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Microporous and Mesoporous Materials 88 (2006) 126–134

MICROPOROUS AND MESOPOROUS MATERIALS

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Preparation and characterization of activated carbons by one-step steam pyrolysis/activation from apricot stones

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Received 10 May 2004; received in revised form 5 September 2005; accepted 7 September 2005
Available online 25 October 2005

Abstract

The activated carbons were prepared from Malatya (a city located in the south-east of Turkey) apricot stones by one-step steam pyrolysis/activation process and characterized for their pore structures. Three kinds of apricot stones that differ in their sulfur content, because of the different drying processes, were chosen for this study to investigate the effect of sulfur in the activated carbon production. The effect of process variables, such as activation temperature, soak time, and particle size range was studied on these samples. The activation temperature and time tested were in the ranges of 650–850 °C for 1–4 h. The activated carbons were evaluated for their chemical (elemental composition), surface (BET surface area, mercury porosimetry), and adsorption (iodine number) properties. Carbonization behavior of the apricot stones was investigated by thermogravimetric analysis. Scanning electron microscopy (SEM) was used to follow the changes in the carbon texture upon activation.

The experimental results revealed that carbons obtained by the same conditions of activation show differences in their pore structures and adsorption characteristics due to their sulfur contents. The highest BET surface area carbon (1092 m^2/g) was obtained from the low sulfur content (0.04%) apricot stone with a particle size range of 1–3.35 mm at the activation conditions of 800 °C for 4 h. The experimental results showed that commercial production of porous activated carbons from Malatya apricot stones is feasible in Turkey.

Keywords: Activated carbon; Physical activation; Surface area; Adsorption properties; Apricot stones

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1. Introduction

Depending on their availability, coal and some agricultural by-products, such as nutshells and fruit stones are widely used for activated carbon production [1–6]. Due to their abundant supply lignocellulosic or agricultural waste products became highly attractive raw materials in activated carbon production compared to coal-based feedstock. Different than the coal-based activated carbon, lignocellulosic or agricultural waste product-based carbon shows higher volatile content and as a result lesser solid yield. However, the increasing demand of adsorption processes in the water treatment industry is encouraging the continuation of the research in the production of activated carbon from alternative precursors including industrial wastes and agricultural by-products [7,8].

Activated carbon is a highly porous form of solid carbon produced from carbonaceous raw materials using chemical or physical activation methods. The physical activation of lignocellulosic chars with steam or carbon dioxide is a conventional manufacturing process of the activated carbon [8]. The physical activation process can be performed by one- or two-step activation methods. The two-step activation involves carbonization of a

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doi:10.1016/j.micromeso.2005.09.003

carbonaceous precursor followed by the activation of the resulting char in the presence of some activating agents such as carbon dioxide, steam or both. In the one-step activation process, pyrolysis and activation were carried out simultaneously in the presence of steam [9]. The one-step steam pyrolysis and activation process has been used to prepare activated carbons from the lignocellulosic materials such as apricot and cherry stones or almond, walnut and coconut shells, and grape seeds [1,9,10]. In this study, activated carbons were prepared from apricot stones by using the one-step steam activation method. The one-step activation method with steam has advantages over the two-step method, due to its simplicity and efficiency in the preparation of activated carbons from lignocellulosic materials [11] and anthracite [12]. The one-step method eliminates the separate carbonization step that is used in the conventional two-step method and employs lower temperatures in the preparation of the activated carbons.

Previously, one-step activation method was applied to apricot stones with steam by several researchers [9,13,14] and preparations of activated carbons were accomplished. Besides the selection of the activation method, activating agent selection is also important to control the porous structure of the activated carbon. Steam and CO_2 are commonly used activating agents. For example gasification with steam produces a more noticeable widening of microporosity to mesoporosity with the increasing effect of activation compared to that obtained by carbon dioxide [15,16]. These differences result from the different reactivities of steam and CO_2, which control the competition between the rates of diffusion and gasification reactions. For example, by steam activation, a higher surface area was developed from anthracite in a shorter time, compared to the CO_2 activation [17]. The major factors that determine the suitability of a raw material for activated carbon production include the carbon and inorganic material contents, ease of activation, bulk density, mechanical strength, cost, availability, and the specific application for the resulting activated carbon [18]. The nature of the precursor, activation method, and activation conditions determine the characteristics of porosity in activated carbons, including pore size distribution, shapes of the pores, and surface chemistry [15,19,20].

Activated carbons with different pore structures can be produced from the same precursor by varying the operating variables and activation agents. The main application of activated carbons is found in purification or recovery of chemicals by selective adsorption. Activated carbons are also used as catalyst supports or catalysts [21].

The main objective of this study was to determine the optimum activation conditions to produce activated carbon using this local raw material in Malatya. Apricot stones are cheap and abundant solid agricultural waste in Malatya, Turkey. 120,000 tons of apricot per year is harvested in Malatya (a city located in the south-east region of Turkey). All the produced apricots are either consumed as fresh fruit or desiccated and exported to all over the world. In the preparation of desiccated apricot, sulfur (in the form of SO_2) rooms are used and a drying method is applied. Due to this drying method, apricots may contain various amounts of sulfur. Annual dried apricot production in Malatya is estimated to be 40,000 tons. The wide availability of these by-products makes them a possible source for activated carbon production in Malatya. High transportation costs can be prevented in the production of activated carbons, using a local raw material. Therefore, it is important to evaluate apricot stones, as an activated carbon resource and as a local raw material in Turkey. Furthermore, apricot stones were also proved to be an excellent precursor for the production of activated carbons [1]. In view of that, the operating variables, activation time and temperature, and raw material particle size range were determined.

Although, in the literature there are a number of studies on the physical and chemical characterization of apricot stones [1,9–11] as activated carbons, there is no research on the stones and their carbons due to their raw material preparation. The abundant production of apricot stones in Malatya/Turkey, make these stones versatile lignocellulosic activated carbon precursors for Turkey, however, the number of techniques used in the preparation of the precursors lead to a different approach in the scientific investigation of their properties as activated carbons. Therefore, different kinds of apricot stones of this region were investigated thoroughly due to their processing techniques along with their activated carbons in this study. A startling difference was found in the elemental composition of these stones (such as, elemental sulfur content) as a result of whether these stones were processed through a desiccation process or not. Therefore, this study brings out a new approach in the investigation of apricot stones depending on their drying process.

2. Experimental

2.1. Precursor preparation

Ten different kinds of apricots are grown in Malatya region. In this present study, apricot stones of one of these types, Kabaaşı, and a mixture of all 10 types were chosen as precursors. Two samples were prepared from Kabaaşı apricots that are dried by different processes: KC01, under the sun and KC02, under the SO_2 atmosphere. The mixture consisted of different types of apricot stones was provided from Turkel Dried Apricot Corporation to represent the industrial waste of apricot stones in Malatya and represented by KC03. Apricot stones were separated from the flesh of the fruits and air-dried for 2 weeks. This was followed by crushing and sieving the stones to obtain four different fractions of particle sizes ranging from approximately 0.85–1.70 mm to 1.70–3.35 mm, 3.35–4.00 mm, and 1.00–3.35 mm. Sieving was conducted to obtain particular size ranges using the same batches of crushed samples.

2.2. Activation method

One-step activated carbons were prepared by pyrolysis of the precursors at 650–800 °C for 1, 2 and 4 h, and at 850 °C for 4 h in the presence of steam. During the experiments, the steam flow rate was kept as 30 g/min. A 50 g sample of apricot stone was used for each experiment.

2.3. Thermogravimetric analysis

The thermogravimetric carbonization experiments of KC01 and KC02 were conducted using a Shimadzu TG 51 Thermal Analyzer. Samples of approximately 10 mg and average particle size of 0.25 mm were heated at 10 °C/min from room temperature to 800 °C under nitrogen flow. The flow of nitrogen was fixed at 10 ml/min throughout the measurements.

2.4. Experimental set-up and procedure

The experimental set-up used for the preparation of activated carbon is adapted from Dr. Ucak-Astarlioglu's thesis [14] and used in our set-up preparation in Malatya Inonu University. The set-up consists of a stainless steel tube reactor, a vertical tube furnace, a steam generator, two water condensers, and a gas flow meter. For activation, the raw material was placed in the middle of the reactor and the reactor was placed in the tube furnace. During the experiments, after heating the furnace to 80 °C to avoid the condensation, the steam was introduced from the top of the reactor at 1 atmosphere pressure. Three thermocouples were employed to measure the temperatures of the reactor, furnace, and the steam generator. To measure the temperature in the reactor, a thermocouple was inserted from the top of the reactor and its tip located on top of the sample without touching it. Once the activation temperature was reached, samples were kept at this temperature for the desired activation time. The dimensions of the reactor and the furnace were 100, 90 cm in length, and 7.5, 8.5 cm in diameter, respectively. During the activation experiments, liquid by-products were collected in a 6 L flask and gaseous by-products were collected for further analyses. After activation, solid samples were cooled to ambient temperature and weighed as-received before grinding by hand with a mortar and pestle. The products were kept in a desiccator for further characterization experiments.

2.5. Physicochemical characterization

The proximate analyses of the apricot stones were performed according to ASTM standards [22].

In the determination of the ash contents, raw material and activated carbon were grinded to pass through a 0.2 mm sieve. One gram of prepared sample was weighed in a tared porcelain basin. Dishes and their contents were placed in a muffle furnace at 815 °C for 2 h, followed by placing the sample in a desiccator and cooling down to room temperature and reweighing the sample. A LECO CHN 600 elemental analyzer was used to determine the carbon, hydrogen, and nitrogen contents, and LECO Sulfur Titrator was used to determine the total sulfur contents of the samples.

BET surface area and micropore volume of each activated carbon were determined from the N_2 adsorption experiments. The activated carbons were characterized by N_2 adsorption at 77 K using a Micromeritics Model ASAP 2010 analyzer. Pore size distributions were determined by using mercury porosimeter, Carlo Erba Model 2000. Before N_2 BET and mercury porosimeter measurements, samples were degassed at 300 °C for 1 h. A computer monitored the adsorbed nitrogen volumes and various equilibrium pressures and BET surface area of each sample was reported. The same adsorption data were also used for calculation of the micropore volume by the *t*-method [23]. The total pore volumes were determined from the amount of nitrogen adsorbed at a relative pressure of 0.95.

Iodine adsorption experiments were conducted as preliminary tests to determine the adsorptive characteristics of the activated carbons. The iodine adsorption was determined using the sodium thiosulfate volumetric method (DIN 53582, 1983) [24]. The amount (in milligrams) of iodine absorbed by 1 g of carbon is called as the iodine number and used in surface area determination.

The microstructures of raw materials and activated carbons produced from apricot stones were examined using scanning electron microscopy (JEOL 840A JXA model SEM).

3. Results and discussion

In this study, "solid yield" term was used to correspond to the percent yield of the activated carbon obtained from apricot stones at different activation parameters. The solid yields were calculated by dividing the mass of the resulting activated carbon by the initial mass of the raw material.

3.1. Starting materials

Table 1 shows the proximate and elemental analyses of the raw apricot stones, which are reported on a dry-basis and dry-ash-free basis, respectively. In the dry basis analyses, ash and volatile matter contents of the apricot stones were calculated on moisture-free basis. In the elemental analyses, samples were dried at 110 °C in a vacuum oven for 24 h and oxygen contents were calculated by difference.

The proximate analyses of the apricot stones show that the moisture, ash, and volatile matter contents vary in the range of 4.4–5.6%, 1.1–3.3%, and 79.8–82.8%, respectively. KC01 has the lowest ash content (1.1%) however; it has the highest volatile matter content (82.8%). On the other hand, KC02 has the highest ash content (3.3%) due to the drying process with sulfur.

Table 1
Proximate and elemental analyses of apricot stones

Sample code	Proximate analysis (wt.%)			Elemental analysis (wt.%)				
	Moisture	Ash	Volatile matter	C	H	N	Total S	O by diff.
KC01	4.8	1.1	82.8	48.07	6.39	0.6	0.04	43.80
KC02	4.4	3.3	82.1	46.71	6.07	1.40	0.29	41.62
KC03	5.6	2.4	79.8	47.32	6.54	0.63	0.24	43.48

The elemental analyses show that the apricot stones have carbon, nitrogen and oxygen contents varying from 46.7%, 0.6%, and 41.6% to 48.1%, 1.4%, and 43.8%, respectively. The apricot stones have relatively low carbon contents, but high oxygen contents. KC01 has the highest C content (48.1%). KC02, on the other hand, has the lowest C (46.7%) and H (6.07%) contents. The differences in the elemental compositions of the raw apricot stones can be attributed to the differences in their lignin and cellulose contents.

As can be seen from Table 1, KC02 and KC03 have higher sulfur contents (0.29% and 0.24%, respectively) compared to KC01 (0.04%), indicating the incorporation of sulfur to the apricot stones during the drying process with sulfur. The proximate analysis clearly indicates that desiccation process has a negative effect on the apricot stones. This affect can be explained by the ash and volatile matter contents of KC01 and KC02. The desiccation process caused an increase in the ash content of KC01 (from 1.1% to 3.3%) and a decrease in the volatile matter content of KC01 (from 82.8% to 82.1%).

3.2. *Effects of temperature and soak time on porosity development*

Many different methods are used to characterize the porous structures of the activated carbons. Table 2 summarizes the activation conditions, solid yields, N_2 BET surface areas, iodine pore volumes, and micropore volumes of the activated carbons prepared.

One can see from Table 2 that activation temperature and time are very important parameters in shaping the pore structure of activated carbons from apricot stones. The activated carbons prepared at 650 and 700 °C have lower pore volumes compared to higher temperatures. It appears that the changes in the solid yields and pore volumes as a function of time are insignificant at lower activation temperatures. This can be attributed to the lesser loss of the volatile matter during pyrolysis/activation at lower temperatures.

The increase in the process temperature and soak time has resulted in decreased solid yield and increased pore volume. At higher activation temperatures, activation of apricot stones becomes more extensive and results in a lower solid yield with a more widened porous structure. At 800 °C, a decrease in the solid yield is observed with the progression of the reaction by time (from 1 to 4 h activation, the solid yield changes are: KC01: 22.1–9.4%; KC02: 18.9–6.2%; and KC03: 19.7–6.8%, respectively). It is observed that KC01 produces higher solid yield compared to KC02 and KC03 at the corresponding activation conditions. This may be explained due to higher sulfur and ash content of KC02 and KC03 initiated by the desiccation process.

In general, at the same activation conditions, the micropore volumes, surface areas, and the solid yields of KC02 and KC03 are found to be relatively lower than KC01. Decreasing solid yield has a profound effect on the carbon structure causing a wider porosity in the activated carbons. The loss of volatile matter results in lower solid yield along with a more porous structure. In this study, the trend observed between the adsorptive properties and the solid yields of KC01 are found to be similar to the trend

Table 2
Activation parameters and adsorptive properties of the activated carbons prepared

Temperature (°C)	Soak time (h)	Solid yield (%)			BET surface area (m^2/g)			Iodine pore volume (cm^3/g)			Micropore volume (cm^3/g)		
		KC01	KC02	KC03	KC01	KC02	KC03	KC01	KC02	KC03	KC01	KC02	KC03
650	1	25.7	24.1	24.4	262	225	242	0.05	0.04	0.04	0.04	0.02	0.02
650	2	25.0	23.8	24.0	327	290	301	0.06	0.04	0.05	0.05	0.03	0.03
650	4	24.5	22.7	23.4	381	335	340	0.07	0.05	0.06	0.06	0.04	0.05
700	1	24.1	22.1	23.0	401	380	395	0.08	0.06	0.07	0.06	0.05	0.06
700	2	23.7	21.0	22.5	445	406	415	0.08	0.08	0.08	0.07	0.06	0.07
700	4	23.0	20.2	22.1	477	426	438	0.09	0.08	0.09	0.09	0.08	0.08
750	1	22.9	19.6	21.6	604	580	595	0.10	0.09	0.09	0.23	0.19	0.21
750	2	19.6	18.1	18.8	690	675	682	0.14	0.13	0.13	0.27	0.26	0.27
750	4	20.2	15.3	16.0	729	645	682	0.14	0.13	0.13	0.29	0.28	0.28
800	1	22.1	18.9	19.7	712	689	704	0.13	0.12	0.12	0.28	0.26	0.27
800	2	15.8	10.4	12.5	830	812	816	0.16	0.16	0.16	0.34	0.33	0.34
800	4	9.4	6.2	6.8	1092	804	824	0.21	0.16	0.16	0.37	0.30	0.32
850	4	11.2	5.2	7.9	850	785	800	0.05	0.04	0.04	0.30	0.26	0.27

reported in the literature, where lesser solid yield leads to a higher BET surface area and a higher porosity [5,7,10]. Despite the fact that, KC02 and KC03 show similar trends to that observed in KC01, it should be noted that their precursors differ from each other only due to their drying processes. The precursors dried in the sulfur rooms, KC02 and KC03, have higher sulfur contents than the sun-dried KC01. Comparing the BET surface areas of the activated carbons and their sulfur contents, an inverse relation is found between the two:

> Decreasing sulfur content order: KC02 > KC03 > KC01.
> Decreasing BET surface area order: KC01 > KC03 > KC02.

This trend between the surface areas and the sulfur contents can be explained due to the formation of a pre-activation stage during the hot vapor-SO_2 treatment to dry the precursor. Although the manufacturer only wanted to dry the sample, the SO_2 environment may have created an acid wash effect on the precursor by increasing the surface functional groups compared to the sun-dried sample. During the one-step pyrolysis/activation treatment of a SO_2-dried sample, an increase in the gasification rate may have occurred due to increased surface functional groups resulting in a lower yield. Moreover, due to higher gasification, reordering of the carbon structure may have blocked nitrogen entrance to the micropores to a lower extent compared to sun dried precursors resulting in lower BET surface areas.

Shorter activation times (<2 h) of KC01, KC02, and KC03 resulted in relatively similar surface areas compared to the longer activation times (>2 h). Such comparable trends are also obtained between the solid yields and the micropore volumes and between the solid yields and the BET surface areas. Lower temperature (650 and 700 °C) activations of the starting materials resulted in carbons with similar micropore volumes. However at higher temperatures ($\geqslant$750 °C), the micropore volumes are found to vary from 0.21 to 0.37 cm^3/g. These results have indicated that employing 800 °C and 4 h activation condition can attain the highest adsorptive properties of the carbons.

Table 2 shows that, with the increasing activation temperature from 650 °C to 800 °C, the solid yield decreases, but both the BET surface areas and the micropore volumes of activated carbons increase. At 850 °C for 4 h soak time, one can see a considerable decrease in the surface areas and micropore volumes of the activated carbons. Obviously, extensive gasification takes place at 850 °C, giving rise to decreasing surface areas and micropore volumes. These results are not unexpected. Numerous studies [10,25,26] reported decreasing surface areas due to pore widening and pore wall collapse after certain solid yield, which is different for different raw materials.

KC01, in general, presents relatively wider microporosity compared to KC02 and KC03 at the same activation conditions. Clearly, longer activation times have lesser impact on the improvement of the pore structure of KC02 and KC03. Since the difference in the starting materials is only due to their varying sulfur content, the wider microporosity observed in KC01 may be attributed to its lower sulfur content. Accordingly, it is deduced that the apricot stones with lower sulfur content are more appropriate in the preparation of activated carbons with higher adsorptive properties.

Table 3 shows the proximate and elemental analyses of the activated carbons obtained from KC01, KC02, and KC03 at 800 °C for 4 h. Compared to their precursors; carbons obtained from desiccated samples show a significant decrease in their total S content (KCO2: from 0.29% to 0.09% and KCO3: 0.24% to 0.07%). A relatively small increase is observed in the ash content of carbons obtained from desiccated samples (KCO2: from 3.3% to 7.0% and KCO3: 2.4% to 5.0%) compared to sun-dried samples (1.1–2.2%). KCO1 has relatively higher carbon content (94.1%) compared to KCO2 (90.4%) and KCO3 (89.8%), which makes KCO1 more carbonaceous material compared to other carbons produced.

Table 4 shows the total pore volumes obtained from N_2 adsorption isotherm and macro- and mesopore accessible volumes obtained from mercury porosimeter. The porous structure of activated carbons contains a wide range of pore sizes. For practical reasons, they are classified into three groups, micropores (pore size smaller than 2 nm), mesopores (pore size up to 50 nm), and macropores (pore size larger than 50 nm) by the International Union of Pure and Applied Chemistry (IUPAC) [23]. Relatively speaking, the total pore volumes obtained from the N_2 adsorption are considerably lower than the summation of the pore volumes obtained from the mercury porosimeter for all activated samples. These results may be explained that activated carbons produced from apricot stones are predominantly microporous. No clear relationship was found between the macroporosities of activated carbon samples and the solid yields.

Table 3
Proximate and elemental analyses of activated apricot stones (800 °C, 4 h)

Sample code	Proximate analysis (wt.%)			Elemental analysis (wt.%)				
	Moisture	Ash	Volatile matter	C	H	N	Total S	O by diff.
KC01	2.4	2.2	6.4	94.1	1.8	0.60	0.02	3.48
KC02	2.1	7.0	4.9	90.4	1.9	1.02	0.09	6.59
KC03	2.3	5.0	4.3	89.8	2.0	0.57	0.07	7.56

Table 4
Pore volumes from N_2 adsorption and mercury porosimetry of activated carbons

Temperature (°C)	Soak time (h)	N_2 adsorption			Mercury porosimetry					
		Total pore volume (cm^3/g)			Mesopore accessible volume (cm^3/g)			Macropore volume (cm^3/g)		
		KC01	KC02	KC03	KC01	KC02	KC03	KC01	KC02	KC03
650	1	0.18	0.15	0.16	0.12	0.11	0.11	0.12	0.10	0.11
650	2	0.20	0.16	0.17	0.13	0.12	0.13	0.14	0.15	0.14
650	4	0.22	0.18	0.20	0.14	0.13	0.15	0.17	0.16	0.15
700	1	0.23	0.21	0.22	0.15	0.13	0.15	0.18	0.18	0.16
700	2	0.25	0.22	0.24	0.16	0.15	0.16	0.19	0.16	0.18
700	4	0.30	0.24	0.30	0.20	0.19	0.18	0.22	0.19	0.21
750	1	0.32	0.30	0.31	0.22	0.21	0.20	0.12	0.10	0.10
750	2	0.36	0.34	0.35	0.23	0.22	0.22	0.14	0.12	0.13
750	4	0.40	0.36	0.37	0.24	0.26	0.25	0.06	0.10	0.10
800	1	0.41	0.37	0.37	0.24	0.25	0.25	0.18	0.10	0.12
800	2	0.45	0.44	0.44	0.25	0.26	0.26	0.20	0.12	0.13
800	4	0.63	0.43	0.44	0.35	0.34	0.33	0.11	0.12	0.12
850	4	0.51	0.42	0.43	0.34	0.22	0.23	0.15	0.18	0.18

The total pore and micropore volumes of carbons prepared by 800 °C for 4 h activation are as following: KC01: 0.63 cm^3/g and 0.37 cm^3/g, KC02: 0.43 cm^3/g and 0.30 cm^3/g, and KC03: 0.44 cm^3/g and 0.32 cm^3/g. At 800 °C for 2 h, KC02 and KCO3 did not show a significant difference in their pore volumes compared to 800 °C for 4 h activation.

Fig. 1 shows the adsorption isotherms of N_2 at 77 K for the activated KC01, KC02, and KC03 with the highest BET surface areas, which are obtained at 800 °C for 4 h. At low relative pressures, a rapid increase in the adsorption isotherms is observed, which is followed by a nearly horizontal plateau at higher relative pressures, indicating Type I of isotherm based on the classification of Brunauer, Deming, and Teller (BDDT) [27]. It is found that, essentially, all the activated carbons are microporous. However, the isotherm of the activated KC01 indicates some mesoporosity development in addition to microporous nature. While the adsorption isotherms of KC02 and KC03 are parallel to the relative pressure axis, KC01 shows a progressive increase in the slope of the isotherm with increasing relative pressures starting from $0.3P/P_0$. At low relative pressures, KC01 isotherm also exhibits a more rounded knee, indicating a widening of the micropores. Therefore, the shape of the KC01 isotherm demonstrates a wider microporosity and the presence of mesoporosity.

Fig. 2 shows the relationship between the iodine number and solid yields of the activated carbons. All the activated carbons show a rapid increase in the iodine number of the activated KC01 upon the decrease of the solid yield. Consistent with the proposed process for the porosity development, this rapid trend of iodine uptake suggests an initial development of microporosity but not mesoporosity at the early stages of activation. The iodine number relatively remains the same for solid yields less than 15% for KC02 and KC03. The steady trend of iodine uptake may be explained by mesoporosity development.

To have a better understanding in pore size distribution of the activated carbons, iodine pore volumes were calculated using the iodine numbers and the results were compared with the pore volumes obtained from N_2 adsorption. The iodine density was used to convert the iodine numbers to iodine pore volumes from iodine adsorption. For iodine adsorption, a sample of 0.10 g of carbon was equilibrated with 25 mL of I_2/KI solution for 1 h. As can be seen from Table 2, in general, the pore volumes calculated from iodine number of activated carbons are

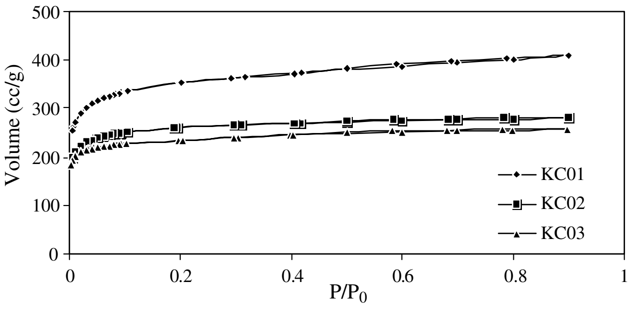

Fig. 1. N_2 isotherms of activated KC01, KC02, and KC03 at 800 °C for 4 h.

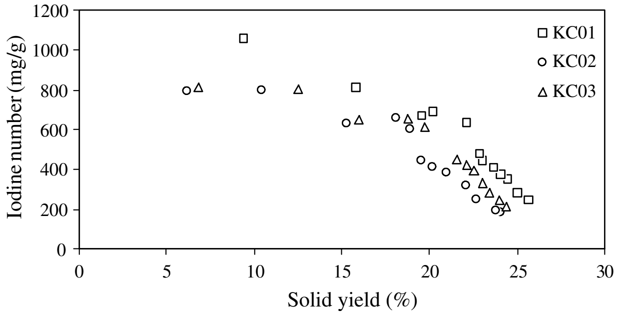

Fig. 2. Iodine numbers versus solid yields of activated KC01, KC02, and KC03.

lower than their corresponding micropore volumes obtained from N_2 adsorption (⩾750 °C). This observation indicated that a predominantly microporous structure is developed in the activated carbons, and pores which correspond to less than two molecular diameters of iodine molecule (<1 nm) are present.

Overall, the optimum activation temperature and time were determined as 800 °C and 4 h, where the highest N_2 surface area (1092 m^2/g) and micropore volume (0.37 cm^3/g from N_2 surface area) were obtained from KC01. KC03 and KC02 follow these values with surface areas of 824 m^2/g, 804 m^2/g and the micropore volumes of 0.32 cm^3/g, 0.30 cm^3/g, respectively.

3.3. Effect of different drying process on the thermogravimetric analyses

To further investigate the effect of precursor desiccation process on producing activated apricot stone, non-isothermal TG experiments were carried out and the weight loss rates upon heating in nitrogen were determined. In Fig. 3, DTG curves of KC01 and KC02 are presented. The DTG curves of KC01 and KC02 showed two major peaks at ~320 and 440 °C. Based on the literature survey [28–31], the first peak (~320 °C) and the second peak (~440 °C) are attributed to cellulose and lignin contents, respectively. At the temperature range of 50–250 °C, two relatively smaller peaks were obtained as seen from Fig. 3. These peaks show moisture and hemicellulose contents of apricot stones (shoulder-like) for the first and the second peaks, correspondingly. In general, both samples presented similar DTG curves; however, the peak temperatures shifted to higher temperatures for KC02. While the peak temperatures of hemicelluloses, cellulose and lignin contents were obtained as 205, 294, and 440 °C for KC01, these temperatures shifted to 220, 331, and 465 °C for KC02.

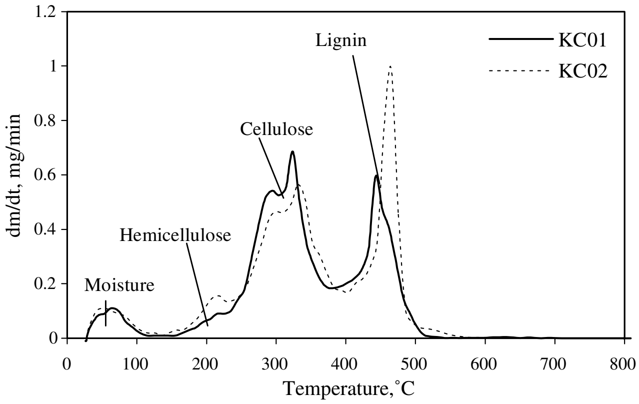

Fig. 3. The carbonization DTG curves of KC01 and KC02.

While the decomposition temperature of KC02 and its main components increase, its reactivity decreases. Decomposition temperature is defined as the temperature where the breakdown of lignin, hemicellulose, and cellulose starts.

As a result, high sulfur content delays the releasing of the lignin and cellulose contents from apricot stones and causes an increase in the peak temperature of KC02. Furthermore, KCO2 shows higher decomposition temperature compared to KCO1. This higher shift in the decomposition temperature (~30 °C) of KCO2 (lignin and cellulose) may be due to higher sulfur content of the desiccated apricot stones.

3.4. Determination of the optimum particle size range of raw materials

In this study, firstly, raw material particle size range was kept constant (1–3.35 mm) to determine the optimum activation conditions. Secondly, predetermined optimum activation conditions were kept constant (800 °C, 4 h) and the effect of raw material particle size ranges on the porosity of activated KC01 were investigated.

Three particle size ranges were analyzed for this part of the study: 4.0–3.35, 3.35–1.7, and 1.7–0.85 mm. Table 5 shows the effect of particle size range on the solid yield, N_2 surface area, and micropore volume of activated KC01. One can see that smaller particles are more readily activated to produce activated carbons with relatively higher surface area. Iodine number values are very close to the corresponding BET surface areas. Compared to the other particle size ranges studied, smaller particles of apricot stones produce carbons with the lowest solid yield (4.7%) and the highest surface area (1157 m^2/g). Although no significant difference in the micropore volumes of the carbons produced from different ranges of particle sizes are observed, 0.85–1.7 mm range yields to the highest micropore volume (0.39 cm^3/g). It should be expected that smaller particles can be readily activated and give high pore structures, particle sizes smaller than 0.85 mm was not used in our activated carbon preparation, due to handling difficulties.

Table 5
Adsorption characteristics of the activated carbons produced from different particle size range of KC01

Particle size range (mm)	Solid yield (%)	BET surface area (m^2/g)	Iodine number (mg/g)	Micropore volume (cm^3/g)
0.85–1.7	4.7	1157	986	0.39
1.7–3.35	9.5	1035	850	0.36
3.35–4	10.5	790	782	0.30
1–3.35	9.4	1092	1057	0.37

3.5. SEM examination of raw material and produced activated carbon

The effect of different drying processes on the apricot stone precursors is clearly observed from the SEM of KCO1, Fig. 4(a) and KCO2, Fig. 5(a). The SEM micrographs show the macropore domain of the material. KC01 dried under sun yields to a more uniform macroporosity in its activated carbon compared to KC02 precursor, which is dried in SO_2 atmosphere. KCO2 also presents a cloudy surface with almost non-porous structure due to its higher ash and sulfur content compared to the sun-dried KCO1. Figs. 4(a) and 5(a) present a big difference between the wall structures of the sun-dried and SO_2-dried apricot stones. Due to the processing differences of the raw apricot stones, their resulting activated carbons also show different porosities.

In Fig. 4(a) and (b), the SEM photographs of the sun-dried apricot stone and its activated carbon are presented, respectively. In the sun-dried apricot stone, a thick wall structure exists along with a little porosity. This thick wall gets opened and a wider porosity is created by the activation of this sun-dried raw material. The comparison of Fig. 4(a) and (b) clearly indicates that increased porosity is achieved by the 750 °C for 4 h steam activation. In Fig. 5(a) and (b), the SEM photographs of the desiccated raw material (dried under SO_2 atmosphere) and its activated carbons are shown, respectively. As it can be seen from the figures, the cloudy surface of KC02 presents a thick wall structure with small cell cavities and non-developed porosity at 750 °C for 4 h.

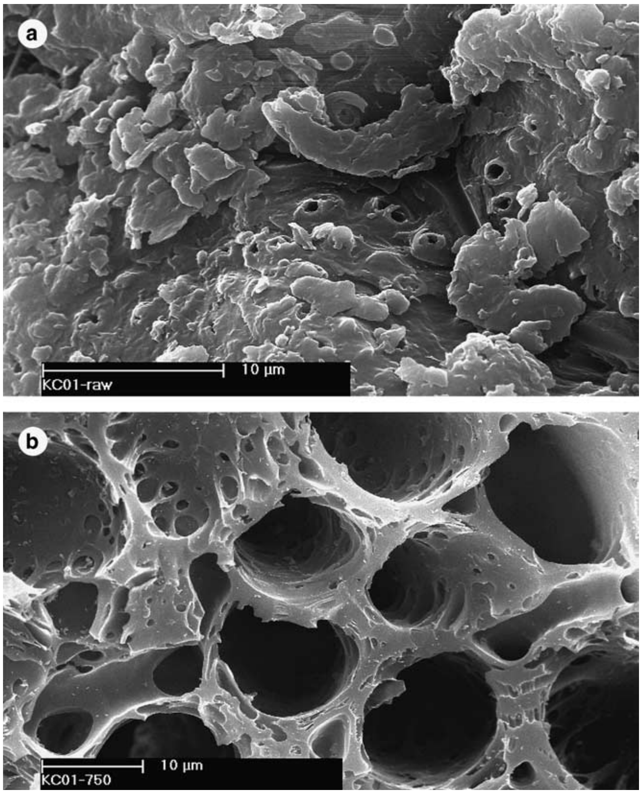

Fig. 4. Scanning electron micrographs of (a) raw KC01 (sun dried) and (b) activated KC01 (750 °C for 4 h).

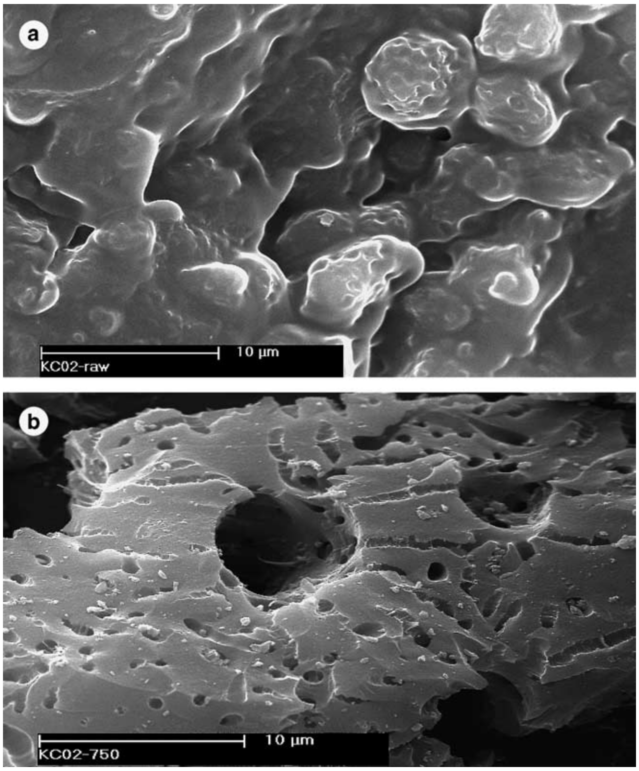

Fig. 5. Scanning electron micrographs of (a) raw KC02 (SO_2 dried) and (b) activated KC02 (750 °C for 4 h).

The SO_2-dried activated carbons show a weak, brittle, porosity compared to solid and well-ordered porosity of the sun-dried activated carbons as shown in Figs. 4(b) and 5(b), respectively.

KCO2 possesses higher sulfur and ash contents as found from the elemental analysis compared to KCO1. The existence of sulfur and ash contents may have caused a cloudier carbon structure in KCO2 than KCO1. Furthermore, the SEM observations of the activated carbons support the findings of relatively lower micropore volumes, surface areas, and yields of KCO2 compared to KCO1. As mentioned earlier, the SO_2 treatment may have created an acid wash effect on the raw material making this material almost non-porous and brittle, and upon activation reordering of the carbon structure results in a weakly porous activated carbon.

4. Conclusions

1. The activated carbons produced from apricot stones exhibited high N_2 adsorption and highly developed micropore structure. The micropore volumes of the resulting carbons varied within the range of 0.02–0.37 cm^3/g as obtained from the BET-N_2 adsorption measurements with corresponding solid carbon yields of 25.7–5.2%, respectively. These results were obtained

by activation of the apricot stones at 650–800 °C for 1, 2 and 4 h. In order to achieve well-developed porosity and high surface area carbons from apricot stones, temperature should be within the range of 750–800 °C and soak time should be kept around 3–4 h.

2. The activation of KCO1 at 800 °C for 4 h gives the highest total pore volume, 0.63 cm^3/g and micropore volume, 0.37 cm^3/g among the other activation parameters studied. In comparison, the total and micropore volumes of the KC02 and KC03 were obtained as 0.43 cm^3/g, 0.30 cm^3/g and 0.44 cm^3/g, 0.32 cm^3/g, respectively, at 800 °C for 4 h.
3. The desiccation process is found to cause higher sulfur content in the apricot stones. It was deduced that the precursor with higher sulfur content exhibits different pore structure in the resulting activated carbon compared to carbon of sun-dried precursor. The KCO1 carbon produced from apricot stone with low sulfur content (0.04%) gave more uniform pore structure than KCO2 which has slightly more sulfur content (0.29%). It is clearly observed from the SEM studies that sun-dried apricot stone yield to a more uniform porosity in its activated carbon compared to SO_2-dried stone.
4. Thermogravimetric studies show that higher sulfur content may have caused a delay in the release of lignin and cellulose requiring higher decomposition temperatures in KCO2.
5. The effect of precursor size is found to be insignificant on the porosity development upon activation. Therefore, feasibility of the activated carbon production can be increased by lowering the time consumption and the cost by not using small sized (<0.85 mm) apricot stones in the activated carbon production.
6. Production of activated carbon from apricot stone harvested in Malatya region is found to be feasible in obtaining activated carbon with high adsorption properties. In terms of the pore volumes obtained, sun-dried or desiccated apricot stones can both be utilized in activated carbon production. Particularly, the apricot stone with lower sulfur content (<0.05%) (i.e. desiccated without using SO_2) is a good activated carbon precursor.

Acknowledgments

This study has been supported by the Scientific and Technical Research Council of Turkey (TUBITAK) through the project MISAG-186. We are grateful for the useful comments of Prof. Harold H. Schobert from The Energy Institute of Pennsylvania State University. The authors also express their thanks to Dr. Tarek Shalaby, who helped to run the experimental studies.

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