

1 The conversion of wood residues, using
2 pilot-scale technologies, into porous activated
3 biochars for supercapacitors

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20 **Abstract**

21 In this study, activated biochar was produced using pilot-scale technologies of fast pyrolysis and
22 activation to create desirable morphology, surface chemistry, and adsorptive properties for
23 application in supercapacitors. First, residues from white birch were converted into biochar by fast
24 pyrolysis ($\sim 450\text{ }^{\circ}\text{C}$). Then, physical (using CO_2) or chemical (using KOH) activation was carried
25 out in a homemade pilot-scale furnace at $900\text{ }^{\circ}\text{C}$. These synthesized materials presented distinct
26 porosity structures: micro-/mesoporous (CO_2 material) and highly microporous (KOH material),
27 reaching surface areas of up to $1700\text{ m}^2\text{ g}^{-1}$. Electrochemical results showed that KOH-activated
28 biochar had higher specific electrical capacitance in both acidic and neutral electrolytes with a
29 maximum specific capacitance value of 350 and 118 F g^{-1} at 1 A g^{-1} , respectively; while, for CO_2 -
30 activated biochar, the maximum obtained values were 204 and 14 F g^{-1} . The greater proportion of
31 oxygenated and nitrogenated functional groups on the surface of the KOH activated biochar, along
32 with its high surface area (with wider porosity), improved its performance as a supercapacitor
33 electrode. Specifically, the low proportion of ultramicropores was determinant for its better
34 electrochemical behavior, especially in the neutral electrolyte. Indeed, these results are similar to
35 those found in the literature on the electrical capacitance of carbonaceous materials synthesized in
36 a small-scale furnace. Thus, the chemical-activated biochar made from wood residues in pilot-scale
37 furnaces is a promising material for use as electrodes for supercapacitors.

38 **Keywords:** Wood residues, biochar, activated biochar electrode, porosity, electrochemistry,
39 supercapacitors

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43 **1. Introduction**

44 Motivated by the growing consumption and restricted availability of fossil fuels, as well as the
45 negative environmental impacts of burning these fuels, researchers have spent considerable effort
46 in recent years to develop environmentally sustainable energy storage devices. Supercapacitors are
47 one example of electrical energy storage devices; supercapacitors consist of two electrodes
48 (separated from each other by an electric insulator) and an ionic electrolyte. These devices are of
49 great interest due to their high energy density, fast charge-discharge time, and long-term operation
50 stability [1]. Currently, these characteristics allow supercapacitors to be used in electric cars,
51 electrical grids, electronic devices (e.g., continuous power supplies, power tools), and military
52 equipment, as well as to be coupled to solar and wind energy systems [2–4].

53 Generally, the performance of supercapacitors depends on the electrode material and its
54 physicochemical structure. Several materials, including conducting polymers, metal oxides, and
55 porous carbons, have been studied to increase the energy density of supercapacitors [5]. Among
56 these materials, carbon-based materials in various forms, such as single- and multi-walled
57 nanotubes, black carbon, graphene, carbon gels, and activated carbons, are the most studied. The
58 feasibility of several biomasses (e.g., lignocellulosic agricultural wastes such as fruit stones, husks,
59 and hulls) has been also reported for the production of highly porous activated carbons not only for
60 the adsorption of gases and pollutants from aqueous solution but also as electrodes for
61 supercapacitors [6,7]. However, scale-up processes are under-explored in the available literature.

62 The forest industry is an important sector in Canada. Globally, Canada is the leader in forest
63 products trade [8]. While the province of Québec covers about 25% of Canada’s forests and only
64 2% of the world’s forests. Québec’s wood-processing sector generates a significant amount of wood
65 residues, which are stored in large wood-residue deposits across the country [9]. The development
66 of innovative materials using wood waste, such as bio-based chemicals and renewable energy to

67 replace the petroleum-derived materials, could provide new market opportunities. In fact, given
68 Canada's commitment to pursuing a national greenhouse gas reduction target of 20% by 2020 [10],
69 the renewable energy sector is expected to grow in the coming years [8]. In this context, the use of
70 clean wood residues from sawmills would be suitable to produce carbon electrodes for
71 supercapacitors and diversify wood-processing markets.

72 Currently, one of the by-products of the thermochemical conversion of biomass (e.g.,
73 torrefaction, slow to fast pyrolysis, gasification) has also been used as a precursor for the production
74 of activated carbon. Biochar, a carbon-rich material, possesses limited porosity (surface area up to
75 $200 \text{ m}^2 \text{ g}^{-1}$), but after activation at high temperature and in the presence of chemicals (KOH, H_3PO_4)
76 and gases (CO_2 , steam), porosity is well developed with the gasification of carbon atoms [11]. The
77 valorization of biochar as a precursor for the production of activated carbons could bring high
78 profitability for biorefineries as the activated carbon market is expected to rise 3.5% per year
79 through 2020 [12]. Additionally, activated biochars that have very high surface areas (up to 2500
80 $\text{m}^2 \text{ g}^{-1}$) were attained, but the properties of activated biochars can be substantially affected by the
81 distinct feedstock chemical composition, and pyro-gasification and activation operating conditions
82 [13].

83 According to González et al. [5], most commercial energy storage devices are manufactured
84 using activated carbon electrodes with a specific capacitance (i.e., the electrical energy stored
85 through the system electrode/electrolyte) of 100 to 120 F g^{-1} . Indeed, chemically activated biochars
86 made with yellow pine [14], woody biomass [15], and spruce whitewood [16] achieved high values
87 of capacitances of 171, 167, and 245 F g^{-1} , respectively. The most important characteristics of
88 porous carbon materials for application in supercapacitors reported so far are surface area, the pore
89 size distribution and pore volume (tailored pore), and amount and nature of some functional groups
90 that can help enhance the electrical capacitance through reversible redox reactions

91 (pseudocapacitance) [17–19]. The porosity of the electrode material directly impacts the
92 supercapacitor performance, due to intrinsic aspects of material on electrochemical behavior such
93 as the available area for the double layer formation, charge and discharge speed of the electrode,
94 and the cell resistance [17,20]. The correlation between the pore size characteristics of carbon
95 materials and their performance as supercapacitor electrodes has been a widely discussed topic by
96 different authors around the world from the beginning of the 1990s [21] to the present time [22–
97 24]. Various models have been proposed to elucidate the different electrochemical behaviors of
98 carbon materials [18–24]. However, the complexity and heterogeneity of their porous structure
99 hinder a conclusive correlation between the textural properties (surface area, size and shape of the
100 pores, etc.) and the electrochemical behavior of the supercapacitor electrode material (electrical
101 capacitance, rate capability, series equivalent resistance, etc.). In addition, the characteristics of the
102 electrolyte (ion size, ion charge, solvation coordination sphere, etc.) increase the level of
103 complexity of the analyzed electrode-electrolyte system. Thus, laboratory experiments, models and
104 interpretations in this field are contradictory. The papers reported by Stoeckli et al. [25] and
105 Chmiola et al. [26] are just examples of these disagreements.

106 Thus, appropriate pore size development and analysis must be carefully considered in order to
107 obtain a more effective match between the pore size and the dimensions of the electrolyte ions.

108 Furthermore, the active functional groups or heteroatoms on the surface of the carbon material,
109 together with the nature and density of the active sites intended for the adsorption of electrolyte
110 ions, play an important role in the performance of electrodes for supercapacitors [18,24]. Indeed,
111 some surface chemical groups may contribute to the improvement of wettability (e.g., oxygenated
112 groups) [27], electronic conductivity (e.g., nitrogenated groups) [28] and the presence of both
113 functional groups may also improve the interfacial capacitance, thereby giving rise to faradaic
114 effects [29,30]. Using pilot-scale technologies, this work aimed to prepare activated biochars that

115 have various textural and chemical characteristics from Québec's forest residues for application as
116 supercapacitor electrodes. The carbon materials were obtained from wood residues from white
117 birch, using two different activation agents, CO₂ and KOH. Different electrochemical parameters
118 of the materials were determined from galvanostatic, potentiostatic, and electrochemical impedance
119 spectroscopy (EIS) experiments using neutral and acid aqueous electrolytes. The electrochemical
120 characteristics of the samples were correlated with their different physicochemical properties,
121 including specific surface area, pore size, and chemical composition.

122

123 **2. Materials and methods**

124 2.1 Activated biochar preparation

125 Wood residues from white birch (WB) sampled from sawmills in Québec, Canada, were first
126 converted into biochars. In summary, the biochar (BWB) was produced through a CarbonFX fast
127 pyrolysis plant (developed by Airex Energy Inc., Bécancour, QC, Canada) at 455 °C in an oxygen-
128 free environment. Chemical and physical activation of the BWB were then achieved using KOH
129 and CO₂ gas, respectively, through an in-house pilot-scale furnace. The furnace is composed of
130 three parts: 1) a feed hopper, 2) a screw conveyor tube placed in a muffle furnace, and 3) a recovery
131 hopper. The details of the furnaces and materials preparation have been described elsewhere [13].
132 For chemical activation, biochar impregnation was achieved by mixing biochar, KOH (in pellets)
133 and water in proportions of 1:1:2 based on mass. The mixture was kept at room temperature for 2
134 h and then dried overnight at 120 °C in an oven. KOH-impregnated biochar was placed in the feed
135 hopper and the screw conveyor was switched on to activate and transport the material (for
136 approximately 1 h) to the recovery hopper under a nitrogen atmosphere once the furnace
137 temperature reached 900 °C. The material was then washed with distilled water until a pH ~ 7 was

138 reached and dried overnight at 105 °C. An almost identical procedure was performed for the
139 physical activation. BWB was placed in the same furnace under nitrogen atmosphere and CO₂ at 3
140 L min⁻¹ injected for approximately 1 h once the temperature reached 900 °C. The final activated
141 biochars were designated as KOHBWB and CO₂BWB, respectively.

142 2.2 Materials characterization

143 After activation, both materials were characterized in terms of porous structure (surface area
144 and pore volume), CHNSO percentage, pHPZC (point of zero charge), and surface chemistry. Pore
145 texture parameters were obtained by N₂ at -196 °C and by CO₂ at 0 °C using a Micromeritics ASAP
146 2460 Surface Area Analyzer (Norcross, GA, USA). BWB and activated biochars were degassed
147 under vacuum for 48 h at 105 and 250 °C, respectively, prior to adsorption testing. N₂ adsorption
148 isotherms were treated to obtain (i) the surface area (S_{BET} , m² g⁻¹) calculated by the Brunauer–
149 Emmett–Teller (BET) model applied to the nitrogen adsorption [31]; (ii) the micropore volume
150 (V_{μ} , cm³ g⁻¹) determined by the Dubinin–Radushkevich (DR) equation [32]; (iii) the total pore
151 volume ($V_{0.97}$, cm³ g⁻¹) calculated from the amount of nitrogen adsorbed at 0.97 relative pressure
152 [33]; (iv) the mesopore volume (V_{m} , cm³ g⁻¹) calculated as the difference ($V_{0.97} - V_{\mu}$); and (v) the
153 average pore diameter (nm). The pore size distribution (PSD) was determined by applying density
154 functional theory (DFT) using N₂ adsorption isotherms [34].

155 CHNS elemental analyzer (Perkin Elmer 2400 CHNS/O Analyzer; Waltham, MA, USA) was
156 used for determining elemental carbon, hydrogen, nitrogen, and sulfur contents by sample
157 combustion in a pure O₂ stream. Oxygen content was obtained by calculating the difference (%O =
158 100 – %CHNS). The point of zero charge (pHPZC), the pH value at which the zeta potential is equal
159 to zero, of activated biochars was carried out in a Malvern Zetasizer Nano ZS90 equipment. Five
160 mg of each material were added into 10 mL of NaCl solution (0.01 M) with pH values adjusted

161 from 2 to 12 with HCL or NaOH solutions and kept for 24 h before measurements. X-ray
162 photoelectron spectroscopy (XPS) spectra were recorded with a Kratos AXIS ULTRA system
163 (Wharfside, MA, UK) equipped with a focused X-ray source (Al K α , $h\nu = 1486.6$ eV) operating at
164 300 W. The survey scans were acquired using a pass energy of 160 eV and a step size of 1 eV. The
165 XPS core level spectra were analyzed using CasaXPS (Casa Software Ltd.).

166 2.3 Electrode preparation and electrochemical measurements

167 The electrochemical analyses were performed in a three-electrode cell with an Ag/AgCl
168 wire (saturated in KCl) as a reference electrode and platinum wire as a counter electrode. The
169 working electrode was prepared through a suspension of 1.1 to 1.4 mg of the analyzed sample in
170 Nafion® (5 wt.%) coated onto a graphite disk (0.29 cm²). The measurements were performed using
171 two different electrolytes, 2 mol L⁻¹ H₂SO₄ (acidic electrolyte) and 1 mol L⁻¹ Na₂SO₄ (neutral
172 electrolyte) aqueous solution. The galvanostatic charge-discharge curves were obtained in a density
173 current range (j) of 1 A g⁻¹ and the cyclic voltammetry in the scan rate of 10 mV s⁻¹, both
174 experiments had a potential range of 0.1 to 0.9 V vs. Ag/AgCl. Electrochemical impedance
175 spectroscopy (EIS) measurement was performed in a frequency range of 3 x 10⁻⁴–2.5 x 10⁵ Hz. All
176 the experiments were performed at room temperature using potentiostat/galvanostat/FRA
177 Vertex.One equipment from Ivium Technologies.

178 The specific capacitance (C_s) of the samples was determined from the charge-discharge
179 curves obtained at different applied current, according to the following equation:

$$180 \quad C_s (\text{F g}^{-1}) = I \cdot t_d / E_2 \cdot m_e \quad (1)$$

181 where I is the constant applied current in amperes (A), t_d is the discharge time in seconds (s), E_2 is
182 the voltage range during the discharge in volts (V), and m_e is the mass of the analyzed sample (g).

183

184 3. Results and discussion

185 3.1 Physicochemical characterization

186 The C, H, N, S, and O content of BWB and activated biochars are presented in Table 1.
187 Compared to BWB, physical and chemical activation increased the carbon content (up to 89.9%)
188 and decreased the heteroatoms (i.e., H, O) from the original biochar structure, enhancing the
189 carbonization process. XPS analysis provided information on the carbon bonding states for the
190 same materials. The XPS C1s peaks were deconvoluted and used to estimate the relative
191 proportions of the functional groups listed in Table 2. The full range of XPS results has been
192 described elsewhere [35]. The main peak, which was lower than 285 eV for all materials, was
193 assigned to aliphatic/aromatic carbon (C–C, C–H, and C=C). The peaks at 285.7–287.1, 286.1–288,
194 and 288–289.4 eV were then attached to the oxygen-containing moieties (i.e., C–O, C=O or
195 O–C–O, and O–C=O, respectively) [36]. The highest percentage of total oxygenated functional
196 groups were found to be in the following order BWB > KOHBWB > CO2BWB. Furthermore,
197 nitrogen functional groups such as pyridinic, pyrrolidonic, quaternary, and N-oxide were also found
198 on the surface of KOHBWB (Table 3), which was confirmed by CHNSO analysis (2% of nitrogen
199 detected) while BWB and CO2BWB possessed less than 1%. In relation to pH_{PZC} results, both
200 activated biochars had the point of zero charge in the acid range. The pH_{PZC} indicates the
201 electrokinetic behavior of the material, which usually varies with the properties of the precursor
202 and the type and temperature of pyrolysis [37]. The acid pH_{PZC} means that mostly acid functional
203 groups are connected to both materials' surface, but KOHBWB, having a much lower pH_{PZC} (2.86),
204 presented more negative charges than CO2BWB (3.95) as evidenced by XPS analysis.

205 3.2 Surface area and porosity

206 Surface area and porosity are among the most important variables for the performance of carbon
207 materials in energy storage. Depending on the type of activation, distinct surface areas and pore
208 size distribution were obtained, as seen in Table 1. For example, KOHBWB had a surface area
209 twofold higher than CO2BWB. However, its pore structure was essentially microporous ($V_{\mu, N_2} =$
210 $0.75 \text{ cm}^3 \text{ g}^{-1}$ and $V_m = 0.00 \text{ cm}^3 \text{ g}^{-1}$) compared to CO2BWB, which had a mixture of micro- and
211 mesopores ($V_{\mu, N_2} = 0.33 \text{ cm}^3 \text{ g}^{-1}$ and $V_m = 0.20 \text{ cm}^3 \text{ g}^{-1}$). The nitrogen adsorption/desorption
212 isotherms at $-196 \text{ }^\circ\text{C}$, the pore size distribution for KOHBWB and CO2BWB and the CO_2
213 adsorption isotherms at $0 \text{ }^\circ\text{C}$ are shown in Fig. 1 a, b, and c, respectively. N_2 isotherms (Fig. 1 a)
214 had different shapes depending on the activation method. Nitrogen adsorption isotherm of
215 chemically activated biochar was Type I, according to the IUPAC classification [38], characteristic
216 of purely microporous solids. The curve was also characterized by a steep rise of the nitrogen
217 amount adsorbed at P/P_0 lower than 0.05, a narrow knee, and a plateau up to P/P_0 equal to 0.99.
218 On the other hand, nitrogen adsorption-desorption isotherm for physically activated biochar was a
219 combination of Type I and Type IV, characteristic of micro-mesoporous solids according to the
220 IUPAC classification [38]. The mesoporosity was also indicated by the slope of the nitrogen
221 adsorption isotherm (in the P/P_0 range from 0.05 to 0.7) and by the prominent hysteresis cycle.

222 CO_2 adsorption-desorption isotherms of biochar-derived materials are shown in Fig. 1 c.
223 KOHBWB presented the highest amount of CO_2 adsorbed compared to CO2BWB. The micropore
224 volume (V_{μ, CO_2}) obtained from this analysis was 0.28 and $0.36 \text{ cm}^3 \text{ g}^{-1}$ for CO2BWB and
225 KOHBWB, respectively. However, taking into account that V_{μ, CO_2} can be mainly related with the
226 ultramicropores (pore size $< 0.7 \text{ nm}$) [11], and considering that the V_{μ, N_2} values are related with
227 the total micropore volume (0.33 and $0.75 \text{ cm}^3 \text{ g}^{-1}$, respectively), it can be concluded that the
228 CO2BWB sample had a much higher proportion of narrower micropores than KOHBWB. CO_2

229 activation involves a reaction between the carbon present in biochar materials and injected CO₂.
230 This reaction (Boudouard reaction) resulted not only in the opening of blocked pores to form new
231 micropores, but also in the widening of existing micropores by a gasification reaction, which caused
232 the formation of mesopores [39]. The high proportion of ultramicropores in CO₂BWB could be
233 then explained by the short residence time during the two-step thermochemical processes in which
234 BWB was produced within (1) a few seconds during fast pyrolysis, and (2) at approximately 1 h
235 during activation. Longer activation residence time result in larger volumes of supermicropores and
236 mesopores, respectively, and a consequent reduction of ultramicropores [40].

237 3.3 Electrochemical performance of activated biochars

238 [Fig. 2](#) shows the cyclic voltammograms obtained at 10 mV s⁻¹ in the acidic ([Fig. 2 a](#)) and
239 neutral ([Fig. 2 b](#)) electrolytes. For both samples, the voltammograms obtained in acidic medium
240 show a broad peak in the potential range of 0.4 to 0.7 V vs. Ag/AgCl. Such behavior is typically
241 related to pseudocapacitive contribution associated with oxygenated surface functional groups in
242 both samples and/or nitrogenated species found on the KOHBWB sample. The reversible redox
243 reactions of C=O, O-C-O, O=C-O, C=NH, C-NHOH groups with the H⁺ ions of the electrolyte
244 enhance the total observed capacitance [17–19,41]. In addition, the pH_{PZC} results ([Table 1](#)) suggest
245 that both materials, especially KOHBWB, have a predominance of acid functional groups (e.g.
246 carboxylic, phenolic, and lactonic) on their surface, due to their amphoteric nature [37]. Those
247 groups might be responsible for the pseudocapacitive reactions observed. These results concur with
248 the available literature on different carbon materials containing such functional groups [42].
249 However, the broad peak observed in both samples using the acidic electrolyte is not seen in the
250 voltammograms obtained with the neutral electrolyte ([Fig. 2 b](#)). In this case, the voltammograms

251 present a quasi-rectangular shape, typical of a pure capacitive behavior, and an absence of
252 pseudocapacitive reactions due to the low concentration of H^+ in the electrolyte.

253 Figs. 3 a and b show galvanostatic curves of the samples using acid and neutral electrolyte,
254 respectively. The curves obtained in neutral medium (Fig. 3 b) have a typical triangular and
255 symmetrical shape of a capacitive material, showing a constant slope along with the potential range
256 of charge and discharge. On the other hand, the curves obtained in acid medium (Fig. 3 a) have a
257 different slope depending on the potential, more clearly observed in the discharge curves, which
258 can be related to the presence of pseudocapacitive reactions in certain potential ranges, as
259 previously discussed.

260 The C_s was determined from the galvanostatic charge-discharge curves according to the Eq.
261 1 and the relationship with j shown in Fig. 4. In the acidic medium, both samples had higher C_s at
262 low current densities ($1 A g^{-1}$), 350 and $204 F g^{-1}$ for KOHBWB and CO2BWB, respectively, which
263 shows a direct correlation with both (i) their respective specific surface areas and (ii) oxygenated
264 and nitrogenated functional group contents (Tables 1, 2 and 3). It is reasonable to assume that a
265 greater portion of the total observed capacitance in the presence of the acidic electrolyte comes
266 from a pseudocapacitive origin due to the presence of pseudocapacitive reactions and their relation
267 with these functional groups. Based on the electrochemical double-layer capacitance for carbon
268 materials ($0.10 F m^{-2}$ in sulfuric acid electrolyte [25]) and the S_{BET} values (Table 1), the expected
269 values for the electrical double-layer capacitance is of $88 F g^{-1}$ and $170 F g^{-1}$ for the CO2BWB and
270 KOHBWB, respectively. The calculated capacitances determined at $1 A g^{-1}$ was $350 F g^{-1}$ for
271 KOHBWB and $204 F g^{-1}$ for CO2BWB. Thus, the estimated pseudocapacitive contribution was 43
272 and 49 %, respectively, which is an important pseudocapacitive contribution in acidic medium. This
273 fact could also explain the apparent contradiction with the potentiostatic results in terms of
274 electrical capacitance when comparing the voltammogram of KOHBWB in an neutral electrolyte

275 with the voltammogram of CO2BWB in an acidic electrolyte (Figs. 2 a and 2 b). Thus, a portion of
276 the electrical capacitance determined for CO2BWB (charge-discharge curves in an acidic
277 electrolyte) cannot be visualized at higher current density due to the characteristics of the
278 pseudocapacitive reactions (i.e., voltage dependence and kinetics), especially in cyclic voltammetry
279 at 10 mV s^{-1} . The capacitance values are similar or higher than other values reported in the literature
280 for similar carbon materials [15,16,18,19,43,44]. Regardless, it is important to highlight that carbon
281 materials analyzed in this work have an additional advantage over materials described in the
282 literature: they were produced from renewable precursors in pilot-scale furnaces, which could
283 reinforce economic incentives for using thermochemical biomass conversion processes, the
284 development of diversified products, and the creation of a local bioeconomy. The high C_s value
285 found for KOHBWB, which is about twofold higher compared to CO2BWB, is also related to the
286 oxygen and nitrogen content. In the neutral electrolyte, the C_s values, determined at low current
287 densities, were lower than in acidic medium, reaching values of 118 and 14 F g^{-1} for KOHBWB
288 and CO2BWB, respectively. These results suggest that the neutral electrolyte ions cannot readily
289 access the overall porosity of the electrode and there is a clear absence of pseudocapacitive
290 contribution from oxygenated and nitrogenated groups in the presence of H^+ ion.

291 Thus, the higher values of KOHBWB samples in acid and neutral electrolytes are probably
292 related to an effective match between the pore size and the dimensions of the electrolyte ions. The
293 KOHBWB presented a larger quantity of micropores detected by N_2 adsorption, while CO2BWB
294 showed a higher proportion of ultramicropores detected by CO_2 adsorption analysis. It has been
295 recently reported that the size of hydrated Na^+ ions (between 0.72–0.9 nm) might be too small to
296 access the ultramicropores found in CO2BWB (between 0.47–0.69 nm) [45]. In fact, the
297 relationship between porosity and the electrochemical performance of materials has been
298 highlighted by different researchers as one of the great challenges to improving the performance of

299 supercapacitors. In order to give a clear and generalized explanation of the differences in the
300 electrochemical behavior of activated biochars, a "universal" model is needed to clarify the
301 mechanisms of energy storage in carbon materials with different textural characteristics. To date,
302 there are many doubts and controversies as to the mechanics and determining factors of charge
303 accumulation in porous materials, especially in materials containing narrow pores (less than 0.7
304 nm) [20–25], similar to the materials studied in this work.

305 In recent years, some authors have shed light on this issue, proposing the basis for the
306 development of a clear model that could explain the enormous and diverse amount of often
307 contradictory experimental results in this field. In this sense, one of the most outstanding studies
308 found in the accessible literature is of the researcher Ali Eftekhari. This author recently published
309 several scientific articles where he decidedly and boldly addressed this problem, proposing the basis
310 of a rational model to explain these different behaviors [22–24]. In these studies, Eftekhari
311 questions the formation of electrochemical double layers inside micropores and highlights the
312 importance of porous surface ion diffusion rather than free ion diffusion in the inner pore volume.
313 He also questioned the importance of counter-ions in the adsorption and diffusion process of the
314 main adsorbed ions. According to Eftekhari's studies, superficial diffusion is also influenced by the
315 chemical and structural characteristics of the electrode's surface.

316 In the present study, the results obtained from the electrochemical experiments and their
317 correlation with their chemical and textural properties allow us to affirm that, regardless of the
318 charge storage mechanism (with or without double layer formation), the capacitance is lower in the
319 presence of the neutral electrolyte compared to the acidic one. This is due to the absence of
320 pseudocapacitive reactions and the lower double layer capacitance obtained in the neutral
321 electrolyte. At this point, it is appropriate to consider the following as to how the electrical
322 capacitance was determined in this study. The capacitance was determined from galvanostatic

323 charge-discharge curves performed on three electrodes and using a positive potential window.
324 Thus, it could be assumed that the non-faradic charge accumulation in both electrolytes are
325 associated with the adsorption of the anion (HSO_4^- and/or SO_4^{2-}). So, why is there a noticeable
326 difference in capacitance values when the electrolyte is changed? And, why is this difference more
327 important in the case of CO2BWB than KOHBWB? Should the capacitance not be similar
328 considering that the adsorption is carried out with the same anion?

329 Taking into account the obtained results, it seems clear that the counter-ion plays an
330 important role in the electro-adsorption and/or diffusion of the main ion. Thus, the surface area
331 associated with larger micropores in KOHBWB might allow a better coexistence (at least near the
332 narrow pore mouth) of the cation with the anion in the neutral electrolyte, resulting in a larger
333 available area for adsorption and internal or superficial diffusion of the anion. The counter-ion's
334 role not only explains the differences in both samples in a neutral electrolyte, but also the
335 differences in capacitance obtained for the same sample using different electrolytes. Although the
336 porosity is the same, the behavior of the adsorbed anion is different since it is affected by the
337 presence of a different cation. These explanations have been highlighted by Eftekhari's publication
338 [22].

339 In summary, the present study does not intend to provide a final answer for all of this
340 controversy, but at least exposes and discusses the importance of a better comprehension of the
341 energy storage mechanism in porous carbon materials through a suitable experimental plan and
342 interpretation of the textural characterization along with a proper correlation of the electrochemical
343 results. Leaving the fundamental analysis to one side and thinking in a more practical way, the use
344 of neutral electrolytes in supercapacitor devices has important advantages over acidic ones. Neutral
345 electrolytes are a non-corrosive dispositive, which reduces health and environmental problems

346 associated with handling and discharge of the material, and they are currently used in commercial
347 technological applications.

348 The Nyquist plots of activated biochars, from the EIS measurements, are shown in Fig. 5.
349 The series resistance (R_s) composed of the electrolyte solution resistance, separator resistance, and
350 electrode resistance [20] were determined from the intersection of the curve with the real axis at
351 high frequency. Both samples show lower R_s values in the acidic electrolyte (Fig. 5 a) than in the
352 neutral one (Fig. 5 b) (see the inset figures), which corresponds with the lower ionic conductivity
353 of the Na_2SO_4 electrolyte. In the acidic electrolyte, the R_s of KOHBWB is lower than the R_s
354 observed for CO2BWB (see inset of Fig. 5 a). R_s is usually associated with the electrical resistance
355 of the electrolyte. Therefore, the difference in R_s values may be associated with a lower electrical
356 resistance of KOHBWB compared with CO2BWB. In addition, this difference is also observed in
357 the Nyquist diagram obtained in neutral medium (larger zoom not shown) which is in agreement
358 with this approach. In the acidic electrolyte (Fig. 5 a) both samples show a typical spectrum of a
359 non-ideal electrochemical capacitor with a semicircle and a sloppy 45° region at high frequency.
360 The diameter of the semicircle can be related to the charge transfer resistance due to the reversible
361 redox reaction (pseudocapacitance), whereas the 45° region can be linked to parameters such as (i)
362 the ion diffusion into the electrode porous structure, (ii) the electrode roughness, and (iii) the active
363 site energy dispersion. The last parameter is especially important in pseudocapacitive materials
364 [18,20]. At low frequencies, KOHBWB shows the most vertical line, suggesting a better capacitive
365 behavior, which is, in general, attributed to a lower resistance of the ion diffusion into the pore of
366 the active electrode. This finding is in accordance with the lower proportion of narrow micropores.
367 In the neutral electrolyte, the Nyquist diagram shows a large, incomplete semicircle due to a higher
368 ion diffusion resistance. Accordingly, the semicircle diameter of the CO2BWB is much higher than
369 the KOHBWB, which also highlights the greater proportion of narrow micropores in the sample.

370 Charge-discharge cycling tests up to 1000 cycles were performed at 2 mA (CO2BWB) and
371 6 mA (KOHBW) in the potential range of 0.1 to 0.9 V. The capacitance retention, expressed in
372 percentage, was calculated from the C_s determined for each cycle divided by the initial C_s from the
373 first cycle. The capacitance retention as a function of the cycle number in the acidic and neutral
374 mediums are shown in Fig. 6 a and b. Both samples show good capacitance retention, from ≈ 98 to
375 ≈ 95 %, indicating a low degradation rate for successive charge-discharge cycles, at least up to 1000
376 cycles. When considering commercial applications of supercapacitor carbon electrodes, 1000
377 cycles are not enough for a long-term cyclability study. Thus, future studies should be done with
378 5000–10000 charge-discharge cycles.

379 Table 4 provides a brief comparison of the electrochemical performances of activated
380 biochars (CO2BWB and KOHBW) with similar porous materials as described in the available
381 literature. As Table 4 demonstrates, the electrochemical results of materials prepared using large-
382 scale technologies and those prepared using carbon materials produced in at laboratory scale using
383 a solution of H_2SO_4 1M as an electrolyte [46–49] are similar. Furthermore, the biochar synthesized
384 in the current project showed a specific capacitance 25% higher using a scan rate 4 times greater,
385 in comparison to a similar material produced in laboratory scale [49].

386 On the other hand, in the presence of Na_2SO_4 as electrolyte, the electrochemical results
387 presented an intermediate maximum specific capacitance value ($118 F g^{-1}$) between an activated
388 carbon [50] and activated biochar [49], both prepared at laboratory scale. However, excellent
389 stability was found even for the greater scan rate used in this study; thus, the specific capacitance
390 of the electrode prepared with KOHBW is still satisfactory as an electrode for supercapacitors.
391 Besides, the application of a neutral electrolyte minimizes the discharge problems of the final
392 device because no corrosive liquid is used in the assembly of the energy storage apparatus.

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394 4. Conclusions

395 This study showed that the scale-up preparation of porous carbon materials for electrodes in
396 supercapacitors were comparable to porous carbon materials prepared at the laboratory scale. Wood
397 residues from white birch are good precursors to obtain activated biochars with suitable
398 characteristics for supercapacitor electrode applications. The KOH activation was a great technique,
399 better than CO₂ activation, for the production of activated biochar. This technique allowed us to
400 obtain a carbon material with a higher specific surface area, suitable porosity, and a high content of
401 oxygenated and nitrogenated functional groups that were able to perform pseudocapacitive
402 contribution. Electrochemical results showed that KOHBWB had a higher specific electrical
403 capacitance in both the acidic and neutral electrolyte. For KOHBWB, a maximum specific
404 capacitance value of 350 and 118 F g⁻¹ were determined at 1 A g⁻¹ in the acidic and neutral
405 electrolyte, respectively, as well as good rate capability and capacitance retention. The results with
406 the neutral electrolyte (Na₂SO₄) present additional advantages due to the sustainability and low cost
407 of the material, a reasonable specific capacitance with a high stability at a high scan rate (1 A g⁻¹),
408 and low impacts on the dispositive discharge because of the non-corrosive nature of the electrolyte.
409 Moreover, the chemically activated biochar has an additional advantage of being synthesized
410 through pilot-scale processes and sustainable bioresourced precursors that could contribute
411 significantly to a circular bioeconomy, with immediate environmental and economic impacts for
412 Québec and the globe.

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521 **Table captions:**

522 **Table 1.** Physicochemical and textural properties of biochar and activated biochars

523 **Table 2.** Quantification of C1s bands in XPS patterns for biochar and activated biochars

524 **Table 3.** Quantification of N1s bands in XPS patterns for the chemically activated biochar

525 **Table 4.** Electrochemical performances in H₂SO₄ and Na₂SO₄ electrolytes of different materials

526 compared to activated biochars synthesized in this work.

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545 **Figure captions:**

546 **Fig. 1.** a) N₂ adsorption–desorption isotherms (full and open symbols, respectively) at -196 °C; b)
547 pore size distribution determined by the DFT model; and c) CO₂ adsorption isotherms at
548 0 °C for both activated biochars KOHBWB and CO2BWB;

549 **Fig. 2.** Cyclic voltammograms obtained for the samples at 10 mV s⁻¹ using a) acidic and b) neutral
550 electrolytes.

551 **Fig. 3.** Galvanostatic charge-discharge curves of the samples obtained in a) acidic at 5 A g⁻¹ and b)
552 neutral electrolyte at 1 A g⁻¹.

553 **Fig. 4.** Specific capacitance vs. current density for the KOHBWB and CO2BWB for a) acidic and
554 b) neutral electrolytes.

555 **Fig. 5.** Nyquist diagram for the KOHBWB and CO2BWB samples in a) an acidic medium and b)
556 a neutral medium. Inset plots represent a zoomed-in selected area of the diagrams.

557 **Fig. 6.** Cyclic performance performed at 2 mA (CO2BWB) and 6 mA (KOHWB) in a) acidic and
558 b) neutral electrolytes during 1000 charge-discharge cycles.

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561 **Table 1.** Physicochemical and textural properties of biochar and activated biochars

	Textural properties											
	pH_{PZC}	<i>C</i> (%)	<i>H</i> (%)	<i>N</i> (%)	<i>S</i> (%)	<i>O</i> (%)	S_{BET} ($m^2 g^{-1}$)	V_t ($cm^3 g^{-1}$)	V_{μ, N_2} ($cm^3 g^{-1}$)	V_{μ, CO_2} ($cm^3 g^{-1}$)	V_m ($cm^3 g^{-1}$)	Average pore diameter (nm)
BWB		75.4	3.5	0.9	0.5	19.4	177*					
CO2BWB	3.95	89.9	0.9	0.4	0.0	8.8	881**	0.53	0.33	0.28	0.20	2.2
KOHBWB	2.86	77.5	1.7	2.0	0.1	18.7	1700**	0.75	0.75	0.36	0.00	1.8

562 S_{BET} obtained from *CO₂ and **N₂ adsorption analysis

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593 **Table 2.** Quantification of C1s bands in XPS patterns for biochar and activated biochars

	Binding energy (BE) (eV) and area of the peak (%)					
	C1s					
	<i>BE < 285eV (graphitic sp² carbon)</i>	<i>285.7 < BE < 287.1 (C-OH)</i>	<i>286.1 < BE < 288 (C=O or O-C-O)</i>	<i>288 < BE < 289.4 (O=C-O)</i>	<i>BE > 290 ("Shake-up" satellites)</i>	<i>Total oxygenated groups</i>
BWB	68.0	17.1	4.6	4.6	5.7	26.3
CO2BWB	72.1	12.8	4.5	2.2	8.4	19.5
KOHBWB	61.8	14.7	7.3	3.4	12.8	25.4

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608 **Table 3.** Quantification of N1s bands in XPS patterns for the chemically activated biochar

	Binding energy (BE) (eV) and area of the peak (%)			
N1s	<i>BE < 399eV (Pyridinic N-6)</i>	<i>399.4 < BE < 399.8 (Pyrrolidonic N-5(O))</i>	<i>400.8 < BE < 401.4 (Quaternary N-Q)</i>	<i>402.5 < BE < 403.62 (Pyridinic N-oxide N-Ox)</i>
KOHBWB	44.7	39.9	10.4	4.9

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611 **Table 4.** Electrochemical performances in H₂SO₄ and Na₂SO₄ electrolytes of different materials
 612 compared to activated biochars synthesized in this work.

Electrode material	Electrolyte	Maximum specific capacitance (F g ⁻¹)	Scan rate (A g ⁻¹)	Cycle number	Stability (%)	Electrode configuration	References
Activated biochar (KOHBWB)	H ₂ SO ₄	350	1	1000	98	3 electrodes	This work
Activated biochar (CO ₂ BWB)	H ₂ SO ₄	204	1	1000	98	3 electrodes	This work
Activated carbon from sugarcane bagasse	H ₂ SO ₄	300	0.25	5000	77	3 electrodes	[46]
Wood-N-doped porous carbon	H ₂ SO ₄	347	2	1000	76	3 electrodes	[47]
Activated carbon from coconut shells	H ₂ SO ₄	258	1	3000	97.2	2 electrodes	[48]
Activated biochar	H ₂ SO ₄	280	0.2	10000	86.7	2 electrodes	[49]
Activated biochar (KOHBWB)	Na ₂ SO ₄	118	1	1000	95	3 electrodes	This work
Activated biochar (CO ₂ BWB)	Na ₂ SO ₄	14	1	1000	95	3 electrodes	This work
Activated biochar	Na ₂ SO ₄	227	0.2	6000	75	2 electrodes	[49]
Activated carbon from banana fibres	Na ₂ SO ₄	74	0.5	500	85	3 electrodes	[50]

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