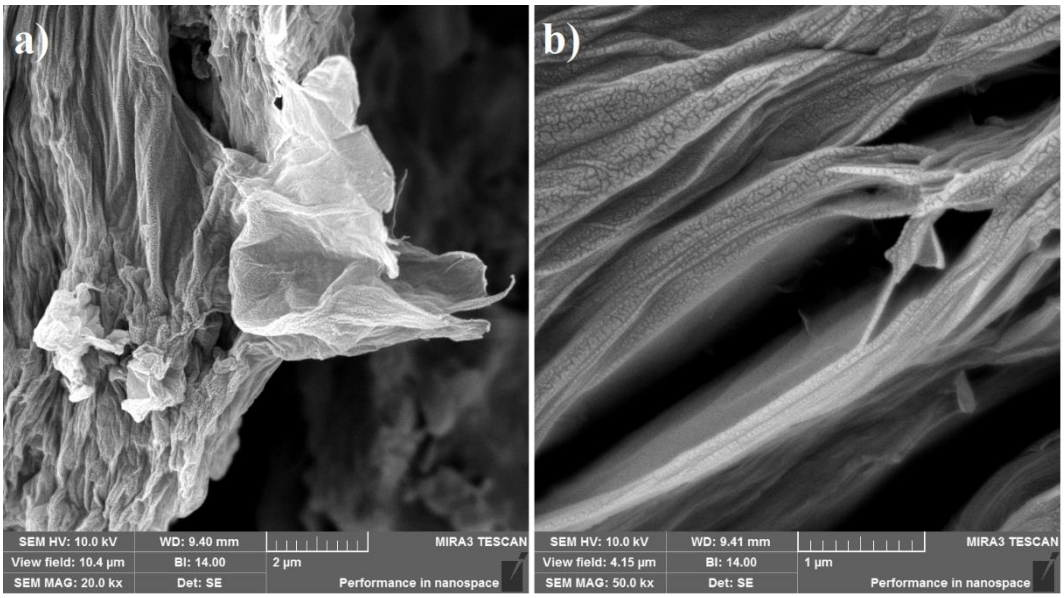

Figure 7. SEM images of RGO from different angles a) 20k magnification b) 50k magnification (Reaction temperature 100 ºC, reaction time 6 hours)

SEM images of the prepared RGO sample at 100 ºC for 6 hours is shown in Figure 7a,b. In Figure 7a, it is seen that there is agglomeration in the structure of RGO. Figure 7b illustrated that multilayer RGO was synthesized. In addition, it seen that prepared RGO sample formed undulating ripple-like layers had the basic properties of graphene (Fig.7b). Also, it is clear that after the GO is reduced, the wrinkled sheets increased and randomly collected [30]. It can be said that oxygen-containing functional groups decrease with increasing reaction temperature and so by removing these groups from the RGO surface, shrinkage occurs [14, 29].

4. Conclusion

Green synthesis has been applied to an environmentally friendly method by using extract instead of harmful chemicals. In this study, the reduction was achieved by removing the functional groups on the GO surface using white cabbage extract. According to the XRD and FTIR data, it can be said that suitable experimental conditions can be provided for the reduction of GO when the reduction

temperature is 100 °C and the reduction time is 6 hours. In the SEM results, it was determined that the morphological structure of RGO is multi-layered. These results revealed that white cabbage extract can be used in the reduction of GO. When the literature is examined, it is seen that the reduction temperature of GO has been tested at different temperatures. However, the commonly chosen temperature in the studies is the range of 95-100 °C. Similarly, the reduction temperature was determined as 100 °C in our study. This study indicates that white cabbage extract can be used as an alternative reducer instead of toxic chemicals, thanks to the polyphenol it contains.

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Authors' Contributions

In this study, Author 1 contributed to the literature review, experiments, evaluation of data and article writing, while Author 2 contributed to the formation of ideas, evaluation of the data, and article writing and editing.

Statement of Conflicts of Interest

There is no conflict of interest between the authors.

Statement of Research and Publication Ethics

The authors declare that this study complies with Research and Publication Ethics

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