

Textural characteristics of activated carbon by single step CO₂ activation from coconut shells

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ABSTRACT

The use of coconut shells as feedstock for the preparation of activated carbons is well adopted industrially, using conventionally two stage activation process, either using steam or CO₂ as the activating agent. The present study attempts to utilize a one-step CO₂ activation to prepare activated carbon from coconut shell, which has received far less scientific attention. Experimental results show that activation temperature, CO₂ flow-rate, holding time and heating rates have significant effects on BET surface area, micropore volume and pore size distribution (PSD). The optimum conditions for activation have been found to be an activation temperature of 900 °C, a CO₂ flow-rate of 200 cm³/min, a holding time of 140 min, and a heating rate of 10 °C/min. The optimum conditions yielded an activated carbon with a BET surface areas of 1667 m²/g and micropore volume of 0.8949 cm³/g, which are significantly higher than the activated carbon produced either using two stage activation process or one-step steam/CO₂ activation for other precursors.

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1. Introduction

Activated carbons with highly developed surface area are being widely used in numerous fields, for separation and purification of liquids and gases, removal of toxic substances, as catalyst support, etc. Activated carbons are noteworthy for their ability to selectively absorb molecules from both liquids and gases. Activated carbons have been traditionally produced by the partial gasification of the char either with steam or CO₂ or combination of both. The gasification reaction results in the removal of carbon atoms, in the process simultaneously produce a wide range of pores (predominantly micropores), resulting in porous activated carbon. Precursors to activated carbons are either of botanical origin (e.g. wood, coconut shells and nut shells) or of degraded and coalified plant matter (e.g. peat, lignite and all ranks of coal). Agricultural by-products are considered as very important feedstock as they are renewable and low-cost materials.

In general, there are two main steps for the preparation of activated carbon: (1) the carbonization of carbonaceous precursor below 800 °C, in the absence of oxygen, and (2) the activation of carbonized product (char), either using physical or chemical

activation methods. Generally physical activation is a two-step process which involves carbonization of a carbonaceous material followed by activation of the resulting char at elevated temperature in the presence of suitable oxidizing gases such as carbon dioxide, steam, air or their mixtures. In the chemical activation process, both steps are carried out simultaneously, with the precursor being mixed with chemical activating agents. Chemical activation offers several advantages which include single step activation, low activation temperatures, low activation time, higher yields and better porous structure. However, the process involves a complex recovery and recycle of the activating agent, which generates liquid discharge that demands effluent treatment.

The one-step activation process is desirable due to lower energy consumption, capital expenditure, processing time that can significantly improve the process economics (Minkova *et al.*, 1991). One-step activation with steam or CO₂ for the preparation of activated carbons from agricultural by-products at laboratory scale has been due to Alaya *et al.* (2000), El-Hendawy *et al.* (2001), Gergova and Eser (1996), Girgis *et al.* (2002), Lua and Guo (2000), Minkova *et al.* (2000, 2001), Rodríguez-Reinoso *et al.* (1985), Savova *et al.* (2001), and Şentorun-Shalaby *et al.* (2006). Table 1 summarizes various works reported in literature in terms of the precursors utilized and experimental conditions, which highlights the significance of one stage activation process.

Coconut shells are suitable for preparing microporous activated carbons due to their excellent natural structure and low ash content (Su *et al.*, 2003). Studies on one-step CO₂ activation of coconut shell

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Table 1

Summary of the various work reported in literature.

Precursors	Activation temperature (°C)	Holding time (h)	Activating agent	References
Plum stones, peach stones	800–850	8 or 16	CO ₂	Rodríguez-Reinoso <i>et al.</i> (1985)
Oil palm stones	650–950	0.5–3	CO ₂	Lua and Guo (2000)
Corn cobs	600, 700	2	Steam	El-Hendawy <i>et al.</i> (2001)
Almond shells, nut shells, peanut hulls, apricot stones, grape seeds	800	1	Steam	Savova <i>et al.</i> (2001)
Apricot stones	650–850	1–4	Steam	Şentorun-Shalaby <i>et al.</i> (2006)
Birch wood, olive stones, bagasse, pelletised straw, miscanthus	700–800	1 or 2	Steam or mixture of steam and carbon dioxide	Minkova <i>et al.</i> (2001, 2000)
Apricot stones	600–800	2–3	Steam	Gergova and Eser (1996)
Date palm wastes, rice husks	600, 700	2	Steam	Alaya <i>et al.</i> (2000)
Olive oil mill wastes	600–800	0.25–2	Steam	Girgis <i>et al.</i> (2000)

have not been reported in literature and hence the present study attempts to prepare activated carbon with well-developed porosity. In addition the present work attempts to assess effects of activation conditions such as CO₂ flow-rate, heating rate, activation temperature and holding time on the pore characteristics of activated carbons to optimize the process conditions.

2. Experiment

2.1. Materials

The precursor coconut shells as received from Vietnam is washed with distilled water and dried at 110 °C for 48 h to reduce the moisture content. The dried samples are then crushed and sieved to particle-size in the range of 4–5.6 mm and stored in air tight containers for further experimentation. The results of the proximate analysis of the coconut shells are listed in Table 2.

Table 2

Proximate analysis results of coconut shells.

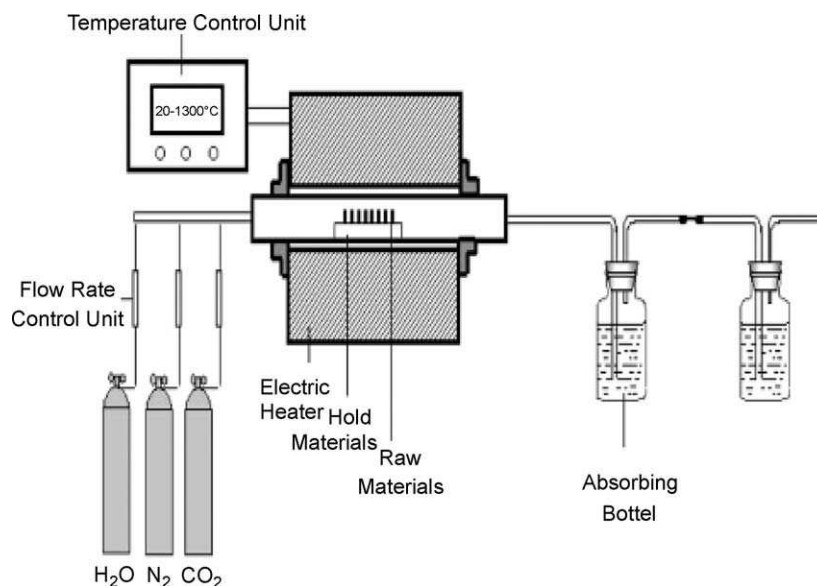
Moisture (wt.%)	Volatile matter (wt.%)	Fixed carbon (wt.%)	Ash (wt.%)
10.53	70.06	18.75	0.66

2.2. Methods

The experimental apparatus utilized in the present study for the preparation of activated carbon is shown in Fig. 1. One-step CO₂ activation is performed in a horizontal tube furnace under desired activation conditions. A metal-mesh holder containing about 30 g of precursors is placed into a stainless-steel reactor (length 450 mm, internal diameter 45 mm) which in turn is positioned into the tube furnace. The sample is heated to the desired temperature with an appropriate heating rate, maintained for a desired holding time, at a desired CO₂ flow-rate. The end of experiment is marked by the termination of CO₂ flow and purging N₂ flow until the samples are cooled to the atmospheric temperature. Experiments are conducted to assess the effect of various influencing parameters such as the activation temperature (750–950 °C), holding time (60–160 min), CO₂ flow-rates (60–600 cm³/min) and heating rate (10, 30, 50 °C/min) on the pore characteristics of the activated carbon, for the sake of process optimization. Selected experiments are repeated to ensure the repeatability of the experimental results.

2.3. Textural characterization

Pore structure of the sample is characterized by nitrogen adsorption at 77 K with an accelerated surface area porosimetry

**Fig. 1.** Schematic of the apparatus setup used in the present study.

system (Autosorb-1-C, Quantachrome). Prior to gas adsorption measurements, the carbon is degassed at 300 °C in a vacuum condition for a period of at least 2 h. Nitrogen adsorption isotherm is measured over a relative pressure (P/P_0) range from approximately 10^{-7} to 1. The BET surface area is calculated from the isotherms by using the Brunauer–Emmett–Teller (BET) equation (Gregg and Sing, 1982). The cross-sectional area of nitrogen molecule is assumed to be 0.162 nm. The Dubinin–Radushkevich (DR) method is used to calculate the micropore volume (Dubinin, 1975). The pore size distribution is ascertained by non-local density functional theory (NLDFT) (Lastoskie et al., 1994) by minimizing the grand potential as a function of the fluid density profile. The total pore volume (Arriagada et al., 1997) is estimated by converting the amount of N_2 gas adsorbed at a relative pressure of 0.95 to the equivalent liquid volume of the adsorbate (N_2). The mesopore volume is estimated by subtracting the micropore volume from the total volume.

3. Results and discussion

3.1. Effects of activation temperature

It is desirable to produce an activated carbon that has relatively high yield, BET surface area and pore volume as the process economy and the market potential improves with the above characteristics. The effects of activation temperature on the yield, BET surface area, total pore volume and micropore volume of the activated carbons are shown in Table 3 covering an activation temperature from 750 to 950 °C, while the other parameters are maintained at a heating rate 10 °C/min, a holding time 120 min and CO_2 flow-rate 200 cm^3/min , respectively.

It could be observed from Table 3 that the yield of activated carbon decreases progressively with increase in activated temperature from 750 to 950 °C. The higher yield at low temperature could be attributed to the slower carbon and carbon dioxide reaction, with the weight loss predominantly due to the release of volatile matters. The lower yield with the increase in activation temperature is due to the higher rate of the carbon and carbon dioxide reaction. The high yield at low temperature results in a carbon with poor textural characteristics, while the decrease in yield at higher temperature is associated with improvement in the textural characteristics. However, there is big difference of the yield at 950 and 900 °C. There are possibly two reasons. One is that volatile amount and C– CO_2 reaction rate rise when activation temperature is raised. The other is when the activation temperature goes up, ash content of chars relatively increases, so it means calcium and sodium content also increase. Because these elements have catalytic effect on C– CO_2 reaction, these elements speed up C– CO_2 reaction rate. The decrease in yield with increase in activation temperature has been well documented in literature.

The effect of activation temperature on the textural properties of activated carbon is also shown in Table 3. The increase in activation temperature enhances the existing pores and forms new pores by continuous devolatilization of chars and carbon burn-off due to the carbon and carbon dioxide reaction, resulting in higher

Table 3
Effects of activation temperature on the pore characteristics of activated carbons.

Temperature (°C)	Yield (%)	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)
750	25.42	638	0.5103	0.2870
800	22.08	834	0.7017	0.4371
850	18.07	1008	0.7805	0.5071
900	13.25	1343	0.9253	0.7004
950	5.92	642	0.4393	0.3368

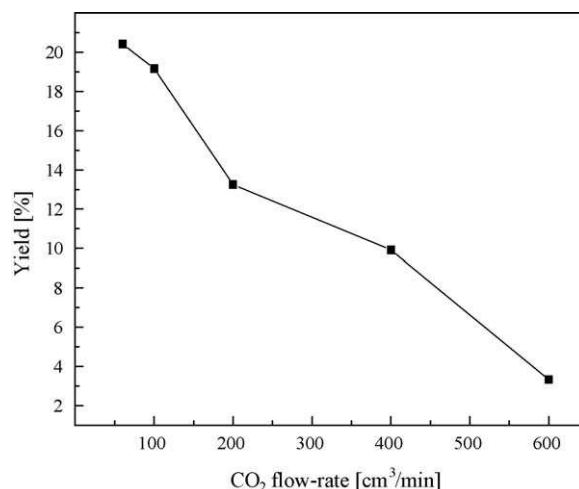


Fig. 2. Yield of activated carbons prepared under different CO_2 flow-rates at activation temperature of 900 °C (holding time 120 min, heating rate 10 °C/min).

BET surface area, total pore volume and micropore volume of the activated carbons. The increase in textural properties is visible until an activation temperature of 900 °C while it is found to decrease beyond 900 °C, possibly due to the further widening of pores that result in collapse of some pore walls. Similar observations of the reduction in textural properties of the activated carbon with increase in temperature beyond the optimum temperature have been reported by Lua and Guo (2000). A BET surface area of 1343 m^2/g with the contribution of micropore volume being 76% of the total pore volume is very significant in comparison with the BET surface area reported in literature. Experiments to assess the effect of other influencing parameters are based on the optimum activation temperature of 900 °C.

3.2. Effect of CO_2 flow-rate

The effect of CO_2 flow-rate on yield of activated carbon is shown in Fig. 2 (an activation temperature 900 °C, a heating rate 10 °C/min and holding time 120 min). It could be seen from the figure that CO_2 flow-rate has significant effect on the yield of the activated carbon, as it controls the rate of reaction of the carbon and carbon dioxide. At high flow-rates the rates of reactions is significantly higher to completely burn of the carbon evidenced by very low yield of less than 4%.

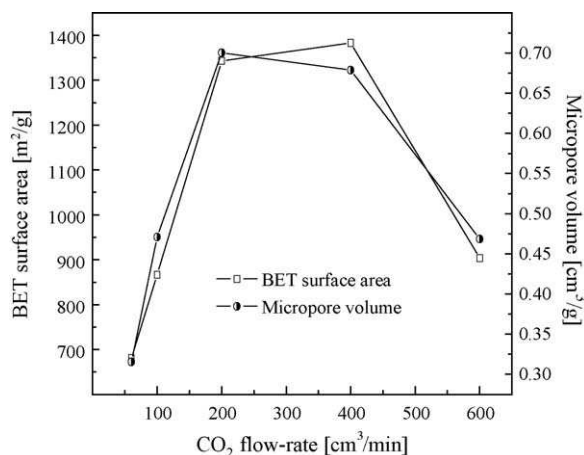


Fig. 3. BET surface areas and micropore volume of activated carbons prepared under different CO_2 flow-rates at activation temperature of 900 °C (holding time 120 min, heating rate 10 °C/min).

The effect of CO₂ flow-rate on BET surface area and micropore volume is shown in Fig. 3, with progressive increment in the BET surface areas and micropore volume, with increase in the CO₂ flow-rate. At lower CO₂ flow-rate, 60 cm³/min the BET surface area and micropore volume are relatively small owing to insufficient amounts of CO₂ gas to diffuse into the sample interior to react with carbon and to effectively remove product gases from the carbon surface. On the other hand when the flow-rate is high, 600 cm³/min, the carbon–carbon dioxide reaction is so fast that it leads to a complete burn-off evidenced by very low yield. The higher rate of reaction and increase in the extent of carbon–carbon dioxide reaction could trigger collapse of pore walls resulting in the reduction of pore volume and surface area. Similar observations of the reduction in textural properties of the activated carbon with increase in flow-rate beyond the optimum flow-rate have been reported by Guo and Lua (2000) and Yang and Lua (2003). Based on the results 200 cm³/min is used as the optimal flow-rate for subsequent experiments.

3.3. Effect of heating rate

The effect of heating rate on BET surface area, total pore volume and micropore volume of the activated carbon is shown in Table 4. BET surface area, total pore volume and micropore volume slightly increase when heating rate is raised from 5 to 10 °C/min, thereafter, these values decrease when heating rate increases from 10 to 50 °C/min. Because the contact time of carbon with CO₂ at 5 °C/min is longer than that at 10 °C/min, carbon ‘burn-off’ is increasing at 5 °C/min, resulting in BET surface area, total pore volume and micropore volume slightly decreasing. However, for heating rate of 30 and 50 °C/min, higher heating rate increases the temperature of material much faster than the lower heating rate as the time required to ramp-up to the desired temperature is less. This effectively alters the contact time of carbon with CO₂, as faster heating rate has shorter effective holding time as compared to the slower heating rate. The shorter effective holding time at higher heating rate could have possibly reduced the extent of carbon–carbon dioxide reaction which explains the reduction in BET surface area, total pore volume and micropore volume at higher heating rate.

Fig. 4 exhibits the nitrogen adsorption isotherms for activated carbons prepared at different heating rate. The isotherms of all activated carbons prepared reflect an intermediate between types I and II of the referred IUPAC classification (Rouquerol et al., 1999), typical of majority in micropores and significant mesopores. As can be seen in Fig. 4, lower heating rate results in a higher volume of nitrogen adsorption generally, which appears to imply that relative low heating rate is conducive for the development of microporosity. Similar observation is also reported by Lua and Guo (2000). It can be concluded that a heating rate of 10 °C/min produces activated carbons with the largest BET surface area, total pore volume and micropore volume and hence it has been chosen as the basis for further experimentation to assess the effects of other parameters.

Table 4
Effects of heating rate on the pore characteristics of activated carbons.

Heating rate ^a (°C/min)	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)
5	1313	0.8962	0.6729
10	1343	0.9253	0.7004
30	1101	0.7800	0.5506
50	1076	0.7629	0.5336

^a Note: activation temperature (900 °C), holding time (120 min), CO₂ flow-rate (200 cm³/min).

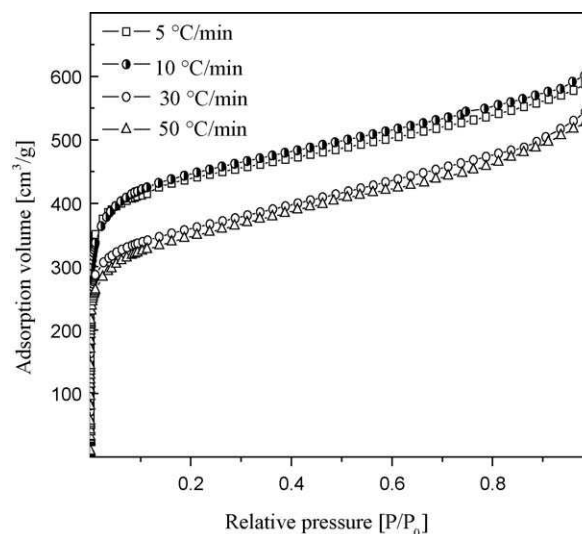


Fig. 4. Effects of the heating rate on Nitrogen adsorption (77 K) isotherms of activated carbons from coconut shells through CO₂ one-step activation (activation temperature 900 °C, holding time 120 min, CO₂ flow-rate 200 cm³/min).

3.4. Effect of holding time

The effect of holding time on yield and textural characteristics of the activated carbon is studied in the ranges of 60–160 min at 900 °C, CO₂ flow-rate of 200 cm³/min and a heating rate 10 °C/min. The effect of holding time on the yield of activated carbon is shown in Fig. 5. It could be observed that the yield of activated carbon decreases with the increase in holding time. This could be expected as the longer holding time would result in higher release of volatiles matter. Further the extent of carbon–carbon dioxide reaction will increase leading to higher carbon burn-off, which well agrees with the current state of knowledge.

Fig. 6 shows the nitrogen adsorption isotherms of activated carbons corresponding to different holding time. It can be seen that the volume of nitrogen adsorbed increases with increase in holding time. The adsorption capacity at relatively low relative pressures (P/P_0) is very high, which indicates the presence of a well-developed microporous structure. According to their shape, all the isotherms in Fig. 6 belong to an intermediate between types I and II of the referred IUPAC classification (Rouquerol et al., 1999). The marginal increase in volume of nitrogen adsorbed at high P/P_0

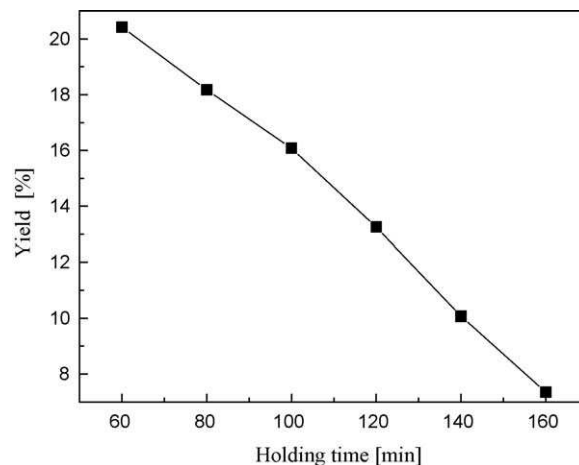


Fig. 5. Yield of activated carbons versus holding time at activation temperature of 900 °C (CO₂ flow-rate 200 cm³/min, heating rate 10 °C/min).

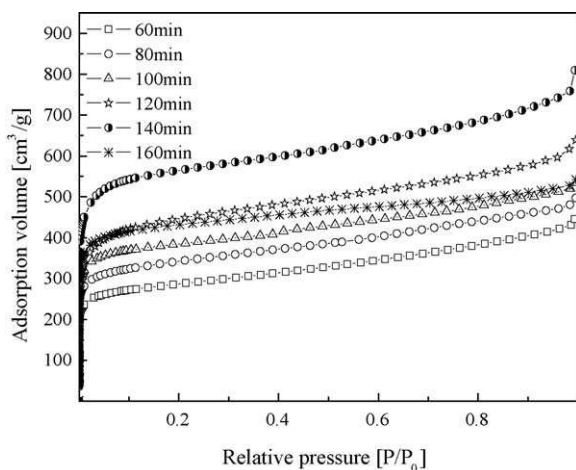


Fig. 6. Effects of the holding time on Nitrogen adsorption (77 K) isotherms of activated carbons from coconut shells through CO₂ one-step activation (activation temperature 900 °C, CO₂ flow-rate 200 cm³/min, heating rate 10 °C/min).

indicates that the carbons are in majority microporous with a relatively well-developed mesoporous structure.

The effect of holding time on porosity development of activated carbon is shown in Fig. 7. With increase in holding time the continual devolatilization and carbon–carbon dioxide reaction, results in the formation of fresh micropores, which increases the BET surface area and micropore volume of activated carbons. However, the increase is limited only up to the optimum holding time of 140 min beyond which a significant reduction in the BET surface area is observed, which could be attributed to the pore wall breakage due to higher extent of carbon–carbon dioxide reaction. A holding time of 140 min based on Figs. 6 and 7 has been selected as the optimum holding time.

3.5. Pore size distribution

Fig. 8 shows the pore size distributions (PSD) of the activated carbon using the non-local density functional theory (NLDFT) for the N₂ adsorption of activated carbons at 900 °C, for various holding time (heating rate of 10 °C/min, CO₂ flow-rate of 200 cm³/min). From the PSD in Fig. 8, the individual contributions by ultra micropores (<0.7 nm), micropores (0.7–2 nm), mesopores (2–50 nm) are calculated. The differential pore volume in all the

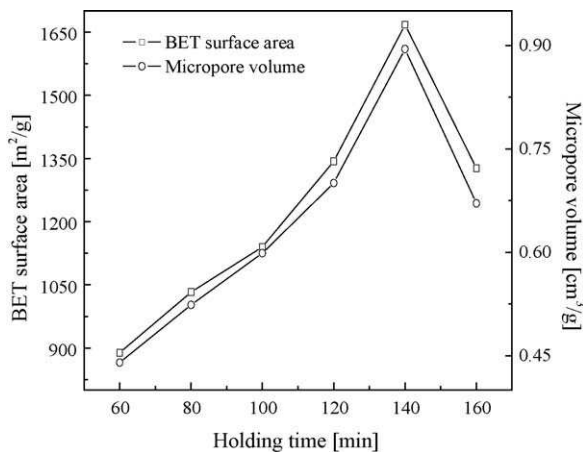


Fig. 7. BET surface areas and micropore volume of activated carbons prepared under various holding time, (activation temperature 900 °C, CO₂ flow-rate 200 cm³/min, heating rate 10 °C/min).

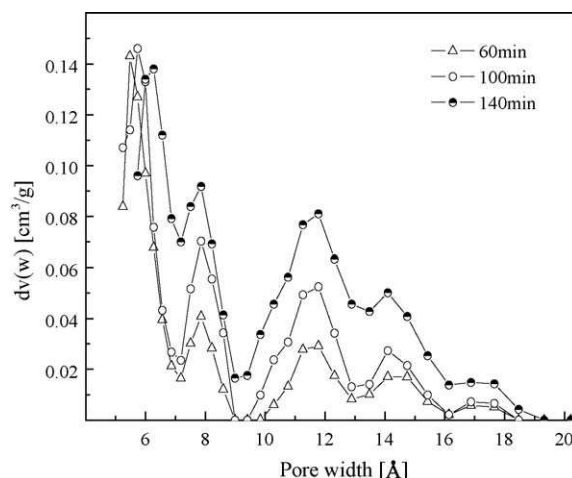


Fig. 8. Pore size distributions of activated carbons prepared at 900 °C for various holding times (CO₂ flow-rate 200 cm³/min, heating rate 10 °C/min).

ranges of micropores, increases with increase in the holding time, with the maximum corresponding to holding time of 140 min, well in agreement with the higher BET surface area and total pore volume reported earlier. However, it can be observed that the ultra micropore volume is very much similar for all the three different holding times, with a marginal variation in the ultra micropore range at lower holding time. It can be concluded that the increase in holding time at 900 °C retains the ultra micropores with significant increase in overall micropore volume.

Fig. 9 shows the PSD at different temperatures for a holding time of 120 min (heating rate of 10 °C/min, CO₂ flow-rate of 200 cm³/min). The ultra micropores are well developed at lower activation temperatures but the pores in micropore ranges are very minimal or otherwise absent. The increase in activation temperature increases the contribution of the pore volume in the micropore range. The pores begin to develop to micropore range only at the activation temperature of 850 °C, still holding the same quantity of ultra micropores corresponding to 750 °C. However, at an activation temperature of 900 °C a significant reduction in the ultra micropore is observed with a significant raise in the micropore range. It can be concluded that the increase in activation temperature increases the pore volume in the micropore range, but in contrast to holding time reduces the ultra micropores. The

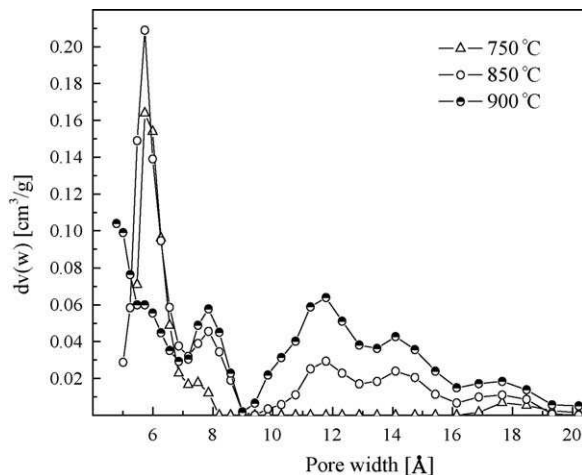


Fig. 9. Pore size distributions of activated carbons prepared at different activation temperatures for 120 min (CO₂ flow-rate 200 cm³/min, heating rate 10 °C/min).

reduction in ultra micropore could be due to enlarging the existing pores, while the increase in total pore volume could be due to cumulative effect of formation of fresh ultra micropores, and enlargement of existing ultra micropores.

3.6. Comparison of pore characteristics

The pore characteristics of activated carbon prepared in the present study, in comparison with the one-step steam or CO₂ activation for other precursors show a significant increase in the surface area and pore volume. Lua and Guo (2000) for oil palm stones have reported a maximum surface area of 1410 m²/g with the corresponding pore volume of 0.71 cm³/g, while Şentorun-Shalaby et al. (2006) for apricot stones using one-step steam activation have reported a maximum surface area of 1092 m²/g with total pore volume of 0.63 cm³/g. The optimum temperature was reported to be 850 °C with an activation time of 120 min by Lua and Guo (2000), while Şentorun-Shalaby et al. (2006) reported an optimum temperature of 800 °C with an activation time of 240 min. However, El-Hendawy et al. (2001) for corn cobs have reported a much lower surface area of 786 m²/g with a total pore volume 0.43 cm³/g at an activation temperature of 700 °C and 120 min activation time. The BET surface area of 1667 m²/g with a pore volume of 1.151 cm³/g is significantly higher than the best of pore characteristics reported by Lua and Guo (2000), could be attributed to the wider range of experimental conditions investigated in the present study and to the variation in the characteristics of the precursor. With the activated carbons produced from coconut shells using physical activation are best sought after industrially due to its physical strength and microporous nature, the successful scaleup of the process could well alter the economics of the activated carbon market.

4. Conclusions

Experimental results testify that high surface area activated carbons could be prepared using one-step CO₂ activation from coconut shells, with relatively well-developed porosity. A wide range of activation parameters investigated in the present study identifies that the activation conditions such as activation temperature, holding time, CO₂ flow-rate and heating rate have dominant impact on the characteristics of activated carbon. The activation temperature of 900 °C, a CO₂ flow-rate of 200 cm³/min, a holding time of 140 min, and a heating rate of 10 °C/min is found to result in activated carbons with a maximum BET surface area of 1667 m²/g and micropore volume of 0.8949 cm³/g.

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