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Optimization of Graphene Oxide Synthesis Using Hummers Method

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Highlights

- Multi-response criterion analysis TOPSIS-based Taguchi application was performed.
- Different auxiliary oxidants have been used in the Hummers method.
- Different purity graphite samples have been used in the Hummers method.
- Pretreatments were applied to graphite samples before Hummers method.

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Graphene oxide
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Abstract

In the processes of nanomaterial synthesis and characterization, it is important to explore and understand the relationships between variables and levels of processes by introducing experimental design methods and statistical approaches. The main goal of this work is to improve the quality of the graphene oxide (GO) that is made by using the TOPSIS-Based Taguchi Method and the $L_9(3^3)$ experimental design. Various parameters were chosen for experimentation, including samples of graphite with varying levels of purity (85%, 99%, and 99.99%). Prior to initiating the reaction, the graphite underwent pre-application, which involved diverse treatments such as no pre-processing, pre-heating at 200 °C, and ultrasonication. Additionally, different types of auxiliary oxidants ($NaNO_3$, H_3PO_4, and $Na_2B_4O_710H_2O$) were employed. Raman spectroscopy was used to measure the peak intensity ratio (D/G) of the D peak and the G peak. X-ray diffraction (XRD) was employed to determine the crystal size (CS-nm). The surface area (SA-m^2/g) was measured using the BET method. The average particle size (PS-nm) and the Zeta potential (ZP-mv) were determined using a Zeta-Sizer. The atomic ratio of carbon to oxygen (C/O) was also studied using scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM+EDX) to get a better understanding of graphene oxide (GO). The quality criteria's findings were assessed for each experiment using the TOPSIS-Based Taguchi Method, and the optimum circumstances were identified. The recovery rates for D/G, C/O, ZP, SA, PS, and CS were computed as 15.88%, 55.55%, 19.23%, -63.23%, -82.77%, and 20.79%, respectively. The utilization of low-purity graphite and boron compounds in the Hummers method yielded a favorable outcome in the synthesis of graphene oxide. When evaluating the experiment from an economic and environmentally conscious perspective, the results are quite impressive.

1. INTRODUCTION

2D materials have attracted interest in the field of material engineering due to their exceptional thermal and optical properties, as well as their large surface areas. Boron nitride, carbon nitride, mxene, and graphene are the most prominent 2D materials [1]. Several methods for synthesizing graphene include chemical vapor deposition, silicon carbide, micro-mechanical exfoliation, chemical reduction, and thermal annealing. Among these strategies, the chemical reduction method can be considered the most advantageous in terms of speed and cost-effectiveness [2]. The chemical reduction technique seeks to manufacture graphene oxide by expanding the interlayer spacing of graphite using chemical means. Graphene oxide, a hydrophilic material, can be synthesized by subjecting graphite to oxidizing chemicals. Graphene oxide is a carbon material that shares a similar structure to two-dimensional graphene. In its basal plane, graphene oxide is different from graphene because it has a small amount of carbonyls and carboxyls, as well as oxygen functional groups like epoxy and oxygen groups that are grouped together. However, to produce a significant quantity of graphene, it is more beneficial to use the graphite oxidation method to create graphite

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oxide. This may then be separated into graphene oxide (GO) and further reduced to give reduced graphene oxide (rGO) [3]. Graphene oxide manufacturing techniques are shown in Figure 1.

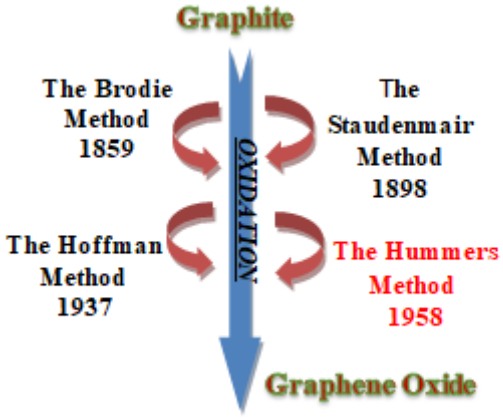


Figure 1. *Schematic representation of the synthesis of graphene oxide synthesis methods from graphite [3]*

The manufacture of graphene oxide has been in progress for around two centuries. In 1859, Brodie performed the inaugural inquiry in the literary field [4]. Brodie's study marked the initial utilization of HNO_3 and $KClO_3$ for oxidation. Furthermore, in 1898, Staudenmaier incorporated H_2SO_4 into the technique [5] as an enhancement to the oxidation mechanism, alongside the Brodie strategy. In 1958, Hummers and Offerman devised a novel methodology for synthesizing graphene oxide. The process of oxidizing graphite involves the use of oxidizers such as $NaNO_3$ and $KMnO_4$ [6]. The Hummers technique offers advantages when compared to the Brodie and Staudenmaier techniques. One of the substances used is $KMnO_4$, a highly effective oxidizing agent that accelerates the process, resulting in rapid completion. Furthermore, the detrimental impact of chlorate on the environment and the potential for explosion are eradicated [7]. Graphene oxide made using Hummer's approach is widely recognized to have a greater abundance of acidic groups compared to the Brodie and Staudenmaier method [8]. Through the modification of the Hummers method, alternative methods that are more ecologically sustainable have been devised. The Hummers tour method employed H_3PO_4 as a substitute for $NaNO_3$. Researchers have favored the employment of the Tour technique over the Hummers approach due to its absence of NOX gas emissions, greater environmental friendliness, and fewer flaws in the structure of graphene oxide [9]. The experimental design in this work used $NaNO_3$, H_3PO_4, and $Na_2B_4O_710H_2O$ to assess performance. $NaNO_3$ exhibits hazardous properties when used in the Hummers method. The ecologically friendly technique of the modified Hummers method involves the utilization of H_3PO_4. $Na_2B_4O_710H_2O$ is a naturally occurring, environmentally friendly substance. In this study, it was utilized for the first time in conjunction with the Hummers method. Various methodologies can be employed to fabricate graphene oxide. Figure 2 shows the oxidation proses for the Hummers method, which is used to make graphene oxide from graphite.

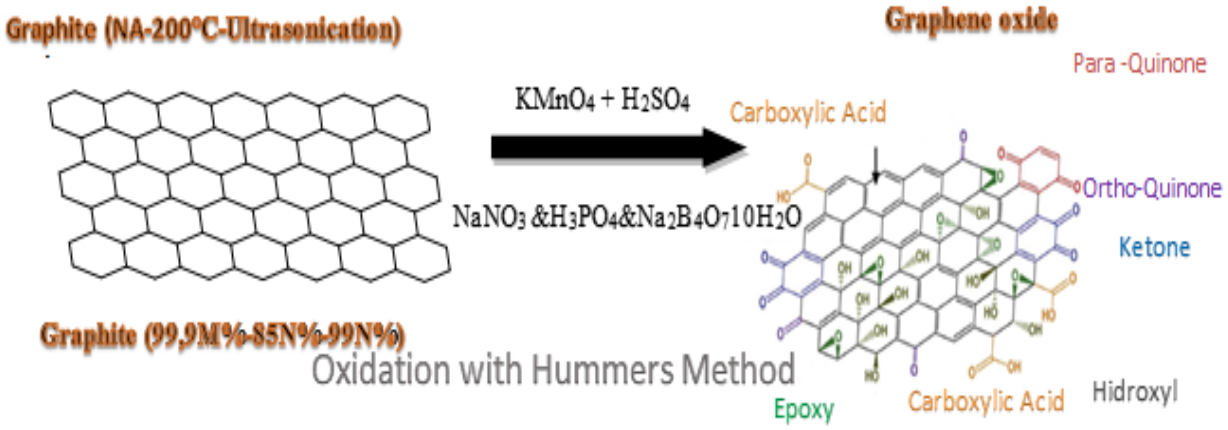


Figure 2. *Synthesis of graphene oxide layers from graphite layers by modified hummers method*

Graphene oxide (GO) is the result of the oxidation and exfoliation of graphite. Graphene oxide serves as a precursor and is utilized in the manufacturing of graphene. It contains oxygen-rich functional groups such as hydroxyl, epoxy, and carboxyl groups, which are suitable for chemical and physical modifications of the carbon structure. Graphene oxide is appealing as an absorbent substance because of its layered structure, large surface area, and straightforward production process. GO contains several oxygenated functional groups, such as hydroxyl, epoxy, carbonyl, and carboxylic acids. At temperatures between 80 and 100°C, the high concentration of oxygen in the structure breaks down into oxygen-containing groups and removes any water that is adsorbed [10-12]. This decomposition occurs even with mild heating. Graphene oxide has a wide range of applications, including electrocatalysis, biomedicine, separation membranes, sensors, energy conversion, and storage [13]. The Hummers method employs sodium nitrate as a substitute for H_3BO_3 in the production of graphene oxide. This procedure adopts an ecologically conscious approach by inhibiting the production of detrimental NO_2 and nitrogen tetroxide N_2O_4 gases. It was also found that the amount of structural flaws decreased while the level of oxidation increased in the graphene oxide samples developed. Utilizing boric acid in the Hummers procedure led to a 10% augmentation in the synthesis yield [14].

This study employed the TOPSIS-Based Taguchi Method to elucidate the synthesis of graphene oxide as a multi-response. The $L_9(3^3)$ experimental design model, which consists of three parameters and three levels, was utilized. The study focused on investigating the effects of different purity levels of graphite (99.99% Merck, 85% Nanokar, and 99% Nanokar) and pretreatments applied to the graphite prior to the reaction. Additionally, an auxiliary chemical was employed to enhance the oxidation performance of sulfuric acid. One of the auxiliary chemicals utilized is $Na_2B_4O_710H_2O$, which is a naturally occurring boron compound and is known for its environmentally favorable properties. Furthermore, no research has been conducted to substitute boron compounds for $NaNO_3$ and H_3PO_4 in the manufacture of graphene oxide and then analyze their impacts using a statistical methodology.

2. MATERIAL METHOD

This study applies the Taguchi-based TOPSIS technique to the characterisation of graphene oxide synthesis utilizing the $L_9(3^3)$ experimental design model and the modified Hummers method from graphite.

2.1. Graphene Oxide Synthesis Procedure

The synthesis of GO using the Modified Hummers Method is characterized by applying the parameters and levels specified in Table 2 to graphite samples of varying purity. This is done using the $L_9(3^3)$ experimental design model. Based on the experimental design, each experiment involves taking five grams of graphite samples (99.99% Merck, 85% Nanokar, and 99% Nanokar) for pre-treatment application. The pre-treatment options include no pre-processing, a pre-heating process at 200 ºC, or a pre-ultrasonication process.

Additionally, five grams of an auxiliary oxidant (sodium nitrate, phosphoric acid, or borax decahydrate) are also taken. For each experiment, volume of 125 ml of pure sulfuric acid is introduced into a double-walled glass reactor. The reaction temperature is regulated using a water circulator bath. The reaction temperature is held at 5 °C, and the mixture is stirred continuously for 1 hour. In order to maintain a robust oxidation process, potassium permanganate is incrementally introduced into the reactor. The reaction temperature is incrementally increased to 35°C, which is the beginning temperature, following the combination of the mixture using a magnetic mixer at 5°C for a duration of 16 hours. The addition of 300 mL of pure water to the solution results in an increase in reaction temperature to 98 °C due to the heat of hydration. At a temperature of 98 °C (the second level of temperature), the reaction is agitated using a magnetic stirrer for a duration of 4 hours. The addition of 200 mL of filtered water and 10 mL of hydrogen peroxide halts the oxidation process. The product is introduced into a 100-mL solution of hydrochloric acid at a concentration of 5% by volume in order to eliminate metal ions. The GO mixture is subjected to decantation until the pH reaches approximately 3–4. Subsequently, the substance is subjected to a drying process in an oven at a temperature of 50 °C.

2.2. Proposed Methodology

Utilizing experimental design techniques such as the Taguchi method rather than random experiments not only reduces costs by minimizing the number of required experiments but also allows for statistical interpretation of the obtained results. The tool can help you find the best mix of Taguchi method factor levels and look at how different factors affect things by using orthogonal sequences. The formula $L_x(y^z)$ represents an orthogonal sequence, where x is the number of combinations of factors used in the experiment, b represents the number of levels for the factors, and z indicates the overall number of factors utilized. The orthogonal experimental design matrix employed in the Taguchi technique enables a decrease in the number of experiments as compared to the full experimental design [15].

The Taguchi technique utilizes the signal-to-noise ratio (S/N) to detect quality parameters that deviate from the desired value. These attributes are typically categorized as smaller, which should be minimized Equation (1), larger, which should be maximized Equation (2), where the goal value should be kept at its best. By utilizing master effect graphs and signal-to-noise ratio graphs, one may efficiently analyze the impact of factors on quality attributes. Using signal-to-noise ratio graphs and major impact graphs makes it possible to study how factors affect quality features in a useful way [16].

The objectives are established to align with a mathematical concept referred to as the Taguchi loss function, which is also commonly known as the signal-to-noise ratio (S/N). The formulae provided in reference [17] are utilized to assess S/N ratios, taking into consideration the conflicting viewpoints that favor both the smallest and greatest values as the optimal choice

when the smallest (lowest) option is best;

$$SN_S = -10Log\left(\frac{1}{n}\sum_{n=1}^{n} y_i^{\,2}\right), \tag{1}$$

when the largest(highest) option is best;

$$SN_L = -10Log\left(\frac{1}{n}\sum_{n=1}^{n} \frac{1}{y_i^{\,2}}\right). \tag{2}$$

In the equations yi: Belonging to experiments i. the result value of the experiment, n: The number of repetitions in the experiments, and: The average of the experimental result [18].

The TOPSIS approach requires determining the deviation values of the decision points in order to establish the sets of deviations from the ideal and negative ideal solutions. The values are represented as the positive ideal difference Equation (3) and the negative ideal variable Equation (4). It will be calculated and the number will naturally be the same as the number of outputs in the experiment's design

$$S_i^* = \sqrt{\sum_{j=1}^{n} (v_{ij} - v_j^*)^2} \tag{3}$$

$$S_i^- = \sqrt{\sum_{j=1}^{n} (v_{ij} - v_j^-)^2} \tag{4}$$

.

The relative distance Equation (5) between the point of determination and the ideal solution is calculated using both ideal and negative ideal differential measurements. This refers to the ratio of the negative ideal measure of separation to the total measure. The formula below is used to calculate the value of the distance relative to the ideal solution. C_i^* takes the value between $0 \le C_i^* \le 1$

$$C_i^* = \frac{S_i^-}{S_i^- + S_i^*} \tag{5}$$

.

For each design analyzed by the TOPSIS method, the ideal resolution distance (C_i^*) is analyzed in the greatest, best way according to the Taguchi method. As a result of the analysis, the optimum conditions for the levels of the parameters are determined based on the results of multiple criteria [19-21].

2.3. Determination of Quality Criteria on $L_9(3^3)$ GO Synthesis

A certain set of quality characteristics is selected for the production of graphene oxide (GO). Optimization studies have been done based on the results of these selected criteria. The D peak at 1350 cm^{-1} in the Raman analysis and the G peak at 1585 cm^{-1} in the G peak serve as the first quality criterion. The elevated D/G peak ratio suggests that an increase in imbalance is to blame for the decrease in the number of layers. Therefore, it is more desirable for the structural defect to be minimal, as a lower intensity of the D/G signal is suitable for the synthesis of GO. Raman spectroscopy analyses using Thermo XDR have been conducted at the Central Research Laboratory of Namık Kemal University. The X-ray Diffraction Pattern (XRD), which is the second criterion for quality assessment, requires a small value for the calculated crystal size. It is evident that the crystal size decreases as the number of layers in the regular plates decreases. X-ray diffraction (XRD) investigations have been conducted at the DAYTAM Central Research Laboratory of Ataturk University, utilizing Empyrean equipment. The third quality criterion is determined through the utilization of scanning electron microscopy and the Energy Dispersive X-Ray Analysis Method (SEM-EDX) to detect the extent of oxidation in the atomic ratio of carbon to oxygen (C/O). Because severe oxidation is necessary for GO, this ratio must be low. The Namik Kemal University Central Research Laboratory employed a Quanta Feg 250 instrument for conducting SEM-EDX investigations. Zeta Potential-Sizer was utilized to measure the fourth and fifth quality criteria. The objective of characterizing GO is to achieve moderate potential values for particle size and zeta potential. The surface area of the GO has been quantified using the BET instrument, and it is considered the sixth quality criteria. The GO's surface area values are intended to be maximized. The Chemical Engineering Research Laboratory at Cankırı Karatekin University has performed BET surface area and Zeta Potential-Sizer analyses using by Quactachrome Nova Touch LX4 and the Malvern Nano-ZS instruments. Explanations for the quality criterias are given above related to the optimization study are provided in Table 1.

Table 1. *Determined quality standards and weights*

Quality Criteria	Symbol	Explanation	Information	The goal for GO	Weighted for TOPSIS-GO	Normalized Weight for TOPSIS-GO
1	ID/IG	The Ratio of the D Peak to the Intensity of the G Peak	Defective in structure	Smaller is better	1	0,167
2	CS	Crystal size (nm)	Disordered carbon materials	Smaller is better	1	0,167
3	C/O	Carbon-Oxygen Ratio	Degree of oxidation	Smaller is better	1	0,167
4	PS	Particle Size	Feature improvement	Larger is better	1	0,167
5	ZP	Zeta Potential	Stable distribution	Smaller is better	1	0,167
6	BET	Surface Area	Degree of porosity	Larger is better	1	0,167
Total					6	1

2.4. Identification of Factors and Their Levels

The components of the graphite structure used in the experimental synthesis of L_9 (3^3) graphene oxide are provided in Table 2. Table 3 displays the specific information regarding the parameters and levels of the L_9 (3^3) experimental design used in the synthesis of graphene oxide. Table 3 displays the effects of graphite pretreatment on the experiment, with column A indicating the specific details. Column B shows the use of several graphite samples with different levels of purity, while column C indicates the chosen auxiliary oxidants used to examine the impact on the quality criteria of graphene oxide production. The experimental design includes both coded and non-coded stages, which are presented in Table 4.

Table 2. *The Purity of graphite used in experiments*

Material	Graphite Grade	Brand	Fly Ash Content %
Graphite	99,99 M %	MERCK	<0,01%
	85 N %	Nanokar Nanotechnology	<15%
	99 N %	Nanokar Nanotechnology	<1%

Table 3. *Parameters and levels of GO synthesized from graphite by the Hummers Method*

	Symbol	Parameters	Levels		
			1	**2**	**3**
Synthesis of Graph	A	Graphite pretreatment	No Pre-Processing	3 hours heat treatment at 200℃	ultrasonic sonication 10 minutes

	B	Graphite purity	99,99 M %	85 N %	99 N %
	C	Auxiliary oxidant	Sodium Nitrate	Ortho-phosphoric Acid	Borax Decahydrate

Table 4. *Experimental design model and uncoded levels of the GO synthesis*

Experiment No.	**Coded Levels**			**Uncoded Levels**		
	A	**B**	**C**	**A**	**B**	**C**
GO1	1	1	1	no pre-processing	99,99M %	Sodium Nitrate
GO2	1	2	2	no pre-processing	85N%	Orthophosphoric Acid
GO3	1	3	3	no pre-processing	99N%	Borax Decahydrate
GO4	2	1	2	3 hours pre-heating 200℃	99,99 M %	Orthophosphoric Acid
GO5	2	2	3	3 hours pre-heating 200℃	85N%	Borax Decahydrate
GO6	2	3	1	3 hours pre-heating 200℃	99N%	Sodium Nitrate
GO7	3	1	3	ultrasonic sonication	99,99M%	Borax Decahydrate
GO8	3	2	1	ultrasonic sonication	85N%	Sodium Nitrate
GO9	3	3	2	ultrasonic sonication	99N%	Orthophosphoric Acid

3. THE RESULTS OF THE RESEARCH AND SUBSEQUENT DISCUSSION

The experimental design models for synthesizing L_9 (3^3) graphene oxide are utilized for the first time to analyze the graphs and pictures representing the quality criteria. This analysis aims to ascertain the recovery rates during the initial phase of the investigation.

3.1. Analysis of Graphs and Images Depicting the GO Synthesis

This section of the study examines the impact of graphite with varying levels of purity (99.99% Merck, 85%, and 99% Nanokar) on the synthesis of graphene oxide (GO) using an experimental design known as L_9 (3^3) in the initial stage. Specifically, it investigates the effects of different pretreatment methods for the graphite (no pre-processing, pre-heating at 200ºC, and pre-ultrasonication), as well as the influence of auxiliary oxidants ($NaNO_3$, H_3PO_4, $Na_2B_4O_7 10H_2O$). The findings are analyzed and interpreted.

3.1.1. Results obtained from the assessment of quality criteria

This component of the research focuses on evaluating the quality criteria of the experiments conducted in the design of the L_9 (3^3) experiment. Figure 3 presents FTIR graphs depicting graphite samples with varying levels of purity.

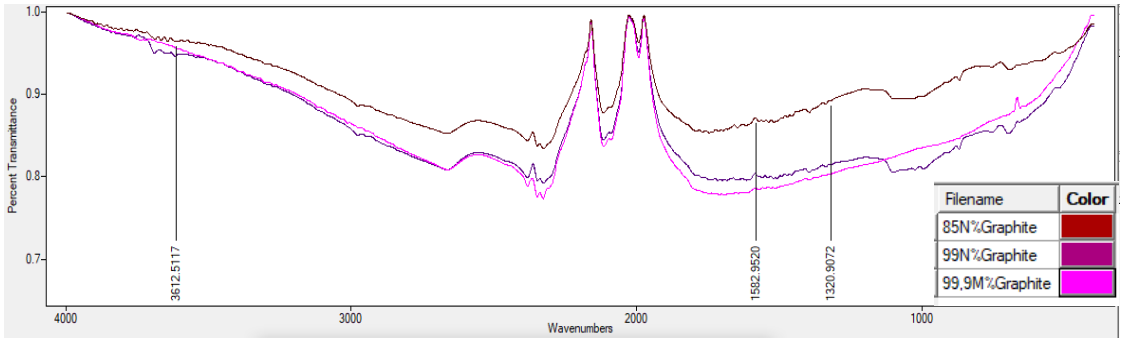


Figure 3. *$L_9(3^3)$ FTIR images of graphites used in GO experimental design*

The FTIR-ATR scanning of graphite from Merck company, which has a purity of 99.99%, has a higher level of regularity compared to other samples. The FTIR-ATR scans of graphite samples from Nanocarbon Nanotechnology company, with purities of 85% and 99% exhibit significant similarities.

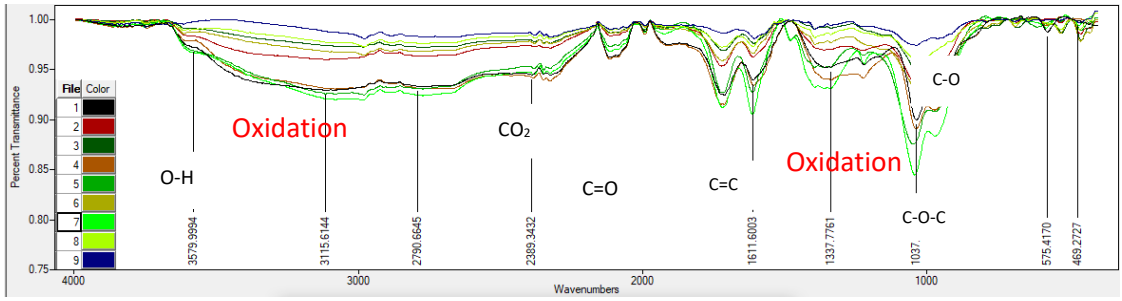


Figure 4. *$L_9(3^3)$ FTIR images of samples of synthesized graphene oxide produced in accordance with the GO experimental design order*

The experimental design for L_9 (3^3) is presented in the initial section of the paper. Figure 4 displays the outcomes of the FTIR-ATR analysis conducted on graphene oxide samples synthesized following the graphite structure's pattern that lacks the carbonyl bond (C=O) at 1721cm^{-1}. The analysis reveals the presence of O-H deformation vibration and groups of peaks at 3115 cm^{-1} and 1410 cm^{-1}, as well as peaks corresponding to the epoxy bond (C-O) at 1221 cm^{-1} and 1046 cm^{-1}. Additionally, an aromatic bond (C=C) peak ranging from 1680 to 1620 cm^{-1} is observed. Examination of the FTIR analysis results demonstrates that oxygen-containing functional groups have been introduced to the structure of graphite and that graphene oxide has successfully been produced from graphite. The L_9 (3^3) experimental setup was used to create Raman scans of graphene oxide samples, as depicted in Figure 5.

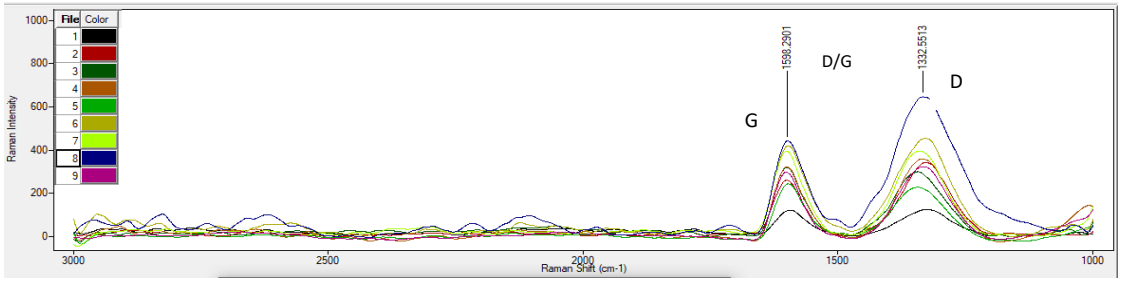


Figure 5. *$L_9(3^3)$ Raman images of samples of synthesized graphene oxide produced in accordance with the GO experimental design order*

Raman spectroscopy detects two distinct peaks. The G peak (1593 cm^{-1}) is observed in all sp^2 hybridized carbonate networks. This peak is caused by the dispersion of sp^2 carbon pairs in the chain due to bond tension. The presence of oxygen functional groups on the carbon's basal plane causes a structural defect, resulting in the appearance of peak D (1357 cm^{-1}) in the spectrum. The X-ray diffraction (XRD) scans of graphene oxide samples produced using the L_9 (3^3) experimental setup are depicted in Figure 6.

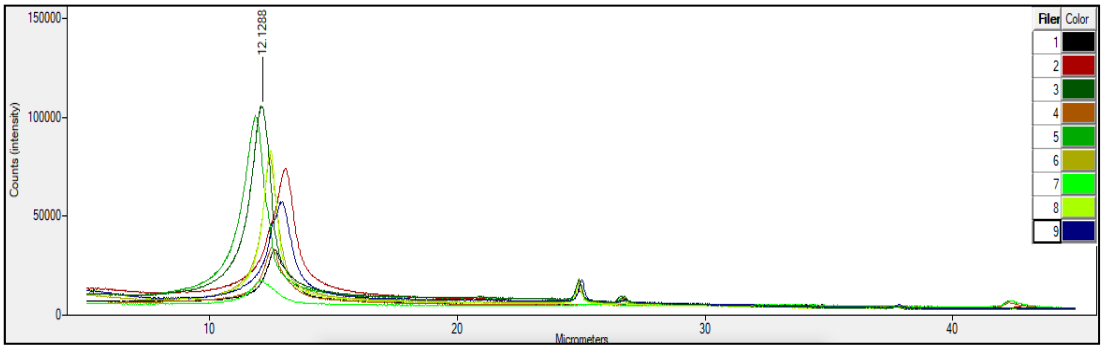


Figure 6. *$L_9(3^3)$ XRD images of samples of synthesized graphene oxide produced in accordance with the GO experimental design order*

The X-ray diffraction (XRD) pattern of graphite has a prominent peak at an angle of 26° (2θ) from its plane, namely in the (002) direction. The structure of graphite undergoes a complete transformation into graphene oxide, resulting in the disappearance of the peak at 2θ =26° and the emergence of a lower peak around 2θ =9-13°. This change occurs due to the presence of functional groups containing oxygen during the oxidation process. This steep peak indicates the increasing distance between the graphite layers. The identification of the formation of oxygenated functional groups on graphite layers during the synthesis of graphene oxide from graphite is of great importance.

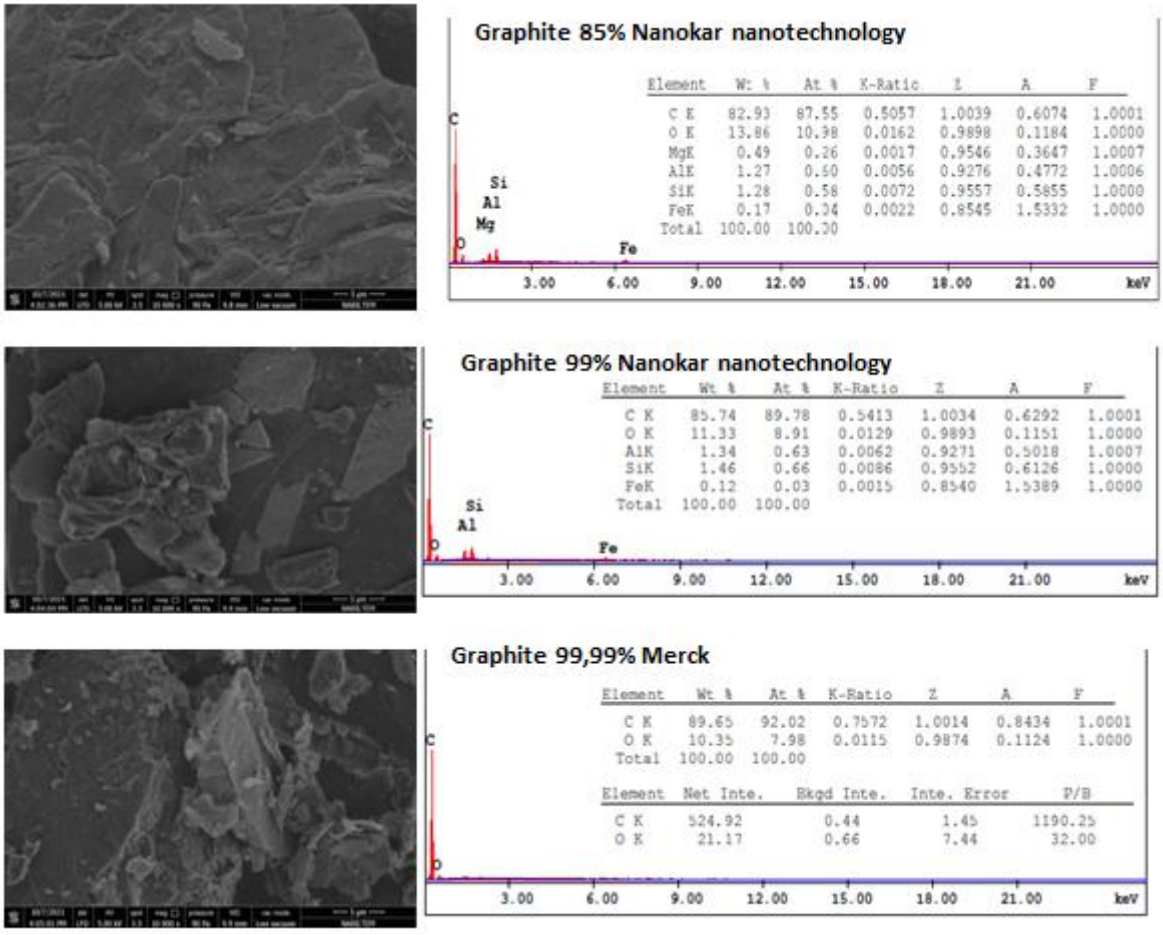
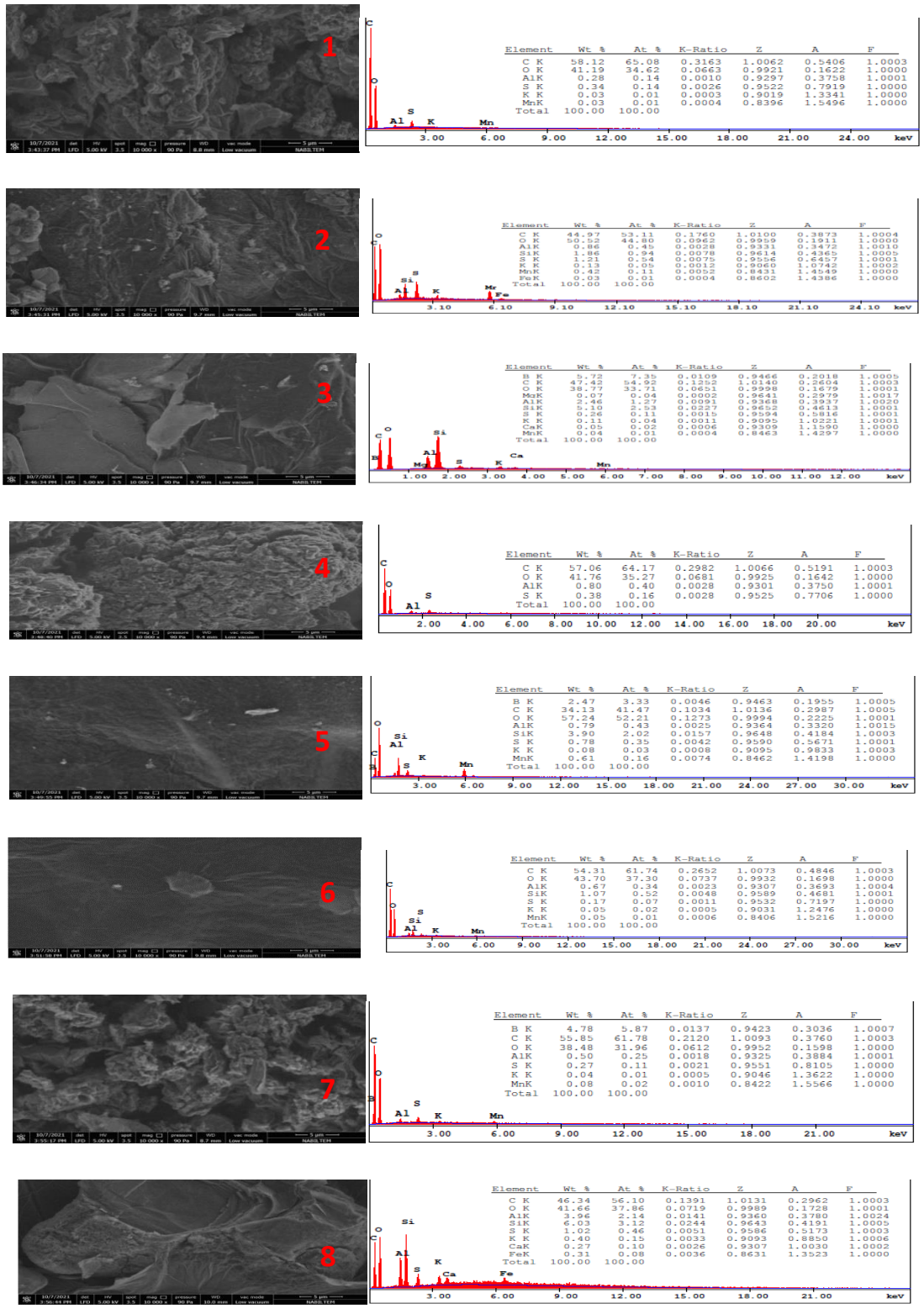


Figure 7. *SEM+EDX images of graphites used in $L_9(3^3)$ graphene oxide experiment design*

Figure 7 displays scanning electron microscopy (SEM) images along with energy-dispersive X-ray spectroscopy (EDX) images of graphite samples with varying levels of purity. These samples are among the factors investigated in the experimental design. Upon examination of the SEM+EDX images of graphene oxide synthesis in Figure 7, it is evident that they are consistent with the SEM+EDX photographs reported by other researchers.



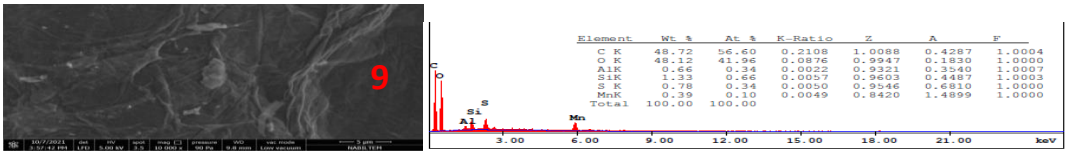


Figure 8. *$L_9(3^3)$SEM+EDX images of graphene oxide samples synthesized according to the experimental design order*

The results of the EDX research are presented in Figure 8. Following oxidation, the C:O ratios decrease from approximately 10 to around 1.9-0.79. The decrease in the C/O ratio can be linked to the formation of additional functional groups that are bonded to carbon. The results indicate that the Hummers approach effectively synthesized graphene oxide from graphite, aligning with previous research findings. The SEM images provide clear evidence of the structural damage to the smooth graphite due to oxidation. The chemical transformation of the structure can be examined by analyzing the EDX results of both graphite and produced graphene oxide, in addition to SEM photographs.

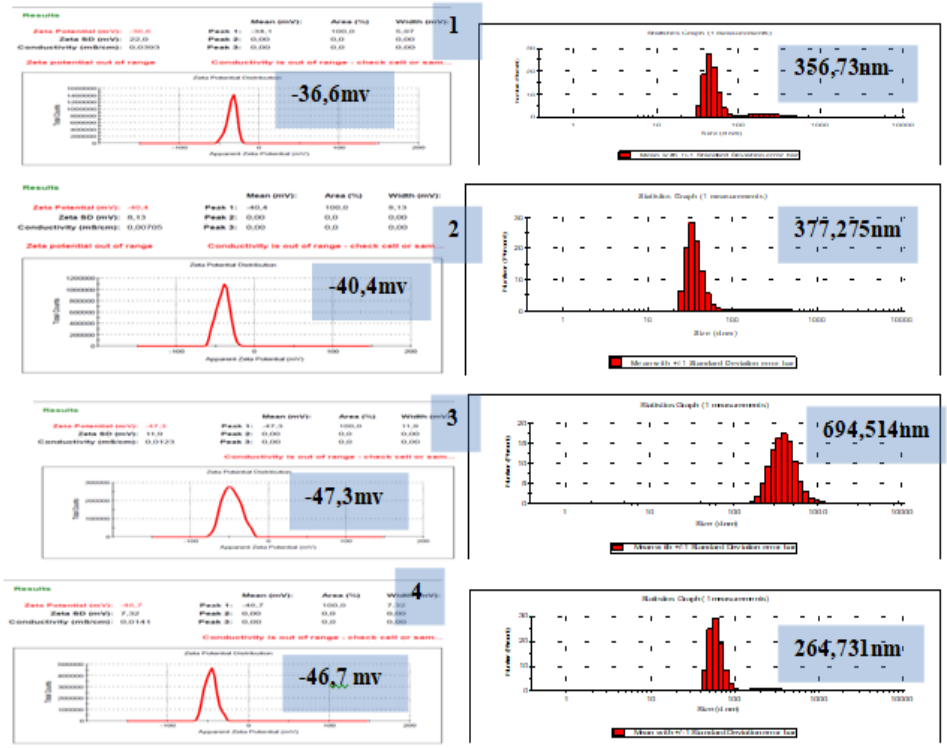


Figure 9. *Results of graphene oxide samples manufactured in accordance with the $L_9(3^3)$ experimental design order in terms of zeta potential and average particle size (Exp1-4)*

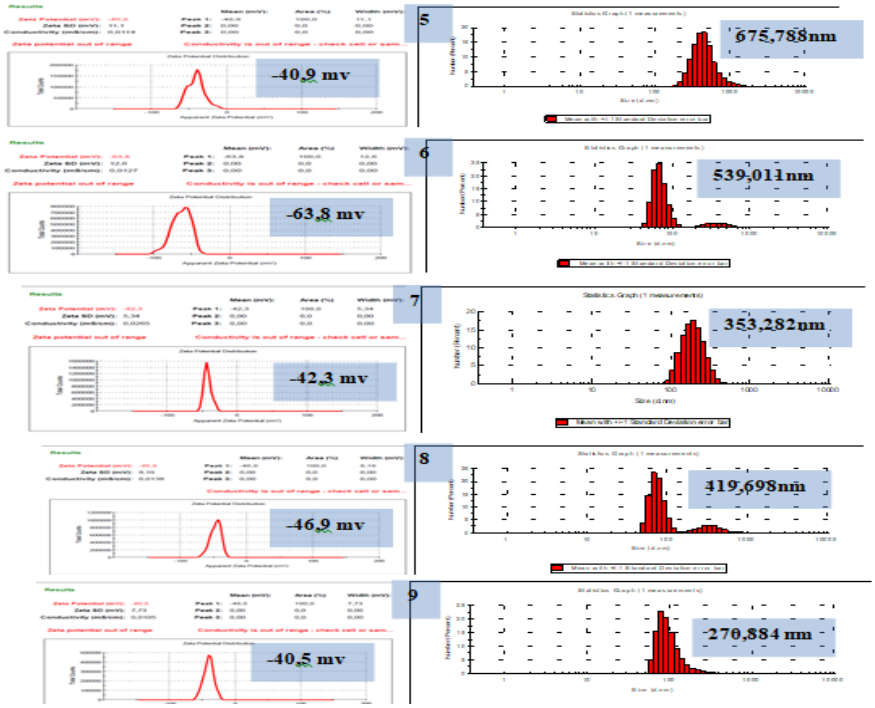
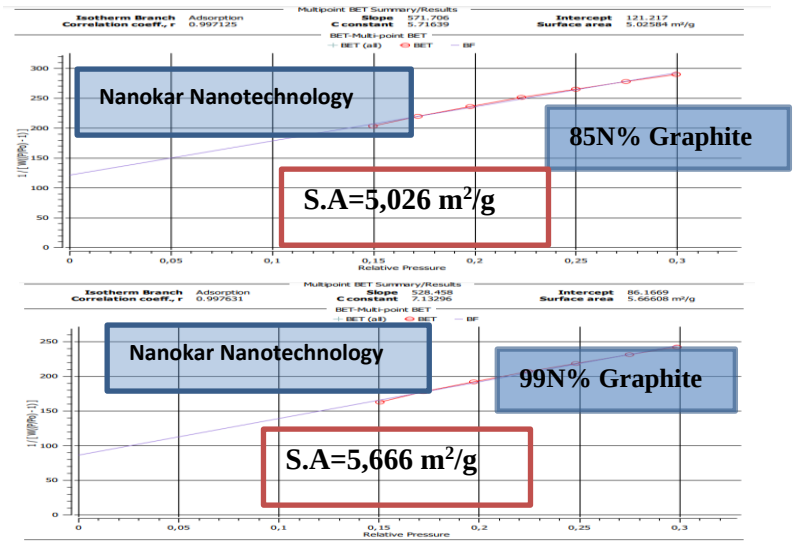


Figure 10. *Results of graphene oxide samples manufactured in accordance with the $L_9(3^3)$ experimental design order in terms of zeta potential and average particle size (Exp 5-9)*

The findings of Zeta potential measurements and particle size distribution analysis are presented in Figures 9 and 10. The experimental setup yielded Zeta Potential values for Graphene oxide ranging from -36.6 to -63.8 mV. The particle size results obtained range from approximately 270,880 to 694,514 nm. Regarding Table 6, the average particle size data indicate that the majority of particles are larger than 100nm. However, the particle size distribution study of graphene oxide reveals the presence of particles that are smaller than 100 nm as well [22]. These findings indicate that the majority of the samples include nanoparticles.



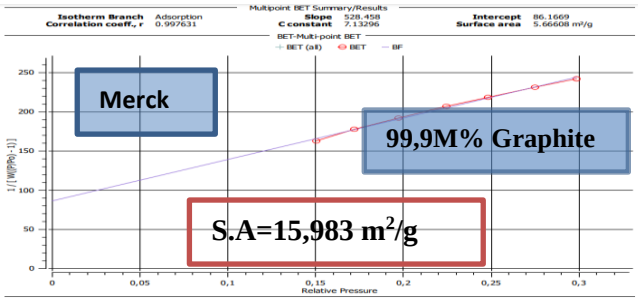
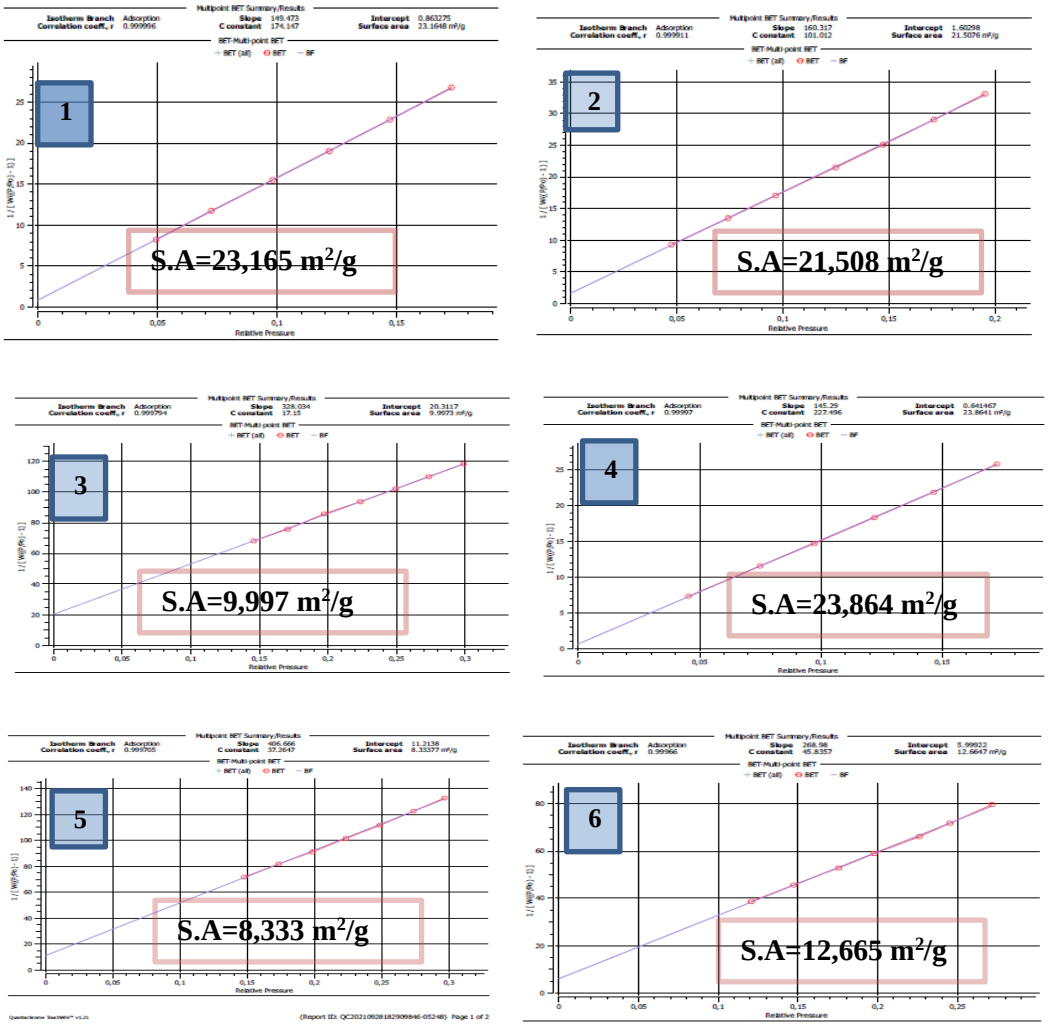


Figure 11. *BET-Surface Area results of graphites used in $L_9(3^3)$ graphene oxide experiment design*

Figure 11 displays BET analysis graphs of graphite samples with varying purities, which is one of the characteristics examined in the experimental design. The surface area of Merck's graphite BET, with a purity of 99.99%, is 15.98 m^2/g. This value corresponds to the first level in the experimental design. The BET surface area measurement of graphite samples from Nanocarbon Nanotechnology with purities of 85% and 99% is approximately 5.03-5.67 m^2/g, respectively. The variation in the surface areas of the items from two distinct firms can be attributed to the presence of contaminants and the manufacturing process employed. BET analysis of samples of graphene oxide produced in accordance with $L_9(3^3)$ the experimental design order in Figure 12. The experimental design yielded values ranging from 8.33 m^2/g to 27.02 m^2/g.



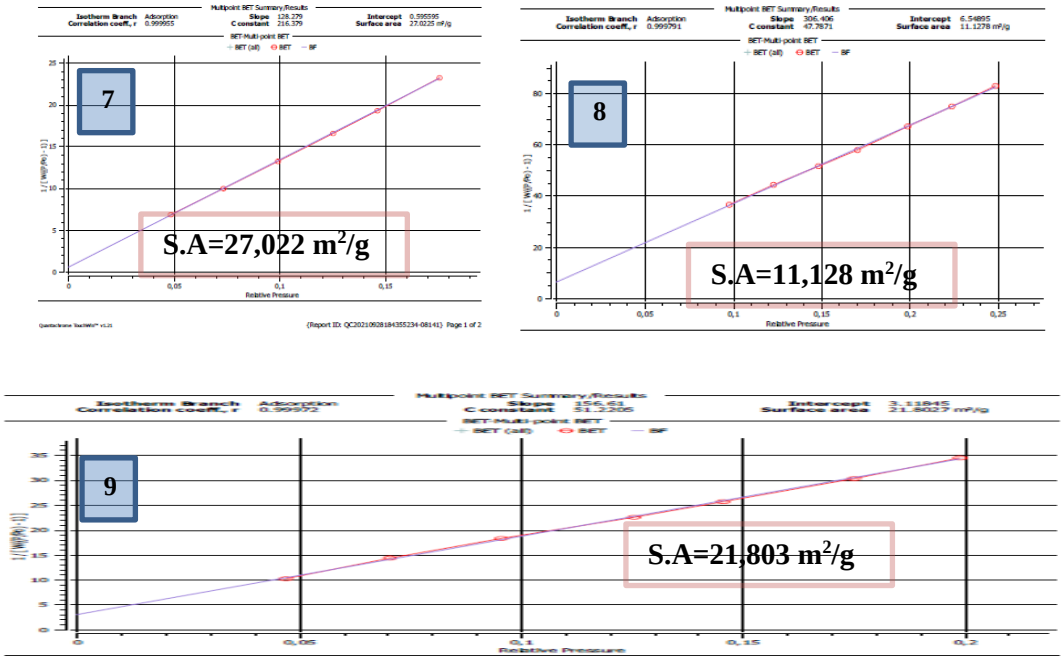


Figure 12. *The findings of the BET analysis of samples of graphene oxide produced in accordance with $L_9(3^3)$ the experimental design order*

4. RESULTS

Table 5 lists the outcomes of multiple tests on the quality standards for the synthesis of L_9 (3^3) graphene oxide in this study. The numbers for D/G in Raman analysis, SA(m^2/g) for surface area in BET analysis, Cs-nm for crystal size in XRD analysis, C/O for C/O ratio in SEM+EDX analysis, A for average particle size, and ZETA for zeta potential measurement are repeatedly presented. The average of these quality criterion's experimental findings is shown in Table 6.

Table 5. *Results of the repeated quality criterion for the samples of GO synthesis in $L_9(3^3)$*

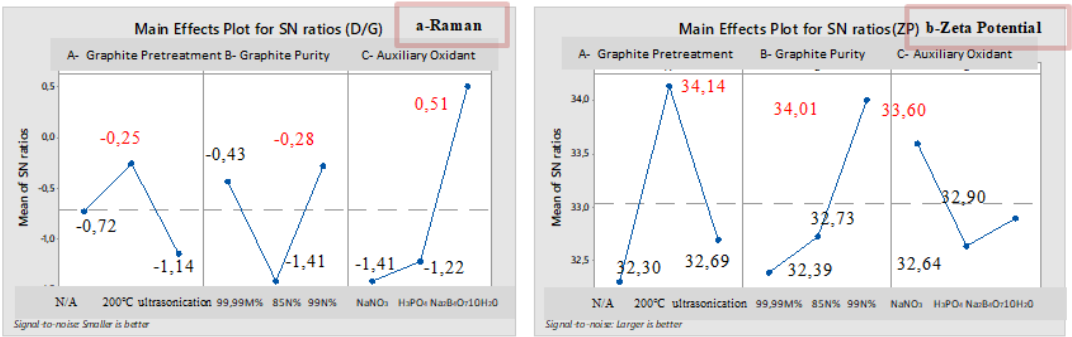
Deney No	ID/IG (Raman)		Zeta Potentail (ZETA-mv)		Particle Size (ZETA-nm)		Surface Area (SA, m^2/g) (BET)		Crystal Size (CS-nm) (XRD)		C/O (Sem+Edax)	
	Serial 1	Serial 2	Serial 1	Serial 2	Serial 1	Serial 2	Serial 1	Serial 2	Serial 1	Serial 2	Serial 1	Serial 2
GO1	1,02	1,11	-36,6	-36,2	380	356,2	23,16	24,11	138,7	140,2	1,88	1,90
GO2	1,31	1,28	-40,4	-40	362,3	377,3	21,51	21,61	138,8	140,3	1,18	1,23
GO3	0,94	0,92	-47,3	-48,3	657,9	527,8	9,99	9,95	118,1	119,3	1,63	1,59
GO4	1,11	1,08	-46,7	-48,5	264,7	257,5	23,86	24,17	118,1	119,4	1,82	1,76
GO5	0,86	0,95	-40,9	-45,8	675,8	669,8	8,34	9,03	109,9	111	0,79	0,89
GO6	1,10	1,10	-64,9	-63,8	549,2	539	12,67	11,23	187,8	189,8	1,65	1,74
GO7	1,00	0,99	-42,3	-41,1	395,7	396,4	27,02	26,61	102,8	103,9	1,82	1,86
GO8	1,46	1,31	-46,9	-46,7	413,8	419,7	11,13	13,25	213	215,3	1,48	1,39
GO9	1,09	1,06	-40,5	-41,7	270,9	270,1	21,80	22,33	110	111,2	1,35	1,32

Table 6. *The average values of the GO synthesis experiment results*

Exp No	ID/IG (Raman)	Zeta Potentail (ZETA-mv)	Particle Size (ZETA-nm)	Surface Area (SA, m^2/g) (BET)	Crystal Size (CS-nm) (XRD)	C/O (Sem+Edax)
	The Series Average	The Series Average	The Series Average	The Series Average	The Series Average	The Series Average
GO1	1,07	-36,4	368,1	23,63	139,45	1,89
GO2	1,30	-40,2	369,8	21,56	139,55	1,21
GO3	0,93	-47,8	592,85	9,97	118,7	1,61
GO4	1,10	-47,6	261,1	24,01	118,75	1,79
GO5	0,90	-43,4	672,8	8,68	110,45	0,84
GO6	1,10	-64,4	544,1	11,95	188,8	1,70
GO7	0,99	-41,7	396,05	26,82	103,35	1,95
GO8	1,38	-46,8	416,75	12,19	214,15	1,44
GO9	1,08	-41,1	270,5	22,06	110,6	1,33

4.1. Determination of Optimum Points in GO Synthesis by Taguchi Method

The data obtained from the L_9 (3^3) Graphene oxide experimental design in Table 2 is subjected to analysis using the Taguchi method. The target values specified in Table 1 for the quality criteria are calculated using Equations (1) and (2) in the minitab application. The optimal points corresponding to the criteria were obtained and are presented in Figure 13. The figure provides the ideal settings for Taguchi analysis of single-response quality criteria for specific parameters. Figure 13a examines the D/G results in Raman analyses. The most favorable outcomes are observed when preheating is conducted at 200 °C, which corresponds to the second level of the graphite pretreatment application parameter. Nanocarbon Nanotechnology received a product with a graphite purity of 99%, which corresponds to the third level of purity. The best outcome for the auxiliary oxidant selection parameter was obtained with borax decahydrate, which is in the third level. The results demonstrated that the application of ultrasonication to the graphite enhanced the influence on the structural fault, while it had a diminished effect on the preheating process. The D/G values decrease significantly when high purity graphites are utilized, resulting in the optimal outcome. Specifically, the third level of graphite purity achieved by Nanocarbon Nanotechnology, with a purity of 99%, yields the optimum result. Regarding the auxiliary oxidant parameter, borax decahydrate yielded the most optimal outcome. Phosphoric acid outperformed sodium nitrate. Upon analyzing the Zeta potential data depicted in Figure 13b, it was observed that the most favorable outcomes were obtained when the graphite was preheated to a temperature of 200 °C, corresponding to the second level of pretreatment. Additionally, the utilization of Nanocarbon Nanotechnology, which represented the third level of graphite purity, resulted in a product with a purity of 99%. The auxiliary oxidant, sodium nitrate the most favorable outcome.



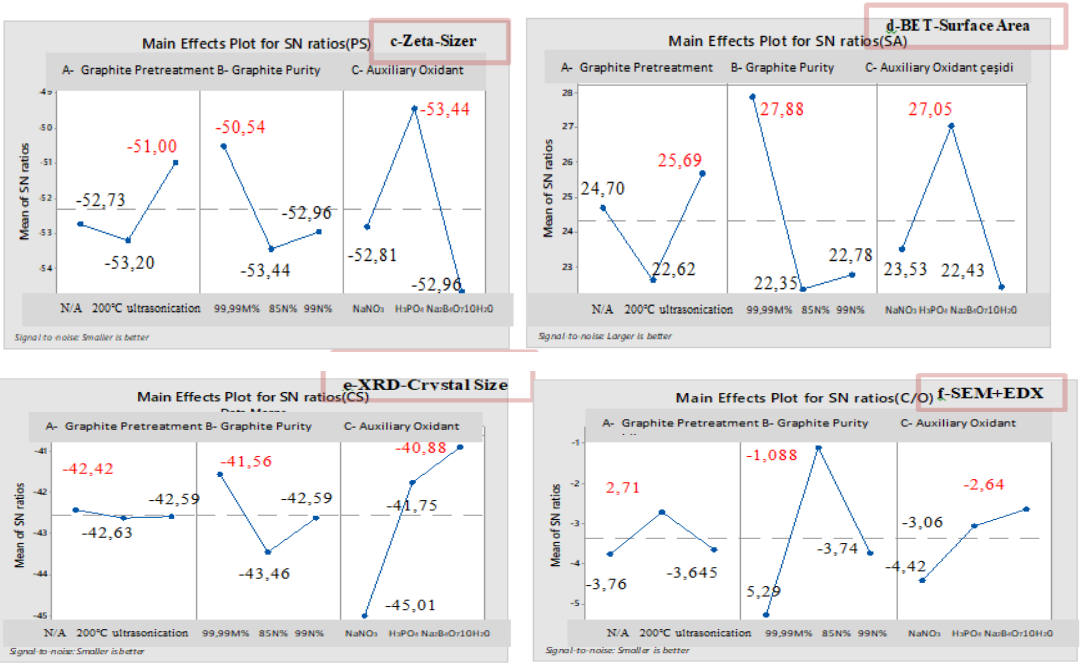


Figure 13. *$L_9(3^3)$ Main effect graphs of S/N values obtained by the Taguchi method in a single response for the experimental design of graphene oxide synthesis*

The results demonstrated that subjecting graphite to ultrasonication enhanced the dispersion qualities of the product by increasing its zeta potential. Conversely, the preheating process had a diminishing effect. The zeta potential performance of the nanocarbon Nanotechnology graphite samples surpassed that of Merck. Sodium nitrate proved to be the most effective supplemental oxidant. Experimental observations revealed that samples in the experimental design containing sodium nitrate had a greater propensity to suspend. The superiority of borax decahydrate over phosphoric acid in terms of performance was acknowledged. The evaluation of Figures 13c and 13d is conducted jointly due to their shared resemblance in attributes. The ultrasonication procedure, as the third step in graphite pretreatment, significantly enhances the particle size and surface area of the Nanocarbon Nanotechnology product. This process also ensures an exceptional purity level of 99%, which is the most attainable for graphite. The auxiliary oxidant has yielded the most favorable outcome with ortho-phosphoric acid at the second level. The results indicated that the application of ultrasonication to graphite had a beneficial impact on particle size and surface area, resulting in a reduction in particle size and an increase in surface area. Conversely, the preheating process had an adverse effect on both of these parameters. The graphite samples from Merck exhibit superior particle size and surface area values compared to those of the Nanocarbon Nanotechnology company. Ortho-phosphoric acid yields the most optimal outcome from the perspective of the auxiliary oxidant. Observations show that the impact of borax decahydrate on both particle size and surface area is the same as the effect of sodium nitrate.

The crystal size measurements of Figure 13e indicate that there is no discernible activity in the pretreatments given to graphite. Merck brand graphite offers the highest level of purity, with a purity rating of 99.9%, which is the best level. The most optimal outcome for the supplementary oxidant was borax decahydrate, which ranked as the third level, closely followed by ortho-phosphoric acid. The findings demonstrated a positive correlation between the purity of graphite samples in Nanocarbon Nanotechnology and the resulting crystal size values, indicating that higher purity led to improved crystal size. The auxiliary oxidant shows that borax decahydrate exhibited significantly superior performance compared to ortho-phosphoric acid and sodium nitrate.

Upon analyzing the EDX findings presented in Figure 13f, it was observed that the Nanocarbon Nanotechnology product exhibited optimal results at a temperature of 200 °C, which corresponds to the second level of graphite pretreatment. Additionally, the graphite purity level was measured at 85%, also corresponding to the second level. The auxiliary oxidant yielded the most favorable outcome when using

borax decahydrate. The results demonstrated that the preheating method had a beneficial impact on the oxidization capacity of graphite. The oxidation capacity of nanocarbon graphite samples in the field of nanotechnology surpasses that of Merck. The auxiliary oxidant, borax decahydrate exhibited superior performance compared to ortho-phosphoric acid and sodium nitrate.

4.2. The TOPSIS-Based Taguchi Method of GO Synthesis

As a consequence of the experiments, the Taguchi Method is used to determine the average results of the quality criteria in the synthesis of graphene oxide, the S/N ratios, and the multiple response quality criteria are transformed into a single response using the TOPSIS Method. The normalized weights from Table 1 were used to build the decision matrices in Table 7.

Table 7. *GO synthesis studies employing the TOPSIS Method and S/N ratios for weighted application*

	Karar Matrisi (S/N Oranları)							**Ağırlıkça Normalize Edilmiş Karar Matrısı**						**S_i^***	**S_i^-**	**C_i^***
Yanıtlar	*D/G*	*ZP*	*PS*	*SA*	*CS*	*C/O*										
Ağırlıklar	***0,167***	***0,167***	***0,167***	***0,167***	***0,167***	***0,167***		v_{i1}	v_{i2}	v_{i3}	v_{i4}	v_{i5}	v_{i6}			
GO1	0,06	0,28	16,83	0,67	1,06	0,01		**0,07[b]**	0,01	0,03	0,05	0,05	0,02	**0,22[c]**	**0,09[d]**	**0,29[e]**
GO2	0,02	0,28	10,61	0,07	1,06	0,04		0,02	0,01	0,02	0,01	0,05	0,04	0,25	0,04	0,13
GO3	0,01	0,71	91,99	0,03	0,85	0,03		0,02	0,03	0,16	0,00	0,04	0,03	0,21	0,16	0,44
GO4	0,02	1,27	5,09	0,22	0,92	0,04		0,02	0,05	0,01	0,02	0,05	0,05	0,23	0,06	0,21
GO5	0,06	3,46	4,24	0,49	0,78	0,07		0,07	0,14	0,01	0,04	0,04	0,09	0,19	0,17	0,48
GO6	0,01	0,78	7,21	1,02	1,41	0,06		0,01	0,03	0,01	0,08	0,07	0,08	0,22	0,11	0,33
GO7	0,01	0,85	0,49	0,29	0,78	0,03		0,01	0,04	0,00	0,02	0,04	0,03	0,25	0,04	0,14
GO8	0,11	0,14	4,17	1,50	1,63	0,06		0,12	0,01	0,01	0,12	0,08	0,08	0,21	0,18	0,47
GO9	0,02	0,85	0,57	0,37	0,85	0,02		0,02	0,04	0,00	0,03	0,04	0,03	0,25	0,04	0,15
	0,14[a]	4,04	94,72	2,06	3,22	0,14	*A** =	0,12	0,14	0,16	0,12	0,08	0,09			
							A- =	0,01	0,01	0,00	0,00	0,04	0,02			

[a] *The square root of the sum of the squares of each value in the columns*
[b] *[ref 20] : 0,167*[(0,06)/(0,14)]=0,07;*
[c] *[ref 20]: {[(0,07)-(0,012)]^2+ ……+ [(0,02)-(0,09)]^2}$^{1/2}$=0,022*
[d] *[ref 20]: {[(0,07)-(0,01)]^2……+ [(0,02)-(0,02)]^2}$^{1/2}$=0,09*
[e] *[ref 20] : 0,09/(0,22+0,09)=0,29*

The Ci* values, which are generated based on the normalized data, are determined using the Taguchi Method, where the highest value is considered the most desirable. The graphs in Figure 14 display the signal-to-noise ratios of the parameters. The optimal points of the parameters in these graphs are calculated by assigning equal importance to the criterion. The optimal conditions for pretreatment of a graphite sample with 85% purity using Nanocarbon Nanotechnology involve preheating at 200℃. Additionally for auxiliary oxidant, sodium nitrate and borax decahydrate are shown nearly same effective factors.

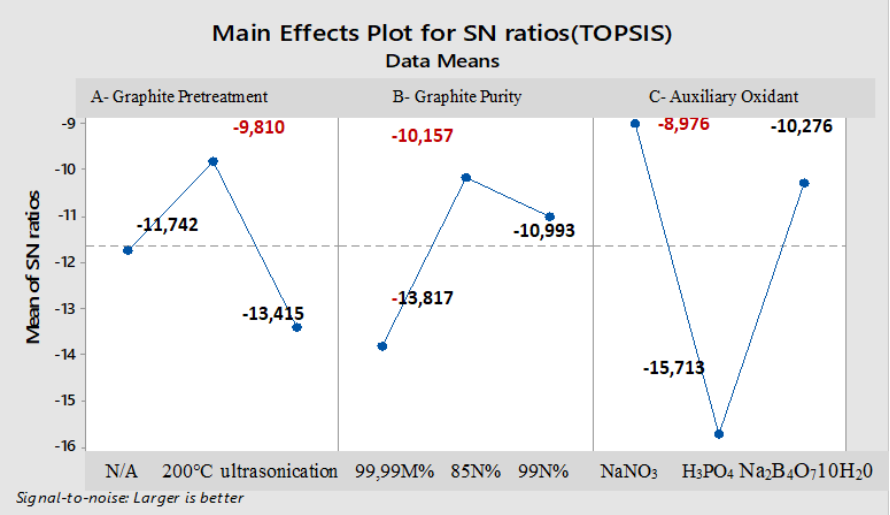


Figure 14. *The main effect graphs of the mean values obtained by using the weight normalized values by the TOPSIS Method for GO synthesis experiments*

The Hummers method is utilized to produce graphene oxide from graphite using the L_9 (3^3) experimental design. The Minitab package application utilizes the TOPSIS-based Taguchi method to determine the optimal point. The GO-5 coded experiment offers the most favorable conditions that closely align with the experimental design. The experimental design of graphene oxide L_9 (3^3) The evaluation of the results of the Taguchi-Based TOPSIS multi-response effect analysis shows that the pretreatment applied at a heating temperature of 200 ℃ has yielded the best result for graphite. Additionally, in terms of purity, the Nanocarbon graphite with 85% purity has yielded the best result in the field of Nanotechnology. Sodium nitrate has demonstrated superior efficacy as supplementary oxidants. The optimal sites for synthesizing graphene oxide are determined using the multi-response Taguchi-based TOPSIS approach, based on equal-weighted normalized values from the L_9 (3^3) experimental design. The experimental design for TOPSIS was designated as experiment code GO-5, and the corresponding experimental circumstances were provided in Table 8. The GO-1 coded experiment, which exhibits the lowest levels, is designated as a reference, whereas the GO-5 coded experiment is identified as the optimal experiment according to the TOPSIS method. The recovery rates were established in Table 9.

Table 8. *TOPSIS Optimum points and levels of GO synthesis according to weighted normalized values*

	Parameters	TOPSIS Optimum Levels GO-5
Synthesis of Graphene Oxide Optimum	(A) Pre-treatment Applied to Graphite	2 (200 ºC heating)
	(B) purity of graphite	2 (85N%)
	(C)Auxilarity oxidant	3 (Borax decahydrate)

Table 9. *Recovery rates of graphene oxide sample under optimal conditions*

Answers	Ref GO1	TOPSİS-GO5	TOPSİS Recovery rates (%)
ID/IG(Raman)[b]	1.07[b]	0.90[b]	15.88[b]
C/O (EDX)	1.89	0.84	55.55
SA(m^2/g)	23.63	8.68	-63.23
PS(nm-ZETA)	368.1	672.8	- 82,77
CS (nm)	139.45	110,45	20.79
ZP(ZETA)	-36,4	-43,4	19.23

Calculation of experiment recovery rates using the TOPSIS approach. using the GO-1 coded sample as a guide

[b] *(1.07-0.90) / 1.07)*100 =15.88 (surplus value means recovery)*

Upon examination of Table 9, it was seen that several criteria had negative recovery rates. The reason for this is the utilization of Merck company's graphite with a purity of 99.99% in design No. 1, specifically in the graphite variety used in the reference experiment coded GO-1, which exhibits the lowest levels in the design. The attributes of the graphite samples from the Merck firm, with a purity of 99.99%, are superior to those of other nanotech companies with purities of 85% and 99%.

5. DISCUSSION

The objective of the study was to enhance the quality of graphite using the Hummers method and a more eco-friendly statistical approach for synthesizing graphene oxide. This study is utilized the Taguchi approach, employing the TOPSIS technique, using the principles of experimental design methodology. The Taguchi approach enables optimization with a single response, whereas the TOPSIS method condenses multi responses into a single solution.

The results of the multiple-response Taguchi-based TOPSIS optimization indicate that the pre-200 °C heating and ultrasonication techniques applied to graphite contribute to the enhancement of graphene oxide characteristics. The performance of graphite samples from nanocarbon nanotechnology with a low level of impurities has yielded unexpectedly positive results. The utilization of the Taguchi optimization criterion revealed that low-purity graphite (85N%) had a detrimental impact on certain criteria while simultaneously exhibiting various responses for all criteria. The Taguchi-based strategy is proven to yield optimal performance when assessed using the TOPSIS evaluation method. Borax decahydrate was found to perform somewhat as nearly same with sodium nitrate when auxiliary oxidants were assessed. This work aims to show that borax decahydrate, as an alternative to sodium nitrate or phosphoric acid, can be used in the Hummers method. The graphs of the single-point Taguchi studies clearly demonstrate that utilizing borax decahydrate as a supplementary oxidant has a beneficial impact on the quality criteria D/G, C/O, and CS. The TOPSIS-Based Taguchi Method was used to look at the results of each experiment and figure out the best conditions for each quality criterion. For D/G, C/O, ZP, SA, PS, and CS, the healing rates were found to be 15.88%, 55.55%, 19.23%, -63.23%, -82.77%, and 20.79%, respectively.

Considered a natural boron molecule, boraxe decahydrate not only adds an environmental perspective to the study but also has mending effects on the degree of oxidation and the structure of graphene oxide. The utilization of various boron compounds in the manufacturing of graphene oxide and its reduction process is highly significant due to the resultant decrease in structural imperfections. This study is demonstrated that boron compounds are applicable in the Hummers method for synthesizing graphene oxide, as well as in the chemical reduction method for producing reduced graphene oxide.

CONFLICTS OF INTEREST

No conflict of interest was declared by the author.

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