

# Effect of different activating agents on the production of activated carbon from Raw Date Fronds of Saudi Palm Trees

Ashfaq Ahmad, Hassan Mohammed Al-Swaidan, Ahmad Hamed Al-Ghamdi

**Abstract**—In this study activated carbon (AC) was prepared from raw date's fronds (RDFs) of Saudi palm trees through a single step chemical activation method using  $H_3PO_4$ , KOH and  $ZnCl_2$ . The effects of different parameters such as, concentrations, carbonization temperature and carbonization time (dwell time), on the BET surface area of ACs were studied. The raw date's frond charcoal (RDFC) and ACs were characterized by Thermogravimetric analysis (TGA), nitrogen adsorption Brunauer-Emmett-Teller (BET) surface area and Scanning Electron Microscopy (SEM). The highest BET surface area  $1901\text{ m}^2\text{g}^{-1}$ ,  $1581\text{ m}^2\text{g}^{-1}$  and  $607\text{ m}^2\text{g}^{-1}$  were obtained at optimum condition of 60 %  $H_3PO_4$ ,  $ZnCl_2$  and 40% KOH concentration respectively at  $400^\circ\text{C}$  carbonization temperature for 3 h carbonization time.

**Keywords**—Activated carbon, Date Fronds, Chemical Activation, Surface area.

## I. Introduction

The properties of ACs are largely depended on the methods of activation and types of precursor materials. Lignocellulosic biomass wastes are very important cheap and renewable materials precursor of ACs. This Agricultural Biomass wastes are significant precursor material for the preparation of ACs. AC synthesized from biomass has high surface area, porosity and high carbon yield. AC is porous, solid and black carbon containing materials [1, 2]. ACs is an outstanding adsorbent due to high porosity, large surface area, surface reactivity, large adsorption capacity and ease of regeneration [3].

ACs is used extensively in different fields like air and gas pollution control, pharmaceutical, food and chemical industries, for the decolorization of vegetable oil, wastewater purification, catalyst support, toxic heavy metals removal from drinking water and recovery of solvents, [4, 5].

Lignocellulosic wastes are low-cost and renewable materials precursor for ACs production. ACs were prepared from

numerous sources of biomass waste materials including coconut shell and husk, palm oil shells, cotton stalks, durian shell, rice husk, jackfruit peel and pomegranate seeds [6-13] etc.

ACs preparation methods are classified as physical and chemical activation. Physical method is two steps, first the carbonization of the precursor materials at high temperature in inert atmosphere followed by activation with oxidizing gases such as steam, carbon dioxide and oxygen etc. Chemical activation is a single step method, in which the carbonization of the precursor materials is carried out at low temperature in the presence of a chemical activating agent [14-16].

The most extensively used chemical activating agents for ACs preparation are phosphoric acid, zinc Chloride, potassium hydroxide, sulfuric acid and hydrochloric acid [17-21].

The most abundant cultivating plant in Saudi Arabia is the date palm. It is one of the cash crops in Saudi Arabia. The date palm trees in the kingdom are more than 20 million. During cutting process about 15 frond branches from each palm tree in per year prune by the cultivator. The weight of each frond branch is about one Kg. These estimates show that in Saudi Arabia about 300000 tons of date fronds are produced per year [22, 23].

In continuation to our previous work, in the present research work the preparation of ACs from biomass (RDF) waste was carried out by chemical activation with  $H_3PO_4$ , KOH and  $ZnCl_2$ . The effect of different concentration, carbonization temperature and carbonization time (dwell time) on the BET surface areas, morphology and chemical changes of the ACs were evaluated.

## II. Experimental

### A. Materials

The RDF samples were collected from Agriculture Research date plants garden in King Saud University Riyadh (KSA). The date's fronds were cut it into small pieces and dried in the sun. The RDFs were washed after completely dried in the sun with water to remove all the impurities. The RDFs were dried in Oven (Gallenkamp size one BS) for 5 h at  $105^\circ\text{C}$ . Finally the completely dried RDFs were crushed using grinder into powder and sieved by 0.160 mm mesh (Retsch 4188 type prufsieb/Sieve). The chemicals used for activation and washing in this study are  $ZnCl_2$  97% (BDH England), hydrochloric acid 37 % (Riedel-de Haen USA),  $H_3PO_4$  85% (MERCK Germany), NaOH 97.5% (BDH England) and KOH 85-100% (BDH England).

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## B. Preparation of activated carbon

AC was prepared by first impregnation of powder RDF in activating agents followed by carbonization. Different concentrations of activating agent solutions were prepared in range of 20 to 100% with the increment of 20% by dissolving all activating agents in distilled water.

Powder RDF were soaked in all activating agent's solutions separately at room temperature and allowed for 24 h. The samples were filtered to remove the excess activating agent's solution and dried in oven at 100°C for 4 h ( $H_3PO_4$ ), 6 h at 120°C ( $ZnCl_2$ ) and at 100°C for 3 h (KOH). The dried samples were carbonized at different temperature and dwell time in muffle furnace (XY-1200 XinYu). After carbonization, the ACs were cooled at room temperature and then washed with 0.5 mol. L<sup>-1</sup> HCl solutions for  $ZnCl_2$ , KOH and 0.5 mol. L<sup>-1</sup> NaOH solutions for  $H_3PO_4$  activated carbon. All the samples were washed with distilled water to remove the remaining chemicals until the effluent PH reached 6.8-7. The washed AC samples were dried in an oven at 110°C. The ACs were prepared from RDF by chemical activation with different concentration of  $H_3PO_4$ , KOH and  $ZnCl_2$  such as 20 to 100% separately, different carbonization temperature 250-550°C with different carbonization time 1 to 5 h with 5°C/min and 20°C/min ramp rate respectively.

## C. Analysis and Characterization

BET surface areas of ACs were determined by using Micromeritics (Gemini VII, 2390 USA) analyser through adsorption of nitrogen ( $N_2$ ) at 77K. The samples were degassed at 150°C under nitrogen flow for 1 h to eliminate moisture and gasses before analysis. Thermogravimetric analysis (TA/TGA Q50) of RDF was carried out with heating rate 20°C/min under  $N_2$  at 25-1000°C temperature, to find the suitable carbonization temperature for ACs preparation. The surface morphology of RDF and ACs at different activating agents were analyzed by scanning electron microscope (SEM) by using JEOL (JSM-6380 LA).

## III. Result and Discussion

### A. Proximate analysis and chemical composition of RDF

The method [24] was used for the proximate analysis, to determine the ash, moisture, fixed carbon and volatile matter content in the RDF are given in Table 1. Before proximate analysis, the precursor was dried in air at room temperature for a week. To calculate the moisture content, 1 g air dried RDF was placed in an oven at 110°C for 3 h until completely dehydration was occurred. To measure the volatile matter contents, dried sample of 1 g was placed for 7 min at 850°C in muffle furnace. The sample was cooled same as above and weighed to get the volatile amount in RDF. 1 g of precursor material was placed at 750°C for 3 h in muffle furnace, to determine the ash contents in RDF. Then crucible was cooled in desiccator and weighed the crucible to measure the ash contents in RDF. To determine the fixed carbon amount,

TABLE.1 PROPERTIES OF RDF DATE PALM TREE

Proximate Analysis (Mass %)				Chemical Composition (%)		
Volatile	Moisture	Ash	Fixed carbon	Cellulose	Hemicellulose	Lignin
74.6	9.1	6.0	10.3	44.0	29.8	26.2

subtract the values calculated for moisture, volatile matter, and ash from 100%. The RDF Chemical composition was carried out [25] and the % of cellulose, hemicellulose and lignin were shown in Table 1.

### B. Thermogravimetric (TGA) analysis

TGA was used to measure the amount of weight loss of sample with respect to temperature. Fig. 1 shows the thermogram of RDF in inert atmosphere of  $N_2$ . The first stage of weight loss start from temperature 25 to 189.67°C, which correspond to the loss of water and some light volatile compounds. The % weight loss at this temperature range is about 4.38%. The second stage start from temperature 210-347°C and about 54.40% weight loss occurred. The decomposition of lignocellulosic structure usually above 200°C begins [26]. This high amount of weight loss occurred because of rapid transfer of hemicelluloses, cellulose than lignin to gases and tars. The formation of carbon also begins in this step [27, 28]. Most of the lignin decomposes in 3rd step that occurs above 350°C up to 1000°C because it is slowly decompose than other two. The weight loss in the 3rd step gradually decreased. Thermogravimetric analysis TGA shows that carbonization of RDF occurred at around 400°C.

### C. Effect of Concentration of Activating Agents on BET Surface Area

The BET surface area of ACs produced at different concentration of  $H_3PO_4$ , KOH and  $ZnCl_2$  measured by  $N_2$

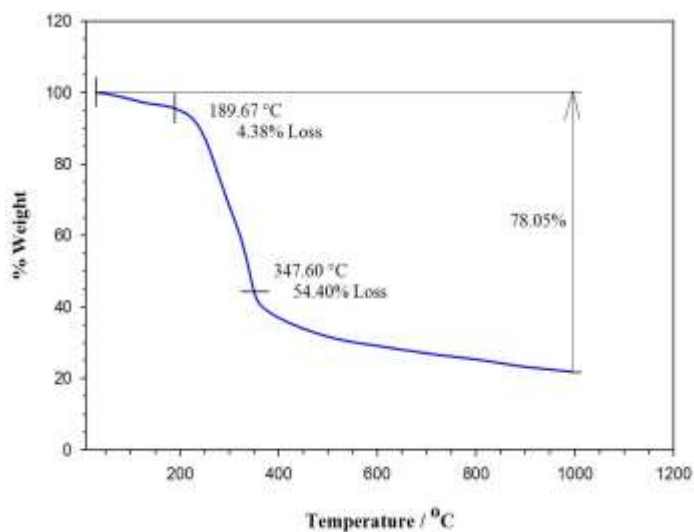


Figure 1. TGA diagram of RDF in a nitrogen atmosphere

adsorption are given in Table 2. The BET surface area of ACs increased with increase in concentration until 40% for KOH and 60% for H<sub>3</sub>O<sub>4</sub> and ZnCl<sub>2</sub>. Further increase in concentrations the BET surface area (Fig. 2) (Table 2) of ACs are decreased. This shows that until 40% and 60% a well porous structure is formed, which is, however, destroyed when the concentration was increased to 100%. The maximum BET surface areas obtained for AC60, AC40 at 60% H<sub>3</sub>PO<sub>4</sub>, ZnCl<sub>2</sub> and 40% KOH are 1901 m<sup>2</sup>g<sup>-1</sup>, 1581 m<sup>2</sup>g<sup>-1</sup> and 607 m<sup>2</sup>g<sup>-1</sup> respectively.

#### D. Effect of Carbonization Temperature on BET Surface Area

The effect of different carbonization temperature from 250 to 550°C on the BET surface area of AC prepared from H<sub>3</sub>PO<sub>4</sub>, KOH and ZnCl<sub>2</sub> are discussed in Table 3. The Raise of carbonization temperature increases the evaporation of volatile components and carbon burn off. The effects of carbonization temperature on the BET Surface area of the synthesized ACs

TABLE. 2 EFFECT OF CONCENTRATION OF H<sub>3</sub>PO<sub>4</sub>, KOH AND ZnCl<sub>2</sub> ON BET SURFACE AREA

Label	H <sub>3</sub> OP <sub>4</sub> BET Surface Area (m <sup>2</sup> g <sup>-1</sup> )	KOH BET Surface Area (m <sup>2</sup> g <sup>-1</sup> )	ZnCl <sub>2</sub> BET Surface Area (m <sup>2</sup> g <sup>-1</sup> )
AC <sup>a</sup> 20% <sup>b</sup>	563	312	572
AC 40%	977	607	1494
AC 60%	1901	503	1581
AC 80%	975	138	753
AC 100%	905	107	857

Note: AC<sup>a</sup>- activated carbon, b-concentration of activating agents

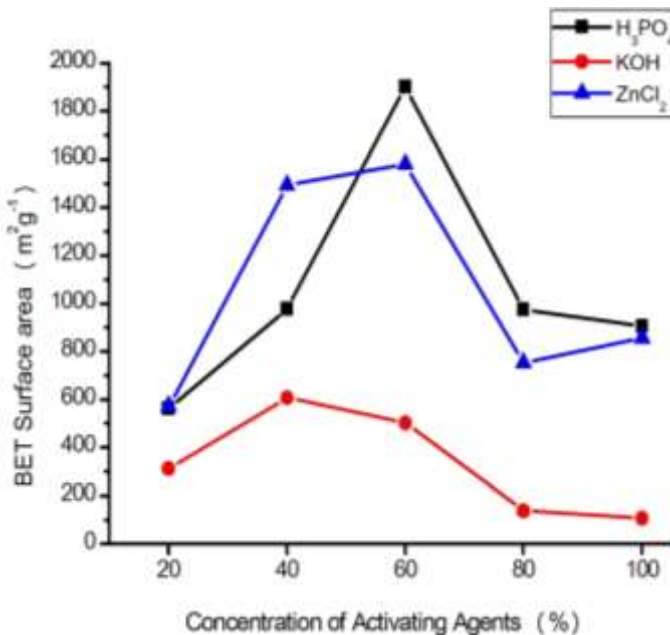


Figure 2. Effect of Concentration of H<sub>3</sub>PO<sub>4</sub>, KOH and ZnCl<sub>2</sub> on BET Surface Area

TABLE. 3 EFFECT OF CARBONIZATION TEMPERATURE ON BET SURFACE AREA

Label	H <sub>3</sub> OP <sub>4</sub> BET Surface Area (m <sup>2</sup> g <sup>-1</sup> )	KOH BET Surface Area (m <sup>2</sup> g <sup>-1</sup> )	ZnCl <sub>2</sub> BET Surface Area (m <sup>2</sup> g <sup>-1</sup> )
AC <sup>a</sup> 250 <sup>b</sup>	1085	343	886
AC 350	1243	520	1167
AC 400	1901	607	1581
AC 450	1510	587	1535
AC 550	1287	497	1303

Note: AC<sup>a</sup>- activated carbon, b-carbonization temperature

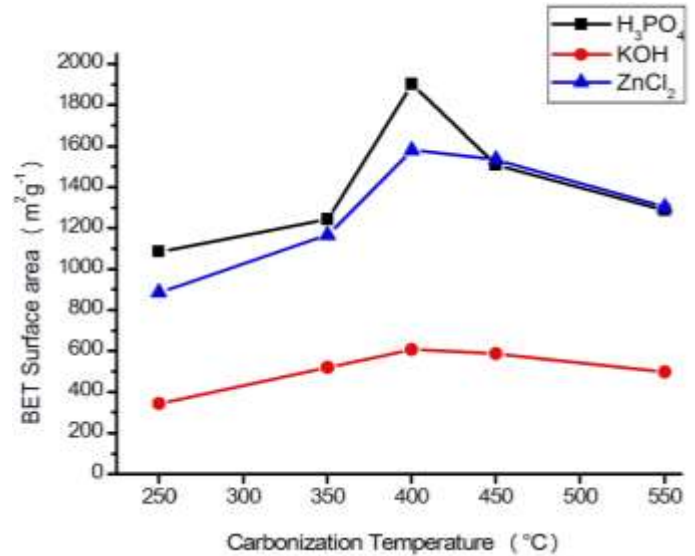


Figure 3. Effect of Carbonization Temperature on BET Surface Area

are stated in Fig. 3. Increasing the carbonization temperature from 250 to 400°C increase the present pores along with the new pores generation. The BET Surface area increasing with increase of carbonization temperature from 250 to 400°C and 400 to 550°C a decreasing trend of BET Surface area was observed. This decreasing trend of BET Surface area may be due rupture of pore (pore fusion) and accumulation of carbon in pores.

#### E. Effect of Carbonization Time on BET Surface Area

The effect of carbonization time 1-5 h on BET Surface area of ACs prepared from various activating agents were examined. The other activation parameters were remains constant, like ramp rate 5°C for H<sub>3</sub>PO<sub>4</sub>, 20°C for KOH, ZnCl<sub>2</sub> and carbonization temperature 400°C for all activating agents. Table 4 shows the results of BET surface area of ACs prepared by various activating agents. The BET surface area increasing with carbonization time till 3 h and then decreasing up to 5 h. High BET surface area was obtained at 3 h carbonization time as shown in Fig. 4. The carbonization time increasing from 1-3 h which effects the production of new pores and increase BET surface area, whereas above the 3 h carbonization temperature or (longer heating duration) pore

widening and collapse of some the pores occurs which decrease the BET surface area.

### F. Scanning Electron Microscopy (SEM)

Figure 5 show the digital images of RDF (a) AC (b) and Scanning electron microscope (SEM) micrographs of RDFC (c), AC-H<sub>3</sub>PO<sub>4</sub> (d) AC-ZnCl<sub>2</sub> (e) and AC-KOH (f) at optimum conditions. There are significant changes among the surface morphology of RDFC and ACs. The micrograph of RDFC shows that surface is in the form of curvy or wavy because of the presence of cellulose, hemicellulose and lignin (Fig. 5 c). There are no pores and no slit like cracks available on the surface of RDFC and look like common lignocellulosic materials. However several large pores and cracks are developed on the surface of AC-H<sub>3</sub>PO<sub>4</sub> due to release of volatile organic and inorganic compounds by chemical activation (Fig. 5 d). The surface of AC-KOH (Fig. 5 e) shows some cracks and small amount of pores. The AC-ZnCl<sub>2</sub> micrograph (Fig. 5 f) shows numerous pores and cracks on surface. The high BET surface area produced with AC-H<sub>3</sub>PO<sub>4</sub> and AC-ZnCl<sub>2</sub> compared to AC-KOH and RDFC is attributed to the presence of numerous pores and cracks.

TABLE 4. EFFECT OF CARBONIZATION TIME ON BET SURFACE AREA

Label	H <sub>3</sub> PO <sub>4</sub> BET Surface Area (m <sup>2</sup> g <sup>-1</sup> )	KOH BET Surface Area (m <sup>2</sup> g <sup>-1</sup> )	ZnCl <sub>2</sub> BET Surface Area (m <sup>2</sup> g <sup>-1</sup> )
AC <sup>a</sup> 1 <sup>b</sup>	1653	443	1290
AC 2	1730	503	1363
AC 3	1901	607	1581
AC 4	1218	545	1392
AC 5	1106	477	1308

Note: AC<sup>a</sup> - activated carbon, b-carbonization time (h)

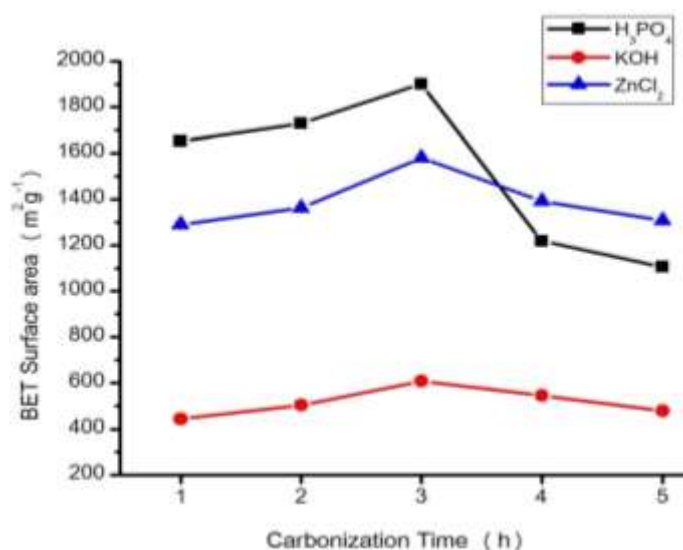


Figure 4. Effect of Carbonization Time on BET Surface Area

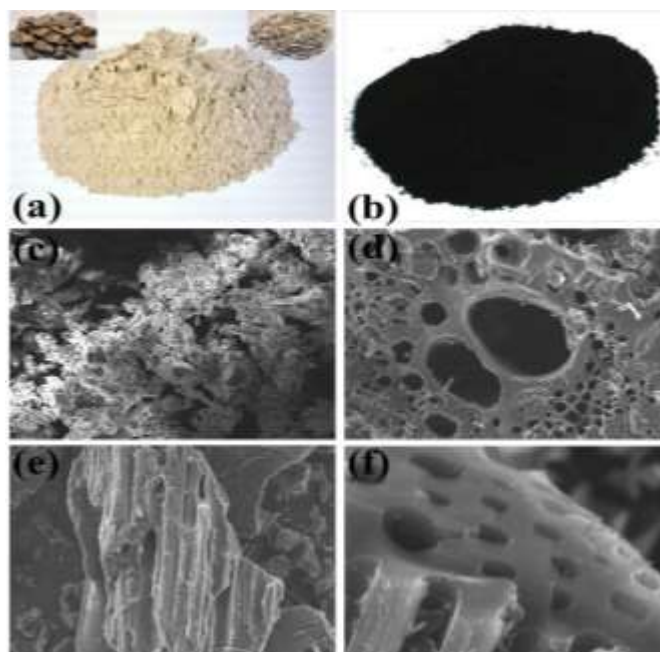


Figure 5. Digital Images (a) RDF, (b) AC and SEM of (c) RDFC (d) AC-H<sub>3</sub>PO<sub>4</sub> (e) AC-KOH (f) AC-ZnCl<sub>2</sub>

## IV. Conclusion

The ACs were prepared from RDF a biomass waste using different chemical activating agents like H<sub>3</sub>PO<sub>4</sub>, KOH and ZnCl<sub>2</sub>. The 60% for AC-H<sub>3</sub>PO<sub>4</sub>, AC-ZnCl<sub>2</sub> and 40% AC-KOH concentration, 3 h carbonization time and 400°C carbonization temperature are the optimum conditions at which the highest BET surface areas were obtained. The High surface area ACs prepared from RDF at lower carbonization temperature and can be used as an adsorbent for purification of industrial wastewater and removal of gases and other hazardous compounds. Therefore, the use of RDF for the ACs preparation is significant from the perspective of economic and environmental aspects as they are available abundantly.

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