Preparation and water vapor adsorption of “green” walnut-shell activated carbon by CO$_2$ physical activation

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Abstract
In this study, activated carbons without any chemical residue were prepared from walnut shells. The preparation method in a tube furnace included a pyrolysis carbonization process and a CO$_2$ activation process. The influences of activation temperature and holding time on the specific surface area, yield, and pore structure were investigated. Adsorption performance of water vapor was also examined in details. Thermogravimetric analysis, N$_2$ adsorption–desorption isotherm, and scanning electron microscope were used to characterize samples. The result shows that the activation energy at different heating rates varies from 30.16 to 64.86 kJ/mol. The highest water vapor adsorption capacity of the sample is 0.3824 g/g and it takes only 30 min to realize regeneration. And the maximum Brunauer–Emmett–Teller specific surface area of 1228 m$^2$/g also occurs in this optimal preparation condition. CO$_2$ physical activation method was found to have a positive effect on pore structure development of activated carbon for water vapor adsorption.

Keywords
Walnut-shell activated carbon, pyrolysis, carbon dioxide activation, activation temperature, holding time, water vapor adsorption

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Introduction
Solid desiccant dehumidification is receiving much attention as a new technology for various dehumidification system applications since it can avoid the disadvantages of the conventional dehumidification based on vapor compression refrigeration system, such as depletion of ozone layer, global warming, harmful to human health, etc. (Sultan et al., 2018). On the other hand, the heat requirement of solid desiccant dehumidification can be satisfied by waste heat and low-grade energy (Sultan et al., 2015), which brings the opportunity to employ renewable energy such as solar energy, biogas, and biomass resources.

In the past few years, many researchers had focused on various aspects of the solid desiccant dehumidification system by mathematical modeling, solid desiccant characterization, and experimental investigations (La et al., 2010). The results show that solid desiccant adsorbents in solar drying dehumidification and regeneration system play an important role in order to maintain the dehumidification performance (La et al., 2010; Wang et al., 2013; Zheng et al., 2014). At present, the widely used adsorbent materials include silica gel and activated carbon (Enteria et al., 2012; Qian et al., 2008). Compared with activated carbon, silica gel may be cracked into powder in high humidity environment, which causes it to lose the adsorption capacity of water vapor (Gu et al., 1998; Ling, 2004; Wang et al., 2016). Activated carbon has been recognized as one of the most popular and widely used adsorbent in the world for a long time. And activated carbon as an adsorbent in solid desiccant dehumidification system has been identified as an effective and economic method for removing water vapor from gas stream because activated carbon has some good performance of large Brunauer–Emmett–Teller (BET) specific surface area, well-developed pore structure, and stable physical–chemical properties (Mazlan et al., 2016; Rodríguez-Reinoso, 2001).

Traditionally, coal, lignite, and wood were often used as raw materials for preparation of activated carbon (Shahkarami et al., 2015). The preparation of activated carbon from these materials not only increases production costs, but also wastes non-renewable resources. In recent years, more and more biomass materials have been used to prepare activated carbon. China is the main producing area of walnut. According to Food and Agriculture Organization of the United Nations statistics, the full production capacity of walnut in China was more than 1.78 million tons in 2016. A large number of the walnut shells are discarded and burned, resulting in serious waste of resources and environmental pollution. In general, most of carbonaceous material can be used as raw materials for preparation of activated carbon. The walnut shell is suitable for preparation of activated carbon due to its advantages of high carbon content and low ash content. Moreover, it not only can save the resources but also reduces cost of preparation process.

In principle, the preparation of activated carbon by a two-step activation method includes carbonization and activation processes (Hindarso et al., 2001). Previously, researchers thought that the carbonization process had little effect on the adsorption performance of activated carbon (Taer et al., 2010). And the activation process was the core of activated carbon preparation because it had a great effect on the adsorption performance of water vapor (Sun et al., 2019). In fact, the carbonization process during the production process of activated carbon also has a certain impact on the adsorption performance because the purpose of the carbonization process is to increase the carbon content of the carbonization material and make a certain initial pore developed over the carbonization material (Yagmur et al., 2008). Therefore, it is necessary to analyze pyrolysis characteristics of the walnut shells.
In general, the activation methods of activated carbon reported in the literature are mainly divided into physical activation and chemical activation (Ruiz-Fernández et al., 2011). The physical activation means that carbon dioxide or water steam is used as an activator to prepare activated carbon. The raw material or char is activated without addition of any chemical reagents. However, the chemical activation means that chemical reagent is selected for preparing activated carbon. The char or raw material is impregnated with certain chemical solution (such as ZnCl₂, KOH, and H₃PO₄, etc.) in the chemical activation process (Gao et al., 2018) and then the treated material is activated under an inert atmosphere. Compared with the physical activation method, activated carbon prepared by chemical activation method has a large BET specific surface area and well-developed pore structure. However, the activated carbon prepared by chemical activation method might have chemical residues and pollute the environment. Although the activated carbon prepared by physical activation method has a smaller BET specific surface area and less-developed pore structure, it has less pollution to the environment and avoids the chemical residue within the activated carbon due to the activating reagent of carbon dioxide or water steam. More important is that the activated carbon prepared by this method is more suitable for the food processing industry because it has no chemical residue.

On the other hand, most agricultural products can be dried in a solar drying system in order to realize long-term preservation. In order to increase the system efficiency and reuse the waste heat, the hot and humid air that is derived from the solar drying system can be returned to this system if the relative humidity in the airflow is reduced by solid desiccant material. Therefore, the solar drying system coupled with dehumidification unit is introduced. In fact, water vapor adsorption performance and regeneration ability of a solid desiccant play an important role in the system’s continuous operation. It is necessary for a new adsorbent to analyze both adsorption performance and regenerability.

In this paper, the walnut shell was identified as a raw material to prepare activated carbon by a two-step method. The preparation process included a carbonization process and a carbon dioxide activation process. The walnut-shell activated carbon was used as an adsorbent for the solar drying system coupled with dehumidification unit. The effects of preparation conditions on the pore structure development and water vapor adsorption–regeneration performance of walnut-shell activated carbon were also investigated. Thermogravimetric (TG) analysis was employed to characterize the pyrolysis characteristics and activation energy of the walnut shell. N₂ adsorption–desorption isotherm was employed to characterize the pore structure development of walnut shells. Morphology of the samples was characterized by scanning electron microscope. Water vapor adsorption–regeneration performance was carried out under a constant temperature and humidity chamber. Adsorption isotherm measurement was made by a dynamic method using a step change in concentration.

**Experiments**

**Material**

Walnut shell as a raw material for activated carbon was obtained from Yangbi county of Southwest China's Yunnan province. The walnut shell was crushed and sieved to 20–60 mesh. And then the starting materials were washed with distilled water and dried at...
100°C for 12 h for preparation. Nitrogen (99.99%) was used to provide an inert atmosphere. Carbon dioxide (99.99%) was used as an activation gas.

**Carbonization and activation process**

A certain weight of the pre-treated raw material was carbonized at 700°C for 10 min in an electric tube furnace (OTF-1200X, Hefei Kejing Materials Technology Co., Ltd, China) under a nitrogen flow rate of 1000 ml/min. And then the char was taken out after cooling to room temperature. The carbonized samples were obtained. In the carbonization process, both heating rate and cooling rate were 10°C/min.

A certain weight of the carbonized sample was placed in the same electric tube furnace. The temperature of the electric tube furnace was first increased from 30 to 350°C under a nitrogen flow rate of 1000 cm³/min, and then the sweep gas was switched to carbon dioxide with the flow rate of 1000 ml/min. Thereafter, the electric tube furnace temperature was further increased to the desired activation temperature. The reactor of electric tube furnace was held at the activation temperature for a given holding time. During the cooling process, when the temperature dropped to 500°C, the flowing gas was changed from carbon dioxide to nitrogen with the flow rate of 1000 ml/min. In the experiment, the nitrogen was used to protect the sample before the desired activation temperature arrives and after the desired activation temperature process was completed. Both heating rate and cooling rates were 10°C/min in the activation process. When the reactor of an electric tube furnace was cooled down to room temperature, the sample was transferred to a beaker filled with distilled water and this beaker was put in an ultrasonic laboratory cleaner operating (KQ-300VDV, Kunshan Ultrasonic Instruments Co., Ltd, China) at a frequency of 45 kHz with an instrument power of 300 W. This ultrasonic process continued for 40 min at 30°C. The activated products were washed with distilled water after the ultrasonic process, and then the sample was dried at 100°C for 12 h in an oven. The influences of activation temperature and holding time on the properties of the final carbon were discussed. The samples were labeled as ACxy. Small x states the activation temperature in tens (°C), while y indicates the holding time. For example, AC703 indicates a typical sample that the preparation conditions are an activation temperature of 700°C and a holding time of 3 h. Total yield can be calculated after the activation process is completed.

**Material characterization**

The surface morphology of the samples was observed by a field emission scanning electron microscopy (55-VP, Supra, Zeiss). TG analysis experiments were used to analyze the pyrolysis properties of walnut shells using a synchronous thermal analysis (DT-4, Shimadzu, Japan). N₂ adsorption–desorption isotherms of the activated carbons were measured using an autosorb gas sorption analyzer (Autosorb-iQ, Quantachrome Instruments, America). The samples of activated carbons were outgassed at 300°C for 12 h under a nitrogen flow before measurement. The isotherms data were recorded at −196°C. The BET specific surface area was determined from the BET equation. The total pore volume was estimated to be the liquid volume of adsorbate (N₂) at a relative pressure of 0.985. The pore size distributions (PSDs) of the different samples were determined by means of the Horvath–Kawazoe (H–K) methods (Lillo-Ródenas et al., 2003).
Water vapor adsorption–regeneration experiment

A certain weight of activated carbon was placed in a constant temperature and humidity chamber (KW-TH-225Z, Dongguan Kewintest Equipment Co., Ltd, China). Samples obtained for the same preparation condition were repeated at least two times to ensure the good accuracy of experimental data. In the adsorption process, the relative humidity was 70% and the temperature was 25°C. The weight of all samples at different time points was measured using an electronic analytical balance (ME204-02, Mettler Toledo, Switzerland) with an accuracy of 0.0001 g. The weighing interval gradually changed from 30, 60, to 120 min. Adsorption equilibrium of activated carbon was defined when the weight did not increase in two consecutive 120 min interval or weight change in two consecutive 120 min interval was less than 3%. Regeneration process after water vapor adsorption process was one of the important performance of activated carbon. After the adsorption process, the regeneration process was carried out under the relative humidity of 20% and the temperature of 90°C. The weighing interval was 10 min. When the sample weight did not decrease in two consecutive intervals or the weight change of less than 3% in two consecutive weighing ranges, the regeneration experiment was complete.

Water vapor adsorption isotherm experiment

Adsorption isotherm experimental system for water vapor is shown in Figure 1. Adsorption isotherm measurement is made by a dynamic method using a step change in concentration. Nitrogen gas from the high pressure cylinder is divided into two paths, one of which is used to carry water vapor and the other is used to dilute the saturated water vapor to obtain the appropriate relative humidity. Their flow rates were controlled by the mass flow controller (Beijing Sevenstar Flow Co., Ltd, China). In order to obtain the saturated water vapor, the water saturator with ultrapure water was heated with a thermostatic water bath and then the super-heated vapor was condensed with a condenser before entering the mixing tank. The wet nitrogen flow rate was 500 ml/min during the experiment. The water vapor concentration at the inlet and outlet of the adsorption column was detected by the temperature and humidity sensor (TRM-SZ1, Jinzhou Sunshine Technology Co., Ltd, China). The outlet concentration of water vapor was increased gradually until adsorption equilibrium where the difference between the

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![Figure 1. Schematic diagram of adsorption isotherm experimental system for water vapor. LTB: low-temperature thermostat bath; MFC: mass flow controller; MTHR: multichannel temperature and humidity recorder; THTB: temperature and humidity sensor.](image-url)
inlet and outlet of the adsorption column concentrations did not exceed 3% within more than an hour. The adsorption amount of water vapor onto the walnut-shell activated carbon was calculated by the integral method. The calculation formula is as shown in equation (1)

\[ q_u = \frac{\int (C_{in} - C_{out}) V \, dt}{m} \]  

where \( q_u \) is the adsorption amount of water vapor onto the walnut-shell activated carbon (g/g), \( C_{in} \) is the concentration of water vapor at the inlet of the adsorption column (mg/m\(^3\)), \( C_{out} \) is the concentration at the outlet of the adsorption column (mg/m\(^3\)), \( V \) is the total flow rate of water vapor and nitrogen (ml/min), \( m \) is the mass of activated carbon (g), and \( t \) is the adsorption time (min).

**Results and discussion**

Preparation process of activated carbon plays an important role in the performance of water vapor adsorption–regeneration. In this paper, the influences of carbonization temperature, activation temperature, and holding time were studied.

**Thermal behaviors**

The purpose of carbonization is to increase the carbon content in the raw material. It makes the carbonized chars have enough initial pores and a certain mechanical strength. In this paper, the carbonization process of the walnut shell was studied by the thermogravimetric analyzer (DSC3+, Mettler Toledo, Switzerland). TG analysis and derivative of TG (DTG) of raw material were investigated in an N\(_2\) flow (30 ml/min). The heating rates were 5, 10, and 20\(^\circ\)C/min, respectively. And the weight loss was automatically recorded in the range 25–1000\(^\circ\)C.

**Analysis of pyrolysis characteristics of walnut shell.** Figure 2 shows the TG and DTG curves of walnut shells at different heating rates. It can be seen that the pyrolysis of walnut shells can be roughly divided into three stages: water loss, rapid pyrolysis, and slow decomposition. The first stage is the stage of dehydration and drying in the range 25–250\(^\circ\)C. At this stage, a small weight loss peak appears at around 100\(^\circ\)C on the curve. This part of the weight loss is mainly the release of moisture inside the sample, including physical water and chemically adsorbed water (Zeriouh and Belkbir, 1995). Simultaneously, hemicellulose also begins to slowly decompose due to its poor chemical stability. The weight loss at this stage accounts for about 2–10% of the entire pyrolysis process. The second stage (250–410\(^\circ\)C) is the rapid pyrolysis stage of the sample. This is the most intense interval for pyrolysis of walnut shells. In this temperature range, two huge peaks appear at about 300 and 350\(^\circ\)C, respectively. In general, hemicellulose begins to largely decompose at around 230\(^\circ\)C (Byrne and Nagle, 1997). This decomposition process destroys the connection between cellulose and hemicellulose, which leads to an increase in the weight loss rate of the sample as the subsequent temperature increases. The 300\(^\circ\)C peak indicates the decomposition of hemicellulose. The subsequent main peak at 350\(^\circ\)C indicates that cellulose begins to decompose.
The weight loss at this stage accounts for about 80% of the entire pyrolysis process. The third stage between 410 and 900°C is mainly due to the slow decomposition of the residue and weight loss of about 5% occurs. As can be seen from the figure, the initial temperatures of rapid pyrolysis stage moves slightly toward the high temperature side with increasing heating rate. And the main reaction interval also reduces with increasing heating rate. The increase in heating rate shortens the time required for the sample to reach the same temperature, which causes this phenomenon to occur. On the other hand, lower heating rate leads to the increase of production costs. Therefore, the optimal heating rate is 10°C/min.

**Kinetic analysis of pyrolysis reaction of walnut shell.** Based on the experience of previous research kinetics, the pyrolysis kinetics analysis of walnut shells is directed to the most severe phase of weight loss during the pyrolysis phase (Uzun and Yaman, 2016; Yang et al., 2019). The walnut shell with an initial mass of \(m_0\) decomposes at a heating rate of \(\beta\). At a certain time \(t\), the mass becomes \(m\) and then the decomposition rate can be expressed by the following formula

\[
\alpha = \frac{(m_0 - m)}{(m_0 - m_\infty)}
\]

where \(\alpha\) is the degree of decomposition at time \(t\) and \(m_\infty\) is the mass at the end of pyrolysis of the sample.

Generally, the thermal decomposition process of biomass is represented by the Arrhenius equation (Açıkalm, 2011), as shown in equation (3)

\[
d(\alpha)/dT = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)f(\alpha)
\]

and

\[
f(\alpha) = (1 - \alpha)^n
\]

where \(E\) is the activation energy of the reaction (kJ/mol), \(A\) is the frequency factor (min\(^{-1}\)), \(R\) is the gas constant (kJ/(mol K)), \(T\) is the absolute temperature (K), \(f(\alpha)\) represents a hypothetical model of the reaction mechanism, and \(n\) represents the reaction order.
Kinetic treatment using the Coats–Redfern method (Wilson et al., 2011), the integral form \( g(x) \) of equation (5) is

\[
g(x) = \begin{cases} 
\frac{-\ln(1-x)}{n} & n = 1 \\
\frac{1 - (1-x)^{1-n}}{1-n} & n \neq 1 
\end{cases}
\] (5)

According to the Arrhenius formula, the graph of \(-\ln \left[ g(x) / T^2 \right] \) against \( 1/T \) should be a straight line. The slope of the straight line is \( E/R \) and the intercept is \(-\ln(AR/\beta E)\) (Fan et al., 2018). Using this equation, the kinetic analysis of the walnut shell at a heating rate of 5, 10, and 20°C/min is carried out. The linear regression effect is shown in Table 1. The kinetic parameters are shown in Table 2.

It can be seen from Table 2 that the Arrhenius equation has a good fitting effect on the rapid pyrolysis stage of walnut shells. Compared with 5°C/min, the heating rate of 10°C/min has a higher linear correlation coefficient. It can be seen from Table 2, when the heating rate is from 5 to 10°C/min, the activation energy is reduced from 35.18 to 30.16 kJ/mol. At the same time, the reduction of activation energy is accompanied by a decrease in the frequency factor. The reason is that the pyrolysis is a severe decomposition reaction. The bursting and breaking phenomenon existing in this process makes the walnut shell form a loose porous structure. Moreover, the reaction surface area caused by the bursting and breaking increases, making the reaction easier and more thorough. An increase in the rate of temperature increase within a certain range leads to more severe bursting and fragmentation.

### Table 1. Correlation coefficients for different reaction orders at different heating rates.

| Reaction order, n | Correlation coefficient, \( R^2 \) |
|------------------|----------------------------------|
|                  | 5 \(^{\circ}\)C/min | 10 \(^{\circ}\)C/min | 20 \(^{\circ}\)C/min |
| 0                | 0.9934 | 0.9975 | 0.9826 |
| 0.5              | 0.9935 | 0.9974 | 0.9826 |
| 1                | 0.9880 | 0.9973 | 0.9930 |
| 1.5              | 0.9784 | 0.9972 | 0.9943 |
| 2                | 0.9664 | 0.9970 | 0.9934 |
| 2.5              | 0.9532 | 0.9970 | 0.9905 |
| 3                | 0.9400 | 0.9968 | 0.9862 |

### Table 2. Pyrolysis kinetic parameters of walnut shell at different heating rates.

| Heating rates \(^{\circ}\)C/min | Fitting temperature \(^{\circ}\)C | Activation energy E (kJ/mol) | Frequency factor A (1/min) | Reaction order |
|-------------------------------|-------------------------------|-------------------------------|----------------------------|----------------|
| 5                             | 244–377                       | 35.18                         | 2.8712 \times 10^8         | 0.5            |
| 10                            | 251–380                       | 30.16                         | 7.7613 \times 10^7         | 0              |
| 20                            | 264–393                       | 64.86                         | 4.7913 \times 10^8         | 1.5            |
Therefore, the dynamic characteristics of walnut shells in the rapid pyrolysis stage show the characteristics of frequency factor and activation energy reduction. When the heating rate is 20°C/min, the activation energy is significantly increased to 64.86 kJ/mol. This may be due to the fact that the temperature rise is too fast and the heat transfer of the sample is delayed. Therefore, reduction of activation energy at 10°C/min indicates that the sample is more susceptible to pyrolysis at this heating rate.

**Characterization of samples**

*Morphology characterization.* Figure 3 shows the morphologies of the walnut shell, char, and activated carbon (AC903). The surface morphologies of these three samples are significantly different. As can be seen in Figure 3(a) and (b), the surface of the walnut shell is rough, with a small amount of pores. After the carbonization process, a small amount of new developed porous structure exists on the surface of the char. These crater-like pores may be formed by pyrolysis of hemicellulose and cellulose and then the sudden escape of hot gases from the walnut shell. It can be seen from Figure 3(c) that the external surface of AC903 is covered with irregular-shaped pores after the CO₂ activation process. Further enlargement here can be seen from Figure 3(d) that interconnected macropores are evident and signs of micropores are also observed. The experimental results are consistent with the

![Figure 3](image.png)

**Figure 3.** Morphology of samples: (a) raw material (walnut shell), (b) char, and (c) and (d) AC903.
When \( \text{CO}_2 \) gas diffuses within the carbon matrix, a \( \text{CO}_2 \) molecule can react with a carbon atom and two \( \text{CO} \) molecules are obtained. When the \( \text{CO} \) gas escapes from the carbon matrix, pore structures of carbon materials can be formed and well developed.

N\(_2\) adsorption–desorption isotherms of the activated carbons: (a) activation temperature and (b) holding time.

| Sample  | Preparation conditions | \( S_{\text{BET}} \) (m\(^2\)/g) | \( V_{\text{total}} \) (cm\(^3\)/g) | \( D_{\text{average}} \) (nm) | Total yield (%) | Water adsorption capacity \(^a\) (g/g) |
|---------|------------------------|-------------------------------|---------------------------------|-----------------------------|-------------------|---------------------------------|
| AC703   | 700°C, 3 h             | 548                           | 0.214                           | 1.8120                      | 26.53             | 0.1300                          |
| AC803   | 800°C, 3 h             | 719                           | 0.328                           | 1.8240                      | 13.15             | 0.1846                          |
| AC903   | 900°C, 3 h             | 1228                          | 0.579                           | 1.8873                      | 11.47             | 0.3824                          |
| AC953   | 950°C, 3 h             | 924                           | 0.345                           | 1.8479                      | 10.21             | 0.2169                          |
| AC901   | 900°C, 1 h             | 961                           | 0.346                           | 1.8488                      | 21.23             | 0.1891                          |
| AC902   | 900°C, 2 h             | 1135                          | 0.531                           | 1.8706                      | 16.67             | 0.2924                          |
| AC903   | 900°C, 3 h             | 1228                          | 0.579                           | 1.8873                      | 11.47             | 0.3824                          |
| AC904   | 900°C, 4 h             | 1184                          | 0.551                           | 1.8721                      | 10.24             | 0.2613                          |

\(^a\) Adsorption conditions: \( T = 25°C, P_0 = 3168.7 \text{ Pa}, \text{ relative humidity (P/P}_0 \) = 70%, \( P = 2218.1 \text{ Pa.} \)

CO\(_2\)-activation mechanism (Wu et al., 2018, 2013). When \( \text{CO}_2 \) gas diffuses within the carbon matrix, a \( \text{CO}_2 \) molecule can react with a carbon atom and two \( \text{CO} \) molecules are obtained. When the \( \text{CO} \) gas escapes from the carbon matrix, pore structures of carbon materials can be formed and well developed.

**\( \text{N}_2\) adsorption isotherms and pore development of the “green” adsorbents.** In this study, \( \text{N}_2\) adsorption–desorption isotherms are measured to study the pore properties of activated carbons and shown in Figure 4. The BET specific surface area (\( S_{\text{BET}} \)), total pore volume (\( V_{\text{total}} \)), average pore diameter (\( D_{\text{average}} \)), and water vapor adsorption capacity (\( q \)) of activated carbons are presented in Table 3. Figure 5 shows the PSDs of activated carbons which are prepared at different conditions.

As shown in Figure 4, the adsorption and desorption branches of the isotherms have a good coincidence. The phenomenon of the nitrogen adsorption is only significant when the relative pressure is less than 0.1. When the relative pressure continuously increases, the amount of adsorption almost keeps constant. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, all the \( \text{N}_2\) adsorption isotherms display a type I shape which indicates that the pore structure of activated carbon is mainly
dominated by micropores. Moreover, it is observed that the accumulative N2 adsorption amounts first increase with the increasing of activation temperature from 700 to 900°C and then decrease significantly. The influence of holding time on accumulative N2 adsorption amounts has the same change tendency. The reason may be that the reaction of CO2 with carbon atom is an endothermic reaction. Appropriately increasing activation temperature and holding time is beneficial for the reaction and enhancing the pores’ development. However, when the activation temperature and holding time exceed to 900°C and 3 h, respectively, excessive reaction of CO2 with carbon atom can result in burning of carbon, decline of activated carbon yield, and hence decrease of pore structure.

As presented in Table 3, these samples after CO2 activation have high SBET (548–1228 m2/g) and Vtotal (0.214–0.579 cm3/g). When the holding time is 3 h, the SBET and Vtotal increase sharply from 548 to 1228 m2/g, from 0.214 to 0.579 cm3/g, respectively, within the range of 700–900°C. And then values of them sharply decrease to 924 m2/g and 0.345 cm3/g, respectively, at an activation temperature of 950°C. In terms of holding time, when the activation temperature is 900°C, the SBET and Vtotal increase significantly from 961 to 1228 m2/g, from 0.214 to 0.579 cm3/g, respectively, with the increase of holding time from 1 to 3 h. And then when the holding time is 4 h, values of them slightly decrease to 1184 m2/g and 0.551 cm3/g, respectively. In other words, activation temperature plays a more important role in pore development of ACs than holding time do.

The PSDs calculated by the H–K methods of ACs are shown in Figure 5. In accordance with IUPAC, the PSDs of the super-micropores are between 0.7 and 1 nm and those less than 0.7 nm are called ultra-micropores. All the PSDs mainly concentrate below 0.7 nm. Compared with other samples, AC903 shows more super-micropores and its PSD peaks at 0.45 nm.

According to the N2 adsorption–desorption isotherms and their corresponding results, the optimal activation temperature and holding time are 900°C and 3 h, respectively. It naturally follows that AC903 is a microporous activated carbon as the optimal adsorbent and suitable for water vapor adsorption applications.

**Total yield analysis.** As shown in Table 3, total yields of ACs decrease with the increase of activation temperature and holding time. When the activation temperature rises from 700 to
800°C, the total yield decreases sharply by 13.38%. And then the total yield decreases slightly with the increase of activation temperature from 800 to 950°C. Compared with the activation temperature, the holding time has less influence on the total yield of ACs where the activation temperature keeps at 900°C. At the same time, the literature also shows that the holding time has less significant effect on activated carbon BET (Nieto-Delgado and Rangel-Mendez, 2011). In short, when the activation temperature exceeds to 800°C, the endothermic reaction energy barrier of CO₂ with carbon atom has been overcome. Increasing temperature is beneficial for 2 mole of CO formation when 1 mole of CO₂ acts with 1 mole of carbon atom. When CO diffuses from the internal structure of carbon material to the external environment, pore structure of ACs is well developed. However, excessive reaction of CO₂ with carbon atom can result in burning of carbon, decline of activated carbon yield, and hence decrease of pore structure.

**Effect of preparation conditions of water vapor adsorption**

*Activation temperature.* In this study, the effect of activation temperature on the adsorption performance of water vapor is studied when the activation time and the heating rate are 3 h and 10°C/min, respectively. As shown in Figure 6, when the adsorption time is 10 h, the water vapor adsorption capacities of AC703, AC803, AC903, and AC953 are 0.1300, 0.1846, 0.3824, and 0.2169 g/g, respectively. The adsorption capacities of ACs increase significantly with the increase of activation temperature from 700 to 900°C and then decrease sharply. This result agrees well with the N₂ adsorption–desorption isotherm characterization. The reason is that well-developed microporous activated carbon is better for gas adsorption. According to these results of pore development and water vapor adsorption performance, the activation temperature of 900°C is selected for the latter investigation.

*Holding time.* When the activation temperature and the heating rate are 900°C and 10°C/min, respectively, the effect of holding time on water vapor adsorption capacity of ACs is studied

![Figure 6. Effect of activation temperature on water vapor adsorption capacity of ACs. Adsorption conditions: T = 25°C, P₀ = 3168.7 Pa, relative humidity (P/P₀) = 70%, P = 2218.1 Pa.](image)
and shown in Figure 7. When the adsorption time is 10 h, the water vapor adsorption capacities of AC901, AC902, AC903, and AC904 are 0.1891, 0.2924, 0.3824, and 0.2613 g/g, respectively. The water vapor adsorption capacity increases slightly with the increase of holding time from 1 to 3 h and then decreases slightly.

According to the N\textsubscript{2} adsorption–desorption isotherms, total yields, and water vapor adsorption performance of ACs, the optimal preparation conditions are an activation temperature of 900°C and a holding time of 3 h. Under the optimal preparation conditions, the sample exhibits a high water vapor adsorption capacity of 0.3824 g/g. The development of microporous structure of activated carbon has a good consistency with the amount of water vapor adsorption.

**Water vapor regeneration experiment.** After the water adsorption process, the exhausted adsorbents are regenerated in the same constant temperature and humidity chamber under the relative humidity of 20% and the temperature of 90°C. Adsorption capacities of water vapor on AC703, AC901, and AC903 are shown in Figure 8. With the regeneration time of 30 min, all the water adsorption capacities for AC703, AC901, and AC903 are close to zero. That is to say, the exhausted adsorbents can be regenerated under a relative humidity of 20% and a temperature of 90°C. The result confirms that the adsorbents can be regenerated with solar energy.

In order to verify the water vapor adsorption of the walnut-shell activated carbon under a relative humidity of 20% and adsorption temperature of 90°C, about 1 g of sample was put into a constant temperature and humidity chamber. After 10 h of the adsorption process, weight changes of three samples are shown in Table 4. The experimental results indicate that the walnut-shell activated carbon has almost not any adsorption at these conditions. Therefore, these conditions can be used for regeneration of the exhausted activated carbon.

![Figure 7](image)

**Figure 7.** Effect of holding time on water vapor adsorption capacity of ACs. Adsorption conditions: $T = 25°C$, $P_0 = 3168.7$ Pa, relative humidity $(P/P_0) = 70\%$, $P = 2218.1$ Pa.
Adsorption isotherm of water vapor

The water vapor adsorption isotherms of ACs are shown in Figure 9(a) and (b), respectively. According to the IUPAC classification, all their adsorption isotherms belong to type V isotherm. The water vapor adsorption performance of activated carbon is poor when the relative pressure of water vapor is less than 0.5. The best sample (AC903) has an adsorption capacity of only 0.1022 and 0.0360 g/g at this relative pressure at 25 and 50°C, respectively. These adsorption amounts account for 28 and 30% of the equilibrium adsorption capacity, respectively. It shows that AC903 still has a certain dehumidification ability under a low relative pressure. On the other hand, the equilibrium adsorption amounts of AC903 at 25 and 50°C are 0.3643 and 0.1214 g/g, respectively, which indicates that the equilibrium adsorption amount decreases with the increase of adsorption temperature and the regeneration of ACs can be realized by increasing the temperature. The results show that the adsorbent can be utilized in solar drying system coupled with dehumidification unit.

Figure 8. Regeneration performance of ACs. Regeneration conditions: \( T = 90°C, P_0 = 70121 \text{ Pa}, \) relative humidity \( (P/P_0) = 20\% \), \( P = 14024.2 \text{ Pa} \).

Table 4. Weight changes of three samples at 90°C at 20% RH.

| Adsorption time (h) | AC703 (g) | AC901 (g) | AC903 (g) |
|---------------------|-----------|-----------|-----------|
| 0                   | 1.0186    | 1.0137    | 1.0186    |
| 0.5                 | 1.0189    | 1.0149    | 1.0197    |
| 1                   | 1.0176    | 1.0138    | 1.0194    |
| 2                   | 1.0226    | 1.0160    | 1.0206    |
| 4                   | 1.0183    | 1.0248    | 1.0159    |
| 6                   | 1.0198    | 1.0148    | 1.0187    |
| 8                   | 1.0194    | 1.0119    | 1.0167    |
| 10                  | 1.0189    | 1.0129    | 1.0186    |

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Conclusion

Walnut-shell activated carbons without any chemical residue were prepared by CO$_2$ physical activation and used for water vapor adsorption in solar drying dehumidification and regeneration system. TG analysis showed that the optimal carbonization temperature and heating rate in the carbonization process were 700°C and 10°C/min, respectively. The activation energy at different heating rates varied from 30.16 to 64.86 kJ/mol. The optimal preparation conditions were an activation temperature of 900°C and a holding time of 3 h. Under the optimal preparation conditions, the sample exhibited a high water vapor adsorption capacity of 0.3824 g/g and it took only 30 min to realize regeneration. And the maximum BET specific surface area 1228 m$^2$/g also occurred in this optimal preparation condition. The development of microporous structure of activated carbon had a good consistency with the amount of water vapor adsorption. Compared with the holding time, the activation temperature had a great impact on the performance of water vapor of activated carbon in the activation process. Higher activation temperature or longer holding time could result in burning of carbon, decline of activated carbon yield, and hence decrease of pore structure. It naturally followed the decline of water vapor adsorption performance of activated carbon. Therefore, AC903 had a more comprehensive range of applications in the field of food processing.

Declaration of Conflicting Interests

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