

## Characterization of activated carbon produced from pistachio shell at different temperatures

H. Dolas

*Harran University, Hilvan Vocational School, Program of Occupational Health and Safety, Sanliurfa 63900, Turkey*

Accepted July 14, 2022

Activated carbons (ACs), which are used as active surfaces in an adsorption process, make the latter successful owing to their high surface area and high volume in terms of micropores. The characteristics of the method used in AC production help to improve the porosity structure of AC and to increase the surface area.

In this work, the effect of different temperatures and H<sub>2</sub>SO<sub>4</sub> on the surface area and porosity structure in obtaining AC from pistachio shells was studied. For this purpose, the collected pistachio shells were kept in 10% NaCl and 10% H<sub>2</sub>SO<sub>4</sub> solution for 24 h. At the end of the period, the material was carbonized for 45 min at 3 different temperatures (500, 700 and 800 °C). The obtained ACs were characterized using a surface area and pore size analyzer, Fourier transform infrared (FT-IR) and scanning electron microscopy (SEM). According to the results obtained, it was found that the AC-800 has the highest surface area compared to the other obtained ACs. So, it had a BET surface area of 2093.063 m<sup>2</sup>/g, and its micropore volume was 1.053 cc/g. All functional groups in the structure of raw pistachio shells were destroyed for pore formation and the resulting porosity is supported by FT-IR and SEM images. With this new method, ACs with a high surface area were obtained and it was understood that the use of H<sub>2</sub>SO<sub>4</sub> decreased the surface area while increasing the temperature increased both the surface area and micropore volume.

**Key words:** Agricultural waste, Carbonization, Activated carbon, Surface area, Micropore volume.

### INTRODUCTION

All living and/or inanimate beings maintain their existence in a certain relationship and cycle in this ecosystem, which we call the environment. As a result of developing technology and other formations, this cycle, which is in a certain order, is disrupted. One of the biggest factors in this deterioration, which is called environmental pollution, is the solid, liquid and gaseous waste. Every breakthrough made to respond to the increasing population and improve the quality of life has led to the development in technology. However, the gas, liquid and solid wastes of the factories established as a result of these developments pollute the air, soil and water, and it is seen that this pollution harms living life [1].

Adsorption is one of the low-cost and easy-to-apply ways to prevent this pollution [2, 3]. Adsorption is the process of chemically or physically adsorbing on the active solid surface (adsorbent) of all charged or uncharged ions and molecules dissolved in the liquid or gas phase. The success of the adsorption depends on the temperature, the physical and chemical state of the ion or molecule to be adsorbed, the ambient pressure and the properties of the active solid surface used. The properties of the active solid surface, especially the surface area and porosity, are of great importance in the adsorption

process. Generally, activated carbon (AC) is chosen as adsorbent in adsorption processes. AC is a kind of adsorbent produced from various carbon-structured materials and has a high surface area and a porous structure, the majority being micropores. Thanks to this porous structure, ACs have a high surface area as they can fit surfaces of thousands of square meters per unit weight.

Generally, the tendency is to use agricultural wastes, which are abundant, completely waste, and have a suitable porous structure by losing the hydroxyl and carboxyl groups in their structure, and also have a quality fiber structure in AC production. The use of agricultural wastes with abundant cellulosic and fibrous structure not only reduces the cost, but also contributes to waste management.

For a long time, various agricultural wastes such as wheat straw [4], banana peel [5], orange peel [6, 7], cane sugar [8], walnut shell [9], peanut shell [10], coconut shell [11], olives [12] were used in AC production [13].

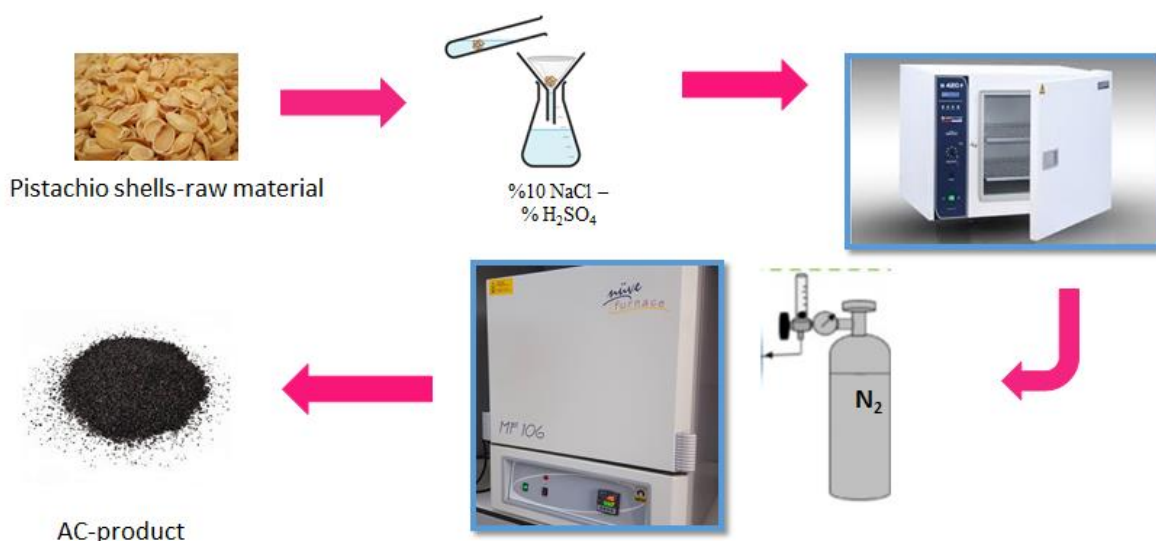
In a previous study, the effect of the use of salt as an activator on the surface area was shown. In this study, it was investigated how the use of acid as an activating agent affects the changes in properties such as surface area, micro, meso and macro porosity, thermal degradation and morphological appearance of ACs obtained from the fistic shell by applying different carbonization temperatures.

To whom all correspondence should be sent:  
E-mail: hacerdolas@harran.edu.tr

## EXPERIMENTAL

**Production of AC.** Pistachio shells (FK) were collected from the fields of Bozova district of Sanliurfa province, Turkey. The collected shells were first cleaned of their soft shell and coarse dirt. They were broken into large pieces and washed with tap water. 20 g of dried shells were weighed and poured into 10% NaCl solution in a 250 ml flask. It was kept in this solution for 1 day. Then, the filtered shells were poured into 10% H<sub>2</sub>SO<sub>4</sub> solution in a 250 ml flask and kept in this solution for 1 day. After the activation process, the filtered peels were thoroughly

washed with distilled water. They were dried in an oven at 80 °C and carbonized in a high-temperature muffle furnace at three different temperatures, 500, 700 and 800 °C for 45 minutes. This process was carried out in an atmosphere of N<sub>2</sub> gas. The carbonized shells were cooled to ambient temperature were again washed with distilled water to remove excess gas in the pores, and the dried shells were ground and sieved. ACs produced in this way were labeled as AC-500, AC-700 and AC-800 based on the temperature to which they were subjected.



**Figure 1.** The route of AC production.

### Characterization

**Surface analysis.** NOVA 4000e-Quantachrome surface area and pore size analyzer device was used to determine the active surface area and pore volume of the produced ACs. Before analysis, ACs were dried at 170 °C under vacuum overnight to open all pores on the AC surface. Based on the nitrogen adsorption method under cryogenic conditions, the adsorption isotherm was obtained at the end of the analysis process. Thanks to the application of this isotherm, the BET surface area [14], Langmuir surface area, pore width, pore volume and micropore surface area by DR method, adsorption energy [15] and BJH method [16] mesopore distribution of AC-800 were determined.

**Thermal analysis.** Thermal analysis SHIMADZU brand DTG-60A simultaneous DTA-TG apparatus was performed from ambient temperature to 900 °C by applying a heating rate of 10 C/min. Meanwhile, the medium was fed with N<sub>2</sub> gas. The gas flow rate was chosen as 50 mL/min.

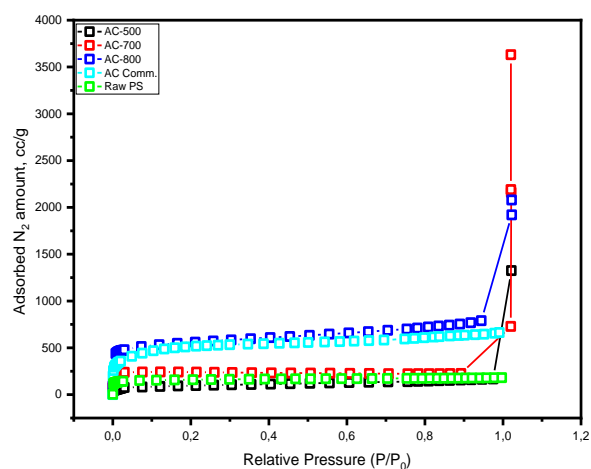
**Structural and morphological analysis.** The spectrum obtained with SHIMADZU IRTracer-100

FTIR was obtained with 4 cm<sup>-1</sup> resolution. The pore network in the structure of the AC-800 was demonstrated using SEM images and the ZEISS brand EVO 50 Model SEM device.

## RESULTS AND DISCUSSION

**Adsorption isotherms.** The activity of ACs produced by carbonization of agricultural wastes under suitable conditions due to their cellulosic structure, is indicated by their active surface areas and porosity structure. ACs obtained for this purpose were subjected to N<sub>2</sub> adsorption. For comparison, the raw material peanut shells and commercial activated carbon and the adsorption isotherms of Ac produced in this study are given in Figure 2. The knee formation observed in these graphs, especially at the relative pressure values of 0-0.01 P/P<sup>o</sup> (low relative pressure), indicates the presence of micropores in the structure and the gas being adsorbed by them. The more gas adsorption has taken place in this region, the more micropores can be mentioned. As a result, a high surface area can be observed. As can be seen from the figure, the activated ACs obtained by

carbonization at different temperatures adsorbed a very high amount of nitrogen compared to the raw material.



**Figure 2.** Adsorption isotherms.

The isotherm of the raw material exhibits a monolayer adsorption isotherm. Capillary condensation in the 0.9-1 relative pressure region is not observed. This corresponds to the Type I monolayer adsorption isotherm in the isotherm classification made by the International Union of Pure and Applied Chemistry (IUPAC). Although micropore formations are mostly observed in the structure of such ACs, meso- and macroporosity are relatively less. The produced AC (AC-500, AC-700 and AC-800) exhibits adsorption isotherm corresponding to type IV of IUPAC classification. In such isotherms, the presence of mesopore formation in the structure and even an adsorption with capillary condensation are mentioned. Relatively high surface areas are obtained from structures exhibiting such isotherms. Comparatively, the micropore volume and surface area and adsorption energy obtained by BET and Langmuir surface area DR method are given in Table 1. As can be seen from the table, peanut shells, which are raw materials, have a BET surface area of 500.275 m<sup>2</sup>/g; ACs produced at different temperatures have BET surface area of, respectively, 422.052 at 500 °C; 1022.031 at 700 °C

and 2093.063 m<sup>2</sup>/g at 800 °C. In this state, ACs with higher beta surface area than the commercially sold ACs were produced. Langmuir surface area, which expresses the monolayer adsorption surface area, reached the highest value at AC-800. The surface area and pore volume of the microporosity in the structure of AC were determined by the DR technique and are given in Table 1. The change in pore volume and surface area with respect to the diameter is shown in Figure 3 by the BJH method.

The results in the figure clearly show that AC with the highest surface area and volume of porosity has a lower pore size. It is understood that the current micropore volume of AC-800 has the highest micropore volume with 1.053 cc/g and the highest microporosity with a micropore surface area of 2963.759 m<sup>2</sup>/g. Therefore, the graph supports the result in the table.

### Thermal analysis

The material obtained before carbonization was subjected to thermogravimetric analysis and compared with the AC obtained after carbonization in order to see how the pistachio shells used as raw material in the production of activated carbon in the study would degrade in the face of heat treatment. The Tg and DTA curves obtained by controlled heating in nitrogen environment from ambient temperature to 800 °C are given in Figure 4.

When the TG curve is examined, it can be observed that the humidity in the building disappears up to about 100 °C, and this covers a low percentage (3%). In addition, the sample decomposed in one step and this decomposition corresponds to the temperature range of 350-500 °C, where the organic content is lost. In this degradation, the loss was determined as 87% (Figure 3 inner graph). The DTA curve clearly shows that the degradation is in the range of 350-500 °C. The DTA curve of the product (AC) obtained at the end of carbonization shows that there is no significant change in (inset) energy. Thus, it can be said that the transformation is completed under the applied conditions.

**Table 1.** BET, Langmuir, DR micropore volume, surface area and adsorption energy.

	BET, m <sup>2</sup> /g	Langmuir, m <sup>2</sup> /g	DR micropore volume, cc/g	DR micropore surface area, m <sup>2</sup> /g	Adsorption energy, kJ/mol
Raw Material	500.275	632.858	0.426	1199.900	9.055
Comm. AC	1648	2479.262	0.659	1849.312	14.976
AC-500	422.052	447.019	0.161	453.86	9.872
AC-700	1022.031	1051.394	0.454	1278.232	14.354
AC-800	2093.063	3939.573	1.053	2963.759	10.927

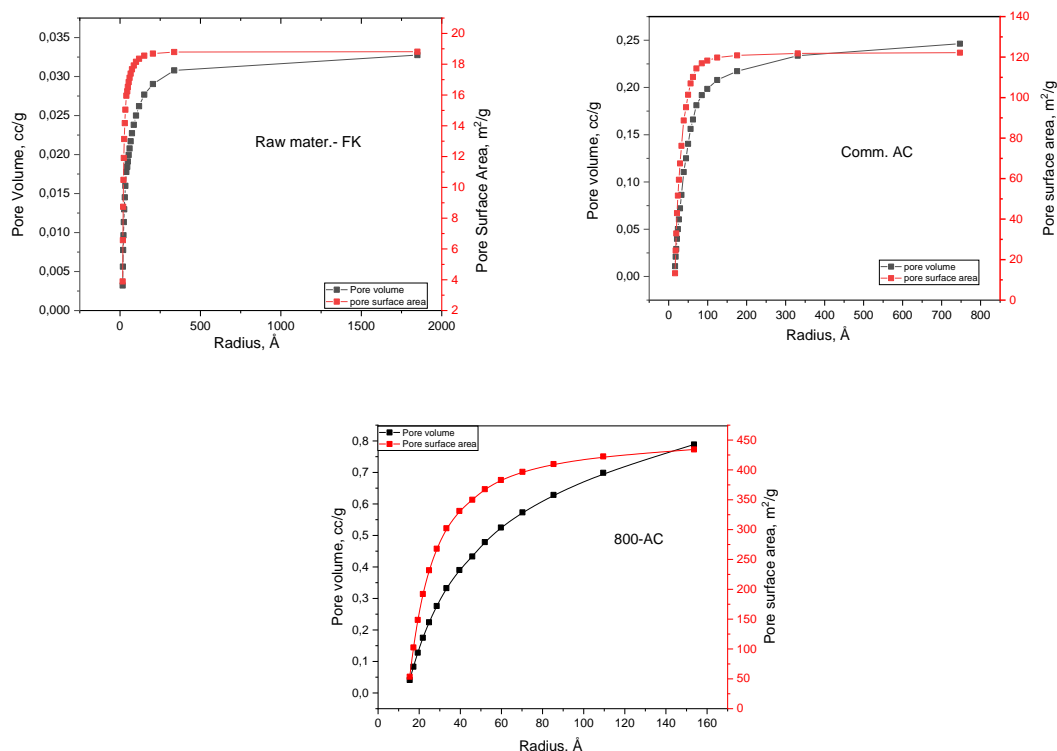


Figure 3. Distribution of pore volume and pore surface area versus radius of AC by BJH method.

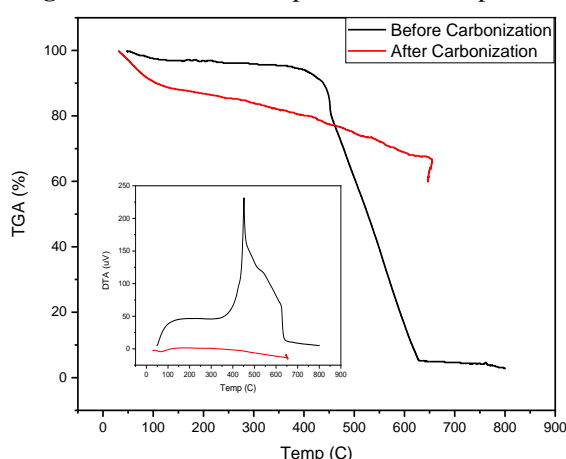


Figure 4. TG curve and DTA curve (inset).

#### Structural analysis

Tg data give the information that the organic structure of the raw material is deteriorated, resulting in the formation of pores in the structure of the raw material. In addition, this information was confirmed by the FT-IR spectrum. The products before and after carbonization of the raw material were compared structurally. The FT-IR results obtained are given in Figure 5.

Peanut shells have a cellulosic structure mostly containing H, C elements and OH groups. In addition, information about the presence of carbonyl, ether, ester, alcohol and phenol groups in pistachio shells is also available in the literature [17].

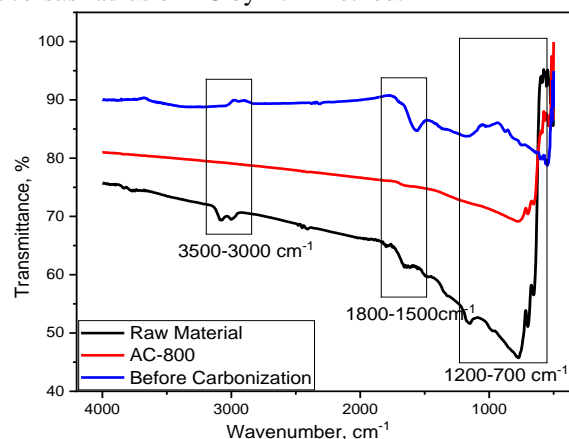


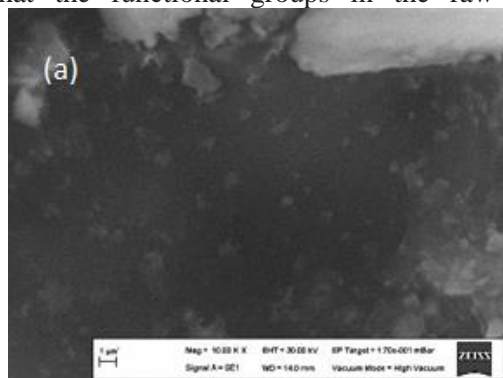
Figure 5. FT-IR spectrum

The vibrations in the raw material structure observed in the FT-IR spectrum were vibrations of functional groups such as  $\text{-OH}$  ( $3600\text{-}3000\text{ cm}^{-1}$  in alcohol and phenols);  $\text{C=C}$  (alkene group,  $2300\text{-}2100\text{ cm}^{-1}$ );  $\text{C=O}$  vibration (carbonyl group in amides,  $1820\text{-}1650\text{ cm}^{-1}$ ), and  $\text{C-O}$  (alcohol, phenol, ester and ether groups,  $1150\text{-}1050\text{ cm}^{-1}$ ). While stretching vibrations related to all bonds of the organic structure in raw peanut shells are observed very little in the activated material before carbonization, they are observed very limitedly and rarely in the AC structure obtained after carbonization. This shows that the structure collapses step by step during the activation process as a result of high temperature.

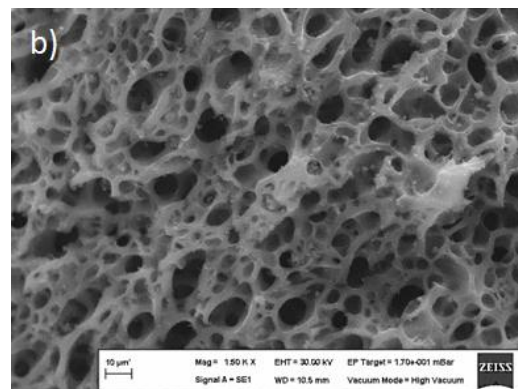


### Morphological analysis

SEM images of AC-800 samples were examined and compared with the raw material in order to show that the functional groups in the raw organic



structure were broken down and a new porous structure was formed. The obtained SEM images are shown in Figure 6.



**Figure 6.** The SEM images of a) raw material and b) AC-800.

SEM images were obtained by applying 30kV energy. While the surface image of the raw material is available in Figure 6a, a distance of 10  $\mu\text{m}$  is given for the AC-800 produced at 800°C as a product in Figure 6b. When both figures are compared, the pores opened in the structure of the raw material can be seen very clearly. The large and small pores formed indicate the structure and high surface area in the AC sample.

### CONCLUSION

As a result, the peanut shells accumulated as agricultural waste were activated for 1 day using 10% NaCl or 10% H<sub>2</sub>SO<sub>4</sub> solution. Afterwards, these shells were thoroughly washed and carbonized using a nitrogen atmosphere for 45 minutes at three different high temperatures, 500, 700 and 800 °C. Appropriate analyzes were carried out to determine the surface area and porosity structure of the obtained ACs. According to the results obtained, it was determined that AC-800 had LARGER surface area and micropore volume than raw peanut shell. Namely, while raw FK HAS 500.275 m<sup>2</sup>/g, AC-800 has a BET surface area of 2093.063 m<sup>2</sup>/g. On the other hand, while raw FK has a micropore volume of 0.426 cc/g and a micropore surface area of 1199.900 m<sup>2</sup>/g; AC-800 has a micropore volume of 1.053 cc/g and a surface area of 2963.759 m<sup>2</sup>/g micropores. In order to obtain this porous structure, the thermal decomposition took place in the range of about 87 to 350-500 °C. The porosity structure of the obtained AC could be observed by SEM. With these properties, it was determined that ACs obtained by applying appropriate activation and carbonization conditions are superior to the raw material FK. It is thought that these applied conditions are suitable for the production of ACs with high surface area and micropore volume from other waste materials.

### REFERENCES

1. M.A. Aly-Eldeen, A A.M. El-Sayed, M.S.A. Salem Dalia, G.M. El Zokm, *Egypt. J. Aq. Res.*, **44**, 179 (2018).
2. T. Fan, J. Zhao, Y. Chen, M. Wang, X. Wang, S. Wang, X. Chen, A. Lu, S. Zhao, *Adsorption Sci. Technol.*, 12 (2021).
3. S. D. Ashrafi, H. Kamani, H. S. Arezomand, N. Yousefi, A. H. K. H. Mahvi, *Desalin. Water Treat.*, **57**, 14051 (2015).
4. J. G. Shang, W. He, C. X. Fan, *Chin. J. Oceanol. Limnol.*, **33**, 169 (2015).
5. H. Gupta, B. Gupta, *Desalin. Water Treat*, **57**, 9498 (2015).
6. J.C. Moreno-Piraján, L. Giraldo, *Coden Echo E-J. Chem.*, **9**, 926 (2012).
7. M.H. Salmania, M. Miria, M.H. Ehrampousha, A. Alahabadib, A. Hosseini-Bandegharai, *Desalin. Water Treat.*, **82**, 157 (2017).
8. N. Rattanachueskul, A. Saning, S. Kaowphong, N. Chumha, L. Chuenchom, *Biores. Technol.*, **226**, 164 (2016).
9. M. C. Tonucci, L. V. A. Gurgel, S. F. D. Aquino, *Ind. Crop Prod.*, **74**, 111 (2015).
10. H. Dolas, O. Sahin, D. C. Saka, *Chem. Eng. J.*, **166**, 191 (2010).
11. R.X. Tang, Dai, C. Li, W.H. Liu, S.T. Gao, C. Wang, *J. Chem.*, 1 (2017).
12. R. Lopez-Cabeza, B. Gamiz, J. Cornejo, R. Celis, *Geoderma*, **293**, 64 (2017).
13. K. Gergova, N. Petrov, S. Eser, *Carbon*, **32**, 693 (1994).
14. S. Brunauer, P. H. Emmett, E. Teller, *JACS*, **60**, 309 (1938).
15. M.M. Dubinin, E.D. Zaverina, L.V. Radushkevich, *Zh. Fiz. Khim.*, **21**, 1351 (1947).
16. E.P. Barrett, L.C. Joyner, P.H. Halenda, *J. Am. Chem. Soc.*, **73**, 373 (1951).
17. A.C. Lua, T. Yang, *J. Colloid Interface Sci.*, **290**, 505 (2005).