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# Characterisation of a new mesoporous active nanocarbon obtained by hazelnut shell charcoal

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## Abstract

In this study, fine granulated commercial hazelnut shell charcoal was mixed together with SBA-15 consist of family of mesoporous silica nanoparticul (MSN) as a template, and then half of it carbonised again together in furnace at 900 °C in nitrogen atmosphere (FC). Other half of it is used without carbonisation (F). Obtained ordered porous carbon material (FC) and obtained other carbon material (F) from hazelnut shell charcoal were characterised by thermal gravimetry (TG/DTA), $N_2$ adsorption-desorption isotherm, X-ray powder diffraction, and SEM (scanning electron microscopy).

As a result, SBA-15 showed very good template properties to obtain ordered mesoporous carbon material. Surface area ordered pore diameter, and pore volume of FC were found to 9005.732 $m^2/g$, 3220.2 nm and 1.003 $cm^3/g$, respectively. Obtained ordered mesoporous carbon material (FC) should be suitable to use as activated nanocarbon material.

**Keywords:** Hazelnut shell charcoal, carbonisation, ordered porous carbon material, activated carbon, SBA-15, template

## 1. Introduction

Active carbon has quite a big surface area, is an excellent amorphous adsorbent. It is produced by using natural sources that contain carbon (root, stem, fruit, seed, shell of plants, etc.), burning fossil fuels (soot), and coal. In this purpose, any carbon source should be carbonised first, then activated with chemically.

Generally, the production of activated carbon is carried out in two stages: activation and carbonization. The activation process is divided into two types: physical activation and chemical activation. In physical activation, activated carbon with a lower surface area, typically used in large-scale industrial applications, is produced at a lower cost. In the chemical activation method, activated carbon with a high surface area, which finds more specific application areas, is obtained [1,2]. In recent years, ordered porous carbon materials (OPCM) have critical applications in many important fields because of their porous structure and huge specific surface area. Some specific properties of ordered porous carbon materials like low density, chemical stability, strong mechanical strength, and very good electrical conductivity provide for using them in specific and advanced technological fields. They get extensive usage in areas especially, as an electrode in electrochemistry, hydrogen storage, heterogeneous catalysis, gas adsorption and as an adsorbent in separation processing. Ordered porous materials are classified based on pore radius (a) microporous (pore size <2 nm), mesoporous (pore size >2 nm<50 nm) and macroporous (pore size > 50 nm).

One of the important agricultural products of our country is hazelnut. After hazelnuts are harvested and cracked of the inner shell, the remaining hazelnut shells cannot be utilized for any significant purpose. Various studies have been conducted to produce activated carbon from hazelnut shells; however, even if the desired surface area is achieved, the required hardness has not been attained [3]. In Turkey, in spite of there are considerable scientific articles about producing commercial activated carbon [4,5], there is no scientific article about ordered porous activated carbon.

In 1992, researchers at the Mobil Group discovered a family of large, regularly mesoporous silica/aluminosilicate molecular sieves (M41S) and began producing them in their laboratories [6,7]. This discovery led to mesoporous materials becoming a focal

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point of interest in the scientific community[8–11]. In 1998, SBA-15 (Santa Barbara Mesostructure No. 15) with pore sizes ranging from 4.6 nm to 30 nm was produced. SBA-15 mesoporous material not only possessed larger pore sizes but also demonstrated thermal, mechanical, and chemical stability, making it a preferred option for use as a catalyst. Uniformly porous, order hexagonal SBA-15 with pore sizes up to 30 nm has been synthesized using amphiphilic triblock copolymers in a strongly acidic environment [12–14].

SBA-15 was synthesized according to the literature [15], and its surface properties were elucidated. Fig. 1 shows the porous structure of SBA-15.

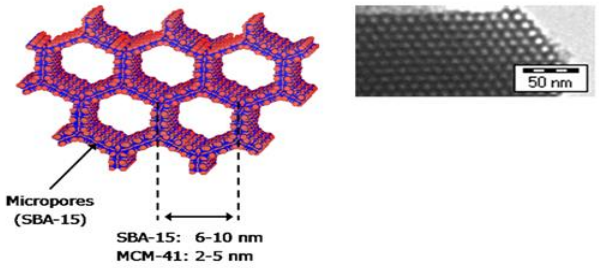


**Figure 1.** Representation of the pore shape and structure of MCM-41 and SBA-15 (Anonymous, 2018).

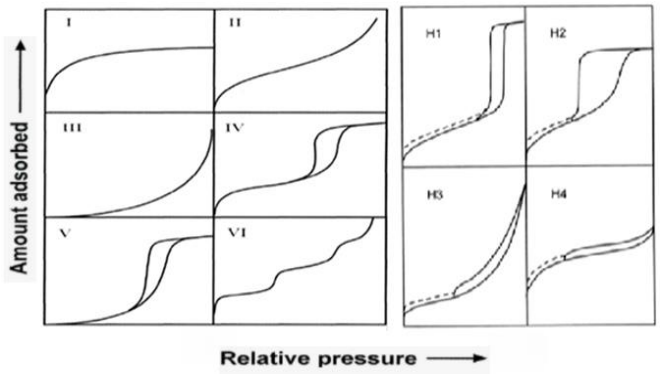


**Figure 2.** According to the IUPAC classification, there are six types of isotherms [16]

These six types of isotherms are shown in Fig. 2. Here, Type I corresponds to microporous, Type II, III, and VI correspond to non-porous or macroporous, and Type IV and V correspond to mesoporous materials [17].

Adsorption-desorption isotherms are also related to the pore structures of the materials. $N_2$ adsorption-desorption isotherm belongs to SBA-15 is given in Fig. 3. According to this isotherm, SBA-15 shows type IV isotherm curve so, it has mesoporous. Besides, porous structure of SBA-15 is relevant to type H1. Type H1 shows cylindrical or spherical porous shapes in porous materials.

In a review published by Lee and colleagues [18], they examined the scientific papers published over the past decade on the synthesis of porous carbon materials up until 2006.

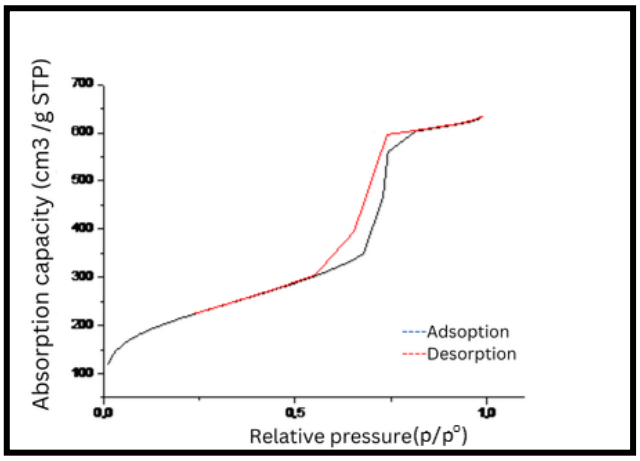


**Figure 3.** $N_2$ adsorption-desorption isotherm of SBA-15.

In this review, it is reported that, porous carbon materials have been synthesized using several different experimental methods, with various pore sizes and pore structures. For example, microporous activated carbons were synthesized via direct activation processes, while regular microporous activated carbon materials were synthesized using a zeolite template. Irregular mesoporous carbon materials have been synthesized using several different methods [15]. These include catalytic activation with various metals, carbonization of polymer/polymer mixtures, carbonization of organic aerogels, and template synthesis using silica nanoparticles. Regular mesoporous carbon materials with various pore sizes have been synthesized using mesoporous silica materials such as MCM-48, HMS, SBA-15, MCF, and MSU-X as templates. Hierarchically ordered mesoporous carbon materials have been synthesized using silica templates prepared in various pore sizes. It has been demonstrated that these mesoporous carbon materials can be successfully used as adsorbents for the adsorption of large (bulky) pollutants, as electrodes for supercapacitors and fuel cells, as hosts for enzyme immobilization, and for hydrogen storage [19].

Eftekhari and Fan (2017), reported methods for obtaining regular mesoporous carbon and their uses, particularly in various electrochemical power sources such as ultracapacitors, supercapacitors, battery systems, fuel cells, and electrochemical hydrogen storage systems in a review [20].

In this study, SBA-15 was used as a template to obtain ordered mesoporous carbon material with higher-surface area from hazelnut shell charcoal. SBA-15 forms a template that imparts its porous structure to the carbon material. So, fine granulated hazelnut shell coal was mixed with SBA-15, and then half of it was carbonised together in furnace at 900 °C in nitrogen atmosphere (FC). Other half of it is used without carbonisation (F). Obtained ordered porous carbon materials (FC and F) from hazelnut shell coal were characterised by thermal

gravimetry (TG/DTA), $N_2$ adsorption-desorption isotherm, X-ray powder diffraction, and SEM (scanning electron microscopy).

## 2. Materials and methods

### 2.1. Materials

The hazelnut shell charcoal was obtained from Nuts Carbon company. SBA-15 (Santa Barbara Amorphous-15) was synthesized according to the literature [15]. 48% HF (hydrofluoric acid) was obtained from Alfa-easier and used without further purification. The following instruments were used for the experiments and analyses: Precision Balance (OHAUS PA 214C, with a sensitivity of 0.0001 g), Oven (WiseVen Fuzzy Control System), Carbonization Furnace (Protherm furnace), XRD (Europe XRD 600), Nitrogen Adsorption-Desorption Device (MicroActive for TriStar II Plus Version 2.02), and TG/DTA Device (SII EXSTAR6000 TG/DTA6200). SEM images (JEOL6610).

### 2.2. Methods

The hazelnut shell charcoal was ground in a blender and sieved through a 35-mesh sieve. 10.00 g of the charcoal passing through the sieve was weighed and gradually added to a mixture of 5.00 g SBA-15 and 50 mL of water, which was stirred at a speed of 250 rpm. The final mixture was stirred with a magnetic stirrer under a reflux condenser in a reaction flask and boiled for approximately 12 hours. The water from this mixture was evaporated, and the residue was transferred to a shallow ceramic crucible and dried in an oven at 250 °C.

The obtained solid (carbon-silica mixture) was weighed (10.32 g) and divided into two portions. 5.00 g was weighed from the first portion of the carbon-silica mixture (CSM1). CSM1 was subjected to carbonization in a furnace under $N_2$ atmosphere, with temperature control (initial temperature: 20.0 °C), ramp rate: 30.0 °C/hour, and final temperature: 900.0 °C for 20 minutes. The carbonized CSM1 was weighed on a precision balance (4.8 g) and then treated with 48% HF, stirred at room temperature for 24 hours to dissolve the silica template (SBA-15). The mixture was filtered to remove all dissolved silica using a plastic funnel and blue band filter paper. The solid remaining on the filter paper was washed five times with deionized water at ambient temperature. The obtained solid carbon material was dried in an oven at 110 °C for 24 hours and then weighed (3.2 g). This solid carbon material was labeled as CF.

The second portion of the carbon-silica mixture (CSM2) was directly treated with 48% HF without undergoing carbonization, resulting in the removal of the silica template (SBA-15). This portion was labeled as F. The physicochemical and surface properties of CF and F were compared in this paper.

SEM analyses, N2 adsorption-desorption isotherms, XRD analysis, and TG/DTA analyses were performed on the non-carbonized (F) and 900 °C carbonized (CF) carbon materials. The synthesis of SBA-15 was carried out according to the literature [15], Structure and surface properties of FC and F were examined, and the results are presented in Table 1.

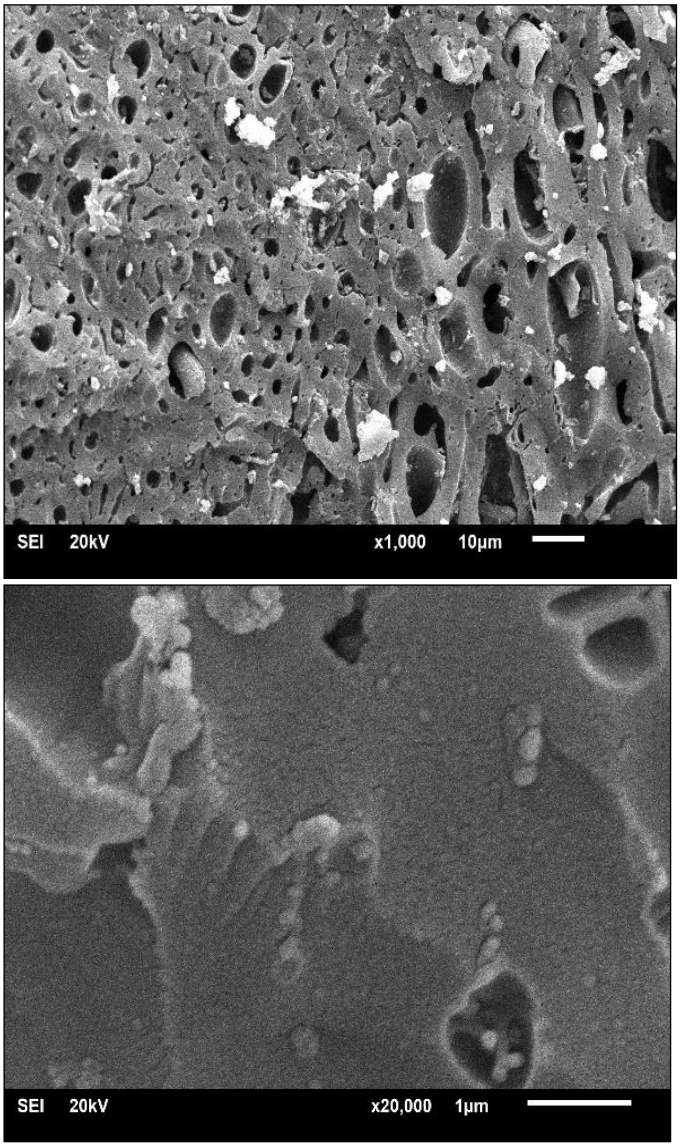


**Figure 4.** SEM image of FC

## 3. Results and discussion

The final yield of FC was calculated 96% after carbonisation at 900 °C and removal of the silica template (SBA-15) by using HF. The physical and surface properties of the obtained ordered mesoporous nanocarbon material (FC) have been elucidated. The reason for carbonisation at 900 °C was to maximize template properties of SBA-15 and to integrate well with hazelnut shell charcoal. Physical and surface properties

of FC were compared with the carbon material (F) that was obtained without carbonization.

### 3.1. SEM (Scanning Electron Microscope) analyses

Fig. 4 shows the SEM image of the ordered mesoporous carbon material (FC) obtained from hazelnut shell charcoal carbonized at 900 °C in the presence of the silica template (SBA-15). In the SEM image of FC, ordered micropores and mesopores are clearly visible.

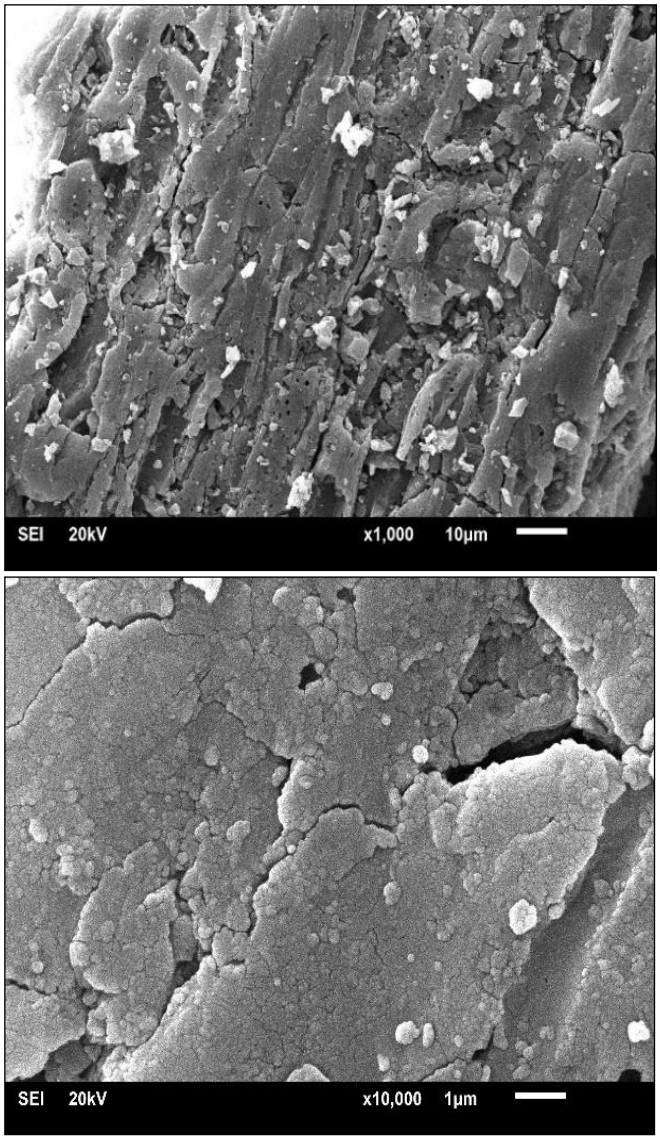


**Figure 5.** SEM image of F

Fig. 5 shows the SEM image of the carbon material (F) obtained from the non-carbonized hazelnut shell charcoal treated with the silica template. In these images, some porosity can be observed, although the pores are not as ordered or abundant as in FC.

In both SEM images, silica that has not been sufficiently removed from the carbon material with HF that visible as white. But at the same time, mesopore structure of FC was seen in SEM image that the most important goal of this paper was to obtain ordered mesoporous carbon material.

### 3.2. XRD analysis

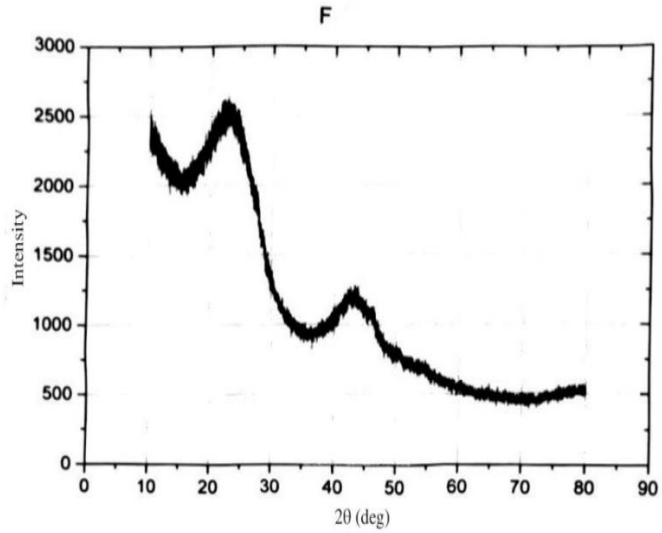


**Figure 6.** XRD pattern of the non-carbonized carbon material (F)

Fig. 6 shows the XRD pattern of the carbon material obtained from hazelnut shell charcoal, which was mixed with the silica template but not carbonized.

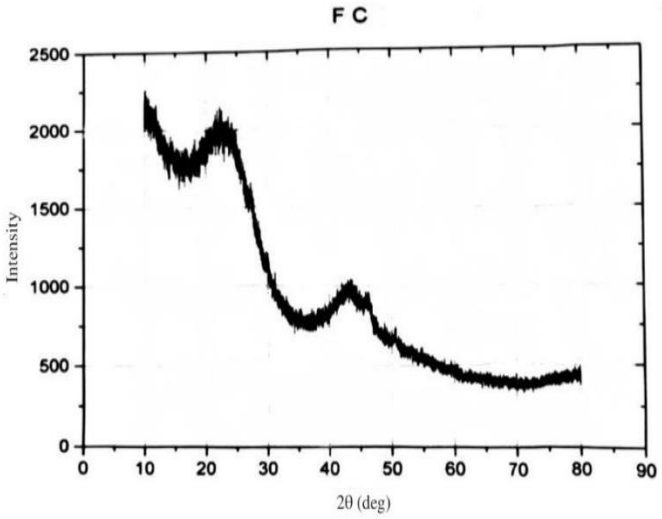


**Figure 7.** XRD pattern of the carbon material carbonized at 900 °C (FC)

Fig. 7 shows the XRD pattern of the ordered mesoporous carbon material (FC) obtained from hazelnut shell charcoal carbonized at 900 °C in the presence of the silica template.

The presence of broad peaks in the XRD patterns indicates that the carbon material is ordered and mesoporous. The 2θ angle shows the (002) plane at approximately 25° and the (004) plane at approximately 45°. According to the literature, these peaks are the ones corresponding to pure carbon (graphite) [19]. When comparing both XRD graphs, it can be observed that the carbon material obtained by carbonization with SBA-15 at 900 °C exhibits a lower density. This indicates that the carbon material exhibits a denser and more homogeneous porosity.

### 3.3. $N_2$ adsorption-desorption (BET) isotherms

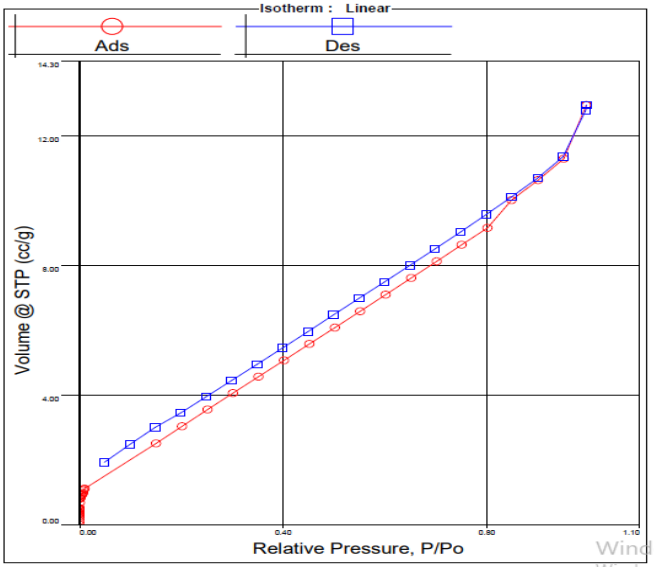


**Figure 8.** $N_2$ adsorption-desorption isotherm of the non-carbonized carbon material (F)

The $N_2$ adsorption-desorption isotherms of the non-carbonized carbon material (F) are shown in Fig. 8. According to these results, the surface area is 9.828 $m^2/g$, the total pore volume is 0.02 $cm^3/g$, the pore diameter is smaller than 2050.9 Å (P/P0: 0.99531), and the average pore volume is 40.7404 Å. Surface area, pore volume, and pore diameter of FC and F were given in Table 1.

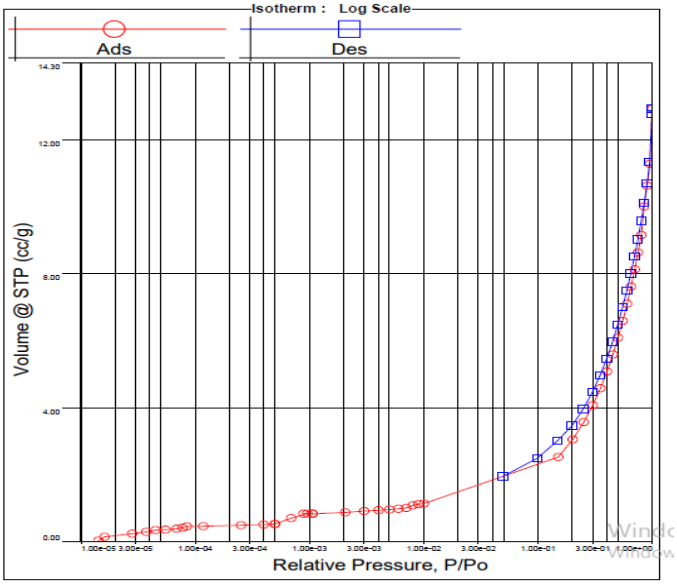


**Figure 9.** $N_2$ adsorption-desorption isotherm of the carbonized carbon material (FC).

The $N_2$ adsorption-desorption isotherms of the carbonized carbon material (F) are shown in Fig. 9. According to these results, the surface area is 9005.732 $m^2/g$, the total pore volume is 1.003 $cm^3/g$, the pore diameter is smaller than 3220.2 Å.

It was seen that the surface area of ordered mesoporus FC (9005.732 $m^2/g$) is bigger than even commercial amorphous activated carbon (937 $m^2/g$) [22].

**Table 1:** BET Analysis Results of SBA-15 [21]

| Sample | Surface Area ($m^2/g$) | Pore Diameter (nm) | Pore Volume ($cm^3/g$) |
|---|---|---|---|
| SBA-15 | 786,8381 | 5,0763 | 0,9614 |
| F | 9.828 | 2050,9 | 0.0200 |
| FC | 9005,732 | 3220,2 | 1,003 |

### 3.4. TG/DTA analysis

TG analysis of F and FC were performed by atmospheric pressure and rising temperature as 10 °C/min. between 30 °C–900 °C.

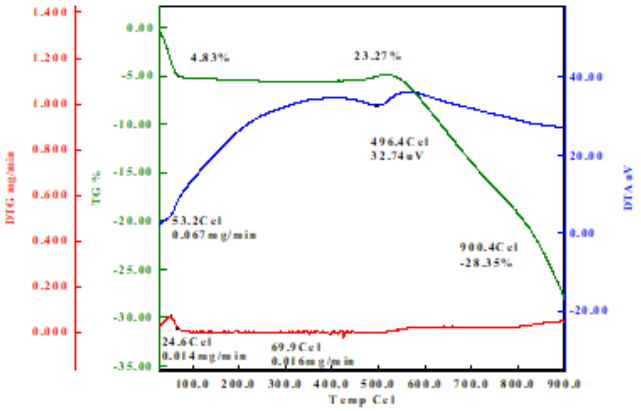


**Figure 10.** TG-DTA graph of FC (the carbonized carbon material at 900 °C)

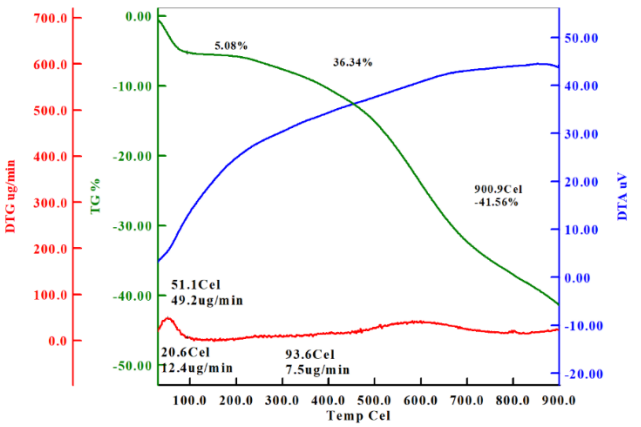


**Figure 11.** TG-DTA graph of F (the non-carbonized carbon material).

Upon examining the TG-DTA curves of the carbon material carbonized at 900 °C (FC) and the non-carbonized carbon material (F), it is evident that both exhibit the characteristic thermal behavior associated with porous carbon materials [23]. Total mass loss was observed as 28.35 % for FC, and 41.46 % for F, so total mass loss with increasing temperature is lower for FC than F. It can be said that, F still has some non-carbonous purities. Most probably, FC has a little silicious purities that couldn't be removed by HF treatment.

## 4. Conclusions

In this study, ordered mesoporous carbon material was obtained from hazelnut shell charcoal.

The ground raw hazelnut shell charcoal was treated with SBA-15 at 250 °C in an air atmosphere (F) and at 900 °C in a nitrogen atmosphere (FC), seperately. Their physicochemical and surface properties were investigated. The yield of FC was found 96 % after all experimental treatment. The surface area and nature of porosity of F and FC was clarified. Structure of FC was shown very good ordered mesoporous carbon material properties.

## Declaration of ethical code

The authors of this article declare that the materials and methods used in this study do not require ethics committee approval or legal special permission.

## Conflicts of interest

The authors declare that they have no conflict of interest.

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