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Characterization of Activated Carbon Produced by Hydrothermal Carbonization Method Using Almond Shells

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In this study, activated carbon was produced by hydrothermal method from almond shells. In the studies, two different techniques were applied. In the first technique, almond shells were processed directly on the hydrothermal device at different times and temperatures without the use of activators. In the second technique, an activator was used after hydrothermal treatment and activated carbon was produced. Characterization of the obtained products was carried out by BET, SEM and EDX analyses. The surface areas of the products obtained from experiments were measured by BET analysis which is an analytical technique utilized for determining specific surface areas and pore size distributions of solid materials. The surface area of the product generated without the use of an activator was measured at 0.95 m^2/g, whereas the surface area of the product created with the use of an activator was measured at 423.56 m^2/g, according to the results of the BET analysis. In a 300 mg/L methylene blue solution, the adsorption efficiency was observed to be 76.37%.

Keywords: *Activated Carbon, Almond Shells, Hydrothermal Carbonization*

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1. Introduction

Activated carbon is a carbon-based material with large surface area, microporous structure, high pore volume and high surface reactivity, and is a versatile and excellent adsorbent [1]. They are usually materials with a pore volume of 0.2 ml/g and a surface area of more than 400 m^2 /g, and they can be produced from various organic and inorganic wastes such as wood, coal, peat, coconut shell, etc. [2, 3]. Activated carbon is used in many areas such as the removal of bad smell and pollution of gases, food industry, waste water treatment, health sector, metal and defense industry [4]. The high cost of activated carbon has led researchers to work on the production of activated carbon from different raw materials. In recent years, the production of activated carbon from agricultural wastes has gained importance [1]. Also, producing activated carbon from biomass waste helps to minimize waste disposal costs and the negative impact on the environment [5].

The hydrothermal process, also known as wet roasting, is an environmentally friendly method used to convert biomass into a high carbon-rich solid product. With a bulk yield of between 35 and 80%, hydrocoal is the primary output of the hydrothermal process. The biomass is treated in an autoclave at predetermined temperatures and times [6]. In this study, activated carbon was produced by hydrothermal carbonization (HTC) method using almond shells, which is an organic waste.

2. Experimental

KOH (Merck CAS NO: 1310-58-3), used as activator, was purchased and used in experiments. An Elektro-Mag M5040P brand oven was used for drying processes, and a Fytronix brand hydrothermal device was used for hydrothermal carbonization experiments.

2.1. HTC experiments without the use of activating agents

Almond shells were first dried in an oven with air circulation at 80ºC for 24 hours in order to remove the moisture in their body. The dried sample was ground in a ball mill for 15 minutes, and it was sieved through a 218µm sieve. After mixing at a ratio of solid/water:1/10 (5 g almond shells/50 ml distilled water), it was treated in a hydrothermal device which was shown in Figure 1, for 12 hours at 100ºC and 200ºC. Hydrothermal device consists of a temperature and time control panel, a hydrothermal reactor and a magnetic stirrer. The hydrothermal reactor is made of stainless steel. The inside of the reactor is designed in such a way that an 80 ml teflon cap can enter. There are two valves and a digital pressure gauge on the cover of the reactor to provide gas inlet and outlet. The mixing process of the reactor is carried out by rotating the magnetic fish in the teflon cap by the magnetic stirrer. The mixing process for the experiments was carried out at 700 rpm. Materials taken from Hydrothermal device were filtered on filter paper. The material remaining on the filter paper was dried in an oven at 80ºC for 24 hours. The obtained samples were kept in ziplock bags for analysis. The flow chart of the experiments performed on almond shells is given in Figure 2.

Fig 1. The hydrothermal device used in the experiments

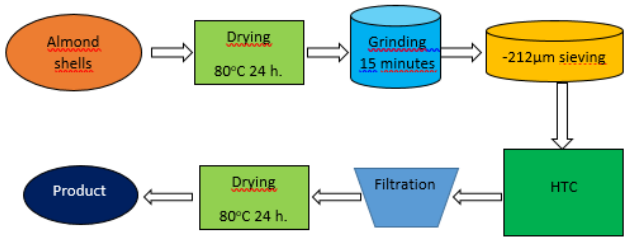


Fig 2. The flow chart of the experiments performed on almond shells

2.2. Experiments performed using activating agent

Almond Shells, which were ground in a ball mill, were carbonized in a muffle furnace at 800ºC for 24 hours. Then, the samples were prepared by mixing the carbonized product/pure water=1/10 (5gr carbonized product/50 ml distilled water). Afterwards, the prepared samples were processed in a hydrothermal device at 200ºC for 12 hours. Carbonized samples obtained from hydrothermal were filtered on filter paper to make solid-liquid separation. The obtained Hidrochar was activated in a muffle furnace at 600ºC for 4 hours by blending KOH/Hydrochar=1/1 and 1/2. The activated product was shaken in a 3 M HCl solution for 1 hour in a vortex device, with activated carbon/HCl solution =1/10, to remove impurities in its pores. After vortexing, the mixtures were filtered through filter paper, the sample remaining on the filter paper was washed repeatedly with distilled water until pH= 4.5-5 and filtered. The washed samples were dried in an oven at 80ºC for 24 hours and stored in ziplock bags for analysis. Figure 3 shows the flow chart of HTC experiments using the activating agent KOH. The flow chart of the experiments performed using activating agent KOH is given in Figure 3.

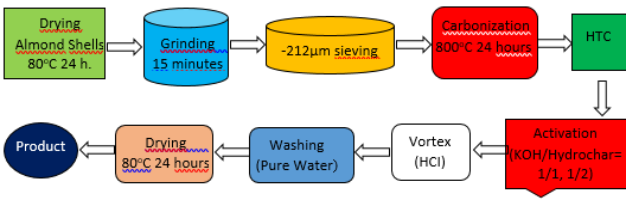


Fig 3. Flow chart of HTC experiments performed using activating agent KOH

3. Results and Discussion

Processes of activation were carried out both without KOH and with KOH added to the system.

3.1. HTC procedures performed without the use of activating agents

SEM, EDX and BET analyses of activated carbon samples produced as a result of experimental studies were performed. SEM images provide important information about the physical morphology of the surface. After the

hydrothermal carbonization process applied to the raw material, the changes occurring on the surface, the micro and mesopores formed can be seen in the SEM images. The SEM image and EDX analysis of the sample before the hydrothermal carbonization process are given in Figure 4. It is seen that the untreated sample does not have a porous structure and the surface is smooth.

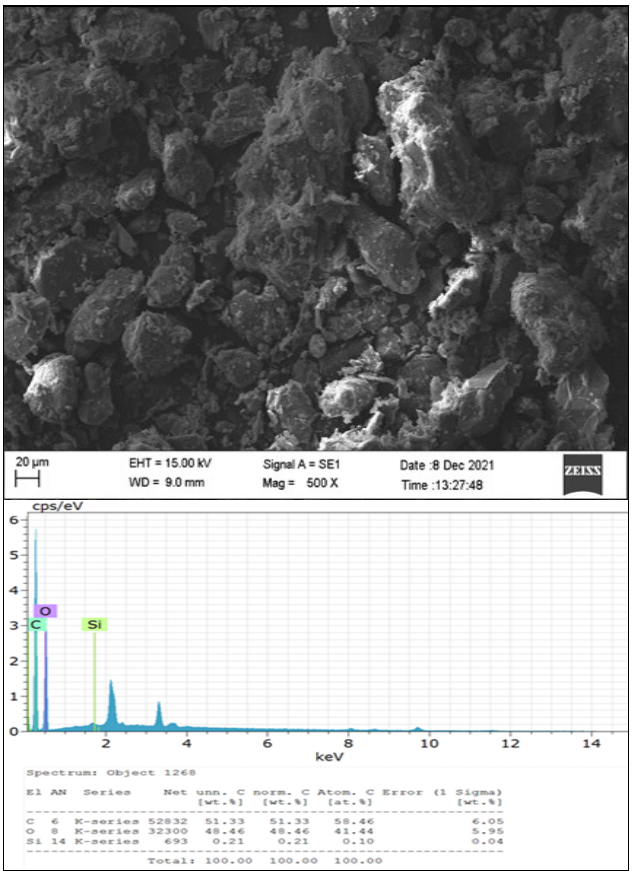


Fig 4. SEM image and EDX analysis of the untreated sample (500x)

The -218 µm sample was subjected to hydrothermal treatment at 100 and 200ºC temperatures for 12 hours and SEM and EDX analyses of the solid part were performed after the obtained sample was filtered. SEM images and EDX analyses of the samples, which were HTC treated for 12 hours at 100ºC and 200ºC, were given in Figure 5 and Figure 6 respectively. It was seen that the pore structures in all samples had an irregular and blocky cavity structure rather than a regular ring structure, and the surfaces were indented and protruding. It was observed that the carbon content of the samples increased depending on the increasing temperature, but components such as Ca, K and Cu also appeared. It is thought that these components exist as inorganic material in the structure of the almond shells and due to the high pressure during the process performed in HTC, they came out of the organic structure and may have adhered to the surface of the sample. In the BET analysis, it was determined that the surface area of almond shells treated for 12 hours at 100ºC was 0.95 m^2/gr.

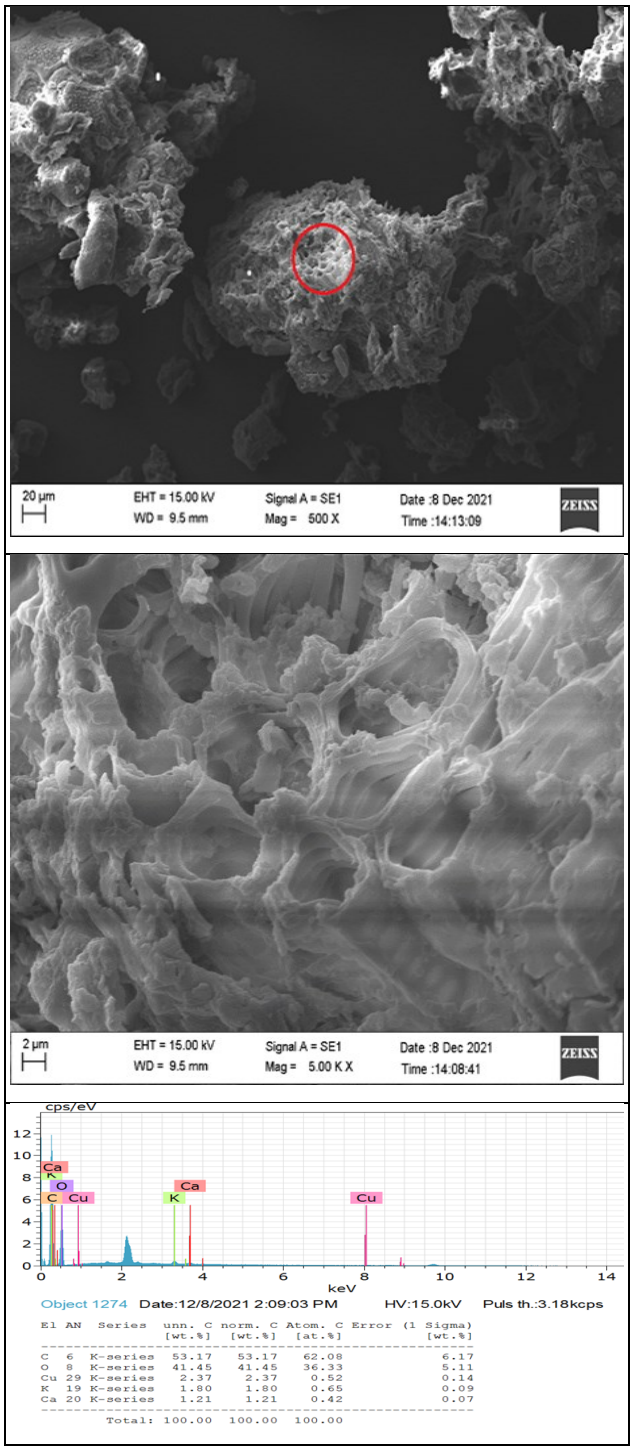


Fig 5. SEM image (500X and 5.00KX), and EDX analysis of the marked region of the 100ºC 12 hours HTC treated sample

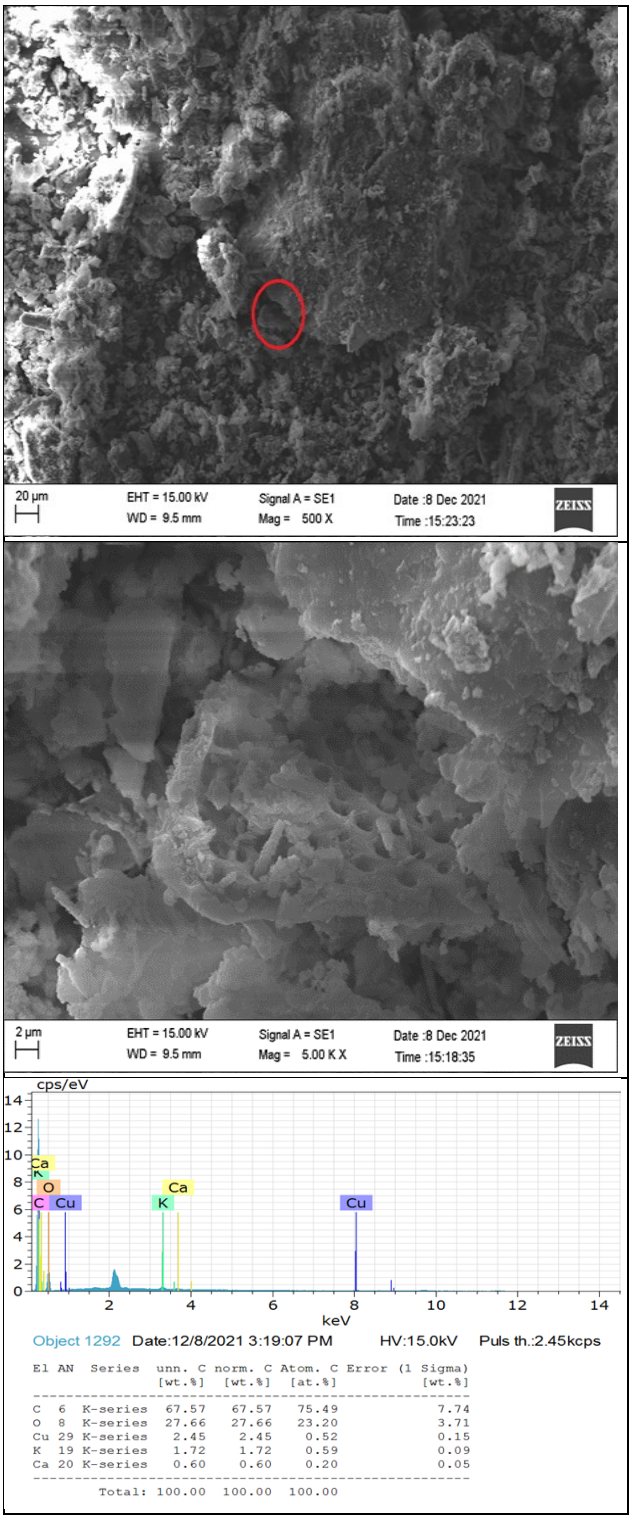
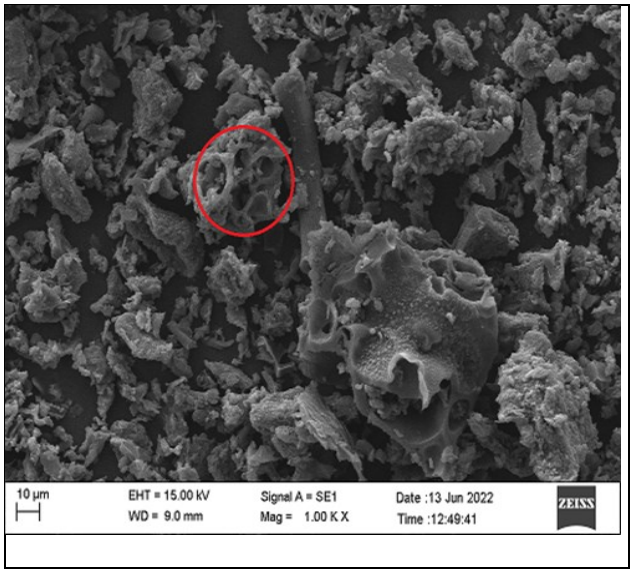


Fig 6. SEM image (500X and 5.00KX), and EDX analysis of the marked region of the 200ºC 12 hours HTC treated sample

3.2. Activation processes by adding KOH

SEM, EDX and BET analysis results of KOH activated samples are given in Figure 7 and Figure 8. According to the SEM images, it was observed that the applied chemical activation process was effective in the formation of the pores. KOH, which is used as an activator, accelerated the degradation of the structure of the raw material during the carbonization process. During carbonization, the structure of the product was largely degraded by thermal decomposition, most of the functional groups were removed from the structure, and a large part of the volatile substances were removed from the structure to obtain a porous structure. After hydrothermal carbonization, the carbonized products obtained from the samples activated with KOH were subjected to surface area analysis by N_2-BET method. Accordingly, the surface area of the sample mixed with KOH/Hydrochar=1/1 ratio was determined as 423.56 m^2/g, while the surface area of the sample mixed with KOH/Hydrochar=1/2 ratio was determined as 335.05 m^2/g. When the C analyses of the samples obtained as a result of the experiments were examined, the carbon ratio(by weight) in the untreated sample was 51.33%, while this ratio was determined as 68.40% after the activation with KOH.



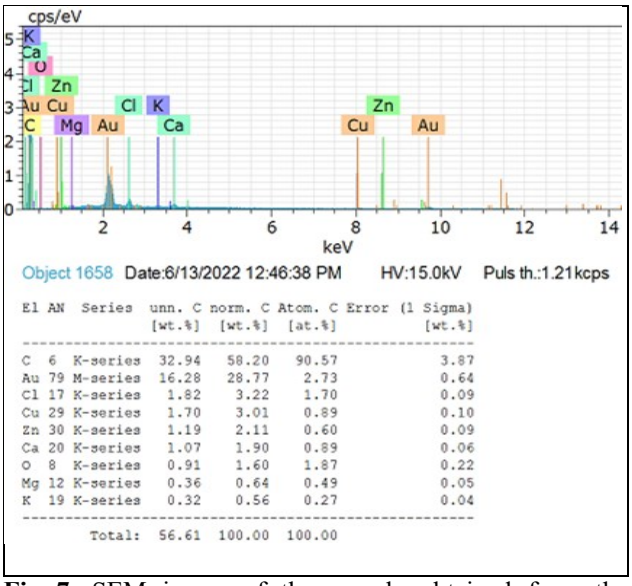


Fig 7. SEM image of the sample obtained from the experiments performed by mixing KOH/Hydrochar=1/1 (1.00KX) and EDX analysis of the marked region

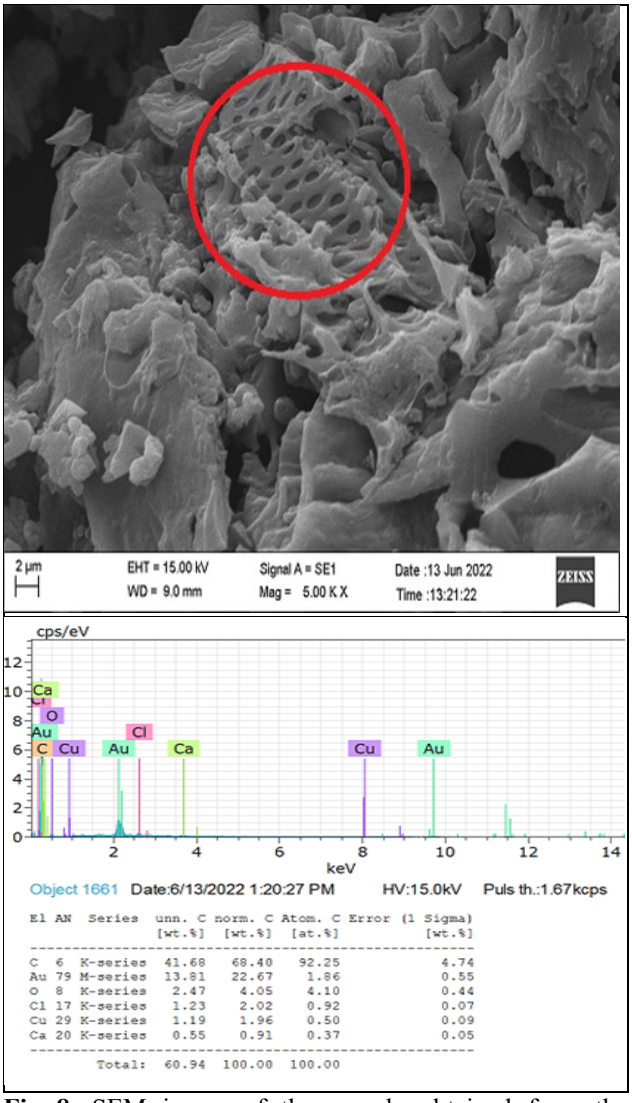


Fig 8. SEM image of the sample obtained from the experiments performed by mixing KOH/Hydrochar=1/2 (1.00KX), and EDX analysis of the marked region

3.3. Methylene blue adsorption experiments and results

The amount of chemicals used for the activation process is an important parameter that affects the activated carbon production process and its economy. In the interaction of lignocellulosic materials with potassium hydroxide, simultaneous reactions occur. These reactions, which start at low temperatures, can be listed as depolymerization of biomass, dehydration of biopolymers, formation of aromatic structures and separation of hydroxyl groups [7].

Adsorption capacities of activated carbon samples obtained from almond shells were determined using methylene blue (MM) solution. Two different concentrated methylene blue solutions of 100 mg/L (100ppm) and 300 mg/L (300ppm) were prepared using 0.07 M sodium acetate-0.03 M acetic acid buffer solution (pH = 4.85). After 50 ml of MM solutions were placed in 250 ml beakers, 0.05 g of adsorbent (activated carbon sample) was added and shaken in a vortex device at 200 rpm for 24 hours. As a comparison sample, sodium acetate-acetic acid buffer solution without MM and containing the same amount of adsorbent was used. At the end of 24 hours, the samples taken from the vortex shaker device were filtered through filter paper. Extraction efficiencies of MM concentrations filtered through the filter were analyzed with an UltraViolet (UV) spectrometer device and calculated. A 660 nm wavelength spectrophotometer was used for UV analyses. MM concentrations of 2, 4, 6, 8, 10 ppm were prepared for UV analyses and a calibration curve was drawn according to these concentrations and the extraction efficiency was calculated according to this curve. In order for the UV device to make accurate measurements, the MM concentrations of our samples were measured after being diluted with sodium acetate-acetic acid buffer solution at the appropriate rate when necessary.

MM adsorption efficiency was calculated with the help of equation (1) below. The MM concentration values of the solutions were measured before (C_o (mg/L)) and after (C_e (mg/L)) the experiments, and these values were written into Equation (1) and the adsorbed MM amounts (q_e, (mg/gr)) per unit amount of adsorbent in equilibrium were calculated [8].

$$q_e = \frac{(C_o - C_e)V}{M_s} \quad (1)$$

M_s (gr) in this equation; indicates the amount of adsorbent used in adsorption, and V (L) indicates the MM solution volume.

In order to see the effect of the amount of activator used in the production of activated carbon, the studies whose conditions are given in Table 1 were carried out and the absorption property of the produced activated carbon was examined in methylene blue solutions prepared at

different ratios. In the absorption studies, the extraction yields seen in Table 2 were obtained. As a result of experiments performed with methylene blue, it was understood that the absorption properties of activated carbon improved as the KOH ratio increased. Moreover, it was observed that the adsorption efficiency was measured as 76.37% in 300 mg/L methylene blue solution (A2 sample).

Table 1. Experimental operating conditions with KOH

Sample Code	Step 1 (Carbonization)		Step 2 (HTC)		Step 3 (Activation)		
A2	Temp. (°C)	Time (h)	Temp. (°C)	Time (h)	Temp. (°C)	Time (h)	KOH/Hydrochar
	800	24	200	12	600	4	(1/1)
A5	800	24	200	12	600	4	(1/2)

Table 2. Methylene blue absorption capacities (In solutions of 100 mg/L and 300 mg/L) of the samples produced in the experiments performed with KOH.

Sample Code	A2	A5
Initial Methylene Blue (ppm)	100	100
Remaining in solution Methylene Blue (ppm)	3.27	7.31
Extraction Yield (%)	96.73	92.70
Initial Methylene blue (ppm)	300	300
Remaining in solution Methylene blue (ppm)	70.88	82.07
Extraction Yield (%)	76.37	72.65

3.4. General results

In this study, almond shells were used to produce activated carbon by the HTC method and the resulting products were characterized. The obtained activated carbon's structural, morphological, and porous characteristics were studied, and the results are as follows.

- The surface on which the porous structures are generated is indented and projecting, and rough surfaces are formed, according to the SEM images of the activated carbon samples acquired in investigations without the application of an activator (KOH). The surface area of the sample, which underwent 12 hours HTC treatment at 100°C, was calculated in the BET analysis to be 0.95 m^2/gr.
- SEM images revealed that chemical activation with KOH following HTC treatment was successful in pore formation. It has been established that the activating agent KOH speeds up the raw material's structural deterioration during the carbonization process.
- In the BET analysis, the surface area of the sample mixed with KOH/Hydrochar=1/1 ratio was determined as 423.56 m^2/g, while the surface area of the sample mixed with KOH/Hydrochar=1/2 ratio was determined as 335.05 m^2/g.
- It was observed that the adsorption efficiency was measured as 76.37% in 300 mg/L methylene blue solution.
- According to the results obtained, it is possible to conclude that the produced material can be used as activated carbon.

Acknowledgement

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