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Synthesis and Characterization of Activated Carbon from Saudi Arabian Dates Tree's Fronds Wastes

Hassan M. Al-Swaidan[+] and Ashfaq Ahmad

Chemistry Department, College of Science, King Saud University, Riyadh, Saudi Arabia

Abstract. Use of date's fronds waste as a raw material for producing activated carbon and characterization was investigated in this work. Date tree's fronds residue production was pyrolyzed using thermogravimetry analysis at 400°C temperature with hold times 3 hours to obtain char from date frond. Activated carbon, with favorable high surface area porous carbons by chemical activation was prepared by soaking these chars in phosphoric acid H_3PO_4. Various concentration of H_3PO_4 (0%, 20%, 40%, 60%, and 80%) is used to optimize the high surface area of carbon obtained and 60% concentration of H_3PO_4 was found the best with the highest surface area of 1139 m^2g^{-1}. The FTIR results shows chemical activation using H_3PO_4 successfully converted the raw material to pure activated carbon and shows similarities between commercial carbon and prepared carbon. FESEM micrographs show the pores and cavity of the prepared activated carbon to get the high surface area. This is further supported by BET results that at 60% H_3PO_4 activated carbon have the highest surface area 1138 m^2g^{-1} compared to the surface area of raw date fronds 4.6 m^2g^{-1}.

Keywords: Date fronds, chemical activation, phosphoric acid, Pyrolysis, activated carbon, Surface area,

1. Introduction

Activated Carbons (ACs) are high surface area and porous carbon has been widely used as an adsorbent for separation, purification, decolorization and deodorization of vegetable oils and fats, water purification and pollution treatment, air and gas purification (cigarette filters, motor vehicles exhaust control) and the food and pharmaceutical industries [1-3]. ACs can be synthesized by two methods, chemical and physical activation. In Chemical activation the starting materials (raw material) is impregnated with a strong dehydrating agent and then followed by Pyrolysis at high temperature to prepare activated carbon. Physical activation method consists of carbonization of the precursor (raw) material in an inert atmosphere and gasification of the resulting char in the presence of steam, carbon dioxide or air. ACs can be prepared from many organic materials having a high content of carbon like coal [4], wood [5, 6], lignite [7] coconut shells [8–10] and recently many agricultural by-products such as walnut shells [11], palm shells[12], pecan shells [13–15], date stones [16–20] almond shells [21], sugar cane bagasse [22,23], cotton stalks [24] and Physic Nut [25], have been used as sources for ACs production.

In this work, AC was produced by chemical activation of Saudi Arabia date palm trees waste. Saudi Arabia is one of the largest date producing countries in the world. The number of date-palm trees is estimated to be more than 18 millions. Every year, about three million trees were pruned. It is estimated that Pruning process of dates tree yield a flow of about 75,000 tons of fronds per year [26]. This has little economical value and are sometimes disposed off as waste or burnt and this might be harmful to the environment. The plenty and easy availability of agricultural by-product make them good source as the raw materials for AC production. Lastly, these agricultural by-products are usually inexpensive and their effective use is desirable.

Saudi Arabia's date frond waste was used for chemical activation due to the abundance availability of date frond as compared to date thorn and foliar. In recent time due to economic and environmental concern phosphoric acid (H_3PO_4) activation has been widely investigated.

[+] Corresponding author. Hassan M. Al-Swaidan Tel.: +96614676008; fax: +96614674365.
E-mail address: hswaidan@ksu.edu.sa.

Many techniques have been used for the characterization of activated carbons. This includes infrared spectroscopy [27], transmission electron microscopy [28], scanning electron microscopy [29, 30], X-ray diffraction [29, 30], optical microscopy [31], apparent surface area estimation by nitrogen adsorption [32-34] iodine number [35], and ion-exchange capacity [36].

In this research, thermogravimetric analysis (TGA) study of dates palm's fronds was carried. The pyrolysis temperature of the raw materials during analysis can determine the exact temperature for decomposition of organic materials, during the activation process for AC production. Finally, the simplest method of obtaining AC by physical activation of the raw materials will carried out and chemical characterized. Using H_3PO_4 for chemical activation, the activation temperature is relatively low (usually around 400^{o}C), while the product yield is of higher grade. Another unique property of H_3PO_4 AC is their remarkable cation-exchange capability, chemical and thermal stability [37].

The main objective of this study is to prepare high surface area carbon by utilizing Saudi Arabia's date frond by optimizing chemical activation using different concentration of H_3PO_4.

2. Experimental Procedures

2.1. Raw Materials

Received date fronds from Riyadh, Kingdom of Saudi Arabia were first washed thoroughly with water to remove all foreign materials, dirt and fibers then cut it to small pieces of about 1 to 4 cm in size. The cleaned fronds are dried at 110 ◦C for 3 hours in a drying oven until it is completely dry.

2.2. Preparation of Activated Carbon

2.2.1 Physical Activation of Raw Materials

Thermogravimetric analysis (TGA) Mettler-TA 4000 was carried out for date's fronds Analysis. Approximately, 5 mg to 10 mg of the samples was heated from 40 to 900 °C with the heating rate 20 °C per minute under controlled atmosphere of nitrogen flow.

About 5 g of raw material (fronds) was weighted in the porcelain. The sample is then activated at 400 °C using Muffle furnace for 3 hours. The temperature was use in corresponds to the TGA results obtained, to reduce any excessive oxidation during physical activation process.

2.2.2. Chemical Activation

5 g of samples date's frond was weight and mixed with 15 ml of 0%, 20%, 40%, 60%, and 80% H_3PO_4 respectively. Then the samples were impregnated in muffle furnace at 100 °C for 2 hour, and then followed by activation for 3 hours at 400 °C still in the furnace. Washing of prepared sample was carried to clean the acid content of the prepared AC. The washing process was continued until pH 7 was attained. The samples were then dried in oven at 110 °C to remove any moisture content. The activated carbon produced was then further characterized using Fourier Transform Infrared (FTIR) analysis and Single Point BET analysis.

2.3. Characterization

2.3.1. Fourier Transform Infrared Spectroscopy (FTIR) analysis

Solid samples of about 1 mg before and after activation were carried. The samples were grinded and milled with 100 mg KBr to form a fine powder. This powder was then compressed into a thin pellet under 7 tons for 5 minutes. The sample was then analyzed using Shimadzu 8300 spectrometer and the spectrum was recorded in a spectral range of 400-4000 cm^{-1}.

2.3.2. Single Point BET surface Area analysis

Specific surface areas and porosities of the samples prepared at various H_3PO_4 concentrations before and after activation were obtained using Single Point BET analysis. This was carried using an automated adsorption apparatus (Micromeritics Pulse Chemisorbs 2705).

3. Results and discussion

3.1. Thermogravimetric analysis of date fronds

Figure 1 is the percentage weight loss during TGA for palm dates frond. Two major weights lost that took place in this graph. The first range of decomposition happened at 40 to 132 °C, which represent 6.1% weight lost. This is most possibly due to the moisture released by the sample during heating. The largest weight loss occurred at temperature range of about 132 to 400 °C. This is due to decomposition of chemical bonded water, cellulose, hemicellulose and lignin to carbon [38-41]. Futher heating above 400 °C reveal a lowering trend of weight loss indicating formation of volatile materials like CO, CO_2 and etc [42].

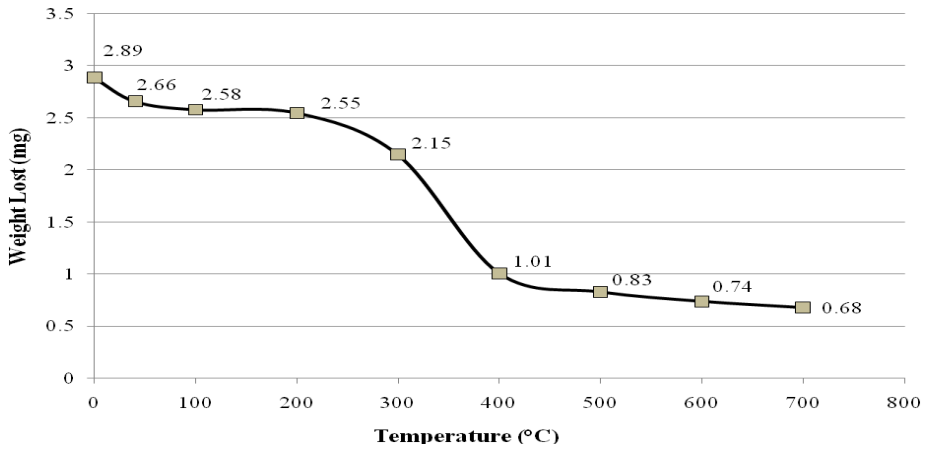


Fig. 1: Thermogravimetric analysis of date fronds

3.2. Effect of H_3PO_4 Concentration

It is proposed that H_3PO_4 has two important functions: it promotes the pyrolytic decomposition of the initial material and the formation of the crosslinked structure [43].

Table 1 illustrate the surface area of AC produced at various concentration of H_3PO_4. The table shows, the surface area of AC obtained increases with the increase of H_3PO_4. It may be spaculated that higher acid concentration would enhance the porosity development. The highest surface area of 1139 m^2g^{-1} of AC obtained is produced using 60% of H_3PO_4. A negative trend of surface area at 80% H_3PO_4 concentration may be recognized to the damage of the structure or formation of polyphosphate layer acting like a skin covering the pore structure. This study is in agreement to those by Girgis which support this finding [44].

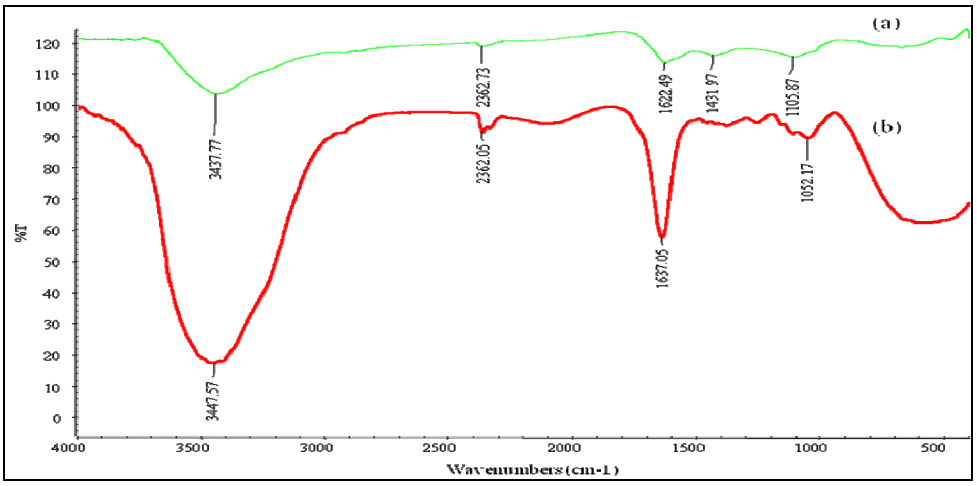
Table 1: Surface area (BET) of activated carbon at different concentration of H_3PO_4.

Label	Concentration of H_3PO_4	Surface Area m^2g^{-1}
Commercial Activated Carbon	H_3PO_4	1069
Raw Date Frond	0% H_3PO_4	4.6
AC-20%	20% H_3PO_4	510
AC-40%	40% H_3PO_4	934
AC-60%	60% H_3PO_4	1139
AC-80%	80% H_3PO_4	776

3.3. Fourier Transform Infrared Spectroscopy (FTIR) analysis

The FTIR spectra can provide valuable information about the chemical compositions of the materials. Figure 2 shows the comparison FTIR spectra of raw date frond (Raw-DF), AC of date frond at 60% concentration of H_3PO_4 (AC-60%) and commercial activated carbon (AC-C) for comparison. Raw date frond (DF) in Figure 2 shows the most complicated and apparent spectrum. A strong and broad adsorption peak appeared at 3434.06 cm^{-1}, which corresponds to the stretching of O – H functional group and this shows the presence of bonded hydroxide in the raw sample. There was another peak observed at 2930.44 cm^{-1} corresponding to the C – H sp^3 stretching. A strong conjugated C=C peak also observed around 1633.83 – 1638.32 cm^{-1}. This sample also shows four important absorption peaks at 1251.06, 1160.53, 1113.89 and 1053.53 cm^{-1} respectively which represent the stretching of C – O functional group. It can be suggested from

the spectrum that the main oxygen groups present in the raw-DF are carbonyl, ethers and alcohols group which are normally present in plant cellulose. In contrast to the FTIR spectrum shown by raw -DF, the spectrum AC-60% and AC-C illustrate less absorption peaks clearly, most of the absorption peaks of functional groups were diminished. Basically all the samples show a weak broad peak around 3425.12 – 3440.32 cm^{-1}, which indicates the presence of OH in the samples. It is most probably of the R-OH bonded like molecule in carbon. Finally, the spectra for the prepared activated carbon from date's frond chemical activated at 60% H_3PO_4 when comparable to the commercial AC, there seem a great similarity. This might indicate that the prepared AC is of similar in grade and standard of that the commercial prepared carbon. The functional groups present in the samples were tabulated in Table 2.



FTIR Spectra for (a) Physical Activation Date Frond, (b) Raw Date Frond

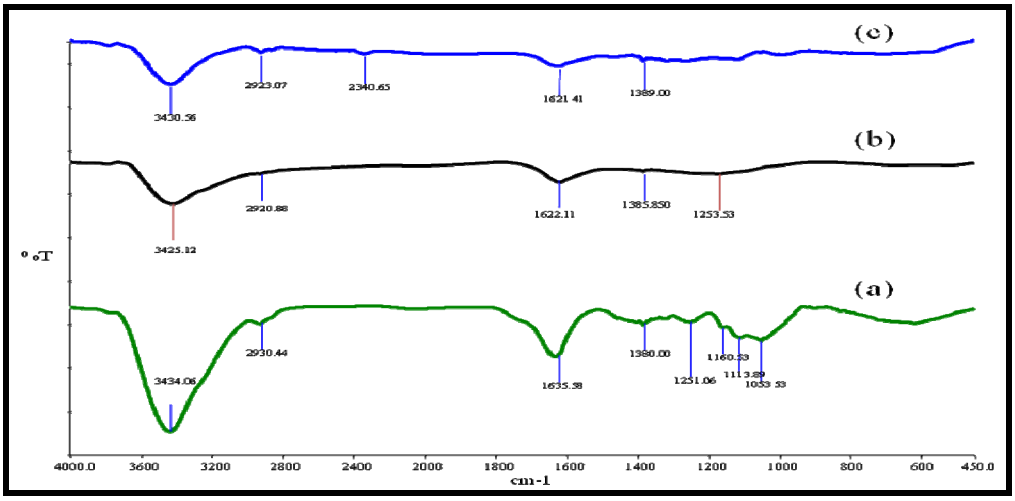


Fig. 2: FTIR Spectra for (a) Raw-DF, (b) AC-60%, (c) AC-C

Table 2: Wave number of some functional groups present in the samples

Sample	Wave Number (cm^{-1})	Functional Group
Raw Date Fronds	3434.06	O – H stretching
	2930.44	C – H (sp^3) stretching
	1635.58	C = C (conjugated) stretching
	1251.06,1160.53, 1113.89,1053.53	C – O stretching
AC-60%	3425.12	O – H stretching
AC-C	3430.56	O – H stretching

3.4. Single point BET Surface Area of Activated Carbon

The single point BET surface area analysis was done to study the effect of different activation method on the surface area of carbon samples. All the data collected, including the raw-DF, AC-60% and AC-C presented in the form a chart in Figure 3. Raw DF gives only 4.6 m^2g^{-1} of BET surface area and for AC-60% is 1139 m^2g^{-1}. Comparatively, the synthesized samples exhibit slightly higher surface area than the commercial activated carbon which only 1069 m^2g^{-1}. This result proposed that the chemical activating agent used, H_3PO_4 has contributed to the higher surface area as compared to the commercial activated carbon.

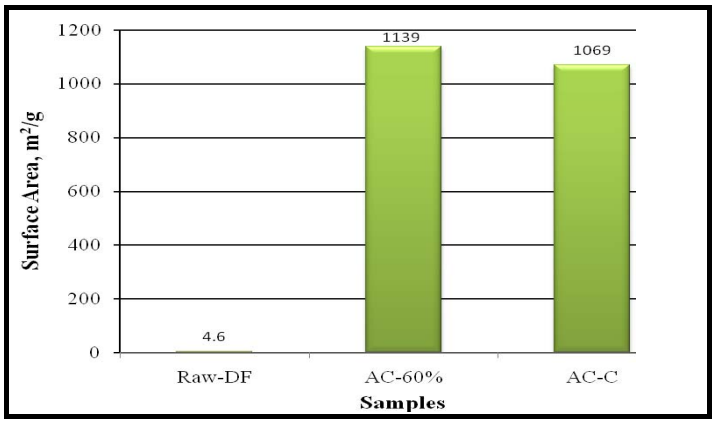


Fig. 3: Single point BET surface area of Raw-DF, AC-60% and AC-C

3.5. FESEM analysis

The FESEM micrographs provide information on the structural changes in the palm date frond for analysis during the activation process. Figure 4 shows raw palm date frond (R-PDF) before and after activation. Figure 4 (a) shows the micrograph of R-PDF at 500x magnification. The surface of R-PDF is curly form resulted from the presence of cellulose, hemicelluloses and lignin in the raw material without any cracks. This would account for its poor or negligible BET surface area. The framework development was so rapid in Figure 4 (b), resulting in extra cavities and leads to crack formation. Due to this well developed pores, the AC-60% possessed high BET surface area. Fig. 4 (b) shows the micrograph of AC-60% at 5000x magnification. The micrograph magnifies the internal cavities, which are now clearly visible. Direct measurement from the micrograph shows that the average pore diameter is 5.23 μm. The surface of the AC-60% seems to be clearer and smoother than R-PDF surface due to the removal of volatile compounds and impurities during the activation process and followed by H_3PO_4–wash. It can be seen that there are solid appeared in the pores of AC- 60% where some small white particles are scattered on the surface of the carbon, maybe due to the remains of the H_3PO_4 which was not washed completely during the activation process.

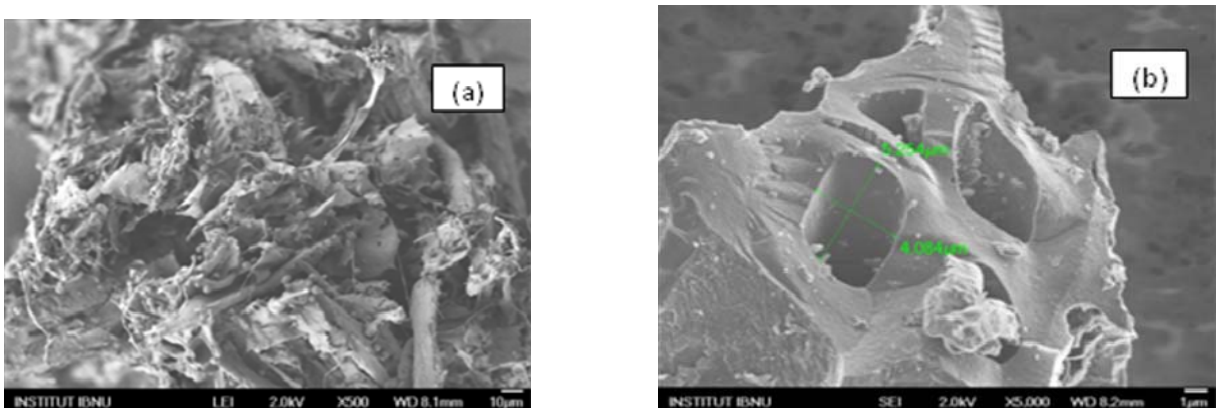


Fig. 4: FESEM of (a) R-PDF and (b) AC-60% H_3PO_4 Acid

4. Conclusion

Preparation of AC from pyrolyzed of date frond was performed in a laboratory-scale facility.The results of TGA reveal that the best temperature for activation is 400^{o}C and any temperature above might effect the production of the high surface area AC. The FTIR shows that before this temperature all the reacted date fronds were uncompleted converted into pure activated carbon. Single point BET surface area for ACs prepared via different concentration of H_3PO_4 indicate AC-60% shows the highest surface area of 1138 m^2g^{-1} compared to the raw date fronds of 4.6 m^2g^{-1} while slightly better to the commercial AC. This study thus suggested that production of high surface area carbon, date palm frond is used, due to its abundance, economical and availability comes from the cutting process on the date palm tree.

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