



# Article Microporous Carbons Obtained via Solvent-Free Mechanochemical Processing, Carbonization and Activation with Potassium Citrate and Zinc Chloride for CO<sub>2</sub> Adsorption

Amonrada Saning<sup>1</sup>, Rabindra Dubadi<sup>2</sup>, Laemthong Chuenchom<sup>1,3,\*</sup>, Decha Dechtrirat<sup>4,5,6</sup> and Mietek Jaroniec<sup>2,\*</sup>

- <sup>1</sup> Division of Physical Science, Faculty of Science, Prince of Songkla University, Songkhla 90110, Thailand; amonrada\_sn@hotmail.com
- <sup>2</sup> Department of Chemistry and Biochemistry, Kent State University, Kent, OH 44240, USA; rdubadi@kent.edu
  <sup>3</sup> Center of Excellence for Innovation in Chemistry, Division of Physical Science, Faculty of Science, Prince of
- <sup>3</sup> Center of Excellence for Innovation in Chemistry, Division of Physical Science, Faculty of Science, Prince of Songkla University, Songkhla 90110, Thailand
- <sup>4</sup> Department of Materials Science, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand; fscidcd@ku.ac.th
- <sup>5</sup> Specialized Center of Rubber and Polymer Materials for Agriculture and Industry (RPM), Faculty of Science, Kasetsart University, Bangkok 10900, Thailand
- <sup>6</sup> Laboratory of Organic Synthesis, Chulabhorn Research Institute, Bangkok 10210, Thailand
- \* Correspondence: laemthong.c@psu.ac.th (L.C.); jaroniec@kent.edu (M.J.)

**Abstract:** In this study, the facile and sustainable synthesis of highly microporous carbons is explored to reduce the extensive use of harsh activating agents and solvents. The role of potassium citrate (PC) as a greener activating agent in addition to the conventional  $\text{ZnCl}_2$  is investigated in the mechanochemical solvent-free preparation of highly microporous carbon materials from chestnut tannin (CT), a biomass-type carbon precursor. A small amount of potassium citrate as a chemical activator coupled with CO<sub>2</sub> activation at 700 °C afforded carbons with higher specific surface area (1256 m<sup>2</sup> g<sup>-1</sup>) and larger micropore volume (0.54 cm<sup>3</sup> g<sup>-1</sup>) as compared to the carbons activated with both PC and ZnCl<sub>2</sub>. The high microporosity of the PC-activated carbon materials, significantly enlarged after CO<sub>2</sub> activation from micropore volume of 0.16 to 0.54 cm<sup>3</sup> g<sup>-1</sup>, makes them favorable for CO<sub>2</sub> adsorption, as evidenced by high adsorption capacity of 3.55 mmol g<sup>-1</sup> at ambient conditions (25 °C, 1 bar). This study shows that the solvent-free mechanochemical processing of tannin in the presence of PC is a promising method for obtaining highly microporous carbon materials.

Keywords: carbon materials; mechanochemical synthesis; tannin; potassium citrate; CO2 capture

## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) is one of the most concerning greenhouse gases these days and most CO<sub>2</sub> emissions are caused by human activity such as industrialization and fossil fuel combustion in vehicles [1]. A rapid increase in the CO<sub>2</sub> emission rate in this century has accelerated global climate change [1]. It has been reported that atmospheric CO<sub>2</sub> concentration has tremendously increased, from 280 ppm in the industrial revolution era to 416.5 ppm in 2020 and is predicted to rise to almost 600 ppm by 2100 [1]. Therefore, the development of CO<sub>2</sub> removal technology is a crucial and challenging issue that urgently needs to be resolved. One of the most popular and effective CO<sub>2</sub> capture strategies is adsorption on solid adsorbents such as metal–organic frameworks (MOFs), zeolite imidazolate frameworks (ZIFs), zeolites, porous alumina, and porous carbon materials, due to their low energy consumption and excellent regeneration ability [1].

Porous carbon materials have been well-known as good adsorbents because of their high  $CO_2$  uptake capability, high surface area and great stability [1]. Many strategies for the synthesis of porous carbon materials have been reported, such as hard templating [2–4], soft



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). templating [5–7] and conventional chemical activation [7–9]. However, these solution-based processes require a large amount of solvent and harsh and/or expensive chemicals, which make them time-consuming and unfeasible [10,11]. For these reasons, the solvent-free mechanochemical synthesis of porous carbon materials has a great potential, because it is a green and sustainable process.

Mechanochemical synthesis has been recognized as an effective, ecofriendly alternative to the conventional preparation methods. The chemical reactions during mechanochemical synthesis are initiated by mechanical forces [11–16] such as shearing, stretching, compression, grinding, etc. [11] The energy provided by mechanochemistry is sufficient to induce the physical and chemical transformation of the materials without applying any additional external energy [11]. During mechanochemical milling, defects are introduced in the precursors, which act as active sites and can propagate into fractures, increasing specific surface area of the resulting porous carbons [11]. Furthermore, the mechanochemical processes can occur in solvent-free conditions or require a minimal volume of solvent [11,12], which not only reduces the amount of solvent used, but also eliminates the sample-drying step. This advantage makes the mechanochemical synthesis an alternative to the conventional wet chemical synthesis procedures, which are complicated and require large amounts of solvents. Moreover, mechanochemical synthesis is recognized as a low-cost [17,18] and reproducible process [18], which has a high potential to be used for industrial-scale production of materials [18]. There are many reports on the mechanochemical synthesis of various types of carbon materials [11,12,19,20], including the fabrication of N-doped carbons with high surface area [21]. Therefore, mechanochemical synthesis was selected in this study.

Tannin is a naturally occurring polymer containing polyphenols that have been widely used as a substitute for conventional phenolic precursors [20] such as phenol and resorcinol [5,22]. Tannin is considered an environmentally benign chemical [20,23,24], despite a similar chemical reactivity to phenol. In addition, tannin is abundant since it can simply be obtained from biomass extraction [24]. The cost of tannin is listed at a significantly lower price than traditional phenolic resources [25]. There are several studies reporting the use of tannin as a carbon precursor to fabricate carbon materials through various synthesis routes. In 2020, Phuriragpitikhon and coworkers [5] successfully prepared ordered mesoporous carbon (OMC) from commercial mimosa tannin through a self-assembly process and one-step  $CO_2$  activation. The as-prepared OMCs, which possessed relatively high specific surface area and well-developed micro-/mesopore texture, were used for  $CO_2$ adsorption applications. In the same year, tannin-derived N-doped mesoporous carbon was mechanochemically synthesized by Zhao and coworkers and used for gas capture application with high adsorption selectivity [26]. Later in 2021, Pérez-Rodríguez and coworkers [24] demonstrated the use of pine tannin to prepare a high surface area biochar  $(2190 \text{ m}^2 \text{ g}^{-1})$  through pyrolysis and a subsequent KOH activation approach. In 2022, sodium-ion battery anode materials were prepared by Tonnoir and coworkers through polycondensation of a commercial mimosa tannin, furfuryl alcohol and formaldehyde [22]. After pyrolysis at high temperature, these materials showed high specific surface area and excellent electrochemical performance [22]. These studies confirm that tannin has a significant potential as a biomass-type carbon precursor.

To achieve high porosity of carbons, various activating agents such as KOH [27–29], NaOH [30,31] and ZnCl<sub>2</sub> [32–35] have been used. Among them, ZnCl<sub>2</sub> has been recognized as an efficient activator to create micropores due to its comparatively small ionic radius [36]. Recently, Głowniak and coworkers [10] successfully prepared tannin-derived porous carbon through mechanochemical synthesis using urea as a nitrogen source, ZnCl<sub>2</sub>/NaCl eutectic salt as a template and potassium salts as activating agents. By coupling the salt-templating and mild chemical activation in a single step of mechanochemical processing, the resulting carbons exhibited high specific surface area and well-developed micropores that were responsible for high CO<sub>2</sub> uptake [10]. Although many researchers reported on the use of potassium salts as activating agents, to our knowledge, there is no comparative study

between the mild potassium salts and conventional activators on the activation effectiveness in the synthesis of porous carbons.

Here, this mechanochemical processing of tannin in the presence of potassium salt as a mild activating agent in combination with conventional ZnCl<sub>2</sub> activator is further explored. In contrast to the research employing potassium salts as activators, studies focusing on the use of potassium citrate (representative of mild potassium salts) as a supplement or substitution for harsh chemical activating agents are rather rare. This work shows the role of potassium citrate as a mild activating agent integrated with ZnCl<sub>2</sub> to create a greener procedure for the preparation of porous carbon materials while retaining high microporosity and great CO<sub>2</sub> adsorption performance.

#### 2. Materials and Methods

## 2.1. Chemicals and Reagents

Commercial chestnut tannin was obtained from Silva-Chimica, Cuneo, Italy. Zinc chloride anhydrous (ZnCl<sub>2</sub>,  $\geq$ 99.995%) was purchased from Sigma-Aldrich, MO, USA. Potassium citrate monohydrate (C<sub>6</sub>H<sub>5</sub>K<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O, >95 wt%) was purchased from Spectrum Chemical Mfg. Corp, NJ, USA. Deionized water (DI water) was used in the material washing step after carbonization.

#### 2.2. Materials Synthesis

In a typical synthesis, as illustrated in Figure 1, 1.0 g of chestnut tannin (CT), 0.25 g of ZnCl<sub>2</sub> (Zn) and 0.2 g of potassium citrate monohydrate (PC) were mechanochemically ground in a PM200 planetary ball mill (Retsch, Germany) at 500 rpm for 3 h. The fine brownish products were then carbonized in a quartz tube under N<sub>2</sub> atmosphere at 800 °C for 1.5 h, using a heating rate of 1 °C min<sup>-1</sup> and N<sub>2</sub> gas flow rate of 75 mL min<sup>-1</sup>. The carbonized products were subsequently washed with hot DI water several times to remove impurities. The obtained products were labeled as CTZnPC. Finally, CO<sub>2</sub> activation was performed on those samples at 700 °C for 3 h, with a ramp rate of 1 °C min<sup>-1</sup> and CO<sub>2</sub> gas flow rate of 75 mL min<sup>-1</sup>, to enhance the microporosity of the resulting carbons. The CO<sub>2</sub>-activated samples were denoted as CTZnPC-A. A control experiment was conducted by directly carbonizing pristine chestnut tannin without any activators at 800 °C and the product was designated as CT-800.



**Figure 1.** Schematic illustration of the synthesis of activated microporous carbon via solvent-free mechanochemical processing of chestnut tannin in the presence of  $ZnCl_2$  (Zn) and potassium citrate (PC) activators, followed by carbonization at 800 °C under N<sub>2</sub> atmosphere and physical CO<sub>2</sub> activation at 700 °C.

# 2.3. Characterization

Surface morphology of pre- and post-activated carbon materials was investigated by scanning electron microscopy (SEM) using an FEI model Quanta 450 FEG at 20 kV. X-ray diffraction spectroscopy (XRD, Rigaku MiniFlex 600) was used to study the turbostratic carbon character of the materials in the 2 $\theta$  range of 10°–90°. Chemical functionality of

the prepared carbon materials was examined by Fourier-transform infrared spectroscopy (FT-IR, vector 33, Bruker) using wavenumbers between 500 and 4000 nm<sup>-1</sup>. Elemental carbon, hydrogen, and nitrogen composition analysis of the materials (CHN analysis) was performed using Elemental Analyzer TruSpec<sup>®</sup> Micro Series, Leco.

Surface area and related porosity parameters of the materials were evaluated by using N<sub>2</sub> adsorption–desorption isotherms measured at -196 °C using an ASAP 2020 volumetric adsorption analyzer (Micromeritics, GA). CO<sub>2</sub> adsorption measurements were performed at 25 °C using a volumetric adsorption analyzer (ASAP 2020, Micromeritics). All samples were degassed at 200 °C for 2 h prior to the N<sub>2</sub> and CO<sub>2</sub> adsorption, to remove trapped gases and moisture from the carbon materials. Specific surface area of all materials was obtained by using Brunauer–Emmett–Teller (BET) equation for N<sub>2</sub> adsorption data at the relative pressure (P/P<sub>o</sub>) range of 0.05–0.2. Total pore volume (V<sub>total</sub>) of the materials was evaluated using the quantity adsorbed at a relative pressure of 0.98. Pore size distribution (PSD), volume of fine micropores (pore diameter < 1 nm, V<sub>ultra</sub>) and micropore volume (pore diameter < 2 nm, V<sub>micro</sub>) of the materials were calculated based on the PSD functions obtained using the manufacturer-provided software, employing 2D non-local density functional theory (2D-NLDFT) calculations. Mesopore volume (V<sub>meso</sub>) of the materials was obtained by subtracting V<sub>micro</sub> from V<sub>total</sub>.

## 3. Results and Discussions

The preparation methodology of carbon materials in this study substitutes the use of hazardous chemicals and extreme conditions with greener chemicals and simplifies the process of making carbon materials, which can be easily scaled up. A series of carbon samples obtained via mechanochemical synthesis by using chestnut tannin as a carbon precursor and potassium citrate monohydrate and zinc chloride as activators are labeled as CTZnPC, where CT refers to the commercial chestnut tannin, PC refers to potassium citrate and Zn refers to zinc chloride. These samples were subjected to CO<sub>2</sub> activation (labeled as CTZnPC-A) to increase their microporosity. Nitrogen adsorption–desorption isotherms measured at -196 °C for these samples are presented in Figure 2, with the corresponding pore size distributions obtained by using the 2D-NLDFT calculation method.

The N<sub>2</sub> adsorption–desorption isotherms for the CTZnPC samples before and after CO<sub>2</sub> activation, which are presented in Figure 2a,b, exhibit mixed type I and type IV isotherms with small hysteresis loops according to the IUPAC classification. The relatively slow increase in adsorption at higher relative pressures and narrow hysteresis loops that could be observed on the isotherms not only indicate a small amount of mesopores in the samples, but also illustrate the well-developed microporosity. The pore size distribution in the micropore range (pore diameter less than 2 nm), calculated by using 2D-NLDFT software, are shown in Figure 2c,d. Before CO<sub>2</sub> activation (Figure 2c), CTZn and CTZnPC show apparent pore size distributions in the fine micropore range, with the highest contribution around 0.5 nm. On the other hand, CTPC, the carbon sample solely activated with PC, shows two distinct pore size ranges at around 0.5 nm and 1.25 nm. After CO<sub>2</sub> activation, Figure 2d shows a higher contribution of small micropores. Especially in the case of CTPC-A (red line), there is an evident development of fine microporosity (pore diameter < 1 nm) after CO<sub>2</sub> activation, which makes it more attractive for CO<sub>2</sub> adsorption [1], while there are only slight changes in the pore size distributions obtained for CTZn and CTZnPC.

The specific surface area, total pore volume, micropore volume and volume of fine micropores for CTZnPC series are presented in Table 1. The control sample without activation, CT-800, was obtained by carbonization of tannin at 800 °C. This sample shows low specific surface area of 49 m<sup>2</sup> g<sup>-1</sup>. Data listed in Table 1 indicate that the use of activating agents in mechanochemical synthesis boosts the surface area of the materials. Surface area improvement occurs even when small amounts of activating agents (0.2–0.25 g per 1 g of tannin) are used, due to the high sensitivity of mechanochemical processing in the presence of additives [11,12,19]. All the samples in CTZnPC series possess considerably high micropore volume (0.16–0.54 cm<sup>3</sup> g<sup>-1</sup>), while the volume of mesopores is noticeably

low (0.01–0.08 cm<sup>3</sup> g<sup>-1</sup>). This result is in agreement with the observed shape of nitrogen adsorption isotherms and small hysteresis loops (Figure 2a,b). Moreover, the use of dual activating agents (CTZnPC) afforded materials with high surface area (816 m<sup>2</sup> g<sup>-1</sup>) and substantial total pore volume ( $V_{total} = 0.37 \text{ cm}^3 \text{ g}^{-1}$ ) in comparison to the tannin-derived carbon sample obtained without activators. After CO2 activation, the specific surface area, and the total pore volume  $V_{\text{total}}$  of all materials are significantly increased. In the case of CTZn-A, the surface area slightly increases from 613 m<sup>2</sup> g<sup>-1</sup> to 723 m<sup>2</sup> g<sup>-1</sup>. While only a small improvement in microporosity is observed, as evidenced by pore size distributions (Figure 2c,d), the mesoporosity is notably enhanced after  $CO_2$  activation due to the possible collapse of some original micropores [37–39]. In contrast, the microporosity of CTPC-A obtained by using PC as a single in situ activator increases remarkably after post-synthesis CO<sub>2</sub> activation, as evidenced by the highest specific surface area and largest micropore volume (0.54 cm<sup>3</sup> g<sup>-1</sup>) in this study. The over three-fold surface area improvement of the CTPC samples from 415 to 1256 m<sup>2</sup> g<sup>-1</sup> and triple enhancement of the sample micropore volume could be the result of the structural development enabled by the combined in situ activation with PC and post-synthetic activation with CO<sub>2</sub>. At temperature < 650  $^{\circ}$ C, PC decomposes into  $K_2CO_3$  [40,41], as presented in Equation (1).  $K_2CO_3$  could function as a structural template [41]. At higher temperature,  $K_2CO_3$  further decomposes into  $CO_2$ and  $K_2O$  [40,41] (Equation (2)). The reactions between these products (CO<sub>2</sub> and  $K_2O$ ) and carbon are relevant at high temperature (Equations (3) and (4)) [40,41] for generating micropores that enhance pore volume and surface area.



**Figure 2.** (**a**,**b**) N<sub>2</sub> adsorption–desorption isotherms for CTZnPC series of samples: (**a**) the materials before CO<sub>2</sub> activation: CTZn (black line), CTPC (red line) and CTZnPC (blue line), (**b**) after CO<sub>2</sub> activation: CTZn–A (black line), CTPC-A (red line) and CTZnPC-A (blue line). (**c**,**d**) Pore size distributions obtained using the manufacturer-provided 2D–NLDFT software for (**c**) non-CO<sub>2</sub> activated carbon samples: CTZn (black line), CTPC (red line) and CTZnPC (blue line) and (**d**) CO<sub>2</sub>–activated carbon samples: CTZn–A (black line), CTPC-A (red line) and CTZnPC-A (blue line).

$$2K_3C_6H_5O_7 \cdot H_2O \to 3K_2CO_3 + 9C + 7H_2O$$
(1)

$$K_2 CO_3 \rightarrow K_2 O + CO_2 \tag{2}$$

$$CO_2 + C \rightarrow 2CO$$
 (3)

$$K_2O + C \rightarrow 2K + CO$$
 (4)

**Table 1.** Surface area and porosity parameters of the carbon samples calculated from  $N_2$  adsorptiondesorption isotherms.

Materials	${S_{BET}}^{1}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_{total}^2$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_{ultra}$ <sup>3</sup> (cm <sup>3</sup> g <sup>-1</sup> )	$V_{micro}^{}  ^4$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_{meso} {}^{5}$ (cm <sup>3</sup> g <sup>-1</sup> )
CT-800	49	0.04	-	0.01	0.03
CTZn	613	0.29	0.26	0.28	0.01
CTZn-A	723	0.38	0.27	0.30	0.08
CTPC	415	0.18	0.05	0.16	0.02
CTPC-A	1256	0.60	0.36	0.54	0.06
CTZnPC	816	0.37	0.29	0.36	0.01
CTZnPC-A	960	0.42	0.39	0.40	0.02

 $^{1}$  S<sub>BET</sub> = specific surface area obtained by Brunauer–Emmett–Teller (BET) method.  $^{2}$  V<sub>total</sub> = total pore volume obtained from the N<sub>2</sub> volume adsorbed at P/P<sub>o</sub> = 0.98.  $^{3}$  V<sub>ultra</sub> = volume of fine micropores (diameter < 1 nm) estimated from 2D-NLDFT PSD;  $^{4}$  V<sub>micro</sub> = micropore volume estimated from 2D-NLDFT PSD;  $^{5}$  V<sub>meso</sub> = mesopore volume = V<sub>total</sub>–V<sub>micro</sub>.

Despite adopting two in situ activators and post-synthetic  $CO_2$  activation, the surface area of CTZnPC-A only slightly increased from 816 m<sup>2</sup> g<sup>-1</sup> to 960 m<sup>2</sup> g<sup>-1</sup> with a small enhancement in microporosity (from 0.29 cm<sup>3</sup> g<sup>-1</sup> to 0.39 cm<sup>3</sup> g<sup>-1</sup>). Combination of ZnCl<sub>2</sub> and PC activators did not improve microporosity. Thus far, this study shows that PC can be used as a single in situ activator, substituting the harsh and corrosive ZnCl<sub>2</sub> for the generation of microporosity in carbon materials.

Surface morphology of carbon materials was investigated by scanning electron microscopy (SEM). Without using an activating agent, the carbonized tannin, CT-800, exhibited a smooth surface on the isolated pieces (Figure 3).



**Figure 3.** SEM images obtained at 20 kV of CT-800 at different magnifications, presenting the surface morphology of the non-activated tannin-derived carbon sample.

Introduction of activating agents drastically changed the surface morphology to a rough surface with numerous aggregated small particles (Figure 4). Figure 4a–c shows the surface morphology of CTZn, CTPC and CTZnPC, while Figure 4d–f presents images for the CO<sub>2</sub>-activated carbon samples (CTZn-A, CTPC-A and CTZnPC-A), which suggest that there is no significant change in the morphology before and after physical CO<sub>2</sub> activation. This conforms with the BET analysis, showing that the activating agents significantly change structure and provide pathways for CO<sub>2</sub> activation to improve microporosity.



**Figure 4.** SEM images obtained at 20 kV represent surface morphology of pre- and post-CO<sub>2</sub> activation carbon materials: (a) CTZn, (b) CTPC, (c) CTZnPC, (d) CTZn-A, (e) CTPC-A and (f) CTZnPC-A.

The X-ray diffraction patterns were collected between  $2\theta$  of  $10^{\circ}-90^{\circ}$ , as presented in Figure 5a. Among CO<sub>2</sub>-activated samples, CTZn-A and CTPC-A diffraction patterns clearly show broad peaks at  $2\theta$  of  $22^{\circ}$  and  $43^{\circ}$ , corresponding to the (002) and (100) of graphitic-like carbon [26,42], whereas these peaks are absent in CTZnPC-A diffraction pattern. This indicates that the carbon substructures of CTZnPC-A may be destroyed during heat treatment [43].



**Figure 5.** (a) X-ray diffraction patterns of CO<sub>2</sub>-activated carbon materials: CTZn-A (black line), CTPC-A (red line) and CTZnPC-A (blue line) from  $2\theta = 10^{\circ}-90^{\circ}$  (b) FT–IR spectra of CO<sub>2</sub>-activated carbon materials: CTZn-A (black line), CTPC-A (red line) and CTZnPC-A (blue line) in the wavenumber range of 500–4000 cm<sup>-1</sup>.

Chemical functionalities of CO<sub>2</sub>-activated porous carbon materials were studied by Fourier-transform infrared spectrometry (FT-IR) in the wavenumber range of 500–4000 cm<sup>-1</sup>. The FT-IR spectra of all samples in Figure 5b show similar patterns, which contain broad peaks around 3218 cm<sup>-1</sup> corresponding to the O-H stretching vibration [35,44] and 2993 cm<sup>-1</sup> referring to the C-H stretching vibration [35], small signals at 1652 cm<sup>-1</sup> belonging to the C=C stretching vibration in aromatic rings [35,44] and small peaks at 1410 cm<sup>-1</sup> representing the C-C stretching vibration [44]. These chemical functionalities are commonly found in carbon-based materials.

Elemental composition of the materials was determined using an Elemental Analyzer to investigate the percentage of C, H and N in the prepared materials. The results in Table 2 show that many of these materials possess about 1% of nitrogen without using a nitrogen

doping source. The presence of nitrogen in tannin-derived samples has been reported elsewhere [45–47] because of fixed protein contaminants [48] introduced during the tannin extraction process [45]. Nitrogen originating from tannin facilitates CO<sub>2</sub> adsorption via Lewis acid–base interactions [49,50], with the nitrogen species acting as Lewis base sites and CO<sub>2</sub> being a Lewis acid.

**Table 2.** CHN elemental composition of prepared carbon materials and  $CO_2$  adsorption performance of CTZnPC series at 25 °C and 1 bar.

Communitor	Elen	CO <sub>2</sub> Uptake at		
Sample –	С	Н	Ν	$25^{\circ}C(1 \text{ bar})$
CT-800	79.51	1.41	0.96	-
CTZn	75.34	1.87	1.01	3.06
CTZn-A	78.23	1.62	1.24	3.13
CTPC	72.70	1.40	0.48	3.17
CTPC-A	59.10	2.86	1.20	3.55
CTZnPC	70.12	1.63	0.78	3.13
CTZnPC-A	79.37	0.68	1.16	3.18

## *CO*<sub>2</sub> *Capture*

 $CO_2$  uptake performance of the materials was studied at 25 °C up to 1.15 bar using a volumetric adsorption analyzer after degassing at 200 °C for 2 h. The  $CO_2$  uptake performance at 25 °C is presented in Table 2, using the data at 1 bar to simulate the real ambient conditions.

The results in Figure 6 and Table 2 show that the CO<sub>2</sub> capture capacities of all CTZnPC samples are in the range of  $3-3.5 \text{ mmol g}^{-1}$ , which are comparable to the reported values for microporous carbons. The sample that shows the highest  $CO_2$  capacity is CTPC-A (3.55 mmol  $g^{-1}$ ), which also exhibits the largest micropore volume (0.54 cm<sup>3</sup>  $g^{-1}$ ) and highest specific surface area (1256 m<sup>2</sup> g<sup>-1</sup>). Additionally, CTPC-A shows that the  $CO_2$ uptake values are comparable to those observed for traditional KOH-activated carbon materials and the materials prepared via wet chemical synthesis routes, zeolite-based porous materials, or metal organic frameworks (Table 3); for many of these processes, the preparation is a multistep, time-consuming, and more costly process [10]. It is worth mentioning that the high fraction of fine micropores (0.36 cm<sup>3</sup> g<sup>-1</sup>) and large contribution of micropores to the total pore volume (~90%) in CTPC-A are crucial for high  $CO_2$  adsorption capacity in comparison to other materials prepared via traditional synthesis routes. Several studies reported that the materials containing pores, which have 2–3 times larger pore diameter than the kinetic diameter of  $CO_2$  molecule (0.3 nm) are the most appreciable porous materials for  $CO_2$  capture [1]. Even though the nitrogen elemental percentage of CTZn-A (1.24%), CTPC-A (1.20%) and CTZnPC-A (1.16%) are similar, the CO<sub>2</sub> uptake capacities of these samples are rather different, as shown in Table 2. This result suggests that the micropore volume and the specific surface area are more beneficial for enhancing  $CO_2$ adsorption capacities than the interaction between Lewis base sites. Therefore, the CTPC-A presented in this study is a good candidate for CO<sub>2</sub> adsorption in ambient conditions. These results prove that the solvent-free mechanochemical synthesis that has been explored in this study has the potential to be a promising alternative process for the preparation of highly porous carbon materials. In addition, it could be noted that potassium citrate is an excellent green activating agent for the synthesis of highly microporous carbons when coupled with physical CO<sub>2</sub> activation, which indicates a promising perspective for the development of carbon materials.



**Figure 6.**  $CO_2$  adsorption isotherms measured for the CTZnPC sample series, studied at 25 °C in the pressure range of 0.01–1.15 bar.

Table 3. CO<sub>2</sub> adsorption capacities at the ambient conditions of previously reported materials.

	S	CO <sub>2</sub> Adsorptio		
Materials	$(m^2 g^{-1})$	CO <sub>2</sub> Uptake	Adsorption Condition	Ref.
<sup>a</sup> NFePC-10-A	1414	3.4	25 °C, 1 bar	[51]
<sup>b</sup> TG-C700-4K	1192	3.6	25 °C, 1 bar	[5]
<sup>c</sup> HS-550–3	1600	4.3	25 °C, 1 bar	[52]
<sup>d</sup> S-doped porous carbon	1463	3.6	25 °C, 1 bar	[53]
<sup>e</sup> KOH-AC	1439	3.5	25 °C, 1 bar	[29]
<sup>f</sup> CS-Py-K100	1051	4.9	25 °C, 1 bar	[54]
g STP-R-A	2710	3.4	25 °C, 1 bar	[7]
h STC-P-500-A	1743	4.4	25 °C, 1 bar	[7]
<sup>i</sup> CS*-P-A	2400	4.6	23 °C, 1 bar	[9]
<sup>j</sup> N-C-800	1018	2.8	25 °C, 1 bar	[55]
<sup>k</sup> T-GU-700-6	1032	2.4	25 °C, 1 bar	[56]
<sup>1</sup> PNK3	901	3.9	25 °C, 1 bar	[57]
<sup>m</sup> IBA-Z4A	32	2.6	25 °C, 1 bar	[58]
<sup>n</sup> MIL-53(Al)	961	2.2	25 °C, 1 bar	[59]
CTPC-A	1256	3.6	25 °C, 1 bar	This work

<sup>a</sup> Activated carbon from tannin, FeCl<sub>3</sub> and KOH; <sup>b</sup> Ordered mesoporous carbon from tannin, glyoxal and potassium oxalate; <sup>c</sup> Carbon materials from hazelnut shells, thiourea and KOH; <sup>d</sup> KOH-activated carbon materials from thiophene; <sup>e</sup> KOH-activated carbon from rice husk; <sup>f</sup> N-doped microporous carbon spheres from pyrrole, formaldehyde, 3-aminophenol and potassium citrate; <sup>g</sup> KOH-activated phenolic resin materials using resorcinol as a phenolic resource; <sup>h</sup> KOH-activated pre-carbonized phenolic resin materials using phloroglucinol as a phenolic resource; <sup>i</sup> KOH-activated phenolic resin-based activated carbon spheres; <sup>j</sup> KOH-activated carbon materials from Taihu blue algae; <sup>k</sup> KOH-activated N-doped graphene oxide; <sup>l</sup> KOH-activated carbon materials from pinewood; <sup>m</sup> Iso-butylamine-modified binder-containing zeolite 4A; <sup>n</sup> Rod-like aluminum terephthalate MOF.

In addition to the presented improvements in the synthesis of porous carbon materials, this study could be used as a guideline for the advancement of the recipes for the preparation of microporous carbons from biomass-based precursors. Also, the microporosity of the prepared carbons can be further improved by examining the effect of potassium salts, activators, carbonization temperature and grinding conditions to obtain materials with high microporosity and large specific surface area that are favorable for gas adsorption. Moreover, the combined use of a low-cost process, solvent-free mechanochemical synthesis and a low-cost carbon precursor, tannin, also shows the high potential of scaling up the production of biomass-derived porous carbons for diverse applications.

# 4. Conclusions

Tannin-derived porous carbon materials were successfully prepared via solvent-free mechanochemical synthesis using ZnCl<sub>2</sub> and potassium citrate as activating agents. The SEM images clearly demonstrate the effect of the activating agents towards surface morphology of the materials by turning smooth surface rough. The carbonized materials show high specific surface area in the range 415–816 m<sup>2</sup> g<sup>-1</sup> after mechanochemical grinding and consequent pyrolysis at 800 °C. These carbon materials were subsequently activated using  $CO_2$  at 700 °C to enhance their microporosity and specific surface area, to enhance the  $CO_2$ uptake. The specific surface area of activated carbon samples increases up to the range of 723–1256 m<sup>2</sup> g<sup>-1</sup>. The CO<sub>2</sub> activation also altered microporosity of the samples. Especially, the micropore volume of the sample activated with potassium citrate shows a significant increase from 0.16 to 0.54 cm<sup>3</sup> g<sup>-1</sup>, which is favorable for CO<sub>2</sub> adsorption. The highest CO<sub>2</sub> capacity, 3.55 mmol  $g^{-1}$  at 25 °C and 1 bar, is obtained for the mechanochemically prepared carbon from tannin using potassium citrate as the activating agent only, which is caused by the highest specific surface area and largest micropore volume. These results suggest that potassium citrate activates carbon materials better and is less corrosive and toxic than  $ZnCl_2$ , which means it could be a promising substitute for  $ZnCl_2$  in the preparation of microporous carbon materials.

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