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Using RSM to optimize crystallite size of rice husk derived graphene prepared by microwave process

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Abstract

In this research work, the optimization of the microwave process is done for the preparation of graphene from rice husk using RSM (Response Surface Methodology) as the graphene has exceptional qualities and is highly used in many industrial applications. The experiments are designed by using Box-Behnken Design (BBD) approach. The characterization of prepared graphene is done by Field Emission Scanning Electron Microscopy (FESEM), UV–Visible spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), X-ray powder diffraction (XRD), etc. The best root to find good quality graphene is the objective of this research. Weight of Ferrocene (gm), rice husk powder (gm), and Furnace Temperature (°C) is selected as input variables within the range of 20-60 gm, 40-80 gm, and 600-800 °C, respectively. The satisfactory correlation between experimental and predictable data is described by a higher value R^2 (0.9979). The obtained optimized minimum crystallite size of graphene is 32.72 nm. The optimized parametric conditions to minimize the crystalline size are at a Weight of ferrocene 57.86 gm, Rice husk powder 79.15 gm, and Furnace temperature of 792.58 °C. The characterization, prediction, and process optimization are made. The validated model confirms that the model can prepare graphene particles from paddy product rice husk. The prediction and optimization of the process parameters are made to synthesize graphene from rice husk. RSM is used as a statistical technique to obtain a quadratic model for the response. As graphene's properties mainly depend upon the size of the particle. So, the prediction of the crystalline size is made by this RSM technique.

Keywords: Carbon materials, Optimization, RSM, Synthesis, Rice husk, Graphene

1. Introduction

A group of materials with structures in layers and a thickness of a few atoms are known as 2D materials. The most quintessential 2D material known as graphene was investigated for the first time by Novoselov et al., using scotch tape [1]. The carbon element has several allotropes like a 3-D diamond, 2-D graphene,1-D nanotubes [2,3]. 2-D carbon allotrope with honeycomb structure, and sp^2 hybridized carbon atom, is called graphene [4]. Graphene is one of the most investigated 2-D materials [5]. Graphene has exceptional qualities, such as outstanding thermal [6] and electrical conductivity [7,8], adaptability, optical straightforwardness, high explicit surface area, and considerably more [9]. These assets make graphene reasonable for different applications, similar to storing energy [10] and harvesting application, the creation of transistors [11,12], biomedical applications [13], health applications [14], and textile applications [14]. Single-layer graphite synthesis was done earlier in 1975 [15], but the researchers synthesized graphene properly in 2004 [16]. Nowadays, many researchers utilize green synthesis procedures to produce it from natural resources[17], as it is non-polluted and non-toxic [17,18]. There are many methods to produce nanoparticles like Chemical Vapor Deposition (CVD), Sol-gel method, etc. [19]. Rice husk was used as the raw material for the CVD technique, which produced graphene with sharp edges. Response Surface Methodology (RSM) was also employed to optimize the process [20,21]. Nanoparticles are superior materials to increase the various properties of existing products like PCM, hybrid composites and Nanofluids, etc. The enhanced properties of materials depend upon the quality and properties of Nanoparticles used in respective materials. The properties of Nanoparticles depend upon the size of that particle, known as crystalline size. As the crystalline size is smaller, that performance in the thermal and other applications enhances. In this research, rice husk is used as the primary raw material. The selection of rice husk is based upon the availability, which is free as paddy waste and the content of carbon in it. The microwave process is easy to use and less time consuming as compare to other processes like CVD, ball mill and sol-gel. The metal nanoparticles prepared from methods like CVD, sol gel and mechanical method etc. but lack of information was there for the preparation of Nanoparticles from crops waste. As the performance of Nano particle is depending upon its crystalline size, like use of Nano particles in Nano fluids and to enhance the performance of phase change materials etc. The Nano particles mainly produced from metallic substances but in this research preparation of Nano particles is done from bio-waste. So here in this reserch main ephasis on the optimization for the same is done. This research aims to develop an RSM based optimized model to predict the crystallite size of graphene prepared by the microwave-assisted process.

2. Materials and methods

Rice husk is used as a primary raw material in this research work. Rice husk is accessible easily from the paddy ground. Rice husk is one of the appropriate raw materials with great ease of silica and carbon. Ferrocene ($Fe(C^5H^5)^2$) (Nano research lab) is used as the catalyst. The washing of raw material (rice husk) was done by ultra-sonication (LMUC-6 40KHz) for 90 min, then drying in regular air heating for 48 h.

Raw Material Graphene Power form of Rice Hush

Figure 1 Schematic diagram of the process optimization to produce graphene from rice husk.

The me chanical method is used to convert rice husk into fine particles. A planetary ball mill with stainless steel grinding balls of 12 mm diameter is used for crushing the rice husk into powder form. The ball mill operates at 410 rpm for 90 min to grind every 50 gm of the sample. After that, the microwave is used for heating at various levels. At unlike levels, rice husk powder is mixed with ferrocene (100 mL each) and ethanol (150 mL each), as shown in Figure 1.

2.1 Parametric investigation

Characterization of prepared graphene is done with the help of zeta-sizer, UV-visible **(**Perkin Elmer Lambda 750), X-ray powder diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) (Magnification of this instrument is lying between 25 to 1,000,000 and accelerating voltage 0.1 kV to 30 kV), and Fourier Transform Infrared Spectroscopy **(**FTIR) (Perkin Elmer RX I FTIR-ATR spectral range of 400–4000 cm^{-1}) [21]. Many properties of graphene are related to the size of particles. Hence, as small as the size of the obtained graphene particle is, the good physical and structural properties it would have.

2.2 Optimization

RSM is the statistical technique used to model and optimize multiple variables, which determine the optimum process variables by merging experimental designs with interpolation by first-or second-polynomial equations in a successive testing procedure. Response surface methodology (RSM) gives the relationships between response variables and several explanatory variables [22,23]. The Box-Behnken is one of the best response- surface designs, also a design central composite design (CCD) given by [24]. Optimization of the process variables by the RSM method involves three primary steps; first, preparing designed experiments statistically; second, mathematical modeling and estimation of variables; at the end, checking the model adequacy and predicting the response within the setup of the experiment [25,26]. RSM develops a second-order mathematical modeling equation for different experimental variables [27]. Thus, the RSM technique is used to optimize the output response to the simple microwave process for producing graphene from rice husk [26,28].

$$Y = \beta_{\circ} + \sum_{i=1}^{n} \beta_{i} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij}\ x_i x_j\ + \sum_{i=1}^{n} \beta_{\circ}\, x_i^2 \tag{1}$$

X_{ij} = Coded values for independent variables

$\beta_0 \ldots, \beta_{ij}$ Regression coefficients

The response variable of the process is Y, and an Xn denotes the independent variable of the system.

In this work, Design-Expert software is used for the optimization of three independent process variables, i.e., the weight of ferrocene (gm), rice husk powder (gm), and furnace temperature (°C) on Crystallite Size (nm), the dependent variable and numerical design is prepared by Box-Behnken Design. Experimentation was done to determine the effect of input variables on output variables. At first, experiments were designed for 20 to 60 gm weight of ferrocene, 40 to 80 gm of rice husk powder, and furnace temperature (varying from 600 to 800 (°C). Low, medium, and high were the levels of every input variable. For developing a quadratic model, the levels were divided in the same manner equally. The values assigned to the input factors are indicated in Table 1 and their corresponding coded levels.

Table 1 Input variables with different levels and their coded values.

Variable	Coded form		
	-1	0	1
Weight of Ferrocene (gm) (A)	20	40	60
Rice husk powder (gm) (B)	40	60	80
Furnace Temperature (°C) (C)	600	700	800

In RSM, seven different steps optimize process variables [29]. The following stages include 1. Selection of output variable (Crystallite Size (nm)), 2. Variables choice and coding of variables, 3. Preparation of experimental design for graphene synthesis, i.e., Crystallite Size (nm), 4. After that regression analysis, 5. Development of an RSM model 6. Development of 3D surface plot and 2D contour of the response variable, 7. Finding optimum operating conditions.

2.3 RSM model Validation

The confirmation of the mathematical model obtained from the RSM technique was done by performing experimentation on the given optimum conditions.

3. Results and discussion

3.1 RSM model development

Table 2 Experimental results according to Box-Behnken Design (BBD) array.

Weight of Ferrocene (gm)	Rice husk powder (gm)	Furnace Temperature (°C)	Crystallite Size (nm)
40	60	700	64.50
20	60	600	56.70
20	80	700	66.58
40	80	600	46.20
40	40	800	42.50
40	80	800	50.50
60	60	800	51.40
20	60	800	64.40
60	60	600	65.54
60	40	700	65.27
60	80	700	45.50
20	40	700	49.50
40	40	600	56.42
40	60	700	63.50
40	60	700	63.50

Table 2 shows the response values according to experimentation done based on the BBD array. Response surface designs customized to fit the experimental results obtained from experimentation done according to BBD. This obtained equation is in the coded forms, where A, B, and C represent the weight of ferrocene, rice husk powder, and furnace temperature. Accordingly, the response, i.e., crystallite size, was computed using Equation 2. Statistical results of the developed model are shown in ANOVA Table 3. The model is significant as from the model F-value 265.61. There is a 0.01% chance that this large F-value could occur due to noise. Significance of model terms indicated by the *p*-values as the *p*-values < 0.0500 implies model terms are significant. In this case, the following linear A, B, C, multiple AB, BC, AC, and square terms A^2, B^2, C^2 are significant model terms. Values > 0.1000 indicate the terms in the model are not significant. As in some cases, if insignificant terms in the prepared model increase, improvement of the prepared model can be increased by reducing the irrelevant values.

Table 3 ANOVA table of quadratic model for crystalline size.

Source	Sum of Squares	DF	Mean Square	F-value	*p*-value	Remarks
Model	1015.32	9	112.81	265.61	< 0.0001	significant
A- Weight of Ferrocene	11.21	1	11.21	26.39	0.0037	
B- Rice husk powder	3.01	1	3.01	7.1	0.0447	
C- Furnace Temperature	32.24	1	32.24	75.91	0.0003	
AB	339.48	1	339.48	799.29	< 0.0001	
AC	119.25	1	119.25	280.76	< 0.0001	
BC	82.99	1	82.99	195.4	< 0.0001	
A^2	11.21	1	11.21	26.38	0.0037	
B^2	290.04	1	290.04	682.87	< 0.0001	
C^2	135.84	1	135.84	319.82	< 0.0001	
Residual	2.12	5	0.4247			
Lack of Fit	1.46	3	0.4857	1.46	0.4317	not significant
Pure Error	0.66	2	0.3333			
Cor Total	1017.44	14				

The lack of fit values should not be significant relative to pure error, as in this case, the non-significance of lack of fit is observed from F-value (1.46). There is a 43.17% chance that a Lack of Fit F-value this huge could happen due to noise. For a model to be a good fit, lack of fit should be Non-significant, as in this study.

$$\text{Crystallite Size(nm)} = 63.8333 + -1.18375 * A + -0.61375 * B + -2.0075 * C + -9.2125 * AB + -5.46 * AC + 4.555 * BC + 1.74208 * A^2 + -8.86292 * B^2 + -6.06542 * C^2 \quad (2)$$

The proficiency of the model prepared in this research also be evaluated by the other parameters like Pred. R^2 (predicted R^2), CV% (coefficient of variation), Adj. R^2 (adjusted R^2), R^2 (coefficient of determination). R^2 and Adj. R^2 values for crystalline size were equal to 0.9979 and 0.9942, respectively. The model developed provides a better predicting response as indicated by the standard deviation value [33], which is very small in this model, and the value of R^2 approaching unity [34].

Table 4 Model Summary of the proposed model.

Std. Dev.	Mean	C V %	R^2	Adj. R^2	Pred. R^2	Adeq. Precision
0.6517	56.8	1.15	0.9979	0.9942	0.9756	44.2358

The difference between Pred. R^2 and R^2 are less than .2; from this, it's clear that there is a good correlation between calculated data and observed data. The model has 44.236 Adeq. Precision value shows that the signal to noise ratio is >4, which is desirable; hence, an adequate signal was indicated for a model [35]. The statistical terms of the RSM model are listed in Table 4.

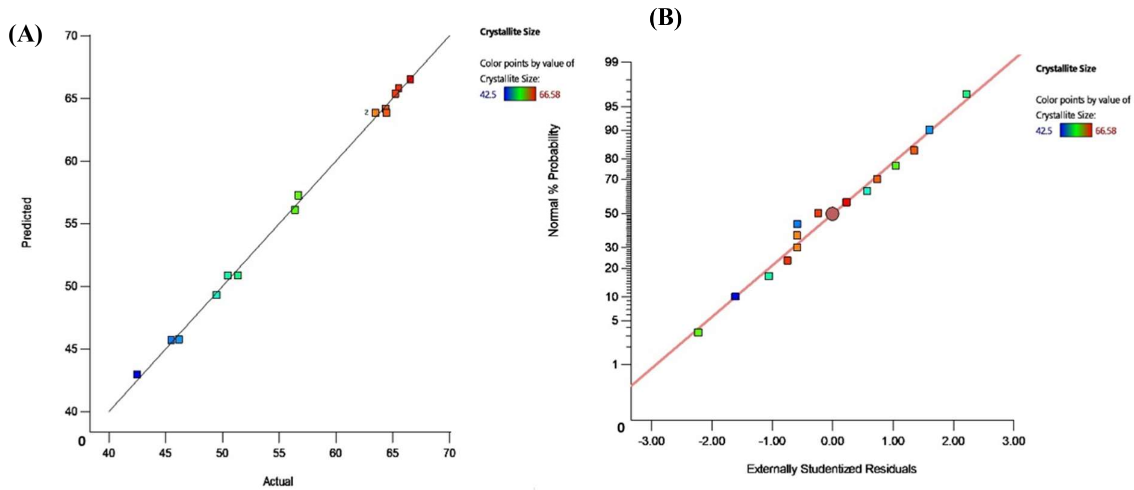

Figure 2 Graphical representation of (A) predicted values vs. actual values for crystalline size and (B) residual error normality plot with 95%.

The statistical terms of the RSM model are listed in Table 3. As from Figure 2., it's clear that the residual error and plot of predicted versus experimental data is normally distributed [35,36,37]. Figure 5. reveals the variation of crystallite size of graphene with input variables. From Figure 3, it is clear that the minimum size of the graphene particle is achieved above 700 ^{o}C furnace temperature and in the range of 35 to 45 gm of ferrocene. The minimum value of output response is achieved beyond 75 gm and 55 gm of rice husk powder and ferrocene. As displayed in Figure 2, the residual errors are within the ±3 range [38]. It can be said that the predicted values of graphene particle size are suitable for further use, and the proposed model is adequate to be used for further studies.

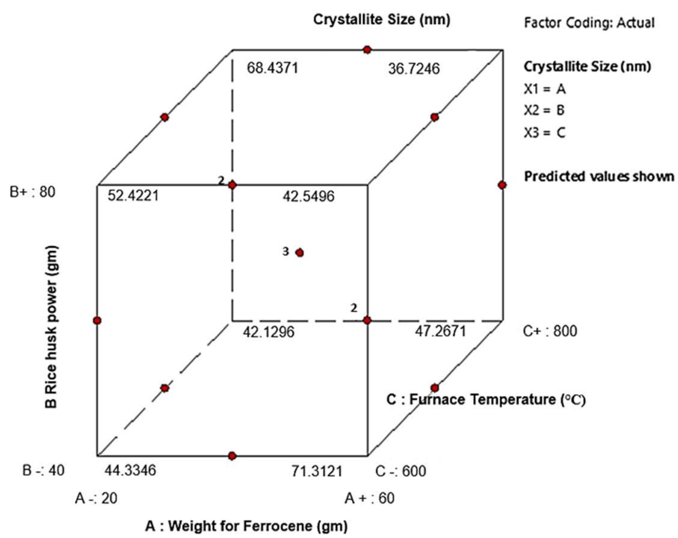

Figure 3 Cube representation of the model with predicted values.

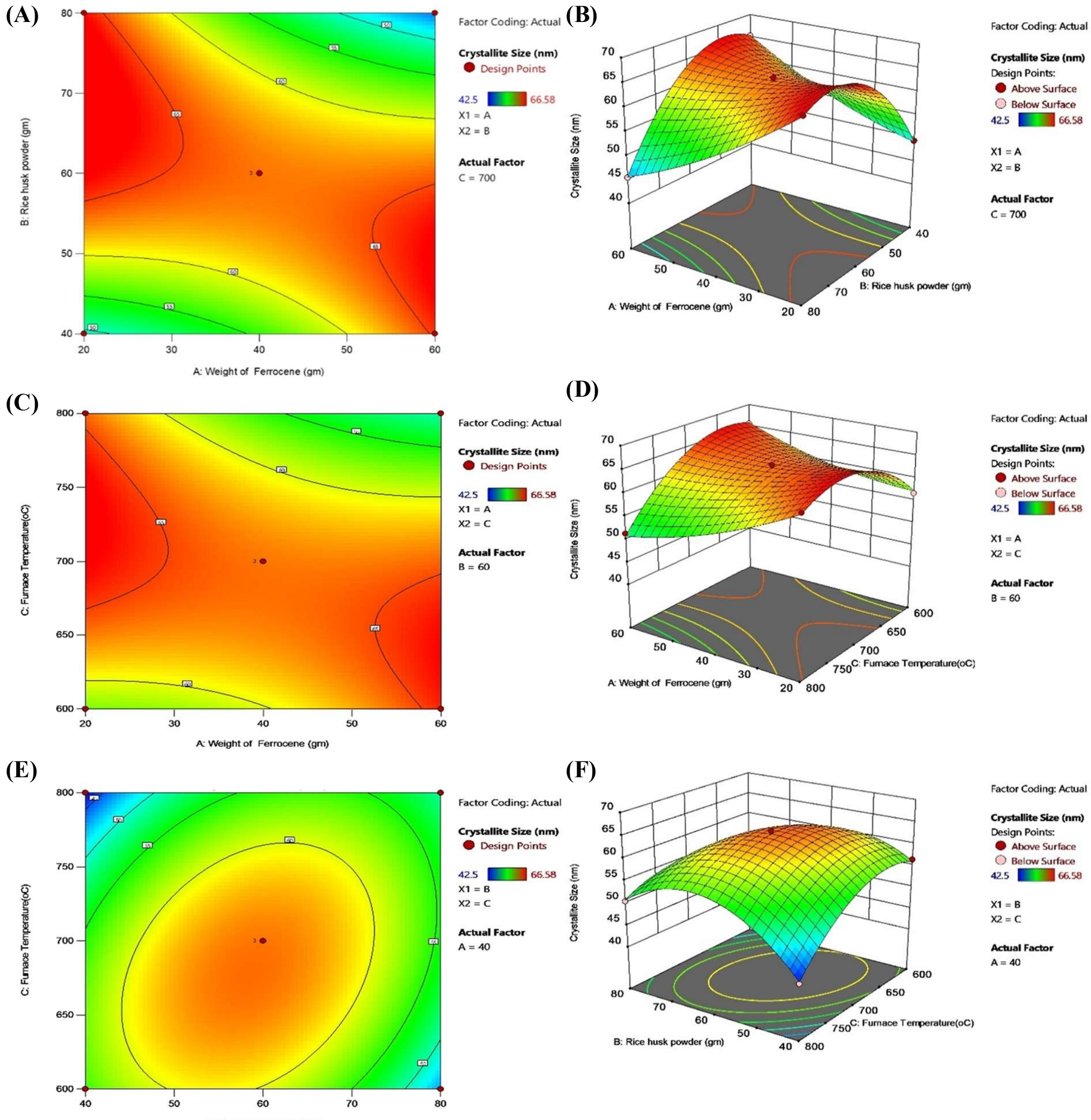

Figure 4 Cube representation of the model with predicted values; (A-F).

Figure 4 is a cube plot for the results of the obtained empirical model. The axis and coordinate point represent all the experimental design factors and the outcome, respectively. The values shown within the cube represent the predicted crystalline size by the process variables used in this study. Minimum crystalline size (36.724 nm) was achieved for high ranges of furnace temperature, rice husk powder, and ferrocene.

3.2 Optimization of the process variable

Experiments designed by BBD were conducted for the graphene preparation and found its crystalline size as response using Design Expert. The limits of the process variables were wisely chosen for minimum particle size to reduce the time of preparation and the process cost.

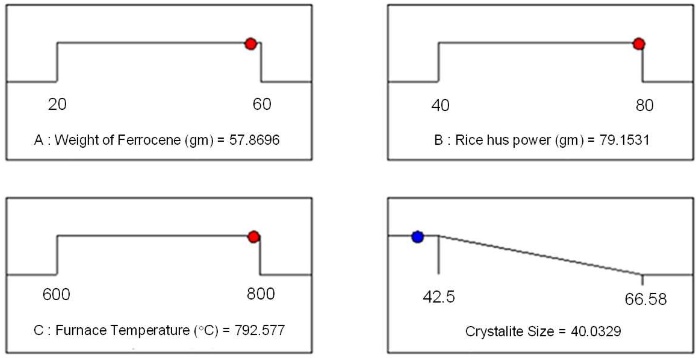

Figure 5 Plot for numerical optimization of the process for the crystalline size of prepared graphene by rice husk.

The response optimization was done to minimize the model function, and different numerical combinations get at the highest desirability. As shown the Figure 5, the optimized parametric conditions to minimize the crystalline size were obtained at a Weight of ferrocene 57.86 gm, Rice husk powder 79.15 gm, and Furnace temperature of 792.58 °C. The desirability approach is used to optimize the response variable; the applicability of the developed model is recognized by the D value, as much as the D-value approaches to 1 are considered the most desirable. At optimized parametric conditions, the 40.03 nm crystalline size of graphene particle was predicted by Equation (2). The obtained optimized result was confirmed by performing an additional set of experiments. The accuracy of the suggested model is confirmed by the confirmatory run by which crystalline size 40.24 nm is obtained. The experimentally observed response values and the model assumed theoretical values agree with each other, showing the efficiency of the response surface model. In this research, the discussion is done about a simple, low-cost method for preparing graphene. Detailed FESEM observation shows that the provided samples have graphene with a honeycomb structure. From the above results and discussion, it is clear that graphene prepared from rice husk should hold excellent physicochemical properties that sort them convenient for energy storage composites, water filters, and various nanocomposites. This process optimization clearly states that this model is adequate for the future research perspective.

3.3 Characterization

In this section, the characterization of prepared graphene and optimization of the output response is done. The minimum experimental value of crystalline size 42.5 nm is obtained at the weight of ferrocene (40 gm), rice husk powder (40 gm), furnace temperature (800 °C), so here are the characterizations for the same. Figure 6 shows the XRD data with h, l, k values corresponding to 2 theta values.

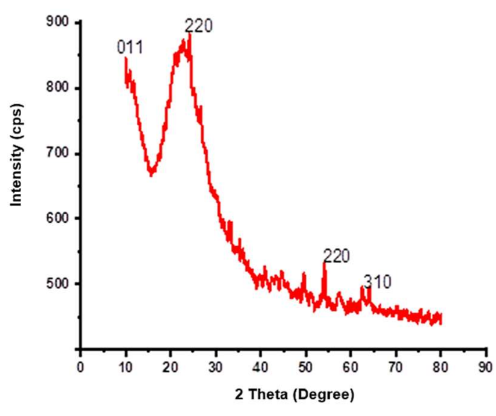

Figure 6 XRD pattern for prepared graphene.

The h, l, k values (0,0,1), (2,2,0), (2,2,0), (3,1,0) are corresponding to 11.23, 26.54,54.10 and 65.24 2theta value respectively. 2 theta values confirm the presence of graphene at 22°-25° [39]. In XRD spectra, a peak near 10°-12° corresponds to 0.7 to 1 nm interspace distance. FTIR (Figure 7 (A)) indicates that the Si-O-Si stretching, presences on –C==C- bond and presence of hydroxyl group, is due to absorption bands, near at the 1102.3, 1623 and 3431.9 cm^{-1} respectively [40].

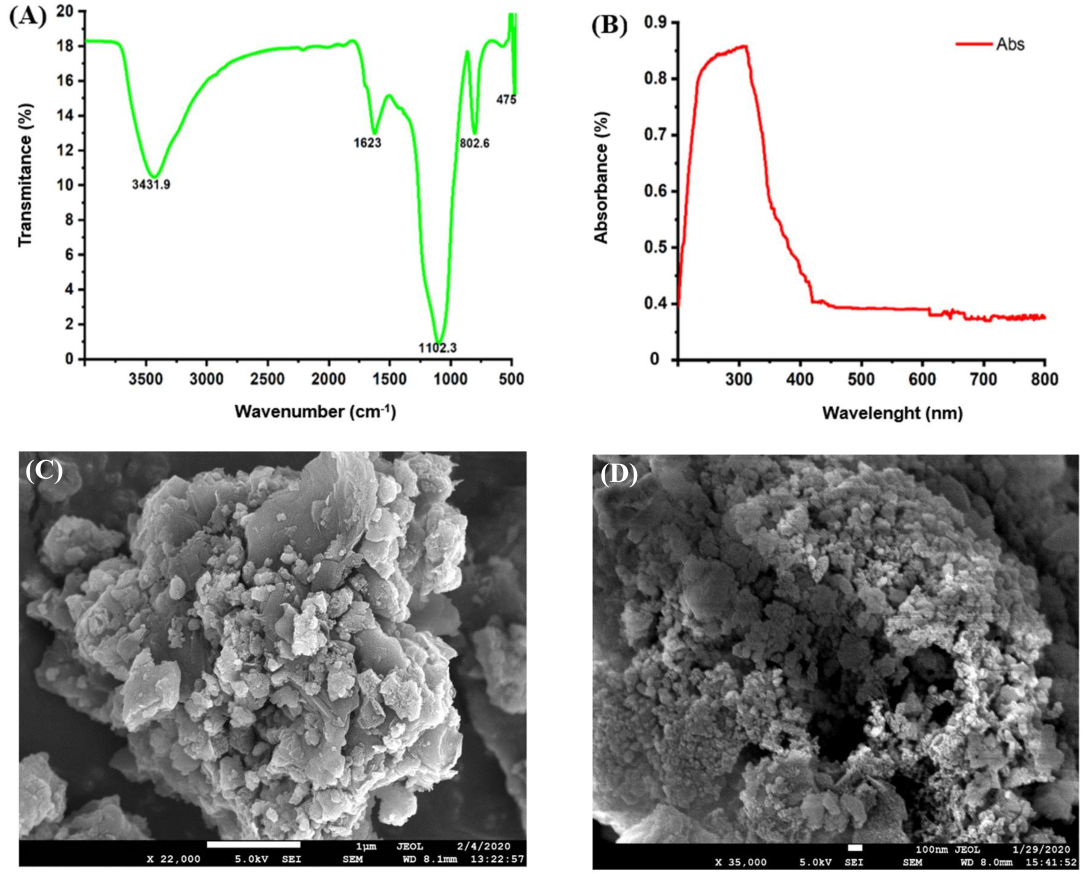

Figure 7 Characterization of prepared graphene by (A) FTIR, (B) UV-Vis, (C-D) FESEM images.

Figure 7 (B) shows the change in n-π* in C=O bonds, leading to the absorption closer to 300- 400 nm. A conversion happens from π-π* in C=C bonds, sp^2 hybridization in carbon core [41,31]. The leading cause for the variations in CNP assets is various preparation techniques or carbon forerunners [32]. It is crystal clear from Figure 7(C), (D) that the obtained graphene has a honeycomb structure, also having a spherical but irregular shape [33]. Carbon, oxygen, and silicon are present by 61.73,30.57 and 7.71 atomic %, respectively.

Table 5 Comparison of the current study with the existing ones for the preparation of graphene Nanoparticles.

Method	Outcomes	References
Micromechanical cleavage	Single-layer up to 300nm size	[5]
Ball milling	100 nm crystalline size	[38]
CVD	Graphene with sharp edges	[19]
Ultrasound-Assisted Method	Graphene of Crystalline size 73.3 nm	[42]
High-power probe sonication	FLG flakes ranged from 200 nm to 2 µm	[43]
Microwave furnace process	Graphene of crystalline size 42.5 nm	Present study

The above table shows the comparison of different methods that were used to produce the graphene nanoparticles with the current study. So, it's evident that the formation of graphene Nanoparticles using the microwave furnace process is suitable for future prospective.

4. Conclusion

Successful optimization of the microwave process is done for the synthesis of graphene with rice husk. The presence of graphene is justified by XRD, UV-vis, and FTIR characterization. The process optimization is completed, and the model is suggested for future perspective as the *p*-value is significant. As the pred-R^2 value is 0.9756, it is revealed that the model, along with its predicted values, of the output variable can be used for future work. The temperature has a high impact on the crystalline size of graphene, followed by ferrocene weight and weight of rice husk. The predicted minimum value of crystallite size of graphene is 36.72 nm obtained from the RSM model. The optimized parametric conditions to minimize the crystalline size are at a Weight of ferrocene 57.86 gm, Rice husk powder 79.15 gm, and Furnace temperature of 792.58 °C. The accuracy of the suggested model is confirmed by the confirmatory run by which crystalline size 40.24 nm was obtained. RSM looks to be a helpful technique for the optimization of process variables.

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