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2 Production, characterization and potential of 3 activated biochar as adsorbent for phenolic 4 compounds from leachates in a lumber industry 5 site

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23 **Abstract**

24 There is growing interest in low-cost, efficient materials for the removal of organic contaminants
25 in municipal and industrial effluents. In this study, the efficiency of biochar and activated biochar,
26 as promising adsorbents for phenol removal, was investigated at high (up to 1500 mg L⁻¹) and low
27 concentrations (0.54 mg L⁻¹) in synthetic and real effluents (from wood-residue deposits in
28 Québec), respectively. The performance of both materials was then evaluated in batch adsorption
29 experiments, which were conducted using a low solid:liquid ratio (0.1 g:100 mL) at different phenol
30 concentrations ($C_0 = 5\text{--}1500$ mg L⁻¹), and at 20°C. Activated biochars presented higher phenol
31 adsorption capacity compared to biochars due to their improved textural properties, higher
32 micropore volume, and proportion of oxygenated carbonyl groups connected to their surface. The
33 sorption equilibrium was reached within less than 4 h for all of materials, while the Langmuir model
34 best described their sorption process. The maximum sorption capacity of activated biochars for
35 phenol was found to be twofold relative to biochars (303 vs. 159 mg g⁻¹). Results also showed that
36 activated biochars were more effective than biochars in removing low phenol concentrations in real
37 effluents. In addition, 95% of phenol removal was attained within 96 h (although 85% was removed
38 after 4 h), thus reaching below the maximum authorized concentration allowed by Québec's
39 discharge criteria (0.05 mg L⁻¹). These results show that activated biochars made from wood
40 residues are promising potential adsorbent materials for the efficient treatment of phenol in
41 synthetic and real effluents.

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44 **Keywords:** Biochar, activated biochar, adsorption, phenol removal, water treatment, synthetic and
45 real effluents, lumber industry sites

46 **1. Introduction**

47 As a main component of many manufactured products, including herbicides, drugs, paints,
48 cosmetics, and lubricants, phenol has been found in various industrial effluents such as those from
49 oil refineries, coking operations, as well as petrochemical, pharmaceutical and resin manufacturing
50 industries (Patterson 1985). Phenol is harmful to organisms even at low concentrations (e.g., 1.0
51 mg L⁻¹) (Mishra and Clark 2013), while human consumption of phenol-contaminated water can
52 cause serious gastrointestinal damage and even death (Baker et al. 1978). The US Environmental
53 Protection Agency and EU regulations consider phenol a priority pollutant; as such, its maximum
54 admissible concentration in drinking water is fixed at 0.0005 mg L⁻¹. The Canadian maximum
55 acceptable concentration for phenol in drinking water is 0.002 mg L⁻¹ (Health Canada 2014).
56 Furthermore, according to Québec municipalities, the concentration of phenolic compounds in
57 sewage systems should not exceed 0.5 mg L⁻¹ after treatment at a municipal wastewater treatment
58 station (MDDELCC 2015a). The phenolic compounds originating in wood-residue deposits can
59 also pose a problem to the environment. Québec's wood-processing sector, for example, generates
60 significant quantities of residues (i.e., bark, sawdust) annually and **discharge/store them in large**
61 **outdoor deposits**. In northern Québec alone, there are 12 large wood waste sites (MDDELCC 1997).
62 The main concerns about these sites relate to leachates that contain phenolic compounds, which
63 may affect the quality of surface and groundwaters. Therefore, Québec's guidelines require
64 concentrations not exceeding 0.05 mg L⁻¹ for phenolic compounds in leachate from wood-residue
65 deposits (MDDELCC 2015b).

66 Several processes are available for the treatment of phenol and its derivatives through
67 separation, destruction, or oxidation, including steam distillation (Kim 2015), solvent extraction
68 (Fu et al. 2014), chemical oxidation (Gümüő and Akbal 2016), membranes (Ren et al. 2017),

69 biological processes (Ganzenko et al. 2014), photo-oxidation (UV irradiation, TiO₂) (Sun et al.
70 2011), enzymatic processes (Ibáñez et al. 2012), and adsorption (Ahmaruzzaman 2008; Nath et al.
71 2013). Adsorption is frequently used since it has the capacity to remove high concentrations of
72 organic and inorganic compounds in water. One of the best adsorbents used for this application is
73 activated carbons prepared from low-cost biomass precursors, together with chemical or physical
74 agents, at high temperatures thermal treatment. Activation is an alternative method for improving
75 the textural properties and chemical composition of biomass precursors with the removal of less
76 organized bound carbonaceous materials (i.e., CO, CO₂, etc.) at high temperatures (Marsh and
77 Rodríguez-Reinoso 2006).

78 As the global demand for commercial activated carbons as adsorbents in environmental and
79 health protection grows, so too does interest among research and industrial communities in
80 converting biochar (a carbon-rich material produced through pyrolysis or gasification of biomass
81 in the absence of oxygen) into activated biochar due to its low porosity and surface area (Freedonia
82 Group 2014). The advantages of activated biochar include low-cost, availability, economic
83 feasibility in large-scale production, and effectiveness in several applications such as energy storage
84 (Dehkhoda et al. 2016), electrodes for batteries and supercapacitors (Gupta et al. 2015), catalyst
85 support (Zhu et al. 2015), and in the treatment of drinking water and wastewater by sorption (Tan
86 et al. 2015).

87 Indeed, some studies have found activated biochars efficient for the removal of organic
88 pollutants such as phenol. By comparing the same adsorbent material to contaminant ratio (0.1
89 g:100 mL), the sorption capacity of steam-activated biochar made from corncobs was reported to
90 be 164 mg g⁻¹ (El-Hendawy et al. 2001), whereas the sorption capacity of activated biochars made
91 from rattan sawdust (Hameed and Rahman 2008) and fir wood (Wu and Tseng 2006), prepared in

92 presence of both physical and chemical agents (KOH and CO₂ gas), were found to be 149 and 275
93 mg g⁻¹, respectively. Furthermore, it has been reported that the adsorption equilibrium of phenol
94 through the use of activated biochar made from palm seed coats (Rengaraj et al. 2002) and rattan
95 sawdust (Hameed and Rahman 2008) was reached within 3 h and 4 h, respectively. However, most
96 of the studies on phenol removal were based on batch sorption of highly contaminated synthetic
97 effluents (Hameed and Rahman 2008; Wu and Tseng 2006; Zhang et al. 2016). Given the fact that
98 the dominant mechanism of phenol removal is sorption, the surface characteristics of solids
99 (specific surface area, porosity, pHPZC (the point of zero charge), the elemental composition C, H,
100 N, S, O, and the content of surface functional groups of carbon and oxygen) are crucial. **Therefore,**
101 **materials with optimal surface characteristics would exhibit better performance.**

102 The production of biochar is usually a two-step process: 1) torrefaction, low to fast pyrolysis,
103 or gasification, and 2) activation, where biochar is introduced in another reactor at laboratory scale
104 with a very low amount of material (< 10 g) in the presence of physical and chemical agents to
105 obtain developed porosity (Shen et al. 2015; Li et al. 2016; Park et al. 2017). In the second step,
106 parameters are easier to control due to the small amount of stationary precursor applied. To date,
107 data on activated biochars prepared from biomass and biochar thermochemical technologies at pilot
108 scale are not yet available.

109 Thus, the objective of the present study was to compare the efficiency of biochars and activated
110 biochars (made from spruce and birch through pilot-scale technologies of pyrolysis and activation
111 in the presence of CO₂ physical agent) as potential adsorbents for the removal of phenol at high (up
112 to 1500 mg L⁻¹) and low (0.54 mg L⁻¹) concentrations, in synthetic and real effluents, respectively.

113 **2. Materials and methods**

114 2.1 Materials

115 Black spruce (BS) and white birch (WB) residues were sampled from sawmills located in
116 Abitibi-Témiscamingue region, Province of Québec, Canada. The residues were milled using a 6
117 mm Hammer-mill's grate (Industrial grinder, Schutte Buffalo, Hammer Mills, Buffalo, NY, USA)
118 and dried to obtain a humidity content below 40% (Dryer, Abri-Tech Inc., Namur, QC, Canada)
119 before being introduced into the pyrolysis process.

120 2.2 Synthesis of biochar and activated biochar

121 The present study was conducted in three steps: 1) production of biochar, 2) activation of
122 biochar, and 3) application of both materials for the evaluation of their comparative performance
123 in phenol adsorption. In the first step, biochars were prepared using the CarbonFX fast pyrolysis
124 technology developed by Airex Energy Inc. (Bécancour, QC, Canada). The biomass was converted
125 into biochar at temperatures either 315°C (600°F) or 454°C (850°F) with little presence of oxygen.
126 The resulting biochars made from BS and WB residues were then milled between 1 and 2 µm
127 (Grinder, Ro-tap RS-29, WS Tyler, Mentor, OH, USA) and placed in a 1 kg charge pilot oven
128 (developed at the CTRI laboratory) for activation. This oven is composed of a feed hopper, a screw-
129 conveyor tube placed in a muffle furnace, and a recovery hopper. The biochar was transported from
130 the feed to the recovery hopper through the screw-conveyor, which is driven by a motor. When the
131 temperature reached 900°C under a nitrogen atmosphere, the flowing gas of CO₂ was introduced at
132 3 L min⁻¹. The biochars were labeled WB315, WB454, and BS454, and after activation, a letter "A"
133 was added to each material's name (e.g., WB315A).

134 2.3 Physical and chemical characterization of biochar and activated biochar

135 Wood residues were characterized before and after modification for their physicochemical
136 parameters: specific surface area and pore volume, pH, pH_{PZC} (i.e., pH value related to zero
137 electrical charge density of the sorbent surface), elemental composition (C, H, N, S, O), surface

138 morphology and surface chemistry. Pore texture parameters were obtained by N₂ and Kr adsorption
139 at -196°C, and CO₂ at 0°C, using a Micromeritics ASAP 2460 automatic apparatus (Norcross, GA,
140 USA). Wood residues, biochars and activated biochars were degassed at 80, 105 and 250°C,
141 respectively, for 48 h under vacuum prior to any adsorption experiment. The Kr adsorption analysis
142 was carried out to measure low surface area of wood residues. Ultramicroporosity was analyzed by
143 CO₂ adsorption, whereas micro- and mesoporosity was analyzed by N₂ adsorption. The N₂ and CO₂
144 adsorption isotherms were treated for obtaining: 1) surface area: S_{BET} (m² g⁻¹) calculated by the
145 Brunauer-Emmett-Teller (BET) model applied to the nitrogen adsorption data in the appropriate
146 range of relative pressures (P/P_0 between 0.01 and 0.05) (Brunauer et al. 1938); 2) micropore
147 volume: V_{μ} (cm³ g⁻¹) was determined by the Dubinin–Radushkevich (DR) equation (Dubinin 1989);
148 3) total pore volume: V_t (cm³ g⁻¹) was calculated from the amount of nitrogen adsorbed at the
149 relative pressure of 0.97 (Gregg and Sing 1991); 4) mesopore volume: V_m (cm³ g⁻¹) calculated by
150 the difference $V_t - V_{\mu}$. The pore size distribution (PSD) was determined by application of density
151 functional theory (DFT) using N₂ adsorption isotherms (Tarazona 1995).

152 Elemental composition of all materials was determined in a CHNS elemental analyzer, Perkin
153 Elmer 2400 CHNS/O Analyzer (Waltham, MA, USA), by combustion of the samples in a stream
154 of pure O₂. Oxygen content was obtained by the difference ($O\% = 100 - \text{CHNS}\%$). The pH was
155 measured using a SevenMulti, Mettler Toledo (Greifensee, Switzerland) equipped with Inlab
156 Routine Pro electrode. The pH_{PZC} was determined for all materials using the solid addition method
157 (Lazarević et al. 2007; Mohan and Gandhimathi 2009; Belviso et al. 2014). The difference between
158 the initial pH (pH_i) and final pH (pH_f) ($\Delta\text{pH} = \text{pH}_i - \text{pH}_f$) was plotted against pH_i . The point of
159 intersection of the resulting curve for each material with pH_i gave the pH_{PZC} . The surface
160 morphology of WB454A before and after phenol adsorption was investigated with a JEOL JSM-
161 5500 (JEOL USA, Inc., Peabody, MA, USA) scanning electron microscope (SEM) after

162 metallization (i.e., the material was mounted on gold studs). X-ray photoelectron spectroscopy
163 (XPS) spectra were recorded with a Kratos AXIS ULTRA system (Wharfside, MA, UK) equipped
164 with a channel electron multiplier detector. The X-ray source had a monochromatic Al K-alpha
165 operated at 300 W under vacuum at 5×10^{-10} Torr. Binding energies for the high-resolution spectra
166 were calibrated by setting C1s at 284.6 eV. The XPS core level spectra were analyzed with Casa
167 software.

168 2.4 Adsorption kinetics experiments

169 Kinetic studies were performed to evaluate the time required to reach the equilibrium in the
170 system containing the adsorbent and the synthetic effluent. The experiments were conducted in 100
171 mL beakers containing 0.05 g of adsorbent material together with 50 mL of synthetic effluent
172 having a phenol concentration of 200 mg L^{-1} . The supernatants were sampled at 2 h, 4 h, 6 h, 8 h,
173 10 h, 12 h, 18 h, 24 h, and 48 h. The beakers were placed on a multi-position stirring plate, at 500
174 rpm, and at room temperature (20°C). The solid (g):solution (mL) ratio was maintained at 0.1:100
175 to compare the performance of all six materials with other activated biochars in the literature (El-
176 Hendawy et al. 2001; Hameed and Rahman 2008; Wu and Tseng 2006). The pH of the supernatant
177 was measured at the beginning and after 48 h of contact time with the adsorbent. The supernatants
178 were filtered, and the residual phenol was measured with an Ultrospec 2100 pro UV/Visible
179 Spectrometer (Biochrom US, Holliston, MA, USA), at 270 nm. This procedure was carried out for
180 all six materials: 3 biochars (WB315, WB454, and BS454) and 3 activated biochars (WB315A,
181 WB454A, and BS454A).

182 The absorbance was recorded and the residual phenol concentration in the final solution was
183 calculated through a calibration equation: $y = 0.0156 \cdot x - 0.0014$ ($R^2 = 0.9995$) where y is the
184 absorbance, and x is the final phenol concentration. Sorption capacity q_t (mg g^{-1}) was calculated
185 with the application of Eq. 1:

186
$$q_t = [C_0 - C_t] \cdot \frac{V}{m} \quad (1)$$

187 where C_0 , C_t , V , and m represent, respectively, the concentrations of phenol in solution (mg L^{-1}) at
 188 the initial and at t moment, the total volume of solution (L), and the amount of the material used
 189 (g).

190 The equations of pseudo-first rate equation of Lagergren, and pseudo-second order model
 191 (Lagergren 1898) were employed to describe phenol adsorption kinetics. The Lagergren model is
 192 the most widely used rate equation in liquid-phase sorption processes, and it can be represented by
 193 Eq. 2. After integration of Eq. 2 for the initial conditions $t = 0$ and $q_t = 0$, the linearized form of the
 194 pseudo-first order rate Eq. 3 is presented as:

195
$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (2)$$

196
$$\log(q_e - q_t) = \log(q_e) - k_1 \cdot \frac{t}{2.303} \quad (3)$$

197 where q_e and q_t refer to the amount of phenol adsorbed (mg g^{-1}) at equilibrium and at any time, t
 198 (h), respectively, and k_1 is the equilibrium rate constant of pseudo-second order adsorption (h^{-1}).
 199 Eq. 3 gives a straight line: $\log (q_e - q_t)$ versus t , if it applies.

200 The pseudo-second order kinetic model is represented by Eq. 4. After integration of Eq. 4 for
 201 the initial conditions $t = 0$ and $q_t = 0$, the linearized form of the pseudo-second order rate equation
 202 is presented as Eq. 5, which can be rearranged to obtain a linear form (Eq. 6):

203
$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (4)$$

204
$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 \cdot t \quad (5)$$

205
$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} t \quad (6)$$

206 where k_2 is the kinetic constant of pseudo-first order adsorption (g (mg h)^{-1}). If Eq. 6 applies, it
207 should have a straight line: t / q_t versus t .

208 Elovich's equation describes the chemical adsorption mechanism and is suitable for systems
209 with heterogeneous adsorbing surfaces (Aharoni and Tompkins 1970). Eq. 7, once rearranged,
210 reads:

$$211 \quad q_t = \frac{1}{b} \cdot \ln(ab) + \frac{1}{b} \cdot \ln(t) \quad (7)$$

212 where a is the initial adsorption rate (mg (g h)^{-1}), and the parameter $1/b$ is related to the number of
213 sites available for adsorption. Thus, the constants can be obtained from the slope and the intercept
214 of a straight line plot of q_t against $\ln(t)$.

215 2.5 Adsorption equilibrium experiments

216 The tests of isotherm adsorption were conducted at different initial concentrations of phenol
217 (5, 10, 20, 50, 100, 200, 500, 1000, and 1500 mg L^{-1}) under the same conditions as the kinetics
218 experiments with synthetic effluent. The pH of the supernatant was measured at the beginning and
219 at the end of equilibrium experiments (after 48 h). The same procedure was used for all six materials
220 (3 biochars and 3 activated biochars). Sorption capacity q_e (mg g^{-1}) was calculated with Eq. 8 where
221 C_0 , C_e , V , and m represent, respectively, the concentrations of phenol (mg L^{-1}) at the initial and
222 equilibrium solutions, the total volume of solution (L), and the amount of the material used (g). The
223 adsorption (%) was calculated with Eq. 9:

$$224 \quad q_e = [C_0 - C_e] \cdot \frac{V}{m} \quad (8)$$

$$225 \quad \text{Adsorption (\%)} = [C_0 - C_e] \cdot \frac{100}{C_0} \quad (9)$$

226 The Langmuir adsorption model is the most commonly used model to investigate the sorption
227 phenomena of an organic pollutant. It assumes that the adsorption is localized, there is no

228 interaction between adsorbate molecules and adsorbent, and that the maximum limiting uptake
 229 corresponds to a monolayer phenol formed on the adsorbent surface (Langmuir 1918). The
 230 Freundlich adsorption model is used to describe the adsorption characteristics of the heterogeneous
 231 surface of the adsorbent (Freundlich 1906). The linearized form of Langmuir and Freundlich model
 232 equations are represented by the following Eq. 10 and 11, respectively:

$$233 \quad \frac{C_e}{q_e} = \frac{1}{b \cdot q_{max}} + \frac{C_e}{q_{max}} \quad (10)$$

$$234 \quad \log q_e = \log k_f + n \cdot \log C_e \quad (11)$$

235 where C_e and q_e have the same meaning for both equations, q_{max} is the maximum uptake per unit
 236 mass of adsorbent (mg g^{-1}) and b is the Langmuir constant related to the adsorption energy (L mg^{-1})
 237 while k_f and n are Freundlich coefficients. The constant b allows the determination of the R_L
 238 equilibrium parameter through Eq. 12:

$$239 \quad R_L = \frac{1}{1 + b \cdot C_0} \quad (12)$$

240 R_L indicates the shape of the isotherm, and the interpretation of the results is based on the
 241 following meaning: at $R_L = 0$, the adsorption is irreversible; $0 < R_L < 1$, the adsorption is favorable;
 242 at $R_L = 1$, the adsorption is linear; and at $R_L > 1$, the adsorption is unfavorable.

243 The Temkin isotherm is a linear model applied for investigating the kinetics of phenol
 244 adsorption (Eq. 13). Temkin and Pyzhev (1940) considered the effect of the heat of adsorption
 245 during adsorbent–adsorbate interactions. Therefore, the heat of sorption of all the molecules in the
 246 layer would decrease linearly with such interactions.

$$247 \quad q_e = k_1 \cdot \ln(k_2) + k_1 \cdot \ln(C_e) \quad (13)$$

248 where k_1 is related to the heat of adsorption (L g^{-1}), and k_2 is the dimensionless Temkin isotherm
 249 constant.

250 2.6 Adsorption of phenol in a real effluent

251 The effluent containing phenol was collected from a wood-residue deposit located in
252 Taschereau, Abitibi-Témiscamingue, QC, Canada. The same solid:liquid ratio (0.1 g:100 mL), and
253 testing conditions (applied for the kinetics and isotherms studies of phenol in synthetic effluents)
254 were also applied for a real effluent. The supernatants were sampled at 2 h, 4 h, 8 h, 24 h, and 48
255 h. To analyze low concentrations of phenol (< 0.015 ppm) in water media, another colorimetric
256 method (Ettinger et al. 1951) was applied. In this last method, the sample was first distilled and
257 then mixed with an alkaline buffer (pH close to 10), potassium ferricyanide and 4-aminoantipyrine
258 solutions to form a colored complex. The coloration was concentrated with chloroform, and then
259 the absorbance of phenol was measured and compared with a calibration curve.

260 2.7 Reutilization and thermal regeneration cycles of activated biochar

261 Reutilization and regeneration tests were performed with an activated biochar (WB454A) for
262 five-cycle adsorption tests. Adsorption tests were conducted using phenol synthetic solution at 5
263 mg L^{-1} (phenol synthetic solution similar to real effluent) under the same conditions as the isotherm
264 experiments. After each cycle, the solid material was recovered and dried in air overnight to be
265 reused or regenerated in the next cycle. Thermal regeneration experiments were performed at 600°C
266 for 1 h in a Netzsch STA 449 F5 Jupiter equipment (Exton, PA, USA), using a He flow rate of 50
267 mL min^{-1} and heating rate of $10^{\circ}\text{C min}^{-1}$. The efficiency of phenol adsorption in both tests was
268 determined using Eq. 9.

269 3. Results and discussion

270 3.1 Characterization of biochars and activated biochars

271 In this study, wood residues from birch and spruce were first converted into biochars and then
272 activated biochars. Both biomass materials presented similar physicochemical characteristics

273 (Table 1). Carbon and oxygen contents of WB were 46.7 and 45.6%, while those of BS were 48.4
274 and 44.0%, respectively. Hydrogen, nitrogen, and sulfur were similar/identical in both materials:
275 6.5, 0.1-0.2, and 1%, respectively. The porosity (obtained from Kr adsorption analysis) was quite
276 low – up to $0.5 \text{ m}^2 \text{ g}^{-1}$ – for each material. The thermal treatment led to higher carbon content in
277 biochar. The latter increased to 60.8% for WB at 315°C and to 75% for both materials, WB and
278 BS, treated at 454°C . The oxygen and hydrogen contents decreased due to the thermal degradation
279 of oxygenated and hydrogenated groups present in wood residues.

280 Biochars did not present developed porosity due to low temperatures (i.e., $< 450^\circ\text{C}$) and the
281 short residence time (approximately 2 s) in the fast-pyrolysis reactor. Moreover, attempts using N_2
282 gas for adsorption analysis of biochars were unsuccessful as the latter is generally highly
283 microporous, presenting ultramicropores (below 0.7 nm). Such limitations of ultramicroporosity
284 analysis using N_2 are due to diffusion restrictions at low pressures, which prevent nitrogen from
285 entering the narrowest micropores. The use of CO_2 , rather than N_2 (-196°C), for adsorption analysis
286 is suggested once the analysis is achieved at moderate pressures and low temperatures (0°C)
287 (Garrido et al. 1987; García-Martínez et al. 2000). The surface areas of biochars through CO_2
288 adsorption were 177 and $208 \text{ m}^2 \text{ g}^{-1}$ (for WB and BS made at 454°C), and $78 \text{ m}^2 \text{ g}^{-1}$ (for WB biochar
289 at 315°C).

290 Activated biochars that presented the highest porosity and surface area were chosen from a
291 preliminary optimization study on different conditions of pyrolysis of WB and BS residues, and
292 posterior activation. From WB, two materials with the same textural properties (up to $880 \text{ m}^2 \text{ g}^{-1}$)
293 (Table 1) were selected to evaluate their performance on phenol adsorption: one prepared at the
294 lowest pyrolysis temperature (315°C), and the other prepared at the highest pyrolysis temperature
295 (454°C) displayed on CarbonFX technology, and posterior activation at 900°C . From BS residues,

296 the activated biochar selected that had the highest porosity ($735 \text{ m}^2 \text{ g}^{-1}$) was prepared at a pyrolysis
297 temperature of 454°C . The nitrogen adsorption-desorption isotherms at -196°C for all activated
298 biochars are presented in [Fig. 1 \(Online Resource 1\)](#). Nitrogen adsorption isotherms were
299 combinations of types I and IV, characteristic of micro-mesoporous solids according to the IUPAC
300 classification (Sing 1985). The existence of a well-developed mesoporosity was confirmed by the
301 presence of a hysteresis cycle. In relation to pore volume, the proportion of mesopores for each
302 material was found to be 31, 38, and 28% for WB315, WB454, and BS454, respectively, with the
303 rest consisting of micropores.

304 The pH of biochars were 5.2 (WB315), 5.6 (WB454), and 6.3 (BS454), whereas activated
305 biochars presented pHs between 9.5 and 9.8. Therefore, biochars decreased the pH of the solution
306 (5–7), whereas activated biochars increased the pH of the solution (6.5–8.5) over time. The same
307 trend for pH_{PZC} was noted for both groups of materials: low pH_{PZC} (6.3–7.0), for biochars and high
308 pH_{PZC} (9.5–10) for activated biochars. The pK_a of phenol was reported to be 9.89 (László and Szűcs
309 2001). Above the pH_{PZC} of the carbon, which practically coincides with the pK_a of phenol, mainly
310 phenolate anions are formed in aqueous solution. At pHs lower than pK_a (i.e., the scenario of the
311 present study), phenol molecules were found to be in non-dissociated form. Most previous research
312 on phenol sorption by activated carbons did not report a change in the pH of the solution (Wu and
313 Tseng 2006; Rincón-Silva et al. 2015; Zhang et al. 2016) (also the case in this study), whereas some
314 studies reported an optimal pH lower than 8 (Hameed and Rahman 2008), between 7 and 8 (Kilic
315 et al. 2011), or lower than 10 (Nabais et al. 2009).

316 The XPS spectra were deconvoluted into the five peaks of graphitic sp^2 , C–OH, C=O or C–O–
317 C, O=C–O, and shake-up satellites. The most intense band is assigned to graphitic sp^2 carbon. The
318 other bands connected to the presence of several C–O bonds. Activated biochars (prepared at

319 900°C) presented higher graphitic sp² carbon content (up to 76.6%) compared to biochars (up to
320 72.0%), whereas biochars (prepared at lower temperature: 454°C) presented higher content of C–
321 O bonds, especially alcohol (C–OH) (up to 18.4%), compared to activated biochars (up to 12.8%).
322 The oxygenated functional groups contents were drastically reduced with pyrolysis, and posterior
323 activation. Several carbon species localized at the materials' surface were deconvoluted into
324 multiple Gaussian components (XPS spectra C1s excitation) as reported in [Table 2 \(Online](#)
325 [Resource 2\)](#).

326 3.3 Kinetics of phenol adsorption

327 Evolution of adsorption kinetics of phenol on biochars and activated biochars shows that higher
328 adsorption capacity of phenol was reached for all activated biochars (184 mg g⁻¹) compared to
329 biochars (71 mg g⁻¹). The majority of materials reached the adsorption equilibrium within less than
330 4 h ([Fig. 2](#)), whereas some, such as WB315 and BS454A, required up to 18 h (with over 50% of
331 equilibrium sorption capacity obtained in less than 4 h). In order to analyze the adsorption kinetics
332 of phenol, pseudo-first, pseudo-second order, and Elovich's equation were investigated. The
333 derived kinetic parameters of these models ([Table 3](#)) show that experimental data obtained from
334 activated biochars were better fitted than biochars, as evidenced by the *R*² coefficients: 0.85–0.97
335 and 0.24–0.74, respectively. Activated biochars reasonably fit all models, but it is difficult to
336 confirm which sorption kinetics can be more satisfactorily applied. To better understand the
337 mechanism involved in sorption kinetics of both materials, the intraparticle diffusion model was
338 proposed by Weber and Morris (1963), assuming that the intraparticle diffusion is considered as a
339 rate-limiting step described by Eq. 14:

$$340 \quad q_t = k_{id} \cdot t^{0.5} + \theta \quad (14)$$

341 where k_{id} is the intra-particle diffusion rate constant ($\text{mg (g h)}^{-0.5}$), and θ is a constant related to the
342 thickness of the boundary layer (mg g^{-1}). If the sorption is controlled by intra-particle diffusion, the
343 plot of q_t versus $t^{0.5}$ gives a straight line. The plots of the kinetics of phenol (q_t) versus $t^{0.5}$ are not
344 linear over the whole time of adsorption (Fig. 3). Therefore, if the sorption is controlled by multi-
345 linear plots (Fig. 3), then there is more than one step controlling the phenol sorption process. First,
346 phenol is transported from the bulk to the external surface of the adsorbent. Second, it is diffused
347 in the film of the boundary layer to the surface of adsorbate. Then, phenol is transported into macro-
348 and mesopores of the adsorbent. Finally, phenol is adsorbed onto active sites or micropores (Singh
349 et al. 2008).

350 For biochars (except for BS454) and activated biochars, two straight lines control the
351 mechanism of phenol adsorption. If the slope of the first straight line is not zero, then the film of
352 boundary layer diffusion controls the initial adsorption rate. The first straight line indicates macro-
353 and mesopore diffusion; then, the second one shows micropore diffusion (Crini and Badot 2010).
354 Activated biochars presented the same slope from the first straight line, indicating a similar rate of
355 phenol adsorption in larger micropores and mesopores (Dąbrowski et al. 2005). On the contrary,
356 biochars showed different slopes that varied due to different mass transfer in the stages of
357 adsorption, except for BS454, which presented just one straight line, indicating that only micropore
358 diffusion of phenol molecules occurred.

359 3.3 Adsorption isotherms

360 Equilibrium experiments in batch sorption were performed with the aim of evaluating
361 pollutants interaction with adsorbent materials. Comparative adsorption isotherms of phenol (Fig.
362 4) show that activated biochars displayed twofold higher phenol sorption relative to biochars.
363 Moreover, the phenol removal for all materials was found to decrease with increases in initial

364 concentrations. Activated biochars removed 90 to 100% of phenol at initial concentrations from 5
365 to 200 mg L⁻¹ (Fig. 5). At higher concentrations (500–1500 mg L⁻¹), the efficiency of phenol
366 removal decreased to 50% or less (not shown in Fig. 5). At the same time, biochars presented much
367 lower phenol adsorption (less than 50%) for almost all initial concentrations. Nevertheless, the
368 amount of phenol adsorbed per unit of biochar or activated biochar mass increased with the increase
369 in initial phenol concentration. Thus, at an initial concentration of 200 mg L⁻¹, the phenol removal
370 capacity was 70.6 and 184.3 mg g⁻¹ for biochars and activated biochars, respectively, whereas at
371 maximum initial concentration (1500 mg L⁻¹), the phenol removal capacity increased to 141.6 and
372 303.2 mg g⁻¹, respectively. An increment of the uptake was closely related to greater mass driving
373 force effect that allows more adsorbates to pass through from the bulk phase boundary to the surface
374 of all carbonaceous materials.

375 Most of the correlation coefficients (R^2) for Freundlich, Langmuir, and Temkin sorption
376 models (Table 4) were higher than 0.90 for all biochars, whereas activated biochars were better
377 fitted to Langmuir with a R^2 equal to 0.99. All equilibrium parameters (R_L) are comprised between
378 0 and 1; hence, the adsorption is considered favorable. The values of q_{max} were found to vary
379 between 159 mg g⁻¹ for biochars (WB454), and 303 mg g⁻¹ for WB454A. The surface morphology
380 differences between WB454A before and after phenol adsorption are illustrated in Fig. 6 a) and b).
381 SEM image of pristine WB454A shows narrow and larger pores structures developed during fast
382 pyrolysis, and posterior activation at 900°C. Based on these results (Fig. 6 b)), it is clearly
383 noticeable that the surface porous structure of WB454A was completely covered with phenol
384 molecules after adsorption.

385 Three mechanisms have been proposed for the sorption of phenol in solution by carbon
386 materials: 1) π - π force interactions, 2) the hydrogen bonding formation, and 3) electron-donor-

387 acceptor complex formation (Rodrigues et al. 2011). The first mechanism, i.e., π - π force
388 interaction, occurs between π electrons present in the aromatic rings of phenol molecule and the
389 delocalized π electrons present in basal planes of the carbon material. Some authors assume that
390 oxygenated surface groups (phenol, carbonyl, lactone, and carboxyl) or acid groups bound to
391 carbon may reduce the π electron density, lowering the π - π interactions, and consequently
392 disfavoring the adsorption of phenol or aromatic compounds (Dąbrowski et al. 2005; Singh et al.
393 2008; Zhang et al. 2016). According to Adamu et al. (2016), the abundance of oxygen-containing
394 functional groups in the basal plane and edge planes of TiO₂-graphene oxide material (compared
395 to thermally reduced graphene oxide) can inhibit delocalization of π -electrons or diminish π - π
396 conjugation of the sp² domain. A mechanism was proposed showing π - π and H-bonding
397 interactions between the thermally treated material (presenting lower amounts of oxygenated
398 groups, the same scenario as for activated biochar) and phenol aromatic rings. On the contrary, for
399 non-thermally treated material (having abundant amount of oxygenated groups, the same scenario
400 as for biochars), there is only H-bonding interactions with phenol molecules, which is the probably
401 reason of its low phenol adsorption performance. The second mechanism assumes that water
402 molecules may form complexes on the surface of carbon materials with oxygenated functional
403 groups, and reduce phenol sorption. The third mechanism is based on the formation of electron-
404 donor-acceptor complexes between the surface carbonyl groups (electron donors) and the aromatic
405 rings of phenol (electron acceptors). In this last case, some authors state that carbonyl groups may
406 act as electron donors with the aromatic rings of phenol (receptors), enhancing phenol adsorption
407 (Terzyk 2003; Zhang et al. 2016).

408 In first and second mechanisms, oxygenated groups were found to be unfavorable to the
409 adsorption by carbon materials whereas in the third mechanism, carbonyl groups enhanced phenol

410 adsorption. Positive correlations were observed in relation to the content of carbonyl groups present
411 in activated biochars ([Table 2](#); [Online Resource 2](#)). The WB454A presented the greatest phenol
412 adsorption (303 mg g^{-1}), the highest surface area, total pore and micropore volumes ($881 \text{ m}^2 \text{ g}^{-1}$;
413 $0.53 \text{ cm}^3 \text{ g}^{-1}$; $0.33 \text{ cm}^3 \text{ g}^{-1}$), and increased proportion of oxygenated groups (19.5%, 4.5% of
414 carbonyl groups). The WB315A (i.e., the activated biochar that exhibited the lowest phenol
415 adsorption (250 mg g^{-1})) had similar surface area and pore volume to WB454A ($873 \text{ m}^2 \text{ g}^{-1}$; 0.48
416 $\text{cm}^3 \text{ g}^{-1}$; $0.33 \text{ cm}^3 \text{ g}^{-1}$) but lower carbonyl groups (3.7%). Therefore, the efficacy of WB454A for
417 phenol uptake, compared to biochars and other activated biochars, is based not only on its
418 developed porosity (high surface and pore volume), but also the presence of micropore volume, as
419 well as the oxygenated functional groups (especially carbonyl groups).

420 3.4 Comparison of phenol sorption capacity

421 A comparison of phenol adsorption capacities by various types of adsorbents reported in the
422 literature with the findings of the present study shows consistent trends ([Table 5](#)). Different phenol
423 adsorption performances were observed when comparing activated carbons due to the different raw
424 materials (e.g., coconut shells, lignocellulosic precursors, coffee grounds, soybean straw, etc.),
425 activation methods (e.g., in presence of chemicals (KOH, H_3PO_4 , ZnCl_2 , NaOH, K_2CO_3)), physical
426 agents (CO_2 or steam) or in presence of both agents (e.g., KOH or CO_2), different adsorbent:phenol
427 effluent ratios, pHs, or initial concentrations of contaminant.

428 It was observed that most of the activated materials followed the Langmuir sorption model,
429 and have great phenol sorption without changing the pH of the effluent. Activation through
430 chemical or a combination of chemicals and physical agents showed highly developed surface area
431 (up to $3000 \text{ m}^2 \text{ g}^{-1}$), and, consequently, higher phenol sorption capacity. Birch- and spruce-activated
432 biochars presented moderated surface area (up to $880 \text{ m}^2 \text{ g}^{-1}$), but great phenol sorption was

433 obtained at 184 and 283 mg g⁻¹ (C₀ of 200, and 500 mg L⁻¹, respectively), compared to rattan-
434 sawdust-activated biochar (at C₀ of 200 mg L⁻¹, 149 mg g⁻¹) or coconut-shell-activated carbon (at
435 C₀ of 500 mg L⁻¹, 206 mg g⁻¹) using the same adsorbent:contaminant ratio (0.1 g:100 mL).
436 Therefore, the efficacy of the activated biochars made from wood residues (WB and BS) through
437 pilot-scale technologies was higher than other prepared activated carbons. These findings suggest
438 that the use of wood residues from northern regions in wastewater treatment has a promising future.

439 3.4 Phenol removal in real residue park

440 The initial concentration of phenol in the lixiviate collected in a wood-residue deposit was 0.54
441 mg L⁻¹, i.e., exceeded the Québec regulatory criteria of 0.05 mg L⁻¹ (MDDELCC 2015b). Activated
442 biochars were highly effective at removing low phenol concentration, i.e., more than 85%
443 (WB315A, WB454A, and BS454A) after 4 h of testing (Fig. 7). In addition, biochars allowed only
444 a gradual removal of phenol of 39, 65, and 79% (BS454, WB454, and WB315, respectively) by the
445 end of the 48 h testing period. After 96 h of testing, phenol removal topped 95% with activated
446 biochars vs. 79% with biochars. The sorption of activated biochars seems to be not affected by the
447 nature of the precursor (BS or WB) after 96h testing. However, only activated biochar WB454A
448 resulted in regulatory conformity with the Québec law after 2 days of testing (0.037 mg L⁻¹ of
449 residual phenol).

450 3.5 Reutilization and thermal regeneration cycles of activated biochar

451 Activated biochar reutilization and regeneration are complementary techniques for industrial
452 applications because the sorbent could be reused after successive adsorption–desorption cycles.
453 After the five reutilization cycles, the efficiency of phenol adsorption was reduced from 99.9% (C_t
454 = 0.003 mg L⁻¹) to 96.7% (C_t = 0.117 mg L⁻¹). To obey the Québec’s regulatory criteria of 0.05 mg
455 L⁻¹ (MDDELCC 2015b) in lixiviate from a wood-residue deposit, WB454A could be reused only

456 after four adsorption-desorption cycles (99.1%; $C_t = 0.047 \text{ mg L}^{-1}$). In relation to WB454A
457 regeneration, the efficiency of phenol adsorption was maintained at 99.8-99.9% ($C_t = 0.003\text{-}0.009$
458 mg L^{-1}), which looks a quite stable trend of variation in five adsorption-desorption cycles.
459 Therefore, the results suggest that WB454A has high regenerability, stable phenol
460 adsorption-desorption efficiency, and suitability for successive adsorption-regeneration cycles.

461 **4. Conclusion**

462 The present study comparatively evaluated the efficiency of biochars and activated biochars
463 (made from birch and spruce residues) in phenol sorption from synthetic and real effluents.
464 Activation of biochars enhanced the physicochemical and textural properties of the final materials,
465 doubling their sorption efficiency compared to biochars. For both materials, the sorption
466 equilibrium was reached in less than 4 h. Activated biochars also proved efficient in phenol removal
467 in a real effluent, collected from a wood-residue deposit, to below the maximum authorized
468 concentration allowed by Québec's discharge criteria. After five successive adsorption-
469 regeneration cycles, the activated biochar exhibited high phenol removal capacity, good stability
470 and high regenerability. In addition, the utilization of activated biochar made from wood residues
471 is also under study in mine water treatment, electrochemical energy storage and conversion, and
472 gas sorption.

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677 **Captions of the tables:**

678 **Table 1:** Textural and physicochemical characteristics of biochar and activated biochar

679 **Table 2:** Contributions to the C1s bands in XPS patterns.

680 **Table 3:** Kinetic parameters obtained from the adsorption of phenol onto biochars and activated
681 biochars

682 **Table 4:** Parameters of phenol adsorption isotherms onto biochars and activated biochars

683 **Table 5:** Comparative sorption capacity of activated biochars, activated carbons and
684 commercial activated carbons for phenol in water

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698 **Captions of the figures:**

699 **Fig. 1:** a) Nitrogen adsorption-desorption isotherms (full and open symbols, respectively) at -
700 196°C; and b) their pore size distribution determined by the DFT method (slit-like
701 geometry) for all activated biochars.

702 **Fig. 2:** Adsorbed amounts of phenol at initial concentration of 200 mg L⁻¹ (q_t) as function of time
703 for all biochars: (◆) WB315, (✱) WB454, (━) BS454 and activated biochars: (□) WB315A,
704 (△) WB454A, (○) BS454A.

705 **Fig. 3:** Kinetics of phenol adsorption on biochars: (◆) WB315, (✱) WB454, (━) BS454 and activated
706 biochars: (□) WB315A, (△) WB454A, (○) BS454A on intraparticle model.

707 **Fig. 4:** Adsorption isotherms of phenol on biochars: (◆) WB315, (✱) WB454, (━) BS454 and
708 activated biochars: (□) WB315A, (△) WB454A, (○) BS454A.

709 **Fig. 5:** a) Phenol adsorption measured in percentage as function of different initial concentrations
710 of phenol (C₀ = 5, 10, 20, 50, 100, and 200 mg L⁻¹) on biochars: (◆) WB315, (✱) WB454,
711 (━) BS454 and activated biochars: (□) WB315A, (△) WB454A, (○) BS454A.

712 **Fig. 6:** SEM images of WB454A before (a) and after (b) phenol adsorption

713 **Fig. 7:** The sorption capacity of phenol present in real effluent (mg L⁻¹) as function of the contact
714 time with biochars: (◆) WB315, (✱) WB454, (━) BS454 and activated biochars: (□)
715 WB315A, (△) WB454A, (○) BS454A.

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718 **Table 1:** Textural and physicochemical characteristics of biochar and activated biochar

	WB	BS	WB315	WB454	BS454	WB315A	WB454A	BS454A
Textural properties								
S_{BET} (m ² g ⁻¹) ^a	0.56 ^o	0.5 ^o	78*	177*	208*	873**	881**	735**
V_t (cm ³ g ⁻¹) ^b						0.48	0.53	0.39
V_{μ, N_2} (cm ³ g ⁻¹) ^c						0.33	0.33	0.28
V_{μ, CO_2} (cm ³ g ⁻¹) ^d			0.05	0.11	0.14	0.29	0.28	0.20
V_m (cm ³ g ⁻¹) ^e						0.15	0.20	0.11
Physicochemical characteristics								
pH	-	-	5.2	5.6	6.3	9.8	9.5	9.8
pH _{PZC}	-	-	6.3	6.6	7.0	9.8	9.5	10.0
C (%)	46.7	48.4	60.8	75.4	75.4	90.6	89.9	88.9
H (%)	45.6	44.0	5.0	3.5	3.8	1.0	0.9	0.6
N (%)	0.2	0.1	1.0	0.9	0.9	0.4	0.4	1.2
S (%)	1.0	1.0	0.8	0.5	0.5	0.0	0.0	0.1
O (%)	6.5	6.5	32.4	19.7	19.4	8.0	8.8	9.2

719 ^a Surface area obtained from °Kr, *CO₂, and **N₂ adsorption analysis; ^b Total pore volume calculated from the amount of N₂
720 adsorbed at the relative pressure of 0.97; ^c Micropore volume determined by the Dubinin–Radushkevich (DR) equation from N₂
721 adsorption analysis; ^d Micropore volume determined by the DR equation from CO₂ adsorption analysis; ^e Mesopore volume
722 calculated by the difference $V_t - V_{\mu, N_2}$

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738 **Table 2:** Contributions to the C1s bands in XPS patterns.
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Binding energy (BE) (eV) and area of the peak (%)	WB315	WB454	BS454	WB315A	WB454A	BS454A
C1s						
BE < 285eV (graphitic sp ² carbon)	69.4	68.0	72.0	76.6	72.1	75.8
285.7 < BE < 287.1 (C–OH)	17.2	17.1	18.4	8.7	12.8	11.7
286.1 < BE < 288 (C=O or O–C–O)	7.2	4.6	3.5	3.7	4.5	3.4
288 < BE < 289.4 (O=C–O)	5.0	4.6	2.2	2.5	2.2	2.4
BE > 290 ("Shake-up" satellites)	1.2	5.7	3.9	8.5	8.4	6.7

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765 **Table 3:** Kinetic parameters obtained from the adsorption of phenol onto biochars and activated
 766 biochars

	<i>Pseudo-first order</i>			<i>Pseudo-second order</i>			<i>Elovich's equation</i>		
	q_e (mg g ⁻¹)	k_1 (h ⁻¹)	R^2	q_e (mg g ⁻¹)	k_2 (mg (g h) ⁻¹)	R^2	a (mg (g h) ⁻¹)	$1/b$ (mg g ⁻¹)	R^2
WB15	122	0.002	0.73	122	0.0001	0.74	6.4	6.0	0.54
WB454	114	0.008	0.24	111	0.00007	0.25	42.1	18.3	0.63
BS454	90	0.002	0.45	90	0.00003	0.45	5.6 10 ⁷	2.8	0.49
WB315A	92	0.004	0.85	92	0.00005	0.88	2.9 10 ¹⁰	6.7	0.89
WB454A	150	0.005	0.95	152	0.00004	0.96	9.0 10 ⁵	12.0	0.90
BS454A	233	0.016	0.87	238	0.00009	0.90	144	38.6	0.97

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798 **Table 4:** Parameters of phenol adsorption isotherms onto biochars and activated biochars

	<i>Freundlich</i>			<i>Langmuir</i>				<i>Temkin</i>		
	k_f	n	R^2	$q_{max}(\text{mg g}^{-1})$	$b (\text{L mg}^{-1})$	R_L	R^2	$k_1 (\text{L g}^{-1})$	k_2	R^2
WB315	1.13	0.65	0.91	125	0.003	0.60–0.98	0.93	17.6	0.16	0.89
WB454	2.51	0.60	0.95	159	0.006	0.46–0.97	0.97	23.0	0.21	0.90
BS454	1.83	0.58	0.87	141	0.004	0.55–0.98	0.93	19.4	0.23	0.86
WB315A	23.3	0.41	0.77	250	0.075	0.06–0.73	0.99	30.0	4.85	0.96
WB454A	24.4	0.40	0.62	303	0.044	0.10–0.82	0.99	37.1	3.67	0.95
BS454A	21.5	0.42	0.64	294	0.035	0.12–0.85	0.99	33.3	3.41	0.86

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832 **Table 5:** Comparative sorption capacity of activated biochars, activated carbons and commercial

833 activated carbons for phenol in water

Effluent type	gAC:mL	pH	AC-raw material	Activation/ S_{BET} ($m^2 g^{-1}$)	q_{max} ($mg g^{-1}$)	Isotherm	C_0 ($mg L^{-1}$)	References
Activated biochars								
SE	-	-	Corncoobs	Steam (607)	164	-	-	(El-Hendawy et al. 2001)
SE/RE	-	6.2	Palm seed coats	CO ₂ (577)	Batch: 18 Column: SE: 72 RE: 55	Freundlich	Batch: 10–60 Column: SE: - RE: 122	(Rengaraj et al. 2002)
SE	0.1:100	-	Fir wood	KOH + CO ₂ (2820)	275	Langmuir	-	(Wu and Tseng 2006)
SE	0.1:100	< 8	Rattan sawdust	KOH + CO ₂ (-)	149	Langmuir	25–200	(Hameed and Rahman 2008)
SE	0.1:100	-	White birch	CO ₂ (880)	303	Langmuir	5–1500	Present study
SE	0.1:100	-	Black spruce	CO ₂ (735)	294	Langmuir	5–1500	Present study
Activated carbons made from biomass residues								
SE	0.67:100	-	Apricot stone shells	H ₃ PO ₄ (1370)	120	Langmuir	60	(Daifullah and Girgis 1998)
SE	0.05:100	-	Coconut shells	KOH (2450)	396	-	-	(Hu and Srinivasan 1999)
SE	0.01:100	6	Kraft Lignin (Eucalyptus)	H ₃ PO ₄ (up to 1460)	227	Langmuir	-	(Gonzalez-Serrano et al. 2004)
SE	-	-	Coffee grounds	ZnCl ₂ + H ₃ PO ₄ (640)	3.2	Langmuir	20	(Namane et al. 2005)
SE	0.1:100	-	Kraft lignin	NaOH (2340) KOH (2920) H ₃ PO ₄ (940)	238 213 107	Langmuir	100	(Fierro et al. 2008)
SE	0.1:100	4	Coconut shells	H ₂ SO ₄ + Steam (380)	50	Langmuir	9.4–94	(Singh et al. 2008)
SE	0.1:100	7	Coconut shells	KOH (1026)	206	Langmuir	100–500	(Mohd Din et al. 2009)
SE	0.1:100	< 10	Lignocellulosic precursors: kenaf (K) / rapeseed (R)	CO ₂ K: 1035 R: 1352	K: 83 R: 84	Freundlich	940	(Nabais et al. 2009)
SE	0.5-8:1000	7/8	Tobacco residues	K ₂ CO ₃ (1635) KOH (1474)	18 0.5	Langmuir	1–12	(Kilic et al. 2011)
SE	-	-	Soybean straw	ZnCl ₂ (up to 2270)	278	Langmuir	10–500	(Miao et al. 2013)
SE	0.01–2:100	-	Cellulose	Steam (1317)	417	Langmuir	150	(Lorenc-Grabowska and Rutkowski 2014)
SE	-	-	Eucalyptus seed	Chemical: NaOH (780) H ₂ SO ₄ (150)	200 29	Langmuir	-	(Rincón-Silva et al. 2015)
SE	1:100	-	Coconut shells	Steam (up to 644)	145	Langmuir	200–1400	(Zhang et al. 2016)

Commercial activated carbons								
SE	-	3	Norit: RGM1 RB2 ROW0.8supra CGran	1152 1380 798 1955	0.9 0.9 1.5 0.2	Freundlich	-	(Jung et al. 2001)
SE	-	-	Commercial AC from coal	Chemical: 1414 Steam: 896 1149	98 226 303	-	200	(Ania et al. 2002)
SE	0.1:100	-	Norit: PAC200 Darco 12 x 40 ROX 0.8	1350 620 102	105 74 137	Langmuir	100	(Fierro et al. 2008)

834 * SE: Synthetic effluent; RE: Real effluent

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