Effect of carbonization temperature on characterization and water vapor adsorption of coffee-shell activated carbon

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Abstract
Coffee shells, which are abundant in cellulose and lignin, are good raw materials to prepare activated carbon. In this paper, coffee shells were selected as raw materials for activated carbon preparation by KOH chemical activation. Influence of carbonization temperature on adsorption capacity of water vapor over activated carbon was researched. Thermogravimetric analysis was employed to select the scope of carbonization temperature. Activation energies of coffee shells pyrolyzed at different heating rates were calculated. Nitrogen adsorption/desorption isotherm and scanning electron microscopy (SEM) were adopted to characterize the activated carbon. And water vapor adsorption isotherms were simulated by the finite simplification model of Do-Do adsorption model. The results show that activation energies of coffee shells pyrolysis process with heating rates of 5, 10 and 20 K/min are 17.21, 18.01 and 57.52 kJ/mol, respectively. The optimal carbonization temperature of coffee shells is 923 K. The adsorption amount of water vapor can reach about 702.3 mg/g under experiment temperature of 298 K and relative humidity of 70%. The highest total pore volume and Brunauer–Emmett–Teller (BET) specific surface area are 1.41 cm³/g and 2817 m²/g, respectively. The simulation results of the finite simplification model are consistent well with water vapor adsorption experiment results. The results show that activated carbon prepared at the optimal condition would be the potential candidate for solar drying system.

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Introduction

Water vapor is one of the most common substances in nature, and its chemical classification belongs to inorganic substances composed of hydrogen and oxygen elements (Robert, 2001). In solar drying dehumidification system, environmental protection, food processing, chemical industry, pharmaceutical refining, aerospace, national defense and other fields, water vapor often co-exists with gas. The existence of water vapor can easily lead to electrochemical corrosion of related equipment, food spoilage and threaten safety of life and property, if content of water vapor is not strictly controlled (Asteman et al., 2000; Sultan et al., 2012). Especially in solar drying systems, too much moisture in the air can seriously affect quality of dry products. Thus, it is very important to dehumidify the air in this system. Solid drying dehumidification which mainly depends on choice of adsorption materials is one of solar drying methods (Wang et al., 2013; Zheng et al., 2014). The most important principles for the selection of adsorption materials are large amounts of cyclic adsorption and lower regeneration temperatures. Commonly used adsorbents are silica gel (Liu et al., 2017), molecular sieve (Wei et al., 2013) and activated carbon (Tso and Chao, 2012). In general, silica gel is utilized diffusely in thermal energy storage (Yu et al., 2014), extraction of water from air (Bar, 2004; Wang et al., 2017), adsorption heat transformation (Gordeeva et al., 2013) and solid desiccant cooling systems (Wang et al., 2009; Zheng et al., 2014). But silica gel cannot be directly used in food production, as dust particles in them could cause cancer in animals and humans (Thoruwa et al., 2000). The complete regeneration temperature of molecular sieve is typically 423 K (Thoruwa et al., 2000). There is incomplete regeneration of molecular sieve based desiccant materials when solar energy is considered as the heat source of regeneration. Activated carbon is diffusely utilized as one of solid adsorbents (Gong et al., 2015; Wang et al., 2011) because of its developed pore structure and favorable adsorption performance (Yu et al., 2019). In addition, its physical and chemical stability is strong and activated carbon is insoluble in water and most other solvents, which make it suitable for solar energy drying system.

Generally speaking, preparation process of activated carbon is usually divided into two steps of carbonization process and activation process. Carbonization is a process in which carbonaceous organic compounds are pyrolyzed and non-carbon elements escape in the form of volatiles to form pores and generate solid pyrolysis products rich in carbon (Teng et al., 1998). The purpose of the process is to obtain a carbonized material which is suitable for activation and owns basic pores and a certain mechanical intension. And nature of the course is organic compounds pyrolysis course in the raw materials, which includes thermal decomposition reaction and polycondensation reaction (Jiang, 2017). During the carbonization process, carbonization temperature directly affects pore structure and strength of carbonization products. At too low carbonization temperature, the carbonization products cannot form enough mechanical strength. If the temperature is too high, it
will promote the orderly change of graphite microcrystals in the carbonization products and reduce void between the microcrystals which affect pore formation during activation process, and then affect water vapor adsorption performance of activated carbon. Therefore, it is necessary to research the influence of carbonization temperature on the porosity characteristics and water vapor adsorption capacity of activated carbon.

At present, there are two kinds of water vapor adsorption mechanisms of activated carbon. The first one is capillary condensation mechanism, and the second one is the cluster growth mechanism. Alcaniz-Monge et al. (2001, 2002) think that adsorption mechanism of water vapor adsorbed over activated carbon surface is capillary condensation mechanism. The theoretical basis of this mechanism is existence of hysteresis loop which is considered to be related to capillary condensation mechanism on water vapor adsorption isotherm. In this mechanism, influence of pore size distribution on the adsorption mechanism is considered, while surface functional group and mineral substance on activated carbon which are recognized as two factors influencing water vapor adsorption are not taken into account. Thus, this mechanism has not been widely accepted and approved. Pierce and Smith (1950; Pierce et al., 1951) proposed cluster growth mechanism firstly, which was perfected by Dubinin and Serpinsky (1981). The mechanism indicates that the water molecules are first adsorbed on activated carbon surface adsorption centers, oxygen containing functional groups and other adsorption center sites. And as the relative pressure increases, water molecules form clusters at these positions by hydrogen bonding. As the relative pressure increases further, water molecules begin to fill the pores. Most investigators who study microporous activated carbon support this mechanism for that the mechanism can explain the influence of surface oxygen-containing functional groups on water vapor adsorption over activated carbon well.

On the other hand, many scholars have tried to use different equations to simulate the water vapor adsorption isotherm of activated carbon. Dubinin and Serpinsky (1981; Dubinin, 1980) are early researchers in the study of water vapor adsorption. They derived DS equation to characterize water vapor adsorption, which was based on the adsorption kinetic theory of water vapor adsorption on adsorption sites of activated carbon. Do et al. (2009) established a new adsorption model, i.e. Do-Do adsorption model, which was on the basis of the water molecular clusters formation and their penetration into micropores. The microporous structure of activated carbon was taken into account and the surface functional groups were assumed to locate at the edges of activated carbon skeleton structure. The hysteresis loop between adsorption isotherm and desorption isotherm is caused by their different mechanisms of water molecules in micropores. The Do-Do adsorption model can not only describe different type’s water vapor adsorption isotherms of porous carbon materials, but also explain the water vapor adsorption mechanism of activated carbon.

This work aims to produce activated carbon from coffee shells to investigate influence of different carbonization temperatures, i.e. 673–973 K, on water vapor adsorption performance and pore properties of coffee shell-based activated carbon. Thermogravimetric analysis of coffee shells is carried out to determine the carbonization temperature range. Activation energies of coffee shells pyrolyzed at different heating rates are calculated. Physical characterization of produced samples are characterized by nitrogen adsorption/desorption isotherm and SEM. And the finite simplification model of Do-Do adsorption model is taken to simulate the water vapor adsorption isotherm of coffee-shell activated carbon (CSAC).
Experimental methods and characterization

Preparation of CSACs

Coffee shells were artificially chosen as precursor for preparing activated carbon. They were wished with deionized water and dried in an oven for latter application. The dried coffee shells were carbonized in Open Type Tube Furnace (OTF-1200X-100) at 673, 773, 873, 923 and 973 K for 40 min, defined as CSAC-C1, CSAC-C2, CSAC-C3, CSAC-C4 and CSAC-C5, respectively. And the whole process was protected by nitrogen with a flow rate of 100 L/h until the temperature was reduced to room temperature. The chars were achieved. Potassium hydroxide (KOH) which was used as activating agent was mixed with chars in a mass ratio of 3:1 (KOH: chars) in crucibles and deionized water was added. 7 mL of water was added into every 1 g of chars. The crucibles were placed in High Temperature Furnace (KSL-1200X-H2) and subsequently activated at 1073 K for 10 min then cooled to room temperature under nitrogen protection with flow rate of 48 L/h. The activated products were washed with hydrochloric acid (1 mol/L) in Ultrasonic Cleaner at 303 K for 40 min, then with hot deionized water until pH value was about 6.5 to 7. After washing, the final product was exsiccated at 383 K in an oven overnight (Yu et al., 2019).

Characterization of samples

Thermogravimetric analysis of coffee shells was measured in Thermal Gravimetric Analyzer (Mettler TGA/DSC3+). Coffee shells were ground into powder whose partical size was bigger than 250 mesh and dried at 378 K for 12 h before experiment. Coffee shells were heated from 298 to 1273 K at 5, 10 and 20 K/min, respectively. Meanwhile, the weight loss was also calculated in this range. And the experiment was under a N₂ atmosphere with 50 mL/min flow.

Nitrogen adsorption/desorption isotherms at 77 K were determined by Automated gas sorption analyzer (Autosorb IQ-XR, Quantachrome instrument). The coffee-shell activated carbon was primarily degassed at 573 K for 10 h before the experiment. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the BET specific surface areas from the isotherms. The t-plot method was utilized to figure the micropore volume and area. The total pore volume of CSACs was defined as the volume of adsorbed liquid nitrogen at relative pressure of p/p₀ = 0.99. Density Functional Theory (DFT) was employed to determine pore size distributions (PSDs) of the different samples. The micro-morpholog of the obtained CSACs was detected by a Tescan Vega3 SBH instrument.

Non-equilibrium adsorption of water vapor over CSACs

The non-equilibrium adsorption of water vapor experimental measurement method and instruments are the same as those in the previous work (Yu et al., 2019). The influences of carbonization temperature on water vapor adsorption capacity of CSACs will be discussed in latter part. The adsorption capacity of water vapor over CSACs (q, mg/g) can be calculated from equation (1).

\[
q = 1000 \times \frac{m_{CSAC-t} - m_{CSAC}}{m_{CSAC}}
\]  

(1)
where $m_{CSAC}$ is the initial mass of CSACs, g and $m_{CSAC-t}$ is the weight of activated carbon sample at an adsorption time of $t$ hours, g.

**Water vapor adsorption isotherm experiment**

An adsorption experiment system for testing water vapor dynamic adsorption performance is shown in Figure 1. Nitrogen is directly introduced into the experimental system from gas cylinder and subsequently divided into two parts: one part is directly connected to the mixing chamber; the other part is traversed through deionized water to get wet gas which would be mixed with dry nitrogen to adjust relative humidity of gas in the system. The two parts airs are controlled by mass flow controller (MFC, D07-19B, Beijing Sevenstar Flow Co., Ltd. China). In order to get saturated wet air, low-temperature thermostat bath (LTB, DKB-2215, Shanghai Jing Hong Laboratory Instrument Co., Ltd., China) is used to heat deionized water to produce superheated water vapor, which is condensed by a condenser to get near saturated water vapor before entering the mixing chamber. All pipelines in the experiment system are insulated by electric heating tapes and aluminum silicate insulation cottons to keep temperature stable during experiment. Relative humidity can be controlled by adjusting the flow rate of nitrogen and wet air. And there is a one-to-one correspondence between relative humidity and relative pressure at the same temperature. Thus, relative pressure can be calculated by relative humidity. In this isothermal adsorption experiment, the flow rate of wet air is maintained at 500 mL/min and temperature of adsorption column is about 298 K. Both inlet and outlet concentrations of water vapor are detected by temperature and humidity sensors (PYS-3, Jinzhou Yangguang Meteorological Science and Technology Co., Ltd., Liaoning, China). The outlet water vapor concentration increases gradually during the adsorption process. When the concentration at the outlet rises to that at the inlet and maintains above 30 min with a change range of no more than 2%, it is considered to be adsorption equilibrium. The equilibrium adsorption capacities of water vapor at a relative pressure of $x$ are calculated by equation (2).

$$q_{l} = \frac{V}{m} \int_{0}^{t} (C_{in} - C_{out}) dt$$

(2)

where $V$ is water vapor flow, m$^3$/min; $C_{in}$ and $C_{out}$ respectively represent water vapor concentration at import and export of the adsorption column, mg/m$^3$; $m$ is the initial mass of CSACs, g.

Do-Do adsorption model (Do et al., 2009) illustrated in equation (3) which consists of early water vapor adsorption on the function group sites (the second item on the equation right hand side) and subsequent formation water clusters inside carbon micropores (the first item on the equation right hand side) is used to fit water vapor adsorption isotherms. It considers that $i$ represents growth of water clusters on functional group sites and has no upper limit to infinity. In fact, when $i$ is greater than or equal to $x + 1$, subsequent formation water clusters inside carbon micropores will happen. Therefore, we assume that $i$ cannot exceed a certain finite number $n$, then the summation of these two series in equation (3) applies only to $n$ terms only, not infinity. Equation (3) is rewritten as equation (4). The first item on the equation right hand side is replaced by the geometric series summation rule and the second is replaced by BET equation. Thus, equation (4) can be described as equation (5).
The finite simplification model of Do-Do adsorption model is also used to fit the relationship between relative pressure \((p/p_0)\) and water vapor adsorption capacity \(q_l\) to compare with Do-Do adsorption model.

\[
q_l = q_{ls} \frac{K_l \sum_{i=2+1}^{i} x^i}{K_l \sum_{i=2+1}^{i} x^i + \sum_{i=2+1}^{i} x^{i-x}} + S_0 \frac{K_f \sum_{i=1}^{i} i x^i}{1 + K_f \sum_{i=1}^{i} x^i} 
\]

\[
q_l = q_{ls} \frac{K_l \sum_{i=2+1}^{i} x^i}{K_l \sum_{i=2+1}^{i} x^i + \sum_{i=2+1}^{i} x^{i-x}} + S_0 \frac{K_f \sum_{i=1}^{i} i x^i}{1 + K_f \sum_{i=1}^{i} x^i} 
\]

\[
q_l = q_{ls} \frac{K_l (x^n - x^a)}{K_l (x^n - x^a) + (1 - x^{n-a})} + S_0 \frac{K_f x}{1 - x} \cdot \frac{1 - (n + 1)x^n + nx^{n+1}}{1 + (K_f - 1)x - K_f x^{n+1}} 
\]

where \(q_{ls}\) is the water vapor equilibrium adsorption capacity in the micropore, mg/g; \(S_0\) is the functional group concentration on the surface, mg/g; \(i\) represents the maximum number of water molecules adsorbed on functional group sites; \(z\) represents the water cluster size within the micropore; \(K_l\) is the equilibrium constant of adsorption and desorption in micropore; \(K_f\) is the equilibrium constant of adsorption and desorption of the functional groups.

**Results and discussions**

**Tg-DTG analysis of coffee shells**

In the pyrolysis process of coffee shells with different heating rates of 5, 10 and 20 K/min, thermogravimetric (TG) curve and differential thermogravimetric (DTG) curve of coffee shells are recorded and illustrated in Figure 2. The coffee shells are mainly composed of cellulose, hemicellulose and lignin. And it is known that pyrolysis temperature ranges of hemicellulose, cellulose and lignin are 493–598 K, 583–673 K and 373–1173 K, respectively (Yang et al., 2007).
A weight loss of coffee shells about 74.8 wt.%–87.6 wt.% in 1273 K is observed and the decomposition can be divided into three stages including dehydration stage, rapid decomposition stage and slow decomposition stage. The first stage occurring in 298–483 K interval is dehydration stage, in which the internal water including physical water and chemical adsorption water is escaped mainly leading to a slight weightlessness. In this stage, a smaller peak appears on the DTG curve, which is mainly caused by water evaporation, and the peak temperature appears between 330–359 K. In the second weight loss stage happening during 483–883 K, the TG curve has a great reduction with approximately the weight loss of 54.9 wt. % – 60.7 wt. %. This stage is probably resulted from the decomposition of cellulose, hemicellulose and lignin. And the corresponding DTG curve represents two peaks. The first peak occurs at 504–530 K, which might be due to the maximum decomposition rate of the cellulose (Wongsiriamnuay and Tippayawong, 2010). And the second peak occurs during 602–620 K resulted from the maximum pyrolysis rate of the hemicellulose. The third stage occurs between 883–1273 K and there is no significant weight loss, it is the further cracking process of coffee shells residues due to lignin decomposition. The results indicate that there will be no more pores formed during carbonization process, when the carbonization temperature is greater than 883 K.

**Pyrolysis kinetic analysis of coffee shells**

In the process of thermal decomposition, coffee shells are decomposed into solid phase products and gas phase products under heating condition. The reaction is assumed as irreversible reaction for that the volatile gases are removed in time by high purity nitrogen. Thus, pyrolysis reaction of coffee shells can be abbreviated as A (solid) → B (solid) + C (gas). The decomposition rate of solid A can be expressed as

\[
\frac{dr}{dt} = kf(r)
\]  

in the equation, \( r \) represents the conversion rate and is defined as: \( r = (m_{CS-i} - m_{CS-f})/(m_{CS-i} - m_{CS-f}) \); \( f(r) \) is a function related to the reaction mechanism, \( f(r) = (1 - r)^n \); \( k \) represents the reaction rate constant and given by Arrhenius equation...
$k = Ae^{-\frac{E}{RT}}$. The pyrolysis process is a constant heating rate process, the heating rate $\beta = dT/dt$, K/min. Thus, equation (6) is rearranged as

$$\frac{dr}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} (1 - r)^n$$

(7)

where $m_{CS-i}$ and $m_{CS-f}$ are the initial and final weights of coffee shells in the pyrolysis process, mg, respectively. $m_{CS-i}$ is the weight at any point in the pyrolysis process. $T$ is the absolute temperature, K. $A$ is the pre-exponential factor, min$^{-1}$. $E$ is activation energy, kJ/mol. $R$ is the universal gas constant, 8.314 J/Kmol. $n$ is order of pyrolysis reaction.

Coats-Redfern method (Coats and Redfern, 1964) is used to kinetic processing. Equation (7) is rearranged and integrated as

$$\frac{1 - (1 - r)^n}{1 - n} = \frac{ART^2}{\beta E} (1 - \frac{2RT}{E})e^{-\frac{E}{RT}}$$

(8)

Take the logarithm of this equation

$$\ln \left[ -\frac{\ln(1 - r)}{T^2} \right] = \ln \left( \frac{AR}{\beta E} \right) - \frac{E}{RT} \quad (n = 1)$$

(9)

$$\ln \left[ \frac{1 - (1 - r)^{1-n}}{T^2(1-n)} \right] = \ln \left( \frac{AR}{\beta E} \right) - \frac{E}{RT} \quad (n \neq 1)$$

(10)

Equations (9) and (10) will make for a straight line with $\ln \left[ \frac{1 - (1 - r)^{1-n}}{T^2(1-n)} \right]$ (or $\ln \left[ -\frac{\ln(1 - r)}{T^2} \right]$), $n = 1$ as the ordinate and $1/T$ as the abscissa. And the activation energy $E$ and the pre-exponential factor $A$ are determined from the slope $-E/R$ and the intercept $-\ln(AR/\beta E)$, respectively.

Figure 3 shows the plots of $\ln \left[ 1 - (1 - r)^{1-n}/T^2(1-n) \right]$ or $\ln \left[ -\ln(1 - r)/T^2 \right]$ versus $1/T$ for coffee shells pyrolyzed at different heating rates and correlation coefficient ($R^2$) versus $n$ curves. From what we observed in Figure 3(d), the pyrolysis process of coffee shells with heating rates of 5 and 10 K/min obey the reaction order of 0.5 and $R^2$ are 0.9925 and 0.9986, respectively. While the reaction order of heating rate of 20 K/min is 2.5 and $R^2$ is 0.9905. Pyrolysis kinetic parameters of coffee shells are shown in Table 1. Activation energies of coffee shells pyrolysis process with heating rates of 5, 10 and 20 K/min are 17.21, 18.01 and 57.52 kJ/mol, respectively.

Influence of carbonization temperature on water vapor adsorption capacity

The influence of carbonization temperature on water vapor adsorption capacity over CSACs is exhibited in Figure 4. It can be seen that the carbonization temperature has a great effect on water vapor adsorption performance of CSACs. In the initial stage of the adsorption process, the adsorption rates of the five samples do not differ significantly. When the adsorption time is 6 h, the adsorption amount of CSAC-C1 and CSAC-C2 tend to equilibrium, i.e., 516.2 mg/g, 615.9 mg/g, respectively, for CSAC-C1 and CSAC-C2.
As the carbonization temperature increases, the water vapor adsorption capacity increases obviously. While carbonization temperature is higher than 923 K, the equilibrium adsorption capacity is no longer increased. In other words, there are no new pores produced when the carbonization temperature is greater than or equal to 923 K.

According to Figure 4, the water vapor equilibrium adsorption capacities of CSAC-C1, CSAC-C2, CSAC-C3, CSAC-C4, and CSAC-C5 are 516.2 mg/g, 615.9 mg/g, 673.1 mg/g, 702.3 mg/g and 686.2 mg/g, respectively. Therefore, the carbonization temperature owns a great influence on the adsorption process of CSACs.

**Table 1.** Pyrolysis kinetic parameters of coffee shells.

| β (K/min) | Temperature interval (K) | Regression equation | E (kJ/mol) | A (min⁻¹) | n | R² |
|-----------|--------------------------|---------------------|------------|-----------|---|----|
| 5         | 452–892                  | y = -2070.1x - 11.221 | 17.21      | 7.73E+08  | 0.5 | 0.9925 |
| 10        | 500–610                  | y = -2166.6x - 11.049 | 18.01      | 1.36E+09  | 0.5 | 0.9986 |
| 20        | 500–640                  | y = -6918.2x - 0.415  | 57.52      | 2.09E+05  | 2.5 | 0.9905 |

**Figure 3.** (a - c): Plots of y versus 1/T, \( y = \ln \left[ 1 - \left( 1 - r \right)^{1-n} / T^2 (1-n) \right] \) for \( n \neq 1 \) and \( y = \ln \left[ -\ln(1-r)/T^2 \right] \) for \( n = 1 \); (d): R² versus n curve.
The standard N₂ sorption method was realized to research the BET specific surface area and the porosity of CSACs. Figure 5 and Figure 6 show N₂ adsorption/desorption isotherms and DFT pore size distributions of CSACs prepared at different carbonization temperatures, respectively. According to the IUPAC classification, the isotherms exhibited in Figure 5(a) belong to type I with typical characteristic of microporous material. The sharp rise in the initial portion of the isotherms and the high N₂ adsorption capacity indicate that lots of micropores exist in the CSACs, and no significant hysteresis loop is observed, indicating that a few mesopores or macropores is present in the CSACs. When the relative pressure reaches nearly 0.2, the adsorption capacity increases slightly and isotherms reach.

**Figure 4.** Non-equilibrium adsorption of water vapor over CSACs with different carbonization temperatures for 40 min.

**Figure 5.** (a) N₂ adsorption/desorption isotherms at 77 K on CSACs, (b) semilogarithmic scale adsorption isotherms, solid symbols – adsorption, open symbols – desorption.

**Characteristics of porosity in activated carbon**

The standard N₂ sorption method was realized to research the BET specific surface area and the porosity of CSACs. Figure 5 and Figure 6 show N₂ adsorption/desorption isotherms and DFT pore size distributions of CSACs prepared at different carbonization temperatures, respectively. According to the IUPAC classification, the isotherms exhibited in Figure 5(a) belong to type I with typical characteristic of microporous material. The sharp rise in the initial portion of the isotherms and the high N₂ adsorption capacity indicate that lots of micropores exist in the CSACs, and no significant hysteresis loop is observed, indicating that a few mesopores or macropores is present in the CSACs. When the relative pressure reaches nearly 0.2, the adsorption capacity increases slightly and isotherms reach.
equilibrium state of adsorption, which indicates a certain amount of mesopores in CSACs. According to Figure 5(a) and (b), N2 adsorption amount increases as carbonization temperature increases when the temperature is inferior to 923 K. Further increasing the carbonization temperature to 973 K leads to a few decrease in N2 adsorption amount. This may be mainly caused by that higher carbonization temperature are favorable for micropore formation, while the temperature beyond 923 K results in pores collapse. The results show that the different carbonization temperatures are effective in producing CSACs with large BET specific surface area. CSAC-C1, CSAC-C2, CSAC-C3, CSAC-C4 and CSAC-C5 show BET specific surface areas of 1420 m²/g, 2009 m²/g, 2289 m²/g, 2817 m²/g and 2644 m²/g, respectively. CSAC-C4 shows the greatest BET specific surface area compared to others.

Figure 6 exhibits the DFT pore size distributions of activated carbon carbonized at different temperatures. All of the samples produce multiple peaks with significant maximum values in micropores region and only a small mesopore region with pore width less than 2.5 nm. The facts of pore size distributions suggest that increasing carbonization temperature is beneficial to form micropores when the temperature is below 923 K. The results are in accordance with the results of activated carbon physical characterization based on the N2 adsorption/desorption isotherms listed in Table 2. And all the physical characterization results are in agreement with the N2 adsorption/desorption isotherms. It is indicated that the BET specific surface area and pore volume increase as carbonization temperature increases when the temperature is inferior to 923 K. The variation of the physical characterization may influence water vapor adsorption performance of the CSACs. CSAC-C4 shows the highest BET specific surface area of 2817 m²/g, total pore volume of 1.41 cm³/g and water vapor adsorption capacity of 702.3 mg/g.

**Textural characterization by SEM**

The scanning electron microscopy (SEM) technique was carried out to observe the surface microstructure of the row coffee shells, precursor of CSAC-C4 and prepared CSAC-C4

![Figure 6. PSDs of produced activated carbon.](image-url)
which are illustrated in Figure 7. Figure 7(a) is the SEM photograph of coffee shells with 2,000 times magnification. From the photograph, there are no porous structure within the microstructure of coffee shells, and, the external surface is uneven. According to Figure 7(b) which is SEM image of precursor of CSAC-C4, a few pores exist within the precursor, which are generated by the decomposition of cellulose and lignin in the carbonization process. As can be seen from Figure 7(c), many clear narrow pores are distinct in CSAC-C4, and well-developed pores can be seen. The SEM images of CSAC-C4 show that the extensive external surfaces with irregular cavitation and porosity were produced during activation stage. These pores are created by the vaporization of the chemical reagent KOH during activation leaving gaps.

**Comparison of simulation and experimental results**

Figure 8 indicates the water vapor adsorption isotherm and derivative model fitting curve. According to the classification of IUPAC, all isotherms shown in Figure 8 belong to type V which is a common adsorption isotherm of water vapor adsorbed over activated carbon. Figure 8(a) shows adsorption isotherms of water vapor adsorbed over CSACs measured under experiment temperature of 298 K. Water vapor adsorption capacities increase

### Table 2. Textural parameters and water vapor adsorption capacities of different samples.

| Samples   | $S_{\text{BET}}$ (m$^2$/g) | $S_{\text{micro}}$ (m$^2$/g) | $S_{\text{ext}}$ (m$^2$/g) | $V_{\text{total}}$ (cm$^3$/g) | $V_{\text{micro}}$ (cm$^3$/g) | Capacity of water vapor adsorption (mg/g) |
|-----------|-----------------------------|-------------------------------|-----------------------------|--------------------------------|-------------------------------|---------------------------------------|
| CSAC-C1   | 1420                        | 1109                          | 311                         | 0.76                           | 0.48                          | 516.2                                |
| CSAC-C2   | 2009                        | 1692                          | 316                         | 0.97                           | 0.71                          | 615.9                                |
| CSAC-C3   | 2289                        | 2009                          | 280                         | 1.08                           | 0.81                          | 673.1                                |
| CSAC-C4   | 2817                        | 2386                          | 431                         | 1.41                           | 1.02                          | 702.3                                |
| CSAC-C5   | 2644                        | 2140                          | 403                         | 1.33                           | 0.91                          | 686.2                                |
gradually with relative pressure increasing. When relative pressure is inferior to 0.3, water vapor adsorption capacities of CSACs are very small and less than 100 mg/g, which may be due to active sites formation on surface of activated carbon during KOH activation process (Long et al., 2012). At low relative pressure, active sites induce water molecules to move, and hydrogen bonds are formed between active sites and water molecules to conduct water vapor adsorption behavior in CSACs. When the relative pressure is high, water vapor adsorption amounts of CSACs gradually increase as relative pressure increases. Water vapor adsorption capacities tend to be saturation, when relative pressure is greater than 0.8, which may be resulted from that water vapor adsorption behavior in CSACs is mainly microporous filling at a high relative pressure (Ohta et al., 2008). Research consequences Brennan et al. (2001) show that water molecules are firstly connected with surface functional groups on activated carbon by hydrogen bonds, at low water vapor relative pressure. After that, with increase of relative pressure, water molecules continue to enter the activated carbon and are adsorbed on the previously adsorbed water molecules to form a bigger water molecular clusters. When the water molecular clusters grow to a certain size, they will fracture and start to fill in micropores. Adsorption rates of CSAC-C1 and CSAC-C2 are significantly lower than those of other activated carbon, indicating that CSAC-C1 and CSAC-C2 formed part of mesoporous structure during preparation process. Figure 8(a) to (f) show fitting results of derivative model for water vapor adsorption isotherm, and relevant fitting parameters are shown in Table 3. It can be seen that the derivative model can fit experimental data well. According to Table 3, values of $q_{0s}$, $z$, and $n$ increase with the increase of the carbonization temperature, when carbonization temperature is lower than 923 K, on the contrary, the values decreases. It may be mainly because high temperature is beneficial for micropores formation, while carbonization temperature above 923 K new pore will not be produced or causes previous pores collapsed. Since activation process of five samples is the same, value of parameter $q_0$ changes very little. While value of $K_\mu$ increases with carbonization temperature resulting from that increase of micropores volume leads to it difficult for microporous filling process in activated carbon reaching equilibrium.
### Conclusion

Carbonization temperature in the preparation of CSAC has a great influence on water vapor adsorption capacity, BET specific surface area and pore volume. The results show that activation energies of coffee shells pyrolysis process with heating rates of 5, 10 and 20 K/min are 17.21, 18.01 and 57.52 kJ/mol, respectively. The optimum carbonization temperature is 923 K. At this carbonization temperature, well-developed porous structure was formed and mainly distributed in micropores region. Water vapor adsorption capacity of CSAC with the optimum carbonization temperature of 923 K is 702.3 mg/g. And the highest pore volume and BET specific surface area are 1.41 cm³/g and 2817 m²/g, respectively. The finite simplification model of Do-Do model can be used to fit water vapor adsorption isotherm accurately. Water vapor adsorption over CSAC is dominated by surface functional groups when the relative pressure is lower than 0.3. However, there is mainly microporous filling of water vapor adsorption at higher relative pressure. The experiment results indicate that the produced activated carbon in this work is the potential candidate for solar drying system.

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**Nomenclature**

\[ A \quad \text{pre-exponential factor, min}^{-1} \]
\[ C_{in} \quad \text{inlet concentration of water vapor, mg/m}^3 \]
\[ C_{out} \quad \text{outlet concentration of water vapor, mg/ m}^3 \]
\[ E \quad \text{activation energy, kJ/mol} \]
\[ i \quad \text{the maximum number of water molecules adsorbed on functional group sites} \]
\[ k \quad \text{reaction rate constant of coffee shells pyrolysis process} \]
\[ K_p \quad \text{equilibrium constant of adsorption and desorption in micropore} \]
\[ K_f \quad \text{equilibrium constant of adsorption and desorption on the functional groups} \]
\[ m_{CSAC} \quad \text{initial mass of activated carbon, g} \]
\[ m_{CSAC-t} \quad \text{mass of activated carbon sample at an adsorption time of } t \text{ hours, g} \]
\[ m_{CS-i} \quad \text{initial weight of coffee shells in pyrolysis process, mg} \]
\[ m_{CS-f} \quad \text{final weight of coffee shells in pyrolysis process, mg} \]
\[ m_{CS-t} \quad \text{the weight at a pyrolysis time of } t \text{ in the pyrolysis process, mg} \]
\[ n \quad \text{order of pyrolysis reaction} \]
\[ q \quad \text{adsorption capacity of water vapor over activated carbon, mg/g} \]
\[ q_p \quad \text{equilibrium adsorption capacity of water vapor at relative pressure of } x, \text{ mg/g} \]
\[ q_m \quad \text{water vapor equilibrium adsorption capacity in the micropore, mg/g} \]
\[ r \quad \text{conversion rate of coffee shells pyrolysis process, mg/mg} \]
\[ R \quad \text{universal gas constant, 8.314 J/K·mol} \]
\[ S_0 \quad \text{functional group concentration on the surface, mg/g} \]
\[ t \quad \text{non-equilibrium adsorption time, h} \]
\[ T \quad \text{absolute temperature, K} \]
\[ V \quad \text{water vapor flow, m}^3/\text{min} \]
\[ x \quad \text{relative pressure, } p/p_0, \text{ Pa/Pa} \]
\[ z \quad \text{water cluster size inside the micropore} \]
\[ \beta \quad \text{heating rate of coffee shells in pyrolysis process, K/min} \]