

## Production of Granular Activated Carbon from Mesquite Trees

Yaseen Mohammed Mosa Salih

Department of Chemical Engineering, University of Kordofan

[yaseen.awal@gmail.com](mailto:yaseen.awal@gmail.com)

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**ABSTRACT** - This paper study the production of granular activated carbon (AC) from mesquite trees, where the previous studies used other materials. Mesquite trees have many problems to agriculture and environment, especially here in Sudan. It's grows quickly and furnish shade and wildlife habitat where other trees will not grow. Activated carbon was prepared through chemical activation using ortho phosphoric acid in a fixed concentration (95%) to activate the raw material at 600, 650 and 700° C in a different time of activation 1.5 and 2 hours respectively, the average yield was approximately 28%. Methylene blue is the parameter of surface area and iodine value is the parameter of porous structure of the AC. 2:lit's the percentage of acid to the raw material that used here. The effect of various process parameters like bulk density at 150°C and pH was determined and evaluated. Almost parameters were in a typical range of preparation, so AC can be prepared commercially to use in many application.

**Keywords:** Activated carbon, mesquite trees, granular activated carbon.

**المستخلص-** هذه الورقة تدرس انتاج الكربون النشط في شكل حبيبات من اشجار المسكيت. اشجار المسكيت تسبب الكثير من المشاكل الزراعية والبيئية خاصة هنا في السودان. فهي تنمو بسرعة، تغطي مساحات كبيرة وتمتص كميات من الماء مما يعيق نمو النباتات الاخرى. تم انتاج الكربون النشط من خلال التنشيط الكيميائي باستخدام حمض الفوسفوريك بتركيز وزني 95% ونسبة 2 من الحامض الى 1 من المادة الخام عند درجات حرارة 600 - 650 و 700° م ولفترة 1.5 و 2 ساعة على التوالي، وتم الحصول على متوسط وزني للكربون النشط يعادل 28% من المادة الخام. تم اجراء تجارب تأكيدية للمنتج لمعرفة مساحة سطحه باستخدام الميثيلين الازرق، كما استخدمت الطريقة الايودية لمعرفة ابعاد المسامات الداخلية للكربون النشط. تم دراسة تأثير عوامل اخرى مثل الكثافة عند درجة حرارة 150° م بالاضافة لتاثير الرقم الهيدروجيني. معظم الخصائص كانت في المدى المرغوب مقارنة مع مواصفات الكربون النشط، وهذا يعطي امكانية انتاجه بكميات تجارية لاستخدامات متعددة.

### INTRODUCTION

Activated carbon is porosity (space) enclosed by carbon atoms<sup>[1]</sup>. Activated carbon is used in gas purification, gold purification, metal extraction, water purification, medicine, sewage treatment, air filters in gas masks and respirators, filters in compressed air and many other applications<sup>[2]</sup>. Naturally occurring carbonaceous materials such as coal and wood are decomposed in an inert atmosphere at a temperature of about 800 K. Activated carbon may be used as a powder, it may also be used in granular form. When the use of carbon is low, it is normally economic to regenerate it, and this is usually the case with powder. Granular carbon is normally regenerated after use<sup>[3]</sup>. AC, has a high adsorption capacity for pollutants such as methylene blue, phenolic compound, lead ions and vapors of some volatile organic compounds<sup>[4]</sup>.

Refineries today faces a big problem in how to separate the mixture of Water/Oil in field of crude oil at a low cost, and how can they use the treated water in further refinery process. In some refineries, wastewater was diverted directly to the environment; because the characteristic of this water was not standard enough to be applied in one of the refinery processing unit.

They are many studies on wastewater treatments by activated carbon, some of these are:

SitiKhadijah, et al.<sup>[5]</sup> studied the utilization of local agricultural waste, which is sugarcane bagasse, in producing AC for groundwater treatment. The AC produced through the carbonization at the temperature of 500°C for two hours after it was impregnated with sulphuric acid to activate a pore surface.

Javier Blanco Castro et al. (2000) <sup>[6]</sup>, they prepared activated carbon from sugar cane wastes (bagasse) by added phosphoric acid with carbonization temperature (300-600°C), the weight ratio of phosphoric acid, carbonization time was (1-3h). Arunrat Cheenmatchaya and Sukjit Kungwan (2014) <sup>[7]</sup>, they prepare activated carbon from rice husk by simple carbonization and chemical activation for using as gasoline adsorbent, to make value-added activated carbons of rice husk and to study the optimum conditions for gasoline adsorption using these activated carbons as adsorbents.

Badie S. et al. (2004) <sup>[8]</sup>, they impregnated dried ground bagasse with 50% inorganic acids and carbonized at 500°C, showed the sequence  $H_3PO_4 > H_2SO_4 > HCl > HNO_3$ , with respect to the efficiency of activation. Treatment with phosphoric acid of different concentrations (30–50 w/w) was followed by carbonization at 300–500°C for 3 h. Nazar A. E. Hamza et al. (2013) <sup>[18]</sup>, they prepare AC from mesquite tree as adsorption of metals (Fe(II), Cr(III) and Co(II)) from aqueous solution, under condition preparation of 1 M KOH and temperature of 600°C for 1 h.

Other studies using membrane bioreactor process coupled with biological activated carbon.

We will use Mesquite trees to generate activated carbon, because it is cheaper than the above kind, and also helping the agriculture lands from the problem of Mesquite trees. Figure 1 shows the raw material that used to produce AC.



Figure 1: Raw material of AC from Mesquite tress.

**Applications in wastewater treatment and desalination:** As indicated, most of activated carbons obtained from lignocellulosic precursors can be used for the removal of both organic and inorganic compounds especially heavy metals, dyes and phenol. Until now, various adsorption kinetic and equilibrium experiments have been performed in the literature to study the adsorption

process of priority water pollutants using lignocellulosic-based activated carbons. In general, these studies have been performed at batch conditions and a limited number of studies using dynamic conditions (i.e., packed bed columns) have been reported <sup>[9]</sup>.

**Mesquite Trees (Prosopischilensis):** Mesquite Trees (*Prosopischilensis*) or *Prosopisjuliflora*. It was introduced to Sudan in 1917 under the name *Prosopisjuliflora*. However, some taxonomists, erroneously, identify it as *P. chilensis*. The name mesquite was given to the trees by the native Americans before the British got to the Americas. Mimosaceae, is the family name, and *Prosopischilensis* is the scientific name, it grows quickly and furnishes shade and wildlife habitat where other trees will not grow. Being a legume, it fixes nitrogen in the soil where it grows, improving soil fertility. Mesquite is a phreatophyte, which means it has deep roots and transpires efficiently. For this reason, one method of managing water loss in arid areas is the removal of mesquite <sup>[10]</sup>.

**Adsorption:** In adsorption, molecules distribute themselves between two phases, one of which is a solid whilst the other may be a liquid or a gas <sup>[3]</sup>. The transfer of the heat liberated on adsorption or consumed on desorption may also limit the rate process or the adsorbent capacity. Again the possible effects of the boundary-film and the intraparticle thermal properties have to be considered <sup>[3]</sup>.

**Classification of AC:** AC are complex product which are difficult to classify on the basis of their behaviors, surface characteristic and preparation methods, some broad classification is made for general purpose based on their physical characteristics <sup>[2]</sup>.

2.1 Powdered Activated Carbon (PAC): Active carbons are made in particulate form as powders or fine granules less than 1.0 mm in size with an average diameter between 0.15 and 0.25 mm. PAC is made up of crushed or ground carbon particles, 95–100% of which will pass through a designated mesh sieve or sieves. Is defined as the activated carbon being retained on a 50-mesh sieve (0.297 mm) and PAC material as finer material, while ASTM <sup>[11]</sup> classifies particle sizes corresponding to 80-mesh sieve (0.177 mm) and smaller as PAC.

2.2 Granular activated carbon (GAC) Granular activated carbon has a relatively larger particle size compared to powdered activated carbon and consequently, presents a smaller external surface. Diffusion of the adsorbate is thus an important factor. These carbons are therefore preferred for all adsorption of gases and vapors as their rate of diffusion are faster. Granulated carbons are used for water treatment, deodorization and separation of components of flow system<sup>[2]</sup>.

**Physical and Chemical Properties**

**Bulk Density:** It is defined as the mass of a unit volume of the sample in air, including both the pore system and the voids among the particles<sup>[13]</sup>. Powdered carbons used for decolorization usually have a bulk density in the range 0.25 - 0.75 gcm<sup>-3</sup>, while granular grades used in gas adsorption have a bulk density of around 0.40-0.50 g cm<sup>-3</sup><sup>[11]</sup>.

**Moisture Content:** Activated carbon it's generally contains different moisture, although occasionally some moisture content is stipulated, e.g., 3, 8, 10%<sup>[14]</sup>. Unless packaged in airtight containers, some activated carbons when stored under humid conditions will adsorb considerable moisture over a long period of time. They may adsorb as much as 25 to 30% moisture and still appear dry for many purposes, this moisture content does not affect the adsorptive power, but obviously it dilutes the carbon. Therefore, an additional weight of moist carbon is needed to provide the required dry weight<sup>[13]</sup>.

**Total Ash content:** The ash content of a carbon is the residue that remains when the carbonaceous materials is burned off<sup>[1]</sup>. The ash consists mainly of minerals such as silica, aluminum, iron, magnesium, and calcium. Ash in activated carbon is not desirable and is considered an impurity. For instance, the ash content may affect the pH of the carbon since the pH of most commercial carbons is produced by their inorganic components. Usually, materials with the lowest ash content produce the most active products<sup>[14]</sup>. The inorganic material contained in activated carbon is measured as ash content, generally in the range between 2 and 10%<sup>[12]</sup>. This test was conducted by European Council of Chemical Manufacturers' Federations in 1986.

**PH value:** Activated carbons exhibit both surface acidity and surface basicity as monitored when carbons are placed into pure water and the system

allowed to reach equilibrium. The pH of the aqueous solution is clearly an important parameter that controlled the adsorption process.

**Iodine number:** Iodine number is the fundamental parameter used to characterize activated carbon performance and giving indication of the internal area of the carbon<sup>[2]</sup>.

**Adsorption Properties:**

**Surface Area:** It is a measurement of the extent of the pore surface developed within the matrix of the activated carbon generally; the larger the specific surface area of the adsorbent, the better its adsorption performance will be<sup>[12]</sup>. The most widely used commercial active carbons have a specific surface area of the order of 600- 1200 m<sup>2</sup>/g<sup>[12]</sup>.

**Pore Structure:** The word pore comes from the Greek word, meaning a passage .In this sense, a pore is a class of void which is connected to the external surface of a solid and will allow the passage of fluids into, out of, or through the material<sup>[12]</sup>. Differences in pore sizes affect the capacity for molecules of different shapes and sizes, and this is one of the criteria by which carbons are selected for a specific application. Porosity is classified by International Union of Pure and Applied Chemistry (IUAC) into three different groups of pore sizes<sup>[12]</sup>.

- i. Micropores- width less than 2 nm
- ii. Mesopores- width between 2 and 50 nm
- iii. Macropores- width greater than 50 nm.

Beside their significant contribution to adsorption, mesopores also serve as the main transport arteries for this adsorbate.<sup>[12]</sup>

The small organic molecules with low solubility have sizes in the range 0.6 to 0.8 nm and can be adsorbed in micropores while large compounds such as color molecules and humid acids have dimensions around 1.5 to 3.0 nm that will favor their adsorption in mesopores, Table 1 below shows minimum pore diameter.

**Table 1: Minimum pore diameter**

Adsorbate	Minimum Pore, Diameter, Å
Iodine	10
Potassium permanganate	10
Methylene Blue	15
Erythrosine Red	19

Source: Nurul'ainJabit, *The Production and Characterization of Activated Carbon using local*

agricultural waste through chemical activation process, (2007).

**Yield Percent:** The yield of activated carbon was calculated on a chemical –free basis and can be regarded as an indicator of the process efficiency for the chemical activation process [15].

**Iodine Value (IV):** Many carbons preferentially adsorb small molecules. It is a measure of activity level, higher number indicates higher degree of activation. It is a measure of the micropore content of the activated carbon (0 to 20 Å, or up to 2 nm) by adsorption of iodine from solution. It is the standard measure for liquid phase applications. Equation (1) giving iodine value:

Iodine value:  $C \times \text{Conversion factor}$ ; mg/g (1)

**Methylene Blue (MB) Adsorption:** This procedure determines the capacity of an activated carbon to decolorize the aromatic dye, methylene blue is a measure of adsorption capacity. Many methods can be used to determine MB, Chevron Carbon method (TM-11) was used here. Some AC have a mesopore (20 Å to 50 Å, or 2 to 5 nm) structure which adsorbs medium size molecules, such as the dye methylene blue [16].

#### MATERIAL AND METHOD

##### Activation Process:

Activated carbon can be prepared by one of the following two methods:

**Partial gasification**, generally called “physical activation.” The activation agents most often used are steam, carbon dioxide, and air or a combination of these. During activation of the intermediate product, the disorganized carbon (depending on the carbonization procedure, 10-20% burn-off) is first removed to expose the surface of the elementary crystallites to the action of the activation agent. The further development of the porosity on increasing burn-off depends on the mechanism of carbon removal via active site formation and the relative rate of reaction in the direction parallel with the plane of the graphitic layers compared to carbon removal in the direction perpendicular to this plane [17].

**Carbonization of lignocellulosic material** starts above 170°C and it is nearly completed.

##### Mechanism of Orthophosphoric Acid as Activating Agent

Phosphoric acid works in two ways : as an acidic catalyst in promoting bond cleavage reactions and formation of crosslink; and by being able to combine with organic species to form phosphate

linkages, such as phosphate and polyphosphate esters [13].

##### Carbonization and Activation Process

Three grams of raw material was impregnated with concentrated orthophosphoric acid (95% w/v) at constant ratios of acid/raw material (2: 1). The first step of activation and carbonization process, was impregnated samples in the acid, then burned in carbolated furnace (CW1200) for 1.5 h and 2 h, at 600°C, 650°C and 700°C with loading time 35 min and heating rate 50°C/min. After cooling to the room temperature, the samples were washed with distilled water to remove any residual phosphoric acid. This was done by washing the carbon with 80-90°C distilled water for several times until remove any acid remains, then filtered through What man filter paper No.3 and dried in the GENLAB oven at 105°C for 2h. The samples were weighed in order to determine the yield of activated. The dried samples were granulated and then stored in air tight bottles ready for use, Figures 2 and 3 below showed granular AC and AC block diagram respectively.



Figure 2, granular AC

##### AC properties

**Bulk Density:** Bulk density was obtained by weighing five grams of the prepared activated carbon and transferred it into a 10 mL graduated cylinder. The cylinder was tamped with a rubber pad while activated carbon was being added until the entire original sample was transferred to the cylinder. Tamping, continued for 5 minutes until there was no further settling. The mass and volume recorded and the bulk density calculated using equation 2 below:

$$\rho = \text{mass/volume occupied} \quad (2)$$

**Moisture Content:** Moisture content was obtained by weighing a petr-dish after being heated in an oven at 150 °C for one hour then

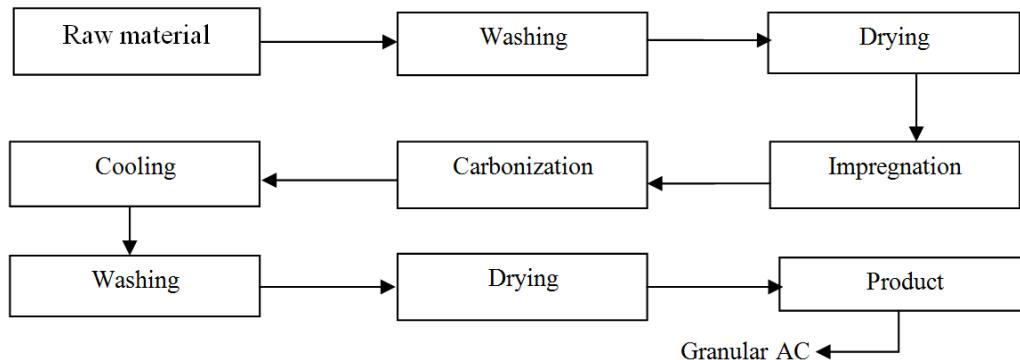


Figure 3: Block diagram of granular AC production, (Sara Y. F. Fadel Alla (2013) <sup>[4]</sup>, unpublished data.

cooled in a desiccator and one gram of mesquite was weighed in the Petri-dish and placed in an oven at 150°C for 3 h, the petr-dish left open during the heating process. Then the petr-dish was removed and cooled in the absence of humidity and reweighed again. The difference between the initial and final mass of the mesquite represents the water content in the sample.

**Total Ash content:** Ash content was measured by burning the prepared activated carbon in a muffle furnace at 650 ± 25°C. One gram of dry mesquite was transferred into a crucible and then was placed in the furnace for 4h, during this test the crucible was left open. The crucible was placed in the desiccator and was allowed to cool toroom temperature. Ash was considered complete when constant weight achieved. The difference between the original and final weight of the carbon represents the ash content per gram. To determine total ash content for prepared AC, one gram of AC was weighed in the petr-dishand was repeated.

**pH value:** Four grams of carbon was weighed into a 250 ml beaker, then add 100 ml of distilled water covered with a watch glass and boiled on a hot-plate for 5 minutes, a thermometer was inserted inside until the bulk of the activated carbon particles were settled. The decanted portion was cooled to room temperature and the pH value was measured to one decimal place <sup>[12]</sup>.

**Yield Percent:** The yield of AC is calculated as the percentage weight of the resultant of AC divided by weight of dried mesquite. The mesquite was weighed before impregnated with acid and it was weighed after activation, the difference between the initial and final weight percent was taken as yield percent. The yield of activated carbon product was calculated based on the activated carbon dried at 105°C by equation 3,

$$\text{Yield \%} = \{W_b / W_c\} * 100 \quad (3)$$

where,  $W_b$  and  $W_c$ ; weight of mesquite and weight of final carbon respectively

**Methylene test solution:** 0.1g AC sample was weighed to 100 ml of 500 mg/l solution in a glass flask, and shaken, then left for 24h to reach equilibrium. All samples were filtered with glass hood and remaining solution was determined. The concentrations of MB in the supernatant solution before and after that remaining adsorption were determined using a Quanova Spectrophotometer at 650 nm. The amount of adsorption at equilibrium,  $Q_e$  (mg/g) was calculated by equation 4:

$$Q_e = (C_o - C_e) V / W \quad (4)$$

where,  $C_o$  and  $C_e$  (mg/L) are the liquid-phase concentrations of the dye at initial and equilibrium state;  $V$  is the volume of the solution (L) and  $W$  is the mass of dry adsorbent used (g).

## RESULTS AND DISCUSION

### Effect of carbonization temperature on activated carbon production

The activation temperature is a very influential parameter on the pore structure of activated carbon, which determines the adsorption capacity. The variation in yield%, methylene blue and iodine values of activated carbon product were investigated as a function of carbonization temperature. Mesquite was used as raw material and activation times were 1.5 and 2 h at 600, 650 and 700°C. As shown in Table 2. The variation in iodine values of activated carbon product was investigated as a function of carbonization temperature.

Iodine value increased and yield values approximately decreased with the increasing carbonization temperature. Thus, it can be concluded that the optimum temperature for the production of activated carbons from mesquite is

approximately 650 – 700°C. Overall weight loss was found to increase with increasing temperature and time, resulting in decreasing yield of activated carbon as temperature increased. The iodine number of the prepared activated carbon increased with increasing carbonization temperature.

**Table 2: shows Iodine Value with different time hours.**

Time/h	IV
2	922
2	1363.1
2	1070.44
1.5	979.61
1.5	1226.76
1.5	1026.95

**Effect of carbonization time on activated carbon production**

The variations in iodine value of the activated carbon produced from mesquite versus the activation time are shown in Table 3. The decrease in iodine value for the time period of 1.5–2 h is considered to be due to the extended activation of product, resulting in the conversion of some micropores into mesopores and mesopores into macropores.

**Table 3 shows Methylene Blue with different Time**

Time/h	Tem	MB
2	700	4
2	650	51
2	600	47.5
1.5	700	6.5
1.5	650	59.5
1.5	600	41

**Table 4 shows yield with different time and temperature**

Time/h	Tem	Yield%
2	700	28.33
2	650	33.6
2	600	22.27
1.5	700	21.73
1.5	650	29.33
1.5	600	24.4

This trend indicates that the activation time of 1.5 h is optimum in this study. As shown in Table 4, the iodine value increased progressively with activation time the pore walls between adjacent pores were probably destroyed and the micropores were destructed, which led to the decrease in iodine value with time. The iodine values were

measured as 979.61 and 1226.76 mg/g after 1.5 hour of carbonization time, respectively. Thereafter, the iodine value gradually dropped to a value of 922.00 mg/g at 2h. A further increase in activation temperature and activation time led to decrease in yield, which may be attributed to the incomplete carbonization.

**CONCLUSIONS**

It can be concluded that the optimum temperature for production of AC from mesquite is approximately 650 – 700°C, this trend indicates that the activation at 1.5 h, with higher IV 1226.76 mg/g is the optimum for making active carbon from mesquite.

The quality of the activated carbon prepared depends on the method and processing conditions such as heating rate, temperature, time of activation and activating agent. So increasing the carbonization temperature increased iodine value and decreased yield %.

The utilization of mesquite tress to prepare AC may have a good positive influence on the environment. Production of AC from mesquite tress, in addition to regenerating, will be a vital item in management of the weed. So, more production of AC from mesquite tress will reduce the problem of mesquite tress to the agriculture land. Also from the results of IV and MB, granular AC can be used as adsorbent AC and suggested as a plausible adsorbent for oily wastewaters.

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