

## Activated Carbon from Dates' Stone by ZnCl<sub>2</sub> Activation

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*Abstract.* A study of the effect of preparation conditions on the yield and quality of activated carbon (AC) produced from dates' stones was made using zinc chloride as an activator. The optimum conditions for AC production was evaluated based on the determination of various adsorption parameters of methylene blue (MB) and phenol. Using MB as an adsorbate it was found that the optimum ratio of activator to dates' stones (R) is 2. The maximum unit capacity for MB was 148 mg/g at carbonization time (Ct) = 1 hour and carbonization temperature (CT) = 600 °C and the corresponding yield was 32%. Milder conditions (Ct = 0.5 hr and CT = 500°C) produced AC with maximum adsorption capacity of 286.3 mg/g with a yield of 31%.

Using phenol as an adsorbate it was found that the optimum value of R = 0.5. The maximum unit capacity for phenol was 19 mg/g at Ct = 3 hours and CT = 600 °C and AC yield of 47.3%. On the other hand milder conditions (Ct = 0.5 hr and CT = 500°C) were required to produce AC with maximum capacity for phenol removal of 75.0 mg/g and AC yield of 64.6%.

*Keywords:* Activated carbon, phenol adsorption, activation, dates' stones, dates' pits

### 1. Introduction

Activated carbon (AC) is an amorphous form of carbon that is specially treated to produce a highly developed internal pore structure and a large surface area, thus, producing reasonably cheap and excellent adsorbent [1-3]. There is a multitude of industrial applications of AC including decolorization, purification and deodorization of vegetable oils and fats, sugar refining and other food industries. Pollution control and

wastewater treatment are growing areas of use to combat environmental pollution<sup>[1-4]</sup>.

Two distinct methods are described in the literature for production of AC, namely, chemical activation (activation with mineral salts) and physical activation (activation using oxidizing agents such as steam or CO<sub>2</sub>). In chemical activation, the precursor is impregnated with an activating agent such as zinc chloride or phosphoric acid followed by carbonization in an inert atmosphere at temperatures ranging from 400 to 800 °C. This is followed by a leaching process to remove the activator<sup>[1,5-6]</sup>. Chemical activation is carried out if the raw material is wood or peat. Possible advantages of chemical activation over physical activation include: higher yield, simplicity (no need of the previous carbonization of raw material), lower temperature of activation and good development of the porous structure<sup>[7]</sup>.

Although the characteristics of the produced AC depend to some extent on the precursor used, the most influential factors are those related to preparation conditions, namely, the impregnation ratio (R), carbonization time (Ct) and, carbonization temperature (CT). R, that is, the weight ratio of the activator to the dry precursor seems to influence the porosity of the resulting products. The activation agent seems to influence the chemistry of pyrolytic processes (acting as a dehydrating agent) so that the formation of tar is restricted to a minimum and the pyrolysis temperature is lowered. This in turn seems to promote the development of a porous structure<sup>[1-3,7]</sup>. Usually micropores predominate at low values of R whereas at higher values wide micropores and mesopores predominate<sup>[8-9]</sup>. The speed and extent of the pyrolysis reaction taking place will depend primarily on the temperature and time of carbonization respectively. These three factors are interrelated in a complex manner and play a crucial role in determining the characteristics of the final product<sup>[1-3, 8-9]</sup>. Many investigators<sup>[6, 19-20]</sup> found that zinc chloride is the best amongst other activators studied.

In the past few years there has been a wide realization of the importance of agricultural waste as a cheap and renewable source of raw materials for AC production. Studies about the production of AC from agricultural wastes included dates stones<sup>[10-13]</sup>, corncob<sup>[14-16]</sup>, coconuts shells<sup>[6, 17-18]</sup>, nuts shells and stones<sup>[19-33]</sup>, oil palm stones and shells<sup>[34-41]</sup>, apple pulp<sup>[8-9]</sup>, chickpea husks<sup>[42]</sup>, rice straw, lignin<sup>[43-47]</sup> and palm tree

branches <sup>[5]</sup>. On the other hand there were few studies in the literature about production of AC from Dates' stones (DS) <sup>[10-13]</sup>. Gergis *et al.* <sup>[10]</sup> used phosphoric acid as an activator and carbonization time of two hours only. Best-developed porosity was at 700 °C. Banat *et al.* <sup>[11]</sup> found that raw date pits are better than activated ones for MB removal. Table 1 summarizes the optimum conditions reported in recent literature for production of activated carbon from dates' stones. We can notice from Table 1 that almost all studies were made using  $H_3PO_4$  as an activator. Also different parameters are used to assess the quality of the produced AC (e.g. phenol number, iodine number, maximum capacity..... etc.). The optimum conditions reported varied widely depending on the method of evaluation where optimum CT varied between 500 to 800 °C and R from 0.4 to 2 depending on the assessment method used and the activator.

**Table 1. Summary of optimum conditions reported in recent literature for production of activated carbon from dates stones.**

Activator	Evaluated Parameter	Maximum Value	Optimum conditions				Comments	Ref.
			Ct (h)	CT (°C)	R	PS (mm)		
$H_3PO_4$	$(q_m)_{MB}$	240 mg/g	2	700	1.2		Only Ct = 2 hr was investigated (see Tables 5 and 6 in this reference).	10
$H_3PO_4$	$k_{MB}$	100 mg/g	2	700	1.2			
$H_3PO_4$	IN	528 mg/g	2	500	1.68			
$H_3PO_4$	PhN	166 mg/g	2	700	1.2			
$H_3PO_4$	IN	495 mg/g	1	800	0.4	0.6	Used fluidized bed	12
None	$(q_m)_{MB}$	80.3 mg/g	NA	NA	NA		Raw dates pits are better than activated ones	11
$ZnCl_2$	PMBR	99%	0.5	600	2			13

$(q_m)_{MB}$  = maximum capacity as estimated from Langmuir isotherm,  $k_{MB}$  = Unit capacity estimated using Freundlich equation, IN = Iodine number, PhN = Phenol number, and PMBR = percentage methylene blue removal. PS = particle size.

The previous discussion clearly shows the need for further investigation about the production of AC from dates' stones to bring about more understanding of the effect of preparation conditions on the quality of the produced AC and the influence of the assessment method in the determination of the optimum conditions.

Also large quantities of dates' stones which can be obtained from more than 830,000 metric tons of dates produced annually in Saudi Arabia <sup>[48]</sup> justify the use of dates' stones as a raw material production of AC. Knowing that dates' stone account for about 10% of fruit weight <sup>[12]</sup> it can be easily shown that about 83,000 metric tons of dates' stones are available annually. A reasonable fraction of this quantity can be reclaimed easily from dates' processing plants and can be used for production of AC.

Therefore, the objective of this study is to explore the effect of preparation conditions on the yield and quality of AC produced from dates' stones. Zinc chloride will be used in this study since little attention has been paid for this activator in literature. The optimum conditions for AC production will be evaluated based on the determination of various adsorption parameters (e.g. unit capacity, maximum capacity, and percentage removal) using methylene blue and phenol as adsorbate.

## **2. Experimental Procedures**

### ***2.1 Preparation of Activated Carbon***

The characteristics of the activated carbon (AC) can be manipulated by controlling three major variables viz. carbonization temperature (CT), weight ratio of activator to dates' stones (R) and, carbonization time (Ct). The range of variables investigated in this study were; CT = 500, 600, and 700 °C, Ct = 0.5, 1, 1.5, 2 and 3 h and R = 0.5, 1.0, 1.5 and 2.0.

Production of activated carbon involves the following steps: pretreatment of the dates' stones, impregnation of the dates' stones with the activator, carbonization of the impregnated stones and finally the removal of activator. Further details are given below.

### **2.1.1 Pretreatment of the Dates' Stones**

Dates' stones were obtained from a dates' packaging factory in Almadinah Almonaorah, Saudi Arabia. Received dates' stones were first washed thoroughly with water to remove all foreign materials, mud and sticky sweet remnants of dates, then, they were spread in one layer over plastic sheets and left to dry in doors. Washed-clean whole dates' stones were then dried in a drying oven at 110 °C to facilitate crushing and grinding. A disk mill was used for grinding.

### **2.1.2 Impregnation**

The required amount of ZnCl<sub>2</sub> (necessary of the desired ratio of ZnCl<sub>2</sub> to dates' stones) was dissolved in 25 ml of distilled water. The zinc chloride solution was then added to 25 g of the crushed dates' stones and then mixed thoroughly. The mixture was left overnight before carbonization.

### **2.1.3 Carbonization**

The impregnated dates' stones were then loaded into cylindrical stainless steel reactor (3.8 cm ID x 13 cm long). The reactor was sealed at one end. The other end had a removable cover with 2 mm hole at the center to allow for the escape of the pyrolysis vapors and gases. The required numbers of reactors were placed in a muffle furnace and heating started by adjusting the furnace temperature to the desired value. The furnace took about 2 to 2.3 hours to reach the desired temperature (the average heating rate was 5 °C/min.). The carbonization times was measured from the moment the furnace reached the desired temperature (not from the start of heating). At prescribed times a sample of each ratio was withdrawn from the furnace and allowed to cool. The activated carbon was then extracted from the reactor and kept in a carefully labeled and tightly closed plastic bottles.

### **2.1.4 Washing**

The next step is the removal of the activator from the carbonization products by through washing. To do this, first the pyrolysis products were grinded into fine powder and the required volume of dilute HCl (3 wt.%) was added to it such that the liquid to solid ratio (LSR) is 10 ml/g. The mixture was then left overnight at room temperature in a conical flask. Next morning supernatant liquid was decanted in a filter paper followed by three successive washings and decantation using distilled

water. In the third washing, the whole carbon was transferred to the filter paper and washing using distilled water was continued on the filter paper till free of chloride ion as indicated by silver nitrate test. Finally the carbon was dried at 110°C for 2 h and kept in tightly closed plastic bottles and carefully labeled.

## 2.2. Adsorption Measurements

### 2.2.1 Percentage Removal of Methylene Blue (PMBR) and Phenol (PPhR)

Rapid screening for assessing the quality of the obtained AC was accomplished using single bottle uptake of MB or phenol from its aqueous solution [10]. For phenol, 0.15 g of AC powder was added to 25 ml of aqueous phenol solution (250 mg/l) in 100 ml Erlenmeyer flask provided with glass stoppers. In case of MB, 0.1 g of AC powder was added to 25 ml of 1200 mg/l MB solution. In each case the mixture was allowed to equilibrate at room temperature for at least 20 hours under continuous shaking. Clear liquid samples (free of carbon particles) were obtained for analysis by centrifugation. The residual concentration of MB or phenol was then determined using UV/V a spectrophotometer (Geneysis 10 UV/V).

The percentage of MB removal (PMBR) was calculated using the formula:

$$\text{PMBR} = [(C_{\text{MB}0} - (C_{\text{MB}})_e) / (C_{\text{MB}0})] \times 100 \quad (1)$$

Where:

$(C_{\text{MB}0}$  and  $(C_{\text{MB}})_e$  = Initial and equilibrium concentrations of MB, in mg/l, respectively.

Similarly, the percentage phenol removal (PPhR) was calculated using the formula:

$$\text{PPhR} = [(C_{\text{Ph}0} - (C_{\text{Ph}})_e) / (C_{\text{Ph}0})] \times 100 \quad (2)$$

Where:

$(C_{\text{Ph}0}$  and  $(C_{\text{Ph}})_e$  = initial and equilibrium concentrations of phenol in mg/l, respectively.

### 2.2.2 Adsorption Isotherms for MB and Phenol

Adsorption data for MB and phenol were collected by equilibrating different weights of AC powder ranging from 0.05 to 0.5 g with 25 ml of an aqueous solution of the adsorbate (1200 mg/l for MB and 250 mg/l for phenol) in 100 ml Erlenmeyer flask provided with glass stoppers. Adsorption tests were made at room temperature under continuous shaking. Preliminary tests have shown that most of the adsorption takes place in the first few hours. All samples were allowed to equilibrate for at least 20 hours. Sample of the supernatant liquid was then withdrawn for analysis using hypodermic syringe fitted with 2  $\mu$ m sintered-steel filter. The residual concentrations of MB and phenol were determined using a Genysis10 UV/V spectrophotometer which was previously calibrated for each adsorbate.

The adsorption data for phenol and MB were fitted to a Freundlich isotherm described by the equation:

$$q_e = k C_e^{1/n} \quad (3)$$

Where:

$C_e$  = equilibrium concentration of the sorbet in mg/l

$q_e$  = the amount adsorbed in mg per gram of AC.

$k$  = the so-called unit capacity factor,

and  $n$  is an empirical parameter that represents the heterogeneity of the site energies<sup>[49]</sup> or the affinity of the adsorbate to the carbon surface<sup>[50]</sup>.

The adsorption data were also fitted to a Langmuir isotherm given by the equation:

$$q_e = q_m (K_L C_e / (1 + K_L C_e)) \quad (4)$$

Where:

$q_m$  = the maximum adsorption capacity or monolayer coverage in mg/g

$K_L$  = the adsorption equilibrium constant in l/mg<sup>[51]</sup>.

Equations 3 and 4 were fitted using nonlinear regression and the values of the constants ( $k$ ,  $n$ ,  $q_m$  and  $K_L$ ) were evaluated and used for comparing the performance of different AC samples.

### 3. Results and Discussion

#### 3.1 Characterization of Dates' Stones

Important physical properties of dates' stones used such as bulk density, moisture content, and particle size distribution of grounded dates' stones are presented in Table 2.

**Table 2. Some physical properties of dates' stone.**

Characteristic	Value	Units	Remarks
Bulk density	0.954	g/ml	For a particle size cut - 2 mm/+1 mm,
Moisture content	10.3	Weight %	Based on drying at 110 °C for 2 hours
Volume of water needed to achieve incipient wetness.	100 ml H <sub>2</sub> O per 100 g dates stones	ml/g	determined in this study
Particle size distribution:		Weight %	
-2 mm/ +1 mm (mesh size: -10/+18)	65.5		
-1 mm/ + 0.5 mm (Mesh size: -8/+35)	25.3		
-0.5 mm (mesh size: -35)	9.2		

#### 3.2 Thermogravimetric Analysis of Dates' Stone

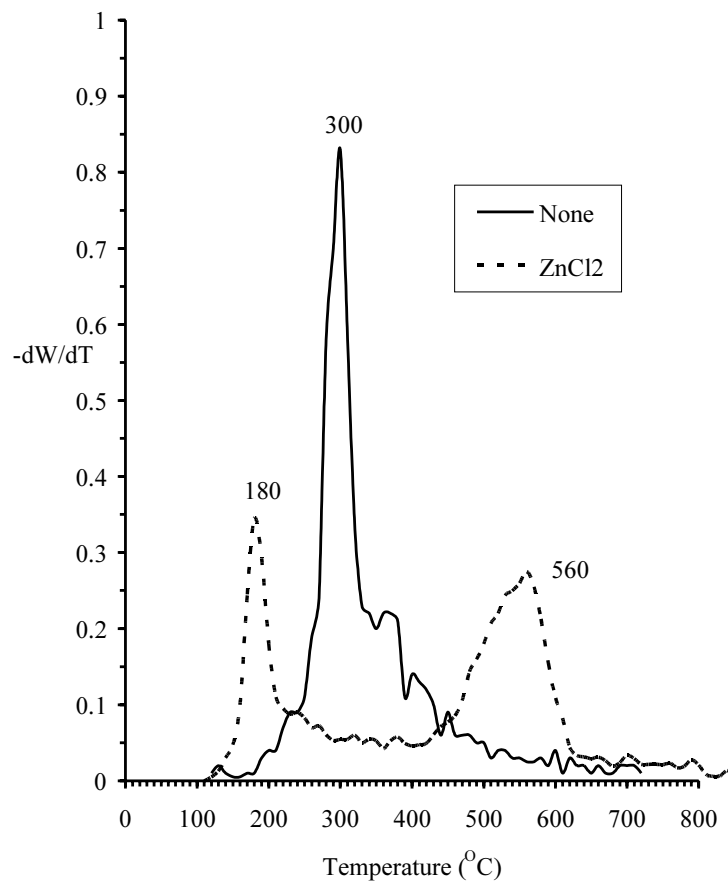
Thermogravimetric analysis (TG) was performed to bring about more understanding of the pyrolysis of dates' stones (DS) and to elucidate the influence of activator on the pyrolysis process. TG and DTG data were obtained in a flow of nitrogen at a heating rate of 10 °C/min. after an isothermal period at 110 °C to allow for the removal of moisture. Figure 1 shows DTG curves for dates' stones (solid line) and



for dates stones loaded with 50 wt.% ZnCl<sub>2</sub> (dotted line). As can be seen from this figure there is only one prominent peak with a maximum at 300°C for dates' stones without activator. Decomposition starts at about 250°C and continues to about 400°C. This peak has a shoulder that extends from 400 °C to higher temperatures. These two peaks are attributed to cellulose and lignin decomposition in the temperature range from 250 to 350 °C and 250 to 500 °C, respectively [52-54]. For dates' stones loaded with activator, two major peaks are observed in the DTG curve. The first peak starts at about 100 °C and ends around 300 °C with a maximum at 180°C. This peak is corresponding to the first peak observed at 300°C for DS without activator but shifted to a lower temperature . Thus it is clear that the presence of ZnCl<sub>2</sub> caused a great reduction in the decomposition and/or dehydration temperature of the cellulose structure of DS. The second major peak observed in the temperature range from 500 to 700 °C is due to the evaporation of zinc chloride (the melting and boiling points of ZnCl<sub>2</sub> are 318 and 732 °C respectively) [55].

### ***3.3 Yield of Activated Carbon***

The yield is defined as the ratio of final weight of the obtained AC after washing and drying to the weight of dried dates stones initially used. Figure 2 shows the % yield of AC obtained as function of R for different values of Ct and CT. For Ct = 0.5 h, the yield depended strongly on CT where a maximum yield of 68.8% was obtained at CT = 500°C and R = 1.0. Similar effect of R was also observed at CT = 600 and 700 °C but the yield was substantially lower and decreased with temperature. For Ct = 1.0 h the yield again depended strongly on CT where a maximum yield of 68.1% was obtained at CT = 500°C and R = 0.5. Similar behavior was also observed at CT = 600 and 700 °C but the yield was substantially lower and decreased with temperature. For Ct greater than 1.0 h, the effect of temperature on AC yield was less pronounced than observed at lower Ct values with maximum yield at R = 0.5 followed by a gradual and slow decrease with increasing R. A similar behavior was reported by Aik and Yang [56] for activated carbon prepared from pistachio-nuts shell using zinc chloride activation where a maximum yield of about 41% was observed at R = 0.25 to 0.33 with CT= 500 °C and Ct = 2 h. They also reported a gradual decrease in yield with increase in R.



**Fig. 1.** Comparison of DTG curves for date's stones with and without Zn Cl<sub>2</sub>. Heating rate = 10  $^{\circ}C/min$ . Sample dried for 2 h before temperature ramping.

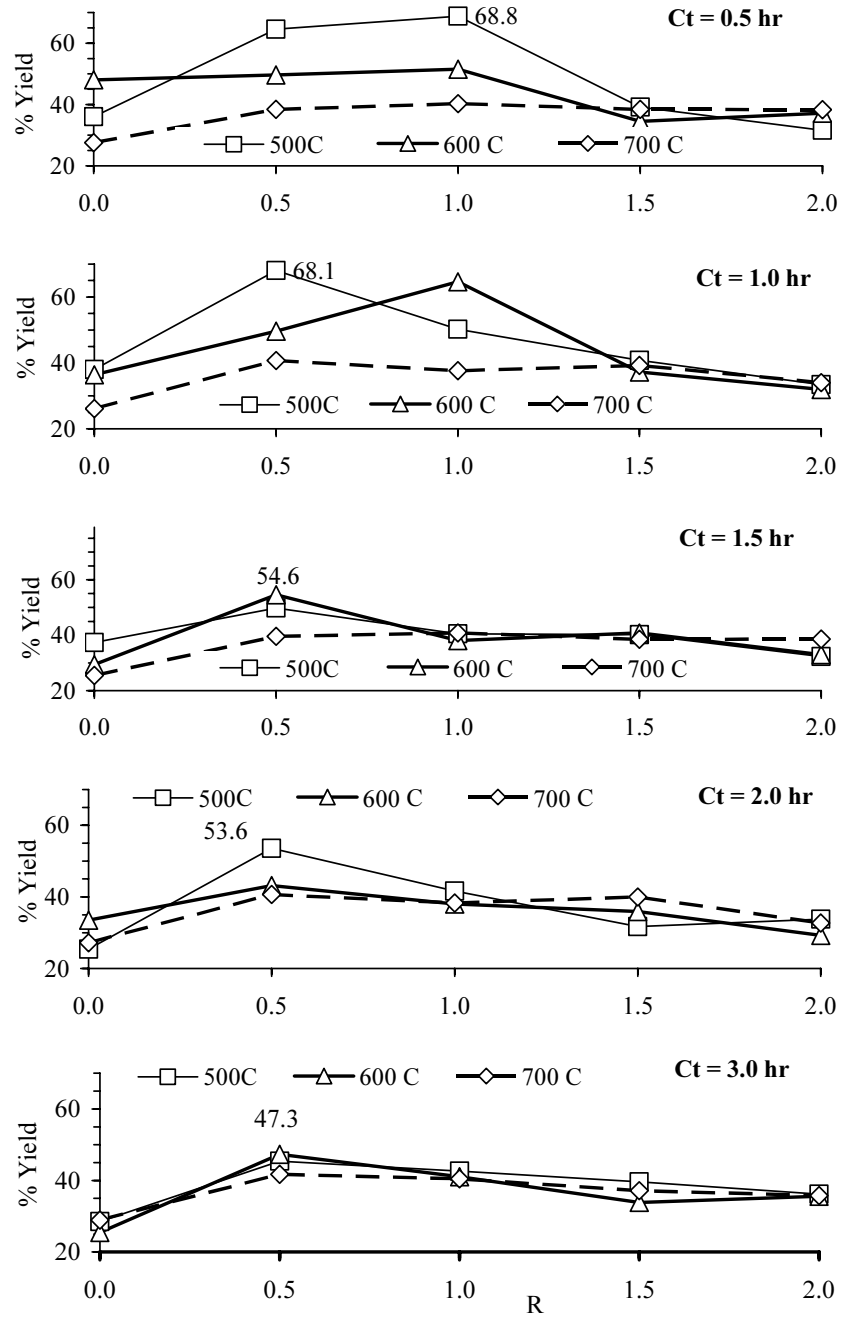


Fig. 2. Yield versus R for AC produced at various carbonization temperature and carbonization times (Ct).

### ***3.4 Effect of Activation Parameters on Percentage Removal***

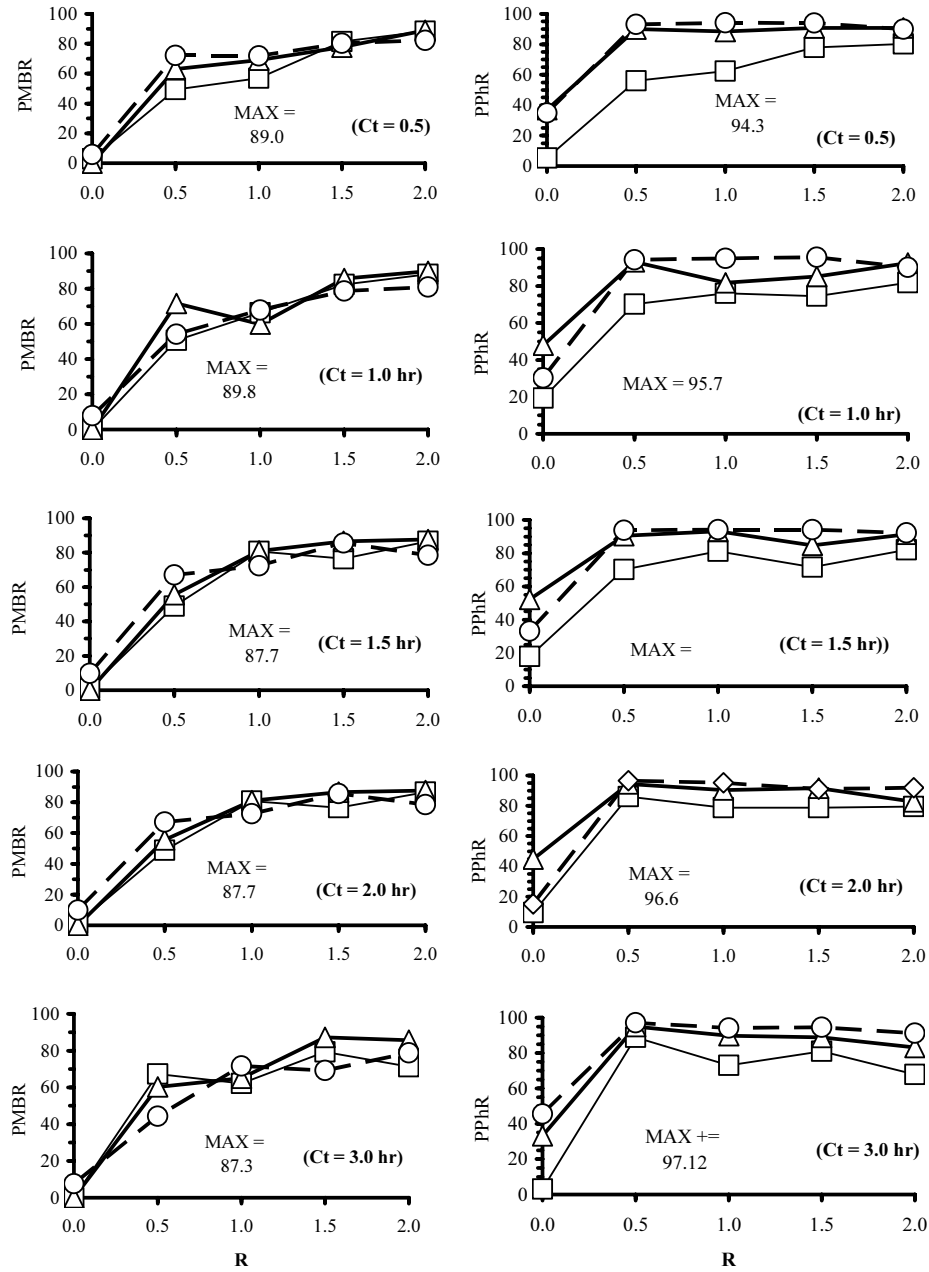
Figure 3 shows the effect of R on PMBR and PPhR for AC produced at different carbonization temperatures ( $CT = 500^{\circ}C$ ,  $600^{\circ}C$  and  $700^{\circ}C$ ) and carbonization times ( $Ct = 0.5, 1.0, 1.5, 2.0$  and  $3$  hr). Maximum value of MBR removal is indicated in each chart. The charts in left hand side of Fig. 3 for PMBR show that for all carbonization temperature there is a gradual increase in PMBR with R. The maximum value of PMBR was obtained at  $R = 2$  and for Ct and CT values used. This maximum value however varied within a narrow range from 87.3 to 89.8. Carbonization temperatures between 500 to  $600^{\circ}C$  give AC with higher PMBR. Based on the PMBR, the optimum conditions are  $Ct = 1$  hr,  $R = 2$  and  $CT$  500 to  $600^{\circ}C$ .

It can be seen from the phenol removal charts in Fig. 3 that there is a considerable removal of phenol even with AC produced without activator ( $R = 0$ ) compared with what was observed with MB removal. The highest value of PPhR (52%), however was obtained at  $Ct = 1.5$  and  $CT = 600^{\circ}C$ . The effect of R on PPhR depended on the CT and Ct. For a given CT and for intermediate values of Ct (1, 1.5 and 2.0 hr), the PPhR did not change significantly with R above  $R = 0.5$ , while for  $Ct = 0.5$  hour, a gradual increase of PPhR with R was observed at  $CT = 500^{\circ}C$ . A maximum PPhR value of 94.3% was obtained at  $R = 0.5$  and  $CT = 700^{\circ}C$  when for this Ct value was 0.5 hr. On the other hand a large Ct of 3 hours resulted in a gradual decrease of PPhR with R. A maximum value of 97.1% at  $R = 0.5$  and  $CT = 700^{\circ}C$  was obtained for the Ct value of 3h.

Depending on the Ct, the maximum value of PPhR varied within a narrow range from 94 to 97% and mostly occurred at  $R = 0.5$ . Based on the PPhR, the optimum conditions that produce AC with the highest PPhR (97.1%) are  $Ct = 3$  hr,  $R = 0.5$  and  $CT 700^{\circ}C$ .

### ***3.5 Effect of Activation Parameters on Unit Capacity***

Another parameter upon which a comparison between the performance of different AC can be made is the unit capacity  $k_{MB}$  and  $k_{Ph}$  of the Freundlich isotherm for methylene blue and phenol, respectively. Such comparison is depicted in Fig. 4 where the effect of R on  $k_{MB}$  and  $k_{Ph}$



**Fig. 3.** Effect of R on PMBR and PPhR for AC produced at various carbonization temperatures (CT = 500°C (squares), 600°C (triangles) and 700°C (circles)) and carbonization times (Ct = 0.5, 1.0, 1.5, 2.0 and 3 hr).

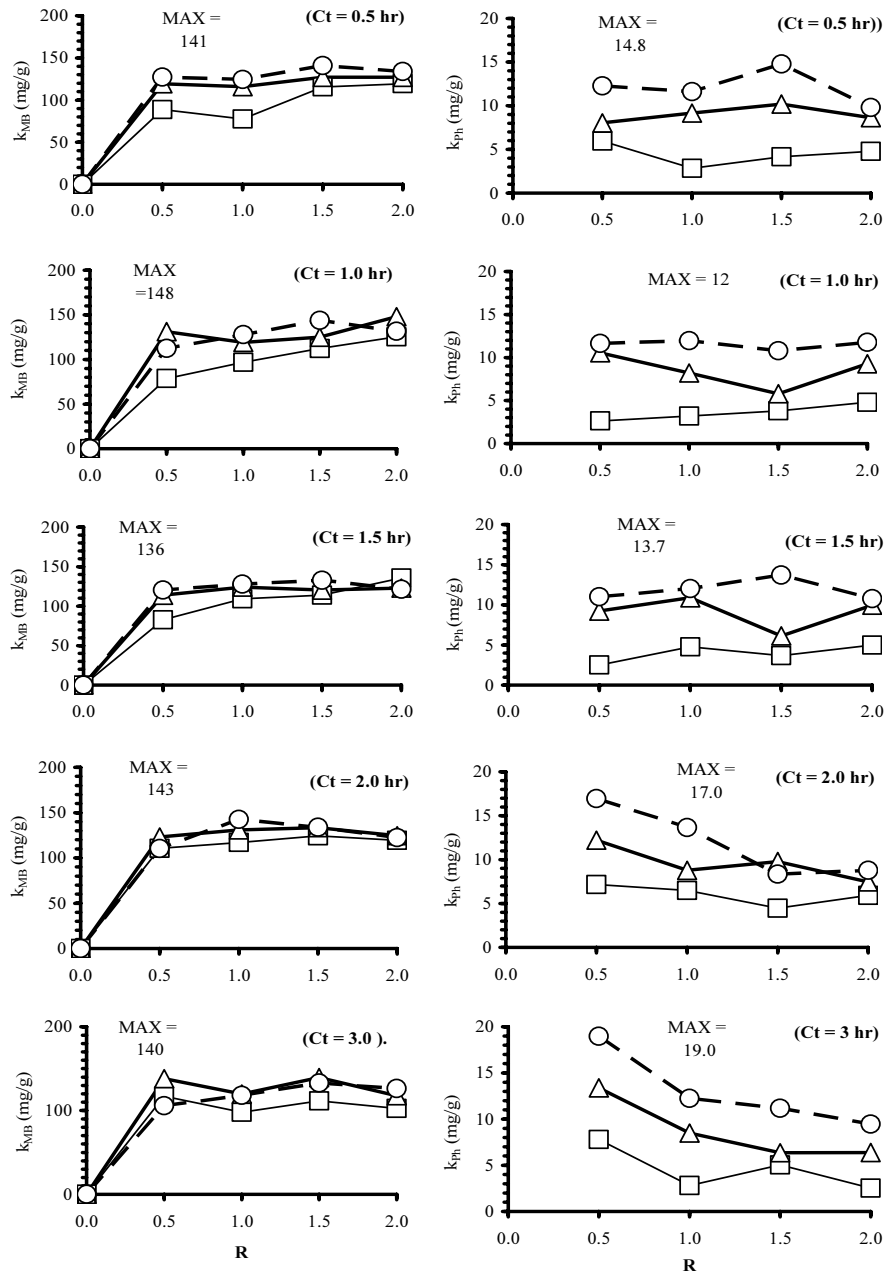
for AC produced at different carbonization temperatures (CT = 500°C (squares), 600°C (triangles) and 700°C (circles)) and carbonization times (Ct = 0.5, 1.0, 1.5, 2.0 and 3 h) is shown. In each chart in figure 4 the maximum value  $k_{MB}$  and  $k_{Ph}$  is indicated on the chart.

For MB adsorption, it can be seen from the charts in the left hand side of Fig. 4 that regardless of the carbonization temperature there is a gradual increase in  $k_{MB}$  with increasing R above R = 0.5 with stronger effect of R at 500 °C at short Ct. The maximum value of  $k_{MB}$  varied between 136 to 148 mg/g depending on Ct and mostly occurred at R = 2 and CT = 600 to 700 °C. Based on  $k_{MB}$ , the optimum conditions are Ct = 1 h, R = 2 and CT = 600 °C, which are similar conditions to those obtained based on maximum PMBR.

The effect of R on the unit capacity for phenol adsorption ( $k_{Ph}$ ) is shown in the charts on the right hand side of Fig. 4. The effect of R on  $k_{Ph}$  depended on both CT and Ct values, where for a given Ct, high CT resulted in higher values of  $k_{Ph}$ . For Ct values less than 2 hours, R did not show a significant effect on  $k_{Ph}$  for most values of CT. On the other hand, for Ct = 2 and 3 hours,  $k_{Ph}$  decreased gradually with R with maximum occurring at R = 0.5, also, higher values of  $k_{Ph}$  were obtained at higher CT. The maximum values of  $k_{Ph}$  varied between 12 and 19 mg/g depending on preparation conditions. Based on the values of  $k_{Ph}$ , the optimum condition for production of AC are R = 0.5, CT = 700 °C and Ct = 3 hours.

### ***3.6 Effect of Activation Parameters on Maximum Capacity***

A third parameter used to compare AC produced at different conditions is the maximum capacity ( $q_m$ ) of Langmuir isotherm, Equation 4. The effect of R on the maximum capacity of MB,  $(q_m)_{MB}$  and phenol  $(q_m)_{Ph}$  are depicted in Fig. 5 for AC produced at different carbonization temperatures (CT = 500°C (squares), 600°C (triangles) and 700°C (circles)) and carbonization times (Ct = 0.5, 1.0, 1.5, 2.0 and 3 hr). In each chart in Fig. 5 the maximum values of  $(q_m)_{MB}$  and  $(q_m)_{Ph}$  are indicated.



**Fig. 4.** Effect of  $R$  on  $k_{MB}$  and  $k_{Ph}$  for AC produced at various carbonization temperatures (CT = 500 °C (squares), 600°C (triangles) and 700 °C (circles)) and carbonization times (Ct = 0.5, 1.0, 1.5, 2.0 and 3 hr).

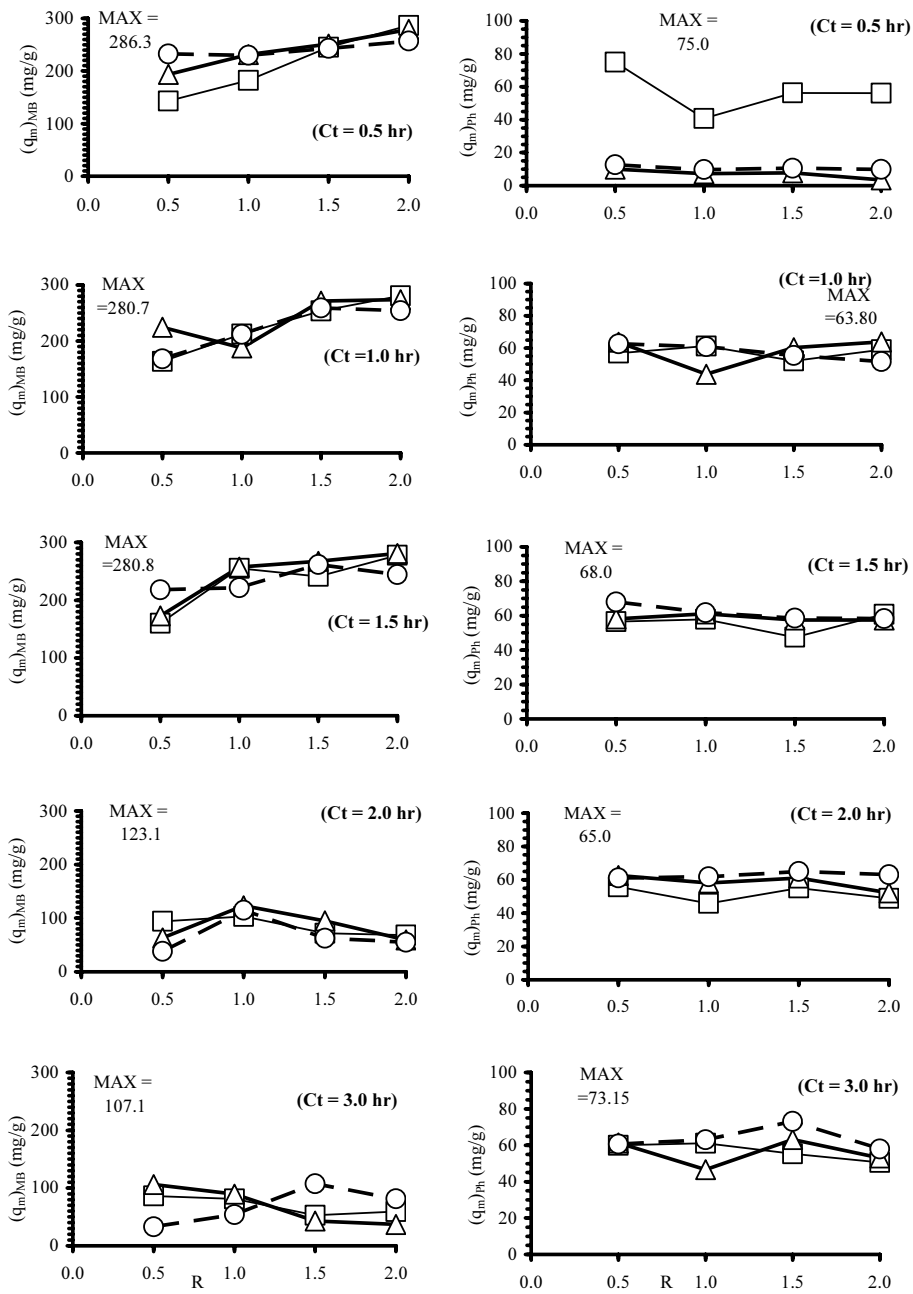


Fig. 5. Effect of R on  $(q_m)_{MB}$  and  $(q_m)_{ph}$  for AC produced at different carbonization temperatures ( $CT = 500$  °C (squares),  $600$  °C (triangles) and  $700$  °C (circles)) and carbonization times ( $C_t = 0.5, 1.0, 1.5, 2.0$  and  $3$  hr).



For MB adsorption, it can be seen from the charts on the left hand side of figure 5 that depending on preparation conditions  $(q_m)_{MB}$  varied widely from as low as 38 to 286 mg/g. For Ct less than 2 hours there is a gradual increase in  $(q_m)_{MB}$  with increasing R. Strong effect of R is observed at CT = 500 °C and short Ct. The maximum values of  $(q_m)_{MB}$  varied between 286.3 and 280.1 mg/g in this range of Ct with the highest value (286.3 mg/g) occurring at Ct = 0.5 hours, R = 2 and CT = 500 °C. A sudden decrease in  $(q_m)_{MB}$  occurred at Ct = 2 and 3 with maximum value of  $(q_m)_{MB}$  of only 123 mg/g. Therefore, the optimum conditions for the production of AC based on  $(q_m)_{MB}$  are Ct = 0.5 h, R = 2 and CT = 500 °C.

As can be seen from the charts on the right hand side of Fig. 5, the effect of R on  $(q_m)_{Ph}$  depended on the CT and Ct with a common observation that for a given Ct, always high CT resulted in a slightly higher values of  $(q_m)_{Ph}$ . For all AC produced,  $(q_m)_{Ph}$  varied within a narrow range from 43.7 to 75 mg/g with the highest value obtained for AC prepared at Ct = 0.5 h, R = 0.5 and CT = 500°C as optimum conditions.

Table 3 shows a summary of optimum conditions for production of AC based on the evaluation of different adsorption parameters. As can be seen from this table, assessment of the AC based on MB adsorption indicates a relatively high R value of 2 is essentially to produce AC with good capacity for MB removal. Due to the relatively large size MB molecule, it is usually adsorbed in mesopores which are formed when high ratios of  $ZnCl_2$  are used<sup>[8-9]</sup>.

**Table 3. Summary of optimum conditions for production of AC based on the evaluation of different adsorption parameters.**

Adsorbate	Parameter	Maximum Value	Optimum conditions			Yield (%)
			CT (°C)	Ct (h)	R	
Methylene Blue (MB)	PMBR	89.8%	600	1.0	2	32
	$k_{MB}$	148 mg/g	600	1.0	2	32
	$(q_m)_{MB}$	286.3 mg/g	500	0.5	2	31
Phenol (Ph)	PPhR	97.1%	700	3	0.5	47.3
	$k_{Ph}$	19 mg/g	700	3	0.5	47.3
	$(q_m)_{Ph}$	75 mg/g	500	0.5	0.5	64.6

On the other hand, the opposite is observed when the AC is assessed using parameters obtained based on phenol adsorption. Again, these phenomena can be explained in terms of the optimum pore size for the adsorption process for a given surface chemistry not forgetting the effects related to the surface chemistry of the AC and the pH of the adsorption medium. Since phenol can be adsorbed in micropores due to its small size and since micropores predominate at low values of  $R$  [8-9], therefore, it is expected that low  $R$  is essential to produce AC with higher capacity for phenol removal.

### 3.7 Comparison with Literature

The AC produced in this study using  $ZnCl_2$  as activator performed better than that produced using  $H_3PO_4$  as activator reported in the literature. For example, Girgis and El-Hendawy [10] reported a maximum value of  $k_{MB}$  as 100 mg /g (see Table 1) compared to 148 mg/g obtained in this study. Also the maximum adsorption capacity reported by them for MB ( $(q_m)_{MB}$ ) was 240 mg/g compared to 286 mg/g obtained in this study. The adsorption capacity obtained in this study is above the lower recommended value for carbon adsorbents (200 mg MB/g AC) [10]. The yield obtained at optimum conditions varied between 31 to 64.6% depending on the assessment method (see Table 4) where the lower yield is associated with high values of  $R$ . On the other, hand the yield reported by Girgis and El-Hendawy [10] was between 38 to 43 using  $H_3PO_4$ . This is consistent with the findings of other investigators [12] who reported that  $H_3PO_4$  gives lower yield than  $ZnCl_2$ . Therefore it can be concluded that  $ZnCl_2$  is a better activator based on the yield of the AC and its ability for removal of MB and phenol. However, AC production should be optimized based on its final use.

## 4. Conclusions

In this study it was shown that the choice of the optimum conditions for production of AC depend on the method of assessment. The conclusions made from the optimization of preparation conditions for AC production based on the determination of various adsorption parameters for methylene blue (MB) and phenol are as follows:

- Using MB as an adsorbate it was found that an optimum ratio of activator to dates' stones (R) of 2 is always necessary.

- The maximum unit capacity for MB was 148 mg/g at carbonization time (Ct) = 1 hour and carbonization temperature (CT) = 600 °C and the corresponding yield was 32%. Milder conditions (Ct = 0.5 h and CT = 500°C) were required to produce AC with maximum capacity of 286.3 mg/g with a yield of 31%.

- Using phenol as an adsorbate it was found that the optimum value of R = 0.5 is always necessary.

- The maximum unit capacity for phenol was 19 mg/g at Ct = 3 hours and CT = 600 °C and the corresponding AC yield was 47.3%.

- On other hand, milder conditions (Ct = 0.5 h and CT = 500°C) were required to produce AC with maximum capacity for phenol removal of 75.0 mg/g and AC yield of 64.6%.

### ***Acknowledgement***

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### **Notations**

AC = activated carbon

Ct = carbonization time (h).

CT = carbonization temperature (°C)

C<sub>e</sub> = equilibrium concentration of the sorbet in mg/l

(C<sub>MB</sub>)<sub>0</sub> = Initial concentration of MB

(C<sub>MB</sub>)<sub>e</sub> = equilibrium concentration of MB

(C<sub>Ph</sub>)<sub>0</sub> = initial concentration of phenol.

(C<sub>Ph</sub>)<sub>e</sub> = equilibrium concentrations of phenol respectively.

IN = Iodine number,

k = the so-called unit capacity factor in Freundlich equation

K<sub>L</sub> = the adsorption equilibrium constant in l/mg.

- $k_{MB}$  = Unit capacity for MB estimated using Freundlich equation.
- MB = methylene blue.
- n = empirical parameter in Freundlich equation.
- PhN = Phenol number.
- PMBR = percentage methylene blue removal.
- PPhR = percentage phenol removal.
- $(q_m)_{MB}$  = maximum capacity for MB estimated from Langmuir isotherm,
- $q_e$  = the amount adsorbed in mg per gram of AC in Freundlich or Langmuir equation.
- $q_m$  = the maximum adsorption capacity or monolayer coverage in mg/g
- R = ratio of zinc chloride to dry dates' stones

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## إنتاج الفحم النشط من نوى التمر عن طريق التنشيط باستخدام كلوريد الزنك

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المستخلص. تم في هذا البحث دراسة تأثير ظروف التحضير على مردود ونوعية الفحم النشط المنتج من نوى التمر باستخدام كلوريد الزنك كمنشط. وقد تم تحديد الظروف المثلى لإنتاج الفحم النشط بناءً على تحديد معاملات الامتزاز المختلفة لأزرق الميثيل والفينول وعند استخدام أزرق الميثيل كمادة ممتزة وجد أن أفضل نسبة من المنشط إلى نوى التمر هي ٠.٢. وتم الحصول على أعلى قيمة لسعة الوحدة لأزرق الميثيل (١٤٨ مجم أزرق الميثيل لكل جرام من الفحم النشط) عند زمن تفحيم مقداره ساعة واحدة ودرجة حرارة كربنة ٦٠٠ م° وكان المردود في هذه الظروف ٣٢٪. ومن الناحية الأخرى فإن ظروفًا أقل حدة (زمن كربنة = ٠,٥ ساعة ودرجة حرارة كربنة = ٥٠٠ م°) ساعدت على إنتاج فحم نشط بسعة قصوى مقدارها ٢٨٦,٣ مجم أزرق الميثيل لكل جم من الفحم النشط بمردود مقداره ٣١٪.

وعند استخدام الفينول كمادة ممتزة وجد أن أفضل قيمة لنسبة المنشط إلى نوى التمر هي ٠,٥. وتم الحصول على أعلى قيمة لسعة الوحدة للفينول (١٩ مجم فينول لكل جرام من الفحم النشط) عند زمن كربنة = ٣ ساعات و درجة حرارة تفحيم = ٦٠٠ م° وكان المردود في هذه الظروف ٤٧,٣٪. ومن ناحية أخرى فإن ظروفًا أقل حدة (زمن كربنة = ٠,٥ ساعة ودرجة

حرارة كربنة = ٥٠٠ م° ( ساعدت على أنتاج فحم نشط بسعة  
قصوى مقدارها ٧٥,٠ مجم فينول لكل جم من الفحم النشط  
بمردود مقداره ٦٤,٦%.