Research Article

Adsorption of Carbon Dioxide onto Activated Carbon Prepared from Coconut Shells

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This study presents the fabrication of high-quality activated carbon (AC) from discarded coconut shells. The effects of experimental parameters such as activation temperature and activation time on the basic characteristics of AC, including charcoal yield, ash content, pH value, Brunauer-Emmett-Teller (BET) specific surface area, total pore volume, and iodine adsorption, are investigated. The results indicate that as the activation temperature and activation time increase, the charcoal yield of the AC decreases. In contrast, iodine adsorption, ash content, pH value, and total pore volume increase with activation temperature. The AC sample activated at 1000°C for 120 min had the highest BET specific surface area and total pore volume and thus the best CO₂ adsorption performance. This sample was compared with 30-mesh commercial AC. The results reveal that coconut-based AC has better instantaneous adsorption capabilities.

1. Introduction

The rapid development of industrial technologies has significantly increased the concentration of greenhouse gases such as CO₂, CH₄, HFCs, and PFCs in the atmosphere. The greenhouse effect of these gases leads to environmental pollution, exacerbates global warming, raises ocean water levels, and affects the balance of the ecosystem. Among greenhouse gases, the greenhouse effect of CO₂ has the greatest impact on global warming [1, 2]. Aggressive efforts are being made to develop technologies to capture CO₂ to mitigate the greenhouse effect. In addition, the captured CO₂, which is nontoxic and inexpensive, can be used to produce various organic solvents, chemicals, and media materials (such as calcium carbonate, glucose, and starch), and thus it can potentially bring substantial commercial benefits.

Porous carbon-based materials have high thermal and chemical stability as well as good adsorption capabilities [1, 3–8]. Their low cost and recyclability make them ideal for pollution prevention [9–11]. Gergova and Eser [12] used apricot stones to fabricate activated carbon (AC) and found a low total pore volume (Vₚ) in AC produced using pyrolysis or incomplete activation. Using formaldehyde resin and chemical and physical activation processes, Teng and Wang [13] created AC with high-density porosity. Scanning electron microscopy (SEM) revealed that physical activation processes produce compounds with a higher Brunauer-Emmett-Teller (BET) specific surface area. Park and Kim [3] fabricated AC using polyacrylonitrile (PAN) carbon fiber fabric and phenolic resin and found that using an activation temperature (T activation) of 900°C led to the highest BET specific surface area. With activation at 1000°C, the pores were easily filled in, collapsed, and formed graphite-like carbon structures, all of which decreased the BET specific surface area [3]. With rockrose as the raw material, Pastor-Villegas and Durán-Valle [14] produced AC using CO₂ and H₂O activation. They discovered that low-temperature activation processes using H₂O (particularly at 700°C) generated a higher total pore volume and a larger pore volume than those obtained with any activation process using CO₂. Wang et al. [15] employed H₂O activation to fabricate polystyrene-based AC spheres and found that spherical AC contains a greater volume of narrow micropores, requires higher temperatures for desorption, and has a higher irreversible adsorption capacity. Huang et al. [16] used Chinese fir wood to create AC and found that higher...
carbonization temperatures contribute to greater quantities of porous structures and a higher BET specific surface area. Using corncobs to produce AC, Liu et al. [17] established that the activation temperature and precarbonization particle size influence the BET specific surface area and pore size distribution of the AC. Furthermore, the corncob-derived AC was found to be effective in hydrogen adsorption.

Since coconut shell carbonaceous adsorbents possess high BET specific surface area and porosity [18], we used discarded coconut shells to produce AC. This work examines the technical feasibility of producing AC from coconut shell wastes. The properties of coconut shell AC and the effects of processing parameters on the CO$_2$ adsorption capabilities are also discussed.

2. Materials and Methods

2.1. Sample Preparation. We used rope coconuts grown in Taiwan to produce AC, the powder of which was subjected to adsorption experiments. The high and unevenly distributed water content in coconuts makes carbonization and activation temperatures difficult to control, which affects the quality of the AC. For this reason, we performed a pretreatment that involved cutting open the coconuts, removing all of the coconut pulp and some of the fibers, and air-drying the remaining shell. For uniform quality in carbonization and activation, the water content of the shells was maintained at between 13% and 16%. The dried shells were cut into pieces with dimensions of 5 cm (length) × 4 cm (width) × 2~3 cm (thickness) and placed in a high-temperature kiln for carbonization.

2.2. Induction Heater. A compact charcoal kiln was used to produce coconut shell AC. Its maximum capacity is about 1 kg of raw materials per batch. Induction heaters, which incorporate a coil directly fed from the electricity supply, were installed in the kiln walls for generating heat energy to carbonize coconut shells. Temperature sensors were placed inside the charcoal kiln for monitoring the carbonization temperature. The carbonization temperature was controlled by setting the temperature of the pyrolysis process. Inert gas (N$_2$) was pumped into the kiln at 10 mL/min to prevent the coconut shells from coming into contact with air during carbonization and activation. During carbonization, the temperature was increased at 15 °C/min to 500°C and held for 60 min. Following the activation process, steam, the activation fluid, was immediately pumped into the furnace at 3 mL/min. Five activation temperatures (600, 700, 800, 900, and 1000°C) and two activation times (60 and 120 min) were adopted for comparing the quality of coconut-shell-based AC. Subsequently, the heater and gas flow were turned off and the carbonized coconut shell AC was allowed to cool naturally inside the kiln to room temperature. Finally, the shells were ground into powder (30 mesh). We used a CO$_2$ adsorption apparatus to evaluate the CO$_2$ adsorption capacities of the samples and compared the results with those of commercially available AC. Figure 1 shows the framework of the procedure for preparing coconut-shell-based AC.

2.3. CO$_2$ Adsorption Test Procedure. Figure 2 shows the structure of the CO$_2$ adsorption apparatus. The procedure for testing CO$_2$ adsorption is as follows.
Figure 2: Structure of CO$_2$ adsorption apparatus: (A) sample case, (B) gas mixing chamber, (C) ball valve, (D) inlet, (E) preadsorption sampling hole, and (F) postadsorption sampling hole.

2.4. Method for Determining CO$_2$ Adsorption Capacity

(1) First, 200 g (30 mesh) of the coconut-shell-based AC is placed into the sample case (A), and the vacuum pump is turned on to draw air from the gas mixing chamber (B) until it becomes a vacuum.

(2) The ball valve (C) is then closed, and CO$_2$ is pumped in through the inlet (D). Preadsorption sampling is conducted at the sampling hole (E) to confirm that the CO$_2$ in the chamber has reached a concentration of 100% at a pressure of 40 cmHg.

(3) The vacuum pump is turned on and the ball valve (C) is opened. With the outflow to the vacuum pump and the gas inflow controlled at equal flow rates, postadsorption sampling can be performed at the sampling hole (F) to extract the CO$_2$ gas following adsorption by the AC for gas chromatography (GC) testing.

(4) The influence of the various AC samples on the CO$_2$ concentration can be observed from the GC tests and Quick Chrom graphs, from which the CO$_2$ concentration can be obtained.

2.5. Gas Chromatography Analysis. The CO$_2$ adsorption capacities of the AC powders were analyzed using GC (Shimadzu GC-8A). GC is one of the most commonly used tools for analyzing volatile and semivolatile organic compounds. We gasified the test samples and pumped them through a column for separation using helium flowing at 40 mL/min as a carrier gas. We filled the column with a solid-phase carrier, which has a liquid film on the surface. As a sample passes this film, the speed at which any compound moves in the column is determined by the net value of the two opposing forces, which varies depending on the compound. The speed differences thus separate the compounds. The adsorption concentration ($M$) can be derived from the geometric ratio of the relative heights ($L$) in the peak graphs produced by the GC analysis program Quick Chrom.

2.6. Determination of Charcoal Yield. The charcoal yield, $Y_{\text{char}}$ (%), produced by a kiln is given by $Y_{\text{char}} = m_{\text{char}}/m_{\text{raw}}$. 

![Image](image_url)
where \( m_{\text{char}} \) is the dry mass of charcoal taken from the kiln and \( m_{\text{raw}} \) is the dry mass of the raw coconut shells loaded into the kiln [19].

2.7. Determination of Ash Content and pH Value. The ash content of coconut shell AC was determined according to CNS 5581 [20], which involved heating the carbonized charcoal in an open crucible (type: L3C6, Chuanhua Precision Co., Germany) to 800 ± 25°C and holding at this temperature for 3 h. The material that remains in the crucible is defined as ash; that is, ash content (%) = 100 \times m_{\text{ash}}/m_{\text{char}}, where \( m_{\text{char}} \) is the initial dry mass of charcoal and \( m_{\text{ash}} \) is the dry mass of ash that remains following combustion of the carbonized charcoal [19]. In this work, the pH value was measured according to CNS 697-698 [21] using a Eutech meter (pH 700, USA).

2.8. Scanning Electron Microscopy Observation. SEM (Philips, CM-200, Japan) was used to analyze the microporous structures of coconut shell AC. SEM was operated at 15 kV in secondary electron imaging mode.

2.9. Iodine Adsorption Value. The iodine value of the coconut shell AC was determined according to ASTM D4607-94 [22], which is based on a three-point adsorption isotherm. The iodine adsorbed per gram of coconut shell AC at a residual iodine concentration of 0.02 N is reported as the iodine value; that is, iodine value (mg/g) = \( A - (DF \cdot B - S) \)/\( M \), where \( A \) and \( B \) are 12693.0 and 126.93, respectively, \( DF \) represents the dilution factor, \( S \) is the volume (in mL) of standard sodium thiosulphate solution, and \( M \) denotes the coconut shell AC used (in g) [19, 22].

2.10. Measurement of Pore Volume and BET Specific Surface Area. Surface area and porosity are two important physical properties that determine the quality and effectiveness of coconut shell AC. In this work, the multipoint (12-point) BET method and the Langmuir method were used to determine the BET specific surface area and adsorption isotherms of nitrogen at 77.3 K using an ASAP 2010 apparatus.

3. Results and Discussion

SEM was used to analyze the microporous structures of coconut-shell-based AC, including the cross-sectional parenchyma cells, thecal pores, and cell walls. Figure 3 shows SEM images of the parenchyma cells and cell wall pores in the AC samples. Figures 3(a)–3(e) show the AC samples activated at 600, 700, 800, 900, and 1000°C, respectively. As shown, the majority of mesopores and micropores were concealed within the macropores, extending layer upon layer. This indicates that the AC had multisized porosity. A comparison of Figures 3(a)–3(e) reveals that as the activation temperature increased, the number of smaller pores in the large pores increased, whereas the number of clogged pores on the surface decreased. This demonstrates that activation removes hydrocarbons and tar, which enhances the adsorption capacity of the AC.

To reduce experimental error, the adsorption characteristics and properties are measured from three different coconut shell AC samples prepared at each activation temperature. The mean values and associated standard errors calculated from the measured raw data are presented in the following figures. Figure 4 shows the averages of charcoal yield, ranging from 20.4% to 34.6%. As shown, due to the pyrolysis and vaporization of hydrocarbons and tar within the AC, charcoal yield declined with increasing activation temperature and activation time. The experimental results are consistent with those reported by Wang et al. [23]. Generally, the main elemental constituents of biomass minerals are K, Na, Ca, Mg, and Si, with smaller amounts of S, P, Fe, Mn, and Al [24, 25]. These inorganic constituents occur as oxides, silicates, carbonates, sulfates, chlorides, and phosphates [25]. Inorganic substances are rarely volatilized during activation, remaining in the ash and thereby increasing the ash content. Figure 5 shows the ash content for various activation temperatures and activation times, ranging between 2.9% and 3.31%. These values conform to the practical limit for the level of ash content allowed in commercial AC (2 to 5%) [26]. The inorganic salts in ash generally possess a high fusion point and largely remain after the water and organic matter have been removed at elevated temperatures. The ash content thus increases with activation temperature and activation time.

The pH value was measured according to CNS 697-698 [21] using a Eutech meter (pH 700, USA). As shown in Figure 6, the pH value increases with activation temperature and activation time. This is attributed to the burning of calcite and the production of lime during the high-temperature pyrolysis steps. Moreover, the activation process increased the surface area and porosity, as well as the surface basicity of AC [27]. As shown, the increase in pH value is most significant between 600°C and 800°C, after which the rate of increase declines. Among the AC samples derived from coconut shells, the one activated at 1000°C for 120 min displayed the highest pH value (9.84). The values correspond to the commercial specifications of coconut-shell-based AC (pH 9–11) [26].

During carbonization, the hydrocarbons attached to the coke structures can often clog up the pores. Increasing the activation temperature and activation time can promote the removal of more hydrocarbons and impurities and increase the total pore volume and BET specific surface area. As shown in Figure 7, the BET specific surface area increases with activation temperature, with the most significant increase being between 600°C and 800°C. When the activation temperature exceeds 800°C, the effect of activation temperature on BET specific surface area gradually weakens. This can be attributed to high activation temperatures allowing easier removal of organic matter, formation of more micropores, and an increase in specific surface area, but also easier collapse of micropores, backfilling, and formation of graphite-like carbon structures, thus decreasing the BET specific surface area [3]. Moreover, the BET specific surface area increased with activation time, with the sample activated at 1000°C for 120 min having the highest BET specific surface area (824 m²/g). Figure 8 presents the negative correlation between BET specific surface area and charcoal yield, which
Figure 3: SEM images (left) and magnified views (right) of pore structures of AC samples activated at (a) 600°C, (b) 700°C, (c) 800°C, (d) 900°C, and (e) 1000°C.
occurs on account of the fact that high activation temperatures allow easier release of volatile substances and tar in the carbon powder, which form micropores, increasing BET specific surface area and reducing charcoal yield.

The formation of pores and changes to the pore structure in AC mostly occur during the activation process. As the activation temperature increases, the hemicellulose, cellulose, and lignin in the coconut shells undergo pyrolysis. The residual carbon molecules reaggregate into coke structures and form numerous micropores. Therefore, higher activation temperatures expedite pyrolysis reactions. Furthermore, as heat and water vapor travel via diffusion and thermal transfer, longer activation periods facilitate the diffusion
of heated water molecules within AC, which then activate more carbon molecules and generate a greater quantity of pores. As shown in Figure 9, total pore volume increases with activation temperature and activation time. Thus, the sample activated at 1000°C for 120 min showed the highest total pore volume ($V_p = 0.502 \text{ mL/g}$). The results are superior to those for the AC produced by Achaw and Afrane [28] with a carbonization temperature of 325°C, activation temperature of 800°C, and activation time of 120 min (BET specific surface area = 524.5 m$^2$/g; total pore volume $V_p = 0.266 \text{ cm}^3$/g). We speculate that this was because Achaw and Afrane employed a lower carbonization temperature, which caused fewer volatile substances and less tar to be released, and produced underdeveloped coke structures. Using a carbonization temperature of 500°C, activation temperature of 900°C, and activation time of 30 min, Azevedoa et al. [29] produced AC with a BET specific surface area of 1,266 m$^2$/g and a total pore volume of 0.731 cm$^3$/g, which are significantly higher than the values in this study. We speculate that this was due to the $\text{ZnCl}_2$ added by Azevedoa et al. to the process as an activating agent. This chemical activation increased the BET specific surface area and total pore volume but produced hazardous gases such as Cl and HCl.

Small pores are adept at adsorbing iodine molecules, and, thus, the quantity of iodine molecules adsorbed is often considered an indicator of the number of micropores in AC [30–32]. As the temperature rises during activation, endothermic reactions between carbon atoms and water vapor are more likely to occur, which produce numerous macropores, mesopores, and micropores. As the activation time increases, water vapor molecules are more able to infiltrate the inner structure of AC. In this work, the iodine adsorption value of coconut-shell-based AC was determined according to ASTM D4607-94 [22], which is based on a three-point adsorption isotherm. As shown in Figure 10, increases in activation temperature and activation time facilitate iodine adsorption, and, at certain temperatures, increasing the activation time has a greater impact on the increase in micropores than does increasing the activation temperature. At activation temperatures of over 700°C, increasing the activation time significantly promotes micropore formation in the AC.

Figure 8: Relationship between charcoal yield and BET specific surface area.

Figure 9: Total pore volume as a function of activation temperature and activation time.
To determine the adsorption performance of the AC samples derived from coconut shells, we used the vacuum pump in the CO$_2$ adsorption analyzer (see Figure 2) to force CO$_2$ through the AC samples. GC was used to analyze the concentration changes of CO$_2$ before and after adsorption to identify the CO$_2$ capture capacity of the AC samples. Figure 11 shows the change in CO$_2$ concentration ($\Delta M_{CO_2}$) for various AC samples at different adsorption times ($t_{adsorption} = 1, 10, 20, and 30$ min). As shown in Figures 11(a) and 11(b), CO$_2$ adsorption performance improves with activation time and activation temperature. In Figure 11(b), the sample activated at $T_{activation} = 1000^\circ$C for $t_{activation} = 120$ min showed the best instantaneous adsorption capacity of $\Delta M_{CO_2} = 14.40$ mg/L at $t_{adsorption} = 1$ min, which is significantly higher than the $12.94$ mg/L for the sample activated at $T_{activation} = 1000^\circ$C for $t_{activation} = 60$ min in Figure 11(a). The reason for this is closely associated with micropore volume and BET specific surface area [33]. At room temperature, the adsorption capacity of AC increases with the number of available adsorption sites on the adsorbent. Extremely small in size, CO$_2$ molecules are easily captured by micropores. Thus, AC with more micropores and a higher BET specific surface area can adsorb more CO$_2$. As the adsorption time increases, the adsorption performance gradually declines, meaning that the pores are being filled with CO$_2$ molecules and that adsorption saturation is imminent.

To understand the adsorption characteristics of the AC derived from coconut shells, we compared the sample activated at $T_{activation} = 1000^\circ$C for $t_{activation} = 120$ min with a commercially available AC with similar specifications (BET specific surface area = $800$ m$^2$/g; ash content = $3.0\%$). Prior to the test, we grounded the AC powders to 30 mesh and tested the CO$_2$ adsorption capacity of these two samples of equal weight (200 g). As shown in Figure 12, soon after adsorption began ($t_{adsorption} = 1$ min), the coconut AC and the commercial AC reduced the CO$_2$ concentration by $14.3$ and $13.2$ mg/L, respectively, which demonstrates that the coconut AC has a higher instantaneous adsorption capacity than that of the commercial AC. The adsorption capabilities of the two powders decrease with time. Following forced adsorption for 30 min, the adsorption capabilities of the two powders dropped to $1.9$ and $1.7$ mg/L, respectively.

4. Conclusion

We prepared various AC samples from coconut shells with various activation temperatures and activation times. The effects of processing parameters on the charcoal yield, ash content, pH value, BET specific surface area, total pore volume, and iodine adsorption of the AC were examined. The experimental results indicate that increasing the activation temperature and activation time increases the ash content and pH value of the AC but reduces the charcoal yield. The coconut-shell-based AC activated at $T_{activation} = 1000^\circ$C for $t_{activation} = 120$ min showed the highest BET specific surface area and total pore volume (824 m$^2$/g and 0.502 mL/g, resp.). The higher activation temperature contributed to the removal of more hydrocarbons and therefore increased the BET specific surface area and total pore volume. However, the high activation temperature also resulted in a significant decrease of charcoal yield. Moreover, increasing the activation time increased BET specific surface area and total pore volume, thereby improving the CO$_2$ adsorption capacity of coconut shell AC. Experiments show that the coconut shell AC has a higher instantaneous adsorption capacity than that of a commercial AC. These results suggest that coconut shell...
Figure 11: Changes in CO₂ concentration (ΔM CO₂) measured after various adsorption times at various activation temperatures (600–1000 °C) and activation times of (a) 60 min and (b) 120 min.

Figure 12: Comparison of CO₂ adsorption capacity in commercial AC and coconut AC at T activation = 1000 °C for t activation = 120 min.

waste is promising for producing high-quality AC via the regulation of process parameters.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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