



Effects of Carbonization Parameters on the COD Reduction of Rhodamine B Dye Aqueous Solutions Using *Elaeis guineensis* Frond Fiber

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PAPER INFO

Paper history:

Received 16 July 2015

Accepted in revised form 23 November 2015

Keywords:

BET surface area

Carbonization duration

Carbonization temperature

Heating rate

Nitrogen gas flow rate.

ABSTRACT

The effects of various carbonization parameters on the COD reduction of Rhodamine B dye aqueous solutions using carbonized *Elaeis guineensis* frond fiber (EGFF) chars have been studied experimentally. The adsorbent with the particle size of <45 µm has been carbonized at temperature from 500-900 °C with carbonization duration of 1-3 h at a heating rate of 10-30 °C/min and nitrogen gas flow rate of 100-500 cm³/min. Carbonization temperature, carbonization duration, heating rate and nitrogen gas flow rate were significantly affecting the carbonization process. Statistical analysis-response surface methodology (RSM)- face centered composite design (FCCD) was used to obtain the optimal carbonization conditions. The optimum condition for carbonization of EGFF was obtained at carbonization temperature of 899 °C, carbonization duration of 2.7 h, heating rate of 10 °C/min, and nitrogen flow rate of 243 cm³/min with 98.88 % of COD reduction of Rhodamine B

doi:10.5829/idosi.ijee.2016.07.02.10

INTRODUCTION

Activated carbon has played a crucial role in the chemical, pharmaceutical and food industries due to well-developed pore structures and high internal surface area. Activated carbons can be prepared from various precursors with high carbon content and low levels of inorganic compounds [1]. The use of agricultural by-products such as bagasse [2], cogongrass [3], rice husk [4], sawdust [5] etc. as adsorbent has been gaining attention recently because of availability and abundant of materials, low cost, easy processing, and waste minimizing [6].

Oil Palm (*Elaeis guineensis*) is nurtured at an enormous scale as a source of oil in West and Central Africa (where it is originated), and in Malaysia, Indonesia and Thailand [7]. In Malaysia, oil palm is one of the most vital commercial crops with world production of 19.22 million tons in year 2013 [8]. The growth of oil palm plantation in Malaysia has generated large amounts of vegetable waste, generating problems in replanting operations, and tremendous environmental concerns [7].

Among various fibrous components of the oil palm tree i.e. trunk, frond, fruit bunch, frond fiber is the longest with an average length of 1.59 mm which is longer than that of most hardwood fibers [7]. Owing to the important availability of the fronds and its high lignin content, the present study utilizes *Elaeis guineensis* frond fiber (EGFF) as adsorbent for the treatment of Rhodamine B dye aqueous solutions.

In principle, activated carbon can be prepared using physical activation and chemical activation. In physical activation, a raw material is first carbonized and then activated using steam, air or carbon dioxide. In the chemical activation, the carbonization step and activation step are carried out simultaneously, with the precursor being mixed with chemical activating agents, as dehydrating agents and oxidants [1]. Carbonization converts organic materials to carbon through thermal conversion process [1, 9]. The carbonization process is also known as aromatic growth and polymerization process, where aromatic is the essential building blocks for carbon [10]. Carbonization temperature, carbonization duration, heating rate, and nitrogen gas

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flow rate are the crucial parameters that affect the Brunauer-Emmett-Teller (BET) surface area of char produced.

The impact of textile wastewater on the environment has been traditionally of immense concern because of its high variation in composition with intense color, varying pH values, high chemical oxygen demand (COD) and relatively low biodegradability with large amount of suspended solids and dissolved salts. COD is used to measure the total quantity of oxygen consuming substances in the complete chemical breakdown of organic substances in water. High COD concentration in water bodies may signify an oxygen deficiency, and aquatic organisms are consequently repelled [2]. Researchers should not only emphasize on the color removal, but also COD reduction of the dye aqueous solutions.

Most previous studies [1, 11, 12, 13] used the univariate method to study the effect of carbonization process on the properties of adsorbent. This might not achieve the real optimal operating conditions. The present study uses response surface methodology (RSM)-face centered composite design to develop, improve, optimize and study the interactions of two or more variables of the carbonization process [14, 15]. The adsorbent was characterized using surface area and pore size analysis, fourier-transform infrared (FT-IR) and scanning electron microscope (SEM).

MATERIALS AND METHODS

Materials

EGFF was obtained from a plantation in Nibong Tebal, Penang, Malaysia. The bark of the frond was removed and cut into pieces. The frond was then cleaned and dried under sunlight. Dried EGFF was ground to fine powder and thorough washed using boiling distilled water until residual solution turned clear. It was then dried in an oven at 100 °C and sieved to attain particle size of <45 µm.

Rhodamine B (C.I. number: 45170; molecular formula: C₂₈H₃₁N₂O₃Cl; molecular weight: 479.02 g/mol; brand: Sigma-Aldrich) was used in the present work (Figure 1) [16]. Distilled water was used throughout the study to prepare the Rhodamine B dye aqueous solutions with the concentration of 200 mg/L.

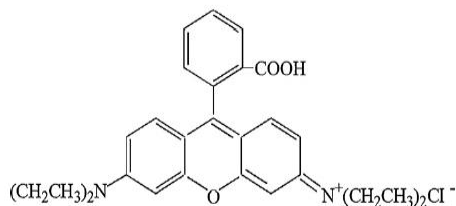


Figure 1. Molecular structure of Rhodamine B

Carbonization process

The dried EGFF with the particle size of <45 µm was carbonized at various temperature (500-900 °C), duration (1-3 h), heating rate (10-30 °C/min), and nitrogen gas flow rate (100-500 cm³/min). The char (EGFF after carbonized) was then crushed and again passed through the sieve of <45 µm.

Adsorption procedure

Batch experimental design using RSM was conducted in 250 mL Erlenmeyer flasks containing 100 mL Rhodamine B dye aqueous solutions (200 mg/L), 0.5 g char, shaking speed 150 rpm, shaking duration 24 h. The solution pH was adjusted using 0.1 M HCl and 0.1 M NaOH. After adsorption, the solution was centrifuged at 4000 rpm for 30 min. The dye concentration of the supernatant was analyzed using a spectrophotometer (Model DR2800) at λ_{max} 547 nm. The percentage of COD reduction of Rhodamine B dye was calculated using

$$\text{COD reduction(\%)} = 100 \times \left(\frac{\text{COD}_0 - \text{COD}_e}{\text{COD}_0} \right) \quad (1)$$

where COD₀ and COD_e are the initial and final COD concentrations, respectively.

Experimental design

RSM was used to study the effect of four factors, namely carbonization temperature A₁ (500-900 °C), carbonization duration A₂ (1-3 h), heating rate A₃ (10-30 °C/min) and nitrogen gas flow rate A₄ (100-500 cm³/min) on COD reduction of Rhodamine B dye aqueous solutions.

The response Y (COD reduction of Rhodamine B) is a function of the levels of independent variables:

$$Y = f(A_1, A_2, A_3, A_4) + \varepsilon \quad (2)$$

where ε is the error observed in the response.

The expected response is:

$$E(Y) = f(A_1, A_2, A_3, A_4) = \eta \quad (3)$$

and the surface area is :

$$\eta = f(A_1, A_2, A_3, A_4) \quad (4)$$

where η is the response surface.

Experimental data was analyzed to fit second-order model:

$$\eta = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum \sum_{i < j} \beta_{ij} x_i x_j \quad (5)$$

where β_0 , β_i , β_{ii} , and β_{ij} are regression coefficients, x_i is coded variable.

The relationship between coded variable and natural variable is

$$x_i = \frac{[\text{natural variable (high level + low level)}] \div 2}{(\text{high level} + \text{low level}) \div 2} \quad (6)$$

Char characterization

Surface area and pore size of the char was characterized using surface area and pore size analyzer (model: NOVA 2200e). The functional groups in a molecule of the adsorbent was obtained using FTIR spectroscopy (model: Thermo scientific FTIR-Is10) within the range of wavelength region between 400-4000 cm^{-1} . The morphologies and the surface structure of the adsorbent before and after adsorption were obtained using a scanning electron microscope (model: Leo supra 50 VP Field Emission SEM equipped with an Oxford INCA 400 Energy Dispersive X-ray Microanalysis (EDS) system).

RESULTS AND DISCUSSION

FTIR analysis

Functional groups contributed to the adsorption process of raw EGFF and char were examined. The spectra are shown in Figure 3. The FTIR spectrum of raw EGFF (Figure 3a) indicates the peaks located at 3418.91 cm^{-1} identical to the N-H group, 2921.29 cm^{-1} is C-H group, 1737.01 cm^{-1} is C=O stretch, 1636.81 cm^{-1} is C=C group, 1426.21 cm^{-1} refers to $-\text{CH}_2$ (alkyl), 1376.19 cm^{-1} is C- CH_3 group, 1247.67 cm^{-1} is CH in plane bending, and 1053.62 cm^{-1} is C-O (anhydrides).

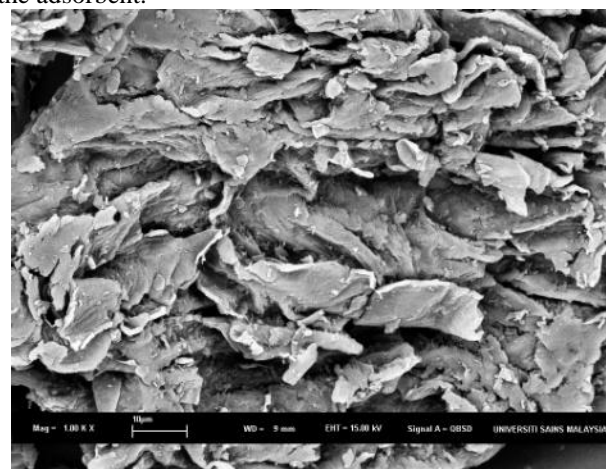
The FTIR spectrum of char (Figure 3b) indicates the peaks located at 3386.19 cm^{-1} identical to the presence of N-H group, 2918.54 cm^{-1} is C-H group, 2846.34 cm^{-1} is two bands of aldehyde, 2361.01 cm^{-1} is $\text{C}\equiv\text{C}$ (alkynes), 2340.64 cm^{-1} is $-\text{COOH}$, 1426.61 cm^{-1} is $-\text{CH}_2$ (alkyl), 1121.66 cm^{-1} is amines group, 874.51 cm^{-1} is CH out-of-plane deformation (two bands), and 808.22 cm^{-1} is out-of-plane C-H derivatives.

After carbonization process a few functional groups have been formed i.e. $\text{C}\equiv\text{C}$ (alkynes), $-\text{COOH}$, amines group, CH out-of-plane deformation (two bands), and out-of-plane C-H derivatives. It is suggested that, these groups are important in the bond formation among carbon atoms.

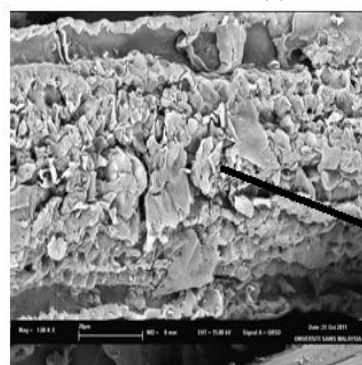
SEM analysis

The morphology of raw EGFF and char with magnification of 1000x is shown in Figure 2a and 3b, respectively. After the carbonization process, the surface of the adsorbent becomes uneven and rough.

Uneven and rough surface increased the surface area of the adsorbent which increase the adsorption efficiency of the adsorbent.



(a)



(b)

Figure 2. SEM micrograph of (a) raw EGFF (b) char

Statistical analysis

Four independent variables i.e. carbonization temperature A_1 , carbonization duration A_2 , heating rate A_3 and nitrogen gas flow rate A_4 affect the COD reduction of Rhodamine B dye. The effect of interaction between independent variables was studied in order to achieve real optimal operating condition. The levels of each independent variable used in this experiment are given in Table 1

The results of 29-run using face centered composite design (FCCD) with four factors covering all possible combinations for various selected levels. The runs are distributed as $24=16$ factorial points, 8 axial points, and 5 replicates at the center. All runs were conducted randomly to prevent unexpected errors in the observed response. The range of COD reduction varied from 14.27-99.54 %. Table 2 shows the results of analysis of variance ANOVA for percentage of COD reduction. It shows that the main linear effect is significant for all selected factors (A_1 , A_2 , A_3 , A_4).

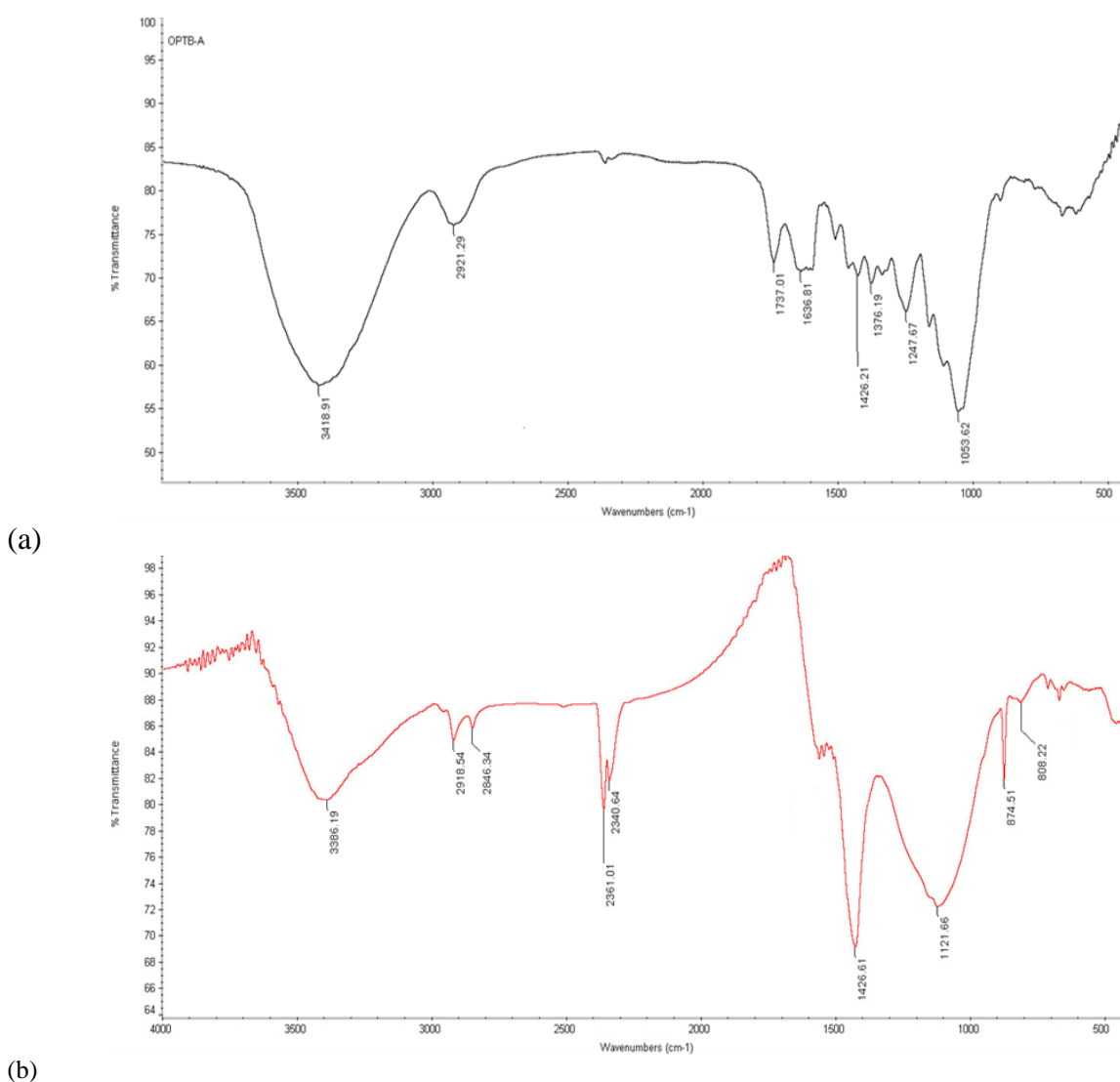


Figure 3. FTIR spectra of (a) raw EGFF (b) Char

The significance of the coefficient term is determined by the p values. Smaller p value shows the more significance of the coefficient term in the carbonization process [9, 17].

The quadratic contribution over the linear effect shows highly significant effect of carbonization temperature A_1 with a p value of 0.0007. Interaction between A_1 and A_2 , A_1 and A_4 , A_2 and A_3 , A_3 and A_4 show significant effect on the percentage of COD reduction of Rhodamine B dye. The regression model was fitted to the data and a model was formed (in coded unit).

$$\begin{aligned} \text{COD reduction (\%)} = & 27.28 + 24.12A_1 + 10.43A_2 - \\ & 6.98A_3 - 5.78A_4 + 29.50A_1^2 - 4.90A_2^2 - 5.88A_3^2 - \\ & 0.23A_4^2 + 10.09A_1A_2 - 4.65A_1A_3 - \\ & 7.39A_1A_4 + 6.11A_2A_3 + 1.41A_2A_4 + 4.25A_3A_4 \end{aligned} \quad (7)$$

Positive coefficients for each term are assigned to the synergistic effect of the factor on the % of COD

reduction, whilst the negative sign indicate the antagonistic effect of the factor on the % of COD reduction [9]. The regression model in Eq (7) is assured as the coefficient of determination value R^2 is 0.9269. This shows more than 92 % of the entire variation is represented by the regression model.

After the regression model was built, the decisive factor for % color removal was determined to obtain maximum of COD reduction. The optimum condition for carbonization of EGFF was obtained at carbonization temperature of 899 °C, carbonization duration of 2.7 h, heating rate of 10 °C/min, and nitrogen flow rate of 243 cm³/min with 98.88% of COD reduction. Authentication experiments were carried out by plotting to ensure the optimum conditions and the results for the predicted and experimental values of color removal are close to each

other (Figure 4). As can be seen that the data points were well distributed and close to a straight line which have the R^2 values of 0.9269. The results suggest an excellent relationship between the experimental and predicted values of the response, and the underlying assumptions of the above analysis are appropriate. The results also indicate that the selected quadratic model is adequate in assuming the response variables for the experimental data.

TABLE 1. Independence factors and levels used in statistical analysis

Factors	Levels	
	-1	1
A ₁ Carbonization Temperature (°C)	500	900
A ₂ Carbonization Duration (h)	1	3
A ₃ Heating Rate (°C/min)	10	30
A ₄ Nitrogen Gas Flow Rate (cm ³ /min)	100	500

Effect of Carbonization Temperature, Carbonization Duration, Heating Rate and Nitrogen Gas Flow Rate

Table 3 shows the BET surface area (S_{BET}) of char and % COD reduction of the Rhodamine B dye prepared under various carbonization temperatures, duration, heating rate and nitrogen gas flow rate. When the carbonization temperature increased from 500 °C to 900 °C the S_{BET} increased from 31.80-555.53 m²/g. The results show that at 900 °C the char has better developed pore structure as compared with that of 500 °C carbonization temperature char. This is because as carbonization temperature increases, polymerization reaction would further proceed. The diameter of char

TABLE 2. ANOVA for COD reduction of Rhodamine B dye.

Source	DF	Prob>F
Model	14	<0.0001
A ₁	1	<0.0001
A ₂	1	0.0012
A ₃	1	0.0169
A ₄	1	0.0415
A ₁ ²	1	0.0007
A ₂ ²	1	0.4823
A ₃ ²	1	0.4011
A ₄ ²	1	0.9730
A ₁ A ₂	1	0.0024
A ₁ A ₃	1	0.1107
A ₁ A ₄	1	0.0171
A ₂ A ₃	1	0.0420
A ₂ A ₄	1	0.6134
A ₃ A ₄	1	0.1423
Residual	14	
Total	28	
R-squared	0.9269	

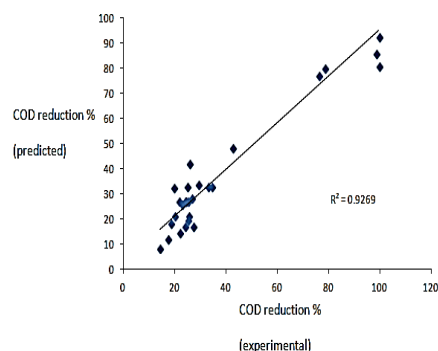


Figure 4. Plot of experimental and predicted values for COD reduction

TABLE 3. BET surface area (S_{BET}) of char and % COD reduction of the dye.

Carbonization temperature (°C)	Carbonization duration (h)	Heating rate (°C/min)	Nitrogen gas flow rate (cm ³ /min)	S_{BET} (m ² /g)	% COD reduction
Effect of carbonization temperature					
500	1	10	100	31.80	29.27
900	1	10	100	555.53	98.62
Effect of heating rate					
900	1	10	100	555.53	98.62
900	1	30	100	398.23	25.77
Effect of nitrogen gas flow rate					
900	1	10	100	555.53	98.62
900	1	10	500	98.97	42.41
Effect of carbonization duration					
900	1	10	100	555.53	98.62
900	3	10	100	555.67	99.54

where Raw EGFF: S_{BET} = 3.60 m²/g

would decrease gradually and the micropores of char would develop, giving rise to increases in the S_{BET} [9]. The percentage of color removal of chars prepared at carbonization temperature of 500 °C and 900 °C, 1h carbonization duration, heating rate of 10 °C/min and nitrogen gas flow rate of 100 cm³/min once again show that higher temperature chars offer higher potential to produce activated carbon of greater adsorption capacity from EGFF.

When the heating rate was increased from 10-30 °C/min, the S_{BET} decreased from 555.53-398.23 m²/g. The carbonization process involves cleavage of C-H and C-C bonds to form reactive free radicals, molecular reassemble, thermal polymerization, aromatic condensation and elimination of H₂ [9, 10, 12]. Low heating rate can reduce adverse effects such as shrinkage, cracking and thermal stresses that may build up during carbonization. The high heating rate reduces the restricted effects of mass transfer and increases the decomposition of the biochar into liquid

product and the mechanical performance of C/C composites deteriorates [9, 18, 19].

A nitrogen gas flow rate of 100 cm³/min shows higher S_{BET} (555.53 m²/g), 98.62 % of COD reduction as compared to nitrogen gas flow rate of 500 cm³/min with S_{BET} (98.97 m²/g) 42.41 % of COD reduction. This is because the sweep gas removes the volatile products from char surfaces and reduces the secondary reactions such as repolymerisation and recondensation. Besides, the nitrogen flow rate affects the residence time of the adsorbent produced by pyrolysis. A rapid flow of 500 cm³/min of N₂ was believed to have cooled down the EGFF rapidly from the hot zone thus minimizing the carbonization reaction to occur [9].

CONCLUSIONS

In conclusion, increasing the carbonization temperature and carbonization duration resulted in an increase in the S_{BET} of char. Heating rate of 10 °C/min has higher S_{BET} (555.53 m²/g) value as compared to heating rate of 30 °C/min (398.23 m²/g). The char prepared under 100 cm³/min nitrogen flow rate exhibits higher BET surface area than that at 500 cm³/min. It is not necessary to have high nitrogen gas flow rate for better COD reduction. The carbonization process has effectively increased the BET surface area of the raw adsorbent by 99.35 %. Higher BET surface area resulted in efficient adsorbent in reducing COD (98.88 % of COD reduction). The present study suggested that nitrogen gas flow rate of <500 cm³/min is suitable for carbonization process.

ACKNOWLEDGMENTS

This study is supported by Ministry of Higher Education Malaysia under the program of MyBrain 15 and Universiti Sains Malaysia through RU-PRGS grant 1001.PTEKIND.845029.

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Persian Abstract

DOI: 10.5829/idosi.ijee.2016.07.02.10

چکیده

تأثیر پارامترهای مختلف کربنی شدن در کاهش COD از رنگ رودامین B محلول های آبی با استفاده از فیبر برگ نخل روغنی (EGFF) کربونیزه شده، به طور تجربی مورد مطالعه قرار گرفت. جاذب با اندازه ذرات کمتر از چهل و پنج میکرومتر در دمای پانصد تا نهصد درجه سانتیگراد با مدت زمان کربنیزه شدن یک تا سه ساعت در نرخ حرارت از ده تا سی درجه سانتی گراد بر دقیقه نرخ دبی گاز نیتروژن از صد تا پانصد سانتی متر مکعب بر دقیقه، کربنیزه شد. دما، مدت زمان، میزان حرارت و دبی جریان گاز نیتروژن به طور قابل توجهی بر فرآیند کربنیزه شدن موثر می باشند. روش سطح پاسخ تحلیل آماری (RSM) (face centered composite design (FCCD) - برای به دست آوردن شرایط مطلوب کربنیزه شدن استفاده شد. شرایط بهینه برای کربنیزه شدن EGFF در دمای هشتصد و نود و نه درجه سانتیگراد، طول مدت دو ساعت و چهل دقیقه، میزان حرارت از ده درجه سانتیگراد بر دقیقه، و سرعت جریان نیتروژندویست و چهل و سه سانتی متر مکعب بر دقیقه با نود و هشت و نه دهم درصد کاهش COD از رودامین B به دست آمد.