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Production of Activated Carbon from Agricultural Residues

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Abstract : The research aim is become to identify the quality of activated carbon product from some agricultural residues. This goal is interested in both of largest amount of agricultural residues and expensive import activated carbon. To achieve research aim, three available of agricultural residues are collected (date kernels, residues of trimming peach trees and corn stalks) and experimentally analyzed under four furnace temperatures of 673, 773, 873 and 973 °K and four pyrolysis times (1.0, 1.5, 2.0 and 2.5 h). The output parameters from pyrolysis of activated carbon such as carbon concentration, yield, surface area, pore volume, ash ratio and SEM (Scanning Electron Microscope) were investigated. The vital carbon concentration were 4.95, 3.61 and 1.28 $mg.g^{-1}$ at pyrolysis time of 2.0, 2.0, and 1.0 h respectively for date kernels, residues of trimming peach trees and corn stalks. Furthermore, the obtained activated carbon can produced at furnace temperature and pyrolysis time of 673 °K through 2 h for date kernels and 973°K during 2 h for peach trees and 673 °K in 1 h for corn stalks.
Keywords : Activated carbon, Agricultural residues, Date kernels, Residues of trimming peach trees, Corn stalks, Temperature, Pyrolysis Time, Chemical activation, Carbon ratio, Surface area, Pore volume, Ash, Yield.

Introduction

Activated carbon plays decidedly important role as adsorbent, due to its unique distinguished properties. Also, it called activated charcoal or activated coal. Scientifically, it is defined as form of carbon that has been processed to make it extremely porous, which obtained and can control for its size by heating speed and good washing [1,2] and thus to have a greatly surface area available for adsorption or chemical reactions[3]. Also, it is widely used in gas purification, gold purification, metal extraction, medicine, sewage treatment, air filters in gas masks and filter masks along with water and wastewater treatment and many other applications[4].

Activated carbon can produced from numerous materials with a high carbon content and low level ash such as coal, woods and bones[4,5]. Many researchers studied the usage of residues from agriculture and agro-industries as raw materials for production activated carbons. These included olive kernels[6], almond shells [7] apricot and peach kernels[8], maize cob[9], linseed straw[10]; saw dust[11], rice hulls[12], cashew nuts[13] and coconut shells, eucalyptus bark, linseed cake, tamarind seeds, and tea waste ash suffocated coal, baggage, ground nut husk, activated bauxite, palm seed coat, de-oiled soya, cement kiln dust[4]. Furthermore, [14]found that the advantages of activated carbon produced from apricot stones had higher sorption and low cost of extraction in compared with other sorbents. Most researches done to propose cheap and new raw materials which produce activated carbon with decline its cost and diminish environmental impact[2]. Also activated carbon can prepared from sugar can stalks by phosphoric acid treatment and used to remove disperse 2BLN dye from industrial water[15].

Methods to produce the activated carbon are physically (dry process) or chemically. Also chemical activation method is used due to the fact that its agents play an important role in the carbonization process, in which they acted as dehydration agents and minimized the formation of tar during carbonization [16]. Furthermore, the temperature range used in chemical activation was lower in comparison to that used in physical activation[17]. Chemical activation, pyrolysis char usually impregnated with some chemical reagents such as H_3PO_4, $ZnCl_2$, KOH, $CaCl_2$, KCl, $Fe_2(SO_4)_3$, H_2O and H_2SO_4[3,18]. Major advantages of chemical activation are lower treatment temperatures and shorter treatment times [19]. Phosphoric acid was selected as the activating agent instead of zinc chloride so as not to aggravate environmental pollution by contamination with zinc compounds and also it is easier to recover the carbon product during processing stage only rinsing with required water [20,21]. [22] noted that Increasing carbonization temperature will decrease yield. H_2SO_4 impregnated material when carbonized for different time of interval results in constant yield. Also concluded that time of carbonization of H_2SO_4 impregnated material has no effect on yield.

The activated carbon obtained by chemical activation exhibits a larger surface area and better developed meso-porosity [4]. By chemical activating, pyrolysis for hazelnut shell was done at 450 °C and 2 h pyrolysis time [3], at 500–800°C for agricultural waste corn cob [23] and at 400°C for seed hulls. [24,25] noted that at activation duration increases the surface area was decreased. This was because longer heating duration caused some of the porous became larger or even collapse, thus contributed to the reduction of surface area. [26] found that mostly micro porous with BET surface area in activated carbons prepared from chitosan between 400 and 2130 m^2 g^{-1} and a pore volume between 0.18 and 1.12 cm^3 g^{-1}. Activated carbons yield from brachystegia eurycoma and prosopis africana seed hulls by physical carbonization at temperatures less of 500^oC was increased by 25% with poor quality [26].

Recent research work, aims to determine the suitable temperature and time during produce activated carbon from some agricultural residuals and at same time identified carbon concentration, yield, moisture content, CNH ratio, ash percentage, surface area and pore volume.

Materials and Methods

Experimental work was carried out as a cooperation between Agricultural Engineering Department, Faculty of Agriculture, Cairo University and Agricultural Engineering Research Institute during the period from September 2013 until September 2015. To produce activated carbon, basically appropriate agricultural residuals must be selected carefully with high content of carbon [4]. Then residues were burned at different engineering variables by chemical methods. After that the produced activated carbon was analyzed as amount and quality for each test. The selected residues were date kernels, (Fig. 1-A) and residues of trimming peach trees, (Fig. 1-B) taken from Horticultural Research Institute in Cairo governorate in summer and winter seasons. But corn stalks (Fig.1-C) were taken from Gimmeza Research in Gharbiya governorate.

A- Dates kernels **B- Residues of trimming peach trees** **C- Corn stalks**

Figure 1. The agricultural residues

The agricultural residues were dried naturally before procedure taken place. Then, some of physic-chemical properties of the selected residues were determined using the traditional methods. There were included moisture content, bulk density, CNH and ash percentage (Table 1). Subsequently, the pyrolysis is performed in sample furnace (Fig. 2) with cupellation inner dimensions of 45×300×2mm diameter, height and thickness, respectively. To activate the agricultural residuals the Ortho Phosphoric Acid (H_3PO_4) were added in ratio of 1: 2 v/w (volume H_3PO_4 / of mass of residuals). During operation in furnace, the stable gas of nitrogen is pumped with a flow rate of 100 cm^3/h.

Figure 2. Oven isolation from the air (Metallurgical Research Center)

The pyrolysis process done at the following variables:

1. Three types of agricultural residues (R). Namely are date kernels, residues of trimming peach trees and corn stalks.
2. Four furnace temperature (T_s) are 673, 773, 873 and 973 °K (400, 500, 600 and 700 °C).
3. Four pyrolysis times (t_p) are 1.0, 1.5, 20 and 2.5 hours.

The randomized factorial experimental designed was done to perform tests with three replicates. To evaluate the obtained activated carbon all samples were: 1) Washed to reach pH7; 2) Methylene blue test is identified to determine the highest carbon concentration as activated carbon in sample; 3) Washed to dry at 378 °K to 24 h.

Determination of carbon concentration

It determined with methylene blue method, and then absorbance data compared with the reference calibration curve according to [28].

Yield ratio

The yield ratio was calculated as a percentage based on the following equation:

$$\text{Yield}\% = \frac{w_c}{w_o} \times 100$$

Where:
w_c : is the dry mass (g) after pyrolysis,
w_o : is the dry mass (g) of precursor.

Moisture content

The moisture content was measured before and after tests. The moisture content of residual samples after air drying (naturally) at 343°K to constant mass. Then after pyrolysis and washing at 378 °K to 24 h.

CNH ratio

To determine the C, N, H elements percentage the automatic analyzer C, N and H. Vario El Ш – Elementary – Germany was used at Cairo Univ., Fac. of Sci., 2015.

Ash in percentage

It determined accordingly [29,30] by using the following equation:

$$\text{Ash} = \frac{\text{Mss of sample before pyrolysis}}{\text{Mass of sample after pyroysis}} \times 100, \quad \%$$

Bulk density

It calculated before and after pyrolysis from the following equation:

$$\text{Bulk density } (g/cm^3) = \frac{\text{mass of dry sample (g)}}{\text{Volume of dry sample } (cm^3)}$$

Characteristics of porous

The surface area, pore volume and size of activated carbon particles were characterized using an apparatus of Nova 2000–made in USA that available in Metallurgical research center. Also, the produced activated carbon were recorded using the Scanning Electron Microscope (SEM) (HITACHI S-3400, Japan) that obtainable in Fac. of Agric. Mansoura Univ.

Results and Discussions

Properties of residues

Before and after pyrolysis, some properties of agricultural residues were illustrated in table (1). The highest percentage of residues moisture content for sun dried samples (natural drying) were 23.3; 19.3 and 9.1% for corn stalks, residues of trimming peach trees and date kernels respectively.

The CNH analysis before and after pyrolysis for date kernels shows that, the “C” and “N” in percentage are ascending by about 1.25 and 1.84 times respectively while the percentage of “H” is descending by about 1.77 time. But for pruning peach trees, the “C” increased by about 1.306 time and vice versa for “N” and “H” by about 17.8 and 7.69 times respectively. While, for corn stalks, the CNH before and after pyrolysis decreased by about 3.15; 1.79 and 1.33 times respectively.

These results may due to the losses in N and H after pyrolysis. But C increased due to the good pyrolysis process at date kernels and residues of trimming peach trees while decreased at corn stalks by excessing pyrolysis process.

On the other side, the ash percentage increasing by about 3.78, 1.50 and 3.0 times for date kernels, residues of trimming peach trees and corn stalks respectively. While, bulk density for all residues were decreased about 5.0, 3.76 and 2.47 times respectively at the previous agricultural residues.

Table (1) Properties of residues before and after pyrolysis.

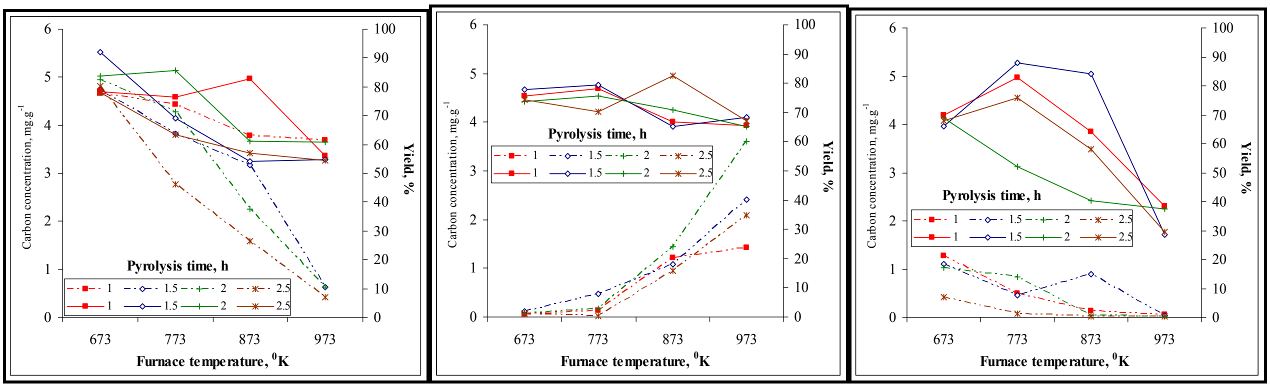
Residues type		Date kernels	Residues of trimming peach trees	Corn stalks
Moisture content (%)		9.1	19.3	23.3
C (%)	Before	45.22	43.18	40.70
	After	56.40	56.40	12.94
N (%)	Before	1.43	0.89	1.59
	After	2.625	0.05	0.89
H (%)	Before	4.40	7.84	4.11
	After	2.48	1.02	3.08
Ash (%)	Before	13.75	6.67	0.00
	After	52.0	10.0	3.0
Bulk density ($g.cm^{-3}$)	Before	0.651	0.263	0.148
	After	0.13	0.07	0.06

Carbon concentration

Figure 3 illustrates the effect of furnace temperatures on carbon concentration (excursive line) at different pyrolysis time for date kernels, residues of trimming peach trees and corn stalks. By increasing the furnace temperature from 673 to 973°K {figure (3 -a and c)} the carbon concentration decreased from 4.95 to 0.41 and from 1.28 to 0.01 $mg.g^{-1}$ for date kernels and corn stalks respectively.

These results explain that the carbonizing process is complete. However, for residues of trimming peach trees, as shown in figure (3-b) recorded a directly trend for carbon concentration with furnace temperature. It increased from 0.03 to 3.61$mg.g^{-1}$ by increasing the temperature from 673 to 973°K. This result may due to the samples of trimming peach trees residues still have some organic components lead to insufficient carbonization.

Furthermore, from the figure, the effect of pyrolysis time on carbon concentration shows the highest carbon concentration were 4.95 $mg.g^{-1}$ during 2.0 h and, 3.61 mg g^{-1} through 2.0h and 1.28 $mg.g^{-1}$ at 1.0 h pyrolysis time for date kernels, residues of trimming peach trees and corn stalks respectively. These results clear that by increasing the pyrolysis time from 1.0 to 2.0h the carbon concentration increased.



a- Date kernels **b- Residues of trimming peach trees** **c- Corn stalks**

Figure 3. Effect of furnace temperature on carbon concentration and yield at different pyrolysis time.

But, it decreased at pyrolysis time of 2.5h. It may be due to too much incineration which causes carbon losses.

Yield ratio

The yield ratio ranging from 54.44% at furnace temperature of 973°K and pyrolysis time of 2.50 h to 91.90% at furnace temperature of 673°K and pyrolysis time of 1.50 h for date kernels (figure-3). However, for residues of trimming peach trees the yield fluctuating from 65.32% at furnace temperature of 973°K and pyrolysis time of 2.00 h to 82.60% at furnace temperature of 873°K and pyrolysis time of 2.50 h. Moreover, for corn stalks the yield ratio ranging from 88.00% at furnace temperature of 773°K and pyrolysis time of 1.50 h to 28.00% at furnace temperature of 973°K and pyrolysis time of 1.50 h. The results clear that the yield ratio increased at decrease furnace temperature and increase in pyrolysis time for both of date kernels and residues of trimming peach trees, but the invers trend obtained for corn stalks. These results due to the properties of lignocellulosic material component for each residues.

Nevertheless, the best highest carbon concentration gave the indicator to the good quality of activated carbon according to [4]. Therefore, as regarded in figure (3), continuous line, the confronted carbon yield ratio of the highest carbon concentrations for the agricultural residues were 83.74% obtained at furnace temperature of 673°K and pyrolysis time of 2.00 h for date kernels, 65.32% at furnace temperature of 973°K and pyrolysis time of 1.00 h for residues of trimming peach trees and 70.00 % at furnace temperature of 673°K and pyrolysis time of 1.00 h for corn stalks.

Quality of activated carbon

a- Surface area and pore volume

Figure (4) explain that the highest surface area and pore volume were 95.57 m^2g^{-1} and 0.00236 cm^3g^{-1} respectively obtained with date kernel, followed by surface area and pore volume form residues of trimming peach trees which were 113.88 m^2g^{-1} and 0.00302 cm^3g^{-1} respectively, then surface area and pore volume form corn stalks were 29.73 $m^2.g^{-1}$ and 0.00579 $cm^3.g^{-1}$ respectively. The results clear that the high pore volume has the benefit surface area [31,4]. Similarly, the obtained results show the lowest differences between the data obtained by date kernels and residues of trimming peach trees which have the high surface area.

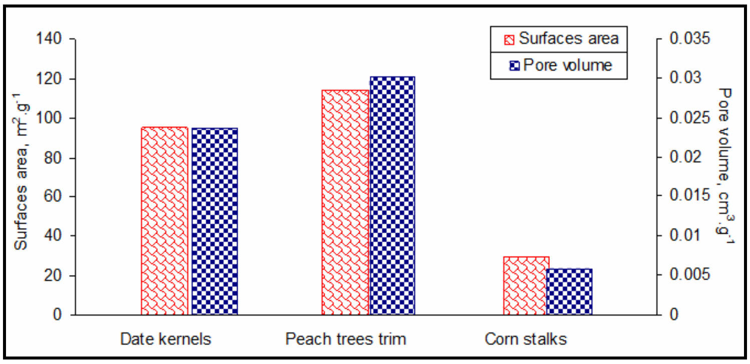
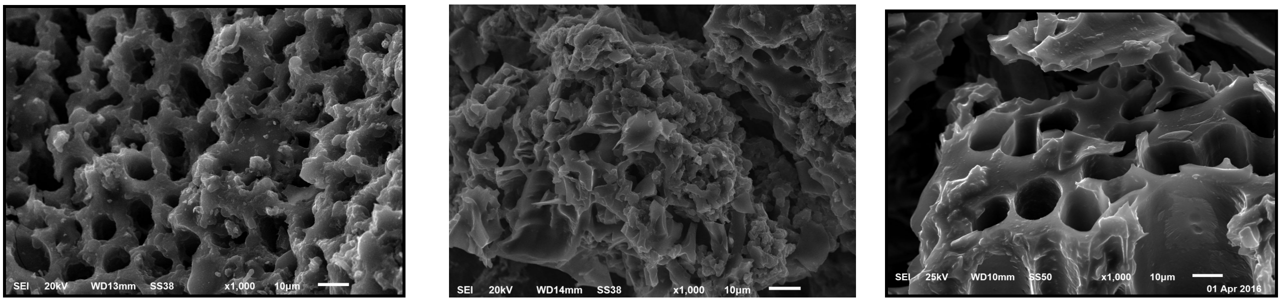


Figure 4. The relationship between surface area and pore volume for different agricultural residues.

B - Scanning electron micrographs (SEM)

Figure (5) shows the scanning electron microscope (SEM) micrographs for optimum obtained activated carbons from the agricultural residues of corn stalks, residues of trimming peach trees and date kernels. The all size of the pores sit in meso-porous categorize [32,33]. While, figure (5) clears that, the high pore size of 12.17 nm shows at Fig. (5-c) for activated carbon from corn stalks, but the medium pore size of 8.27 nm found at Fig. (5-a) for activated carbon from date kernels. While the minimum pore size of 2.78 nm shows in Fig. (5-b) for activated carbon from residues of trimming peach trees.



a- Date kernels **b- Residues of trimming peach trees** **c- Corn stalks**

Figure 5. Scanning electronic micrograph for different agricultural residues.

Conclusions

From the results it can concluded that the agricultural wastes can give the activated carbon with high carbon concentration of about 4.95, 3.61 and 1.28 $mg.g^{-1}$ for date kernels, residues of trimming peach trees and corn stalks respectively. At these concentrations the yield of activated carbon are 83.74, 65.32 and 70.00% respectively. The obtained activated carbon can produced at furnace temperature and pyrolysis time of 673 °K for 2 h, 973°K for 2 h and 673 for 1 h respectively for the previous agricultural residues. Also the properties of the activated carbon produced is high in surface area, pore volume, low pore size. This concluded allow to applied using different agricultural residues and structure the furnace suitable for the amount rate of agricultural residues as a movable project.

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