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# Preparation and Study of Properties of Activated Carbon Produced from Agricultural and Industrial Waste Shells

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## Abstract

*The activated carbon was prepared from carbonaceous agricultural waste Almond shell and walnut shell by chemical activation using ortho-phosphoric acid at 800 ± 5 °C. Walnut shells and almond shells were carbonized in an inert atmosphere and then the char was mixed with a solution of ortho-phosphoric acid. The mixture was then activated thermally in a nitrogen atmosphere and finally washed and dried to obtain the activated carbon. The objectives of this work were to develop a modified method to produce activated carbon from almond shell and to compare its physical and morphological characteristics with the activated carbon obtained from walnut shell. The internal structure of both the carbon was analyzed with scanning electronic microscopy (SEM) and the dye adsorption capacity of each carbon was determined according to the ASTM specifications (American Society for Testing and Materials). The results of FTIR ( Fourier-Transform Infrared Spectroscopy) strongly support significant chemical and spectral changes occurring with the activation of the almond shells for phosphoric acid treatment. Activated carbon obtained from the almond shell showed a heterogeneous carbonaceous structure compared to walnut shell. The prepared activated carbon was characterized for dye adsorption and was found that methylene blue adsorption capacity of walnut shell activated carbon is 51% less compared to almond shell.*

**Keywords:** Activated carbon, spectra, methylene blue number, phosphoric acid, adsorption capacity.

## Introduction

Agricultural and food industries create various waste matters that need to be utilized and convert in value added product. Carbonaceous materials such as coconut shell, palm shell, saw dust and tropical wood are some of the most common agricultural wastes shells used to produce activated carbon. In the present study the activated carbon was prepared from two carbonaceous agriculture waste almond shell and walnut shell by chemical activation using ortho-phosphoric acid ($H_3PO_4$) at 800 ± 5 °C. These nutshells are waste materials generated in various industries and can be collected on community basis for reuse. Both nutshells are abundant, inexpensive and readily available lignocellulosic material. The national walnut production in India oscillates between 40,000 to 45,000 tons per year. The walnut shell represents 67% of the total weight of the fruit[1]. The process involved to obtain unshelled walnut, generates more than 25000 tons of shell. Also, production of almond is 17000[2] tons per year generating approximately 11000 tons of almond shell waste as 80% of total almond weight comprises of shell that are of no further use. On account of the success in the cultivation of new trees, the waste matter produced will be greater in the near future[3]. Activated carbon is one of the mostly used and important microporous adsorbents due to its tremendous adsorptive capacity (milligrams of adsorbate retained per gram of carbon) and ability to be custom-tailored to suit specific application[4]. They can adsorb different types of substances from gaseous or liquid phases. Therefore, activated carbons are widely used in many fields, e.g., water and air purification, separation of industrial gases, for discoloring in pharmaceutical and chemical industries, and in making oral carbon tablets[5-7].

General process for production of activated carbon involves carbonization of raw material to obtain the char or carbonaceous material, which is activated at elevated temperature to yield the highly porous final product. At present, there are two different activation processes: (1) steam activation, (2) chemical activation. In steam activation, steam is introduced in the temperature range of 600-1200°C, whereas in chemical method, the starting material is impregnated with an agent and the blend of both is heated at a temperature of 500 - 800°C. Chemical activation reduces the formation of tar and other by-products, thereby increasing carbon yield[8-10]. The processes involve elimination of hydrogen and oxygen from the raw material to produce a carbon skeleton possessing a latent pore structure (crude char). The conversion of raw material to activated carbon involves gasification of the crude char at an oxidizing atmosphere that increases the pore volume and surface area of the resulting product. Both activation methods yields 30-35 % of activated carbon on average, but in chemical activation yield is normally higher than physical method (based on weight of starting material)[9-12].

This work had as a primary objective to obtain activated carbon from walnut shell and almond shell and to analyze their internal structure through Scanning Electronic Microscopy (SEM) and Fourier-Transform Infrared Spectroscopy (FTIR). Moreover, it was proposed to measure their dye adsorption capacity.

## Material and Methods

Walnut shells and Almond shell were collected from local market, cleaned, grinded with a roller mill to use as starting materials. The product was passed through sieves to obtain three samples with different particle size: from 1 to 2 mm (sample 1), from 0.5 to 1 mm (sample 2) and minor than 0.5 mm (sample 3). The samples were carbonized separately in a furnace in nitrogen atmosphere at 500°C during 1 h. These conditions were selected from the literature[13-16]. Samples 2 and 3 were incinerated completely, thereby they were discarded. The char obtained from sample 1 was cooled at room temperature and then mixed with a solution of ortho-phosphoric acid, in a ratio of 2:1 ($H_3PO_4$ solution /char, W/W). This ratio was selected from previous experiments in our laboratory, which show that the adsorption capacity increases remarkably with increasing $H_3PO_4$ /char ratio up to 2:1. The mixture was dehydrated at 250°C for 3 h and subsequently activated at 800°C in absence of air for 1 hour. These conditions were used by R. Arrigada[17] reported that higher temperatures (900°C) favor the production of an adsorbent with larger adsorption capacity due to an increase in micropore size. The products formed were thoroughly washed with deionized water and dried in oven at 100°C for 2 hours. The prepared activated carbons were stored in dessicator for later studies.

The surface morphological features of activated carbon was examined by using a JEOL Scanning Electron Microscope (JSM-6380 Model No). The pore formation of activated carbon is mainly attributed to the addition of phosphoric acid which causes the material to swell and it opens the surface structure. Phosphoric acid is a strong dehydrating agent, it has been reported that $H_3PO_4$ accelerated the bond cleavage reactions leading to the early evolution of volatiles at below 300°C and generation of empty spaces. At high temperatures the reactive sites leave a hard aromatic porous carbon structure for adsorption[18].

Figures-2 and 3 below shows the surface morphology of activated walnut and almond shells. In activated walnut shell carbon there are smaller pores of regular size randomly arranged whereas it can be observed from figure-2 that the surface of activated almond shell shows a lot of grooves, cracks and crevices in the matrix after activation. The macropores are highly developed deep inside the surface. It indicates that the precursor material and method for preparation of activated carbon is adequate for the purpose.

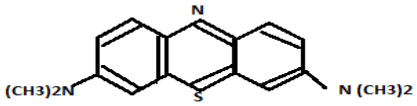


**Figure-1**
**Structure of methylene Blue Dye**

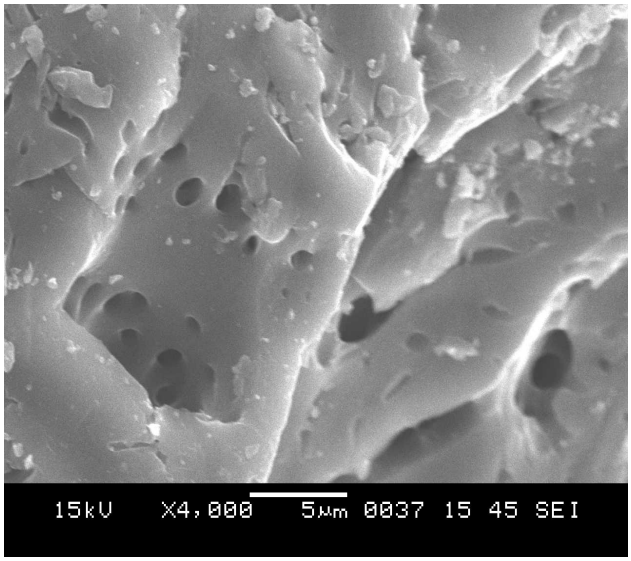


**Figure-2**
**Activated charcoal from walnut shell**

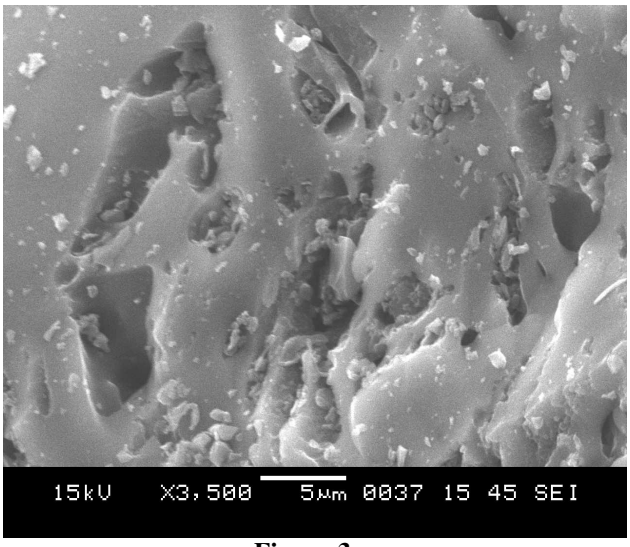


**Figure-3**
**Activated charcoal from Almond shell**

The adsorption capacity was measured according to the ASTM D 2330-02 specifications[19]. The methylene blue dye used in the investigation was discovered by Caro in 1878. It is a basic cationic dye, heterocyclic aromatic chemical compound with molecular formula: $C_{16}H_{18}N_3SCl$, Molecular weight = 319.85.

The structure of methylene blue is shown in figure-1. Methylene blue dye (Merck) was dried to constant weight before use and Stock solutions of 20.00 g/l and 1.00 g/l concentration was prepared. Three representative samples of both, walnut and Almond activated carbons obtained as described previously, were weighted and transferred separately to a 250 ml Erlenmeyer flasks equipped with ground glass stoppers. Exactly 80 ml of methylene blue solution (20 grams per litre) was added to the flask, Shaken at about 150 oscillations per minute for 20 minutes using a mechanical stirrer. Immediately after the stirring period, contents in the flask were filtered, through a Buchner funnel under vacuum, using Whatman No. 3 filter paper. The first 10 to 15 ml of the sample filtrate was discarded and the remainder was collected for spectrophotometric determination.

The UV-VIS spectrophotometer (Perkin Elmer Lambda 35) was used to prepare a standard curve using methylene blue concentrations of 0.4, 1.0, 3.0 and 5.0 mg/lit prepared from 1 g/lit methylene blue stock solution. The concentration of methylene blue filtrate was determined by analyzing it in reference to the standard curve at $\lambda_{max}$ = 660nm [20]. The methylene blue No. was found by referring to standard Tables given in ASTM D 2330-02.

## Results and Discussion

Carbon prepared from waste walnut shall and almond shells were found effective in removing dye from aqueous solution. Iodine no. is a measure of the micropore content of the activated carbon (0 to 20 Å, or up to 2 nm) more accurately defines the small pores or micropore volume of a carbon and reflects its ability to adsorb lowmolecular weight, small substances, while methylene blue no. defines a mesopore (20 Å to 50 Å, or 2 to 5 nm) structure which adsorbs medium size molecules. The Iodine adsorption capacity per gram for the walnut shell carbon was 907 mg of Iodine/gm of carbon, while the one corresponding to the almond shell carbon was 947 mg of iodine/g of carbon. On the other hand, the methylene blue adsorption capacity per gram for the walnut shell carbon was 198 mg of methylene blue, while the one corresponding to the almond shell carbon was 387 mg of methylene blue/g of carbon. Therefore, each carbon showed a characteristic pore size depending on the starting material used. It is evident from the values of Iodine No. and methylene blue no. as given in table-1, that microporous carbons are obtained from walnut shells and are more effective to retain small molecules. On the contrary, micro as well as mesoporous carbons are obtained from almond shell and are better to adsorb large molecules also, e.g., dye molecules. The structure of the dye is also influenced on adsorption. Both the carbons prepared are comparable on commercial basis for methylene blue adsorption. The surface morphology studies using SEM proves that, almond shell contains more pores providing more sites for adsorption.

**Table-1**
**Table showing values of Iodine No. and Methylene Blue No. of prepared activated carbon.**

| Activated Carbon | Iodine No. (mg/g) | Methylene Blue No.(mg/g) |
|---|---|---|
| Walnut shell | 907 | 198 |
| Almond shell | 947 | 387 |
| Commercial | 700-1100 | 150-200 |

Details of functional groups present on the surface of carbon materials are obtained from FT-IR studies as shown in figures-4 and 5. A sharp band at 3689 $cm^{-1}$ is ascribed to isolated nonbonded hydroxy (OH) groups and around 3526 $cm^{-1}$ is due to carboxylic acid group. A wide, intense band in the range of 3200-3600 $cm^{-1}$ with a maximum at about 3445 $cm^{-1}$ is assigned to the O-H stretching mode of hydroxyl groups and adsorbed water, are seen in both the prepared activated carbons[21].

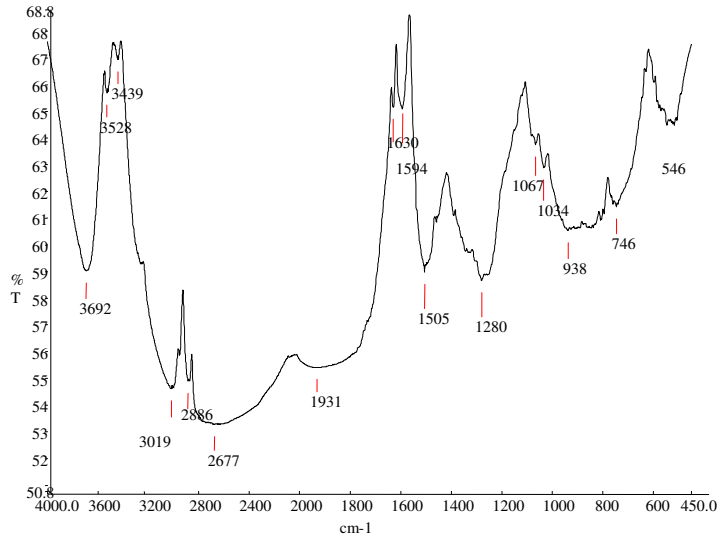


**Figure-4**
**FTIR Spectra of walnut shell AC**

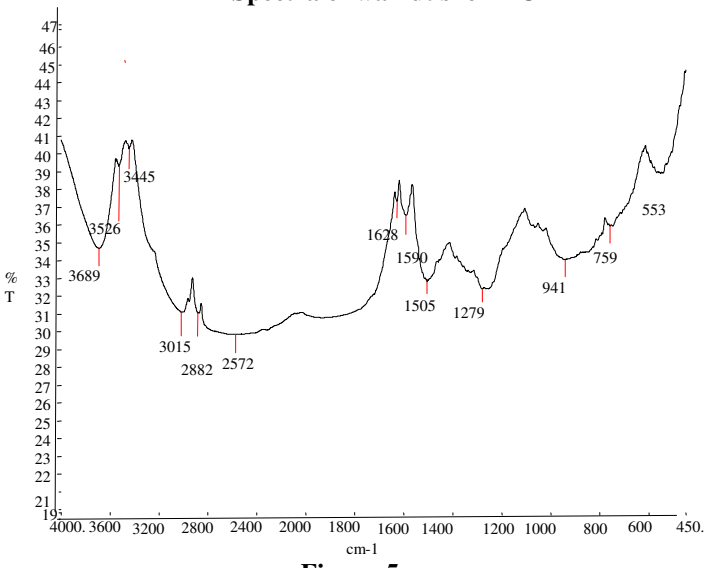


**Figure-5**
**FTIR Spectra of almond shell AC**

The carbonization yields were 22.7% for walnut shell and 26.5% for almond shells. The activation yields were 19.2 % and 17.2 %, respectively.

## Conclusion

This work provides a simple method to obtain carbonaceous adsorbents of controlled pore size, from two industrial wastes walnut shell and almond shell. The activated carbon obtained from walnut shell shows a heterogeneous structure with smaller pores than those of the widely dispersed almond shell carbon.

The Iodine adsorption capacity of both the carbons are approximately equivalent while, the methylene blue adsorption capacity of Almond shell carbon was 51% higher than that of the walnut shell. Thus it can be concluded that high iodine adsorption capacity do not signify high methylene blue adsorption, therefore carbon properties depend upon the raw material used and the preparation condition to get a carbon that can be used for removal of very specific pollutant.

The adsorption capacity may be increase by changing the activation conditions, such as temperature, activation time and concentration of activating agent. Higher activation conditions favor the production of adsorbents with a high adsorption capacity and wider pore size distribution. Furthermore, the utilization of walnut and almond shells to make activated carbon could be promising materials to produce carbonaceous adsorbents at low cost, economically viable and eco-friendly for the treatment of dye house wastewater.

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## References

**1.** The Indian walnut market, Production and trade statistics, (**2011)**

**2.** www.indexmundi.com, Jamadi al Awwal, 1444 AH; April (**2012)**

**3.** Walnut Market and Forecasts, March (**2013)**

**4.** Ismadji S., Sudaryanto Y., Hartono S.B., Setiawan.L.E.K. Ayucitra. A., Activated carbon form char obtained from vacuum pyrolysis of teak sawdust: pore structure development and characterization, *Bioresource Tech*. **96** ,1364-1369, (**2005**)

**5.** Toles C., Marshall W.E., Johns M.M., Granular activated carbons from nutshells, *Carbon*, **v 35**, 1407-1414, (**1997**)

**6.** Arwa M.O., Preparation Of Sulfurized Granular Activated Carbon From Beji Asphalt Using Concentrated $H_2SO_4$, *T. J. Pure Science*., **13(3),** (**2008**)

**7.** Martin R. J., Activated carbon product selection for water and wastewater treatment. *Ind. Eng Chem. Prod. Res. Dev*., **19**, 435–441 (**1980**)

**8.** Lillo-Rodenas M.A., Cazorla-Amoros D, Linares-Solano A., Understanding chemical reactions between carbons and NaOH and KOH. An insight into the chemical activation mechanism, *Carbon* **41**, 267–75, (**2003**)

**9.** Gonza lez Serrano E., Cordero T., Rodriguez Mirasol J., Rodriguez J.J., Development of porosity upon chemical activation of kraft lignin with ZnCl2. *Ind Eng Chem Res*, **36**, 4832–4838, (**1997**)

**10.** Evans M.J.B., Halliop E., MacDonald J.A.F., The production of chemically-activated carbon, *Carbon*, **37(2),** 269-274, (**1999**)

**11.** Mcketta J. J., Encyclopedia of Chemical Processing and Design, **6**, 110 (**1978**)

**12.** MacDowall, US Patent 5162286, November **10,** (**1992)**

**13.** Gonzales J.C.,Sepulveda-Escribano A., Molina-Sabio M, Rodriguez-Reinoso F., Micropore size distribution in carbon molecular sieves by immersion calorimetry COPS IV, *Royal Soc. Chem*, **9**,16 (**1997**)

**14.** Halil Hasar., Adsorption of nickel (II) from aqueous solution onto activated carbon prepared from almond husk, *J.of Hazardous Materials,* **B97**, 49, (**2003**)

**15.** Arons G.N, Macnair R.N., Activated Carbon Fiber and Fabric Achieved by Pyrolysis and Activation of Phenolic Precursors, *Textile Research Journal,* **42 (1), 60-63, (1972)**

**16.** Suh Cem Pang., Wai Hwa Khoh., Suk Fun Chin., Synthesis and characterization of Magnetite/Carbon Nanocomposite Thin Films for Electrochemical Applications, *J. of Mat. Sc. and Tech.*, 27, 873-878, (2011)

**17.** R.Arriagada, R.Garcia, M.Molina-Sabio and F.Rodriguaz-Reinso, Effect of steam activation on the porosity and chemical nature of activated carbons from *Eucalyptus globulus* and peach stones, *Microporous Materials*, 8, 123 (1997)

**18.** Guillermo S.M., Geoffrey D. F., Sollars C.J., Study of the characteristics of activated carbons produced by steam and carbon dioxide activation of waste tyre rubber, *Carbon,* **41,** 1009–1016, **(2003)**

**19.** Tentative method of test for methylene blue adsorption number of carbon, ASTM D 2330-02.

**20.** Ansari.R., and Mosayebzadeh.Z., Removal of Basic Dye Methylene Blue from Aqueous Solutions Using Sawdust and Sawdust Coated with Polypyrrole *, J. Iran. Chem. Soc.,* **7(2),** 339-350, (**2010**)

**21.** Rao M M., Ramesh A, Rao G.P.C., Seshaiah.K., Removal of copper and cadmium from the aqueous solution, by activated carbon derieved from ceibapentandra hulls, *J. of Haz. Mat.* **129(1-3),** 123 (**2006**)