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Preparation and Characterization of Activated Carbon from Walnut *(Jaglansregia)* Shells by Chemical Activation with Zinc Chloride ($ZnCl_2$)

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Abstract
Activated carbons (ACs) were prepared from Walnut *(Jaglansregia)* shells powder (WSP) by chemical activation with Zinc Chloride ($ZnCl_2$) carbonized at different temperatures: 400°C, 500°C, and 600°C in inert atmosphere for 3 hours. The ratio of WSP: $ZnCl_2$ was fixed to 1:1 by weight. The activated carbons thus obtained at 400°C (WSP-4), 500°C (WSP-5) and 600°C (WSP-6) were characterized by XRD, FTIR, Iodine adsorption number and Methylene blue number. In XRD patterns the broad peaks of the prepared ACs can be indexed to amorphous carbon; diffraction is from (002) and (100) planes. FTIR spectroscopy showed the presence of functional groups on the surface of ACs. Iodine number values of Commercial Activated Carbon (CAC), WSP-4, WSP-5 and WSP-6 were found to be 940.57mg/gm, 1053.44 mg/gm, 1040.90 mg/gm and 990.739 mg/gm. The methylene blue numbers of CAC, WSP-4, WSP-5 and WSP-6 were 496.21mg/gm, 499.54 mg/gm, 499.15 mg/gm and 479.68 mg/gm respectively. It was observed that the WSP-4 have higher value of iodine number and methylene blue number than CAC. Thus WSP-4 can be use for the adsorption of dyes and pollutants from water.

Keywords
Activated Carbon, Walnut shell, Zinc Chloride ($ZnCl_2$), Chemical Activation, Methylene blue number, Iodine number

1. Introduction

Activated Carbon (AC) is a porous carbon material which has a high adsorption capacity. It is widely used in industrial waste water and gas treatment as the adsorbent due to its great specific surface area, ability to reactivate, desired pore structure, good chemical resistance, and different oxygen-containing functional groups on the surface. Nowadays, AC can be produced from a large number of accessible and low cost materials containing a high carbon content and a low inorganic content such as coconut shell, cherry stone[1], rice husk[2], peanut shell[3],walnut shell, etc. The general process to produce activated carbon is based on carbonizing and activating the original carbonaceous material[4].

Activation may be achieved either physically or chemically. A typical physical method consists in a thermal treatment that is carried out in two stages: (1) carbonization of the precursor and (2) controlled gasification (steam flow, temperature, heating rate, etc.) of the crude char. In the chemical method, the starting material is impregnated with a chemical agent, such as KOH, NaOH, K_2CO_3, $ZnCl_2$, $FeCl_3$, H_3PO_4, and H_2SO_4 and the blend is heated to a temperature of 450–700°C.Chemical activation reduces the formation of tar and other byproducts, thereby increasing carbon yield[5]. The type and the amount of the chemical agents used are important to enhance the quality and quantity of the activated carbon obtained. Among the chemical activation agents, $ZnCl_2$ is the most widely used since it resulted in high surface areas and high yields[6].

Activated carbon is classified into one of three types, such as powder, granular, and fibrous according to its size and shape, and each type has its specific

application[7]. Raw materials for activated carbon are chosen depending on their purity, price, potential extent of activation, and stability of supply. Presently, the materials being used to produce carbon are usually coal, wood, petroleum residue, sawdust, coconut shell, pulp sludge, and pitches resulting from the pyrolysis of fossil fuel.

The most important properties of activated carbons are the large specific surface area and, arising from this, the high micropore volume, but good mechanical strength, resistance to abrasion and the possibility of regeneration are also desirable characteristics. Pores of activated carbons can be divided into three group according to their radii. Micropores with pore radii (r_0) smaller than 1.5-1.6 nm, mesopores (1.6<r_0>100 nm) and, macropores (100 nm<r_0)[8]. Micropores determine the adsorption equilibrium characteristics. Mesopores represent adsorption capacity only at high relative vapour pressure range,when capillary condensation effects occur. Mass transfer properties of the adsorbents are primarily determined by macropores.

In this study, waste walnut shell was utilized as the raw material for the production of activated carbon by chemical activation. The activating agent used was Zinc Chloride and conditioning variables examined was temperature. The change in the microstructure of the raw material and produced activated carbon was examined by scanning electron microscopy (SEM). The low-cost walnut shell-based activated carbons were fully characterized, compared with Commercial Activated Carbon(CAC) and subsequently used as an adsorbent for methylene blue removal.

2. Materials and Methods

2.1 Preparation of Activated Carbons

Walnut shells used in this study were obtained from local market. The ultimate analyses of this material are shown in Table 1 [4]. This agricultural waste is considered as a good candidate for conversion to activated carbon because of its relatively high carbon content and low ash.

Table 1: Ultimate analysis of walnut shell

	Ultimate analysis(dry basis,wt%)		
Parameter	C	H	N
Value	66.3	4.74	0.435

The precursor was washed with distilled water for several times to remove dust and other inorganic impurities, oven-dried for 24 h at 110°C to reduce the moisture content, crushed, and sieved to a particle size of 250µm. Zinc chloride was dissolved in water and then impregnated into the shells with a impregnation ratio (defined by the weight ratio of $ZnCl_2$ to walnut shell)of 1:1. The mixture was kept at 110°C for 24 h to incorporate all the chemicals in the interior of the particles, and then carbonized for 3 h in a horizontal furnance at 400°C (WSP-4), 500°C (WSP-5) and 600°C in inert condition of N_2 gas.

The resulting activated carbons were thoroughly washed with 0.1 M hydrochloric acid and distilled water to remove the residual $ZnCl_2$ until the pH value of the washed solution was between 6 and 7. The sample was then dried at 110°C and sieved to a particle size of 100µm to obtain a powder for subsequent analyses and uses. The complete process flowchart is shown in Fig 1.

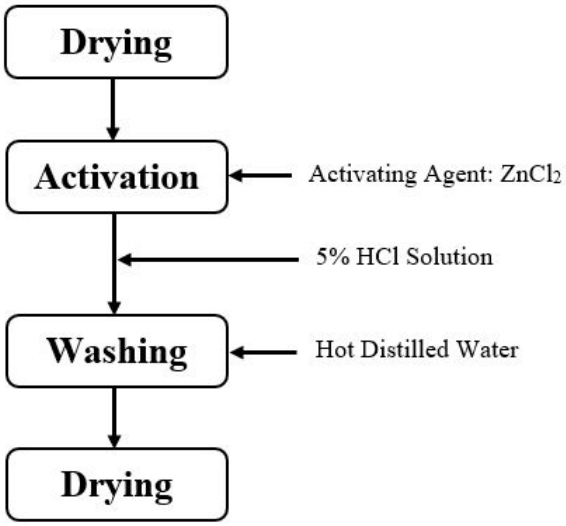

Figure 1: Process for the prepration of Activated Carbon

2.2 Characterization of Activated Carbon

The Iodine value and Methylene Blue number for produced activated carbon was measured by titration to evaluate its adsorption capacity, FTIR was done to investigate the presence of functional groups, XRD to check the crystalline or amorphous nature of the carbon and SEM was employed for the observation of surface microporous structure.

Iodine number: It is the amount of iodine adsorbed (in milligrams) by 1gm of carbon when the iodine

concentration of the filtrate is 0.02 N. In determining the iodine number, 10 ml of 5 % by weight HCl was added to 0.1 gm of activated carbon in a conical flask and the flask was swirled until the carbon was wetted. Then 10 ml of 0.1N iodine solution was added and the content was shaken vigorously for 4 minutes and filtered. The 10 ml of filtrate was titrated with 0.1 N sodium thiosulphate (hypo) in presence of starch as indicator. The concentration of iodine adsorbed by activated carbon was calculated as amount of iodine adsorbed in milligrams[9].

$$Iodine\,Number = C * f$$

Where, f is the conversion factor which is calculated as:

$$f = \frac{Molecular\,weight * Normality * 10}{Weight\,of\,AC * Blank\,reading}$$

where,

$$C = (Blank\,reading - volume\,of\,hypo\,consumed)$$

Methylene Blue Adsorption: Methylene blue is a syntetic cationic thiazine dye of an amorphous nature with a molecular formula $C_{16}H_{18}ClN_3S.XH_20$. It is dark green powder, with a characteristic deep blue color in aqueous solution where it dissociates into an MB cation and a chloride anion.Its chemical structure is shown in Fig 2.

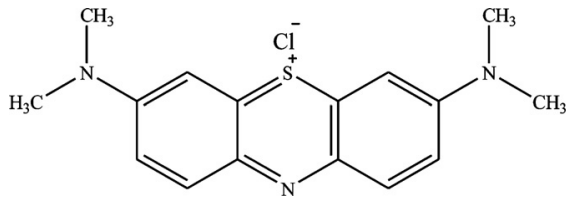

Figure 2: The chemical structure of methylene blue

Methylene blue number is defined as the maximum amount of the dye adsorbed on 1.0 g of adsorbent. Adsorption experiments of the molecules of methylene blue are easy and habitually done to characterize activated carbons with the purpose of obtaining information on the adsorption capacity of the materials. According to the dimentions of the methylene blue molecule, it is mainly adsorbed in mesopores, the pores having diameter 20-500A^0 [10]. Methylene blue number can be calculated by the following formula

$$MBN(mg/gm) = \frac{(C_o - C_e) * V}{M}$$

Where C_o and C_e are initial and equillibrium concentration of MB(mg/L) respectively, M is the mass of adsorbent in gram(gm) and V is the volume of the solution in liter(L) and MBN is Methylene blue number.

Fourier Transform-Infrared(FTIR) Spectroscopy: Surface carbon-oxygen functional groups of the activated carbons were determined recording FTIR spectra. The percentage of transmission of the samples was recorded over 400-4000 cm^{-1}[11].

X-ray Diffraction(XRD): An X-ray diffractometer was used to investigate the diffraction patterns of the activated carbons.Diffraction profiles were recorded for all samples.

Scanning Electron Microscopy(SEM): A scanning electron microscope was used to observe the surface pore structure of the activated carbons prepared on a carbon tape.

3. Results and Discussion

3.1 Iodine number

Iodine adsorption capacity was affected by the activating temperature.Iodine number of carbon activated at 3 different temperature is shown in Table 2. Table 2 shows that the iodine number of carbon activated at 400°C is much higher that at other temperature. Comparing with the value for CAC the result is quite significant. The higher Iodine number of the activated carbon has been attributed to the presence of large micropore structure which might have resulted due to the reactivity of the activating agent $ZnCL_2$.

Table 2: Iodine Number

Sample	WSP-4	WSP-5	WSP-6	CAC
Iodine No.(mg/gm)	1053.44	1040.9	990.739	940.57

3.2 Methylene Blue Number

Methylene Blue Number of carbon activated at 3 different temperature is shown in Table 3. Table 3 shows that the Methylene Blue Number of carbon activated at 400°C is slightly higher that at other temperature.The low value of Methylene Blue Number at 600°C is due to thermal degredation.

Comparing with the value for CAC the result is quite significant. The higher Methylene Blue Number of the activated carbon has been attributed to the presence of large macropore structure which might have resulted due to the reactivity of the activating agent $ZnCL_2$.

Table 3: Methylene Blue Number

Sample	WSP-4	WSP-5	WSP-6	CAC
Methylene Blue No.(mg/gm)	499.54	499.15	479.68	496.21

Fig 3 shows the comparison of both Iodine number and Methylene Blue number for the carbon at 3 different activation temperature and comparing the result with commercial carbon.

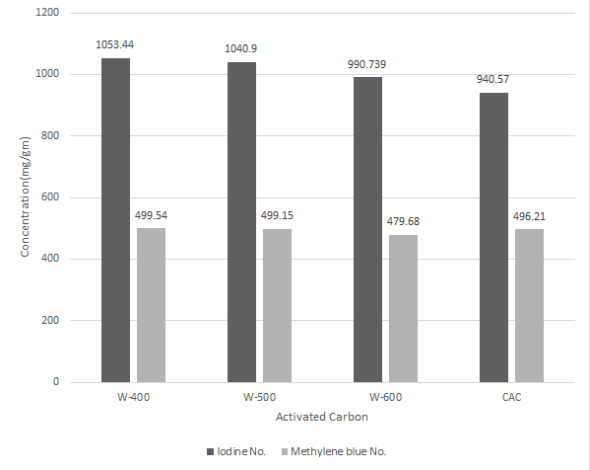

Figure 3: Comparison of Iodine and Methylene Blue Number

3.3 SEM analysis

Scanning electron microscopy(SEM) showed that carbon texture and development of porosity was strongly affected by characterstics of the starting materials and activating temperature. Carbon obtained from walnut shells had an homogeneous structure with a perdominance of macropores. The SEM technique was used to observe the surface physical morphology of the raw material and the prepared activated carbon. Fig. 4a presents the micrographs for walnut shell employed as the raw material for the preparation of activated carbon. The material presents a surface morphology in the form of particles, possibly with a low specific surface area. However, after activation, the compact structure of the sample turned to be crispy and porous.

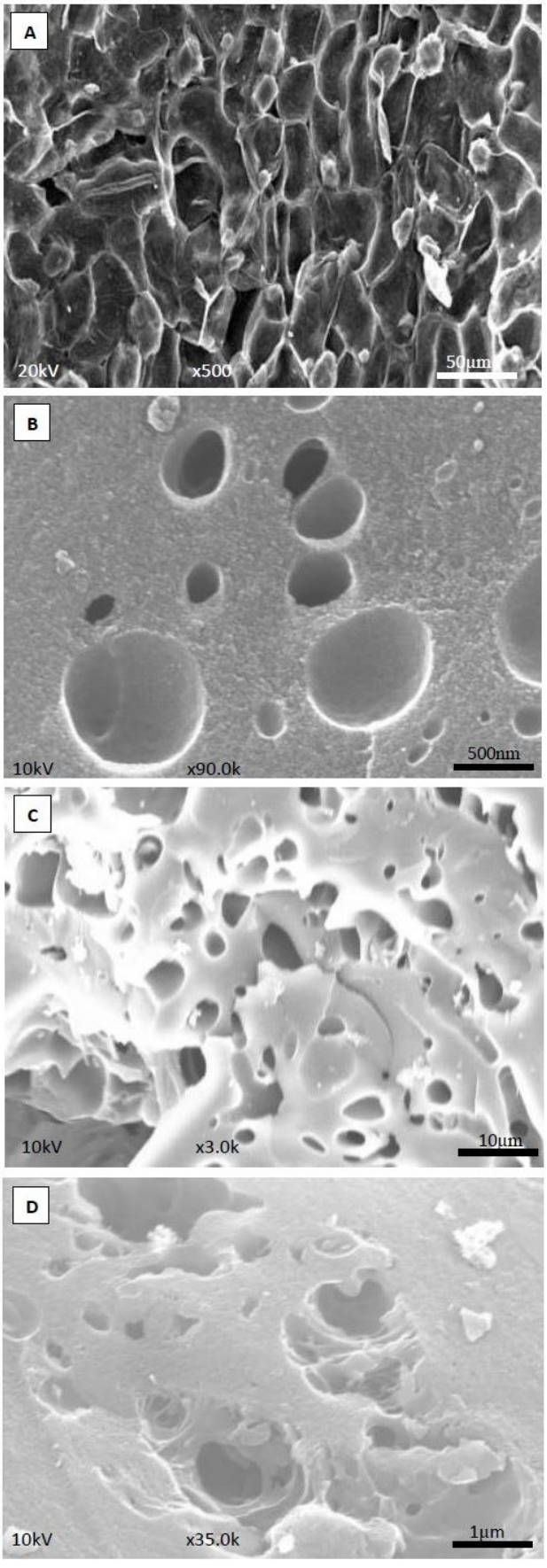

Figure 4: SEM Analysis of Raw Walnut(a), carbon at 400°C(b), carbon at 500°C(c), carbon at 600°C(d))

Fig 4b shows the surface of the WSP-4 activated carbon.At 400°c the pores are clearly visible. Fig 4c shows the surface morphology of WSP-5 activated carbon. In WSP-6 carbon the macropores are not seen due to thermal degradation as shown in Fig 4d. All three surface is smooth and different from the rough surface of the raw walnut shell. All of the pores observed by SEM are macropores.

3.4 FTIR analysis

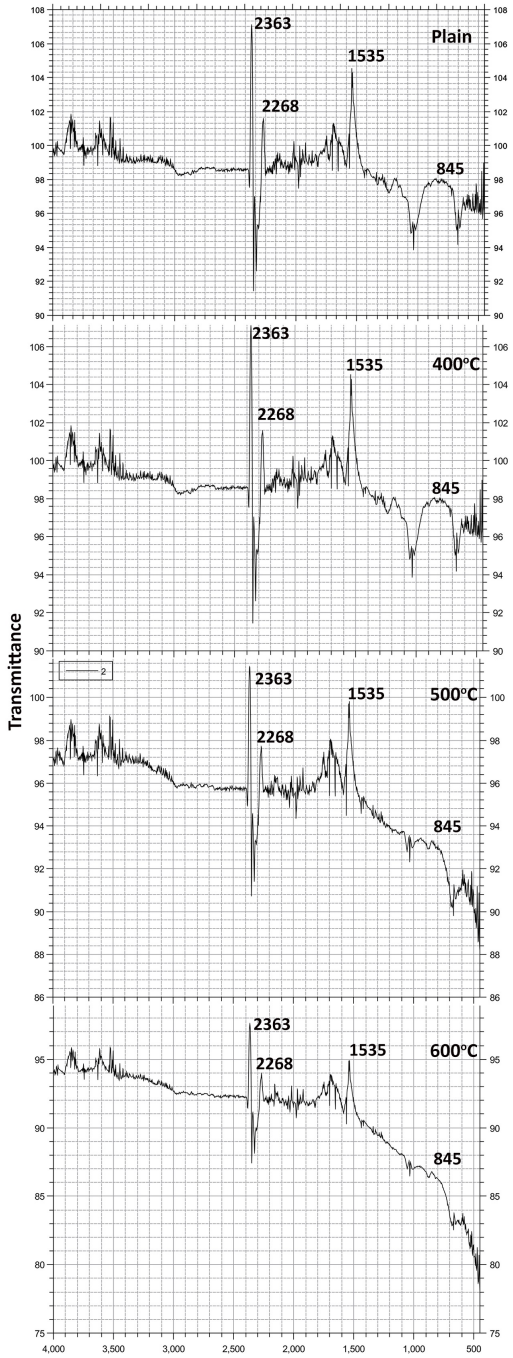

Figure 5: FTIR analysis of the carbon prepared at different temperature

The adsorption capacity of an AC depends not only on its porosity but also on the presence of many chemical functional groups on its surface.FT-IR spectra of the walnut shell-based AC are given in Fig 5.

The raw walnut shell shows indications of various surface functional groups. The wide peak, which located at around 3325cm^{-1} is typically attributed to hydroxyl groups or adsorbed water. The bands located at around 2363cm^{-1} and 2347cm^{-1} correspond to C–H stretching vibrations in methyl and methylene groups. The band appearing at 1694cm^{-1} is ascribed to carbonyl (CO) groups. The olefinic C=C stretching vibrations adsorptions cause the band at about 1535cm^{-1} while the skeletal C=C vibrations in aromatic rings cause another two bands at about 1513cm^{-1} and 1428cm^{-1}. The appearance of a band at 1322cm^{-1} can be attributed to C–O stretching vibrations in carboxylate groups. Finally, the band caused by O–H out-of-plane bending vibrations band is located at 609cm^{-1}.

The FTIR spectra of activated carbon prepared under the optimum conditions is also shown in Fig.5. Fewer functional groups were detected, indicating that the surface functional groups of walnut shell experienced chemical changes during pyrolysis. Compared with the walnut shell, the C–H vibrations in methyl and methylene groups (at 2921cm^{-1} and 2852cm^{-1}) become much weaker after activation, suggesting the carbonization of the material is almost complete. As the release of light volatile matters in the heating process, a new band at 2362cm^{-1} appears that can be ascribed to C=C stretching vibrations in alkyne groups. The peak at 1744cm^{-1},which is observed in the starting material, belonging to carbonyl groups, disappears with the thermal treatment. Many other bands decrease dramatically indicating the decrease in functionality in the main matrix.

3.5 XRD analysis

The X-ray diffraction profiles of the raw shell, the char carbonized at 400°C, 500°C and 600°C are illustrated by Fig 6. The raw material has a less organized structure with no indication of any specific crystalline structure probably due to the various organic impurities and volatile matters present within the structure. There is only one peak centered at around 21, which is assigned to the reflection from the (002) plane. However, as for the char, there are two broad peaks centered at around 23 and 43, which are assigned to the reflection from the (002) plane and the

reflection from the (100) plane, respectively.

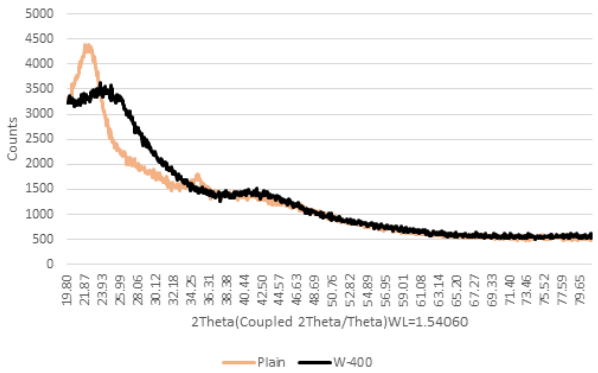

Figure 6: XRD analysis of the carbon prepared at different temperature

4. Conclusion

The results of this study showed that activated carbons prepared from walnut shells by chemical activation exhibit well developed porosity. The properties of the activated carbons were closely related to the activation temperature. The maximum Iodine Number of 1053.44 mg/gm and Methylene Blue Number of 499.54 mg/gm was obtained for carbon activated at 400°C.The FTIR results showed the presence of many oxygen groups and olefinic and aromatic carbon structures in the raw walnut shell. During the activation, the functionality in the main matrix was decreased. SEM micrographs showed that the prepared activated carbon had a well developed porous structure so that the prepared activated carbon is a good candidate for water treatment to remove some organic pollutants.

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