Preparation Of Graphene Oxide And Its Reduction By Lemon Peel To Graphene And Diagnosed By Several Techniques

Rusul Rifat Jameel[#1] & Liqaa Hussein Alwan[2]

[#1,2]*Department of Chemistry, College of Education, University of Samarra ,Samarra-Iraq.*
barabio86@gmail.com

Abstract**: -The research included the preparation of graphene oxide by Hummer and Modified Hummer method through a simple chemical reaction and in the presence of plant extracts, as the product was reduced by an aqueous extract of lemon peel, and the result was diagnosed using several techniques, including Fourier-transform infrared spectroscopy (FT-IR) and scanning electron Microscope (SEM) and X-ray diffraction (XRD) BET surface area, as the results of the (FT-IR) spectrum showed the appearance of oxygen groups in graphene oxide that were reduced into wafers. The results of XRD showed that the average crystal size of the prepared particles was 3.11nm, and the (SEM) showed that the prepared graphene minerals with enlargement strengths of 4.16µm and 41.6µm with diameters (1-10µm) had a large number of pores, and were in the form of transparent and thin plates And in a fluffy and folded shape, the results of the BET measurements indicated that the prepared graphene has a surface area of 169.16 m2 g / with an average pore diameter of about 3.58nm. In addition to studying some of the physical characteristics of graphene, such as the pH and the percentage of moisture, where the moisture content was (8.1%) and the pH was (7.1).

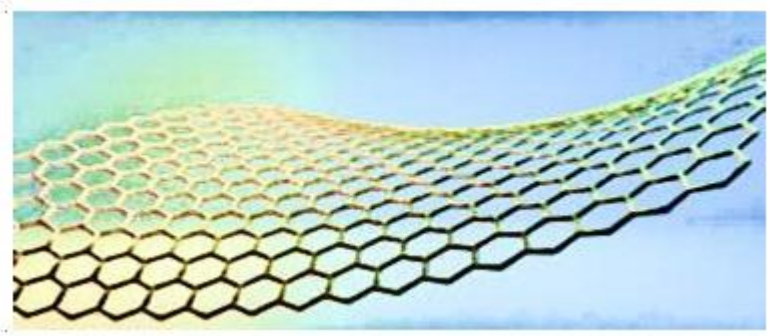
Key words: graphene, graphene oxide, lemon peel, BET surface area

INTRODUCTION

The discovery of graphene in the field of nanomaterial technology has made it an interesting material and has various applications [(1)], among which it is used as a conduction in medicines [(2)], hydrogen storage [(3)], fuel cells manufacturing [(4)], super capacitors and batteries manufacturing [(5)], the manufacture of solar cells and the manufacture of electromagnetic shields [(6)], reinforcement of polymer materials, ceramics and metal matrix [(7,8)], while the disadvantages of graphene are less significant or even desirable [(9,10)].

The graphene is two-dimensional flat plates, the thickness of these plates is the diameter of one carbon atom, and the hybridization process between carbon atoms is in the form of sp^2 for graphene. As for graphene oxide, the hybridization between carbon atoms is in the formula sp^3, where graphene is the basic building unit of graphite sp^3, but its electronic structure is different from that of graphite.

When collecting many levels of graphene, we get graphite, the substance in the pencil, and the forces that bind the graphene layers together are the weak Vander Walz forces [(11)] as in Figure (1)



The structure of graphene (1)

There are many processes for the production of graphene, including the Chemical Exfoliation Process of Graphene [12], where in recent years this method has been dispensed with and replaced by another method through the introduction of well-reduced natural substances such as green tea extract [13] and black tea [14] Red tea, Vitamin C, ascorbic acid [15].

Because ascorbic acid is a green alternative to conventional reducing agents for GO (such as hydrazine hydrate) it is an inexpensive and abundant substance that can reduce GO to an acceptable extent) [16].

The aim of the research

- Preparing nanoparticles graphene from a simple chemical reaction and reducing it with an aqueous extract of lemon peel.
- Diagnosis of the prepared material with (FT_IR, EDX, SEM, BET) techniques.
  - Practical part:
  - Practical devices: A number of devices were used, such as the Sartorius Lab Sensitive Balance. BL210S, UV_VIS Spectrophotometer 1650PC of Shimadzu of Japanese origin, FT-IR Spectrophotometer type 1S-IR Affinity equipped by Shimadzu company of Japanese origin, PH Meter Type 211 supplied by Hanna Company of Korea, Drying Oven Type (Termaks - S - NO 104544), X-ray Diffractometer-6000 device supplied by Shimadzu Company and Scanning Electron Microscopy Type - AIS2300C, Atomic Microscopy Type - SPM AA3000, BET method (Brunauer Emmett and Teller), Shaking Water Bath Type - YCW012S.

Chemicals used

In this research, I used concentrated sulfuric acid prepared from (B.D.H), sodium nitrate prepared from (Merck), potassium permanganate prepared from (Merck) company, an hydrogen peroxide prepared from (Scharlau), noting that all these materials are of high purity.

Preparation of the raw material

Preparing the graphite: a number of (VERTEX ® OffiCe V-1102) pencils were taken, the wooden part was removed from them and only the graphite was taken, then it was cleaned well from the wood residues and it was ground by a pestle (mortar) at home, so approximately 3 gm of graphite were obtained.

Preparation of the reduced aqueous solution: an amount of lemon peel was taken (because it contains ascorbic acid) and washed well, then carefully peeled, took 5 gm of

it and added 100 ml of ion-free water, then heated for 30 min until it reached a boil, then after The heating was filtered with a regular filter paper and the volume was completed to 100 ml and kept in the refrigerator in a degree less than 20 k, where it was adopted as a working solution with a concentration of 5% for the purpose of using it in reducing the graphene oxide to turn into graphene.

- Preparation of graphene: The preparation process was carried out in two parts:

♦ Preparation of graphene oxide stage: the graphene was prepared using the Modified Hummer method [17] as follows:

1. (46ml) of concentrated H_2SO_4 hydrochloric acid was placed in an ice bath, then 1g of $NaNO_3$ sodium nitrate was slowly added to it and stirred by a magnetic stirrer at 0ºC for a period of (30 min).
2. (0.5g) of graphite powder is added slowly so that the addition process takes 20min
3. We add to this mixture (6g) of $KMnO_4$ potassium permanganate slowly, and the process of adding it takes (30min).
4. Leave the mixture in an ice bath for (10min), then remove the beaker containing the mixture from the ice bath, and leave it to stir by the magnetic stirrer for a period of 2hor.
5. After that, (92ml) of distilled water is added very slowly, so that it is initially in the form of a drop by drop. The process of adding it continues for more than (40min), then the temperature is raised to (98 C) for a period of (40min).
6. Then warm distilled water (280ml) is added, then hydrogen peroxide H_2O_2 with a concentration of 30% is added by (18ml) so that the color of the mixture turns into a greenish yellow color.
7. This mixture is left to stir for about (30min) by the magnetic stirrer, after which it is left to cool and filter, then after a period of filtering out, we rinse the suspension with distilled water several times to get rid of the acid residue. We measure the acidity of the last filter and try to make it neutral by adding drops of sodium hydroxide (0.1M From NaOH).
8. We let the filter paper dry at laboratory temperature, then we skim the material on it.
9. Then it was ground with a pestle and collected in a plastic bottle where (0.33g) of non-reducing graphene oxide was obtained, as shown in figure (2

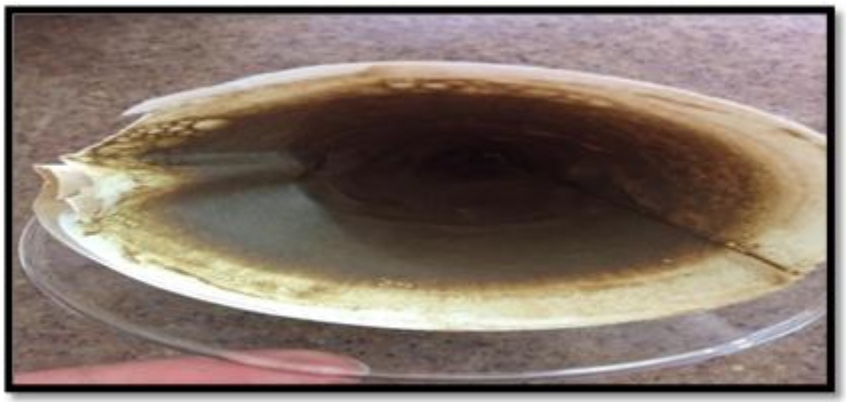


Figure (2): The non-reducing graphene oxide filtration process

- Preparation of reduced graphene oxide:

A weight of (0.3g) was taken from the prepared graphene oxide and added to it (50ml) of aqueous solution of lemon peels with a concentration of (5%), which was heated for a

period of (2hor) at a temperature of (55 ˚C), where it was observed that the color of the graphene oxide changed from greenish yellow to greenish. The black color is evidence of RGO reductive graphene formation, as shown in Fig. (3).

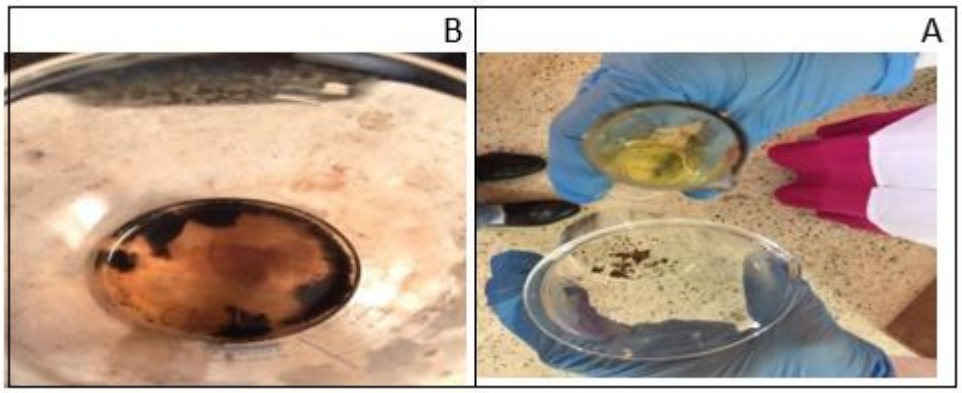


Figure (3) A- The image before mixing graphene oxide with the aqueous solution of lemon peel. B - An image of RGO reductive graphene.

Take some measurements to evaluate the characteristics of the graphene:

- set the humidity:

1gm of graphene was weighed in a ceramic ladle and pre-weighed, placed in a drying oven at 115 ° C for 2 hor. The model was left in the dryer until it was cooled to the laboratory temperature, then weighed and then the percentage of humidity calculated.

Estimating the pH of graphene:
1gm of graphene was added to 10ml of distilled water, then the solution was shaken well for half an hour by shaking at a laboratory temperature of 25 ºC, then filtered and the pH of the filtrate was measured.

RESULTS AND DISCUSSION

During the past decade, upon the discovery of carbon-based nanomaterials such as carbon nanotubes and fullerene, graphene has gained great interest, due to its potential as a multifunctional material and a wide range of applications in various types of devices [(19)].

As graphene was isolated in 2004 by scientists Kostya Navoseiov and Andre Geim at the University of Manchester, and in 2010, both scientists won the Nobel Prize in Physics for their experiments on the structure of graphene, so we were able to record properties that are distinguished It contains graphene from other minerals such as diamond and copper [(20)].

In this paper, the moisture content of graphene was calculated, as it was found that it contains a moisture content of 8.1%, and the acidic function was measured by the pH meter of the filtrate of graphene, where the pH value was (7.1) and this indicates that the prepared graphene is neutral and is prepared This characteristic is one of the good qualities, and the prepared graphene has been diagnosed using the following techniques:

Infrared spectrum (FT-IR)
When the infrared spectrum of graphene was analyzed, it was found that a clear shift in the absorption values of the group (O - H) reached 3412.08 cm^{-1} due to the lack of oxygen

between its molecules [20], and the value of the vibration of the band (C = O) decreased at 1579.06 cm^{-1}. Also, we notice the presence of the alkoxy group (C-O) even after the reduction of graphene oxide to reduced graphene oxide, which shows its bundle at 1055 cm^{-1}, and there is also the organic carboxyl group (C-O), whose value reaches 1350.17 cm^{-1}, and As shown in (4).

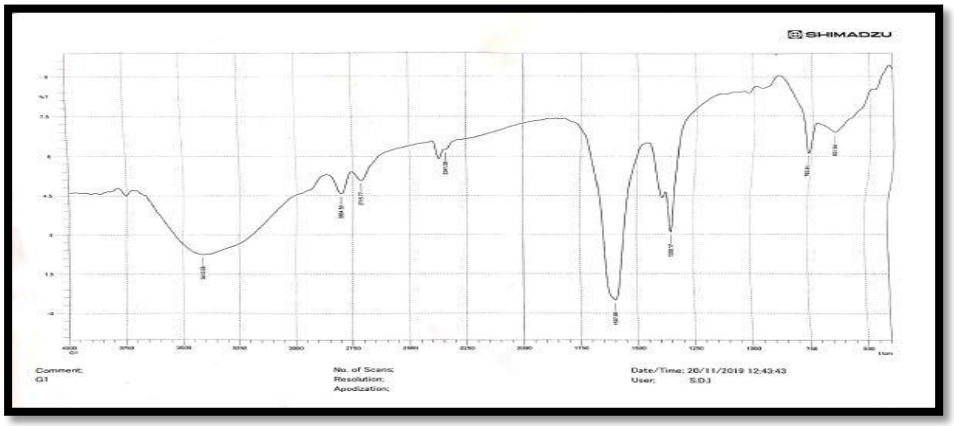


Figure 4: FT-IR spectrum of reduced graphene oxide.

X-Ray Diffraction Spectroscopy:
An X-ray diffraction device (X-RD) was used to know the crystalline properties of the reduced graphene oxide through Miller coefficients. The purity of the reduced graphene oxide as well as the size of the nanoparticles were determined using the Debye Scherer Equation (21)(22). -

Where D = particle size in unit nm, and K = is the Debye Shearer constant whose value is, $\lambda = 0.9$, the X-ray wavelength of 1.5104 A of the copper element ($\lambda = 0.15104$ nm) is converted into a nanometer unit since each $1A = 10^{-1}$ nm, Therefore, β = the total width at the greater half of the summit and its abbreviation FWHM, measured by deg, and converted into a Radian unit, so that the sample was examined by fixing it on a glass slide so that it was prepared in the form of paper on which the material was placed and scanned at 2θ within the range 5 - 75 degrees, Figure (5) shows the X-ray diffraction spectrum of the reduced graphene oxide:

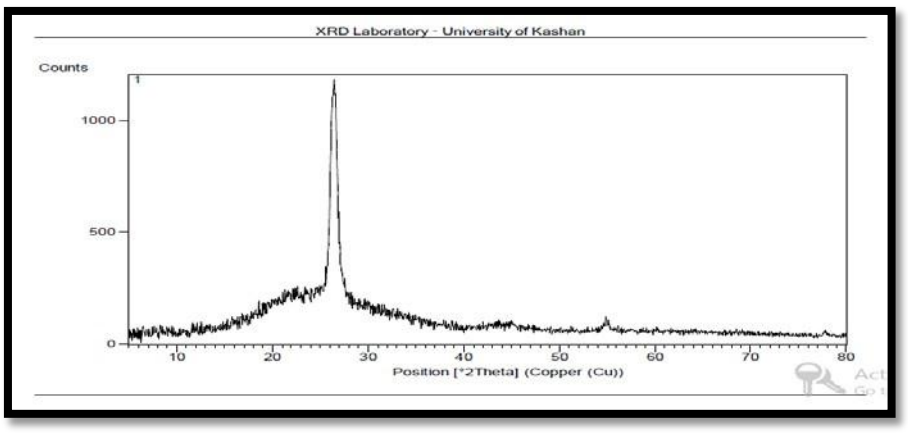


Figure (5) X-ray diffraction spectrum of reduced graphene oxide

Table (1) shows the values of diffraction angles, interlayer distance, Miller index, and intensity of the X-RD spectrum for the strongest three beams, which were used to calculate the average crystal size of the reduced graphene oxide grains.

Table (1) Crystal size according to Miller Index

No>	Peak No.	2 Theta (deg)	D Nm	II/I	FWHM	Intensity (counts)	Integrated (counts)
1	53	26.6841	3.33804	100	0.21600	41	**467**
2	59	28.2918	3.15190	71	0.33250	29	**486**
3	67	31.1769	2.86649	39	0.29000	16	**205**

We note from Table (1) that the average size of granules d is 3.338nm, and that the crystal size of the reduced graphene oxide is within the nanoscale, but it is less than the crystal size of the unreduced graphene oxide according to the literature. This is due to the presence of the oxygen-containing groups in the oxide minutes Graphene because it is between the oxide plates, which leads to an increase in the interlayer space between its layers, and thus this leads to a decrease in its crystalline size, but when the oxide is reduced, the functional groups containing oxygen diminish, which makes the crystalline particles of graphene converge and merge, and as a result, its crystal size will increase [23].

Scanning Electron Microscopy Spectroscopy

In this spectroscopy, the surface properties of the reduced graphene oxide particles were diagnosed from the size and shape of the micro-particles, and it is observed from the scanning electron microscope images obtaining fine particles in different shapes, including the semispherical, transparent and thin layers in the form of fluffy and folded, and minutes were obtained The prepared graphene has a magnification of 4.16µm and 41.6µm, as it was found that it has a large number of pores, with diameters (1-10µm), as shown in Figures (6.7).

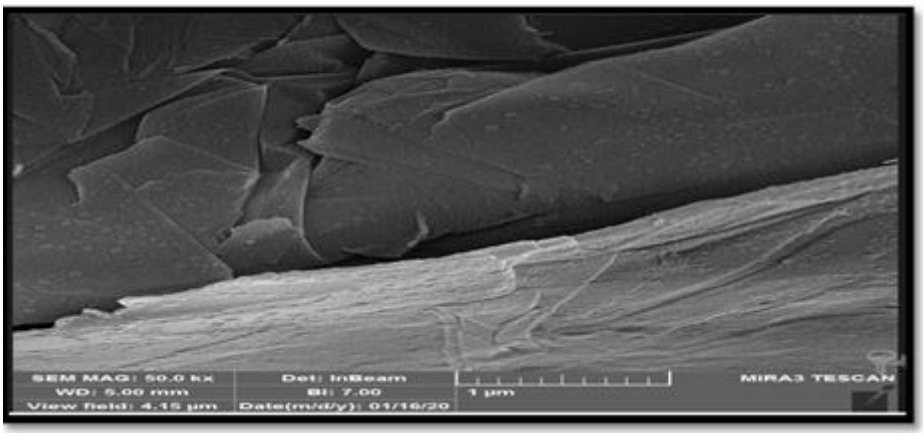


Figure (6): Image of a scanning electron microscope of reduced graphene oxide at 1µm scale

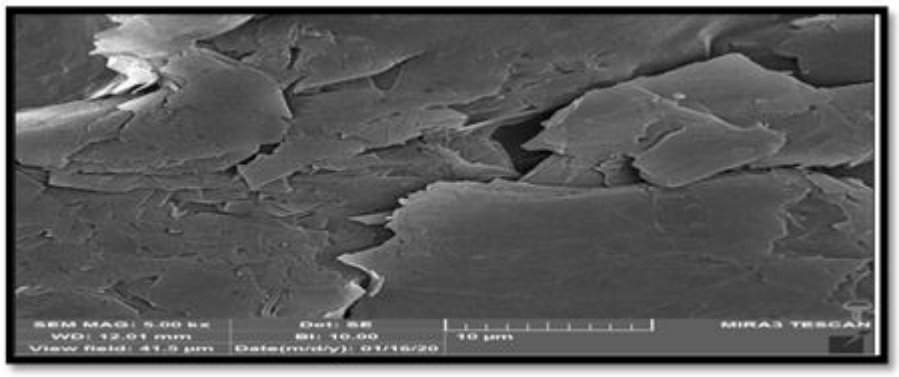


Figure (7) Image of a scanning electron microscope of 10µm reduced graphene oxide.

Analysis of The Surface Area and The porosity nature of Surface (BET,BJH)

The surface area of the prepared graphene was studied, as well as some surface properties such as the distribution of pore diameters and the pore size. We used the method of BET isotherms (adsorption - extortion).

As well as the BJH method for distributing the pore diameters, whereby H_2O and CO_2 were removed from the sample before performing the surface analysis, then it was measured through an adsorption-extortion process at 77k and using liquid nitrogen.

It is possible to use gas adsorption on the surface of the adsorbent material (graphene) in calculating its surface area. In order to determine the surface areas, nitrogen is often used at its normal boiling point

- 195.8C°. The surface area of the prepared nanoscale graphene was measured at different temperatures using a surface area measuring device (Prep 060 and Gemini BET machine) for the purpose of calculating the surface area based on the (Brunauer, Emmett and Teller) equation:

$$\frac{p}{V(p^\circ - p)} = \frac{1}{Vm} + \frac{C-1}{VmC}\frac{p}{p^\circ} \qquad \ldots\ldots\ldots\ldots \quad (1)$$

V: volume of adsorbed gas at equilibrium pressure (p), Vm: capacity of adsorbent monolayer, pº: saturated vapor pressure of adsorbed gas at measured temperature, C: is constant,

Figure 8 illustrates the isotherm of the adsorption and desorption processes that take place on the prepared material.

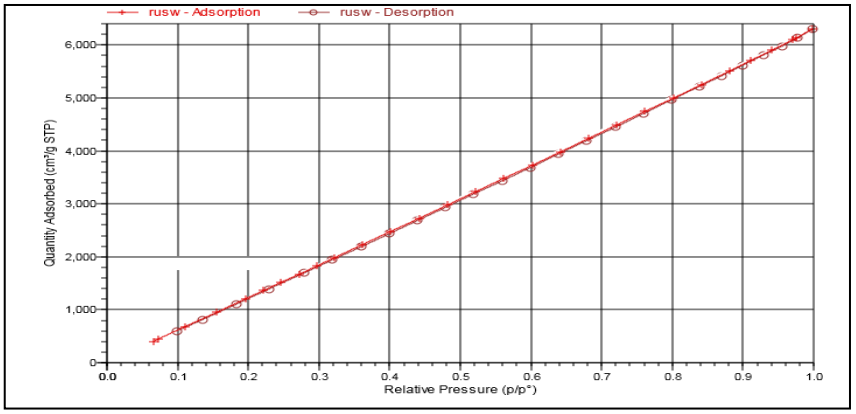


Figure 8: Adsorption / Extortion Isotherm.

Fig. (9) and (10) show the value of the prepared graphene surface area, average pore volume and average pore diameter. We note that the prepared graphene has a surface area of 169.16m^2 / g, and that this surface area in relation to the previously mentioned in the literature is very suitable for using the prepared material in Medical or industrial field

On the other hand, that the size of the pores is in the range of 9.706 cm^3 / g, and this size is very suitable for the completion of activating reactions (catalytic) and adsorption processes , On the other hand, the size of the pores was measured using the BJH method (Barrett-Joyner-Halenda) and it was found that the size of these pores can be used to produce long carbon chains that are wrapped around each other hyper branched and branched molecules, which gives a distinctive characteristic that the adsorbed molecule cannot exit from the pores due to The average pore diameter of the prepared graphene is large and very suitable, which is 3.58 nm. This is called shape in the battle, as the average pore diameter is very excellent for catalysis and adsorption processes.

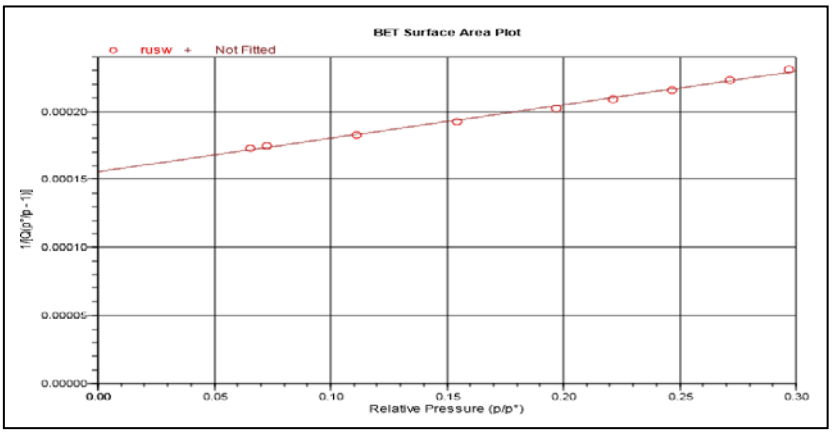


Figure (9): The surface area of the graphene prepared by BET method

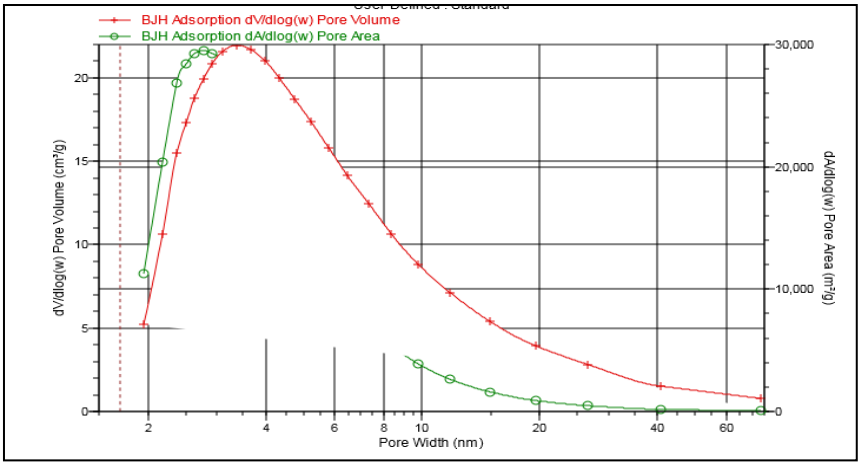


Figure (10): Average follicular volume by BJH method

CONCLUSIONS

1- Successfully preparing graphene sheets and graphene oxide from pencils (graphite pens) using Hummer and the modified Hummer's method.
2- All techniques and microscopy confirmed the nanolayer of the prepared materials.
3- The results of the SEM showed that the prepared graphene is fluffy and in the form of very thin plates or sheets.
4- Using plant extracts (lemon peel) to complete the reduction process.
5- The IR results show the oxygenation groups in graphene oxide and their reduction in graphene sheets.
6- Through X-ray diffraction it is found that the sample of reduced graphene oxide belongs to the hexagonal crystal system.
7- BET measurements showed that the prepared graphene has a surface area of 169.16 m^2 / g.

REFERENCES

[1] Novoselov, K. S. et al. A roadmap for graphene. Nature 490, 192–200 (2012).
[2] Wang, Y., Li, Z., Wang, J., Li, J. & Lin, Y. Graphene and graphene oxide: biofunctionalization and applications in biotechnology. Trends Biotechnol. 29, 205–212 (2011)
[3] Dimitrakakis, G. K., Tylianakis, E. & Froudakis, G. E. Pillared graphene: a new 3-D network nanostructure for enhanced hydrogen storage. Nano Lett. 8, 3166–3170 (2008).
[4] Qu, L., Liu, Y., Baek, J.-B. & Dai, L. Nitrogen-doped graphene as efficient metal-free electrocatalyst for oxygen reduction in fuel cells . ACS Nano 4, 1321–1326 (2010).
[5] Li, Y. et al. Superior energy capacity of graphene nanosheets for a nonaqueous lithium-oxygen battery. Chem. Commun. 47, 9438–9440 (2011).
[6] Wang, C. et al. The electromagnetic property of chemically reduced graphene oxide and its application as microwave absorbing material. Appl. Phys. Lett. 98.7, 072906 (2011).
[7] Walker, L. S., Marotto, V. R., Rafiee, M. A., Koratkar, N. & Corral, E.L. Toughening in graphene ceramic composites. ACS Nano 5, 3182–3190 (2011).
[8] Kim, Y. et al. Strengthening effect of single-atomic-layer graphene in metal–graphene nanolayered composites. Nat. Commun. 4, 2114 (2013).
[9] Wang, C. et al. The electromagnetic property of chemically reduced graphene oxide and its application as microwave absorbing material. Appl. Phys. Lett. 98.7, 072906 (2011).
[10] Banhart, F., Kotakoski, J. & Krasheninnikov, A. V. Structural defects in graphene. ACS Nano 5, 26–41 (2010).

[11] Dato et al., "Substrate-Free Gas-Phase Synthesis of Graphene Sheets", Nano Lett., Vol. 8, pp. 2012-2016, (2008).
[12] Parvez, K., Chemical exfoliation of graphene and its application in organic electronics and energy storage devices , (Doctoral dissertation, Johannes Gutenberg-Universität Mainz) , 2014 ,1- 3.
[13] Al-Marri, A., Khan, M., Shaik, M., Mohri, N., Adil, S., Kuniyil M., Alkhathlan, H., Al-Warthan, A., Tremel, W., Tahir, M. and Khan,M., Green synthesis of Pd graphene nanocomposite: Catalyst for the selective oxidation of alcohols , Arabian journal of chemistry ,2016,9,835-845.
[14] Firdhouse, M. and Lalitha, P., J, Eco-friendly synthesis of graphene using the aqueous extract of Amaranthus dubius , Carbon – Science and Technology , 2013 , 5 , 253 - 259.
[15] Abdolhosseinzadeh, S., Asgharzadeh, H. and Kim, H., Fast and fully– scalable synthesis of reduced graphene oxide ,Scientific Reports,2015, 5 ,1-10 .
[16] Zhang, J. et al. Reduction of graphene oxide via L-ascorbic acid. Chem.Commun. 46, 1112–1114 (2010).
[17] Akhavan, O. The effect of heat treatment on formation of graphene thinfilms from graphene oxide nanosheets. Carbon 48, 509–519 (2010).
[18] Sharon Maheshwar, Sharon Madhuri.Carbon nanoforms and applications. New York: McGraw-Hill: 2010.
[19] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Firsov AA. Electric field effect in atomically thin carbon films, Science 2004; 306:666–669.
[20] Loryuenyong, V., Totepvimarn, K., Eimburanapravat, P., Boon- chompoo, W. and Buasri, A., Preparation and characterization of reduced graphene oxide sheets via water-based exfoliation and reduction methods. Advances in Materials Science and Engineering, 2013 , 2013 , 1-5 .
[21] Mohammadyani, D., Hosseini, S.A. and Sadrnezhaad, S.K. Characterization of nickel oxide nanoparticles synthesized via rapid microwave-assisted route. Int. J. Mod. Phys. Conf. Ser. 2012,5: 270-6 .
[22] Mahal, M. H., Hussein, A. L., Mohammed, H. E., Thamer, H. A., & AL-Samarraie, M. Q. EFFECT OF AQUEOUS EXTRACT OF GRAPE SEEDS ON THE CERTAIN BIOCHEMICAL PARAMETERS IN FEMALE MICE WITH HYPERPROTEINEMIA INDUCTION. Biochem. Cell. Arch. Vol. 19, Supplement 1, pp. 2525-2529, 2019.
[23] Choi, E., Han, T., Hong, J., Kim, J., Lee, S., Kim, H. and Kim, S., Noncovalent functionalization of graphene with end-functional polymers. Journal of Materials Chemistry, 2010 , 20 , 1907-1912.