

The Effect Of Boron Compounds The Pore Formation And Surface Area Of Activated Carbon Obtained From Pistachio Shell

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Abstract

It was reported the effect of boron compounds to the pore formation and surface area of activated carbon (AC) obtained from pistachio shell. Pistachio shells were activated by using two different methods and five different compound. These methods and compounds were washing/waiting with phosphoric(H_3PO_4) as acid solution or sodium hydroxide (NaOH) as base solution and waiting in boron compounds solution such as borax, boric acid and ammonium baborate. Shells were carbonized in high temperature furnace 900 °C, 45 minute under CO_2 washed H_2O atmosphere. Obtained results were compared with untreated shells, only carbonized. The shells have 1518 m^2/g of BET surface area, 2.086cc/g DR pore volume and 5865,632 m^2/g of DR micropore surface area for waiting in %10 ammonium baborate solution. The pore width as radius of obtained ACs and adsorption energy were 18,932 Å and 6,867 kJ/mol for waiting in %10 ammonium baborate solution (ABB-PS). It was found that ABB-PS have higher micropore surface area, higher pore volume and lower adsorption energy. It was concluded that the pore structure and BET surface area of AC obtained from pistachio shell were developed by treating with boron compounds by compared of other compound in same conditions.

Keywords: Pistachio shell, boron compounds, activated carbon, BET surface area

INTRODUCTION

Adsorption is a process providing to take hold the ions or molecules solvated in gas or liquid phase on a porous surface by bounding physical or chemical. The achievement of the process based on mostly high removal of pollutants, heavy metals or dyes from environmental sources. Adsorbent plays an important role in this success. Activated carbon (AC) is an adsorbent having the thousands square meters of high surface area and hierarchical pore structure per 1 gram. Adsorbents were produced from many materials such as plastic (Fan et.al, 2021), silica (Villaruel-Rocha et.al., 2021), polymer (Gong et. al., 2021) and agricultural wastes (Rodriguez-Mirasol et.al., 1993). For decades agricultural wastes have attracted attention to investigate the performance of using as adsorbent because of they have in cellulosic and fibrous structure, been abounded in nature and cheap. Cellulosic and fibrous structure gain the AC high surface area and porous structure. For this reason, ACs were preferred in many applications such as water purification (Imran et.al., 2006), removal from heavy and hazardous metals, textile (Carrott et.al., 2001), food (Zhang 2018), health, in energy storage capacitor manufacturing as electrode materials (Adekunle et.al., 2015; Wu et.al., 2015) and catalyst support (Lam et. al., 2016; Jüntgen 1986). The surface area and the pore structure of AC produced from agriculture wastes were affected applied activation method and conditions such as activating agent, activating time, furnace temperature, time held in furnace, furnace atmosphere gas, activation method. By time, many researchers were studied many agriculture wastes such as pistachio-nut shell (Lua et. al., 2005), orange peel (Carlos et. al., 2021), corncob waste (Wu et. al., 2021). To

develop the surface area and pore formation of AC, various activating chemical compounds having different acidity values were used. Phosphoric acid (H_3PO_4) (Vernersson et. al., 2002; Liou 2010), zinc chloride ($ZnCl_2$) (Lua et. al., 2005) could be counted among these compounds. Wastes were modified by using some metals such as Copper (Cu) (Taghizadeh et. al., 2018). In previous study carried out by our group, a new method based on salt using as activating agent was suggested. We reported the positive effect of salt using on surface area and pore size distribution of activated carbon produced from pistachio shell (PS) as agricultural waste. In present study, the effect of boron compound using as activating material on the development of surface area and the formation of pore in structure of AC produced from pistachio shell was investigated. The obtained results were compared with untreated PS (un-PS) by means of BET surface area, DR micropore volume, DR micropore surface area, DR adsorption energy.

MATERIALS AND METHOD

Material

Pistachio was gathered from pistachio trees growing up on land of Sanliurfa, Turkiye. Hydrochloric acid (HCl) as an acid, sodium hydroxide (NaOH) as a base, boric acid, borax and ammonium baborate as boron compounds were using as activating agent. All used chemicals were purchased from Merck. Solutions were prepared with pure water (PW).

Method

The production of activated carbon

In this stage, PSs were obtained by separating the edible soft part of gathered pistachios. Then PSs were washed with PW to clean any contaminants. They were waited in room conditions in air to dry. Suitable amount

of Pistachio shell (PS) was weighted by analytical balance and then added in activating agent included solution. PSs were held in the solution for 24 h in room temperature. For example, PSs were weighed in the desired amount and washed with 10% HCl solution in first stage. PSs were washed by pure water until pH was 6-7 after they were washed with the solution for 1 h. Filtrated and washed with pure water PSs were carbonized by using the high temperature furnace 900 °C and 45 min.

in CO₂ atmosphere passing into water. Obtained activated carbons were washed with pure water again and dried in 85 oC. Before characteristic analysis, AC was grinded into suitable particular size. Obtained AC was named H-PS. Other ACs from different activating solution were named according to activating process. Table 1 shows this naming. HCl, NaOH, boric acid, borax and ammonium baborate solutions were prepared as 10% (w/w).

Table 1. The naming of obtained AC

Activation condition	Washing PW-raw material	Washing HCl	Washing NaOH	Waiting HCl	Waiting NaOH	Waiting Boric Acid	Waiting Borax	Waiting Amm. BB
Name	Un-PS	A-PS	B-PS	AW-PS	BW-PS	BA-PS	BB-PS	ABB-PS

Surface and pore size analysis (BET-DR-BJH)

ACs produced from different activating conditions were characterized by using NOVA 4000e-Quantchrome instruments Surface area and pore size analyzer. In this method, measurements were based on the nitrogen adsorption of AC at -196 °C. The surface areas of AC were determined from calculating by using nitrogen adsorption isotherms via the Brunauer-Emmett-Teller (BET) equation (Gregg et.al., 1982) micropore volume and micropore surface area were calculated using Dubinin-Radushkevich (DR) equation (Dubinin et.al., 1947). The pore size distribution was determined by using Barrett-Joyner-Halenda (BJH) model (Barrett et.al., 1951).

Thermal gravimetric-differential thermal analysis (TG-DTA)

Before they were treated by high temperature, the decomposition curves of PSs were recorded by used Thermogravimetric-differential thermal

analysis (TG-DTA) instrument marked SHIMADZU. The curves were taken to determine the stability of the PSs to high temperature.

Fourier transform infrared (FT-IR) spectroscopy

Structure analysis was performed using FT-IR device to determine how the structures of activated carbons obtained by activated and carbonized by these processes were affected by the applied processes.

Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) technique was used to visualize the porosity structure of the raw material at the end of the processes.

RESULT AND DISCUSSION

Isotherms

In this section it was investigated how the acidic or basic activating materials treatment methods changed the active surface area and pore development of the untreated PS with any material. Adsorption isotherms give

the information about the existence of micro and/or mesopores in AC structure, whether the pores are filled with adsorbate or not and that adsorption is monolayer or multilayer. For this reason, to obtain these informations, the adsorption isotherms of the obtained

ACs were given in Figure 2. For comparison, raw PSs were processed the same carbonization without activating materials. Obtained AC was named untreated AC (un-PS). Its adsorption isotherm was added in the figure for comparison.

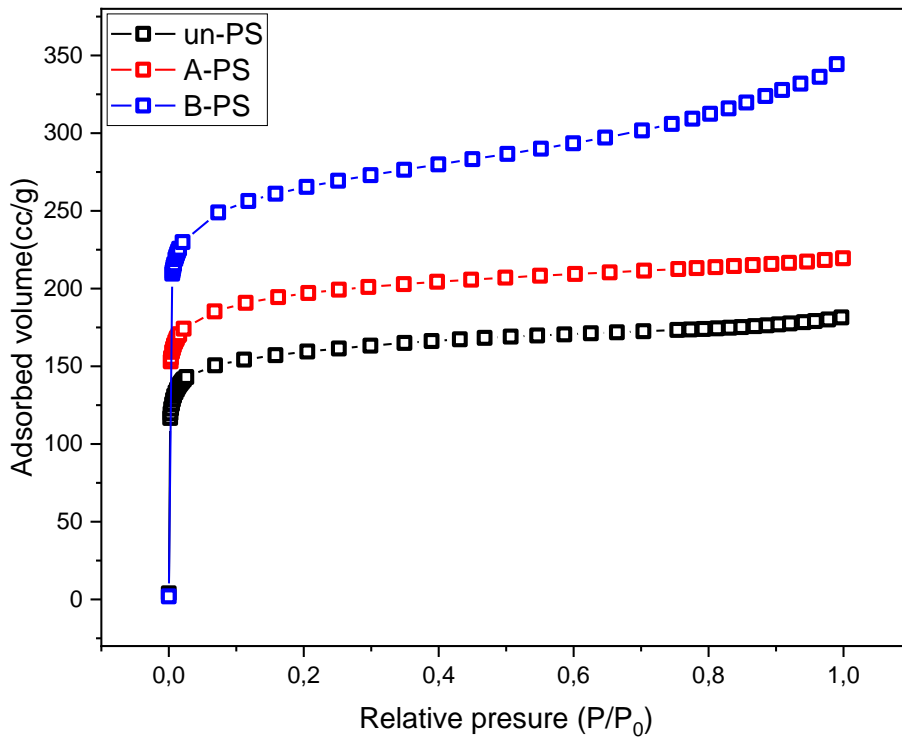


Figure 2. The effect of washing method with activating materials on the AC adsorption isotherms. (activating material concentration: 10% w/w; time passed during washing: 1 h, carbonization temp.: 900°C; carb. Time: 45 min.)

IUPAC classifies the isotherm as type-I, II, and so on. When micropores in AC structure adsorb the adsorbate in monolayer form, a shoulder and then a plateau are seen at the isotherm in starting and at during adsorption, respectively. This type isotherm is Type I. So, the isotherm of un-PS was Type-I as seen in the figure. The AC possessed microporous structure due to the formation of shoulder at isotherm curve at starting of adsorption. Adsorption was monolayer for un-PS. the isotherm of A-PS showed a shoulder and plateau as like

un-PS. The isotherm of A-PS was Type-I, but the adsorbed adsorbate volume was more in A-PS than un-PS. This can be attributed the usage of acidic activating material. The material increased the formation of micropore. This effect was seen the usage of ZnCl₂ as activating material in previous study (Dolas et. al., 2011), too. Basic activating material B-PS caused increased and developed microporous structure compared with A-PS due to the irritation effect of basic activating material. It was though that this effect caused more micropore and

electrostatic effect between the AC and adsorbate. So, multilayer adsorption was seen at the middle relative pressure, which was increased adsorbed adsorbate volume middle and middle high relative pressure. As second stage PSs were

waited in 10% activating solution for 1 day. Filtered PSs from the solutions were washed by pure water until pH was 6-7. Figure 3 illustrated the adsorption isotherm of dried ACs in comparison with the obtained isotherms in first stage.

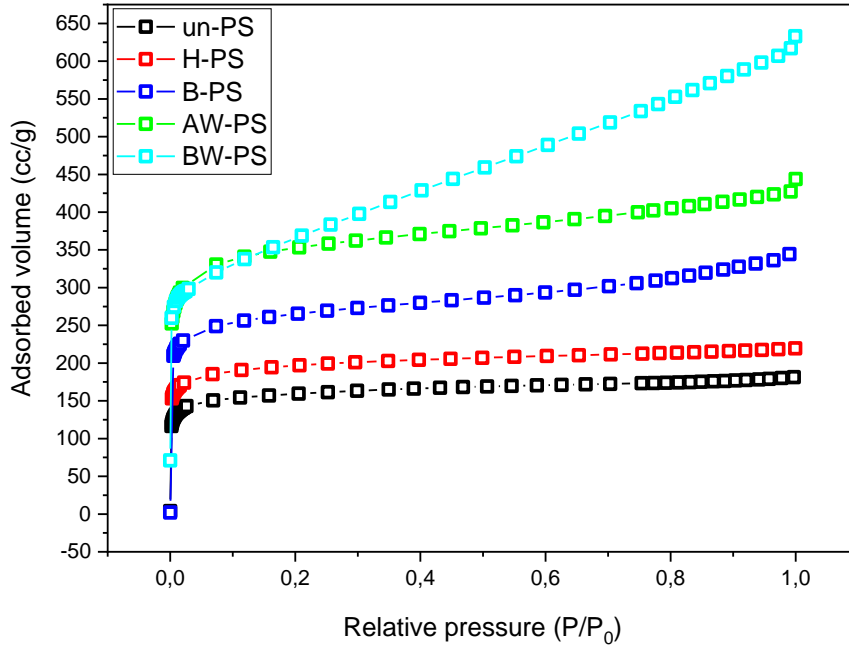


Figure 3. the effect of waiting method in activating solution on AC adsorption isotherm 2nd stage. (activating material concentration: 10% w/w; time passed during waiting: 1 day; carb. temp.: 900°C; carb. time: 45 min.)

It was clearly said that the activation method increased and promoted the porous structure of AC by investigating the isotherms in the figure. Waiting method in activating material solution increased adsorbed adsorbate volume. This effect can be attributed to increasing the micropore volume in AC structure (Dolas et. al., 2011). At the same time,

multilayer adsorption and capillary condensation in pores were seen at AW-PS and BW-PS samples, increasing adsorbed adsorbate volume at 0,999 P/P^o. The pore width, adsorption energy, pore volume and micropore surface area obtained by the DR method of the obtained ACs was given in Table 2 in comparison with the BET surface area.

Table 2. The DR method parameters, in comparison with the BET surface area

AC	Pore width, A ^o	Adsorption energy, kJ/mol	Pore volume, cc/g	Micropore surface area, m ² /g	BET surface area, m ² /g
Un-PS	14,357	9,055	0,426	1199,900	500,021
A-PS	6,212	20,928	0,293	825,048	620,036
AW-PS	7,099	18,313	0,520	1462,949	838,521
B-PS	19,290	6,736	1,269	3572,151	1117,291
BW-PS	10,965	11,856	0,639	1798,129	1302, 547

When the table was examined, the effect of the activation method and activating material on the parameters and the synergistic effect of these parameters on the BET surface area were seen. As the pore width increased, the surface area was expected to decrease as meso and macro pore structures were formed. Because high surface areas have been obtained in ACs with high micropore structure. Also, it was observed that the adsorption energy changed inversely with the pore width (given in Figure 4). For this reason, it could be said that the adsorption energy played an important role in determining the micropore surface area. It was observed that the method of acid washing enabled to obtain AC with smaller pore width from un-PS. Resulting ACs had a pore width of 6,212 Å in the method of the washing with acid solution, while in the method of the waiting in acid solution had a pore width of 10,965 Å. Adsorption energy decreased from 20,928 kJ/mol to 18,313 kJ/mol. As the pore volume increased

from 0,293 cc/g to 0,520 cc/g the surface area increased from 825,048 m²/g to 1462,949 m²/g. On the other hand, washing with base solution and waiting in base solution caused an increasing in pore width. Un-PSs with a pore width of 14,357 Å reached a pore width of 19,290 Å in the base washing process. Pores with a width of 10,965 Å were obtained by waiting in the base solution. It was expected that the surface area would decreased with the increase in width. But, it was determined the surface area was high. This result was attributed to the low adsorption energy because of that the adsorbate adheres more because it was not difficult in these pores. Due to the high pore volume, the surface area was also determined high. A surface area of 3572,15 m²/g was obtained by washing with base while the area was 1798,129 m²/g by waiting in base solution. Since waiting in the base solution caused pore destruction, the pore volume and thus the surface area were decreased.

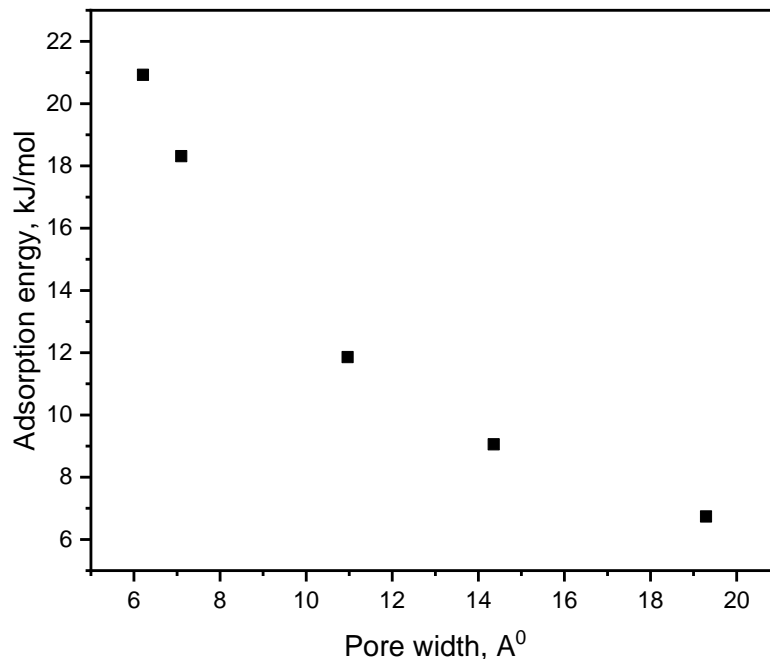


Figure 4. The changing of pore width with adsorption energy.

The adsorption isotherm of all activated carbons obtained in this study are given in Figure 5, comparatively. In order to compare the surface area and pore

structures of activated carbon obtained by using boron compounds, the relevant isotherms were given in Figure 5.

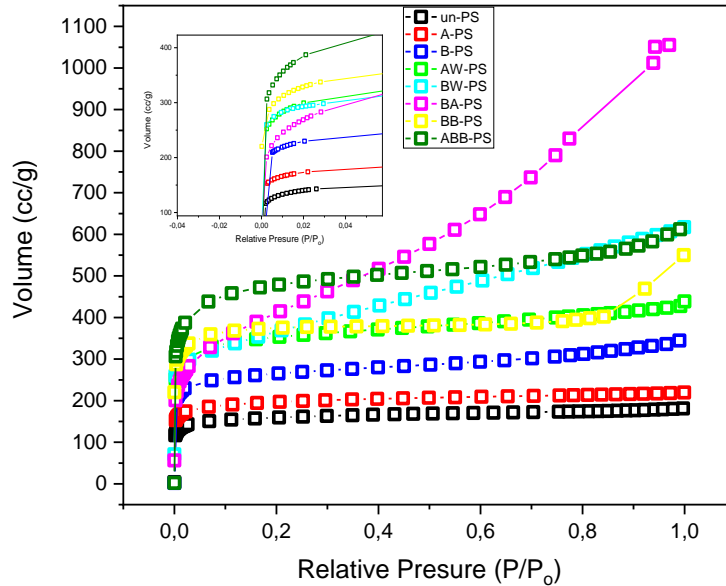


Figure 5. The isotherms of all obtained ACs

It was observed that when boron compound is used as the activating material, the micro-porosity in the structure of ac increases and even in the use of ammonium baborate, both micro-porosity and capillary condensation occur. So, the changing of the pore volume and pore surface area according

to the radius of the ACs were given in Figure 6. These data were determined by BJH method. As seen from the data, the micropore volume and surface area of ABB-PS were higher than other ACs. Such that the pore volume in the 0-200 Å range was 2,1 cc/g and the surface area was 110 m²/g.

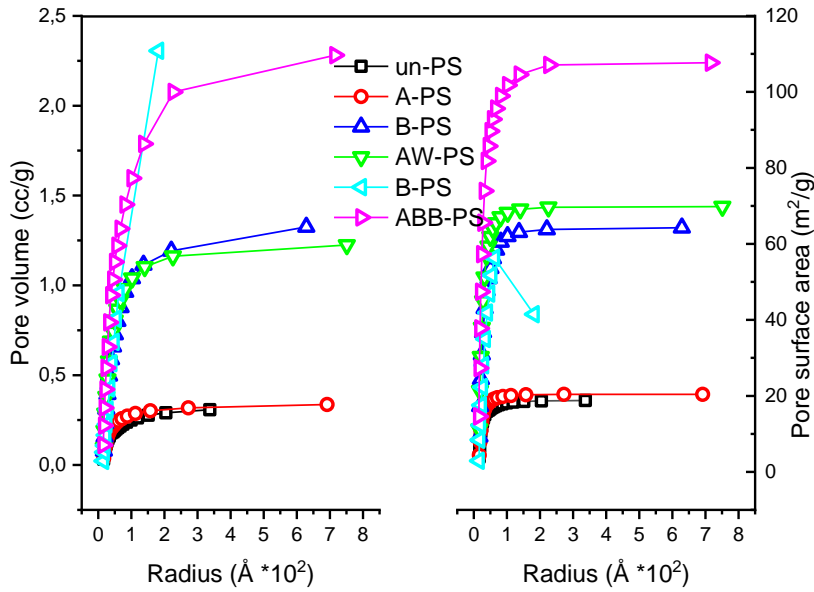


Figure 6. The changing pore volume and pore surface area of the ACs

Table 3 showed the BET surface area, pore radius, adsorption energy, pore volume and micropore surface area data of ACs activated with boric acid, borax or ammonium baborate (BA-PS, BB-PS or ABB-PS). These data were determined by DR method. It was seen

that the micropore surface area of ABB-PS was the highest as 5865,632 m²/g. This result was obtained because ABB-PS had the highest micropore volume, as well as the formation of meso- and macro-pores formations.

Table 3. The data of ACs activated with boric acid, borax or ammonium baborate (BA-PS, BB-PS or ABB-PS)

Aktivating Material	Boric Acide	Borax	Ammonium Baborate
BET surface area (m ² /g)	1441	1471	1518
Pore radius (A°)	9,918	6,44	18,932
Ads. Energy(kJ/mol)	13,108	20,176	6,867
Pore volume (cc/g)	0,532	0,56	2,085
Micropore surface area (m ² /g)	1495,734	1571,18	5865,632

The BET surface area of the obtained all activated carbons were given Table 4, comparatively. It was seen that the ABB-

PS had the highest BET surface area as 1518 m²/g.

Table 4. The BET surface area of all obtained ACs

AC	Un-PS	A-PS	B-PS	AW-PS	BW-PS	BA-PS	BB-PS	ABB-PS
BET	500	620	838	1117	1302	1441	1471	1518

Thermal characterization

It was thought that if the raw material having cellulosic and organic structure was delayed its thermal decomposition, active structure for adsorption would increase in obtained AC after carbonization. Because the losing of C in raw material could be decreased by delaying decomposition. Thus, boron compounds such as Boric acid (H_3BO_3 -BA), sodium tetra borate decahydrate ($Na_2B_4O_7 \cdot 10 H_2O$ -borax,

BB) and ammonium baborate ($(NH_4)HB_4O_7 \cdot 3H_2O$ -ABB) were used as activating material due to the fire delaying feature of boron compounds. To see the delaying of thermal decomposition of PSs, thermal gravimetric analysis was performed for un-PS, BA-PS and A-PS before carbonization. Figure 7 showed the weight loss with temperature of these materials.

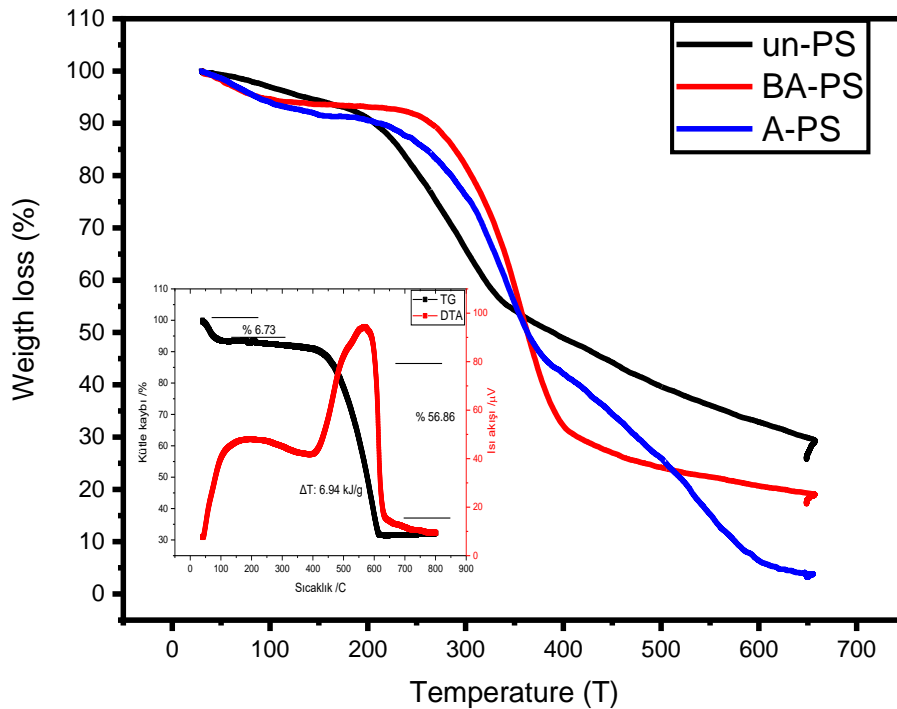


Figure 7. TG curves for un-PS, BA-PS and A-PS. (temp range: 30-650 C; heating rate: 10 C/s; in nitrogen atmosphere)

According to given curves the waiting in BA solution added the durability and stability to the structure of raw PS and thus decomposition was delayed. The un-PS, BA-PS and A-PS were decomposed about at 198 °C, 257 °C and

228 °C, respectively. Their weight loss percentage were 60% for un-PS, 95% for A-PS, 80% for BA-PS. Although the remaining part of the raw material was large, the porous structure had not been formed since the PSs did not treated with

activating material. For this reason, its surface area is lower compared with the other ACs. Inset figure showed the TG and DTA curves of ABB-PS. The treatment with ABB delayed the decomposition more than other materials. Decomposition was seen at 430 °C and its weight loss percentage was about 63%. Decomposition enthalpy

was calculated as 6,94 kJ/mol. The features of obtained ACs was evaluated with terms of formed pore width, micropore volume, micropore surface area and adsorption energy. Results were presented above in Table 2. And Table 3. Here, the heat and mass losing % data by determined TG-DTA analysis were given in Table 5.

Table 5. The mass losing and heat data of ACs.

Activating material	Mass losing /%	Heat /kJ/g
None	%60	1,92
H ₃ PO ₄	%85	8,1
Borik asit	%65	1,7

Thermal decomposition of cellulosic materials mostly proceeded in three steps. In the first step, the moisture in the structure of the material is removed at approximately 70-100 °C, and the second step in which the degradation of hemicellulosic structure and the release of organic volatiles occurs between 100-200 °C. The third step is the step in which the cellulose and lignin structure degrade at approximately 450-650 °C. decomposition in the un-PS sample started at 200 °C. in this example, since the PSs were not activated, volatile organics that would cause the destruction of cellulose and lignin in the structure and pore formation did not occur. It can be seen from the table and the graph that the mass loss remained et 60%. On the other hand, the degradation took place in 3 steps in the A-PS sample. It is understood from the 85% loss of mass

and the degradation step that the acid breaks down the cellulose and lignin structure. It was expected that the surface area and pore volume would be higher than the mass loss. However, the surface area and pore volume were low. This result can be explained by the collapse of the pores and the decrease in the surface area. In the activation with boron compounds, degradation started in one step with BA at 300 °C and with ABB at 430-500 °C. Accordingly, sufficient temperature and mass loss were obtained for proper pore development.

Morphological characterization

The morphological changing was presented in figure 8 by SEM images. Formed porous structure on and in the AC surface. The images belonged to the ABB-PS surface. These images proved TG-DTA due to porous structure formed by decomposing of raw material surface.

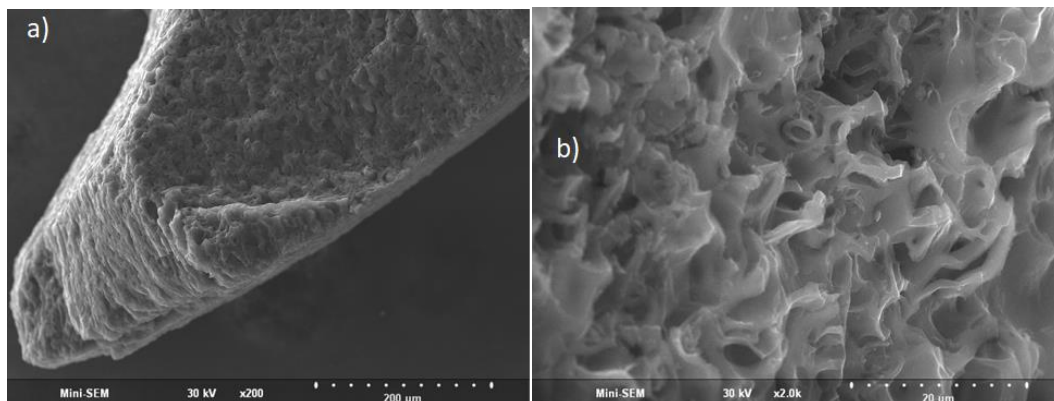


Figure 8. The SEM images of ABB-PS.

CONCLUSION

In the production of AC, materials such as acids and bases frequently used as activators. In this study, the effects of boron-containing chemicals on the production of activated carbon and on the surface area, micropore pore volume, pore surface area and degradation process the obtained ACs were investigated. According to the results obtained, BA-PS, BB-PS and ABB-PS ACs activated with boron chemicals have higher BET surface area and DR micropore volume than ACs obtained by other methods, while ABB-PS has the highest surface area among themselves. has been determined. This result was obtained because ABB-PS had the highest micropore volume, as well as the formation of meso- and macro-pores formations. Decomposition was seen at 430 °C in one step and its weight loss percentage was about 63%. Decomposition enthalpy was calculated as 6,94 kJ/mol. It was thought that the decomposition of ABB-PS at higher temperature may be the reason for its high surface area.

The PS had 1518 m²/g of BET surface area, 2.086 DR pore volume and 5865,632 m²/g of DR micropore surface

area for waiting in %10 ammonium baborate solution, when untreated shells have a 500 m²/g of BET surface area, 0,426 DR pore volume and 1199,900 m²/g of DR micropore surface area. The pore width as radius of obtained ACs and adsorption energy were 18,932 Å° and 6,867 kJ/mol for waiting in %10 ammonium baborate solution, when they were 6,212 Å° and 20,928 kJ/mol for washing with acid. It was found that obtained activated carbon by waiting in %10 ammonium baborate solution have higher micropore surface area, higher pore volume and lower adsorption energy. It was concluded that the pore structure and BET surface area of AC obtained from pistachio shell were developed by treating with boron compounds by compared of other compound in same conditions.

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