Optimization of activation temperature on the preparation of sliced porous activated carbon from date fronds by physical activation

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Abstract

Saudi Arabia is the major date producer in the world. In order to get the maximum production from date tree there is a need to prune the trees on annual basis and is considered as a serious environmental threat. The single step procedure for the synthesis of porous activated carbon (AC) from Saudi date tree fronds using mixture of gases (N_2 and CO_2) was carried out at different carbonization/activation temperatures staring from 700 to 1000 °C at a ramp rate of 10 °C/min. Alloy 330 horizontal reactor was used in tube furnace. Flow rate of N_2 and CO_2 gases were kept at 150 and 50 ml/min, respectively. Results revealed that at 850 °C larger surface area was achieved and can offer higher potential to produce activated carbon of greater adsorption capacity from date fronds waste. The BET surface area of the activated carbon prepared at 850 °C after 30 min activation time is 1094 m^2/g.

Keywords: activated carbon, physical activation, gaseous mixture, Saudi date fronds, agro waste.

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Any cheap material, with a high carbon content and low in organics, can be used as a raw material for the production of activated carbon (AC) [1]; agricultural by-products have proved to be promising raw materials for the production of activated carbons (ACs) because of their availability at a low price. They can be used for the production of activated carbon (AC) with a high adsorption capacity, considerable mechanical strength, and low ash content [2]. Literature survey indicates that there have been many attempts to obtain low-cost activated carbons (AC) or adsorbent from agricultural wastes [3–7].

Saudi Arabia is the major date producer in the world. In order to get the maximum production from date tree there is a need to prune the trees on annual basis. About twelve million of date-palm trees exist in Saudi Arabia. Approximately about three million trees were cut and then pruned every year. It is reported that about 75,000 tons of palm tree fronds, also consisted of foliar parts and thorns, are left during pruning process [8]. This quantity is either disposed off as waste or burnt and ultimately ends up with a harmful effect to the environment. Carbonaceous material can be used to produce activated carbon. Many studies have been reported for the preparation of activated carbon (AC) through agricultural waste material [9–14]. Therefore, the plenty of this agriculture waste material (palm tree fronds) is available in Saudi Arabia and considered as an ideal source as a precursor for production of activated carbon (AC). For the manufacturing of activated carbon (AC) two methods have been reported, *i.e.*, physical and chemical activation [15–20]. In the present study the aim is to prepare activated carbon (AC) of high surface area and porosity using physical method.

Pyrolysis is one form of energy recovery process, which has the potential to generate char, oil and gas product [21]. Because of the thermal treatment, which removes the moisture and the volatile matter contents of the biomass, the remaining solid char shows different properties than the parent biomass materials. The remarkable differences are mainly in porosity, surface area, pore structures (micro pores, mesopores and macropores) and physicochemical properties such as composition, elemental analysis and ash content. These changes in the properties usually lead to high reactivity, and hence, an alternative usage of char as an adsorbent material becomes possible [22]. Thus, the char becomes an attractive by-product, with applications including production of activated carbons (ACs), which is useful as a sorbent for air pollution control [23]. Activated carbons (ACs) are carbons of highly micro porous form with both high internal surface area and porosity, and commercially the most common adsorbents used for the removal of organic compounds from air and water streams.

EXPERIMENTAL

The fronds were dried at 105 °C for 8 h to reduce the moisture content, sliced with sophisticated wood cutter to a size range of 2–3 mm. Pyrolysis of the palm fronds and activation of the resulting chars were both

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carried out in a horizontal stainless-steel tube alloy reactor Alloy 330 (UNS N08330) having ID 30mm, OD 36 mm by Sandmeyer steel company, which was placed in a Carbolyte MTF 12/38/250 tube furnace. During the pyrolysis process, about 10 g of sliced precursor was used in high alumina sample tray to prepare the chars. Grade 5 (99.999%) nitrogen gas at a flow rate of 150 ml/min was passed through the reactor right from the beginning of the pyrolysis process. The furnace temperature was increased at a rate of 10 °C/min from room temperature to 850 °C now activation gas carbon dioxide gas was introduced at a flow rate of 50 ml/min for 30 min. Inside reactor the pressure was maintained at 0.25 bar for all the samples. The prepared activated carbon was characterized by calculating surface area, pore size, pore volume, SEM and FTIR. The schematic of the process is shown below in Fig. 1 [15,24].

RESULT AND DISCUSSION

Proximate and chemical analysis of date fronds

Date palm tree fronds were used as the precursor in the present study. The proximate and chemical analysis of the precursor is given in Table 1.

Proximate analysis of date palm tree fronds was conducted as per the method given in [22]. The method was effectively applied to determine the ash contents, moisture, fixed carbon content and volatile matter in the date palm tree fronds. The properties of the precursor are given in Table 1. To calculate the moisture content in fronds, air dried 1.0 g of date palm tree fronds was loaded in a crucible and placed in an oven at 110 °C for 3 h until total dehydration was occurred. In order to measure the amount of volatile 1.0 g of air dried sample was placed in a muffle furnace at 850 °C for 7 min. The sample was weighed after cooling in the desiccator to get the volatile contents present in the starting material. For the determination of ash content about 1.0 g of starting material was placed in the muffle furnace for 3 h at 750 °C. After 3 h the crucible was placed in desiccators for cooling. The crucible was then weighed to get the ash contents present in the sample. Subtracting the calculated values for moisture, ash content and volatile matter from 100% fixed carbon content was calculated. Chemical composition of date palm tree fronds was conducted as per the method [25] and the results were shown in terms of lignin, hemicellulose and cellulose.

Thermo gravimetric Analysis (TG) of date fronds

Thermo-gravimetric (TG) experiments were carried out by a thermo-gravimetric analyzer (Netzsch STA 409) to study the pyrolysis behavior of date fronds. The dried fronds was directed to analyze in the temperature range of 25–900 °C at heating rate 10 °C/min under nitrogen with a holding time at 900 °C for 15 min. Figure 2 [24] illustrates the TG curve of raw date frond by % weight loss under N_2 atmosphere and at a heating rate of 10 °C/min.

During the first stage, *i.e.*, from 250 to 375 °C cellulose and hemi-cellulose of the fronds decomposed to (acetic acid, methanol and, wood tar) that are considered as a condensable gases and (CO, CO_2, CH_4, H_2 and H_2O) are non-condensable gas. A little loss in wt. % can easily be seen below 250 °C in Fig. 2 [24], as the

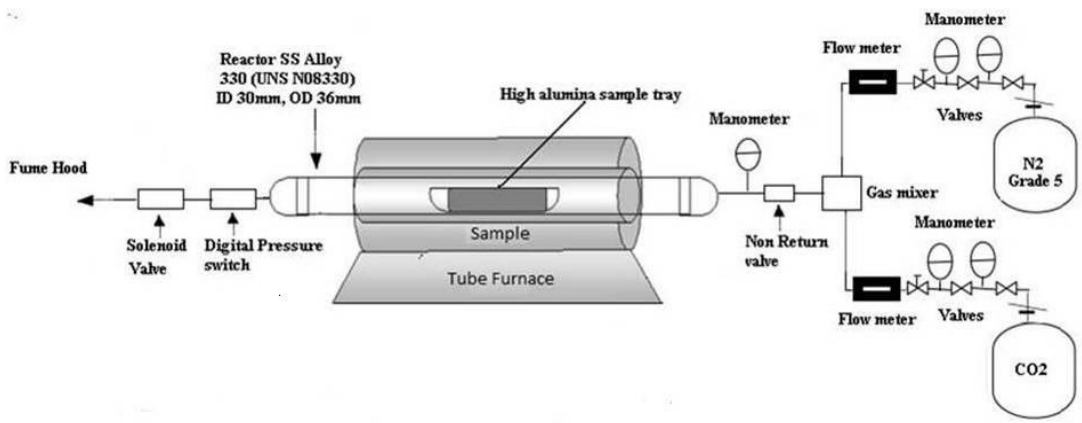

Fig. 1. Schematic of Process [24] ("Reprinted from Biomass and Bioenergy, Vol 73, M. Shoaib, H. M. Al-Swaidan, Optimization and characterization of sliced activated carbon prepared from date palm tree fronds by physical activation, 124-134, Copyright (2015), with permission from Elsevier").

Table 1. Properties of the palm tree fronds

Proximate analysis, wt.%				Chemical composition, %		
Moisture	Volatile	Fixed carbon	Ash	Cellulose	Hemicellulose	Lignin
9.1	74.6	10.3	6.0	44	29.8	26.2

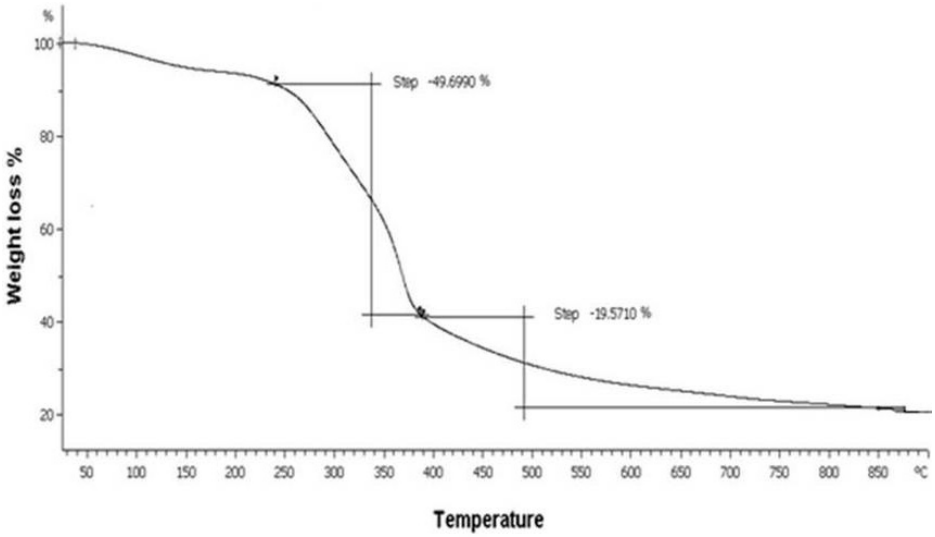

Fig. 2. Thermogravimetric Analysis (TG) of date fronds (this material is reproduced with kind permission of Elsevier) [24] ("Reprinted from Biomass and Bioenergy, Vol 73, M. Shoaib, H. M. Al-Swaidan, Optimization and characterization of sliced activated carbon prepared from date palm tree fronds by physical activation, 124-134, Copyright (2015), with permission from Elsevier").

frond had been dried under 105 °C for 8 h. Curve at temperature over 850 °C showed the weight unchanged at this stage. The carbon at this stage is acceptable as a precursor for producing activated carbon because a carbon with 10–15% volatile is not too tight, and can easily react with activating gas to produce big surface and huge pore volume. So it is apparent that date frond can be as good raw material.

BET surface area, pore size and pore volume

Specific surface areas pore size and pore volumes of the activated carbons were determined by N_2 gas adsorption at 77 K with an automated adsorption instrument (Gemini VII, 2390 Micromeritics). Prior to the determination, the sample (about 0.05 g) was degassed for 45 min at 15 °C under nitrogen to remove moisture and other volatiles from the sample. The surface areas of activated carbon produced at various activation temperatures are shown in Table 2.

Increasing temperature causes increasing release of volatiles and increasing carbon burn off due to carbon–CO_2 reaction. Hence, the yield decreases with increasing temperature. For an activation temperature of 100 °C, the yield has reached at 8.5% and it mainly contains the ash whereas at 850 °C 18.75% yield was obtained with high surface area and pore volume as shown in Table 2. Increasing the activation temperature enhances the existing pores and forms new pores from 700 to 850 °C by continual devolatilization of the chars and carbon burn off due to the carbon–CO_2 reaction, resulting in increasing BET surface area, pore volume, and non-pore volume. A decreasing trend from 900 °C and above was also observed and this is maybe because of the accumulation of carbon in the pores. The pore size may have started increasing and pore fusions might occur, causing decrease in surface area. The highest surface area 1094 $m^2\ g^{-1}$ for AC prepared at 850 °C was obtained.

Fourier transform Infrared spectroscopy (FTIR)

FTIR spectra give details about different functional group information of the materials. Figure 3 illustrates

Table 2. Activation temperature effect on surface area, pore volume, pore size and yield %age of activated carbon; : a-b-c-d-e-f denotes sliced activated carbon: activation temperature (°C), heating ramp rate (°C/min), activation dwell time (min), CO_2 flow rate (ml), reaction vessel pressure (bar)

Sample No.	Sample name	Surface area, m^2/g	Pore volume, cm^3/g	Pore size, Å	Yield, %
1	Raw date frond	2	–	–	–
2	SAC^a-700^b-10^c-30^d-50^e-0.25^f	385	0.1663	17.27	28.42
3	SAC^a-750^b-10^c-30^d-50^e-0.25^f	587	0.2562	17.44	24.65
4	SAC^a-800^b-10^c-30^d-50^e-0.25^f	633	0.2716	17.14	20.62
5	SAC^a-850^b-10^c-30^d-50^e-0.25^f	1094	0.4382	16.09	18.75
6	SAC^a-900^b-10^c-30^d-50^e-0.25^f	727	0.3063	16.83	16.0
7	SAC^a-950^b-10^c-30^d-50^e-0.25^f	515	0.2270	17.38	14.3
8	SAC^a-1000^b-10^c-30^d-50^e-0.25^f	ND	ND	ND	8.5 mainly ash

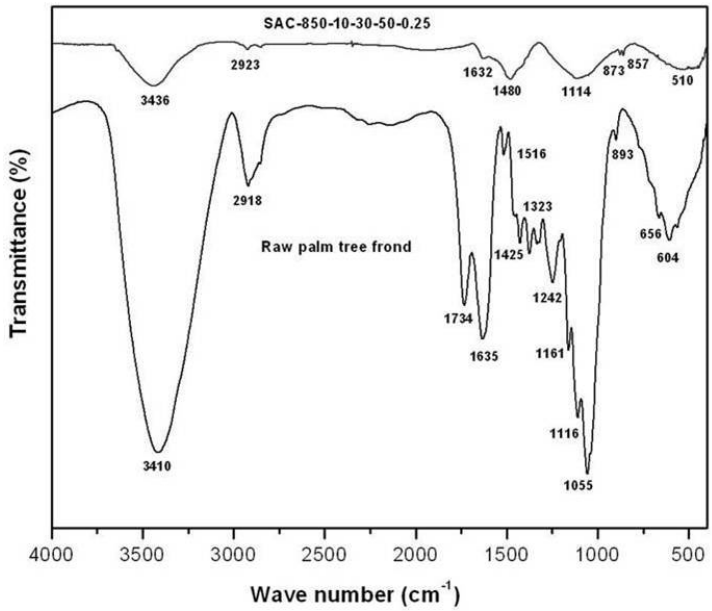

Fig. 3. FTIR spectra for date palm tree frond and SAC-850-10-30-50-0.25 [24] ("Reprinted from Biomass and Bioenergy, Vol 73, M. Shoaib, H.M. Al-Swaidan, Optimization and characterization of sliced activated carbon prepared from date palm tree fronds by physical activation, 124-134, Copyright (2015), with permission from Elsevier").

the FTIR spectra of Raw Date Frond, SAC-850-10-30-50--0.25. Strong absorption band between 3600–3400 cm^{-1} can be seen in all the spectra's shown in Fig. 3 [24], which is the characteristic of OH group and the broadening of the band is due to the high degree of hydrogen bonding. The Raw date frond in Fig. 3 shows the most crowded spectrum. A strong and broad adsorption peak appeared at 3386.23 cm^{-1}, which is due to the stretching of O–H group in the raw date frond sample. Peak observed at 2923.75 cm^{-1} belongs to the alkane C–H stretching. The peak at 1733.44 cm^{-1} is a C=O stretching and a C=C peak also observed around 1618.30 cm^{-1}. The peak at 1425.46–1375.25 corresponds to C–H bends and rock in alkane, respectively. Absorption peaks at 1330.98, 1160.53, 1243.99 and 1055.98 cm^{-1} which is the characteristic of C–O group can also be observed. The spectrum for SAC-850-10-30--50-0.25, in Fig. 3 shows reduction in absorption peaks because most of the groups are reduced at 850 °C.

Scanning electron microscopy (SEM)

SEM analysis was carried out by using Jeol JSM-6380 LA instrument. Figure 4a shows the scanning electron micrographs for the raw date fronds. The image clearly shows the surface is curvy due to cellulose, hemicelluloses and lignin and with less slit like fractures or cracks. Mesoporosity can be seen in Fig.4b. Microporous and mesoporous combination can easily be interpreted in Fig. 4c and small pores, transitional pores, and slit like pores with different shapes could also be clearly identified in Fig. 4d. SEM images account for the higher BET surface area and pore volume.

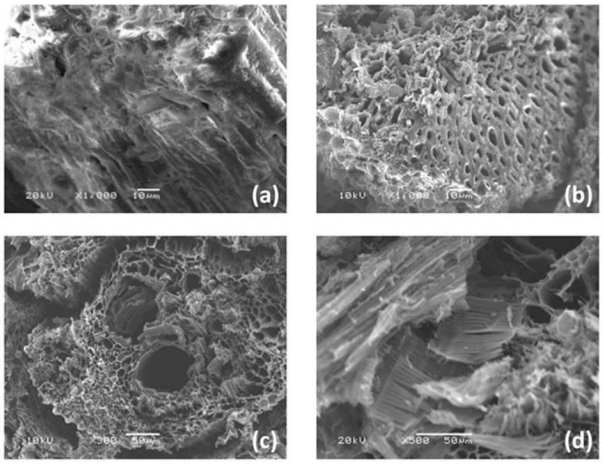

Fig. 4. SEM micrographs showing the surface morphologies of: a) raw date frond, b) mesopores, c) micropores and mesopores and d) slit like pores for SACa-850b-10c-30d-50e-0.25f [24] ("Reprinted from Biomass and Bioenergy, Vol 73, M. Shoaib, H. M. Al-Swaidan, Optimization and characterization of sliced activated carbon prepared from date palm tree fronds by physical activation, 124-134, Copyright (2015), with permission from Elsevier").

Nitrogen adsorption isotherm

The N_2 adsorption isotherms of the selected five activated carbons are presented in Fig. 5. Here the quantity of N_2 adsorbed is plotted against the relative pressure p/p^0 of N_2. It can be seen that the N_2 adsorption isotherm of Sample SAC-850-10-30-50-0.25 shows the maximum adsorption, which indicates predominantly the presence of micro porosity with minor

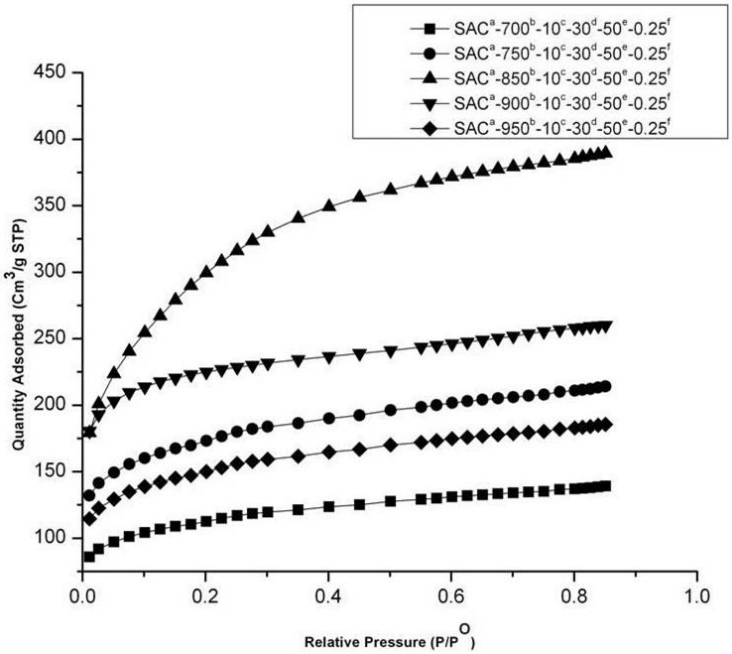

Fig. 5. Adsorption Isotherm for synthesized activated carbon [24] ("Reprinted from Biomass and Bioenergy, Vol 73, M. Shoaib, H. M. Al-Swaidan, Optimization and characterization of sliced activated carbon prepared from date palm tree fronds by physical activation, 124-134, Copyright (2015), with permission from Elsevier").

presence of mesoporosity in the activated carbon. This result is similar to as observed in SEM studies.

Nitrogen adsorption-desorption isotherm

Figure 6 shows the nitrogen adsorption-desorption isotherm at 77 K of the activated carbon prepared from 700 to 950 °C. The effects of temperatures provided different performances of the nitrogen isotherms. All the nitrogen isotherm curves significantly increase in the low-relative pressure (p/p^0 < 0.2) indicating the presence of pore structures with the Type I isotherm indicates the presence of mono layers. However, at higher relative pressure (p/p^0 > 0.2), the knee of nitrogen isotherm curves became more open and steadily

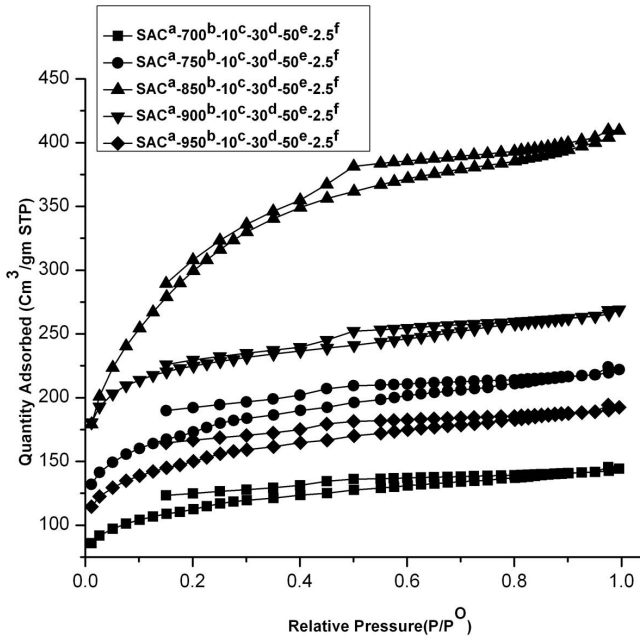

Fig. 6. Nitrogen adsorption desorption isotherm of activated carbon synthesized at various temperatures [24] ("Reprinted from Biomass and Bioenergy, Vol 73, M. Shoaib, H. M. Al-Swaidan, Optimization and characterization of sliced activated carbon prepared from date palm tree fronds by physical activation, 124-134, Copyright (2015), with permission from Elsevier").

increased to the maximum relative pressure (p/p^0 ≈ ≈ 0.9). These results suggested that large amount of nitrogen was adsorbed during the adsorption process indicating the presence of wider porosity (mesopores) with the Type IV isotherm. The entire relative pressure ranges suggested that the nitrogen adsorption exhibited a combination of the Type I and IV isotherms, indicating the presence of micro and mesoporosity in the activated carbon. Additionally, the presence of hysteresis loops with H4 type in the desorption isotherms closure at p/p^0 ≈ 0.4 indicates presence of small mesopores. This hysteresis was associated with capillary condensation in micro and mesopores. This phenomenon shows that the activated carbon production may have a combination of micro and mesopores. The lower curves being an significance of microporosity [26], whereas the upper curves look like a Types H4 that also verifies the presence of slit-shaped pores as shown in SEM images.

CONCLUSION

The optimum activation temperature conditions for the synthesis of activated carbon from date palm tree fronds using the physical activation were a temperature of 850 °C. The above conditions verified that the activation has occurred, BET surface area of 1094 m^2/g has been achieved moreover the synthesized activated carbon has predominantly microporous. SEM images verified the presence of porosities and pore development during the pyrolysis and activation process. Thus, it is feasible to produce high-quality porous activated carbon from date frond agro waste using N_2 carbonization followed by physical activation with CO_2 and N_2 mixture.

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IZVOD

OPTIMIZACIJA TEMPERATURE AKTIVACIJE ZA PRIPREMU POROZNOG UGLJENIKA DOBIJENOG IZ LISTOVA URME FIZIČKOM AKTIVACIJOM

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(Stručni rad)

Saudijska Arabija je vodeći proizvođač urmi u svetu. U cilju postizanja maksimalne proizvodnje koristeći drvo urme, postoji potreba da se drveće seče na godišnjem nivou, što se smatra ozbiljnom pretnjom za životnu sredinu. U radu je prikazan jednostavan postupak (u jednom koraku) za sintezu poroznog aktivnog uglja (AC) iz urminog drveta iz Saudijske Arabije, korišćenjem smeše gasova (N_2 i CO_2). Postupak je izveden na različitim temperaturama karbonizacije/aktivacije od 700 to 1000 °C pri brzini od od 10 °C/min. Horizontalni reaktor tipa Alloy 330 je korišćen u cevnoj peći. Protok gasova N_2 i CO_2 je bio 150 i 50 ml/min, redom. Rezultati pokazuju da je za 850 °C dobijena veća površina, i ovi uslovi mogu ponuditi veće mogućnosti za proizvodnju aktivnog uglja sa većim adsopcionim kapacitetom iz otpada od lišća urme. Površina aktivnog uglja, određena BET analizom, dobijenog na 850 °C posle vremena aktivacije od 30 min je iznosila 1094 m^2/g.

Ključne reči: Aktivni ugalj • Fizička aktivacija • Mešavina gasova • Urme iz Saudijske Arabije • Agro otpad