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Synthesis and Characterization of ZnCl2 Activated Carbon Derived from Betel (Areca Catechu) Nut

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Abstract

In this study, activated carbon (AC) was prepared from Betel nut by chemical activation with zinc chloride acid in nitrogen atmosphere at 400 °C. Thermogravimetric analysis of Betel nut was carried out to study the thermal behavior of Betel nut. The resultant activated carbon was characterized by iodine number, methylene blue number, scanning electron Microscopy (SEM), fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). Iodine number, methylene number and surface area of the resultant AC were found to be 874 mg/g, 351 mg/g and 908 m2/g respectively. These values are also comparable to that of commercial carbon. SEM micrograph showed that, the AC is highly porous in nature. The results of FTIR analysis showed the presence of oxygenated functional groups such as hydroxyl, carbonyl, and carboxyl on the AC surface. XRD patterns indicated that, the AC has amorphous structure. The experimental result showed that, Betel nut AC prepared by ZnCl2 activation can be used as a potential adsorbent for water treatment..

Keywords: *Activated carbon, betel nut, zinc chloride, chemical activation.*

1. Introduction

Activated carbons are the most important commercial adsorbents which are widely used to remove pollutants from contaminated water. Its first use came into prominence through its use as an adsorbent for certain poisonous gases in gas masks during World War I. [1]. The most widely used commercial activated carbons have a specific surface area of the order of 600- 1200 m^2/g [2]. The main characteristics of activated carbon are specific surface area and developed pore structure. The pores of AC are classified in three groups: micropores (diameter < 2) nm,

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mesopores (2 nm < diameter < 50 nm), and even macropore (diameter > 50 nm) [3]. The porous texture of the activated carbons depends strongly on both, the activation process and the nature of the precursor.

The methods used for activated carbon synthesis are physical activation and chemical activation. In physical activation, the precursor is first carbonized in an inert atmosphere and then activated in a stream of carbon dioxide or steam. On the other hand, in chemical activation, the precursor is impregnated with a dehydrating agent, usually zinc chloride or inorganic acids, prior to carbonization in an inert atmosphere. Among the different activating agents that can be used, most common are H_3PO_4 and $ZnCl_2$. Chemical activation has several advantages compared to physical activation such as (i) Single step process (ii) High carbon yield (less weight loss) (iii) Better porous structure and (iv) Low activation temperature. Chemical activation is the method usually preferred when the raw material is of lignocellulosic origin [4].

Almost all the carbonaceous materials can be treated as precursor to produce activated carbons. Most of the commercial activated carbons are prepared from fossil fuel–based precursors, such as coal [5] and petroleum [6], which made them expensive and harmful to the environment. This has prompted considerable researches into the low-cost alternatives for the production of activated carbon from agricultural wastes. They are renewable, locally available in large quantities and inexpensive. Consequently, a wide variety of agricultural by-products and wastes has been investigated as cellulosic precursors for the production of activated carbon. These precursors include: coconut shell [6], palm shell [6] pistachio-nut shells [7] nut shells [8] almond shell and hazelnut shell‖ [10].

Betel nut (Areca catechu), fruit of the Areca palm tree is native to south-east Asia. It is an edible fruit and extremely common in many Asian cultures and have a long history of human use. The literature survey reveals that Areca husk carbon [11], Areca nut heartwood [12], and Areca nut coir [13] had been used for the preparation of AC for various application. Moreover, little work has been reported on the production of activated carbon using Betel nut. The aim of this work was to synthesize and characterize activated carbon from Betel nut by chemical activation with zinc chloride.

2. Experimental

2.1. Materials

Betel nuts were purchased from local market, Kathmandu, Nepal. The chemicals used for this investigation and analysis were all analytical grade, purchased from Qualigen, India. Ultra high pure (UHP) nitrogen was used for inert atmosphere during carbonization. Betel nuts were washed with distilled water and dried in an oven at 110 ^oC for 24 hrs and then crushed and grinded into powder. The seed stone powder was then sieved to obtain the fraction of size 212 μm.

2.2. Preparation of carbon

The dried powdered betel nut powder was processed to obtain plain carbon and $ZnCl_2$ activated carbon as described below.

2.3. Carbonizing in inert atmosphere

20 g of dried Betel nut powder was carbonized in a tubular furnace at 400 °C under a continuous flow of nitrogen (75 ml/min) for 3 hrs. The prepared carbon was washed with warm distilled water *till* it becomes neutral. The carbon were then dried at 110 ^oC for 24 hrs and sieved to get the particles of size 106 μm.

2.4. Chemical activation with $ZnCl_2$

20 g of dried Betel nut powder was mixed with 20 g zinc chloride ($ZnCl_2$) in ratio of 1:1 by weight. To the mixture, little amount of distilled water was added, stirred with magnetic stirrer at 70^oC till dry mass was obtained.

Then, the sample was dried in air oven at 110°C for 24 hours. Then, the dried sample was transferred to a quartz tube and placed in horizontal tubular furnace (Accumax, India) and heated at 400 °C under a continuous flow of nitrogen (75 ml/min) for 3 hrs. The prepared AC was washed with warm distilled water *till the filtrate becomes neutral.* The samples were then dried at 110 ºC for 24 hrs and sieved to get the particles of size 106 μm. The resulting AC samples were used for characterizations.

2.5. Characterization of precursor

Thermo gravimetric analysis (TGA) of Betel nut was carried out by a thermogravimetric analyzer (EXSTAR 6300 SEIKO TG/DTA, Korea).

2.6. Characterization of Carbons

Characterizations of activated carbons were performed by determining iodine number, methylene blue number, Scanning electron microscopy (SEM) and Fourier and Transform-Infrared (FTIR) spectroscopy.

Iodine number of activated carbons was determined according to ASTM D4607-94 method [14]. Methylene blue number of activated carbons was determined by single point adsorption isotherm studies according to Standard Method [15]. Surface area of activated carbons was estimated by iodine and methylene blue numbers using multiple regressions [16]**.** Surface functional groups of the $ZnCl_2$ activated carbon were determined by recording FTIR spectra on the Thermo Electron Corporation, Nicolet 4700 at room temperature. The % of transmission of samples was recorded over 500–3500 cm^{-1}. Surface morphology of the prepared activated carbon was studied using scanning electron microscope U-8000, Hitachi Co. Ltd. Japan.

3. Results and Discussion

3.1. Characteristics of precursor and carbon

3.1.1. Thermogravimetric analysis (TGA) of Betel nut

In order to predict thermal behavior of the Betel nut, the rate of weight loss of the sample as a function of temperature was studied. TGA graph of Betel nut is shown in Figure 1.

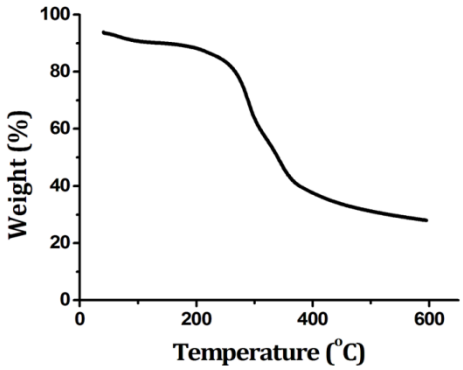


Figure: 1 TGA graph of Betel nut.

Thermal degradation of Betel nut was divided into three zones, corresponding to the decomposition of their main components (cellulose, hemicellulose and lignin). A little mass from 30 to 200ºC is primarily due to the evaporation of free water present. After that, mass loss decreases significantly from 200 to 400 ° C. It might be caused by decomposition of cellulose, hemicellulose. Since lignin is the most stable and complex of these three components, it is much difficult to decompose. The mass loss corresponds to the degradation of lignin takes place between 400 and 600ºC. Therefore, 400°C was selected as the carbonization temperature in this study.

3.1.2. Iodine number and methylene blue number of activated carbon

Iodine number, methylene blue number and surface area of carbons are shown in figure: 2.

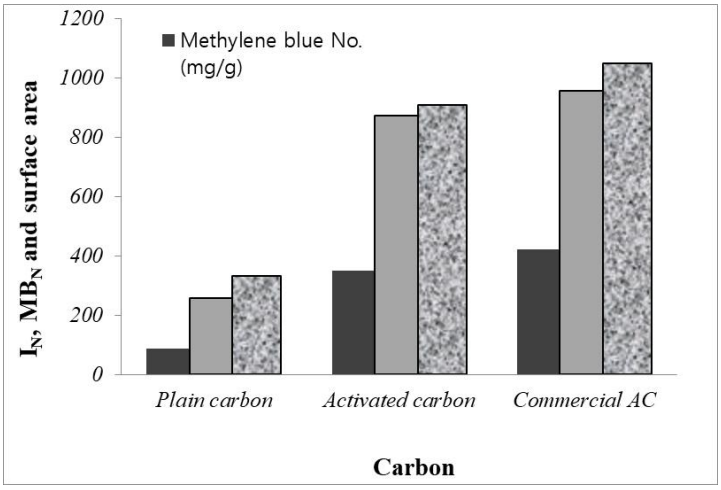
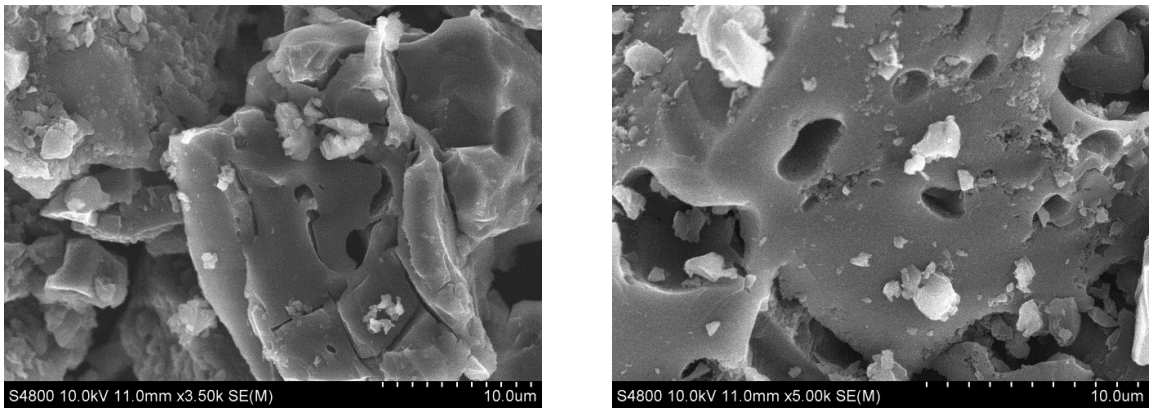


Figure 2. Iodine number, methylene blue number and surface area of carbons.

Iodine number and methylene blue number are useful indicators to evaluate the adsorptive capacity of activated carbon. Iodine number is the amount of iodine adsorbed (in milligrams) by 1 g of carbon [16]. It is a measure of micropore content (micropores having pore diameters of less than 2 nm) of the activated carbon and relates to the ability of activated carbon to adsorb low molecular weight substances. Methylene blue number is defined as the milligram of methylene blue adsorbed onto 1.0 g of carbon [15]. It is a measure of mesopore content (mesopores have a diameter between 2 and 50 nm) and indicates ability of activated carbon to adsorb high molecular weight substances. As shown in the figure.1, iodine number, methylene blue number and surface area of activated carbon are much higher compared to the plain carbon. It suggested that $ZnCl_2$ activation highly increased microporosity, mesoporosity of char. The values are also found to be comparable to that of commercial activated carbon indicating the better developed porosity with surface area. Hence, the prepared AC has high adsorption capacity for various compounds.

3.2. Scanning electron microscopy (SEM) image

SEM images of the plain carbon and activated carbon is shown in Figure: 3.



(a) Plain carbon (b) Activated carbon

Figure: 3 SEM Images of the plain carbon and activated carbon.

The SEM image shows that the plain carbon (Figure: 3 a) has a relatively smooth surface with no significant pore structure whereas; the activated carbon (Figure: 3 b) contains cylindrical pores and cavity of different size and shape on its surface. It seems that the pores and cavities on the surfaces of carbons resulted from the evaporation of the activating agent (zinc chloride) during carbonization, leaving the space previously occupied by the activating agent. These pores can be regarded as channel to the porous systems which increases the surface area for adsorption. During chemical activation of lignocellulosic materials with $ZnCl_2$, it acts as dehydrating agent. Zinc chloride promotes the extraction of water molecules from the lignocellulosic structures leading to generation of porosity. Impregnation with $ZnCl_2$ first results in degradation of the material and, on carbonization, produces dehydration that results in charring and aromatization of the carbon skeleton and creation of the pore structure [17]. A similar result was also observed in development of nanoporous structure in carbons by chemical activation with zinc chloride [18].

3.3. Fourier Transform Infrared (FTIR) Spectra

The surface functional groups of activated carbon determine its adsorption capacities. These characteristics are highly dependent on the surface oxygen/nitrogen containing functional groups. Acidic oxygen containing functional groups based on carboxyl and phenolic hydroxyl groups contribute to the polarity of adsorbents thus increase their adsorption capability for polar compounds [9]. Surface functional groups on the carbon surface were determined by FTIR spectra. FTIR of plain carbon and activated carbon is shown in Figure: 4.

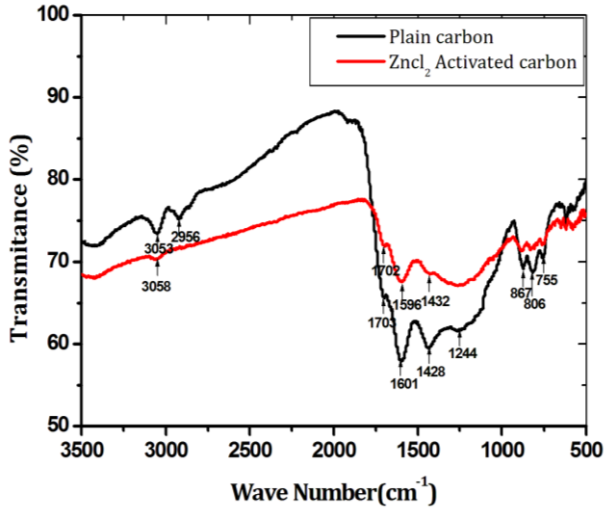


Figure: 4 FTIR of plain carbon and activated carbon.

The FTIR spectra of both carbons exhibited a broad band at around 3400 cm^{-1} assigned to the O–H stretching vibration of hydroxyl functional groups in phenols and alcohols [18]. However, the intensity of the band in activated carbon is weaker than in plain carbon. It is probably due to the loss of hydroxyl groups and elimination of volatile molecules from plain carbon. The band located at around 1700 cm^{-1} is related to the stretching vibration of C=O in ketones, aldehyde, lactone, and carboxyl. The band around 1600 cm-1 is attributed to the C=C stretching vibrations of conjugated C=C in aromatic ring or oxygen-aromatic bonding in aromatic ether [19]. The FTIR spectra suggested that, the AC contains oxygenated functional groups such as hydroxyl, carbonyl which may be the potential active sites for interaction with polar adsorbate molecules. Similar results were also found in the activated carbon prepared oil palm shell by chemical activation with KOH [20].

X-Ray Diffraction can be used to provide information about the structure of crystalline or amorphous material. Amorphous materials has a broad hump and no any sharp diffraction peaks, the presence of sharp diffraction peaks

is an indication of crystalline material. The XRD patterns of plain carbon and activated carbon samples are shown in Figure.5.

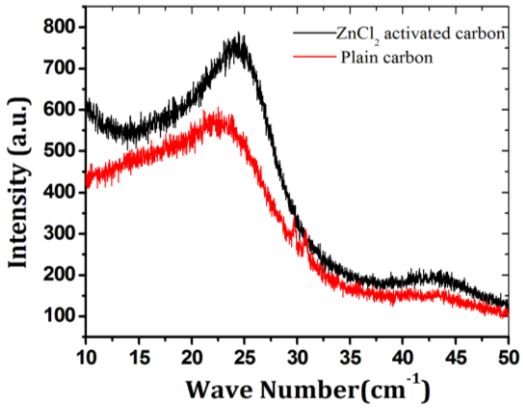


Figure 5. XRD patterns of plain carbon and activated carbon.

XRD patterns of both carbon samples show diffraction patterns with two broad peaks at diffraction angles (2θ) of around 23 and 43 degree. The diffractions assigned to the reflection are coming from (002) and (100) planes respectively. There is no sharp diffraction peak was observed in the XRD pattern, attributing to the non-crystalline (amorphous) nature of the carbon. Hence it indicated that both plain carbon and activated carbon were amorphous in structure. The XRD pattern of the AC is similar to the KOH activated oil palm empty fruit bunch, bamboo stem, and coconut shell carbon [21].

4. Conclusion

In the present study, activated carbons with a well-developed pore structure are prepared from Betel nut by chemical activation with $ZnCl_2$. Iodine and methylene blue adsorption also indicates that activated carbon is highly micro and mesoporous with high surface area. These values are comparable to that of commercial activated carbon. The porous nature is also indicated by SEM image. FTIR results indicate that activated carbon contains –OH, >C=O as oxygen containing surface functional groups. The prepared $ZnCl_2$ activated betel nut carbon can be effectively used as an adsorbent for removing hazardous compounds from industrial waste gasses and wastewaters.

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