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# PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBON FROM DATES' STONE

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## ABSTRACT

*In this paper, the results of a laboratory scale study about the preparation of activated carbon from dates' stones using the physical activation method are presented. The preparation method entails the impregnation of the dried and crushed stones with an activating agent such as ZnCl2 followed by carbonization at high temperatures. The effects of carbonization temperature (500 to 700 °C) carbonization time (0.5 to 3 hours) and, weight ratio of zinc chloride to dry stones (2:1, 1:1 and, 0.5:1) on the quality of activated carbon obtained were investigated to determine the optimum operating conditions. The quality of the Activated Carbons (AC) produced was assessed by their ability for methylene blue removal from aqueous solutions. Characteristics of selected samples of the AC, such as specific surface area, solid density and phenol adsorption isotherm were measured.*

*Based on methylene blue adsorption experiments and economical considerations, it was concluded that the optimum operating conditions tested for production of activated carbon from date's stones are: carbonization time = 0.5 hour; temperature of carbonization = 600°C; and, zinc chloride to wood ratio = 2:1. In addition, it was found that carbons with specific surface area in excess of 1100 $m^2/g$ were obtained. Considering phenol adsorption, the study showed that the best conditions which produce carbons with good phenol adsorption capacity are, carbonization temperature = 700°C, carbonization time = 1.5 hours and R = 2:1. Compared to Commercial AC, carbons prepared in this study were slightly inferior with respect to phenol adsorption. Nevertheless, it was shown that activated carbon with good characteristics can be obtained from dates' stone.*

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

## الملخص

في هذه الورقة نقدم نتائج بحث معملي لتحضير الكربون النشط من نوى التمر بإستخدام طريقة التنشيط الفيزيائي. وتشتمل طريقه التحضير على تحميل النوى المجفف والمجروش بعامل منشط مثل كلوريد الزنك ثم بعد ذلك يتم تفحيمه عند درجات حرارة مرتفعه ثم يتم إزالة العامل المنشط بواسطة الأحماض مثل حمض الهيدروكلوريك .لقد تم دراسة تأثير درجه الحراره ( ٥٠٠ إلى ٧٠٠ م٥ ) وزمن التفحيم (٥و٠ إلى ٣ ساعات ) ونسبة كلوريد الزنك إلى النوى المجفف (٥و٠: ١ ، ١: ١ ، ٢: ١) على نوعيه الكربون الناتج وذلك لتحديد الظروف المثلى لعمليه التصنيع . ولقد تم تقييم نوعيه الكربون بناء أ على مقدرته في إزالة صبغه أزرق المثيلين من المحاليل المائية. كما تم تعيين خواص

الكربون لأخرى لبعض العينات المنتجة مثل المساحة السطحية وكثافة الكربون الصلب ومقدرتـه غلـى أد مصـاص الفينول. وبناءا على قياس أد مصاص أزرق المثيلين فأنه وجد أن أفضل الظروف هي التفحيم لمدة نصف سـاعة عنـد درجه حرارة ٦٠٠ م٥ واستخدام نسبه من كلوريد الزنك إلى النوى تبلغ ٢ :١. بالأضافه إلىذلك فقد تم الحصول على عينات كربون ذات مساحة سطحيه أكثر من ١١٠٠ م٢ /جم. وعند الأخذ بالاعتبار عمليه ادمصاص الفينول فقد وجـد أن أفضـل الظروف هي درجه حرارة تفحيم تبلغ ٧٠٠ م٥ ولمده ساعة ونصف ونسبه كلوريد الزنك إلى النوى تبلـغ ٢: ١ وبالمقارنة مع الكربون النشط التجاري فأن الكربون المحضر في المختبر أظهر كفاءة أقل في أدمصاص الفينول. ولكن على الأقل لقد تم إثبات أمكانية الحصول على كربون نشط بمزايا جيده من نوى التمر.

## 1. INTRODUCTION

Activated carbon is manufactured by carbonizing the raw material under appropriate conditions. Two distinct methods, namely, chemical activation and physical activation are described in the literature [Hasler, 1974 and Mattson and Harry, 1971]. In chemical activation, the starting material is impregnated with a mineral salt, such as zinc chloride, followed by pyrolysis at high temperatures. The carbonized product is cooled and the activation agent is then extracted from it. In case of zinc chloride, extraction is achieved by using HCl [Hasler, 1974]. Chemical activation is usually carried out at temperatures from 400 to 1000 °C, for $ZnCl_2$, the optimum temperature is between 600 and 700 °C. These temperatures are lower than those needed for activation with gaseous agents (physical activation) such as steam or $CO_2$. The low carbonization temperature promotes the development of a porous structure [Hasler, 1974].

Cheap and readily available adsorbents such as activated carbon are widely used for controlling air and water pollution. Growing need for activated carbon in Saudi Arabia justify the search for raw materials suitable for local production of activated carbon. One of these sources of raw materials is agricultural waste from palm tree (e.g. palm tree branches and Date's stones). Current statistics show that there are at least 15 million palm trees in the Kingdom [Basha et al., 1409H and, Al-Baker, 1392 H). This renewable resource could be exploited economically for the production of activated carbon.

The scientific literature presents ample examples about studies dealing with the production of activated carbon from agricultural waste such as almond shells [Ruiz et al., 1984a, 1984b and Rodriguez-Reinosos et al., 1982, 1984] beech wood shells [Eherburger and Lahaye, 1982], rice husk [Abraham, 1979], coconuts shells [Kirubakaran et al. 1991] and palm tree branches [Alhamed and Abdulsalam, 1995]. Although one of the investments opportunities presented by Gulf Organization for Industrial Consulting (GOIC) is the manufacture of AC from local waste materials such as Dates' stones, there is no literature available about laboratory scale studies dealing with the effect of preparation conditions on the quality and characteristics of AC obtained from Dates' stones.

Therefore, the objective of this work is to investigate, in a laboratory scale, the effect of preparation conditions on the quality of AC produced from dates' stones as determined by methylene blue adsorption. Also, selected samples of the prepared AC will be characterized by the determination of their specific surface and solid density. Comparison of prepared carbons with commercial brand with respect to phenol removal from aqueous is another objective of this study.

## 2. EXPERIMENTAL PROCEDURES

The experimental part consists of three major sections, namely, preparation of activated carbon, characterization of activated carbon and adsorption measurements.

### 2.1 Preparation Method

The dates' stones were first dried in an oven at 100 °C for 24 hours, grinded, and sieved. Fractions of average size of 2 mm were used. Zinc chloride was dissolved in water and added to dates' stone. The amount of solution was adjusted to obtain the desired ratio of zinc chloride (dry basis) to dry stones. Excess water was then evaporated by heating on a hot plate followed by drying in an oven at 120 °C for 2 hours to remove the last traces of water.

The impregnated stones were packed into a 2.5 cm ID, 30 cm long Pyrex tubes. The tubes were nearly filled with the dry impregnated mixture then sealed leaving an opening of 0.5 mm at the end of the tube. The desired number of tubes containing samples impregnated with various ratios of zinc chloride to dates' stones (R), namely 2:1, 1:1 and 0.5:1, were placed inside a furnace and heated to the desired temperature. At a given temperature one sample of each ratio was withdrawn at predetermined time intervals, namely after 0.5, 1, 1.5, 2 and 3 hours. The time to withdraw the samples from the furnace is calculated from the moment the furnace reaches the desired temperature.

After cooling the samples, the carbonization products were grinded into a fine powder in a mortar followed by washing thoroughly using distilled water. 100 ml of diluted hydrochloric acid were added to each sample in 250 ml conical flask and the samples were left for one day. After that the samples were filtered and washed with distilled water thoroughly. The filtered water was then tested for the presence of chloride ion using silver nitrate. If chloride ion was still present, washing was continued till no chloride ions can be detected in the washing water. Finally the samples were dried at 120 °C for two hours, cooled and stored in closed containers.

### 2.2. Adsorption Measurements

Before conducting adsorption measurements AC was washed with double distilled water the dried at 120 °C in an oven for at least 2 hours. The adsorption of methylene blue (MB) from aqueous solution was used to assess the quality of the AC obtained. For this purpose, 0.25 g of each the AC samples was added to 50 ml of MB solution (0.35 g/L) in 200 ml conical flask and allowed to equilibrate at room temperature (23 °C) for an hour under continuous shaking. The carbon was then filtered and the concentration of MB in the filtrate was determined using a spectrophotometer.

Adsorption of phenol was used to assess the quality of the obtained carbon as compared to industrial carbons. Adsorption isotherms were constructed by making adsorption measurements at room temperature. For this purpose the desired amount of AC (previously washed with double distilled water then dried at 120 °C in an oven for at least 2 hours and kept in a closed container) is added to 25 ml of 500 PPM phenol solution in a tightly closed conical flasks. The samples are shaken for two hours. This time was sufficient to establish equilibrium between the carbon and the solution. The carbon is filtered out and the residual concentration of phenol is determined using a UV-V spectrophotometer. Absorbance at 260 nm was used for quantification of phenol. The adsorption data were fitted to a Freundlich isotherm described by the following equation:

$$X = k\, C_e^{\,n}$$

where; $C_e$ is the equilibrium concentration of the adsorbate, X is the amount adsorbed per gram of carbon and k and n are constants.

### 2. 3 Characterization

Surface area of selected samples of activated carbon was determined using Qauntchrom Jr adsorption apparatus. Adsorption measurements of nitrogen at its boiling point were conducted and surface area was estimated employing the BET method. The solid density was measured using a pychnometer.

## 3. RESULTS AND DISCUSSION

Figures 1A, 1B and 1C show the percent methylene blue removal (%MBR) versus carbonization time at various temperatures and impregnation ratios (R) of 2:1, 1:1, and 0.5:1 respectively. It is clear from these Figures that the shape of the %MBR versus time curve depends strongly on R. For R= 2:1 and carbonization times higher than 1 hour, %MBR was independent of carbonization temperature and it reaches a constant value of about 99%. For R = 1:1 (Figure 1B) and R = 0.5:1 (Figure 1C), %MBR increases with carbonization time

then reaches a plateau. The time required to reach this plateau depends on the carbonization temperature where shorter times are required for higher temperatures. For example for R = 0.5:1 and carbonization temperature = 550 °C, the time required to reach a plateau value of 94 %MBR is 2 hours while at 700 °C it is only 0.5 hour. This is consistent with fact that the pyrolysis reaction is strong function of temperature. Based on the %MBR and taking into account economical aspects, the optimum operational conditions are temperature = 700 °C, R = 2:1 and carbonization time = 0.5 hour.

For carbonization time of 1.5 hour and carbonization temperature of 600 °C, the effect of R on surface area (SA), solid density (SD) and %MBR is depicted in Figure 2. It can be seen from this figure that the surface area is a strong function of R. For R ranging from 0:1 to 2:1, the corresponding variation in SA is from 35.5 to 1132 $m^2/g$. The degree of impregnation (R) mainly influences the total pore volume. For small values of R, the increase in the total pore volume of the product is due to the increase in the number of small pores that have a high contribution to surface area. On the other hand, when the degree of impregnation is further raised, the number of pores with lager diameter increases (lager pores have low contribution to surface area) and therefore the SA versus R reaches a plateau and becomes invariant with R. As can be seen from Figure 2, %MBR is 85 for R = 0:1 and reaches 95 for R = 2. This narrow range of variation in %MBR (85 to 95) does not reflect the large variation in surface area (35.5 to 1132 $m^2/g$). The increase in surface area is attributed to the increase in the number of small pores. These pores may not be accessible by the large molecule of methylene blue and/or the adsorption of methylene blue occurs on specific sites.

Table 1 compares the physical characteristics of carbon samples prepared at a carbonization time of 1.5 hours and R = 0.5:1, 1:1, and 2:1 and temperatures from 500 to 700 °C. It can be seen from this table that for R = 1:1 or 2:1, the effect of temperature on the surface area (SA) and %MBR is not significant while for R = 0.5, both SA and %MBR increase with temperature. Furthermore, Table 1 indicates that the solid density (SD) vary within a very narrow range (1.324 – 1.568 g/ml). Generally, SD increases slightly with increasing temperature and decreases with increasing R. A high value of SD may be taken as an indication that the carbon structure is stronger. The largest value of SD obtained was at 700 °C with R = 0.5:1.

Phenol adsorption isotherms for selected samples are presented in Figure 3 along with the adsorption isotherm for a commercial carbon (IND). The designation of each carbon, preparation conditions, Freundlich equation parameters (k and n), SA, and %MBR are summarized in Table 2. It can be seen from this table that the values of both k and n and %MBR depend on the preparation conditions. For the same carbonization temperature (500°C) and R, as the carbonization time increases, n decreases while k and %MBR increase. At this low carbonization temperature (500°C), it is evident that there is a strong positive correlation between the improved performance of the carbon in phenol adsorption (higher k)

and %MBR. On the other hand, for the same carbonization time and R, as the temperature increase, n decreases, k increases and SA and %MBR remain essentially constant.

The k and n values for carbons prepared in our laboratory ranged from 0.44 to 4.05 and 0.83 to 0.49 respectively. Considering the adsorption of phenol, it can be seen from Figure 3 that the best conditions are those used for preparing S58 (carbonization temperature = 700 °C, Carbonization time = 1.5 hours and R = 2:1). It is clear from Table 2 and Figure 3 that the industrial carbon performed better than carbons prepared in this study with k and n values of 26.6 and 0.24 respectively. The commercial carbon is a NORIT peat- based carbon activated using steam. It is clear that further optimization of the preparation conditions, use of other activating agents and/or use of steam activation should be considered for improving the adsorption characteristics of the carbon obtained from the dates' stones. Nevertheless, the study indicates that activated carbon with reasonably good characteristics can be obtained from dates' stone.

## 4. CONCLUSIONS

Based on methylene blue adsorption experiments and economical considerations, it was concluded that the optimum operating conditions tested for production of activated carbon from date's stones are: carbonization time = 0.5 hour; temperature of carbonization = 600°C; and, zinc chloride to wood ratio = 2:1. In addition, it was found that carbons with specific surface area in excess of 1100 $m^2/g$ were obtained. Considering phenol adsorption, the study showed that the best conditions which produce carbons with good phenol adsorption capacity are, carbonization temperature = 700 °C, carbonization time = 1.5 hours and R = 2:1. AC prepared in this study was slightly inferior with respect to phenol adsorption compared to commercial AC. Nevertheless, it was shown that AC with good characteristics could be obtained from dates' stone.

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Table 1: Physical characteristics for carbon samples produced by carbonization for 1.5 hours

| T (°C) | R = 0.5 | | | (R) = 1 | | | ratio (R) = 2 | | |
|---|---|---|---|---|---|---|---|---|---|
| | SA ($m^2$ /g) | SD (g/ml) | %MBR | SA ($m^2$ /g) | SD (g/ml) | %MBR | SA ($m^2$ /g) | SD (g/ml) | %MBR |
| 500 | 768 | 1.324 | 84.0 | 826 | 1.362 | 99.2 | 1148 | | 99.1 |
| 550 | 723 | 1.396 | 85.0 | 802 | 1.430 | 99.2 | 1010 | 1.355 | 98.5 |
| 600 | 731 | 1.412 | 93.2 | | 1.451 | 99.1 | 1132 | 1.456 | 99.0 |
| 700 | 977 | 1.568 | 98.8 | 880 | 1.462 | 97.8 | 1162 | 1.533 | 98.5 |

Table 2: Comparison between Freundlich equation parameters k and n and surface area of selected samples and a commercial sample.

| Sample | Carbonization | | Ratio ( R ) | Freundlich equation parameters | | Surface area $m^2/g$ | %MBR |
|---|---|---|---|---|---|---|---|
| | Time (hr) | Temp. (°C) | | k | n | | |
| S6 | 0.5 | 500 | 0.5 | 0.44 | 0.83 | | 36.9 |
| S7 | 1 | 500 | 0.5 | 0.6 | 0.79 | | 40.8 |
| S8 | 1.5 | 500 | 0.5 | 4.03 | 0.49 | 768 | 84.1 |
| S13 | 1.5 | 500 | 2 | 0.76 | 0.8 | 1148 | 99.1 |
| S43 | 1.5 | 600 | 2 | 2.45 | 0.6 | 1132 | 99.0 |
| S58 | 1.5 | 700 | 2 | 4.05 | 0.53 | 1162 | 98.5 |
| IND | NORIT steam activated- peat based activated carbon | | | 26.6 | 0.24 | | |

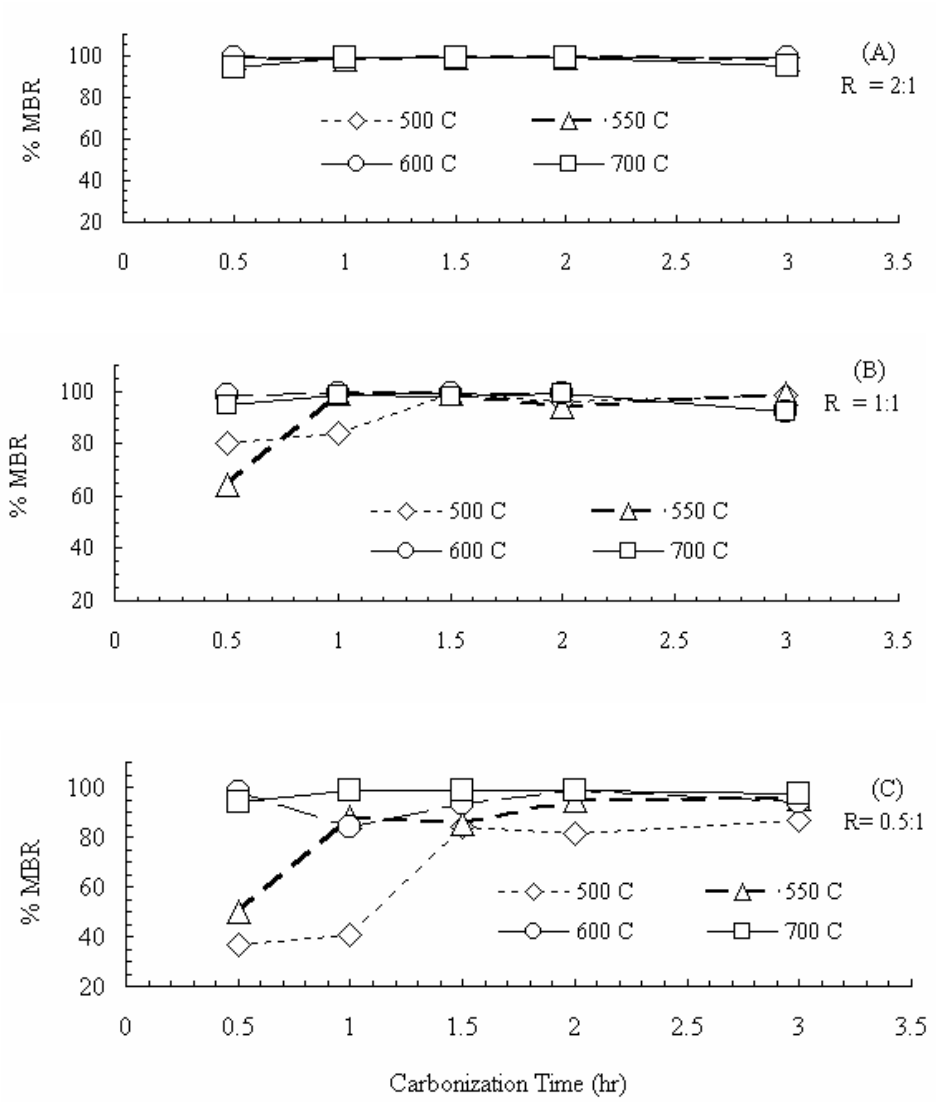


Figure 1: Effect of carbonization time on methylene blue removal (%MBR) by activated carbons prepared from date's stones by chemical activation at various carbonization temperatures and at various weight ratios of zinc chloride to dry date's stones (R).A: R = 2:1, B: R = 1:1 and C: R = 0.5:1.

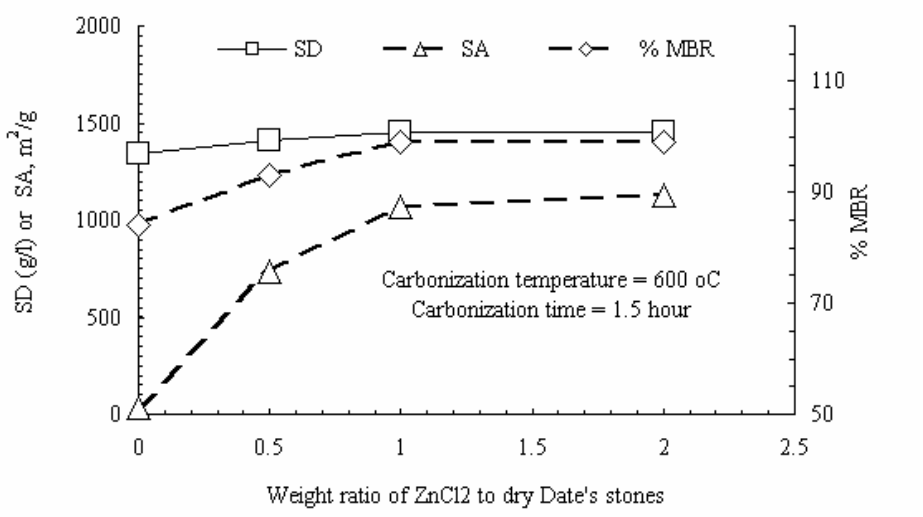


Figure 2: Effect of weight ratio of zinc chloride to dry dates' stones on % methylene blue removal blue (% MBR), solid density (SD) and specific surface area (SA) for activated carbons carbonized for 1.5 hour at 600 °C.

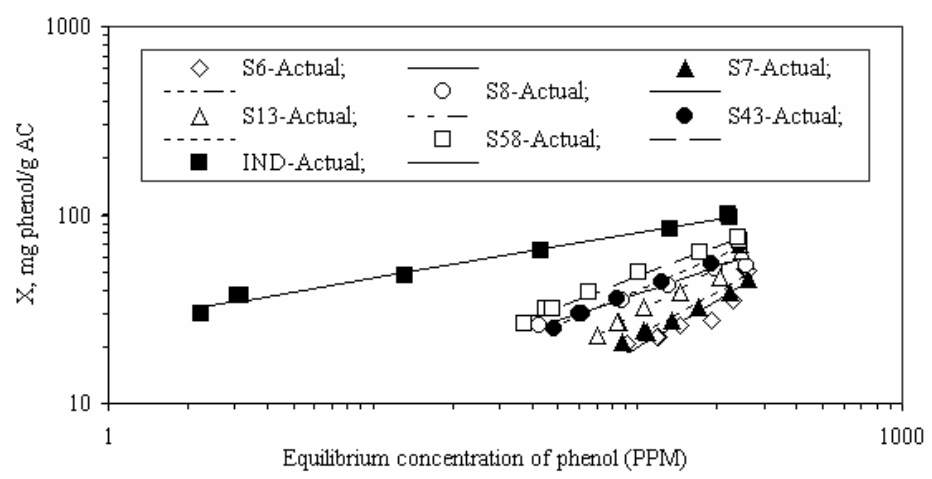


Figure3: Freundlich isotherm representation for adsorption of phenol on carbons prepared at various conditions and for an industrial activated carbon sample. See Table 2 for sample designation and preparation conditions.