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Araştırma Makalesi / Research Article

Examining and Optimizing Production Conditions for Producing Mesoporous Activated Carbon from Pepper Stems

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Abstract

In this study, in order for the activated carbon obtained by using pepper stems to reach the mesoporous structure, production conditions such as activating agent type (KOH, NaOH, NaOH- Na_2CO_3), agent ratio (10%, 20%, 30%, 40%, 50% w/w), activating time (1 day, 3 days, 5 days, 7 days, 9 days) and carbonization temperature (700 ºC, 750 ºC, 800 ºC, 850 ºC and 900ºC) were examined. Additionally, the obtained ACs were characterized thermally, structurally and morphologically using TG-DTA, FT-IR, X-ray diffraction, and SEM devices. The BJH method was used for calculate and determine the pore size distribution. NaOH-Na_2CO_3, which has a basic character, had a higher micro and meso porous structure than other activating agents. 30% as agent rate, 5 days for activating time and 900ºC as carbonization temperature were determined as ideal conditions to reach the mesoporous structure. By applying these conditions, the maximum pore diameter observed in raw BS was increased from 207 Å to 799 Å, and the pore volume density value was increased from 0.024 cc g^{-1} to 0.484 cc g^{-1}.

Keywords: Pepper stems, activated carbon, production conditions, BJH method, mesopore volume

1. Introduction

Pores are gaps that occur during production in many active structures (carbon, zeolite and glass, etc.). These cavities are called micropores, mesopores and macropores in the IUPAC classification according to their diameters. Accordingly, those smaller than 2 nm (or 20 Å) are classified as micropores, those in the range of 2-50 nm (or 20-500 Å) are classified as mesopores, and those greater than or equal to 50 nm (or 500 Å) are classified as macropores (Naito et al., 2018).

The pores in the structure of the active material play a role in increasing the activity of the material. Because extra surface area is gained thanks to the pores, the effectiveness of the material will continue on this gained surface. For example, as the surface area of activated carbon increases, it means more active surface and more adsorption when used as an adsorbent. In materials with a catalytic function, the efficiency increases due to porosity and a faster reaction occurs. In addition, the size of the pores on the surface is important depending on the purpose. While the presence of micro-structured pores in the structure of the material as an adsorbent makes the material more effective, the material used in super capacitor electrodes has pores at the meso and macro (mostly meso) level, making the material effective. What is important here is the contact at the electrode-electrolyte interface. While micropores add extra surface area to the adsorbent; Since mesopores enable rapid mass transport of electrolytes to micropores (Lv et al., 2012; Xing et al., 2009; Wang et al., 2016), it is very important that the super capacitor electrode material contains a high percentage of mesopores. The formation and control of mesoporosity in AC production is mostly achieved by methods such as single-stage chemical activation (Hadoun et al., 2013; Saygılı et al., 2016; Marrakchi et al., 2017; Jawad et al., 2017; Nasrullah et al., 2019; Borhan et al., 2019; Lee et al., 2021), two-stage chemical activation (Tseng, 2006; Tseng et al., 2005; Muniandy et al., 2014; Khamkeaw et al., 2020), hydrothermal (Xin et al., 2020; Hossain et al., 2018) and chemical activation with dual activation agents (Le Van et al., 2019). For this reason, the size of the pores formed in material production can be controlled the factors such as the type and amount of activating agent, interaction time and carbonization temperature because of that these factors affect the pore size.

While microporous structures are generally obtained by physical activation method, chemical agents such as KOH also cause more micro-porosity in the structure. In addition, since KOH is a strong base, its corrosive effect makes it disadvantageous. In the literature, mesopore formation has been investigated using acids such as $ZnCl_2$ (Ashfaq et al., 2023**)**, K_2CO_3 (Nagalakshmi et al., 2015), Na_2CO_3 (Yanhong et al., 2017) or phosphoric acid (Zhe et al., 2021; Reffasa et al., 2010). Studies have shown that mesoporosity can be created in the activated carbon structure, but it has not been examined to what extent all production conditions will change meso-porosity.

In our previous study, activated carbon was obtained from pepper stems and its adsorption was examined (Dolas, 2023a, 2023b). However, these studies focused on the micro-porosity of activated carbon. In this study, we wanted to focus on meso-porosity and the availability of limited information in the literature to determine the optimum conditions, especially in the production of activated carbon containing mesopores, is the trigger for this study. In this context, the mesoporosity process was examined by using pepper stalk as raw material and applying different production conditions. The mesopore formation processes of different activating agents (KOH, NaOH and NaOH- Na_2CO_3 mixture) at different rates (10%, 20%, 30%, 40% and 50 %,w/w) for different periods of time (1 day, 3 days, 5 days, 7 days and 9 days) and at different carbonization temperature (700 ^oC, 750 ^oC, 800 ^oC, 850 ^oC and 900 ^oC) were examined using the BJH method.

2. Materials and Methods

2.1. Materials

The raw material pepper stems (BS) used as carbon source were obtained from a local producer in Şanliurfa. KOH, NaOH and Na_2CO_3 and commercial activated carbon were purchased from Merck. Solutions were prepared with pure water.

2.2. Methods

Measurements and calculations were made using the NOVA 4000e-Quantachrome instruments device. The surface area of the AC obtained at each stage was given as the Brunauer-Emmett-Teller (BET) surface area (Gregg et al., 1982). Pore size distribution was performed using the Barrett-Joyner-Halenda (BJH) model, and mesoporosity was selected from these calculations (Barrett et al., 1951). Pepper stalks to be used as raw material to obtain activated carbon (AC) were first washed and dried to get rid of external pollution. The material was cut into small pieces and kept in a solution containing the activating agent at the desired rate. At the end of the required time, the BSs taken from this solution was washed with pure water to prevent any residue on the surface and was taken to the physical activation (carbonization) section (Figure 1). In this section, production was carried out within the desired time by applying the desired temperature in the $CO_2 + H_2O$ gas mixture atmosphere. The obtained ACs were kept in water to completely open the pores. The ACs taken from here were dried, ground and sieved. An AC range of 600-400 microns was used in the measurements.

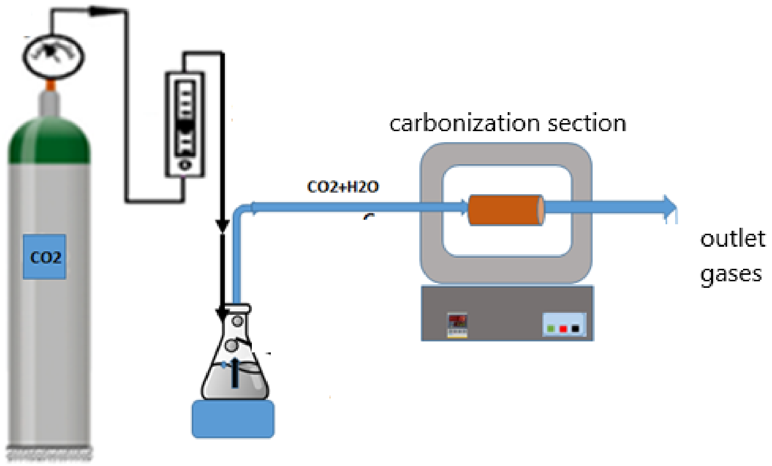

Figure 1. Physical Activation (carbonization) scheme

The resulting ACs were structurally analyzed by Fourier-transform infrared spectroscopy (FT-IR ATR) in the wavenumber range of 4000–400 cm^{-1} using a Bruker Vertex 70 FTIR instrument. Thermal characterization by Thermal Gravimetric-Differential Thermal Analysis (TG-DTA-) was performed in a nitrogen atmosphere at a heating rate of 10 °C min^{-1} using the Shimadzu DTG-60H Simultaneous DTA-TG apparatus). X-ray diffraction patterns were obtained using morphological characterization and crystal structure by scanning electron microscope (SEM) (ZEISS Evo/LS 10 electron microscope). It was performed by X-ray diffraction spectroscopy (RJGAKU-DMAX-2200).

3. Result and Discussion

3.1. The characterization of AC

The TG-DTA graph taken with a temperature range of 25-1000 °C and a heating rate of 10 °C min^{-1} in a nitrogen atmosphere gave information about the thermal decomposition of the raw material (BS) (Figure 2a).

Accordingly, the material undergoes initial decomposition in the range of 100-300 °C and experiences a 40 % structural degradation. It undergoes the second decomposition at approximately 700-900 °C. A loss of 33 % was observed here. Both of these structure degradations showed us that the organic structure of the material was destroyed by heat and a porous structure was formed in the meantime, and this process started at approximately 150°C. These results were taken into account in physical activation.

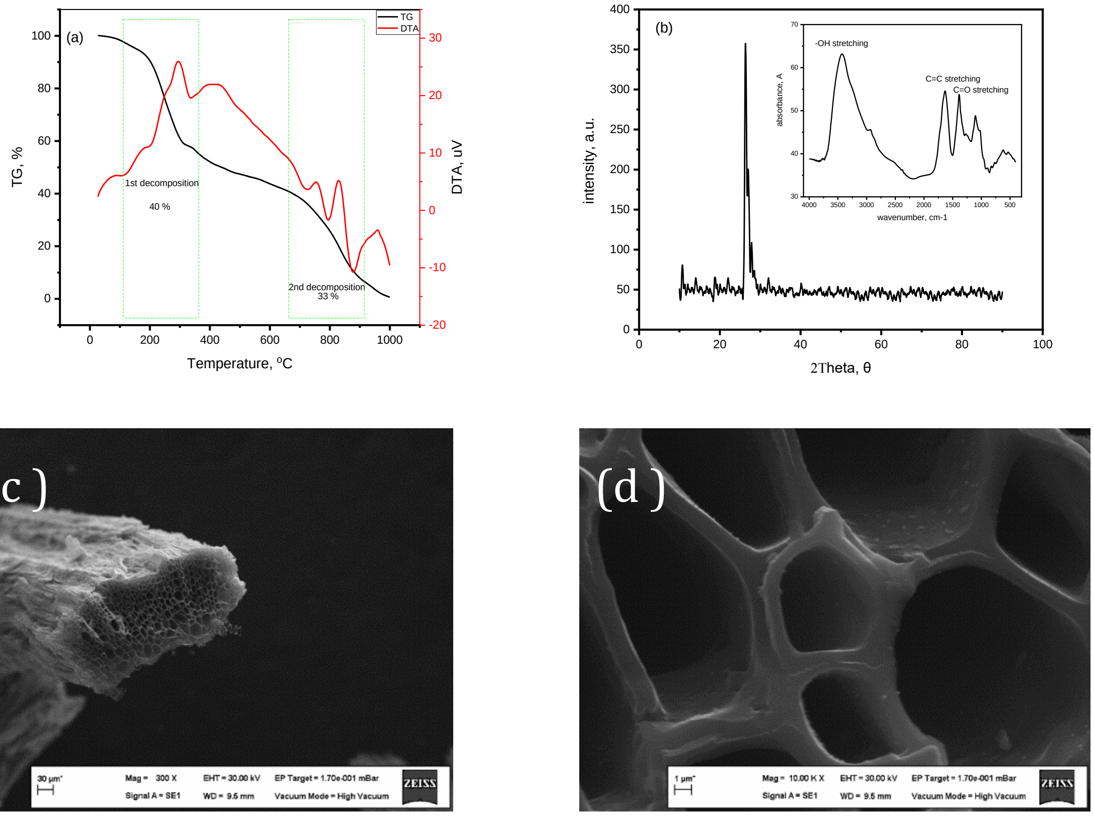

Figure 2. a) The TG-DTA thermogram of BS, b) The x-ray pattern of AC (inset: The FT-IR spectrum of AC), c and d) SEM images of AC. (agent ratio: 30 %w/w, activating time: 5 days, carbonization temperature: 900 °C)

The x-ray pattern of AC is given in figure 2b and the IR graph is given as figure 2b-insert graphic. A strong peak is observed in the range $2\theta = 25^\circ$-30°. This result indicates the presence of graphite crystals in the AC structure.

When the obtained products were examined structurally, peaks were observed in the relevant regions of the –OH in its structure and the C-C, C=C and C-O bonds that form the inorganic carbon skeleton (Figure 2). The sharp peak at 3400 cm^{-1} - 3600 cm^{-1} belongs to –OH stretching, 1641 and 1387. C=O stretching peaks were observed at cm-1. This result indicated that the ACs obtained had a mesopore structure (Zhigang et al., 2014).

SEM images clearly showed the pores formed in the structure (Figure 2 c-d). During thermal decomposition, all the carbon walls of the raw material collapsed and pore formation occurred. All these results show the formation of pores in the structure, but the most consistent information about the diameter and distribution of the formed pores could be obtained with isotherms and pore distributions.

3.2. The effect of activating agent

At this stage, KOH, NaOH, NaOH-Na_2CO_3 were used as activating agents, each at 30% by mass (w/w). The aim here was to determine the contribution of the activating agent to mesoporosity. In this context, a solution of 30 % of each substance by mass was prepared, added to the BS and subjected to chemical activation. The results obtained as isotherms are given in Figure 3.

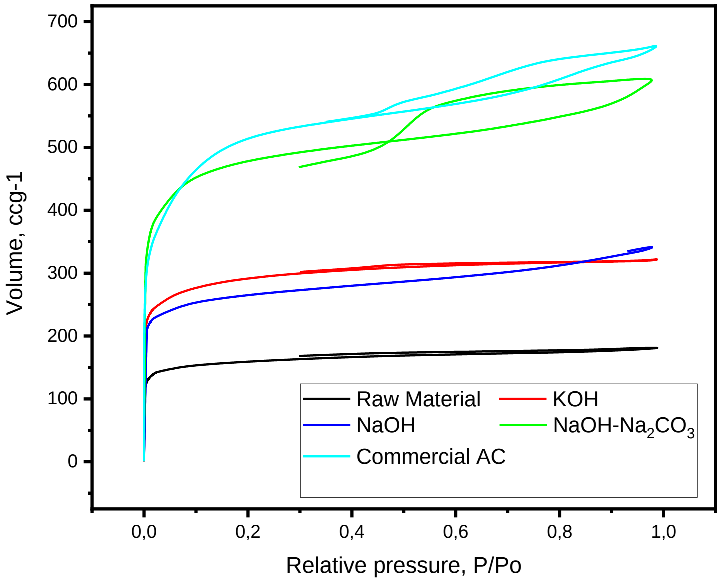

Figure 3. The comparison of the isotherm of AC obtained by using different activating agents. (agent ratio: 30 %w/w, activating time: 5 days, carbonization temperature: 900 ºC)

Isotherm shapes are closely related to the pores in the structure. The micropores in the structure fill at very low relative pressure values, and then, after being covered with a monolayer, the mesopores begin to fill and the volume increases. This occurs around 0.1-1 relative pressure, then if there are macro pores in the structure, capillary condensation occurs and the volume increases upwards in the region where the relative pressure is 1. Another existence of mesopores is that desorption will occur in mesopores and macropores. With this information and graphics, as can be seen from the figure, it could be said that the mesoporous structure was achieved with NaOH-Na$_2$CO$_3$. Pore distribution graphs obtained by the BJH method are given as pore volume and pore surface area versus pore diameter (Figure 4).

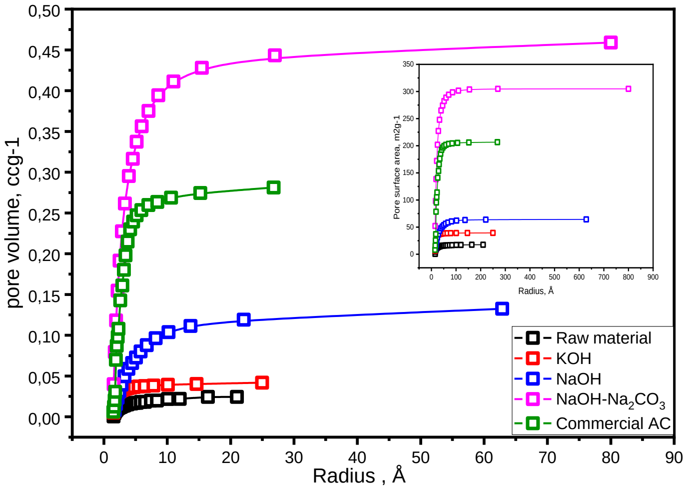

Figure 4. The comparison of the effect of different activating agents. (the agent ratio: 30 %, activating time: 5 days, carbonization temperature: 900 ºC) (inset: radius vs pore surface area graph)

According to the data obtained, the raw material had a volume density of 0.024 cc g^{-1} from pores with a maximum diameter of 207 Å and 0.007 cc g^{-1} from pores with a diameter of 22 Å. Commercial AC had a volume density of 0.282 cc g^{-1} from 266 Å diameter pores and 0.09 cc g^{-1} from 20 Å diameter pores. When KOH was used, mesopores formed a volume density of 0.039 cc g^{-1} up to 251 Å, while with NaOH, pores up to 628 Å formed a volume density of 0.132 cc g^{-1}. When using NaOH-Na_2CO_3, a volume density of 0.48 cc g^{-1} was achieved through pores with a diameter of 799 Å. As seen that OH- and CO_3-2 anion groups increased both the volume density micro and mesopores. Parallel to the pore volume values, the highest pore surface area values were reached with the use of NaOH-Na_2CO_3. For this reason, NaOH- Na_2CO_3 duo was used as the activating agent.

3.3. The effect of activation agent ratio

Since the rate at which the activating agent was used is an effective parameter in opening the pores by breaking down the carbon walls of the cellulose structure, NaOH (30 %) was kept constant and the amount of Na_2CO_3 was used in 5 different rates (10 %, 20 %, 30 %, 40 % and 50 %). The obtained data are given in Figure 5.

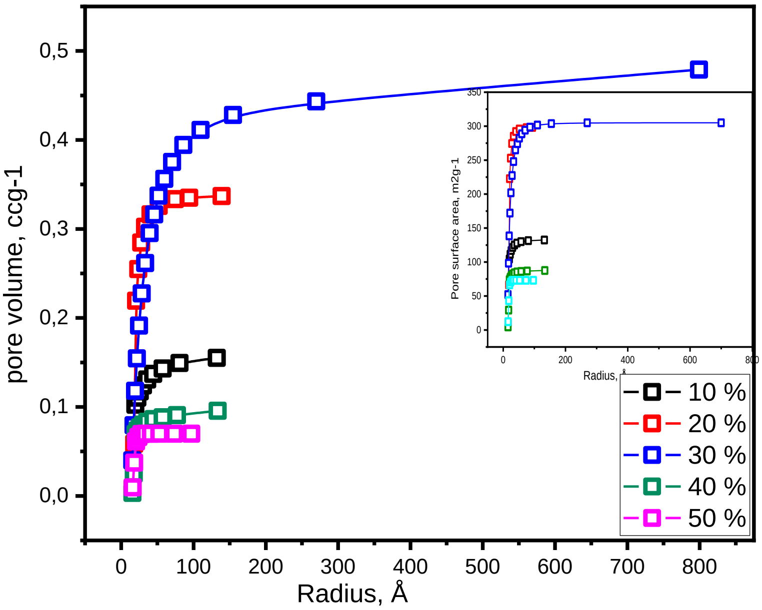

Figure 5. The comparison of the effect of activating agent (Na_2CO_3) ratio. (NaOH ratio: 30 %, activating time: 5 days, carbonization temperature: 900 ºC)

According to the data obtained, it is very important to determine the ratio of the agent as it will cause effects such as micropore formation, opening of the existing pores and formation of mesopores. Accordingly, the diameter and pore volume values obtained with the use of 10 %, 20 % and 30 %, respectively, were 12 Å -0.154 cc g^{-1}, 135 Å -0.337 cc g^{-1} and 799 Å -0.484 cc g^{-1}. At 40% and 50% ratios, these values were determined as 133 Å -0.097 cc g^{-1} and 100 Å -0.071 cc g^{-1}, respectively. A decrease in both mesoporosity and micro porosity was observed, apparently due to the destruction of the pores formed with excessive agent use. This is an expected result. Because pore destruction means excessive deterioration of the structure and disappearance of pores. This effect is also observed in the graph. In terms of mesopore formation and pore volume, the ideal ratio under these conditions was determined as 30 % Na_2CO_3 and was used for other applications.

3.4. The effect of activating time

It is also important how long the raw material of cellulosic structure, which is the carbon source, will be kept in the solution containing the ideal activator at the ideal rate. For this reason, BS was kept in a solution containing 30 % NaOH-30 % Na_2CO_3 for 5 different periods of time (1 day, 3 days, 5 days, 7 days and 9 days). The results obtained are given in Figure 6.

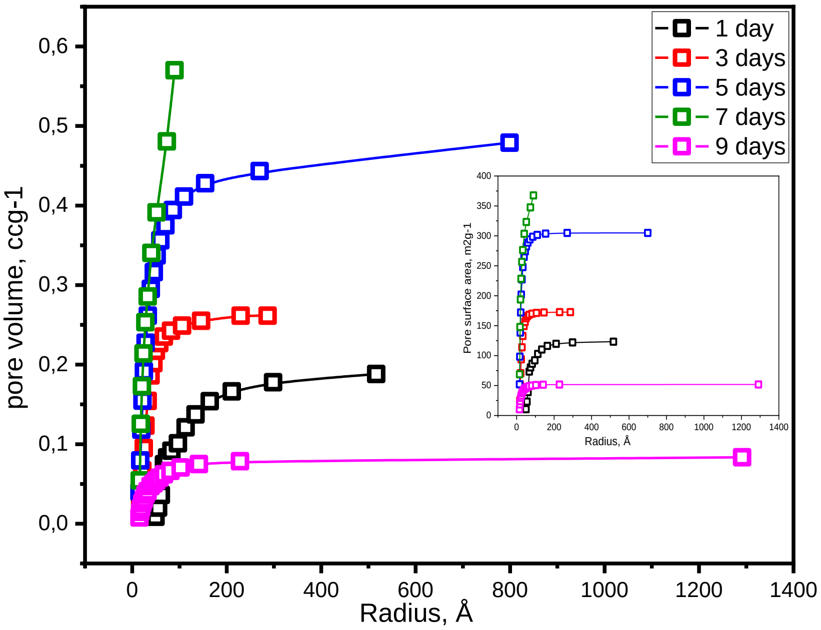

Figure 6. The comparison of the effect of activating time. (the agent ratio: 30%, carbonization temperature: 900 ºC)

According to the graphs, as the number of day increases, micro porosity and mesoporosity increase, but after a certain number of days, a change is observed in the size and amount of the pores, as in the ratio of the activating agent. The maximum pore diameter and pore volume data obtained after 1, 3, 5 days of waiting were 526 Å - 0.193 cc g^{-1}, 283 Å -0.26 cc g^{-1}, 799 Å - 0.484 cc g^{-1}, respectively. At around 20 Å, an increasing pore volume was observed for up to 5 days. High micro porosity was observed only in the structure for 7 days. Thus, pores with a maximum diameter of 85 Å and a volume of 0.57 cc g^{-1} were obtained. In 9 days, the majority of the micropores (21 Å -0.048 cc g^{-1}) in the structure were reduced by further opening and pores with a maximum diameter of 1292 Å and a volume of 0.086 cc g^{-1} were obtained. As a result, it was concluded that the ideal holding time was 5 days in terms of mesoporosity.

3.5. The effect of activating temperature

Apart from all these, the temperature value used in physical carbonization also affected the pore size. To see this effect, the material prepared by keeping it in a solution containing 30 % NaOH-30 % Na_2CO_3 for 5 days and carbonized by applying different temperatures (700 ºC, 750 ºC, 800 ºC, 850 ºC and 900 ºC) are given in Figure 7.

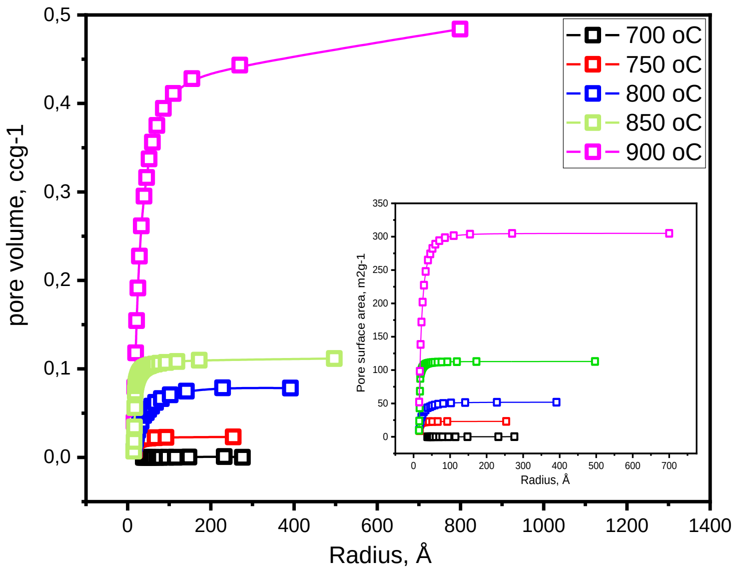

Figure 7. The comparison of the effect of carbonization temperature. (the agent ratio: 30 %, activating time: 5 days)

According to the data obtained, low temperature (700 ^{o}C) could not cause sufficient pore formation. The maximum reached pore diameter is approximately 300 Å and its volume is 0.0019 cc g^{-1}. As the temperature increased, an increase in the pore diameter and volume was observed. This effect reached its ideal level at 900 ^{o}C. Accordingly, the ideal temperature was determined as 900 ^{o}C.

4. Conclusion

Knowing that the size of the pores and their control are of vital importance, especially depending on the area of use of the material, AC was obtained using pepper stems in this study, and the mesoporous conditions of the obtained AC were examined and optimized in terms of production conditions such as activating agent type, activating agent ratio, activating time and carbonization temperature. KOH, NaOH and NaOH-Na_2CO_3 were used as activating agents. Based on the desorption curve from the obtained isotherm graph, it was found that NaOH- Na_2CO_3 agent had the highest value in terms of mesopore pore volume. In the calculations made with the BJH method, the pore volume of raw BS had a maximum of 207 Å and the pore volume of 0.024 cc g^{-1} increased to 799 Å pore diameter and 0.484 cc g^{-1} with the use of NaOH- Na_2CO_3. Keeping the NaOH amount constant at 30%, 5 different ratios (10, 20, 30, 40 and 50% w/w) were tried, and the Na_2CO_3 ratio was found to be 30% higher and more appropriate than other ratios. So much so that while the highest pore volume was observed at 30%, a higher volume decrease was observed. This effect was not interpreted as the transition of micropores to meso and macro dimensions, since a decrease in pore size was also observed. The soaking time in activating solution was compared for 5 different periods. Accordingly, it was determined that the ideal duration was 5 days. High pore volume within the limits of 20 Å and a maximum pore diameter of 799 Å and a pore volume density of 0.484 cc g^{-1} for this diameter were obtained for 5 days. It was observed that for over-holding, first only micro porosity turned into micro porosity and then all micro pores turned into macro (maximum diameter of 1292 Å and a volume of 0.086 cc g-1). According to the results of 5 different carbonization temperatures (700 °C, 750 °C, 800 °C, 850 °C and 900 °C), the ideal temperature was determined as 900 °C. While a maximum of 300 Å pore radius and 0.0019 cc g^{-1} pore volume density were obtained at 700 °C, 799 Å pore diameter and 0.484 cc g^{-1} pore volume density were obtained at 900°C. it was determined that 30 % of NaOH-Na_2CO_3 should be used to obtain mesoporous AC from BS, 5 days should be selected for the activating time and 900 °C would be suitable as the carbonization temperature.

As a result, it was thought that mesoporosity, which is important in areas requiring special use such as super capacitor electrode material, will be achieved in the production stage of activated carbon from carbonaceous wastes such as pepper stalks, if NaOH-Na_2CO_3 is selected as 30 % as the activating agent, 5 days as the activation time and 900 °C as the carbonization temperature, the optimum micro and mesoporosity rate will be achieved.

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