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Production of Activated Carbon from Sugarcane Bagasse by Chemical Activation with $ZnCl_2$: Preparation and Characterization Study

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Abstract

A protocol producing the activated carbon (AC) with high surface area and porosity with large adsorption capacity from non-toxic and low cost precursor source was developed. The ACwas prepared from sugarcane bagasse with $ZnCl_2$as activating agent. Three preparing temperatures including 400°C, 500°C, and 600°C were investigated to compare the structural difference of the ACs. The properties of the ACsfabricated at these temperatures were determined using relevant techniques such as scanning electron microscopy (SEM), X–ray diffraction (XRD), thermo–gravimetric analysis (TGA),Fourier transform infrared (FT–IR) spectroscopy and nitrogen adsorption/desorptionmeasurement.Characterization results showed that the maximum BET surface area of the AC is1502.1 m^2/g at 500°C. XRD patternsand SEM micrographs revealed that the ACshave the amorphous structure and heterogeneous surface. IR spectra also proved the presence of functional groups O–H, O–N asymmetric and C–C aromatic in the carbon. Moreover, the maximum AC yield of 45.7% was achieved at 500°C.

Keywords: Activated carbon; Sugarcane bagasse; Chemical activation; Structural characterization; $ZnCl_2$.

Introduction

The rapid industrialization is accompanied with adverse effects on living environment and human health. Solutions for greenhouse gas emissions and hazardous component contamination in groundwater have attracted the attention of environmental scientists around the world[1]. Recently, many studies on absorbability of novel material generation have been promoted towards sustainable development tendency[2]. However, some considerable impediments such as expensive production cost and energy dilapidation have restricted the application scope of those materials[3]. Among the prominent materials such as zeolites, metal–organic frameworks, biomass, and silica/polymer materials, ACs have emerged as potential materials with extensive applications[4–6]. Because ACs contains a number of remarkable characteristics, for example high specific surface area, high porosity and favorable pore–size distribution, AC preparation protocols have been long discussed among material researchers[7].

Synthesis of ACs from sugarcane bagasse precursoris considered as a highly feasible solution because this agricultural bio-waste is cheap, abundant and locally available. Yearly, the fined sugar manufacturing factories in Vietnam dispose of thousands of tons of sugarcane bagasse from surrounding sector. Consequently, untreated sugarcane bagasse eliminationis not only responsible for useless loss of a large amount of carbonaceous precursors, but also might cause several serious environmental issues. Accordingly, utilizing sugarcane bagasse for the purpose of low–cost AC spreparationis one of potential approaches towards green production[8]. Generally, ACs can be manufactured through a continuous two–step procedure including chemical activation and physical activation[9]. In the chemical activation step, the raw materials are impregnated with strong dehydrating chemical agents such as $ZnCl_2$, H_3PO_4, KOH and K_2CO_3[10]. The significant role of activating chemicals is to generate new vessels and to expand the structure of pores. Moreover, the chemical agents inhibit the formation of tar during the pyrolysis, in which the decomposition of the precursor releases none–carbon ingredients such as vapor and volatile compounds[11]. Among a number of effective activating agents, $ZnCl_2$ illustrates its efficient impregnation in realizable conditions[12]. For instance, several publications proved that $ZnCl_2$ can support formation of micro–porosity, giving extremely high surface area and increase in AC productivity[13]. In addition, $ZnCl_2$is utilized as a Lewis acid with crucial performance is to enhance the reaction of aromatic condensation[14]. As a result, hydrogen molecules are eliminated from hydro–aromatic structure of the precursor to create the active sites on surface. Regardless of some strict rules of zinc presentin the food and pharmaceutical industries, agent $ZnCl_2$with its outstanding advantages for preparation of ACs was used more widely than other chemicals[15,16].

This study concentrates on the fabrication and characterization of AC synthesized from the sugarcane bagasse. The ACs are obtained via two–step procedure including chemical and physical activation. Structure analysis were employed using a number of characterization techniques including XRD, SEM, FT–IR, N_2 adsorption/desorption for determination of surface area, pore volume and pore distribution.

Materials and Methods

Preliminary treatment of precursor: Sugarcane bagassewas collected from local cane–juice shops in Ho Chi Minh city, Vietnam. They were initially washed with hot distilled water several times before drying under the sunshine. The materials were then ground with diameters of approximately 1.0 mmand stored in sealed plastic bags for further experiments.

Production of AC: The ACs were synthesized by the following protocol. In the chemical activation step, 30g of dried sugarcane bagasse was soaked in $ZnCl_2$ solution at room temperature for 24h. The impregnation ratio (IR) of $ZnCl_2$ solid and the pretreated sugar bagasse was 1.0. The impregnated samples were then dried at 105^{o}C for 24h. In the physical carbonization step, $ZnCl_2$–impregnated sugar bagasse samples were heated with a N_2 flow (400 cm^3/min) in anelectric furnace (Carbolite, England.) for 1h. The heating rate was 10^{o}C/min and the calcination temperatures range was from 400^{o}C to 600^{o}C. Thechar was repeatedly washed with deionized water in order to eliminate zinc residual until the solution is neutralized to achieve activated carbon. Finally, product of ACs were ground to fine powder and stored for further uses. The AC yields were quantified by the following equation:

$$Yield(\%) = \frac{w_c}{w_o}.100,$$

Where: w_c and w_o are the weight of activated carbon (g) and the weight of dry precursor (g), respectively.

Materials and instruments: The XRD measurements of ACs were implemented on D8 Advance Bruker powder diffractomete with a Cu–Kα excitation source. The diffraction spectra were recorded with glancing rate of 0.02^o/s. The angle range (2θ) was investigated between 0^o and 50^o. All samples were performed at room temperature and beneath the atmosphere for this study. The FT–IR spectra of samples were recorded by using the Nicolet 6700 spectrophotometer instrument. The solid mixture of potassium bromide crystals and AC particles was ground to fine powder. The spectra were then recorded at room temperature with the wave number range of 4000 – 400 (cm^{-1}). The morphology of material surface was identified by SEM technique. The instrument S-4800, Japan utilized an accelerating voltage source of 10 kV with magnification of 7000. Moreover, the characterizations of surface morphology were observed at various length equivalents from 5 µm to 1 mm. Thermo decomposition of the materials were performed using TGA Q500 Universal V4.5A instrument. The experiments were performed under nitrogen atmosphere with flow rate of 40 cm^3/min and maintained during the decomposition. The heating rate was 10^{o}C/min from the ambient temperature to 1000^{o}C. In addition, the AC samples were positioned in a platinum plate and degassed in vacuum in prior to use.

The N_2 adsorption/desorption isotherms were obtained by using the Micromeritics 2020 volumetric adsorption analyzer system. The BET isotherm equation is used to calculate the specific surface area. The Dubinin–Radushkevich (DR) approach is employed to measure the micro–pore volume. The pore size distribution is illustrated by non–local density functional theory (NLDFT)[17]. Moreover, in order to eliminate impure components from the pores, the samples were activated beneath vacuum pressure in prior to analysis.

Results and Discussion

In this study, the characteristics of sugarcane bagasse were identified by proximate analysis method with the results shown in Table-1.

The structure of the AC samples prepared from sugarcane bagasse at activation temperatures of 400^{o}C, 500^{o}C, and 600^{o}C was characterized by XRD technique (Figure-1). Generally, the appearance of shape peaks at 32.2^o, 34.8^o, and 36.1^o illustrates the presence of residual zinc chloride[18]. On the other hand, the X-ray diffraction diagrams reveal negligible change of the AC structure regardless of temperature fluctuations between 400^{o}C and 600^{o}C. Although the broad of diffused peaks were appeared at narrow angles, the AC structures are considered as amorphous nature and they possess heterogeneous surface[19].

FT-IR spectra were recorded to characterize the functional groups available on the as-synthesized AC surface (Figure-2). It is well known that the agricultural comodities are largely composed of cellulose, hemicellulose and lignin. As provided by the FT-IR spectra, a stretching wave number range at about 3421–3392 (cm^{-1}) reveals the existence of O–H functional groups. The presence of nitrogen compounds in the structure is confirmed by O–N asymmetric stretch peak at 1541 cm^{-1}. Moreover, the band wave number of around 1560 cm^{-1} proves that porous carbons contain the C–C stretching for aromatic ring. Herein, the functional groups identified by FT–IR technique are relatively consistent with the previous publication[20].

The morphological micrographs of material surface for three samples (SC400, SC500, and SC600) synthesized at various temperatures were shown in Figure-3. SEM images of AC samples showed that ACs have irregular and highly porous surface. Importantly, a number of pores, defects and vacancies available on the AC are expected to contain highly active sites supporting its adsorption property[21]. It is worth noting that the higher activation temperatures led to the formation of more irregular surface with larger amount of fragments.

Table-1
Proximate analysis of sugarcane bagasse

pH (30°C)	Moisture (%)	Ash (%)	Volatiles (%)	Fixed carbon (%)
7.1	11.54	2.67	56.76	29.03

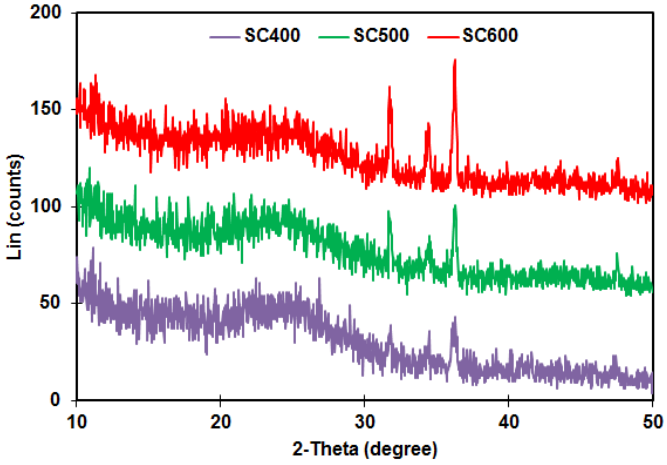


Figure-1
XRD spectra of the AC samples SC400, SC500 and SC600

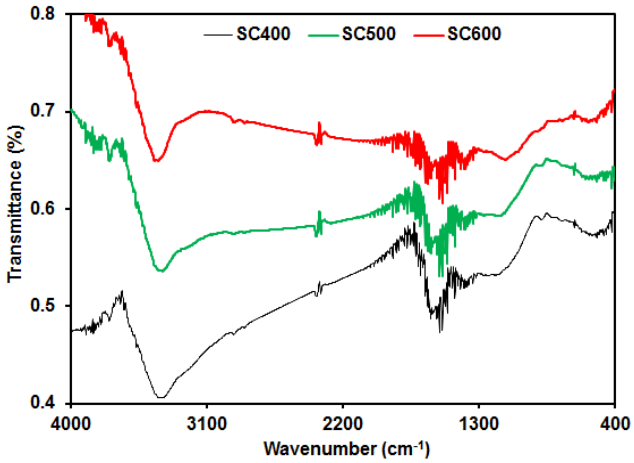
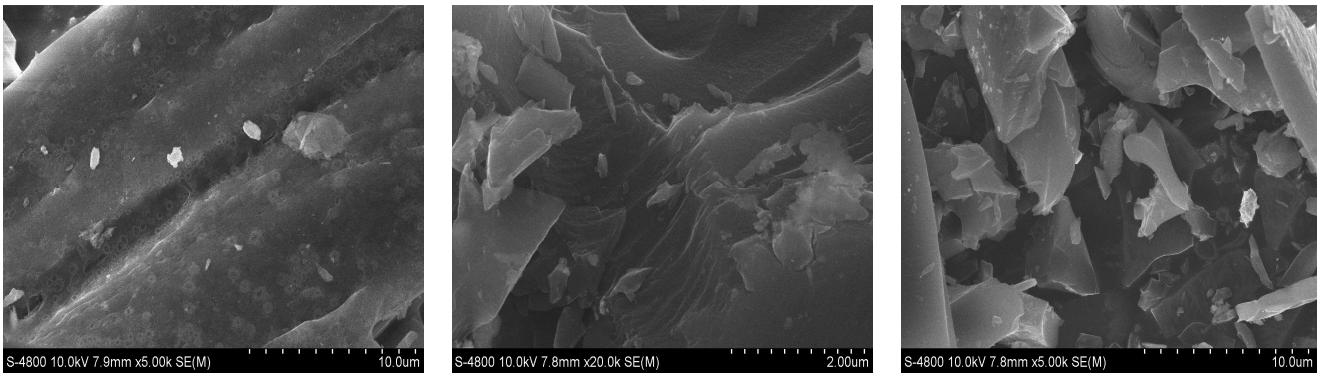


Figure-2
FT-IR spectra of the AC samples SC400, SC500 and SC600



SC400 **SC500** **SC600**

Figure-3
SEM micrograph of the AC samples SC400, SC500 and SC600

Figure-4 shows the decomposition behaviors of the activated carbons prepared from different activation temperatures. Generally, as the temperature increased, the more AC sample weight lost was observed. Among the AC samples, the weight loss of SC600 is negligible (approximately 10%) while the weight loss of SC400 is significant (approximate 35%) and the weight loss of SC500 is slight (approximately 15%). In details, decrease of sample weight during the decomposition takes place in two stages. In the first one, loss of absorbed water is about 2 – 5 (%) at temperature below 100°C. In the second stage, the significant decrease of AC weight occurs in the temperature range of 400°C - 850°C much likely resulted from the decomposition of lignin and hemicellulose components[22].

The distribution of pore size of the ACs can be found in Figure-5. In details, the calculation data demonstrates a negligible difference of average pore size for all three samples. The average pore diameter is 8.5 (Å) for SC500 and SC600 while this value is 8.7 (Å) for SC400. On the other hand, measurement results of micro–pore volume are provided in Table-2. It is evident that the activation temperature strongly affects Dubinin–Astakhov (DA) micro–pore volume. The moderate temperatures (400°C and 500°C) facilitate the development of micro–pore volume, 0.82 and 0.86 cm^3/g, respectively. The higher temperature (600°C) gave lower micro–pore volume of 0.63 cm^3/g.

Dependence of nitrogen adsorption/desorption capacity of the synthesized ACs on temperature and relative pressure was shown in Figure-6. Determination of the structural characterization for the prepared ACs was conducted using physisorption technique (Figure-6). Measurement results of BET specific surface of the ACs are reported in Table-2. Correspondently, the investigated values illustrate that ACs possess a very high specific surface area and large micro–porous structure. The AC activated at 500°C (SC500) has the highest specific surface area, 1502.1 m^2/g. This achievement indicates that the ACs can be utilized as a potential gas and liquid adsorbents.

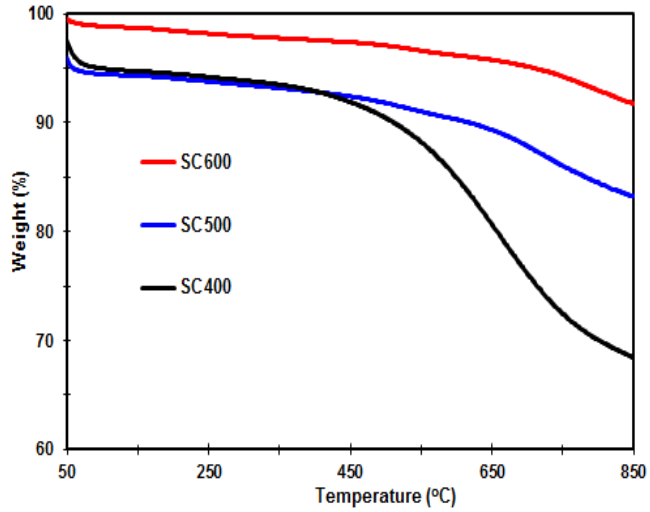


Figure-4
TGA analysis of the AC samples SC400, SC500 and SC600

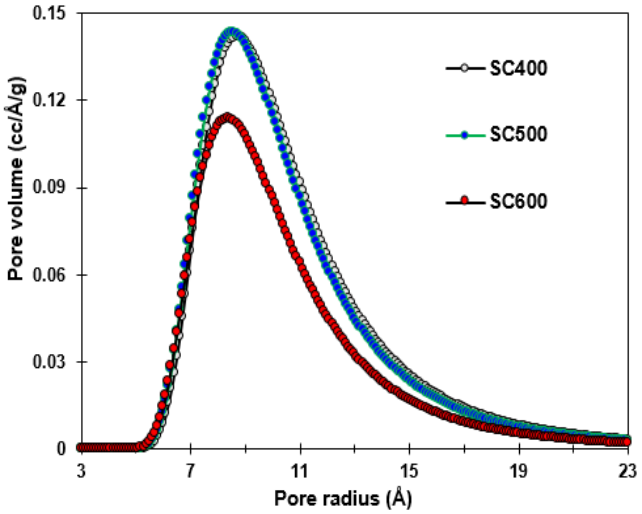


Figure-5
Pore size distribution of the AC samples SC400, SC500 and SC600

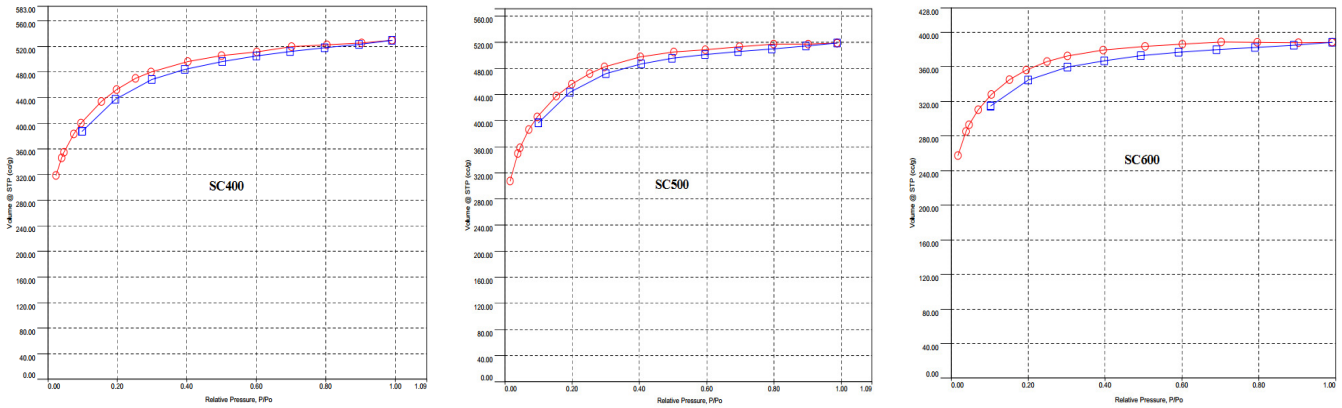


Figure-6
Nitrogen adsorption/desorption isotherm of the samples of SC400, SC500 and SC600

Table-2
Summary comparison of the AC samples

Samples	Activation agent	Activation temp. (°C)	Impregnation ratio (-)	AC yield (%)	Pore size (Å)	BET (m^2/g)	DA volume (cm^3/g)
SC400	$ZnCl_2$	400	1.0	41.3	8.7	1495.57	0.82
SC500	$ZnCl_2$	500	1.0	45.7	8.5	1502.10	0.86
SC600	$ZnCl_2$	600	1.0	40.0	8.5	1143.84	0.63

Conclusion

In the present study, the effects of activation temperatures including 400°C, 500°C and 600°C. $ZnCl_2$ activated ACs were successfully synthesized from the low-cost sugarcane bagasse with high carbon yield values ranging from 40.0% to 45.7%. According to the analysis results, the as-prepared activated carbons have highly irregular structure with a number of surface functional groups neccesary for adsorption property. The higher activation temperature offered higher irregularity and porosity; the highest surface area of about 1500 m^2/g was found with the activation temperature of 500 °C. The advanced property of the as-synthesized sugarcane baggasse-based activated carbon is very promising for application in many areas involving adsorption processes.

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