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STORAGE OF HYDROGEN IN ACTIVATED CARBONS AND CARBON NANOTUBES

ABSTRACT

Activated carbons and carbon nanotube were synthesized with chemical and microwave processes of olive leaf in media with and without ultrasonic waves, and chemical vapor deposition method, respectively. The samples were characterized by x-ray diffraction, calorimetry, Brunauer, Emmett and Teller method, scanning electron microscopy/energy-dispersive X-ray, and zetasizer nano S90 instruments. The activated carbon synthesized in the ultrasonic bath had a higher surface area. The hydrogen adsorption capacity of carbon structures including activated carbons and carbon nanotube was measured as a function of pressure at 77 K. The hydrogen storage capacity of the carbon nanotube is 300% and 265% higher than the hydrogen storage capacity of activated carbons synthesized in medium without and with ultrasonic waves, respectively. Results showed the correlation between hydrogen storage capacity and specific surface area. The highest H₂ storage value was obtained with carbon nanotube at 77 K. As a result, activated carbon and carbon nanotube can be used in hydrogen storage and therefore, the olive leaf can be converted into a high added value product in the energy field.

Keywords: *Olive leaf, carbon nanotube, activated carbon, hydrogen energy*

INTRODUCTION

In parallel with the increasing population and urbanization of the world, the energy demand is increasing day by day. Considering the fact that the fossil fuels are used to meet a large part of the world's energy needs, which will be consumed in a very short time, should be replaced by alternate energy sources [1,2]. In the researches carried out by different research centers, universities and private firms, the fuel that is at the forefront at present is hydrogen. Hydrogen has one of the highest energy density values per mass. Its energy density is between 120 and 142 MJ/kg [3]. However, the problems associated with the transport and storage of hydrogen are the most important obstacles in the transition to hydrogen energy [4]. Current hydrogen storage approaches involve compressed hydrogen gas tanks, liquid hydrogen tanks, complex metal hydrides, chemical hydrogen materials such as chemical hydrides, and carbon-based adsorbents. Although the storage, transport or use in gas or liquid phase of hydrogen is possible, the storage or use in gas phase of hydrogen requires very large volumes and the storage in liquid phase requires both very high pressure and high costs [5]. The storage of hydrogen in a safe, effective, and cheap system is necessary for practical applications, and

therefore hydrogen storage in the solid matrix is the only alternative. Hydrogen can be stored in solid materials such as metal hydrides, organo-metal structured compounds, zeolites, and nano carbon derivatives [6]. It can be said that nano carbon derivatives with the porous structure and high surface area are the most appropriate storage material. The two most important derivatives of nano carbons are carbon nanotube (CNT) and activated carbon.

CNTs were discovered in 1991 by Sumio Iijima [7]. They are one-atom thick sheet of graphite rolled into a tube with a diameter of around one nanometer. CNTs can be produced as single-wall or multi-wall. In recent times, the application of CNTs in various fields such as medicine, engineering, environmental science, energy, catalysis and catalyst supports has been reported by different authors [8-12]. This is largely attributed to their inherent properties such as large surface area and pore volume. Dillon et al. [13,14] first time discovered the hydrogen storage capacity of carbon nanotubes. Hydrogen storage capacities of carbon nanotubes have varied as depending on the type of the nanotubes (single-walled, multi-walled), whether the tubes are closed or open, tube dimensions (tube diameter, length etc.) and the activity of the tube surfaces [15]. CNTs have been synthesized by different methods such as arc discharge method, laser method, chemical vapor deposition and ball milling [16]. Hydrogen storage capacities of some carbon nanotubes synthesized from different sources have been given in Table 1. As can be seen from the table, the hydrogen storage capacity of carbon nanotubes varies in the ranges of 0.2 to 5% by weight.

Table 1. Hydrogen storage capacities of some carbon nanotubes

CNTs	Temperature (K)	Pressure (MPa)	H ₂ (% weight)	References
SWCNT	298	10	4-5	[17]
SWCNT	295	0.1	0.93	[18]
SWCNT	at room	4.8	1.2	[19]
SWCNT	323	-	4.77	[20]
SWCNT	-	3	0.8	[21]
MWCNT	-	0.005	2	[22]
MWCNT	77	0.1	0.54	[23]
MWCNT	298	10	0.2	[24]
MWCNT	425	3	3.8	[25]
MWCNT	143	7.5	3.5	[26]

Activated carbon can be defined as carbonaceous materials with a very high pore size and internal surface structure, which cannot be characterized by structural formula or chemical analysis in any way. The fact that activated carbons have a high pore size and internal surface area allows these materials to be used as an effective adsorbent on an industrial scale [27]. One of the first studies on the use of activated carbon in the storage of hydrogen was carried out by Kidnay and Hiza in 1967 [28]. They determined hydrogen adsorption isotherms at 76 K and different pressures of activated carbon samples from coconut shells and found that 20.2

g of hydrogen at 25 atm was adsorbed by 1 kg of activated carbon. Jorda-Beneyto et al. [29] measured the hydrogen storage capacities of a series of chemically activated carbon samples at different temperatures and pressures. They found that the amount of hydrogen adsorbed on activated carbon at 298 K depended on both the micropore volume and micropore size distribution, and that the storage capacities of hydrogen on the chemically activated carbon at 20 and 50 bar pressures at 298 K were 1.2 and 2.7% by weight, respectively. Jimenez et al. [30] examined hydrogen storage capacities of various carbon samples containing activated carbon and carbon nanofibers as a function of pressure and temperature. They found that the adsorption capacity values at room temperature and 10 bar pressure were less than 0.1% by weight and that the highest hydrogen adsorption capacity at 77 K and 10 bar was 2.02% by weight. Akasaka et al. [31] synthesized microporous carbon samples with KOH activation of the coffee core. They found that the hydrogen adsorption capacity of the samples at 298 K increased linearly with increasing surface area and that the hydrogen adsorption capacities of sample with 2070 m²/g surface area at 290 and 77 K were 0.6 and 4%, respectively.

As can be seen from the above studies, there are not any studies on the production of activated carbon from olive leaf and its use in hydrogen storage. Moreover, the effect of the ultrasonic waves on some properties of activated carbon was not investigated and at the same time, the hydrogen storage capacities of the carbon nanotube and activated carbon were not also compared with each other. For this reason, in this study, firstly olive leaf was ground in a Fritsch Planetary ball mills, and activated carbons were then synthesized by chemical and microwave process in media with and without ultrasonic waves. Secondly, carbon nanotubes were synthesized according to the method of chemical vapor deposition from acetylene gas. The synthesized samples were characterized using x-ray diffraction (XRD), Brunauer, Emmett and Teller method (BET), scanning electron microscopy/energy-dispersive X-ray (SEM/EDX), and zetasizer nano S90 instruments. The hydrogen storage capacities of the samples were also measured at 77 K using the Hiden IMI PSI device.

MATERIAL AND METHODS

All chemicals used in study were purchased in analytical grade and used without further purification. Olive leaf was obtained from Edremit-Balikesir in Turkey.

Synthesis of activated carbon

The olive leaf obtained as wet was first washed with tap water, and then with distilled water five times. The olive leaf removed from the dusts was dried at 105 °C for 2 days. Dried

leaf was grinded to the ball mill and then sieved to a size of 100 µm with Retsch GM 200 sieving. Samples with particle sizes less than 100 µm were ground in a Fritsch Planetary ball mills to reduce the particle size of the olive leaf powders below 200 nm. The ball-milling process was conducted at room temperature with a rotation speed of 500 rpm for 45 minutes. The mass ratio of ball to olive leaf was fixed at 100:1. For chemical activation, these samples were firstly mixed with 0.5 M ZnCl₂ (CAS Number: 7646-85-7) at 1/3 ratio and activated in an ultrasonic and non-ultrasonic bath for 24 hours. The activated samples were

filtered, washed with distilled water and then dried at 105 °C for 48 hours. The dried samples were subjected to a microwave process at 600 watts for 15 minutes. Synthesized samples were exposed to ultrasonic waves to allow for separation of the nested samples. The activated carbon samples were then characterized and measured their hydrogen storage capacity [31, 32].

Synthesis of carbon nanotube

Carbon nanotube was synthesized according to the method of chemical vapor precipitation from acetylene gas [33].

Characterization of activated carbon and carbon nanotubes

The techniques used in the characterization of olive leaf, activated carbon samples and carbon nanotube have been given below.

BET surface area analysis

BET surface areas of the samples were measured using a Quantachrome Nova 2200e series instrument. Before analysis, the samples were degassed at 200 °C for 24 hours and then their surface areas were measured using pure nitrogen gas as adsorbent in liquid nitrogen (77 K) media.

Calorimetric Analysis

Calorimetric measurements of activated carbon samples were performed using the IKA Analysentechnik C5000 instrument.

Particle size analysis

The particle sizes of the ground olive leaf powders were measured using a Malvern zetalyzer nano S90. Olive leaf powders in measuring of particle size were dispersed in water.

XRD analysis

XRD measurements of the samples were performed with Malvern PANalytical Philips X'Pert-Pro X-ray diffractometer. The device with copper cathode and monochromator $\lambda=1.54$ nm was analyzed at 30° at 2°/min scan speed and 5-80° at 40 kV.

SEM/EDX analysis

Surface morphology of samples was measured with a Zeiss EVO LS 10 scanning electron microscope. Prior to examining the morphology of the samples, the olive leaf, activated carbons and carbon nanotube were fixed on the conductive carbon tape and Au-Pd coating was applied for 15 seconds under a current of 20 μ A.

Hydrogen storage analysis

Hydrogen gas adsorption measurements of activated carbon and carbon nanotube samples were carried out at -198 °C with the Hiden IMI PSI gas storage device.

RESULTS AND DISCUSSIONS

Particle size analysis

Prior to particle size analysis, the olive leaf was washed, dried, ground and sieved from 0-100 μm sieves. It was then ground at 500 rpm for 45 minutes in a Fritsch Planetary ball mills to reduce the particle size of the sieved olive powders below 200 nm. The particle size analysis of the ground samples was measured using zetasizer nano S90 device. As seen in Figure 1, the particle size of the ground olive leaf powder was below 200 nm. The most important goal when the particle size is reduced below 200 nm is to increase the BET surface area of sample, and to synthesize microporous activated carbons during the activation process.

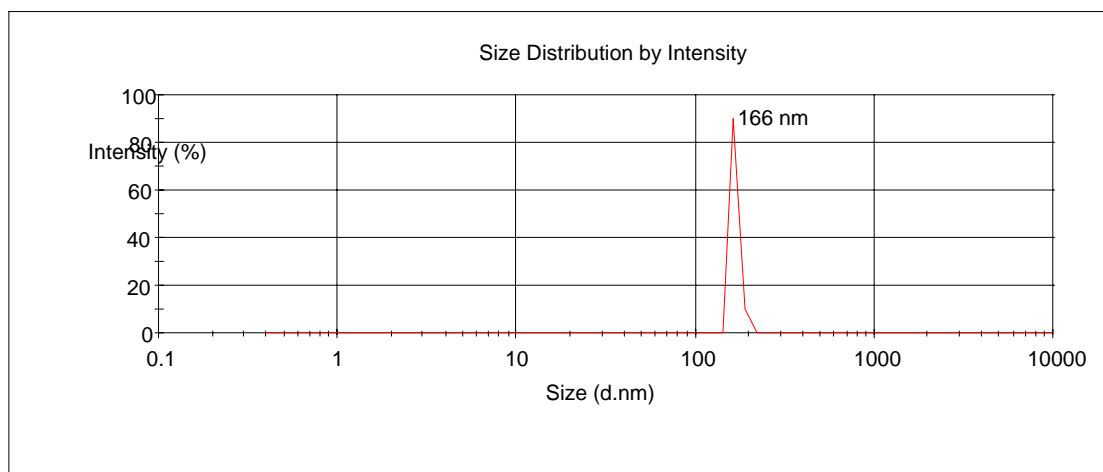


Fig. 1. Particle size measurement of olive leaf powders

Calorimetric analysis

Calorimetric analyzes of olive leaf and activated carbon samples were made to determine their heat values. When the values in Table 2 were examined, it can be concluded that heat values of the samples are increased by chemical activation and microwave process, and that both chemical activation and microwave process are important parameters in activated carbon synthesis. It can be said that the heat values of the samples exposed to ultrasonic waves from the values in Table 2 are slightly higher than the heat value of the samples synthesized in the non-ultrasonic media. This result reveals the importance of ultrasonic waves in the activation process. That is, ultrasonic waves have influenced the activation in a positive way.

BET surface area analysis

The BET device is used in the measurement of surface areas of dust or bulk samples and in nano, meso and macro pore size analyzes. As the particle sizes of the samples decrease, the surface areas generally increase. BET surface areas of samples were measured by degassing at 200 °C for 24 hours. The results in Table 2 show that the activated carbon synthesized in the ultrasonic bath has a higher surface area than the activated carbon synthesized in non-ultrasonic media. This can be due to the fact that the activating agent with the effect of ultrasonic waves penetrates better into the olive leaf.

Table 2. Some physicochemical properties of olive leaf and activated carbons

Samples	Heat values of samples (kcal/g)	BET surface area (m^2/g)	Elemental content (%)			
			C	O	N	S
Olive leaf	2.03	5	51.6	43.7	4.8	0.1

Activated carbon (Non-Ultrasonic)	4.66	92	62.3	33.8	3.8	0.1
Activated carbon (Ultrasonic)	4.69	172	73.4	22.9	3.7	0.0

XRD patterns of olive leaf, activated carbons and carbon nanotube

Figure 2a shows the XRD patterns of olive leaf, activated carbon (ultrasonic) and activated carbon (non-ultrasonic), and Figure 2b XRD pattern of the carbon nanotube. Figure 2a shows that there is no significant change in the crystal structure of the activated carbons synthesized by the chemical activation and microwave process of the olive leaf in ultrasonic and non-ultrasonic bath, and the active carbons are in the amorphous structure. On the other hand, when the XRD structure of the carbon nanotube is examined, it is seen that it has a small peak of about $2\theta=43^\circ$. This peak shows the XRD peak of the graphite sheets forming the structure of the carbon nanotube [33].

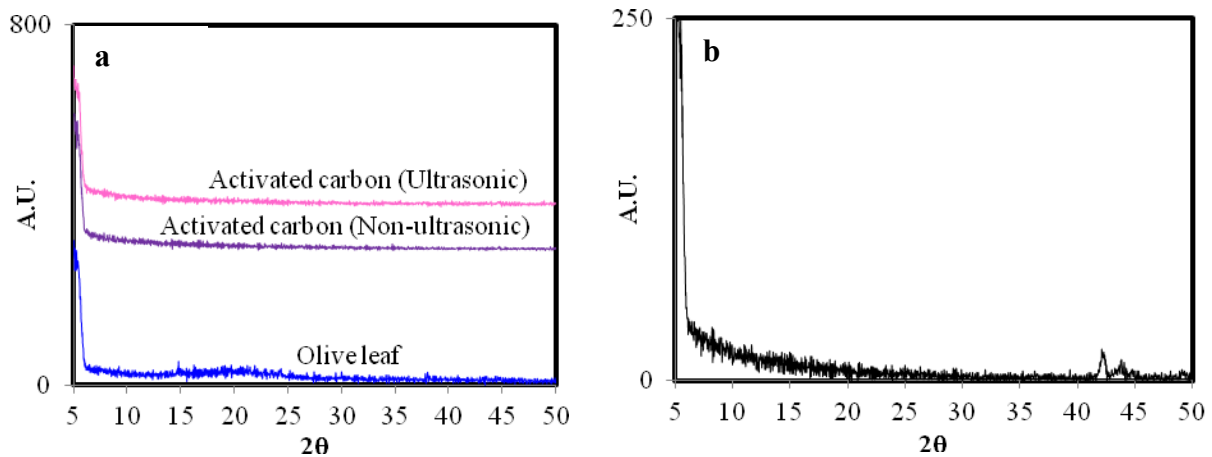


Fig. 2. XRD patterns of: a) olive leaf, activated carbon (non-ultrasonic) and activated carbon (ultrasonic) b) carbon nanotube

SEM/EDX analysis

SEM images of olive leaf, activated carbon (non-ultrasonic), activated carbon (ultrasonic) and carbon nanotube have been given in Figures 3a-6a, and EDX analysis of those in Figures 3b-6b. From SEM images, it can be said that the activated carbons synthesized in media with and without ultrasonic waves have much more porous structure according to olive leaf. When EDX graphs are examined, it is seen that mainly C, N, O and S are found in the structures of activated carbons. Table 2 shows the elemental contents of olive leaf, activated carbon (non-ultrasonic) and activated carbon (ultrasonic). When the results were examined, it was found that the carbon content of the samples increased with the chemical activation and the microwave process, while the oxygen, nitrogen and sulfur contents decreased. Furthermore, ultrasonic waves in activated carbon synthesis have an important effect on activating and forming a porous structure. The increase in carbon content of the samples by chemical and microwave processes can be used as an indication of the synthesis of the activated carbon. Again, when the experimental results in Table 2 are examined, it is shown that the activated carbon synthesized in the ultrasonic bath has higher carbon and lower nitrogen, oxygen and sulfur contents than the activated carbon synthesized in the non-ultrasonic bath. This shows that zinc chloride with ultrasonic waves penetrates into the inner parts of the olive leaf and

accelerate the chemical activation. As a result, a more porous structure occurs. It is seen from Figure 6 that the carbon nanotubes are synthesized and they are in tube form.

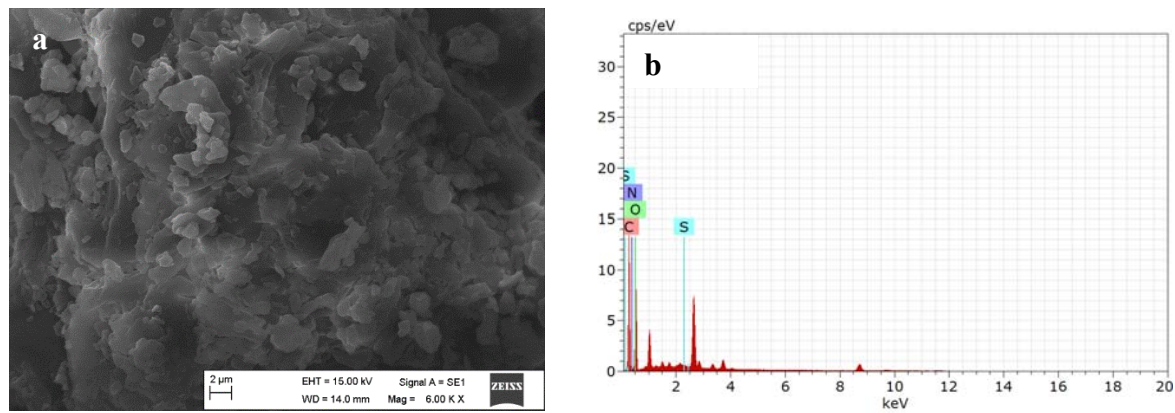


Fig. 3. a) SEM and b) EDX images of olive leaf

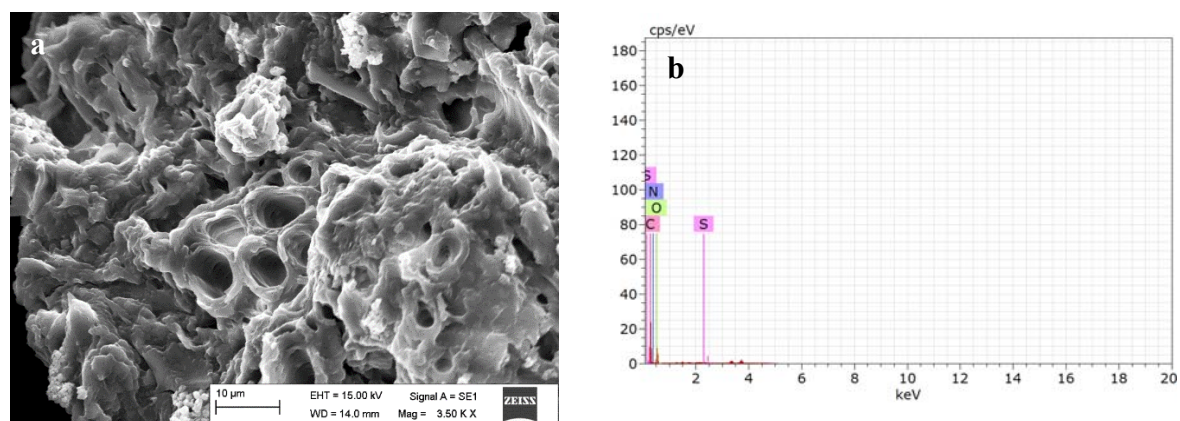


Fig. 4. a) SEM and b) EDX images of activated carbon (non-ultrasonic)

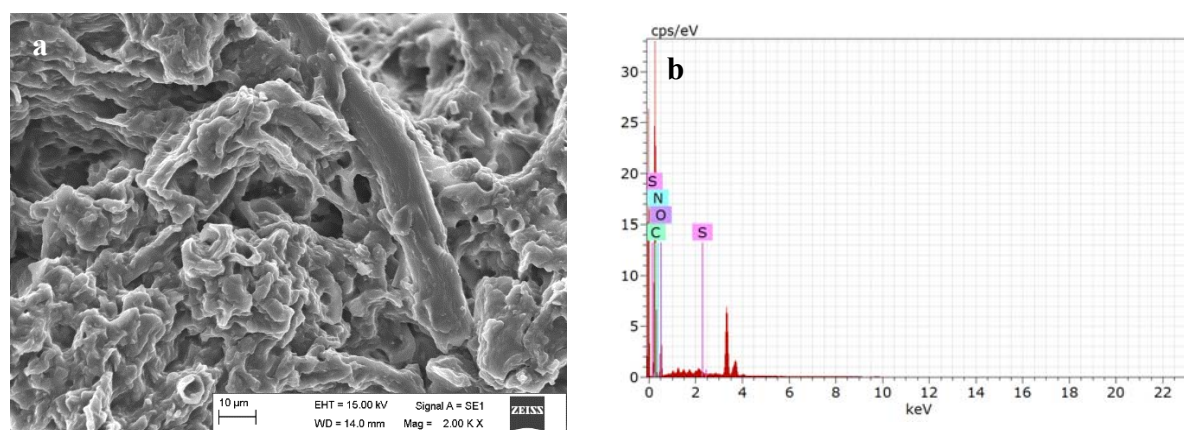


Fig. 5. a) SEM and b) EDX images of activated carbon (ultrasonic)

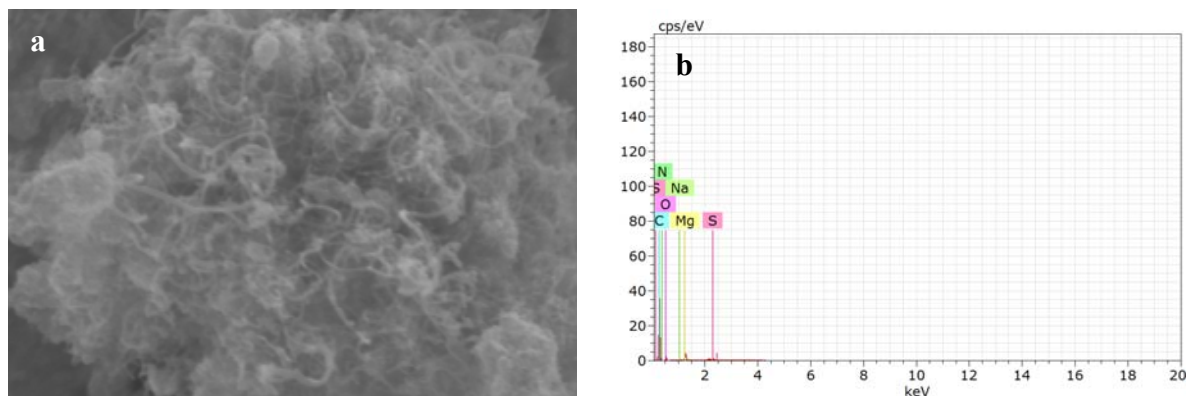


Fig. 6. a) SEM and b) EDX images of carbon nanotube

Hydrogen storage analysis

The potential of activated carbons and carbon nanotube as hydrogen adsorption materials was investigated at 77 K. Figure 7 demonstrates the H₂ adsorption isotherms for two activated carbons and carbon nanotube at 77 K in the pressure range of 0-80 bar. Experiments should be carried out at low temperatures to increase Van der Waals interactions between adsorbent and hydrogen [34]. For this reason, the samples in the experiments were immersed in a Dewar tank filled with liquid nitrogen under vacuum. Because weak interactions that hold hydrogen molecules together are more important at cryogenic temperatures (77 K) and/or higher pressures [15]. In general, in hydrogen storage systems it is desirable to adsorb hydrogen to the adsorbent surface in a reversible manner with physical forces. A physical sorption is a process in which the hydrogen molecule is bound to the adsorbent surface by weak Van der Waals interactions. In this process, hydrogen molecules retain their molecular forms and do not participate in any chemical reaction such as decomposition. For this reason the physical sorption is a very fast and completely reversible process [35]. H₂ adsorption isotherms for activated carbons and carbon nanotube show similar behavior. However, their hydrogen storage capacities are different each other. Among these activated carbons, activated carbon synthesized in media with ultrasonic waves has the highest H₂ uptake because of the high surface area. At the pressures studied, it can be observed that hydrogen is near to reach the plateau for all adsorbents. Hydrogen storage capacities of all samples have increased with increasing pressure. Hydrogen uptake of porous materials at low pressure is usually dominated by pores in the sub-nanometer range. The continuous increase in the adsorption isotherms at high pressure can be considered as evidence that an important contribution of the pores in the near-mesoporous region is developed in the samples. The hydrogen storage capacities of activated carbons synthesized in medium without and with the ultrasonic waves and carbon nanotube at 77 K and 80 bar were 0.38, 0.43 and 1.14 g/g, respectively. The fact that the carbon nanotube has more hydrogen storage capacity than the activated carbon may be due to increasing of Van der Waals forces at cryogenic temperature and due to more hydrogen adsorption on the inner and outer surfaces of carbon nanotube. The carbon nanotube can be thought of as a porous tubular structure. Hydrogen storage capacity of activated carbon samples is directly proportional to BET surface area and pore size distribution. As can be seen from the SEM/EDX images and the BET surface areas, the activated carbon synthesized in the presence of ultrasonic waves has both a higher porosity and carbon content and a higher BET surface area.

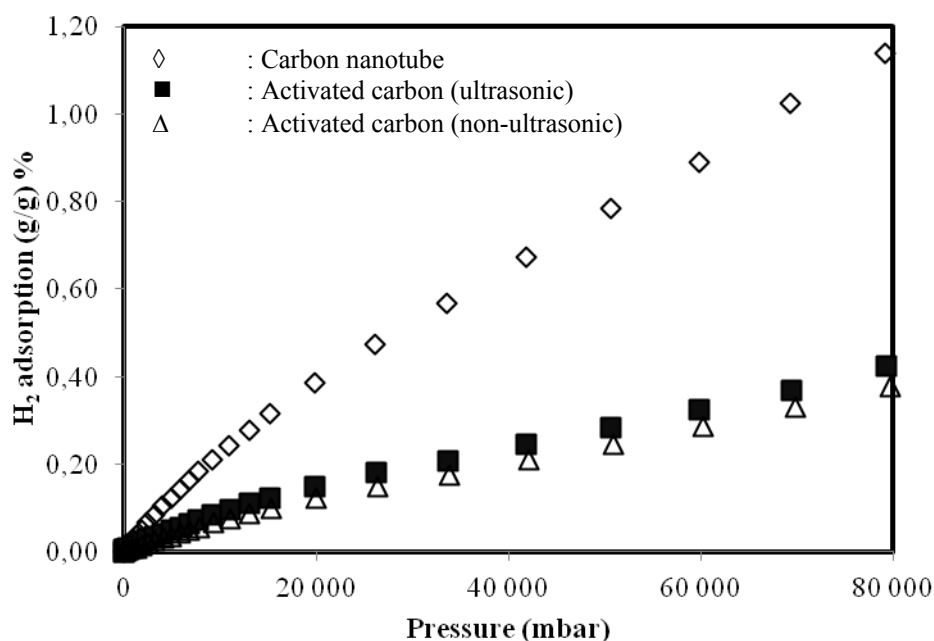


Fig. 7. Hydrogen storage capacities of activated carbon (non-ultrasonic), activated carbon (ultrasonic) and carbon nanotube

Hydrogen storage capacities of the activated carbon samples synthesized from different sources were measured by various researches in the literature. Jorda-Benyto et al. [26] found that the chemically activated carbon had hydrogen storage capacities of 1.2 and 2.7% at 20 and 50 bar pressure at 298 K, respectively. Jimenez et al. [30] investigated the hydrogen adsorption capacities of various carbon samples such as activated carbon and carbon nanofibers as a function of pressure and temperature. They found that the adsorption capacity values obtained at room temperature and 10 bar pressure were less than 0.1% by weight and that the highest hydrogen adsorption capacity at 77 K and 10 bar was 2.02% by weight, depending on temperature and pressure. Akasaka et al. [31] synthesized microporous carbon samples with KOH activation of the coffee core. They found that the hydrogen adsorption capacity of the samples at 298 K linearly increased with increasing surface area, and that the hydrogen adsorption capacity at 298 and 77 K of the sample with 2070 m²/g surface area was 0.6 and 4%, respectively. When the hydrogen storage capacity of carbon nanotubes is compared with the values in the literature (Table 1), it can be seen that similar results were obtained with some studies.

CONCLUSIONS

In this study, it was obtained the following results:

- By grinding in a Fritsch Planetary ball mills of the olive leaf, olive leaf powders with less particle size than 200 nm were obtained.
- The activated carbons were amorphous structure.
- The activated carbon synthesized in the ultrasonic bath had a higher surface area. The BET surface area values were 5 m²/g for olive leaf, 92 m²/g for activated carbon

synthesized in medium without the ultrasonic waves and 172 m²/g for activated carbon synthesized in medium with the ultrasonic waves.

- The heat values of the activated carbon samples were considerably higher than that of the olive leaf.
- The activated carbon according to olive leaf had a more porous structure.
- The activated carbon samples had higher carbon content than the olive leaf. The carbon content of the olive leaf used as starting material was 51.6%, while the carbon content of the activated carbon obtained in the ultrasonic bath increased to 73.4% and the carbon content of activated carbon prepared without ultrasonic effect increased to 62.3%.
- The hydrogen storage capacity of the carbon nanotube was higher than the activated carbon. The hydrogen storage capacities of activated carbons synthesized in medium without and with the ultrasonic waves and carbon nanotube at 77 K and 80 bar were 0.38, 0.43 and 1.14 g/g, respectively. The hydrogen storage capacity of activated carbon synthesized in medium with ultrasonic wave is 13% higher than that of activated carbon synthesized in medium without ultrasonic waves. On the other hand, the hydrogen storage capacity of the carbon nanotube is 300% and 265% higher than the hydrogen storage capacity of activated carbons synthesized in medium without and with ultrasonic waves, respectively.

The results of this study show that olive leaf can be used in high heat release activated carbon synthesis and regarded as an important adsorbent especially in hydrogen storage.

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