Production of Activated Carbon from Raw Date Palm Fronds by $ZnCl_2$ Activation

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Summary: Annually a large volume of date palm frond waste is produced in Saudi Arabia as a result of the pruning of date palm trees. In this research activated carbon (AC) was prepared from date frond through a single step chemical activation method by $ZnCl_2$. The influence of $ZnCl_2$ concentrations (in the range of 0, 20, 40, 60 and 80%) on the surface areas, pore volumes and carbon yield of ACs prepared from raw date frond (RDF) was studied with various analytical techniques. The RDF and ACs were characterized by Thermogravimetric Analysis (TGA), nitrogen adsorption Brunauer-Emmett-Teller (BET) for surface areas and pore volumes, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) for surface morphology and elemental composition respectively. In the present study we have obtained the highest BET surface area 1581.67 m^2g^{-1} and total pore volume 0.629 cm^3g^{-1} at 60 % $ZnCl_2$ concentration. The % yield of ACs increased with increase in $ZnCl_2$ concentration and reached to 39% at 60 % $ZnCl_2$ concentration. The surface area obtained in the present study is highest amongst the results report in literature.

Keywords: Activated carbon, Date Palm Fronds, Zinc Chloride Activation, Surface area.

Introduction

Agricultural wastes are important starting material for the production of ACs. Agro waste produced AC have large surface area and high content of carbon materials. ACs is porous, solid and black carbonaceous materials [1, 2]. ACs is excellent adsorbents because they have high porosity, extremely high surface area, surface reactivity, large adsorption capacity and ease of regeneration [3-5]. ACs are widely used in various fields such as environmental (for gas and air treatment, and wastewater purification), medical (in pharmaceutical), food (for the decolorization and purification of vegetable oil and fats) and chemical (for the recovery of solvents and as catalyst support) industries [6, 7]. ACs are available in three different forms e.g. powder, granular and fibrous. The most frequently used precursor materials for the synthesis of ACs are coals, polymers, agro biomass (RDF (lignocellulosic)) and some petroleum based products [8]. The properties of ACs are largely dependent on the methods of activation and type of the precursor materials. Lignocellulosic biomass wastes are very important as these are abundant in nature and cheaply available precursor materials for ACs. Many researchers have reported the production of ACs from various sources of lignocellulosic waste materials including coconut shell and husk, [9,10] palm oil shells, [11] cotton stalks [12] durian shell [13] rice husk, [14] jackfruit peel [15], pomegranate seeds [16] sugar cane bagasse [17], hazelnut shell [18], almond shell [19], Woods [20], Olive stone [21], date stone [22], Walnut shell [23] etc.

Physical and chemical activation methods are used for preparation of ACs. In physical method, the carbonization of the carbonaceous materials is carried out at high temperature range of 700-1100 ºC in inert atmosphere followed by activation with oxidizing gases (activating agents) such as oxygen, steam and CO_2. However, in chemical activation the carbonization of the precursor materials is carried out at comparatively low temperature (400-700 ºC) in the presence of a chemical activating agent.

The carbonization and activation during chemical activation method occurs at the same time. The advantages of chemical activation method over physical activation are: (i) it is a single step process, (ii) it is carried out at lower temperature and usually have a better effect on pores development, and (iii) high carbon yields and low energy cost [24-30].

Many researchers have used chemical activation method for the production of ACs. In chemical activation the biomasses are impregnated in various chemical activating agents such as phosphoric acid (H_3PO_4) [31], zinc Chloride ($ZnCl_2$) [32], potassium hydroxide (KOH) [33], sulfuric acid (H_2SO_4) [34], hydrochloric acid (HCl) [35], nitric acid (HNO_3) [36], pyrophosphoric acid ($H_4P_2O_7$) [37], sodium hydroxide (NaOH) [38], sodium chloride (NaCl) [39], potassium carbonate (K_2CO_3) [40], ammonium chloride (NH_4Cl) [41], sodium carbonate (Na_2CO_3) [42], ferric chloride ($FeCl_3$) [43], hydrogen peroxide (H_2O_2) [44] etc.

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The plenty cultivating plant and cash crop in Saudi Arabia are the date palm. According to the recent Figures, over 20 million date palm trees are in Saudi Arabia. During the pruning process around fifteen branches of frond from each date palm tree are pruned (trim) annually by the cultivator. The weight of each branch of frond is approximately 1 Kilogram. These estimates show that around 300,000 tons of RDFs are produced annually in Saudi Arabia [45, 46].

KOH was used as an activating agent for preparation of ACs from RDF in our previous research article [6]. In continuation to our previous study, in the current research work the synthesis of ACs from RDF were carried out by $ZnCl_2$ activation. The influences of various concentration of $ZnCl_2$ on the surface areas, pore volumes, % yields, morphological and elemental composition of the ACs were investigated.

Experimental

Materials

RDFs were collected from date plants garden in Riyadh (KSA). RDFs were cut it into pieces of 1 to 3 cm. The pieces were thoroughly washed first with tap water and then with distilled water to remove the dust, fibers and impurities, etc. The washed RDFs were dried, at 105°C for 5 h in oven (Gallenkamp size one BS oven), to remove the moistures content. The dried RDFs were crushed into powder and sieved by 0.160 mm mesh (Retsch 4188 type prufsieb/Sieve). Analytical grad chemical such as $ZnCl_2$ 97% (BDH England) and hydrochloric acid 37 % (Riedel-de Haen USA) were used for activation and washing respectively in this research. Double distilled water was used in the solution preparation and distilled water was used for washing.

Preparation of Activated Carbon

ACs were prepared by first impregnating RDFs in $ZnCl_2$ solution followed by carbonization at 400^{o}C for 3 h. Various concentrations such as 20, 40, 60 and 80% of $ZnCl_2$ solutions were prepared by dissolving $ZnCl_2$ in distilled water [47]. The powder RDFs (11g) were separately socked in 40 mL $ZnCl_2$ solutions at room temperature and allowed for 24 h. The samples were filtered to remove the excess $ZnCl_2$ solution and dried in air circulated oven for 6 h at 120°C. The dried samples were carbonized at 400°C for 3 h in muffle furnace (XY-1200 XinYu). The Prepared ACs were cooled at room temperature and then washed with 0.5 mol.L^{-1} HCl solution to remove the excess chloride ions. All the samples were washed several times with hot water and distilled water to eliminate the remaining chemicals. This filtration and washing were continued until the effluent became neutral. The pH was determined by Thermo Scientific (Orion 2 Star) pH meter. The washed ACs samples were dried at 110°C in an oven. The charcoal prepared from RDF at 400°C carbonization temperature for 3 h with 20°C min^{-1} ramp rate without chemical activation was indicated as RDF 400-3-20. The ACs prepared from RDF at 400°C carbonization temperature for 3 h with 20°C min^{-1} heating ramp rate and various concentration of $ZnCl_2$ such as 20%, 40%, 60% and 80% were designated as AC20 400-3-20, AC40 400-3-20, AC60 400-3-20 and AC80 400-3-20 respectively.

Analysis and Characterization

The surface areas and pore volumes properties of ACs and RDF samples were determined through the adsorption of nitrogen (N_2) gas (at 77K) using Micromeritics (Gemini VII, 2390 Surface Area and Porosity analyzer). The samples were degassed under nitrogen flow for 1 h at 150°C to eliminate moisture and gasses before analysis. TGA (TA/TGA Q50) was used for thermal behavior of RDF with heating rate 20°C min^{-1} under N_2 atmosphere until 1000°C. The surface morphology and elemental composition of RDF and ACs at different $ZnCl_2$ solutions were analyzed by scanning electron microscope (SEM) and Energy Dispersive X-ray (EDX) by using JEOL (JSM–6380 LA).

Result and Discussion

Thermogravimetric (TGA) analysis

TGA was used to measure the amount of weight loss of the RDF with respect to temperature. Fig. 1 shows the TGA plot of RDF in N_2 atmosphere. The first stage of weight loss start from 50 to 189.67 °C temperature range, which correspond to the loss of water and some light volatile compounds. The % weight loss at this temperature range is about 4.38%. The temperature range of the second stage start from 210-347°C and about 54.40% weight loss occurred. The decomposition of lignocellulosic structure usually starts above 200°C [48]. The high weight loss occurred in this step was attributed to the swift transformation of hemicelluloses and cellulose to gases and tars. On the contrary lignin conversion to gases and tar was slow. Further, the formation of carbon also begins in this step [49, 50]. The weight loss in the 3rd step gradually decreased. Most of the lignin decomposes above 350°C and up to 1000°C in this step. Thermogravimetric analysis TGA reveals that carbonization RDF occurs at~ 400°C.

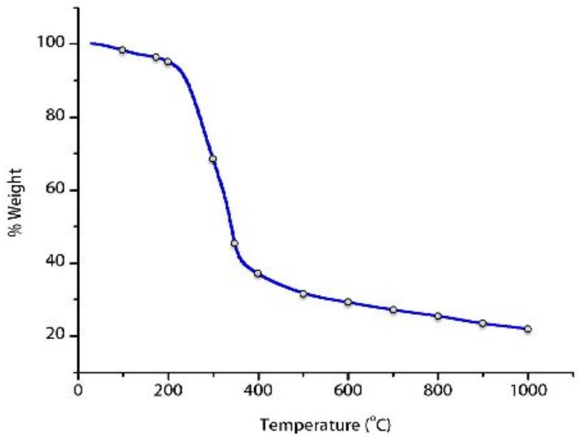

Fig. 1: Typical TGA diagram of Date Fronds in a nitrogen atmosphere.

BET Surface Areas, Pore Volumes

The BET, micro and mesopore surface area, total pore volume (V_{total}) and micropore Volume (V_{micro}) of ACs prepared at different $ZnCl_2$ concentrations and RDF measured by N_2 adsorption are given in Table-1. RDF showed low surface area 4.5 m^2g^{-1}, which revealed that RDF has a highly compact structure with almost no porosity. The BET, mesopore surface area and mesopore volume of ACs increased with increase in the $ZnCl_2$ concentration until 60%. Further increase in the $ZnCl_2$ concentration to 80%, the mesopore volume (calculated using equation1) [16] and the BET surface area of ACs are decreased. This shows that until 60% a well porous structure is formed which is, however, destroyed when the concentration was increased to 80%. The maximum BET, mesopore surface area and mesopore volume obtained for AC at 60% $ZnCl_2$ are 1581 m^2g^{-1}, 1507 m^2g^{-1} and 0.610 cm^3g^{-1}, respectively.

$$V_{meso} = V_{total} - V_{micro} \qquad (1)$$

where V_{meso} is the mesopore volume, V_{total} is the total pore volume and V_{micro} is the micropore volume.

The BET surface area and total pore volume of the present work were compared with ACs prepared from different raw materials and activated by physical and chemical methods in Table-2. It could be observed that the AC produced in this research work indicated a high BET surface area of 1581 m^2g^{-1} as compare to the values reported in literature. Based on the above results, $ZnCl_2$ is a promising activating agent for AC preparation from RDF.

Yield of Activated carbon

Fig. 2 shows the % yields of ACs prepared with $ZnCl_2$ concentrations of 20%, 40%, 60% and 80%. The % yield of ACs is calculated using equation 2. Similar to the BET, mesoporous surface area and mesopore volume, the % yield of the ACs increased with increase in the concentration of $ZnCl_2$ until 60%, however, further increase in the $ZnCl_2$ concentration results in the decrease of the % yield. This decrease in the % yield is attributed the increase in dehydration, degradation and condensation reaction in lignocellulosic precursor with increase in $ZnCl_2$ concentration. These reactions result in increased evolution of gaseous products from the hydroaromatic structure of carbonized char.

$$\text{Yield (\%)} = W_{AC} / W_R * 100 \qquad (2)$$

where W_{AC} is the dry weight (g) of final AC and W_R is the dry weight (g) of RDF.

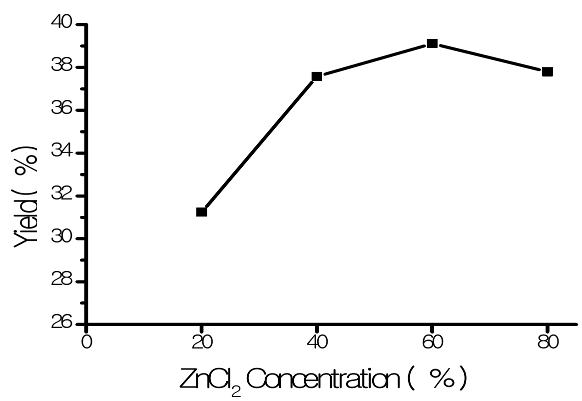

Fig. 2: Effect of $ZnCl_2$ Concentration on yield of ACs.

SEM Analysis

Fig. 3 shows the SEM micrographs of RDF (a) and AC60 (b) at optimum concentration of $ZnCl_2$ (i.e. 60%). Significant changes among the surface morphologies of RDF and AC60 can be observed. The micrograph in Fig.3a shows a wavy or curvy surface for RDF. This curvy surface was attributed to the presence of cellulose, hemicellulose and lignin. Further no pores and cracks were observed on the surface of RDF. The surface morphology of RDF is found similar to that of common lignocellulosic materials. On the contrary, AC60 exhibited several large pores and cracks on the surface. The development of these pores is attributed to release of volatile organic and inorganic compounds (Fig. 3 b). The high BET surface area of the AC prepared with 60% $ZnCl_2$ is attributed to the presence of these pores and cracks.

Table-1:BET, Surface Areas, Pore Volumes of RDF and $ZnCl_2$ ACs.

Label	BET Surface Area(m^2g^{-1})	Micropore Surface Area(m^2g^{-1})	Mesopore (External) Surface Area(m^2g^{-1})	Total Pore Vol. (cm^3g^{-1})	Micropore Vol. (cm^3g^{-1})	Mesopore Vol. (cm^3g^{-1})
RDF 400-3-20	**4.6**	**1.93**	**2.67**	**0.003**	**0.001**	**0.002**
AC20[a] 400[b]-3[c]-20[d]	**572**	**267**	**304**	**0.237**	**0.114**	**0.123**
AC40 400-3-20	**1494**	**85**	**1409**	**0.595**	**0.025**	**0.570**
AC60 400-3-20	**1581**	**74**	**1507**	**0.629**	**0.019**	**0.610**
AC80 400-3-20	**753**	**235**	**518**	**0.309**	**0.099**	**0.210**

Note: RDF-Raw Date Frond, AC- activated carbon, a-$ZnCl_2$ concentration, b- activation temperature (°C), c- activation time (h), d-ramp rate (°C /min)

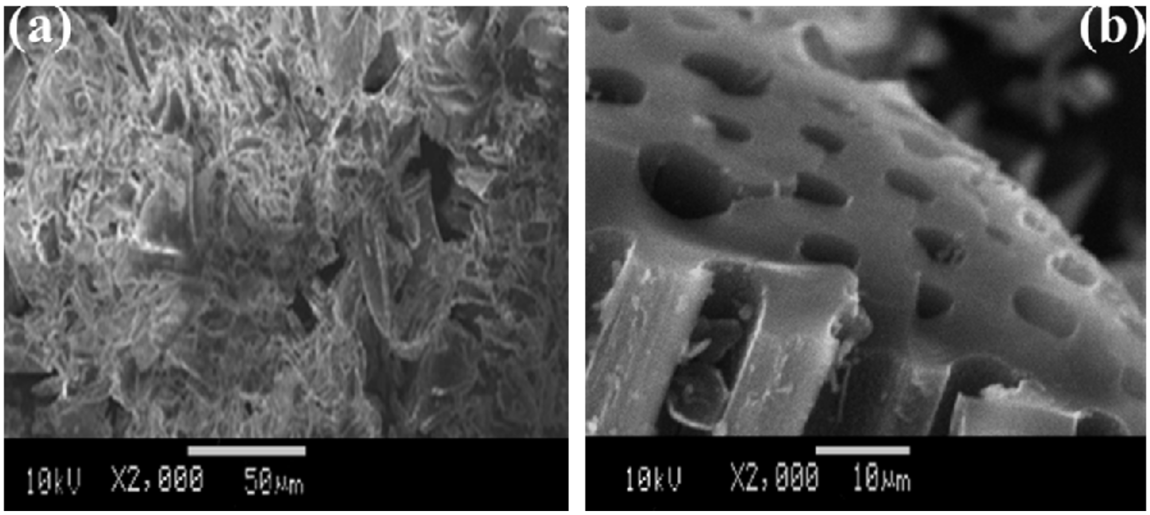

Fig. 3: SEM of (a) RDF (b) AC60.

Table-2:Comparative data of the various adsorbent activated by physical and chemical methods

Activation Method	Raw Materials	Activating Agent	BET Surface Area (m^2g^{-1})	Total Pore Vol. (cm^3g^{-1})	Micropore Vol. (cm^3g^{-1})	Mesopore Vol. (cm^3g^{-1})	Refs.
	Palm shell	**CO_2**	**984**	**0.76**	**-**	**-**	**51**
	Almond shell	**Steam**	**1234**	**0.90**	**0.36**	**-**	**52**
	Coconut shell	**Steam**	**1054**	**0.517**	**0.092**	**0.019**	**53**
Physical Activation	**Date stone**	**CO_2**	**604**	**0.34**	**0.29**	**-**	**22**
	Date palm branches	**Steam**	**560**	**0.292**	**0.259**	**0.068**	**54**
	Date palm leaves	**Steam**	**525**	**0.309**	**0.199**	**0.089**	**54**
	Raw Date Frond	**CO_2**	**1094**	**0.438**	**-**	**-**	**55**
	Tea Fruit Peel	**H_3PO_4**	**1024**	**0.746**	**0.285**	**0.463**	**31**
	Pomegranate seeds	**$ZnCl_2$**	**978**	**0.563**	**0.283**	**0.280**	**16**
Chemical Activation	**Palm kernel shell**	**KOH**	**217**	**0.12**	**0.11**	**-**	**56**
	Date stone	**$ZnCl_2$**	**951**	**0.456**	**0.355**	**-**	**57**
	Date palm stem	**H_3PO_4**	**1100**	**1.15**	**-**	**-**	**58**
	Grape stalk	**$ZnCl_2$**	**1411**	**0.723**	**-**	**-**	**32**
	Raw Date Frond	**KOH**	**250**	**0.082**	**-**	**-**	**6**
Chemical Activation	**Raw Date Frond**	**$ZnCl_2$**	**1581**	**0.629**	**0.019**	**0.610**	**Current Paper**

EDX Analysis

The elemental composition of RDF and AC60 was carried out by Energy Dispersive X-ray (EDX) analysis. The elemental analysis of RDF and AC60 prepared at optimal concentration of 60 % $ZnCl_2$ are shown in Table-3. The carbon, oxygen and some other elements contents were determined. Carbon and Oxygen contents are the major and mainly observed elements in both samples. The carbon content in AC60 is 95.03%, which is greater than the RDF 59.17% and Oxygen percentage in RDF 34.66%, which is greater than AC60 2.19%. The high Carbon% and low Oxygen % in AC60 are attributed to the volatilization of Oxygen and Hydrogen atoms.

Table-3: Elemental Analysis of (RDF) and AC60.

Elements (%)	RDF	AC60
Carbon (%)	59.17	95.03
Oxygen (%)	34.66	2.19
Others (%)	6.17	2.78
Total	100	100

Conclusion

The ACs were prepared from RDF biomass at different $ZnCl_2$ concentrations (i.e. 20%, 40%, 60% and 80%). The 60% $ZnCl_2$ is the optimum concentration at which the highest BET surface area 1581 m^2g^{-1}, pore volume 0.629 cm^3g^{-1} and mesopore volume 0.610 cm^3g^{-1} were obtained. The ACs prepared from RDF at low carbonization temperature and with high surface area can be used as an adsorbent for purification of industrial wastewater, removal of gases and other hazardous compounds. The use of RDFs for the production of ACs is significant from economic and environmental perspectives as these are abundantly available.

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