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REDUCED GRAPHENE OXIDE FROM POLYETHYLENE TEREPHTHALATE (PET) WASTE SYNTHESIS AND CHARACTERIZATION

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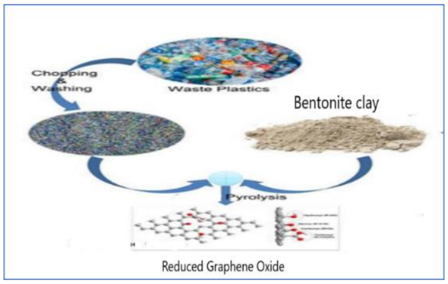
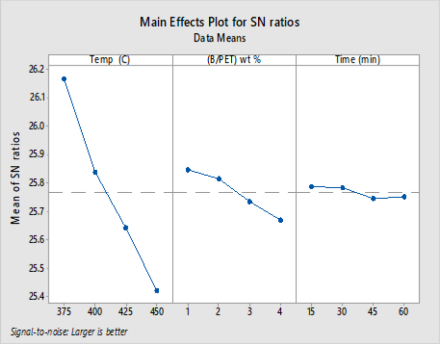
Graphical abstract





Abstract

In this work, reduced graphene oxide was successfully synthesized from Polyethylene terephthalate (PET) waste in the catalytic reactor. The effects of the production variables such as temperature (375-450 C), weight of bentonite catalyst (1-4%), and holding time (15-60 min) were investigated. The physiochemical properties of reduced graphene oxide were determined by employing various analytical techniques, like X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR), Field Emission Scanning Electron Microscopy (FESEM), Energy-Dispersive X-ray (EDX), and Raman Spectroscopy. Taguchi method was used to investigate the effects of these factors on the production of reduced graphene oxide. Taguchi design methodology was used with an L16 orthogonal system to find the best operating conditions. The results of the experimental analysis showed that the most effective factors in each experimental design response were pyrolysis temperature and holding time. The best-conditions for reduced graphene oxide production from Polyethylene terephthalate (PET) waste were found to be as follows: pyrolysis temperature of 375 °C, the weight of bentonite catalyst 1%, and time of 15 min.

Keywords: Polyethylene terephthalate PET, Reduced Graphene Oxide, Taguchi method

1.0 INTRODUCTION

Recently, with increasing global demand for plastic material, the total amount of waste plastics generated by human society is increasing and becoming a danger to the environment [1]. Polyethylene terephthalate (PET) bottles are one of the most find optimal conditions for an examined process. [2]. solid plastic wastes that accumulate day after day in our surroundings cause a huge problem during their disposal without contaminating the environment [2-3]. The traditional methods of disposal of waste plastics are landfill and incineration, but they waste resources and harm the environment. Convert carbon sources such as Polyethylene terephthalate (PET) waste to high-value-added carbon nanomaterials such as reduced graphene oxide has become an emerging method [3]. Graphitic Nano products with value-added and cost-effectiveness can be synthesized from polymeric materials by pyrolysis at a catalytic reactor. High carbon materials such as polypropylene (PP), polyethylene (PE), and polystyrene (PS) are considered to be the most precursor materials for the synthesis of carbon Nano products[4]. PET polymer has a high value of carbon 63%. Despite this high value, PET pyrolysis results in a significant mass loss of 80% or more giving only 20% or less mass remaining during PET thermal degradation [4-5]. Carbon nanomaterials such as CNTs, carbon spheres, carbon nanofibers, and graphene Nano sheets (GNs) have been synthesized from wastes of plastic. Moreover, various catalysts for instance transition metals (Ferrocene, Ferrous Chloride, Nickel Oxides, or Cobalt acetate) or in elemental forms (Iron or Nickel)have been studied in the processes [6-7]. Essawya *et al.* [8] Synthesized graphene from Polyethylene terephthalate (PET) waste. The plastic wastes were cut first and washed with hot water to remove impurities. The plastic wastes was introduced into a stainless-steel autoclave reactor and heated to 800 °C for 1 h at an electric furnace. Finally, the product is cooled to room temperature, and the product is classified as graphene. Gong *et al*. [9] used the up-cyclization process to convert of waste polypropylene (PP) into high-yield graphene flakes. A degradation agent such as an organically modified catalyst (OMMT) was used in this process, at 700 °C and under an inert environment. *Kamali, et al.* [10] synthesized, graphene nanostructure from waste plastic bottles by pyrolysis with a heating rate of 10 °C/min to 1300 °C in a tube furnace, graphene cooled overnight by air drying at 80 °C. Hu *et al.* [11] a new, safe, and controllable method has been developed to prepare highly crystalline few-layer graphene (FLG) sheets using waste expanded polystyrene (EPS) by dense iron cluster catalyst. Three-layer graphene sheets were acquired at 700 °C due to the coordinated catalysis of a dense Fe cluster array. More than 70% of FLG sheets were produced from waste EPS, providing an efficient way the recycle EPS waste.

In the present work, synthesized reduced graphene oxide from Polyethylene terephthalate (PET) waste using a thermal catalytic reactor with a bentonite catalyst was studied. The design of experiments was considered in the Taguchi method to find the optimum conditions to produce reduced graphene oxide that has almost the same characteristics as conventional reduced graphene oxide prepared from natural graphite. The physiochemical properties of reduced graphene oxide were determined by employing various analytical techniques, such as field emission scanning electron microscopy (FESEM), energy-dispersive X-ray (EDX), X-ray diffraction (XRD), Fourier transform infrared (FTIR), and Raman spectroscopy.

2.0 METHODOLOGY

2.1 Materials

Bentonite clay with (100 micrometers), HCL with concentration >36 wt. % and PET waste were used in this study. Bentonite clay was supplied by Sigma-Aldrich (St. Louis, MO, USA). Polyethylene terephthalate (PET) waste was collected and crushed into small pieces after removing the labels and caps from the sample. To remove any dirt the collected bottles were washed with hot water and then dried in the oven at 70 ◦C, for 24 h.

2.2 Synthesis of Reduced Graphene Oxide from Waste PET Bottles

Reduced Graphene Oxide (rGO) was synthesized by pyrolysis of PET waste in a catalytic reactor using bentonite clay as a catalyst. PET waste were cut into small pieces (10*5 mm) and mixed with bentonite catalyst for 15 min before being subjected to pyrolysis at a heating rate of 10 ◦C/min in the stream of nitrogen as shown in Figure 1. The (rGO) was obtained thoroughly washed with distilled water and HCL to remove excess impurities and finally dried in an oven at 100 ◦C for 24 h.

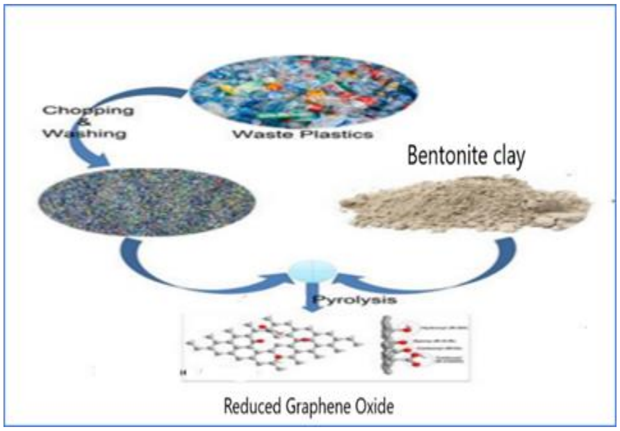


Figure 1 Schematic of the present process for synthesis of reduced graphene oxide from PET waste

2.3 Production Optimization

Taguchi method was used to optimize the production of reduced graphene oxide from PET waste by using orthogonal arrays (OA). Levels of experimental parameters pyrolysis temperature (X1), (B/PET) ratio (X2), and time (X3) were summarized in Table 1. The responses were selected as rGO Yield. Since a higher yield of rGO was the aim of this study. The larger is better was selected to S/N. The "ANOVA" was used for data analysis of the matrix with three factors (X1, X2, and X3) and 16 trials[12].

Table 1 Levels of experimental parameters

Factors	Unit	Symbol	levels			
			1	2	3	4
Temperature	°C	X_1	375	400	425	450
(B /PET) ratio	Wt. %	X_2	1	2	3	4
Time	min	X_3	15	30	45	60

2.4 Reduced Graphene Oxide Yield

The reduced graphene oxide yield is usually expressed as the final weight of reduced graphene oxide produced after pyrolysis, washing, and drying divided by the initial raw material waste plastic and bentonite clay.

$$Y_i\% = \frac{Wt_{rGO}}{Wt_{rm}} 100 \qquad \dots\dots(1)$$

Where Y_i% represented the reduced graphene oxide yield, wt_{rGO} represented the final dry weight of the reduced graphene oxide product, and wt_{rm} represented the dry weight of raw material of waste plastic and bentonite clay[13-14].

3.0 RESULTS AND DISCUSSION

3.1 Taguchi Analysis of the Responses and S/N Ratio

The results of runs experiments and the tested S/N ratios are presented in Table 2. The values of the S/N ratios for all experimental parameter levels and their effect on the yield of rGO are summarized in Table 3. The main effect plots of experimental parameters (X1, X2, and X3) on the S/N ratio of rGO yield were shown in Figure 2. This figure shows that S/N ratio of rGO yield decreased with increased pyrolysis temperature from 375 °C to 450 °C. The best value of S/N ratio was 26.17 at the 375 °C as shown in Table 3.

Table 2 Results of Taguchi experiment design for yield of reduced graphene oxide

Exp. No.	Real Values			Response	S/N
	Temp °C	(B/PET) wt.%	Time (min)	Yield %	
1	375	1	15	20.590	26.2731
2	375	2	30	20.520	26.2435
3	375	3	45	20.200	26.1070
4	375	4	60	20.050	26.0423
5	400	1	30	19.800	25.9333
6	400	2	15	19.700	25.8893
7	400	3	60	19.500	25.8007
8	400	4	45	19.350	25.7336
9	425	1	45	19.250	25.6886
10	425	2	60	19.208	25.6696
11	425	3	15	19.160	25.6479
12	425	4	30	18.980	25.5659
13	450	1	60	18.830	25.4970
14	450	2	45	18.750	25.4600
15	450	3	30	18.600	25.3903
16	450	4	15	18.500	25.3434

Table 3 Signal to Noise Ratios Response table (larger is better)

Level	Temp °C	(B/PET) wt.%	Time (min)
1	26.17	25.85	25.79
2	25.84	25.82	25.78
3	25.64	25.74	25.75
4	25.42	25.67	25.75
Delta	0.74	0.18	0.04
Rank	1	2	3

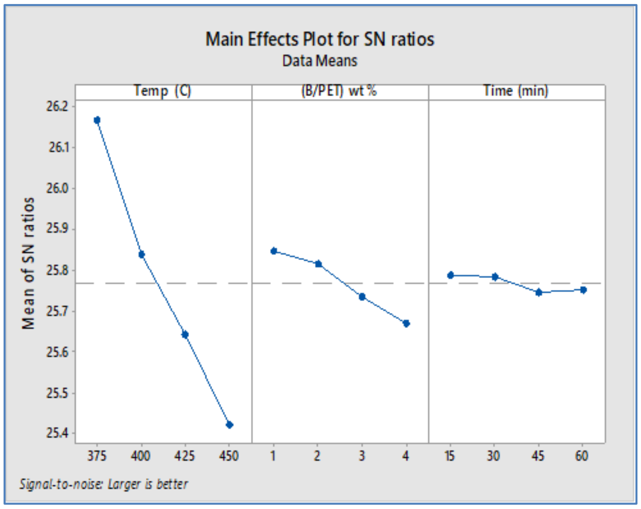


Figure 2 Main effect plots of SN ratios for reduced graphene oxide yield

The S/N ratio of rGO yield dropped dramatically with increasing (B/PET) ratio from (1 to 4 wt. %). The best value of the S/N ratio was 25.85 at level 1 as shown in Table 3. Also, the S/N ratio of rGO yield marginally decreased with time. The optimum S/N ratio attributed to pyrolysis time was 25.79 at 15 min as shown in Figure 2 and Table 3. The optimum conditions for the rGO yield are temperature = 375 °C, the (B/PET) wt. % = 1, and time =15 min. The order of effect of the factors is Temperature °C > (B/PET) ratio wt. % > Time (min).

The regression equation that describes the model for reduced graphene oxide yield response is represented in Equation 2.

$$\text{Yield } (Y_1)\ \% = 47.35 - 0.1119\, X1 - 0.1372\, X2 - 0.00239\, X3 + 0.000109\, (X1)^2 \qquad (2)$$

Where X1 is temperature °C, X2 is (B/PET) ratio wt. %, and X3 is time (min).

The result of the ANOVA analysis for Yi responses is represented in Table 4. Based on the correlation coefficient values R^2. It is the variability between the experimental data and the predicted data. In this research, the predicted equation had a squared value equal to (0.9983), which explained that 99.83% of experimental data agreed well with the predicted data. Higher values of the sum of squares indicate relative importance on the response. An f-value of more than (4) means that the control factors have a strong influence on the response. While a p-value above (5%) indicates that the parameter is not important for the response[15-16].

Table 3 Analysis of variance for reduced graphene oxide yield response

Source	DF	Seq SS	Adj SS	Adj MS	F-Value	P-Value
Temp °C	3	6.03	6.03	2.01	1115.3	0.00
(B/PET) wt. %	3	0.38	0.38	0.12	71.26	0.00
Time(min)	3	0.32	0.32	0.01	5.95	0.031
error	6	0.01	0.01	0.001	-	-
total	15	6.46	-	-	-	-
Model	**S**	**R^2**	**R2 (adj.)**	**R^2(pred.)**	-	-
	0.042	99.83%	99.58%	98.81%	-	-

The influence of the pyrolysis time on the yield of rGO has been presented at 15, 30, 45, and 60 min by applying the multiple regression models equation and the results are illustrated in Figure 3 at temperatures 375 °C for each weight percent of (B/PET).

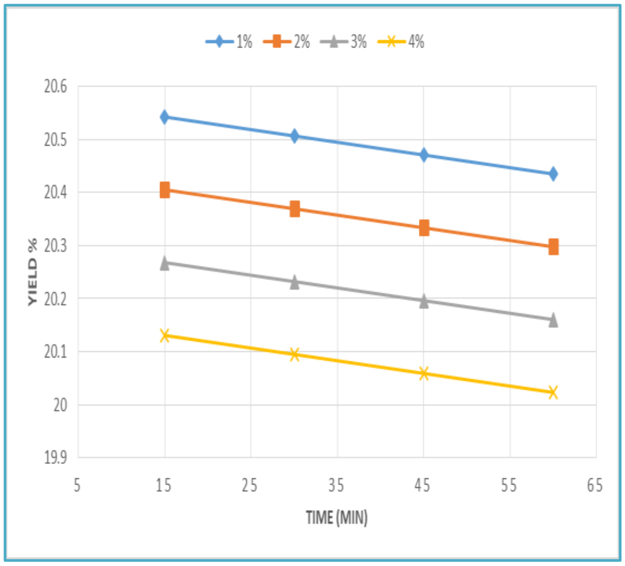


Figure 3 Effect of pyrolysis time on rGO yield % at 375 °C

Figure 4 shows effect of temperatures on rGO yield by applying the multiple regression models equation. As the temperatures increases yield percentage of rGO decreases with increasing in (B/PET) ratio.

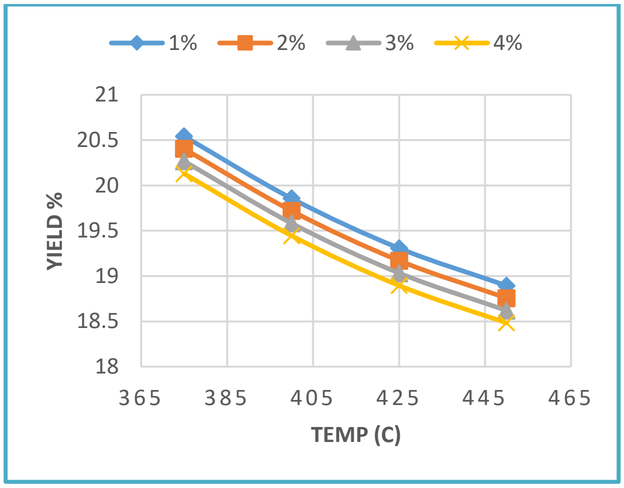


Figure 4 Effect of Temperature on rGO yield % at 15min

3.2 Reduced Graphene Oxide Characterization

3.2.1 *FT-IR spectrum*

The performance of rGO functional groups was investigated by FTIR spectroscopy. Figure 5, shows the position of the rGO absorption peaks. Stretching vibrations for hydroxyl groups (-OH) are shown at Peak (3449.92 cm^{-1}), while, the stretching vibration of (C=O) appeared at the peak (1708.99 cm^{-1}) for carboxyl and carbonyl groups. Moreover, the (C=C) bonds is corresponding to the peak center of (1,613 cm^{-1}) [17]. Besides, there are various peaks at (1539.25 cm^{-1}, 1396.5 cm^{-1}, 1238.34 cm^{-1}) which are assigned to (O–C=O) of a carboxyl group, vibrational stretching of the ketonic functional group, and the (C-O) stretching vibration of the epoxide ring. furthermore, stretching vibrations (C–O–C) usually appear at bands (1091.75 cm^{-1}) [18-19].

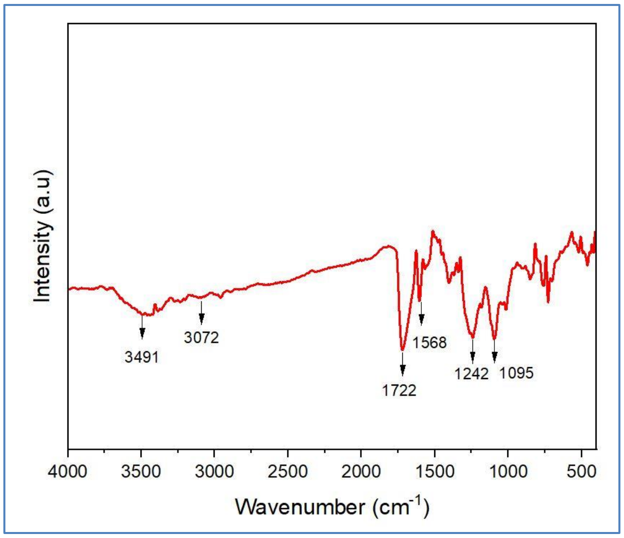


Figure 5 FT-IR spectra of reduced graphene oxide

3.2.2 *X-Ray Diffraction*

The XRD diffraction of rGO in Figure 6 shows peak at 2θ = (23.06°) corresponding to an interlayer distance of (0.386 nm) which indicates that oxygen functional groups are still present during synthesized reduced graphene oxide from PET waste in pyrolysis [20-21]. Average crystal size was 2.32 nm, the number of graphene layers was calculated by dividing the average crystal size by d-spacing was 8 layers.

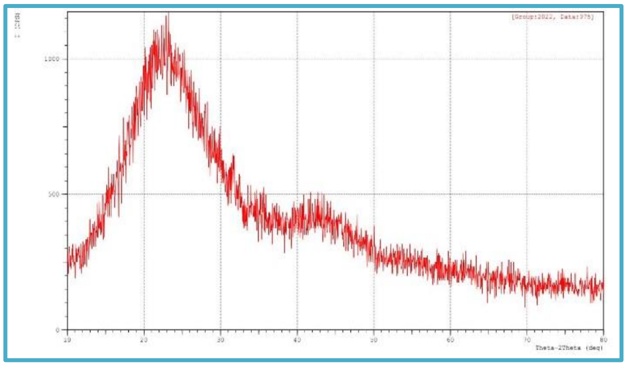


Figure 6 X-ray diffraction of reduced graphene oxide

3.2.3 *BET Surface Area & Pore Volume*

According to the Brunauer–Emmett–Teller (BET) test, graphene has a surface area (SBET), pore volume (VP), and pore diameter (D) of 31.04 m^2/g, 0.038 m^3/g, and 4.78 nm respectively.

3.2.4 *Raman Spectroscopy*

Raman spectroscopy of reduced graphene oxide synthesized from waste plastic is shown in Figure 7. It can be seen that rGO has a sharper G band that appears at 1607 cm^{-1} which indicates a higher sp^2 domain and lower degree of the disorder, while, the D*and D band, is observed at 1265 cm^{-1} and 1428 cm^{-1} [22-23].

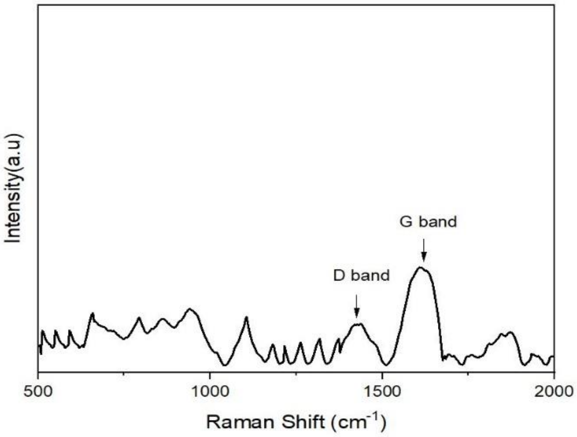


Figure 7 Raman Shift of reduced graphene oxide

3.2.5 *Field Emission Scanning Electron Microscopy (FESEM), Energy-Dispersive X-ray (EDX)*

Field emission scanning electron microscopy (FESEM) of the reduced graphene oxide has been shown in Figure 8 with magnification strength of 500 nm. It seemed that rGO was in the form of sheets [24].

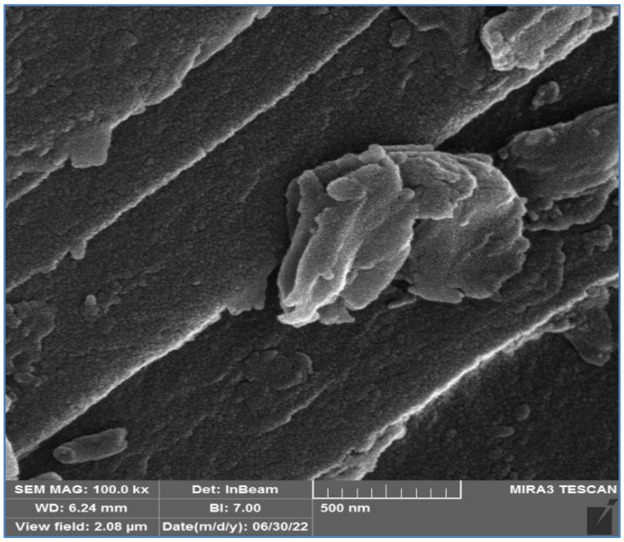
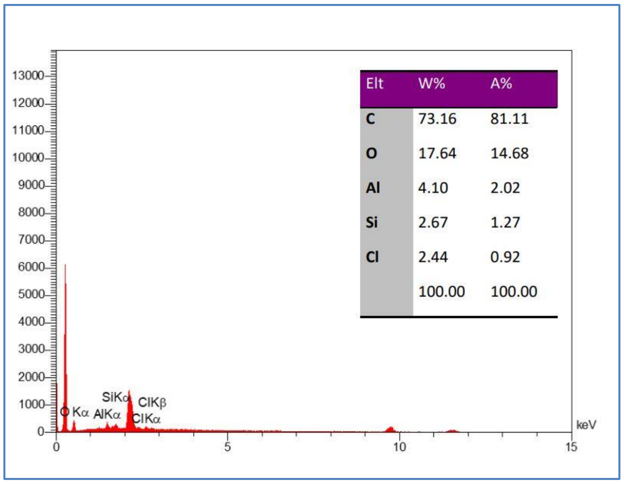


Figure 8 FESEM of reduced graphene oxide

While EDX profile of rGO composite is given in Figure 9. From the date, it is clear that rGO consist of C and O as its major elements (73.16% and 17.64%) respectively. In addition, some quantities of AL,Si and Cl are observed with total amount less than 10% which may be due to used bentonite clay as catalyst in pyrolysis [25-26].



Elt	W%	A%
C	73.16	81.11
O	17.64	14.68
Al	4.10	2.02
Si	2.67	1.27
Cl	2.44	0.92
	100.00	100.00

Figure 9 Energy-dispersive X-ray (EDX) of reduced graphene oxide

4.0 CONCLUSION

Conversion of plastic wastes (PET bottles) to reduced graphene oxide by pyrolysis using a bentonite catalyst and its use it as catalytic support was one of the objectives of the present work. The use of low-cost, readily available, and reproducible raw materials such as (PET bottles) for the production of reduced graphene oxide is of great economic and environmental importance. The Taguchi method was used to analyze experimental results. The maximum yield of rGO was at a pyrolysis temperature of 375 °C, the weight of bentonite catalyst 1%, and time 15 min. The XRD spectra showed that the rGO has a diffraction peak 2θ = (23.06°) corresponding to an interlayer distance of (0.386 nm). Average crystal size was 2.32 nm and number of layers were 8. The peak signal for major functional groups could also be found in FTIR analysis that confirmed the presence of an oxygen functional group of rGO. The surface area (SBET), pore volume (VP), and pore diameter (D) of rGO was of 31.04 m^2/g, 0.038 m^3/g, and 4.78 nm respectively.

Conflicts of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

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