

A NOVEL ACTIVATED CARBON FROM NON LIVING LICHEN CETRARIA ISLANDICA (L.) ACH

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ABSTRACT

Activated carbons obtained from different sources are used for a wide variety of purposes. For example, they are frequently used in wastewater treatment, energy storage, gas purification, catalysis support materials and removal of environmental pollutants. As far as we know, lichens are rarely used in activated carbon production. However, it is more economical and sustainable to produce activated carbon from lichens. Lichens, which can be found in many regions of the world and have a wide variety of species, are organisms consisting of symbiotic combination of fungi and algae. In this study, activated carbon was produced using *Cetraria islandica* (L.) Ach. lichen (LCI) collected from Çankırı region in Turkey. Chemical activation was performed with $ZnCl_2$. Carbonization was carried out in an ash furnace under nitrogen atmosphere at 768 °C for 1 hour. The surface area and pore size distribution of the ACCI and LCI were determined by BET analysis. Physicochemical properties of both the ACCI and LCI were examined by FTIR and TGA analysis. Morphological properties were analysed by XRD and SEM techniques. The BET surface area of the ACCI and LCI was found as 394.417 m^2g^{-1} and 1.103 m^2g^{-1} , respectively. While the LCI had a heterogeneous surface morphology, the synthesized ACCI had a homogeneous and porous surface structure. It was found that activation and carbonization processes caused very significant changes in the LCI molecular structure and surface morphology. As a result, a novel activated carbon with relatively high surface area was successfully synthesized.

Keywords: Activated carbon, Lichen, chemical activation

Introduction

An activated carbon can be defined as a carbonaceous material with increased surface area and pore volume by physical or chemical activation of substances with a high content of carbon. It is known that the most important parameter for activated carbon is the surface area (Yagmur, 2008). In order to determine the surface area, the BET method, in which the physical adsorption of nitrogen gas on the activated carbon, is generally applied and the surface is expressed as the BET surface area (m^2g^{-1}). Another important feature is porosity. IUPAC classified the adsorbents according to their pore size radii as follows: Macro ($r > 25$ nm), mezo (25 nm $>$ 1 nm), micro (1 nm $>$ $r >$ 0.4 nm) and submicro (0.4 nm $>$ r) (Dolas, 2011). The pore structure is effective in determining the adsorption capacity, and the active regions and functional groups on the surface determine whether the adsorption will be feasible or not. Carbonization and activation (physical or chemical) processes are performed to increase the volume and radius of the pores and to create new pores (Rafatullah, 2010). Since the chemical activation process is carried out at a lower temperature and in a shorter time, it is more preferred than physical activation. Zinc chloride is also a frequently preferred activation chemical in chemical activation processes

Of course, most substances with sufficient carbon content, easily available and low cost can be used to produce activated carbon. However, the raw material used in the production of activated carbon significantly affects the chemical and physical properties of the produced activated carbon. In recent years, some biological materials such as agricultural waste, some plants, fruit peels are preferred to produce low cost activated carbons by the researchers (Danish, 2018, Chieng, 2015, Ioannidou, 2007, Jain, 2003, Koyuncu, 2020). *Cetraria islandica* (L.) Ach. (LCI) which is a kind of lichens species, occurs in damp places such as coastal plains, lichen woodlands, bogs and tundra, usually on rocks or the conifer-hardwood trees (Meli, 2018, Crawford, 2015, Koyuncu, 2020). To the best of our knowledge, the production of activated carbon from LCI has not been investigated (Koyuncu, 2020). In this study, a novel activated carbon (ACCI) was obtained from LCI, and characterizations of both the ACCI and the LCI were examined by Brauner-Emmett-Teller surface area (BET), X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR), thermogravimetric analysis (TGA) and scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) techniques at the first time (Koyuncu, 2020).

Materials and Methods

Firstly, the LCI samples were collected from Yapraklı Forest in Çankırı (Turkey). Then non-lichen foreign materials were carefully removed manually under the microscope and the samples were washed several times with

distilled water to remove soil, dust and some salts (Koyuncu, 2020). The biomass sample was dried in an oven at 105 °C for 24 hours and ground in agate mortar using liquid nitrogen. Then it was sieved through a 230 mesh sieve and chemically activated with zinc chloride at a 1/1 (w/w) impregnation ratio. The mixture was dried and carbonized in an ash furnace under nitrogen atmosphere at 768 °C for 1 hour. Chloride and zinc ions were removed by washing and filtration processes, and the sample was dried and sieved again (Koyuncu, 2020).

The synthesized ACCI and the LCI were characterized by using BET (Micrometrics-Tristar II), FT-IR (Nicolet-IS50), XRD (Bruker AXS/Discovery), TGA (TA/SDT650) and SEM/EDX (Zeiss GeminiSEM 300) (Koyuncu, 2020).

Results and Discussion

According to the IUPAC (International Union of Pure and Applied Chemistry) classification, the LCI complies with type III isotherm and the ACCI complies with type I isotherm (Figure 1) (Koyuncu, 2020). It is known that the pore size distribution is predominantly in the micropore region in materials fit the type I isotherm. As shown in Figure 1, the pore size distribution of the ACCI was in the micropore region, whereas, it was in mesopore region for the LCI (Koyuncu, 2020, Koyuncu, 2014). Besides, the BET surface area, Barrett-Joyner-Helenda (BJH) adsorption total volume of pores and BJH adsorption average pore diameter of the LCI and ACCI were determined as 1.103 m²g⁻¹ and 394.417 m²g⁻¹, 0.0044 cm³g⁻¹ and 0.1216 cm³g⁻¹, 140.18 Å (14.02 nm) and 12.768 Å (1.28 nm), respectively (Koyuncu, 2020).

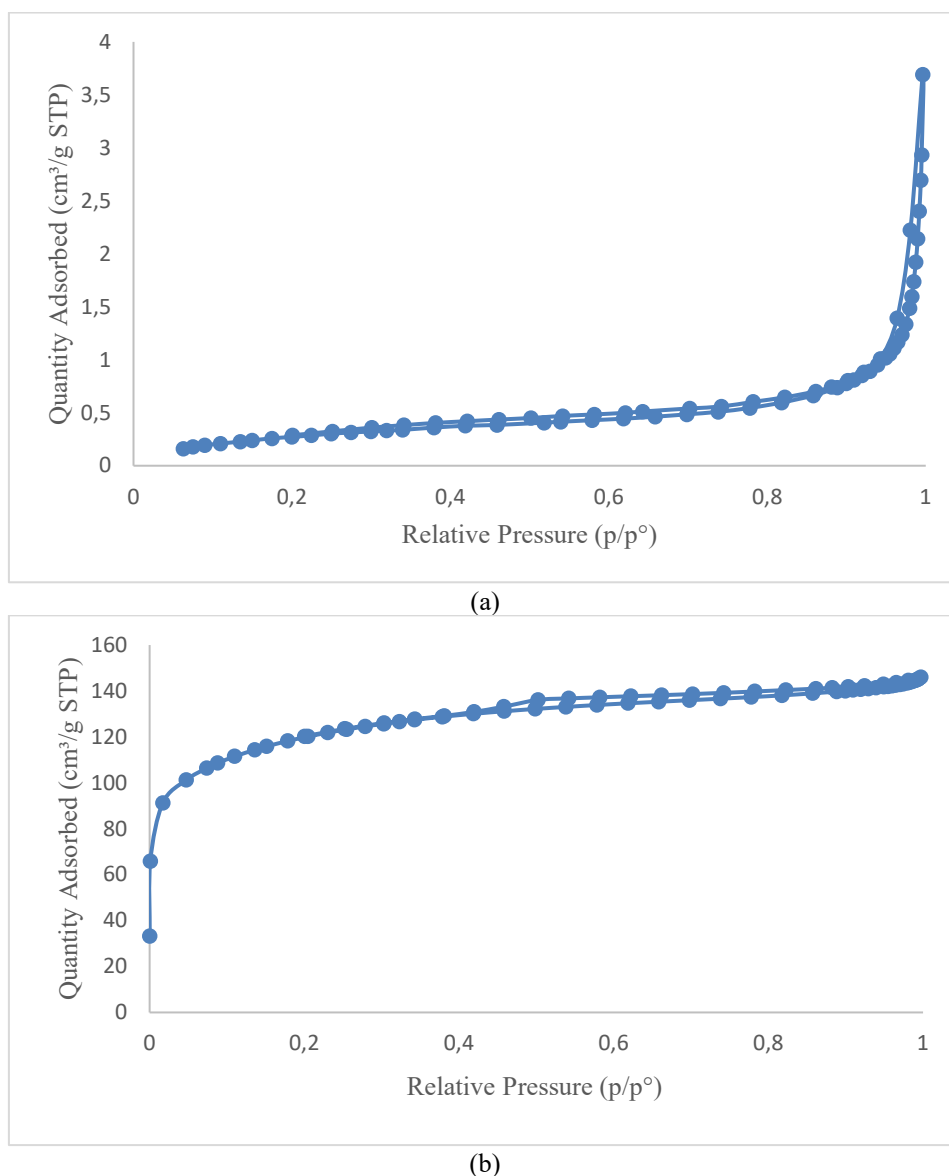


Figure 1. BET isotherms of the LCI (a) and ACCI (b).

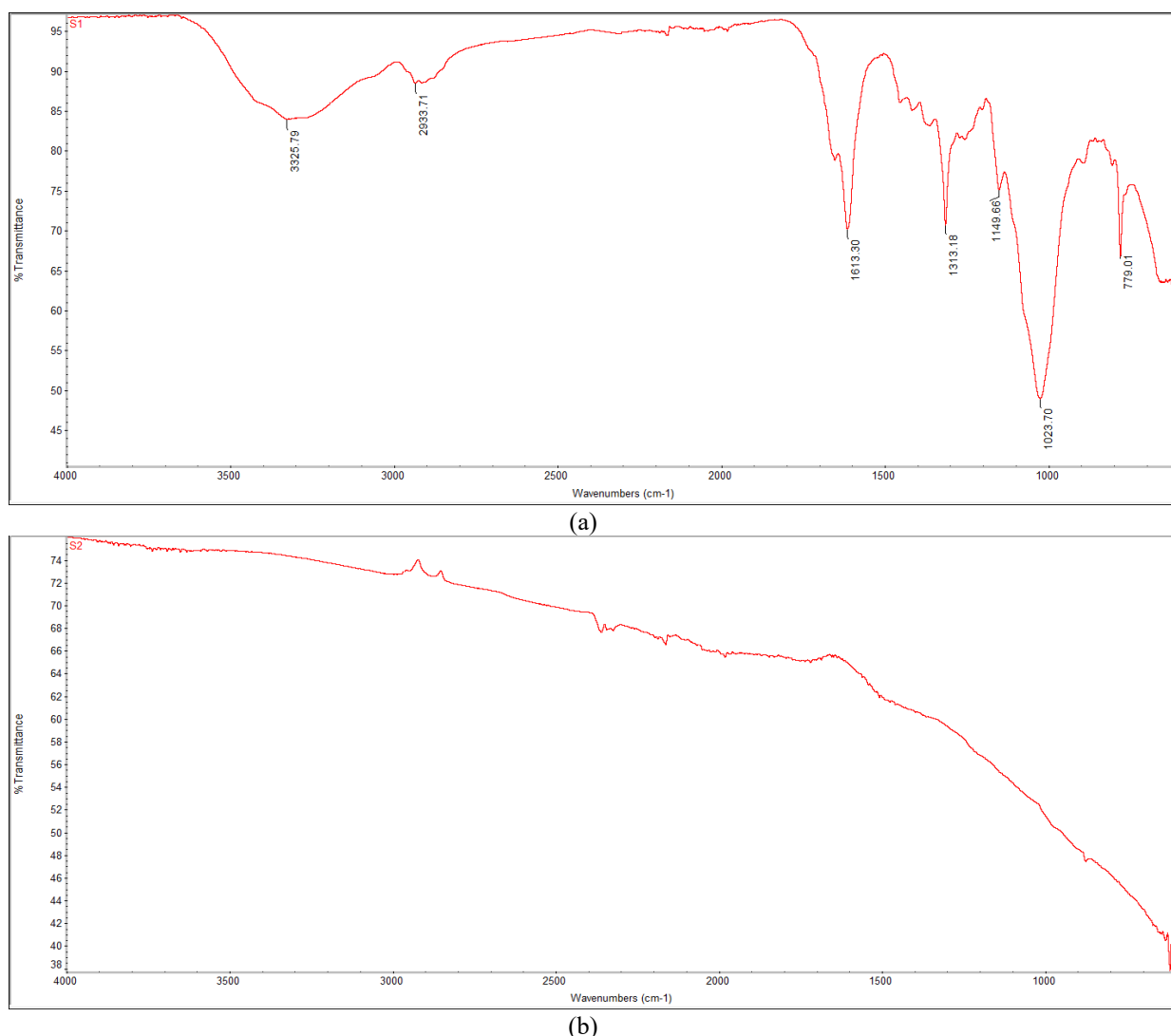


Figure 2. FTIR curves of the LCI (a) and ACCI (b).

The FT-IR ATR spectrums of the LCI and ACCI were shown in Figure 2 (a, b) (Koyuncu, 2020). The wide band around 3300 cm^{-1} was due to stretching vibrations of $-\text{OH}$ groups (Koyuncu, 2020). The peaks at about 2933 cm^{-1} and 1610 cm^{-1} was related to aliphatic $\text{C}-\text{H}$, and aromatic $-\text{C}=\text{O}$ and $-\text{C}=\text{C}$ bonds stretching, respectively. The peaks at 1155 cm^{-1} and 1294 cm^{-1} were from stretching vibrations of the ester group and symmetrical vibration of $-\text{COO}$ bond, respectively (Koyuncu, 2020). The peak observed at 1023 cm^{-1} was assigned to stretching vibration of $\text{C}-\text{O}$ bonds. As can be seen from the Figure 2b, there was a significant change in functional groups in the structure with the effect of the chemical activation and carbonization processes (Koyuncu, 2020). In addition, the results of these effects on the molecular and crystalline structure of the LCI biomass are shown in XRD diffractograms (Figure 3 a,b). We can say that the ACCI contains sharp peaks indicating more crystalline structure, and the peaks at $2\theta = 31.8^\circ, 34.5^\circ, 36.5^\circ$ belong to activated carbon (Koyuncu, 2020).

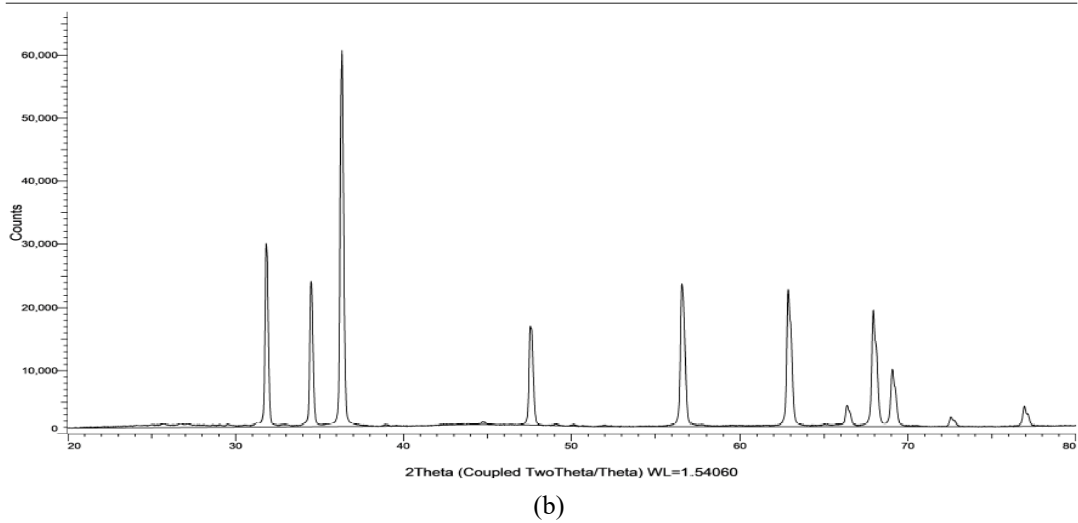
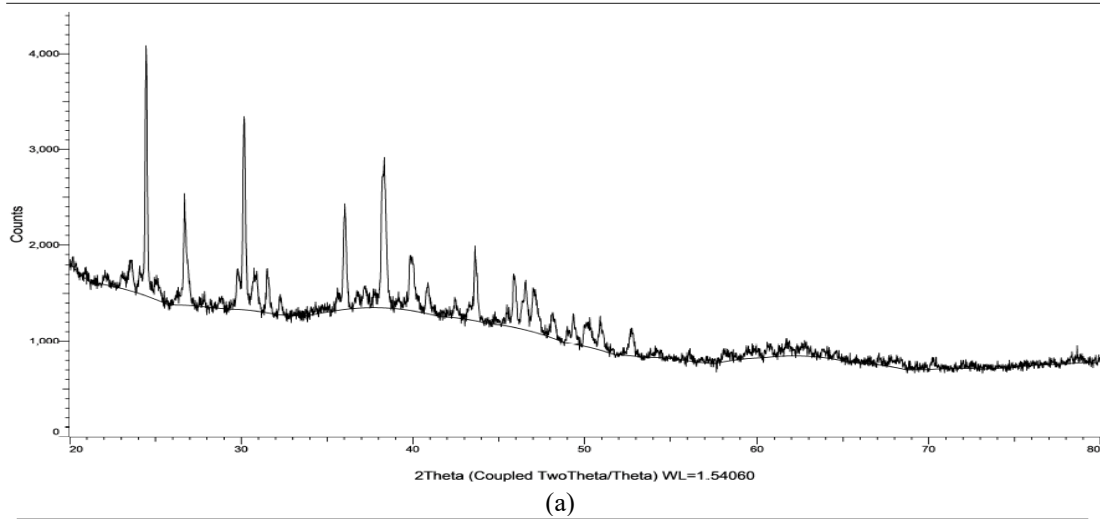
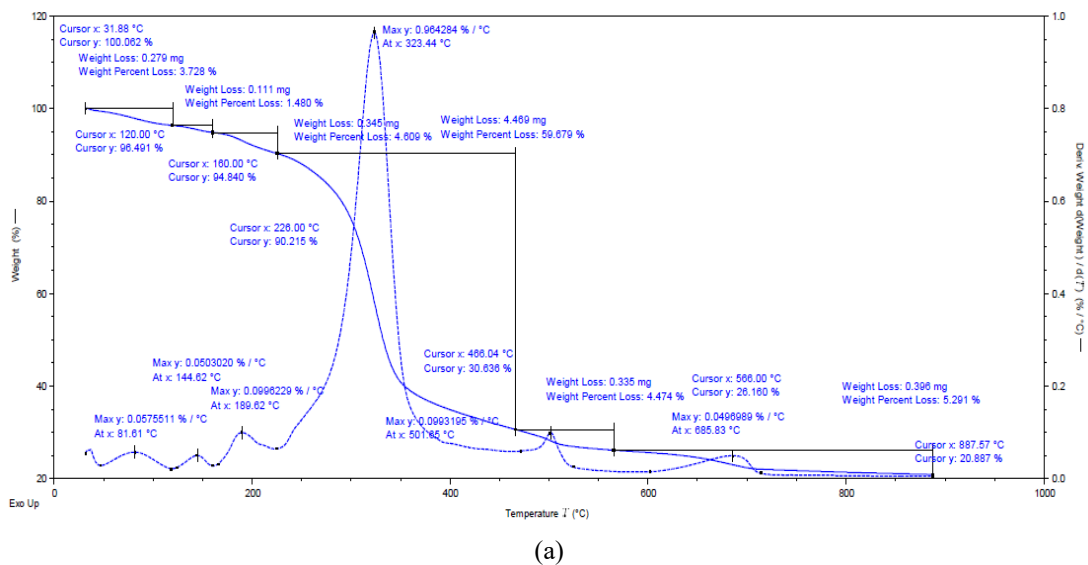
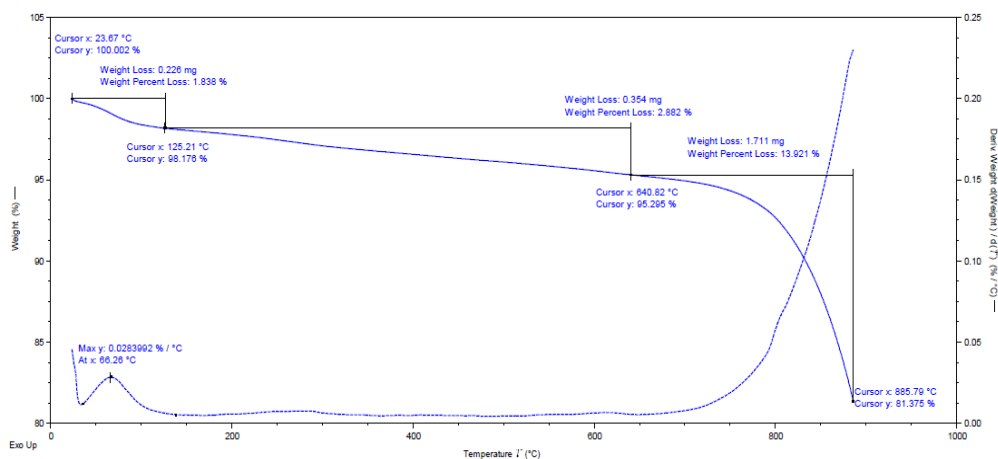


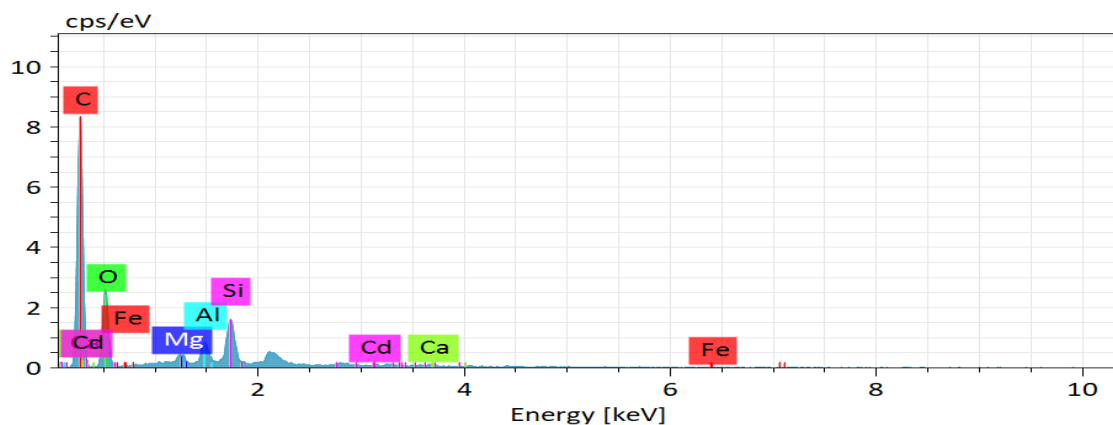
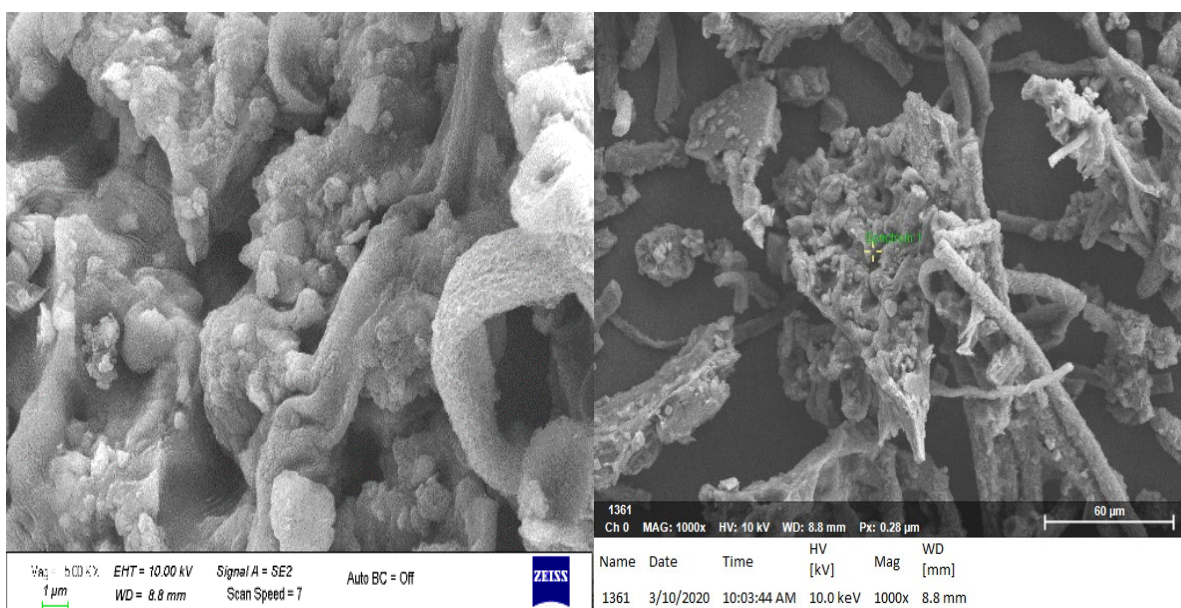
Figure 3. XRD patterns of the LCI (a) and ACCI (b).

Thermogravimetric analysis results of the LCI and ACCI were shown in Figure 4. Except the initial moisture loss, no significant degradation of the LCI was observed up to 350°C (Figure 4a) (Koyuncu, 2020). However, the ACCI showed very stable temperature profile, and almost no degradation was observed until 750°C (Figure 4b) (Koyuncu, 2020).

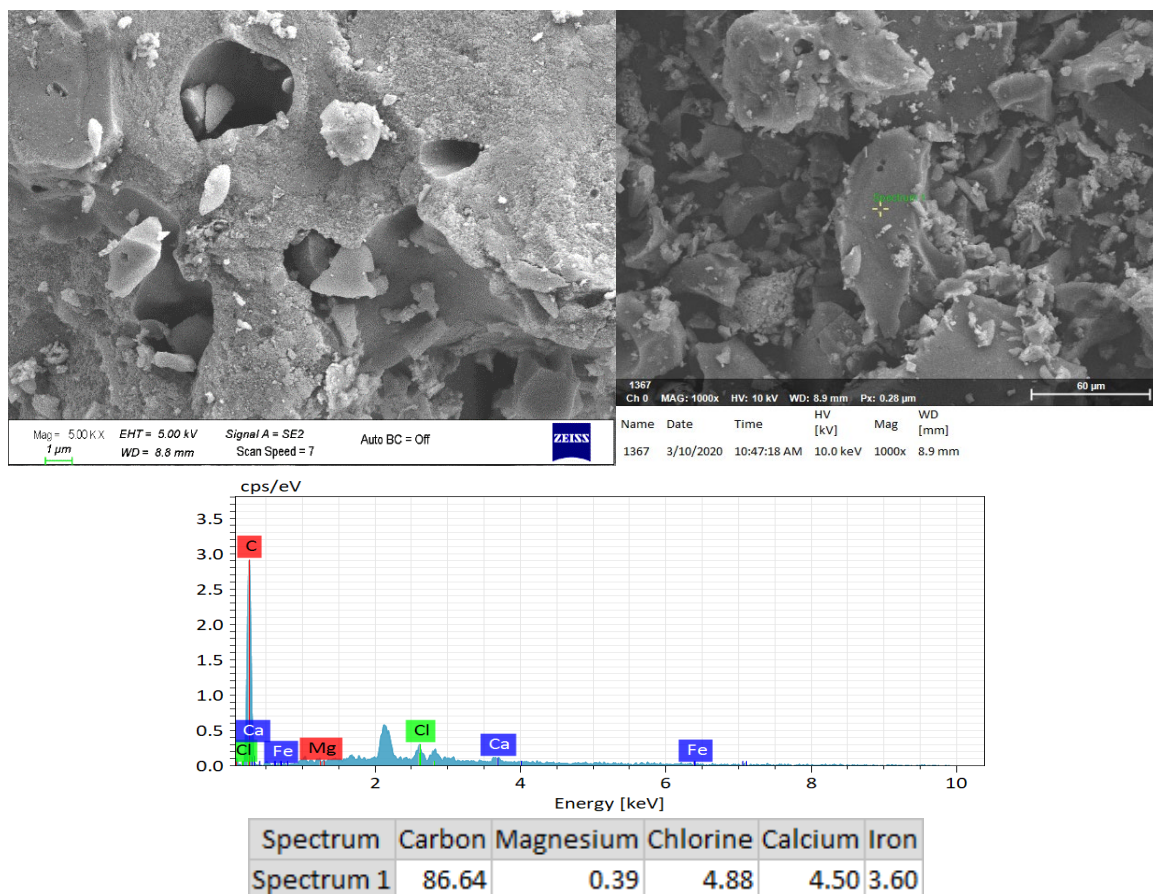




(b)
Figure 4. TGA curves of the LCI (a) and ACCI (b).



(a)



(b)
Figure 4. SEM/EDX results of the LCI (a) and ACCI (b).

SEM images and EDX results of the LCI and ACCI were given in Figure 4 (Koyuncu, 2020). As can be seen from the Figure 5a, the LCI has heterogeneous surface, and the elemental compositions of the LCI surface consist of 61.66% carbon, 25.95% oxygen, 0.91% magnesium, 2.24% aluminium, 7.48% silicon, 0.79% calcium, 0.73% iron and 0.25% cadmium. It should also be noted that the chemical composition is not the same at all points for heterogeneous surfaces.

The carbonization and the chemical activation processes led to have a more homogeneous and porous surface of the ACCI (Figure 4b) (Koyuncu, 2020). The elemental compositions of the ACCI surface are determined with EDX analysis, and found as 86.64% carbon, 0.39% magnesium, 4.88% chlorine, 4.50% calcium and 3.60% iron. As a result, the carbon composition (in percent) of the ACCI was increased from 61.66% to 86.64% by the activation and carbonization processes.

Conclusion

A novel activated carbon was produced from the non-living LCI for the first time, and the physicochemical and morphological properties were characterized. The BET surface area of the ACCI was determined as 394.417 m² g⁻¹. The pore size distribution of the ACCI was in the micropore region, and the pore diameter found as 1.28 nm.

The effects of chemical activation and carbonization processes on the surface were evaluated using different analysis techniques. Summarizing, we can say that the ACCI surface was more crystalline structure, more stable temperature profile and more porous and homogeneous surface than that of the LCI surface.

As a result, we think that the ACCI with high surface area can be utilized in many industrial fields as an effective biosorbent.

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