Activated carbon preparation from biomass feedstock: Clean production and carbon dioxide adsorption

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Activated carbon preparation from biomass feedstock: clean production and carbon dioxide adsorption

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Abstract

The current methods used for the production of activated carbon (AC) are often chemical and energy intensive and produce significant amount of chemical waste. Thus, clean production of AC is important to reduce its overall production cost and to limit the adverse effect on the environment. Therefore, the main aim of this study is to develop a clean method for AC production from woody biomass with low chemical consumption. Herein, this study reports a facile strategy for reducing chemical usages in the production of high-performance AC, by introducing a crucial pre-pyrolysis step before chemical activation of biomass. The ACs prepared were characterised using scanning electron microscopy, Fourier transform infrared spectroscopy, nitrogen and carbon dioxide gas adsorption measurements. All these characterisations indicated that produced ACs have similar physicochemical properties. The strategy reduced chemical use by 70% and produced high-performance ultra-microporous ACs with excellent carbon dioxide adsorption capacity (4.22-5.44 mmol m\(^{-2}\)). The facile pre-pyrolysis method is recommended for further research as a cleaner activated carbon preparation method from biomass feedstock.

**Keywords**: Activated carbon; Biomass; CO\(_2\) adsorption; Chemical activation; Surface area
1. Introduction

There is a long history of the production of activated carbon (AC) (Yagmur et al., 2008), which has shown excellent performance in a number of process applications. For example, AC has been used for the removal of heavy metals arsenic and chromium from aqueous solution (Asadullah et al., 2014; Niazi et al., 2018), and for the removal of pharmaceutical compounds from sewage effluent (Grover et al., 2011). AC has also been used for electrical energy application (Arena et al., 2016), greenhouse gas adsorption (Sawant et al., 2017), selective CO$_2$ capture and adsorption (Rashidi et al., 2017), H$_2$ storage, air pollution control (Nor et al., 2013), and as ultra-capacitors (Kim et al., 2016). There are essentially two methods for preparing AC based on physical and chemical activation (Dias et al., 2007). In general, chemically activated AC has higher surface areas and smaller pore sizes and finds broader applications compared to physically activated AC. Physical activation is a two-step process of carbonisation and then activation in carbon dioxide or steam whereas in chemical activation, the carbonisation and activation steps proceed simultaneously in the presence of an activating agent. Chemical activation is conducted with varying ratios of activating agents to biomass as a way to tune the properties of the resultant AC (Dobele et al., 2012; Hayashi et al., 2000). For example, ZnCl$_2$ to biomass ratios range from 1.00:1.00 to 8.00:1.00. The 1.00:1.00 ZnCl$_2$: biomass ratio gave promising results with respect to production temperature (473.00-1,173.00 K) and process conditions (e.g. reactor design, biomass type) (Angin 2014; Saygılı et al., 2016). Similarly, the 4.00:1.00 (KOH: biomass) ratio produced promising results in most of the cases, with respect to different preparatory conditions (Luo et al., 2018; Zhu et al., 2014). Other activating agents (e.g. K$_2$CO$_3$, NaOH, HNO$_3$, H$_3$PO$_4$) were also employed to produce AC at different biomass to chemical ratios. However, extensive use of activating agents will increase the preparation cost and hence decrease the profitability of AC production, as it is often difficult to recover the activating agents (Dobele et al., 2012).
On the other hand, CO$_2$ capture and separation has recently been regarded as an important means to reduce CO$_2$ emission into the atmosphere from fossil fuel combustion and to control global warming (Zhang et al., 2016). Different materials such as AC (Zhang et al., 2016; Sawant et al., 2017), biochar (Huang et al., 2015), carbon nanotube (He et al., 2019), graphene oxide (Zhou et al., 2019) and nitrifier enriched activated sludge (Sepehri and Sarrafzadeh, 2018) can capture CO$_2$ under varying conditions. Moreover, CO$_2$ gas is also used to measure the surface porosity, surface area and other characteristics of carbonaceous material. Therefore, this study used CO$_2$ gas to assess the prepared ACs for their surface areas, porosities and materials characteristics.

Pyrolysed or pre-pyrolysed biomass, hydrochar, char, and biochar have been utilised to produce AC. For example, Azargohar et al. (2006) and Park et al. (2013) used biochar, Dobele et al. (2012) and Lee et al. (2014) used pyrolysed or pre-pyrolysed biomass/carbon, and Parshetti et al. (2015) used hydrochar as precursor to produce AC. However, so far the chemical uses between pre- and post-carbonisation/pyrolysis process to produce AC have not been critically assessed and measured. In this regard, this study has applied pre-pyrolysis as a facile process that reduces the chemicals required to produce AC from biomass. The physicochemical properties and CO$_2$ adsorption capacity of the produced ACs were compared with the results from other studies. Therefore, the key resolution of this study is to reduce the chemical consumption of ACs production while maintaining excellent physicochemical properties that has not been carried out up to now. In addition, the subsequent objective of this study is to evaluate the performance of all ACs in adsorbing CO$_2$ gas at two different temperatures. Thus, the results presented in this study will help to produce clean AC with high adsorption capacity of CO$_2$ for practical industrial application, so as to combat the increase of temperature in the atmosphere.
2. Material and Methods

2.1. Chemicals and biomass

ZnCl$_2$, KOH, NaOH and HCl were purchased from Sigma-Aldrich, Australia. Slash pine (scientific name *Pinus elliottii*) wood was donated by HQ Plantations Pty Ltd, Queensland, Australia. Pine wood was used for this study due to its wide availability in Australia.

2.2. Activated carbon preparation

2.2.1. Pyrolysis step for preparation of activated carbon

Slash pine wood first cut into small sizes and dried before going further steps. Pyrolysis of biomass was carried out using a fixed-bed reactor. Before pyrolysis, 60 mL of 25% (w/v) ZnCl$_2$ solution was added to 15 g of slash pine wood particles (impregnation ratio 1.00: 1.00 i.e. 15 g biomass and 15 g ZnCl$_2$ in 60 mL water) and mixed thoroughly. The resulting mixture was left for 22 h and then dried at 373.00 K for 2 h, and pyrolysed at 853.00 K with an average heating rate of 10.00 K min$^{-1}$ (starting temperature 295.00 K) and held for 2 h under continuous flowing nitrogen at 1.00 psi. The AC produced was poured into deionised water, and pH adjusted to 7.00 using 1.00 N HCl with vigorous stirring and recovered after filtration and drying at 378.00 K. The produced AC was named as AC-1.

The same procedure was repeated, but using KOH as the activating agent to prepare another AC (AC-2). Briefly, 40 mL of 100% (w/v) KOH solution was added to 10 g of slash pine wood (impregnation ratio 1.00: 4.00) with the rest of the procedure as described above.

The AC yield and activation burn-off were calculated using equations (1) and (2):

\[
Y (%) = \frac{W_{ac,final}}{W_{initial}} \times 100
\]

\[
Y_0 (%) = \frac{W_{initial} - W_{ac,final}}{W_{initial}} \times 100
\]

where $Y$ represents the yield of AC after activating agent removal by washing, while $Y_0$ represents the activation burn-off. $W_{initial}$ and $W_{ac,final}$ denote the weight of initial biomass weight and final weight of AC on dry basis.
2.2.2. Pre-pyrolysis method

In this method, biomass was first pyrolysed at 633.00 K for 1 h and the product, termed pyrolysis carbon (PC), was chemically activated to AC following the procedure in section 2.2.1. Briefly, 18.70 mL of 25% ZnCl₂ solution was added to 4.67 g of PC (giving a PC to ZnCl₂ ratio of 1.00:1.00) and left for 22 h before drying at 373.00 K for 2 h. Pyrolysis conditions, product isolation and drying were similar as described earlier. This product was named as PC-AC-1. An identical procedure was used to produce AC using KOH (PC: KOH = 1.00: 4.00) as the activating agent, and the product was referred to as PC-AC-2.

The yield of AC produced from PC and normalised activation burn-off of biomass was calculated using the following equations:

\[
Y_{pc} (%) = \frac{W_{pc,final}}{W_{initial}} \times 100
\]  
(3)

\[
Y_{peac} (%) = \left(\frac{W_{pc,final}}{W_{initial}} - \left(\frac{W_{pc,final} - W_{peac,final}}{W_{initial}}\right)\right) \times 100
\]  
(4)

\[
Y_n (%) = \frac{W_{initial} - W_{peac,final}}{W_{initial}} \times 100
\]  
(5)

where \(Y_{pc}\) represents the yield of PC, \(Y_{peac}\) represents the normalized yield of AC derived from PC, and \(Y_n\) represents the normalized activation burn-off of biomass. \(W_{pc}\) and \(W_{pc,final}\) denote the weight of pyrolysed carbon and final weight of AC derived from PC, respectively.

2.3. N₂ and CO₂ gas adsorption

N₂ and CO₂ gases were used to measure the surface porosity, surface area and other characteristics of carbonaceous material. The textural properties were evaluated by N₂ and CO₂ adsorption measurements at pressures up to 1.00 atm. The adsorption and desorption isotherms (0–1.00 atm) were measured at 273.00 K and 285.00 K (for CO₂), and at 77.00 K (for liquid nitrogen). N₂ and CO₂ adsorption studies were carried out using the volumetric technique on a Quantachrome Autosorb MP instrument using high purity nitrogen (99.99%) and carbon dioxide (99.99%) gases. Degassing procedure was carried out by heating at 150.00
under dynamic vacuum for 12 h. Surface areas were determined using Brunauer-Emmett-Teller (BET) calculations and Density Functional Theory (DFT) calculations. Pore size distributions were calculated using the QSDFT kernel for N\textsubscript{2} at 77.00 K on carbon with slit/cylindrical pores and NLDFT kernel for CO\textsubscript{2} at 273 K and 288.00 K as implemented in the Quantachrome software (v 3.0). The enthalpy of adsorption as a function of CO\textsubscript{2} loading was calculated by application of the Clausius-Clapeyron equation to CO\textsubscript{2} isotherms measured at 273.00 K and 288.00 K:

\[
\ln P = A - \frac{Q_{st} \cdot 1}{RT}
\]  

where \(Q_{st}\) (kJ mol\(^{-1}\)) is the isosteric enthalpy of adsorption, \(R\) (0.0821 J mol\(^{-1}\) K\(^{-1}\)) is the gas constant, \(T\) (K) is the adsorption temperature, and \(A\) is the coefficient.

2.4. Other characterization methods

The Fourier-transform infrared spectroscopy (FTIR) spectra were obtained at 4.00 cm\(^{-1}\) resolution between 600.00 and 4,000.00 cm\(^{-1}\) using 40.00 scans on an ATR Miracle-10 cell (Shimadzu, Japan). The morphology of ACs was obtained using scanning electron microscopy (SEM; Zeiss Evo-LS15 SEM instrument) and with the use of Bruker SDD XFlash 5030 detector. Differential scanning calorimetry-thermogravimetric analysis (DSC-TGA; SDT Q600 V209 Build 20) was used to record mass change and differential heat flow of slash pine biomass from 295.00-873.00 K at 5.00 K min\(^{-1}\) (starting temperature 295.00 K) under a nitrogen flow of 130 mL min\(^{-1}\).

3. Results and Discussion

3.1. DSC-TGA of slash pine wood

Proximate analysis of the slash pine wood indicated that it contains 0.14% ash; 73.36% volatile carbon and 26.50% fixed carbon. It is clear from Fig. 1 that the melting or glass transition of small molecules in slash pine biomass (initial weight was 7.93 g) starts at 315.00 K (Guo et al., 2016). The thermal degradation of slash pine biomass starts by losing 9.61%
mass up to 423.00 K in an endothermic process consistent with the loss of moisture from the sample. Exothermic devolatilisation starts at 483.00 K for decomposition of cellulosic and hemicellulosic components with the major derivative weight loss around 624.00 K indicating maximum devolatilization at this temperature. Devolatilization of biomass is related to the differences in the elemental and chemical compositions of the samples (Idris et al., 2010; Munir et al., 2009). A smaller, less observable evolution profile is evident between 633.00 and 723.00 K with no significant mass loss observed after 723.00 K. It was on this basis that 633.00 K was selected as the temperature for the preparation of PC (Fig. 1).

![Fig. 1. Differential scanning calorimetry-thermogravimetric analysis (DSC-TGA) profile of slash pine wood.](image)

3.2. Structural, textural and surface functional properties of ACs

ZnCl₂ and KOH influence the pyrolytic decomposition of biomass by degradation of the cellulosic fraction, therefore, developing a high porosity carbon skeleton *en route* to a porous AC structure. SEM reveals the ZnCl₂-activated AC particles (AC-1 and PC-AC-1) are flake-like in structure with well-defined smooth surfaces and pores (Figs 2a and 2b). KOH-activated ACs, on the other hand, exhibited an apparent fine cellular-like texture with an
irregular but highly porous surface structure (Figs 2c and 2d). Therefore, there are no significant morphological differences between the pairs of AC materials (i.e. ACs produced from pre-pyrolysis and conventional processes) but tremendous differences in materials activated using ZnCl$_2$ or KOH.

![SEM images of AC materials](image)

**Fig. 2.** SEM images of AC materials. (a) AC produced from slash pine wood using ZnCl$_2$ (AC-1); (b) AC produced from PC using ZnCl$_2$ (PC-AC-1); (c) AC produced from slash pine wood using KOH (AC-2); (d) AC produced from PC using KOH (PC-AC-2).

Surface functional groups of AC samples were characterized using FTIR technique. The FTIR spectra of all the AC samples derived from slash pine wood with ZnCl$_2$ and KOH activation have many similar features, i.e., presence of similar functional groups on their surface (Fig. 3). The bands located in the regions near 3,838.00, 3,734.00, and 3,472.00 cm$^{-1}$ were attributed to –OH functional groups of phenol, alcohol, and carboxylic acid (Martins et al., 2007; Molina-Sabio et al., 2004; Romanos et al., 2011). The relatively intense bands at 2,320.00 cm$^{-1}$ can be attributed to O=C=O formed by the esterification reaction between the
carboxyl and phenolic groups during preparation stages (Li et al., 2017). The intense band at ~2,325.00 cm\(^{-1}\) could also be ascribed to the stretching vibration of C≡C bonds present in alkyne bonds. The peaks observed at 1,695.00 cm\(^{-1}\) were due to C=O stretching in ketones while peaks at ~1,524.00 cm\(^{-1}\) were due to C≡C stretching. However, the other peak at 1,026.00 cm\(^{-1}\) was ascribed to C–O–C stretching that may be present in ethers (Heidari et al., 2017).

![FTIR spectra of produced activated carbon materials.](image)

**Fig. 3.** FTIR spectra of produced activated carbon materials.

### 3.3. Chemical saving in two different strategies

The yield of AC-1 using ZnCl\(_2\) as an activating agent was 28.81% (standard deviation (SD) = 1.80%), which is only marginally higher than for PC-AC-1 at 26.80% (SD = 1.2%). In comparison, a higher yield of PC-AC-2 (24.52% ± 1.60%) was obtained in relation to AC-2 (19.51% ± 2.80%) (Table 1). The slight variations of yield might be due to the adjustment of the porosity while pyrolysis process was carried out. The yield of PC, as calculated using
equation 3, was 31.15%. Chemical consumption (CC) reduction for producing ACs using pre-
pyrolysis method was calculated using equation (7):

\[
CC \text{ reduction (\%)} = \frac{CC \text{ for AC production from biomass} - CC \text{ for AC production from PC}}{CC \text{ for AC production from biomass}} \times 100
\] (7)

The same 1.00:1.00 or 1.00:4.00 ratios of biomass/PC to an activating agent were used to
prepare ACs with conventional and pre-pyrolysis processes as described in this study.
Therefore, the chemical consumption was reduced by 70% in the pre-pyrolysis process
compared to conventional one-step chemical activation to produce the same amount of AC.
This establishes the dramatic reduction in chemical usage in the production of AC. Further
investigation is required to calculate the overall cost of AC production especially that of
energy consumption.

### Table 1

Activating agents, yields and chemical usage reduction for AC produced in this study.

<table>
<thead>
<tr>
<th>Type of activated carbon</th>
<th>Activating agent</th>
<th>Biomass/PC to activating agent ratio</th>
<th>Y (%) (±SD)</th>
<th>Yn (%)</th>
<th>Y_pcAC (%) (±SD)</th>
<th>Yn (%)</th>
<th>Chemical usage reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-1</td>
<td>ZnCl₂</td>
<td>1.00:1.00</td>
<td>28.80±1.80</td>
<td>71.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC-AC-1</td>
<td>ZnCl₂</td>
<td>1.00:1.00</td>
<td>26.80±1.20</td>
<td>73.20</td>
<td>69.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AC-2</td>
<td>KOH</td>
<td>1.00:4.00</td>
<td>19.50±2.80</td>
<td>80.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC-AC-2</td>
<td>KOH</td>
<td>1.00:4.00</td>
<td>24.50±1.60</td>
<td>74.50</td>
<td>70.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3.4. Physicochemical properties of the ACs

To assess the prepared ACs for their surface areas, porosities and materials characteristics,
this study recorded gas sorption isotherms for N₂ at 77.00 K and CO₂ at 273.00 K and 288.00
K. The N₂ isotherms of AC-1, PC-AC-1 and AC-2 are essentially of Type I, according to the
IUPAC classification, suggesting the materials are exclusively microporous (Figs A.1 & A.2).
Sample PC-AC-2 has very small hysteresis loop indicative of some macro-porosity (Figs A.1
& A.2). In all cases, the CO₂ isotherms were closed due to the same adsorption and
desorption branches. The specific surface areas, as calculated through the BET method, for AC-1, PC-AC-1, AC-2 and PC-AC-2 were 1,384.00; 1,122.00; 906.00 and 1,011.00 m² g⁻¹, respectively. Similarly, the DFT specific surface areas for AC-1, PC-AC-1, AC-2 and PC-AC-2 were 1,332.00; 1,155.00; 1,112.00; and 982.00 m² g⁻¹, respectively (Table A.1). These data indicate that the pre-pyrolysis method produces ACs of the comparable surface area to conventional chemical activation.

3.5. \( \text{CO}_2 \) adsorption performance

This study used \( \text{CO}_2 \) adsorption to obtain greater insight into the porosities of produced ACs and to show how these compared to related materials. Fig. 4 shows the \( \text{CO}_2 \) adsorption-desorption isotherms of all ACs recorded up to 1 atmosphere at 273.00 K. AC-2 showed the highest \( \text{CO}_2 \) adsorption capacity (4.92 mmol g⁻¹) with PC-AC-2 having a capacity of 4.26 mmol g⁻¹. Such differences are likely due to their different BET surface areas. On the other hand, the \( \text{CO}_2 \) adsorption capacity of PC-AC-1 (4.46 mmol g⁻¹) was slightly higher than AC-1 (4.32 mmol g⁻¹). Similar explanation might apply for slightly higher adsorption capacity of PC-AC-2. NLDFT pore size distribution calculations on \( \text{CO}_2 \) isotherms at 273.00 K show that ACs produced by KOH activation had pores distributed around 0.53 nm and ACs produced by ZnCl₂ activation around 0.57 nm (Table 2, Fig. 5). This shows the pre-pyrolysis conditions support the development of defined micropores and excellent textural properties of AC as pre-pyrolysis notably decreases the oxygen-containing functional groups which are available to react with the activating chemicals (Dobele et al., 2012). \( \text{CO}_2 \) adsorption-desorption isotherms at 288.00 K was also recorded and data is presented in Table 3. The \( \text{CO}_2 \) adsorption capacities scale with surface area and the high adsorption of \( \text{CO}_2 \) by AC-2 are explained by its large surface area (1,185.00 m² g⁻¹) in combination with attractive Van der Waals interactions in the narrow ultra-micropore system (0.524 nm) (Borchardt et al., 2017; Lee et al., 2011; Thommes et al., 2015). This could have resulted from KOH activation etching the carbon surface (Macwan et al., 2011; Presser et al., 2011; Thommes et al., 2015) and justify its
excellent carbon dioxide adsorption performance (Idree et al., 2018). Similarly, the high CO₂ adsorption capacities by ZnCl₂ activated carbons (i.e. AC-1 and PC-AC-1) can also be ascribed to their solely ultra-microporous nature (Heidari et al., 2014).

Fig. 4. CO₂ adsorption-desorption isotherms at 273.00 K (rectangular symbols for adsorption and red circle symbols for desorption) on slash pine wood derived ACs. (a) AC-1, (b) PC-AC-1, (c) AC-2 and (d) PC-AC-2. CO₂ adsorption-desorption isotherms at 288.00 K were also recorded with data being presented in Table 3.

Table 2

Porous properties of ACs as calculated by DFT from CO₂ adsorption at 273 K.

<table>
<thead>
<tr>
<th>Type of activated carbon</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Pore width (nm)</th>
<th>Lower confidence limit (nm)</th>
<th>Fitting error</th>
<th>Surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-1</td>
<td>0.37</td>
<td>0.57</td>
<td>0.42</td>
<td>0.02%</td>
<td>1,081.00</td>
</tr>
<tr>
<td>PC-AC-1</td>
<td>0.36</td>
<td>0.57</td>
<td>0.42</td>
<td>0.03%</td>
<td>1,093.00</td>
</tr>
<tr>
<td>AC-2</td>
<td>0.35</td>
<td>0.52</td>
<td>0.42</td>
<td>0.02%</td>
<td>1,185.00</td>
</tr>
<tr>
<td>PC-AC-2</td>
<td>0.32</td>
<td>0.52</td>
<td>0.42</td>
<td>0.02%</td>
<td>979.00</td>
</tr>
</tbody>
</table>
ACs are recognised for high adsorption capacity for CO$_2$ (Heidari et al., 2014; Xu et al., 2014) but with a crucial parameter in their performance being the heat of adsorption, i.e., isosteric enthalpy ($Q_{st}$). This is a balance between adsorption strength for selectivity and potential regeneration cost (Xu et al., 2014). $Q_{st}$ for CO$_2$ adsorption was calculated and found to follow the order AC-2 (39.70 kJ mol$^{-1}$) > PC-AC-1 (29.60 kJ mol$^{-1}$) > PC-AC-2 (27.80 kJ mol$^{-1}$) > AC-1 (27.60 kJ mol$^{-1}$). These values indicate physisorption. The relationship between $Q_{st}$ and the amount of CO$_2$ adsorbed followed a decreasing linear trend with increasing adsorption capacity (Fig. 6a) and changes based on the type of activation. Moreover, CO$_2$ adsorption capacity of the ACs also increases with the increasing micropore surface area of the ACs (Fig. 6b).

**Fig. 5.** Cumulative pore volume and pore sizes based on Density Functional Theory (DFT) calculations for (a) AC-1, (b) PC-AC-1, (c) AC-2 and (d) PC-AC-2 for CO$_2$ gas adsorption at 273.00 K.
Table 3 lists metrics for comparing these materials against other top-performing ACs prepared using KOH or ZnCl₂ activation. It is well known that the biomass source has a significant impact on properties of the resultant ACs. However, it is evident that the CO₂ adsorption capacities of ACs are in line with these top-performing materials, which maintain the relationship between the surface area and CO₂ capacity (Hong et al., 2016; Deng et al., 2014; Samanta et al., 2011; Serafin et al., 2017). The CO₂ adsorption capacity of 7.00 mmol g⁻¹ at 1 atm and 273.00 K for Paulownia sawdust was obtained using a high activation temperature (1,073.00 K) and KOH as the activating agent. It is believed that results from this study are very good for KOH activated ACs considering the type of biomass source (slash pine), chemical consumption and activation temperature against the surface area and CO₂ adsorption metrics. This becomes clearer from the values of the normalized adsorption capacity values (normalized by surface area). It can be seen that synthesized materials are highly competitive with the top performing ACs (Table 3). Also, AC prepared by the pre-pyrolysis route (PC-AC-1) showed one of the highest capacities for CO₂ (4.46 mmol g⁻¹) compared to ACs using ZnCl₂ as an activator.
Fig. 6. (a) Heat of adsorption versus volume of CO$_2$ adsorbed for the ACs, and (b) comparison of CO$_2$ adsorption capacities and surface areas for all ACs at 273.00 K.
Table 3

Physical properties and CO$_2$ adsorption capacities of different ACs produced using ZnCl$_2$ and KOH as the activating agent.

<table>
<thead>
<tr>
<th>Biomass source</th>
<th>Production temperature (K)</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>Activating agent</th>
<th>Activating agent to biomass ratio</th>
<th>Adsorption capacity (mmol g$^{-1}$) at 273 K</th>
<th>Adsorption capacity (10$^{-3}$ mmol m$^{-2}$) at 273 K</th>
<th>Adsorption capacity (mmol g$^{-1}$) at (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slash pine (AC-2)</td>
<td>853.00</td>
<td>906.00</td>
<td>KOH</td>
<td>4.00:1.00</td>
<td>4.93</td>
<td>3.86 (288.00)</td>
<td>This study</td>
<td></td>
</tr>
<tr>
<td>Pyrolysed Slash pine (PC-AC-2)</td>
<td>853.00</td>
<td>1,011.00</td>
<td>KOH</td>
<td>4.00:1.00</td>
<td>4.26</td>
<td>3.12 (288.00)</td>
<td>This study</td>
<td></td>
</tr>
<tr>
<td>Eucalyptus camaldulensis wood</td>
<td>1,173.00</td>
<td>2,595.00</td>
<td>KOH</td>
<td>3.50:100</td>
<td>6.10</td>
<td>4.10 (303.00)</td>
<td>Heidari et al., 2014</td>
<td></td>
</tr>
<tr>
<td>Paulownia sawdust</td>
<td>1,073.00</td>
<td>1,555.00</td>
<td>KOH</td>
<td>4.00:1.00</td>
<td>7.14</td>
<td>4.80 (298.00)</td>
<td>Zhu et al., 2014</td>
<td></td>
</tr>
<tr>
<td>Paulownia sawdust</td>
<td>1,173.00</td>
<td>1,293.00</td>
<td>KOH</td>
<td>4.00:1.00</td>
<td>4.24</td>
<td>3.33 (298.00)</td>
<td>Zhu et al., 2014</td>
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</tr>
<tr>
<td>Fir bark</td>
<td>973.00</td>
<td>1,242.00</td>
<td>KOH</td>
<td>4.00:1.00</td>
<td>6.10</td>
<td>4.99 (303.00)</td>
<td>Luo et al., 2018</td>
<td></td>
</tr>
<tr>
<td>Bamboo</td>
<td>1,073.00</td>
<td>2,000.00</td>
<td>KOH</td>
<td>4.00:1.00</td>
<td>7.00</td>
<td>4.50</td>
<td>Wei et al., 2012</td>
<td></td>
</tr>
<tr>
<td>Celtuce leaves</td>
<td>1,073.00</td>
<td>3,404.00</td>
<td>KOH</td>
<td>4.00:1.00</td>
<td>6.04</td>
<td>4.36 (298.00)</td>
<td>Wang et al., 2012</td>
<td></td>
</tr>
<tr>
<td>Black locust</td>
<td>1,103.00</td>
<td>2,511.00</td>
<td>KOH</td>
<td>6.00:1.00</td>
<td>5.86</td>
<td>3.75 (298.00)</td>
<td>Zhang et al., 2016</td>
<td></td>
</tr>
<tr>
<td>Wheat</td>
<td>1,073.00</td>
<td>2,192.00</td>
<td>KOH</td>
<td>3.00:1.00</td>
<td>5.70</td>
<td>3.48 (298.00)</td>
<td>Hong et al., 2016</td>
<td></td>
</tr>
<tr>
<td>Longan shells</td>
<td>1,073.00</td>
<td>3,260.00</td>
<td>KOH</td>
<td>2.00:1.00</td>
<td>5.60</td>
<td>4.30 (298.00)</td>
<td>Wei et al., 2017</td>
<td></td>
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<tr>
<td>Empty fruit bunch (H250)</td>
<td>1,073.00</td>
<td>1,720.00</td>
<td>KOH</td>
<td>5.00:1.00</td>
<td>5.22</td>
<td>3.70 (298.00)</td>
<td>Parshetti et al., 2015</td>
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<td>Eucalyptus sawdust</td>
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<td>2,850.00</td>
<td>KOH</td>
<td>4.00:1.00</td>
<td>5.20</td>
<td>3.00</td>
<td>Sevella et al., 2011</td>
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<td>Slash pine (AC-1)</td>
<td>853.00</td>
<td>1,384.00</td>
<td>ZnCl$_2$</td>
<td>1.00:1.00</td>
<td>4.32</td>
<td>3.12 (288.00)</td>
<td>This study</td>
<td></td>
</tr>
<tr>
<td>Pyrolysed Slash pine (PC-AC-1)</td>
<td>853.00</td>
<td>1,122.00</td>
<td>ZnCl$_2$</td>
<td>1.00:1.00</td>
<td>4.46</td>
<td>3.20 (288.00)</td>
<td>This study</td>
<td></td>
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<td>Olive stone</td>
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<td>1,253.00</td>
<td>ZnCl$_2$</td>
<td>1.00:1.00</td>
<td>4.50-4.70</td>
<td>0.36 - 0.24</td>
<td>Balsamo et al., 2014</td>
<td></td>
</tr>
<tr>
<td>Commercial AC</td>
<td>1,073.00</td>
<td>1,374.00</td>
<td>ZnCl$_2$</td>
<td>1.00:0.500</td>
<td>2.00-2.20 (313.00)</td>
<td>2.00 (303.00)</td>
<td>Thote et al., 2015</td>
<td></td>
</tr>
<tr>
<td>Soybean</td>
<td>873.00</td>
<td>811.00</td>
<td>ZnCl$_2$</td>
<td>1.00:1.00</td>
<td>2.20</td>
<td>2.00 (303.00)</td>
<td>Thote et al., 2015</td>
<td></td>
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</table>
3.6. Significance and future research

In this study, a facile process used for the clean production of AC for CO\textsubscript{2} adsorption has been reported in laboratory scale experiments. The results are significant by producing high-performance ultra-microporous ACs with excellent carbon dioxide adsorption capacity while reducing chemical consumption by 70%. In order to further assess the feasibility of the process and the performance of the produced AC, long-term laboratory as well as pilot-scale study should be carried out for practical implementation of this process. So far, the performance was evaluated based on single pure gas (only CO\textsubscript{2} adsorption). Thus, it is important to study the effect of other gases such as methane, carbon monoxide, nitrous oxide on the adsorption of CO\textsubscript{2}. In addition, to ensure the reusability of the produced AC, several adsorption and desorption cycles of ACs should be completed. Furthermore, a detailed cost estimation (production, operation, and maintenance) would be beneficial to highlight the cost-effectiveness of this process.

4. Conclusions

ACs produced by the facile technique showed excellent CO\textsubscript{2} adsorption performance, compared to ACs produced by the conventional chemical activation. Up to 70% reduction in chemical usage was achieved by employing pre-pyrolysis strategy hence minimizing environmental impacts. The CO\textsubscript{2} sorption capacity using AC produced in this study showed reasonably good performance in comparison with the other AC. The findings indicate that this approach should be promoted in future AC preparation from biomass feedstock, especially at commercial scale. The produced AC can be used for a wide variety of applications like commercial AC, although further investigations will be beneficial especially on the energy consumption of AC production using this method. Furthermore, long term pilot studies considering the effect of other gases on CO\textsubscript{2} adsorption and the reusability of the produced AC are required to ensure the process sustainability.
Acknowledgments

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Appendix. Supplementary data

Supplementary data associated with this article is attached.

References


Highlights

• Pre-pyrolysis reduced chemical consumption by 70.00% for AC production.
• Pre-pyrolysis produced high-performance ultra-micropore AC.
• Excellent CO$_2$ capture performance for ZnCl$_2$ activated AC.
• All AC showing similar physicochemical properties.