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ORIGINAL ARTICLE

Characterization of acid-leaching cocoa pod husk (CPH) and its resulting activated carbon

Wen-Tien Tsai[1] · **Po-Cheng Huang**[2]

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Abstract

In order to enhance the adsorption capacity of activated carbon (AC) from cocoa pod husk (CPH) and reuse the solution after the acid-leaching of CPH as a liquid fertilizer, CPH was first leached by acid and then used as a precursor (CPH-A) for preparing ACs by physical activation at a temperature range of 650–850 °C in this work. Based on the proximate analysis, mineral compositions, thermogravimetric analysis, and thermochemical properties, the differences between CPH and CPH-A were investigated. The chemical and pore properties of the resulting ACs were further studied. The results show that the pretreatment of CPH with hydrochloric acid led to removal of over 90% of the ash content in the CPH, mainly composed of potassium minerals. The Brunauer-Emmet-Teller (BET) surface area of the AC derived from CPH-A at 650 °C is 355.8 m^2/g, significantly larger than that (i.e., 1.1 m^2/g) of the AC derived from CPH. The higher activation temperature (e.g., 900 °C) is beneficial to the pore development of the resulting AC (e.g., BET surface area > 1300 m^2/g). In addition, the carbon (C) and sulfur (S) contents of the resulting ACs indicate an increasing trend as the temperature increased from 650 to 850 °C, but a decreasing trend in the hydrogen (H), nitrogen (N), and oxygen (O) contents.

Keywords Cocoa pod husk · Acid-leaching · Physical activation · Activated carbon · Pore property

1 Introduction

Carbon materials have been widely used in a variety of industrial and environmental applications such as energy materials in supercapacitors and adsorption materials for purification/remediation [1]. In this regard, activated carbon (AC), used as adsorbents, antidotes, and catalysts (or catalyst supports), may be one of the most important carbon materials for removal of contaminants and for purification of valuable chemicals [2]. Practically, the carbonaceous precursors for producing ACs are mainly based on coals, coconut shell, and wood because they have high carbon contents, large amounts (i.e., low-cost raw materials), or low ash compositions (inorganics) [3]. However, commercial AC products are relatively expensive, suggesting that it is necessary to find new low-cost starting materials for producing them. Therefore, many researchers have recently adopted the reuse of agricultural by-products (biowaste materials, or agricultural residues) as precursors for AC production [4–6]. Due to their amounts in abundance, many efforts on upgrading their available reuses have attracted much attention. On the other hand, some of them discarded directly into soils as organic fertilizer could cause environmental problems, including greenhouse gas (i.e., CO_2 and CH_4) emissions, unpleasant odor, and inoculum sources for plant diseases (e.g., black pod rod) because of their lignocellulosic components and biodecomposition features [7].

Cocoa is an important fruit in the tropical countries because its seeds (beans) are commonly processed to make chocolate products and other foodstuffs. However, the cocoa industry will generate large amounts of agricultural by-products during the cocoa bean-producing process. Cocoa pod husk (CPH) is the most significant one. It represents over 50% of the whole weight of the cocoa fruit [8, 9]. More significantly, the mass ratio of CPH to cocoa beans may be up to 10 [10], accounting for over 10 million tons of CPH being generated every year [11]. Although CPH was often discarded as an organic

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✉ Wen-Tien Tsai
wttsai@mail.npust.edu.tw

[1] Graduate Institute of Bioresources, National Pingtung University of Science and Technology, Pingtung 912, Taiwan

[2] Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, Pingtung 912, Taiwan

fertilizer on the farm, it has some alternative applications [12], which include animal feed, food antioxidants, biomass fuel for boilers, potash (from CPH) for soft soap manufacturing, filling material for bioplastics and biocomposite, biosorbent for removal of pollutants in water, precursor for AC production, dietary fibers. Based on its lignocellulosic content and plentiful amount, CPH seems to be one of excellent precursors for AC production, suggesting that there is the potential for its value-added utilization.

The methods for manufacturing AC include physical activation and chemical activation. Although the latter process can be carried out in a single step, thus providing a lower activation temperature (energy consumption), a higher carbon yield, and larger pore properties [13], the former is a cleaner process commonly used in the industrial production because it does not involve the release of chemical activating agents such as zinc chloride ($ZnCl_2$) [2]. Regarding the researches on the reuse of CPH as a low-cost precursor for producing AC by physical activation, only a few investigators have conducted in recent years. The CPH-based AC was produced at carbonization of 800 °C followed by CO_2 activation at 850 °C, showing that the largest surface area of the resulting AC was about 560 m^2/g [14–16]. The authors further treated the CPH-based AC with hydrochloric acid (HCl), resulting in higher surface area because of ash leaching and new pore development. The biomass acid pretreatment studies also reported similar findings [17, 18]. Furthermore, other authors investigated the CPH-based AC production using carbonization at 500 °C and subsequent CO_2 activation at 700 °C for 2 h [19]. Their results indicate that the resulting AC only offers the surface area of 503 m^2/g.

The ash content in the precursor also plays a vital role in the pore properties. In some circumstances, these minerals in the precursor or its resulting AC will hinder pore development during activation, or act as a catalyst during steam regeneration [20]. Due to the significant potassium content involved in CPH, the acid-leaching solution may be reused as a liquid fertilizer. In this work, CPH was initially treated with inorganic acid (HCl) to permit the reduction of ash content because of leaching by acid dissolution. In order to compare the pore properties of ACs from original CPH and leached CPH, a series of physical (CO_2) activation experiments were performed at different temperatures (i.e., 650, 750, and 850 °C) held for 30 min. Regarding their variations on the chemical and pore properties, the resulting ACs were further characterized by the N_2 adsorption-desorption isotherms and elemental analyses.

2 Materials and methods

2.1 Materials

The CPH samples were collected from a local cocoa farm in Neipu Township (Pingtung County, Taiwan). To avoid the material deterioration and fermentation odor generated, the wet samples were put into an oven set at about 105 °C for several days (denoted as-received CPH). Subsequently, this dried CPH was crushed and then screened to get the fraction of − 20/+ 40 mesh (particle size 0.63 mm on average) as the feedstock samples, which were used in the thermochemical characterization measurements and physical activation experiments.

2.2 Acid pretreatment

Acid pretreatment (i.e., acid-leaching) was performed to remove minerals (i.e., ash) from the CPH sample by mixing 100 ml 3 M HCl and 10 g feedstock in a 250-ml Erlenmeyer flask. The mixture solution was stirred on a hot plate (Corning Co., USA; Model: PC-420D) at about 80 °C (353 K) for 30 min, and then cooled to room temperature for decanting (solid-liquid separation). Finally, the solid fraction was washed with hot (about 90 °C) deionized water (150 ml each batch) for three times using a vacuum filter. The de-ashed CPH sample (labeled as "CPH-A") was then dried in a heated air circulation oven at about 105 °C (378 K) overnight. The washing also plays a role on the increase of the pore properties of the AC from CPH-A because of the removal of water-soluble components in the AC precursor [17].

2.3 Thermochemical characterization analyses of CPH and CPH-A

2.3.1 Proximate analysis

According to the Standard Test Method set by the American Society for Testing and Materials (ASTM), the proximate analysis was used to determine the contents (wt%, dry basis) of volatile matter, ash, and fixed carbon. The fixed carbon is determined by subtracting the weight percentages of volatile matter and ash from a sample. Volatile matter was determined by the difference between the CPH mass and its residual mass after heating at 950 °C for 7 min under inert atmosphere. The ash contents of the precursors (i.e., CPH and CPH-A) play a vital role in the production and characterization of AC. The samples were burnt in the muffle furnace at about 750 °C for a minimum of 4 h. Ash composition was further analyzed with an inductively coupled plasma-optical emission spectrometer (ICP-OES).

2.3.2 Ultimate (elemental) analysis

In general, the ultimate analysis refers to the contents of organic elements except for its moisture and inorganic constituents (ash) [21]. An elemental analyzer (vario EL III; Elementar Co., Germany) was used to determine its elemental concentrations, including carbon (C), hydrogen (H), nitrogen

(N), sulfur (S), and oxygen (O). In this analysis, each sample (1–3 mg) was analyzed in duplicate, showing that the repeated measurement error is within 1% of the mean value.

2.3.3 Thermogravimetric analysis

In order to evaluate the pyrolysis conditions for producing char under the inert atmosphere, the thermogravimetric analysis (TGA) curves for the dried CPH and CPH-A samples were obtained using a thermal analyzer (TGA-51; Shimadzu Co., Japan). The sample of known weight (about 0.2 g) was placed in a quartz crucible and then heated from room temperature to 1000 °C at a constant rate of 10 °C/min under a N_2 flow environment (50 cm^3/min). Furthermore, the derivative thermogravimetric (DTG) analysis curves can be obtained by converting mass loss data into mass loss rate as a function of temperature.

2.3.4 Higher heating value analysis

It is well known that the ash content of biomass lowers its calorific value or higher heating value (HHV). Herein, the HHV is a measured value of the specific energy of combustion for unit mass of a biomass (or fuel) burned in oxygen in an adiabatic bomb. In the work, the HHVs of dried CPH and CPH-A samples (about 0.5 g) were obtained by a calorimeter (Calorimeter ASSY 6200; Parr Instrument Co., USA).

2.3.5 Trace element analysis

The inorganic elements in the ash are alkali metals, alkaline earth metals, transition metals, and other elements, depending on its starting material. An inductively coupled plasma-optical emission spectrometer (ICP-OES) (Agilent 725; Agilent Co., USA) was used for the determination of 20 relevant elements. They include arsenic (As), aluminum (Al), barium (Ba), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), phosphorus (P), lead (Pb), silicon (Si), strontium (Sr), titanium (Ti), and zinc (Zn). Prior to the ICP-OES analysis, the concentrated HNO_3/HCl/HF solution was employed for the dissolution of the dried CPH and CPH-A samples (about 0.05 g) in a microwave digester at two stages (first 170 °C for 20 min, then 190 °C for 20 min).

2.4 Physical activation experiments

In order to produce AC with a cleaner process, the method of physical activation was employed using gasifying gas carbon dioxide (CO_2) in this work. However, this process involves the carbonization of the starting precursor at temperature below 600 °C, followed by the gasification at higher temperature (above 700 °C). In this study, a series of carbonization-activation experiments was carried out to produce the CPH-based ACs from the CPH and CPH-A samples in a vertical fixed-bed furnace [22, 23]. For each experiment, about 5 g of the dried CPH sample was poured into a mesh-made holder, and then placed at the center of the reaction system. The precursor was subjected to the carbonization at a ramp of 10 °C/min under N_2 flow (500 cm^3/min) by heating to 500 °C. Subsequently, the activation of the resulting carbon was carried out by switching to a CO_2 flow (50 cm^3/min), heating to specified temperature (i.e., 650, 750, or 850 °C) and then maintaining for 30 min. The yields of the resulting ACs are within the range 18–38 wt%, indicating a decreasing trend with activation temperature increased. According to the CPH precursor and activation temperature, the CPH-based AC products in this work were coded as AC-CPH-650, AC-CPH-650, AC-CPH-A-650, AC-CPH-A-750, and AC-CPH-A-850, respectively.

2.5 Characterization of CPH-based activated carbons

Pore properties of CPH-based ACs were measured by the surface area and porosity analyzer (ASAP 2020; Micromeritics Co., USA). The nitrogen molecules adsorbed by monolayer coverage must be determined in order to calculate the specific surface area (SSA). In this regard, the method for SSA (denoted as S_{BET}) is based on the Brunauer-Emmett-Teller (BET) theory. The BET equation was applied to the relative pressure (P/P_0) range of 0.05–0.25 in this work [24]. The total pore volume (V_t) was determined by the N_2 adsorption isotherm at P/P_0 close to unity (i.e., 0.95). It was suggested that all the pores are of straight and cylindrical geometry. The average pore diameter can be roughly calculated from V_t and S_{BET} [25, 26]. Regarding the microporous properties, the *t*-plot method was employed to permit the determination of micropore volume and surface area [26]. The pore size distribution was obtained from the desorption branch of the N_2 adsorption-desorption isotherm by the modified Kelvin equation, called as the Barrett-Joyner-Halenda (BJH) method [26].

As described above, the ultimate analysis of the CPH-based AC is expressed in terms of its weight percentages (on a dry basis) of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S) by an elemental analyzer (vario EL III; Elementar Co., Germany).

3 Results and discussion

3.1 Thermochemical characterization of CPH and CPH-A

Table 1 indicates the data in terms of the proximate analysis, ultimate analysis, and calorific value for the precursors (i.e.,

Table 1 Thermochemical properties of cocoa pod husk (CPH) and acid-leaching CPH (CPH-A)

Property	CPH	CPH-A
Proximate analysis[ac]		
Ash (wt%)	9.8 ± 0.1	0.4 ± 0.4
Volatile matter (wt%)	74.3 ± 0.1	73.2 ± 0.6
Fixed carbon[b] (wt%)	15.9 ± 0.1	26.4 ± 0.9
Ultimate analysis[cd]		
Carbon (wt%)	43.25 ± 0.04	50.23 ± 0.02
Hydrogen (wt%)	6.06 ± 0.05	6.50 ± 0.00
Oxygen (wt%)	44.34 ± 0.04	41.30 ± 0.08
Nitrogen (wt%)	1.03 ± 0.04	0.77 ± 0.01
Sulfur (wt%)	0.34 ± 0.02	0.35 ± 0.04
Calorific value (MJ/kg)[ac]	17.83 ± 0.31[e]	20.21 ± 0.10

[a] The mean ± standard deviation for three determinations

[b] By difference

[c] On a dry basis

[d] The mean ± standard deviation for two determinations

[e] Source [27]

CPH and CPH-A) used in the AC production. The value (i.e., 9.8 wt%) of ash content in the CPH agrees very well with those found in the literature [28]. Clearly, the acid-leaching of CPH with 3 M HCl results in removal of over 90% of the ash content. It is well known that the ash constituents in the biomass consist mainly of silica, alumina, iron, alkaline, and alkaline earth metals [29]. Consequently, ash was easily leached out by acid solution. On the other hand, it indicates the increased fixed carbon in the CPH-A, representing more carbon fractions left after the drive-out of volatiles during the acid treatment. This result is consistent with the data on ultimate analysis and calorific value (Table 1). For example, the carbon content of CPH-A (50.23 wt%) is obviously larger than that of CPH (43.25 wt%).

In order to verify the difference of inorganic compositions between CPH and CPH-A, Table 2 lists the total contents of main inorganic elements and trace metals. It shows that inorganic element in the CPH is mainly K, which could be the presence of oxides, carbonates, bicarbonates, or hydroxides [30]. Minor inorganic elements are Mg, P, Ca, and Mn. It is noteworthy that trace amounts of heavy metals and other elements (Table 2), including Al, As, Ba, Cd, Co, Cr, Cu, Fe, Na, Ni, Pb, Si, Sr, Ti, and Zn, were found in CPH and CPH-A. Similar data have been found in the previous study [27] and other researches [31, 32]. These findings suggest that the emissions of toxic metals from the combustion of cocoa processing by-product will be negligible.

The thermogravimetric and its derivative thermogravimetric (TG/DTG) curves of the dried CPH (blue lines) and CPH-A (red lines) precursors at a heating rate of 10 °C/min can be seen in Fig. 1. Obviously, it revealed the slight weight loss at temperatures less than 200 °C, which is probably due to the

Table 2 Contents of relevant elements of CPH and CPH-A

Inorganic element	CPH (wt%)	CPH-A (wt%)	Method detection limit (ppm)
Potassium (K)	3.73	ND	–
Magnesium (Mg)	0.277	ND	–
Calcium (Ca)	0.230	ND	–
Phosphorus (P)	0.160	ND	–
Manganese (Mn)	0.022	ND	–
Silicon (Si)	ND [a]	ND	11.3
Aluminum (Al)	ND	ND	17.4
Iron (Fe)	ND	ND	6.6
Sodium (Na)	ND	ND	11.4
Barium (Ba)	ND	ND	0.3
Copper (Cu)	ND	ND	7.2
Nickel (Ni)	ND [a]	ND	19.2
Strontium (Sr)	ND	ND	0.3
Zinc (Zn)	ND	ND	4.2
Lead (Pb)	ND	ND	17.4
Chromium (Cr)	ND	ND	7.8
Titanium (Ti)	ND	ND	1.2
Cadmium (Cd)	ND	ND	2.4
Arsenic (As)	ND	ND	0.5
Cobalt (Co)	ND	ND	20.4

ND not detectable

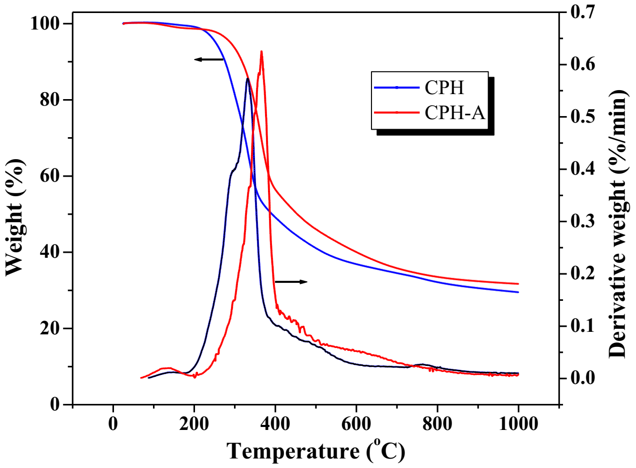

Fig. 1 TG and DTG curves of CPH and CPH-A at a heating rate of 10 °C/min

releases of adsorbed water and poorly bonded materials. As shown by sharp DTG peaks, a significant weight loss subsequently occurs at 200–400 °C, which is corresponding to the release of the volatile matter from the thermal decomposition of the hemicellulose and cellulose contained in the biomass precursor. These results suggest that the carbonization condition should be set at the temperature higher than 400 °C to prepare a carbon-rich product used in the next activation process. On the other hand, the TGA/DTA curves in the CPH-A sample are shifted to higher temperatures by about 30 °C, indicating that it has a higher thermal stability than the CPH sample between 200 and 400 °C. This result could be attributed to the acid-leaching treatment in the CPH-A sample, leading to the crystallinity of cellulosic biomass increased [17].

3.2 Pore properties of CPH-based activated carbons

Table 3 summarizes the pore properties of the CPH-based ACs obtained from the CPH and CPH-A at different activation temperatures. Obviously, their pore properties indicate an increasing trend with activation temperature. For example, the BET surface area significantly increased from 1.1 m^2/g (AC-CPH-650) to 289.5 m^2/g (AC-CPH-750). The activation at higher temperature would enhance the diffusion and reaction of gasification gas (CO_2) in the physical activation and thus increase the pore properties of the resulting AC. On the other hand, these data in Table 3 further show that the acid pretreatment has resulted in more developed pores, thus increasing the specific surface area and pore volume of the resulting AC. It is seen by the fact that the BET surface area significantly increased from 289.5 m^2/g (AC-CPH-750) to 427.8 m^2/g (AC-CPH-A-750). Comparing the data in Table 3 also demonstrates that the average pore width gradually decreases with increasing activating temperature, indicating the development of more fine pores at higher temperature from 650 to 850 °C. To assure the higher pore properties of the resulting ACs at higher temperature and longer time in the CO_2 activation experiments, AC-CPH-A-900 was produced at 900 °C, holding 90 min. Due to the serious burn-off at higher activation temperature and longer holding time, the BET surface area of AC-CPH-A-900 increases significantly to about 1330 m^2/g, but its yield reduces rapidly to 8.0%, as compared to the yield of 26.4% for AC-CPH-A-850.

Figure 2a, b shows the corresponding N_2 adsorption-desorption isotherms (at − 196 °C) and the Barrett-Joyner-Halenda (BJH) desorption pore size distribution curves of the resulting ACs, respectively. These AC products prepared

Table 3 Pore properties of activated carbons (ACs) produced from CPH and CPH-A

Pore property	AC-CPH-650	AC-CPH-750	AC-CPH-A-650	AC-CPH-A-750	AC-CPH-A-850
Surface area (m^2/g)					
Single-point surface area [c]	0.9	280.0	345.5	414.7	618.1
BET surface area[d]	1.1	289.5	355.8	427.8	637.7
t-plot micropore area[e]	1.4	198.6	317.8	391.7	579.2
Pore volume (cm^3/g)					
Total pore volume[f]	0.00075	0.149	0.179	0.213	0.319
t-plot micropore volume[e]	0.00069	0.102	0.154	0.190	0.281
Average pore width (nm)[g]	3.36	2.16	2.12	2.11	2.00

[a] Cocoa pod husk (CPH)-based activated carbons (AC) produced at 650 and 750 °C

[b] Cocoa pod husk (CPH)-acid treatment (A)-based AC produced at 650, 750, and 850 °C

[c] Calculated by the single-point BET method at relative pressure of ca. 0.3

[d] Calculated by the BET method at relative pressure range of 0.05–0.25 (6 points)

[e] Calculated by the *t*-plot method

[f] Calculated by the single-point adsorption at relative pressure of ca. 0.95

[g] Calculated from the ratio of the total pore volume (V_t) and the BET surface area (S_{BET}) if the pore is of cylindrical geometry (i.e., average pore width = $4 \times V_t/S_{BET}$)

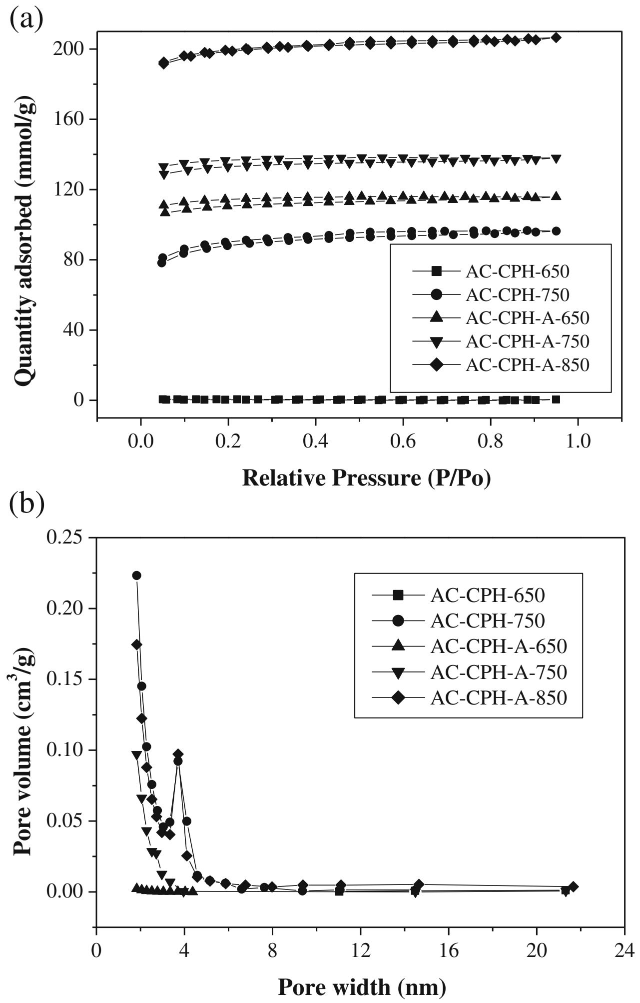

Fig. 2 **a** N_2 adsorption-desorption isotherms. **b** Pore size distributions of CPH-based ACs

from the CPH and CPH-A at different activation temperatures exhibit the shape of the type IV isotherm according to the classification by the International Union of Pure and Applied Chemistry (IUPAC) [26]. In the case of physical adsorption, this type is often encountered in microporous materials where the high adsorption uptake is observed at low relative pressures because of the narrow pore width and the high adsorption potential. These features are also demonstrated in the pore size distribution curves, where the pores of the resulting ACs have narrow pore size distributions at less than 2.0 nm (20 Å) depicted in Fig. 2b. It is interesting that the mesoporous structure is also present in the resulting ACs; there are slight hysteresis loops for AC-CPH-750 and AC-CPH-A-850 when relative pressure increases to 0.4 or more. This result provides the fact that the rigorous reaction at higher activation temperatures is beneficial to the development of mesoporous structure, thus converting the narrowly distributed micropores into the wider pore size distribution with little mesopores created [2].

3.3 Chemical properties of CPH-based activated carbons

Table 4 provides the data on the elemental analysis of the resulting ACs produced from CPH and CPH-A. Obviously, the CPH-A-based AC products are rich in carbon (O), ranging from 85 to 90%. Compared to the data in Tables 1 and 4, this can be further confirmed by the increase in the content of C from 50 to 85% or more, clarifying that the contents of O and H in the lignocellulosic precursor (i.e., CPH-A) significantly decrease during the activation process. In addition, the precursor (i.e., CPH) for producing AC contains a significant ash content, which should be attributed to the fact that most of the potassium-containing minerals are likely remained in the resulting ACs, thus resulting in relatively high in oxygen contents (> 30 wt%) and low in carbon contents (< 60 wt%). Furthermore, increasing the activation temperature from 650 to 850 °C will induce more gasification reaction, thus indicating an increase in the C and S contents of the resulting ACs (Table 3), and a decreasing trend of H, N, and O contents.

4 Conclusions

Based on the proximate analysis, mineral compositions, thermogravimetric analysis, and thermochemical properties, the chemical and thermochemical differences between cocoa pod husk (CPH) and acid-leaching CPH (CPH-A) were investigated in the present study. It shows that the pretreatment of

Table 4 Ultimate analyses of CPH-based ACs

Activated carbon	Carbon (C, wt%)	Hydrogen (H, wt%)	Nitrogen (N, wt%)	Sulfur (S, wt%)	Oxygen (O, wt%)
AC-CPH-650	57.89	1.95	1.11	0.41	30.38
AC-CPH-750	40.96	2.17	1.21	0.40	34.88
AC-CPH-A-650	85.54	2.13	1.44	0.11	10.67
AC-CPH-A-750	89.33	1.98	1.28	0.23	6.95
AC-CPH-A-850	89.45	1.93	1.13	0.45	7.01

Dry basis (moisture free)

CPH with hydrochloric acid led to removal of over 90% of the ash content in the CPH, mainly composed of potassium minerals. This work further studied the effect of CPH-A on the pore properties and chemical compositions of the resulting ACs, which were prepared from the physical activation at different activation temperatures (650–850 °C). The Brunauer-Emmet-Teller (BET) surface area of the AC derived from CPH-A at 650 °C is 355.8 m^2/g, significantly larger than that (i.e., 1.1 m^2/g) of the AC derived from CPH. In addition, the activation at higher temperature is beneficial to the pore development of the resulting ACs. These results suggest that the de-ashed CPH provides an excellent precursor for preparing microporous ACs. More significantly, the solution after the acid-leaching of CPH may be reused as a liquid fertilizer because it is abundant in potassium ions.

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