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1 **Paracetamol removal by Kon-Tiki kiln-derived**  
2 **biochar and activated carbons**

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13 **Abstract**

14 Biochar was obtained from Eucalyptus pruning residues with a non-conventional device  
15 named Kon-Tiki kiln. The average heat of combustion of the biochar,  $27.3 \text{ MJ kg}^{-1}$ , was  
16 higher than that of Eucalyptus wood,  $17.8 \text{ MJ kg}^{-1}$ . Activation with  $\text{CO}_2$  was performed by  
17 varying the activation time from 0 to 60 minutes. The activated carbons (ACs) and the carbon  
18 precursor have been characterised and tested for paracetamol removal in the liquid phase,  
19 studied in both kinetic and equilibrium aspects. ACs presented an increase in BET area (up to  
20  $845 \text{ m}^2/\text{g}$ ), total pore volume and microporosity with the activation time. The pseudo-second  
21 order model was the one that best fitted the experimental data. Elimination of paracetamol  
22 was much faster when using ACs, 5h, than when using the biochar, 3 days. However,  
23 pollutant removal was greater than 95% for all materials, which is a promising result for low-  
24 cost biochars in a difficult economic context. All the adsorption equilibrium experiments  
25 exhibited multilayer behaviour, showing values up to  $98 \text{ mg g}^{-1}$  for the maximum monolayer-  
26 adsorption capacity.

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35 **Keywords:** Kon-Tiki kiln; activated carbon; biochar;  $\text{CO}_2$  activation; paracetamol adsorption.

## 36 **1. Introduction**

37 Pharmaceutical and Personal Care Products (PPCPs) are emerging pollutants, which are  
38 increasingly found in treated urban and industrial wastewaters, as well as in watercourses  
39 (Kolpin et al., 2002). PPCPs are not listed as pollutants in the World Health Organization  
40 guidelines for drinking water quality (WHO, 2004) and, therefore, they are not regulated. For  
41 this reason, studies on their effects on human and environmental health are still rare  
42 (Daughton and Ternes, 1999). Although PCPCs are present in low concentrations in aquatic  
43 ecosystems, typically at trace levels ( $\text{ng L}^{-1}$  to  $\mu\text{g L}^{-1}$ ), they can still induce adverse effects due  
44 to cumulative effects and continuous exposure (Boudrahem et al., 2017; Dordio et al., 2009).

45 Paracetamol (N-4-hydroxyphenylacetamide or acetaminophen), a common analgesic and  
46 anti-inflammatory for humans and animals, is usually chosen as a model molecule (García-  
47 Mateos et al., 2015; Lladó et al., 2015; Mestre et al., 2015, 2011; Spessato et al., 2020;  
48 Terzyk, 2001; Terzyk et al., 2003; Terzyk and Rychlicki, 2000) because it is a pharmaceutical  
49 compound used worldwide and does not require medical prescription. Depending on the  
50 source, 58 to 90% of the ingested paracetamol and its metabolites are excreted by the human  
51 body without being metabolised (Correia et al., 2016; Wu et al., 2012). In surface waters, the  
52 median concentration of paracetamol detected was  $0.055 \pm 0.051 \mu\text{g L}^{-1}$  (Bound and  
53 Voulvoulis, 2006; Gros et al., 2006; Wiegel et al., 2004) although higher concentrations have  
54 been measured. Paracetamol has been found in concentrations up to  $6 \mu\text{g L}^{-1}$  in effluents from  
55 European sewage treatment plants, up to  $10 \mu\text{g L}^{-1}$  in USA natural waters, and higher than  $65$   
56  $\mu\text{g L}^{-1}$  in the Tyne River in the UK (Wu et al., 2012). In raw wastewater, paracetamol was  
57 detected at a median concentration of  $48 \pm 75 \mu\text{g L}^{-1}$  but in raw hospital effluents and some  
58 wastewater effluents, paracetamol concentrations can even exceed  $150 \mu\text{g L}^{-1}$  (Wu et al.,  
59 2012).

60 Activated carbons (ACs) have been widely studied to remove contaminants from water,  
61 and PPCPs are no exception (Acosta et al., 2016; Baccar et al., 2012; Marques et al., 2017;  
62 Mestre et al., 2009, 2007; Selmi et al., 2018). Pyrolysis of biomass at the laboratory scale for  
63 the production of ACs requires specific and expensive equipment both for carbonisation and  
64 activation steps. Commercial carbons are usually physically activated with steam, CO<sub>2</sub>, air or  
65 mixtures, or are chemically activated by adding zinc salts, KOH or H<sub>3</sub>PO<sub>4</sub> to the carbon  
66 precursors (Zhang et al., 2004). After chemical activation, an extensive washing step with  
67 water and sometimes HCl is needed (Fierro et al., 2006; Schaefer et al., 2016). Despite the  
68 desired chemical and textural properties are successfully achieved by chemical or physical  
69 activation, the overall yield of the process is sometimes quite low, especially by KOH  
70 activation (Basta et al., 2009; Szczurek et al., 2014).

71 This study focuses on the development of low-cost adsorbent production strategies. In this  
72 sense, Schmidt and Taylor designed a non-conventional carbonisation device named Kon-Tiki  
73 kiln, which allows the production of large amounts of carbonaceous material with minimal  
74 infrastructure and without external energy supply, promoting the reuse of agricultural by-  
75 products (Schmidt and Taylor, 2014). It follows the principle of pyrolysis of biomass layer  
76 after layer in an open metal kiln, conical in shape, easy to use, fast and resulting in low  
77 greenhouse gas emissions (Cornelissen et al., 2016). The process of carbonisation using this  
78 device resembles the carbon production by ancient civilisations and small contemporary  
79 communities, which proves that it is well known, easy to reproduce and cheap. Kon-Tiki kiln-  
80 derived biochar has been used for soil amendment as it possesses chemical properties and  
81 agronomic effects similar to those seen for biochars produced in other types of kilns (Pandit et  
82 al., 2017).

83 The aim of this study was to produce biochar from Eucalyptus pruning residues in a Kon-  
84 Tiki kiln and to use them *as such* or more carbonised and activated with CO<sub>2</sub>, for the removal  
85 of paracetamol removal in water.

86

## 87 **2. Materials and Methods**

### 88 *2.1 Biochar and activated carbons (ACs) preparation*

89 Biochar was obtained from the urban pruning of Eucalyptus branches from La Plata,  
90 Argentina. Charring was performed in a Kon-Tiki kiln according to the procedure presented  
91 by Schmidt & Taylor (2014). In short, fire was first produced inside the kiln with small  
92 branches (diameter  $d$  about 1 cm) and, as soon as a layer of ash was perceived, new larger  
93 branches were added to the kiln ( $d < 4$  cm). The kiln was fed constantly using the same  
94 criteria until all the selected biomass was consumed. Apart from the addition of more  
95 feedstock when the flames are low, the temperature in the Kon-Tiki kiln cannot be controlled,  
96 but the operating and investment costs are much lower than those of traditional carbonisation  
97 kilns. The maximum temperature recorded before quenching was 700°C and was measured by  
98 using a copper-aluminium K-type thermocouple sheathed in an alumina tube and coupled to a  
99 digital thermometer. Figure SI 1 shows an image of the device in operation. Then, distilled  
100 water was poured to put out the fire. The biochar thus obtained was then filtered and dried at  
101 105°C for 48h. The biochar was ground and sieved, and the particle fraction used in this study  
102 was 600-250 µm (mesh 30-60, ASTM). The material was labelled as CV.

103 Physical activation with CO<sub>2</sub> was carried out in a quartz tube reactor installed in a  
104 horizontal furnace. The inner diameter of the quartz tube was 3.5 cm and its length was 100  
105 cm. A quartz boat containing between 0.5 and 0.6 g of CV was located in the centre of the  
106 quartz tube and the system was purged for 1 h with a 100 mL min<sup>-1</sup> nitrogen flow to eliminate

107 any trace of oxygen before heating. Then, the oven was heated at  $5^{\circ}\text{C min}^{-1}$  to  $900^{\circ}\text{C}$ , and the  
108 latter temperature was held for 1h. Then, the nitrogen flow was switched to a  $25\text{ mL min}^{-1}$   
109  $\text{CO}_2$  flow, which was maintained for a given time of 15, 30 or 60 min. After this time, the  
110 sample was cooled under  $\text{N}_2$  flow. The resultant activated carbons (ACs) were labelled as  
111 CV15, CV30 and CV60, respectively. The ACs obtained were weighed and the yield of the  
112 process ( $Y$ ) was calculated according to equation (1):

$$113 \quad Y = \frac{W_C}{W_{CH}} \times 100 \quad (1)$$

114 where  $W_{CH}$  is the initial weight of biochar and  $W_C$  is the weight of the sample after activation.  
115 A reference carbon material was prepared by heating CV up to  $900^{\circ}\text{C}$  for 1h without  $\text{CO}_2$   
116 activation and it was labelled CV0.

## 117 *2.2 Materials characterisation*

118 Carbon, hydrogen, nitrogen and sulphur contents in all carbonaceous materials were  
119 determined using an elemental analyser (Vario El Cube, Elementar). Oxygen was also  
120 determined in the same equipment in a second step. The measurements were performed in  
121 duplicate. The ash content was estimated by difference.

122 The morphology of the samples was studied with a Scanning Electron Microscope (FEG-  
123 SEM Hitachi S 4800) equipped with an EDX (Energy Dispersion of X-rays) instrument. The  
124 latter was used for semi-quantitative analysis and element mapping.

125 Calorific tests were carried out in a 6200 Isoperibolic Calorimeter (Parr) in order to  
126 determine the enthalpy of combustion of the raw biomass (Eucalyptus wood) and the biochar  
127 (CV). For that purpose, sample weights between 0.6 and 0.9 g were used and the variation of  
128 temperature while burning in an excess of oxygen was recorded. The measurements were  
129 performed with a resolution of  $0.0001^{\circ}\text{C}$  over a working range of 20 to  $40^{\circ}\text{C}$ .

130 The porous texture was characterised by N<sub>2</sub> adsorption-desorption at -196°C and by CO<sub>2</sub>  
 131 adsorption at 0°C, using an automatic equipment (ASAP 2020, Micromeritics). First, the  
 132 samples were outgassed at 110°C under secondary vacuum for at least 48h. The N<sub>2</sub> isotherms  
 133 were used to estimate the apparent surface area,  $A_{\text{BET}}$  (m<sup>2</sup> g<sup>-1</sup>), by applying the BET equation  
 134 in the adequate range of relative pressures ( $p/p_0$ ), and the total pore volume,  $V_{\text{T}}$  (cm<sup>3</sup> g<sup>-1</sup>), at  
 135  $p/p_0 = 0.97$ . The  $p/p_0$  range was chosen by plotting  $V_{\text{ads}} \times (1 - p/p_0)$  as a function of  $p/p_0$ ,  $V_{\text{ads}}$   
 136 being the STP adsorbed volume, and we took the range of values of  $p/p_0$  for which  $V_{\text{ads}} \times (1 -$   
 137  $p/p_0)$  increased with  $p/p_0$ . The micropore volume,  $V_{\text{DR}}$  (cm<sup>3</sup> g<sup>-1</sup>), was determined from the  
 138 application of the Dubinin-Radushkevich (DR) equation to the N<sub>2</sub> adsorption,  $V_{\text{DR,N}_2}$ , and to  
 139 the CO<sub>2</sub> adsorption isotherms,  $V_{\text{DR,CO}_2}$  (Dubinin, 1989). The mesopore volume,  $V_{\text{MESO}}$  (cm<sup>3</sup> g<sup>-</sup>  
 140 <sup>1</sup>), was calculated as the difference between  $V_{0.97}$  and  $V_{\text{DR,N}_2}$ . The average pore size,  $L_0$  (nm),  
 141 was calculated using the following equation:

$$142 \quad L_0(\text{nm}) = \frac{10.8}{E_0 - 11.4} \quad (2)$$

143 where  $E_0$  (kJ mol<sup>-1</sup>) is the characteristic adsorption energy derived from the application of the  
 144 DR method to the N<sub>2</sub> adsorption isotherms (Stoeckli et al., 2000). The 2D NLDFT-HS  
 145 method was applied to obtain the pore size distributions (PSD) from both the N<sub>2</sub> and CO<sub>2</sub>  
 146 adsorption isotherms. Surface areas,  $S_{\text{NLDFT}}$  (m<sup>2</sup> g<sup>-1</sup>), micropore volumes,  $V_{\mu, \text{NLDFT}}$  (cm<sup>3</sup> g<sup>-1</sup>),  
 147 and total pore volumes,  $V_{\text{T, NLDFT}}$  (cm<sup>3</sup> g<sup>-1</sup>), were also obtained from the PSDs.

148 The textural information was supplemented by mercury porosimetry (Autopore IV,  
 149 Micromeritics) to obtain macro and mesopore size distributions. The skeletal density of the  
 150 solids was obtained by helium pycnometry (AccuPyc II 1340, Micromeritics), using samples  
 151 previously degassed at 100°C under vacuum.



152 Given that the material yield is as important as the surface area, the total surface area,  
153  $A_{\text{TOTAL}}$  ( $\text{m}^2 \text{g}^{-1}$ ), can be used as a criterion for selecting materials for further testing (Acosta et  
154 al., 2016; Fierro et al., 2010). It reads:

$$155 \quad A_{\text{TOTAL}} = \frac{A_{\text{BET}} \times Y}{100} \quad (3)$$

156 The pH at the point of zero charge,  $pH_{\text{PZC}}$ , which is the pH where the net charge of the  
157 surface is zero, was determined according to Carrott et al. (Carrott et al., 2001). Briefly, 15  
158 mg of material was added to 15 mL of  $\text{NaNO}_3$  solution ( $0.1 \text{ mol L}^{-1}$ ), bubbled with  $\text{N}_2$  for 2  
159 min, sealed and placed in a stirrer. The initial pH of the solution was recorded, and, after 48h  
160 of stirring, the suspension was filtered and the equilibrium pH was measured.

161 The amount of proton-binding groups was also measured. For that purpose, 0.1g of  
162 activated carbon was suspended in 50 mL of  $\text{NaNO}_3$  solution ( $0.01 \text{ mol L}^{-1}$ ) as support  
163 electrolyte and was stirred overnight to equilibrate. The suspension was then titrated with  
164  $\text{NaOH}$  ( $0.1 \text{ mol L}^{-1}$ ) under saturation with  $\text{N}_2$  (Jagiello, 1994) using an automatic titrator (905  
165 Titrand, Metrohm controlled by Tiamo® V2.2 software). The titration curves, pH vs volume,  
166 were transformed to proton-binding isotherms,  $Q$  vs pH, using the proton balance equation.  
167 Here,  $Q$  is equal to the total amount of protonated sites on the material. The relationship  
168 between the experimental proton-binding isotherms and  $pK_a$  values is given by an integral  
169 equation (Jagiello et al., 1995). The integration of this function over finite intervals, arbitrarily  
170 defined, gives the amount of sites whose  $pK_a$  values belong to these intervals. For the  
171 evaluation of the unknown distribution,  $f(pK_a)$ , the numerical SAIEUS-pK-Dist program was  
172 used.

173

174

## 175 2.3 Paracetamol adsorption studies

### 176 2.3.1 Kinetic studies

177 The materials were tested as paracetamol adsorbents in liquid phase. A paracetamol stock  
178 solution of concentration  $180 \text{ mg L}^{-1}$  was prepared without adjusting the initial pH, which was  
179 equal to 6. 98% pure paracetamol (Acros Organics) was used. The 2D and 3D structures of  
180 paracetamol are shown in Figure SI 2.

181 For kinetic studies, 15 mg of carbon and 15 mL of paracetamol solution were mixed in a  
182 glass flask that was introduced into a water bath at  $30^\circ\text{C}$  and stirred at 500 rpm in a 15-  
183 position stirring plate (Mutistirrer 15, VELP Scientifica). After the desired contact time, an  
184 aliquot was removed and the amount of paracetamol remaining in the solution was  
185 determined by UV spectroscopy at 243 nm (Lambda 35 UV/VIS Spectrometer, Perkin  
186 Elmer). All tests have been carried out in duplicate. The effect of the initial paracetamol  
187 concentration, 10, 20 and  $40 \text{ mg L}^{-1}$  was studied.

188 The paracetamol uptake was calculated according to the following equation:

$$189 \quad q_t = \frac{(C_0 - C_t)}{W} V \quad (4)$$

190 where  $q_t$  ( $\text{mg g}^{-1}$ ) is the amount of paracetamol removed at time  $t$ ,  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial  
191 concentration of paracetamol,  $C_t$  ( $\text{mg L}^{-1}$ ) is the concentration of paracetamol at time  $t$ ,  $V$  (L)  
192 is the volume of the solution and  $W$  (g) is the weight of dry carbon.

### 193 2.3.2 Kinetic modelling

194 Two different kinetics models were applied to describe the experimental data. The first was  
195 the pseudo-first order (PFO) kinetic model proposed by Lagergren (Lagergren, 1898),  
196 mathematically represented by equation (5):

$$197 \quad \frac{dq_t}{dt} = k_1(q_e - q_t) \quad (5)$$

198 where  $q_t$  and  $q_e$  are the adsorbed amounts ( $\text{mg g}^{-1}$ ) at time  $t$  and at equilibrium, respectively,  
199 and  $k_1$  ( $\text{min}^{-1}$ ) is the kinetic rate constant of pseudo-first order.

200 The second kinetic model applied was the pseudo-second order (PSO) kinetic model  
201 proposed by Ho and McKay (Ho and McKay, 1999), and mathematically represented by  
202 equation (6):

$$203 \quad \frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

204 where  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the pseudo-second order rate constant.

205 The product  $k_2 q_e^2$  represents the initial adsorption rate,  $h$ . The half-life time,  $t_{1/2}$ , which is  
206 the time required for the adsorbent to uptake half of the adsorbate at equilibrium and which is  
207 often used as a measure of adsorption rate was also calculated. For PFO kinetic model, it is  
208 calculated according to equation (7) and, it is calculated according to equation (8) for the  
209 PSO:

$$210 \quad t_{1/2} = \frac{\ln 2}{k_1} \quad (7)$$

$$211 \quad t_{1/2} = \frac{1}{k_2 q_e} \quad (8)$$

### 212 *2.3.3 Equilibrium tests*

213 Adsorption studies at equilibrium were carried out at 20, 30 and 40°C by varying the  
214 paracetamol concentration ( $5 - 180 \text{ mg L}^{-1}$ ) for the materials CV and CV15. After 5 days and  
215 24h of stirring, respectively, to guarantee equilibrium, the sample suspensions were filtered  
216 and diluted if necessary. Then, the concentration of paracetamol remaining in solution at  
217 equilibrium ( $C_e$ ) was determined, and the corresponding uptake ( $q_e$ ) was calculated using  
218 equation (4). Experiments were done in duplicate.

219 The isotherms were modelled with the Langmuir, Freundlich and Sips equations (9), (10)  
220 and (11), respectively:

221 
$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (9)$$

222 where  $q_e$  and  $C_e$  have the same meaning as before,  $K_L$  ( $\text{L mg}^{-1}$ ) is the Langmuir constant, and  
 223  $q_m$  ( $\text{mg g}^{-1}$ ) is the monolayer adsorption capacity.

224 
$$q_e = K_F (C_e)^{1/n} \quad (10)$$

225 where  $K_F$  ( $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ ) is the Freundlich constant and  $n$  (dimensionless) is the Freundlich  
 226 exponent.

227 
$$q_e = \frac{q_m (K_S C_e)^{1/n_S}}{1 + (K_S C_e)^{1/n_S}} \quad (11)$$

228 where  $K_S$  ( $\text{L mg}^{-1}$ ) is the Sips constant, and  $n_S$  (dimensionless) is the heterogeneity factor.

229 The BET liquid adsorption equilibrium model was also fitted to the experimental data,  
 230 since this model considers the possibility of multilayer adsorption. The model is  
 231 mathematically represented by equation (12).

232 
$$q_e = \frac{q_m K_{BET} C_e}{(C_S - C_e) [1 + (K_{BET} - 1) \frac{C_e}{C_S}]} \quad (12)$$

233 where  $K_{BET}$  ( $\text{L mg}^{-1}$ ) is the BET constant, and  $C_s$  ( $\text{mg g}^{-1}$ ) is the saturation concentration of  
 234 paracetamol in water.

#### 235 *2.3.4 Parameter estimation*

236 All the parameters were estimated using as an objective function the sum of the square of  
 237 errors, obtained through equation (13):

238 
$$F_{OBJ} = \sum_{i=1}^{n_{dat}} (Y_{i,exp} - Y_{i,mod})^2 \quad (13)$$

239 where  $F_{OBJ}$  is the objective function value,  $n_{dat}$  is the number of experimental points and  $Y_{i,exp}$   
 240 and  $Y_{i,mod}$  are respectively the experimental and predicted value for the experimental point  $i$ .

241 The method of Nelder and Mead was applied to such optimisation, using the mathematic  
242 software Maple®.

### 243 3. Results and discussion

#### 244 3.1. Characterization of the carbon materials

##### 245 3.1.1 Calorific value and elemental composition

246 The average heat of combustion of CV (27.3 MJ kg<sup>-1</sup>) was higher than that of wood (17.8  
247 MJ kg<sup>-1</sup>). These calorific values are consistent with what has been reported in the literature for  
248 different species of Eucalyptus (Gaqa et al., 2014; Heidari et al., 2014; Khider and Elsaki,  
249 2012; Kumar et al., 2010) and are slightly lower than for Eucalyptus-derived chars produced  
250 by fast pyrolysis using a pilot-scale fluidised bed reactor (Heidari et al., 2014). These trends  
251 have also been reported for other agroforestry tree crops (Fuwape, 1993; Khider and Elsaki,  
252 2012) and for other types of biomass such as corn crop residues (Mullen et al., 2010). The  
253 calorific value obtained here indicates that CV can be potentially used as fuel.

254 Table 1 presents the elemental analysis of the different materials studied. The carbon  
255 content in the original sample (CV) was 81.8 wt. % and it slightly decreased after  
256 carbonisation at 900°C to 80.6 wt. %. Activation with CO<sub>2</sub> further decreased the carbon  
257 content due to evolution of volatiles and enrichment in ashes of the activated carbons. Thus,  
258 the ash content of the CV sample was 4.4 wt. %, and increased up to 10.7 wt. % after  
259 carbonisation at 900°C and even to 46.4 wt. % after CO<sub>2</sub> activation for 60 min. The hydrogen  
260 and nitrogen contents were low, and there was no significant difference between the materials.

261 **Table 1.** Elemental composition (wt. %), yield  $Y$  (%) and  $pH_{PZC}$  of the materials.

Sample	C	H	N	O	S	Ash*	Y (%)	$pH_{PZC}$
CV	81.8	1.8	0.4	11.6	0.0	4.4	100	8.3
CV0	80.6	0.8	0.4	7.5	0.0	10.7	81.7	10.3

<b>CV15</b>	80.5	0.8	0.5	7.2	0.0	11.0	61.4	11.3
<b>CV30</b>	74.9	0.9	0.7	9.3	0.0	14.3	41.1	11.7
<b>CV60</b>	40.2	1.4	0.5	11.5	0.1	46.4	10.8	-

262 \* Calculated as 100 – all other element weight fractions.

263 The SEM images in Figure 1a show that the wood structure was preserved after  
264 carbonisation and activation, and an increase in the ash content can be observed with  
265 activation, see Figure 1b. Thus, CV60 contained nearly 50 wt .% of ashes, clearly seen in the  
266 photo. A basic characterisation of this material was done just to illustrate trends, but no  
267 further paracetamol adsorption tests was performed on it. EDX analysis allowed to identifying  
268 and mapping inorganic components in the ashes, see Figure 1c. Among these, calcium was  
269 the major element identified ranging from 6 wt. % in CV to 30 wt. % in CV30. Mg, K, Fe and  
270 Al contents ranged between 2 wt. % and 6 wt. %, with no clear trend. Other elements such as  
271 Si, P, Na, Cu and Mn were identified but at lower percentages (<1 wt. %). These results are  
272 consistent with already reported ash composition of Eucalyptus wood (Girón et al., 2012;  
273 Khanna et al., 1994).

274 Figure 1

### 275 3.1.2 Textural properties

276 Figure 2a shows the N<sub>2</sub> adsorption/desorption isotherms of the materials. The original  
277 sample (CV) presents, according to the IUPAC classification, a type I isotherm with a marked  
278 knee in the region of low relative pressure and a slight slope at higher relative pressures  
279 (Thommes et al., 2015). This is characteristic of essentially microporous materials with a  
280 narrow micropore size distribution and an absence of significant mesoporosity, as also shown  
281 by the PSD (Figure 2d). The longer the activation time, the wider the knee and the higher the  
282 slope, indicating a widening of the micropore size distribution and the development of  
283 mesoporosity. The hysteresis loop appears and becomes more marked with the activation  
284 time, which is attributed to capillary condensation in the mesopores (Lin and Teng, 2002).

285

## Figure 2

286 It is well known that following the activation step, which is a controlled gasification of the  
287 carbon, part of the material is lost (called burn-off,  $BO (\%) = 100 - Y (\%)$ ). The extent of the  
288 activation influences the morphology and the textural properties of the activated carbons (Al  
289 Bahri et al., 2016). As shown in Table 1, the carbon yield decreased with the activation time:  
290 from 81.7% for the reference material (CV0) to 10.8% after 60 minutes of exposure to  $CO_2$ .  
291 Concerning the BET area ( $A_{BET}$ ), see Figure 3, activation with  $CO_2$  increased it from 392 to  
292  $845 \text{ m}^2 \text{ g}^{-1}$  from CV to CV30, respectively.  $CO_2$  developed the pore texture over the entire  
293 range of pore diameters, in particular the microporosity by opening closed pores as well as  
294 widening existing ones, in agreement with previous studies (Rodríguez-Reinoso et al., 1995).

295 The pore texture parameters of all carbon materials are presented in Figure 3 and in Table  
296 SI 4. By comparing CV to CV0,  $A_{BET}$  increased from 392 to  $498 \text{ m}^2 \text{ g}^{-1}$ , due to the usual  
297 volatile evolution when increasing the temperature from  $700^\circ\text{C}$  (typical Kon-Tiki charring  
298 temperature) to  $900^\circ\text{C}$ . The tars produced during pyrolysis at  $700^\circ\text{C}$  could partially block the  
299 micropores that would be opened at  $900^\circ\text{C}$  (Ibarra et al., 1991), as suggested by the values of  
300  $L_0$  that did not change when increasing the pyrolysis temperature from 700 to  $900^\circ\text{C}$  (i.e.,  
301 from CV to CV0, see Table SI 4).  $A_{BET}$  reached a maximum value of  $845 \text{ m}^2 \text{ g}^{-1}$  after 30 min  
302 of  $CO_2$  activation but decreased by around 10% when the activation time was 60 min (Figure  
303 3 and Table SI 4). Despite the fact that the ash-free fraction of CV60 may have a very high  
304 surface area, this material also has a high ash content and ashes do not have a significant  
305 surface area. Except for CV60, all the materials had higher  $V_{DR, CO_2}$  values than  $V_{DR, N_2}$ ,  
306 suggesting that a significant part of the microporosity was not accessible to  $N_2$  at the  
307 equilibrium times given for this analysis. This also means that, to give an accurate overview  
308 of the textural properties of the materials, both  $N_2$  and  $CO_2$  adsorption isotherms must be  
309 taken into account, as this has been shown in Figure 2c. Therefore,  $V_{DR, N_2}$ ,  $V_{DR, CO_2}$  and  $V_{0.97}$

310 are given for comparison with textural data reported in the open literature, but  $V_{\mu, \text{NLDFT}}$  and  
311  $V_{\text{T, NLDFT}}$  give a more precise indication of the microporosity and total porosity, respectively  
312 (see Figure SI 3 and Table SI 4).

313 Figure 3 shows the evolution of the  $A_{\text{BET}}$ ,  $A_{\text{TOTAL}}$ ,  $S_{\text{NLDFT}}$ , the total and micropore volume  
314 and the average pore size with the burn-off (BO, wt. %). While  $A_{\text{BET}}$  and  $S_{\text{NLDFT}}$  showed a  
315 marked increase from 392 to 845  $\text{m}^2 \text{g}^{-1}$  and from 600 to 1000  $\text{m}^2 \text{g}^{-1}$  at 30 min of activation  
316 (58.9 % BO), respectively,  $A_{\text{TOTAL}}$  only slightly increased from 392 to 415  $\text{m}^2 \text{g}^{-1}$  at 15 min of  
317 activation (39.6% BO) and markedly decreased afterwards. The microporosity fraction  
318 decreased with the increase in the burn-off. Based on previous studies (Acosta et al., 2016;  
319 Basta et al., 2009; Selmi et al., 2018), we selected CV15 for further paracetamol adsorption  
320 studies because a good compromise between  $A_{\text{BET}}$  and  $Y$  was reached.

321 Figure 3

322  
323 Figure 2d shows that CV presented a bimodal PSD, with a narrow peak centred at 0.4 nm  
324 and some pores with a diameter of 0.75 nm. The PSD widened with the activation time up to  
325 CV30 at the same time as the pores narrower than 1 nm increased. CV60 showed a  
326 continuous PSD with an enlargement of the pore size. Besides, mercury porosimetry suggests  
327 a higher volume of mesopores in the activated carbons (Figure 4).

328 Figure 4

329 Figure 4 shows the PSD in the mesopore (2-50 nm) and macropore (> 50 nm) ranges.  
330 However, the equipment used for mercury intrusion, with a maximum intrusion pressure of  
331 414 MPa, only allows access to pores with diameters greater than 3.6 nm. CV and CV0  
332 showed very similar PSDs, but the amount of pores narrower than 100 nm decreased  
333 compared to those of larger diameter, in agreement with the higher ash content of ACs



334 produced at longer activation times. The bulk density of the materials calculated at a mercury  
335 intrusion pressure of 0.0036 MPa decreased from 0.21 g cm<sup>-3</sup> for CV to 0.16 g cm<sup>-3</sup> for CV60,  
336 which suggests the increase of porosity of the materials with the activation time, not only in  
337 the micropore range already evidenced by N<sub>2</sub> + CO<sub>2</sub> adsorption, but also in the mesopore and  
338 macropore ranges.

### 339 3.1.3 Surface chemistry

340 With respect to surface chemistry, the values of  $pH_{PZC}$  shown in Table 1 suggest that CV  
341 and derived ACs have a basic nature. Although the ash contents were only quantified for raw  
342 eucalyptus biomass and CV, a simple visual analysis of Figure 1b and the estimation  
343 presented from the elemental analysis revealed that ashes became noticeable as the activation  
344 time increased, and were evident in CV60. Then, a basic nature of the ACs was expected and  
345 it should be greatly influenced by the ash content.

346 A more detailed analysis was performed on samples CV and CV15 to study the  
347 modification of surface functionalities with the activation process. Figure 5 shows the results  
348 of the potentiometric titration of these materials. Activation increased the density of  
349 functional groups from 0.63 to 1.04 mmol g<sup>-1</sup> (see Table 2). The number of peaks,  
350 representing different types of functional groups, was 4 and 5 for CV and CV15, respectively.  
351 The  $pK_a$  distributions showed the predominance of strongly basic species such as lactol- or  
352 hydroxyl-containing functional groups with  $pK_a > 8$  (Seredych et al., 2015). The basicity of  
353 CV and CV15 materials was confirmed by the high value of  $pH_{PZC}$ , around 8 and 11,  
354 respectively (see again Table 1).

355 Figure 5

356 **Table 2.** Results of potentiometric titration measurements: peak position and number of types  
357 of functional groups (mmol/g, in brackets); the  $pH_{PZC}$  is also recalled.

Samples	$pK_a$ 3-5	$pK_a$ 5-7	$pK_a$ 7-8	$pK_a$ 8-10	$pK_a$ 10-12	All (mmol g <sup>-1</sup> )	pH <sub>PZC</sub>
CV	3.79 (0.02)	5.35 (0.05)	-	8.16 (0.09)	11.33 (0.46)	0.63	8.3
CV15	4.41 (0.08)	6.21 (0.04)	7.78 (0.19)	9.63 (0.22)	10.91 (0.51)	1.04	11.3

358 This analysis is relevant given that changes in the surface chemistry of activated carbons  
359 can also affect the adsorption process of pollutants by dissociation of functional groups on the  
360 adsorbent surface (Ruiz et al., 2010).

### 361 3.2 Removal of paracetamol in the liquid phase

#### 362 3.2.1 Paracetamol adsorption kinetics

363 Figure 6 shows the kinetics of paracetamol adsorption at 30°C on CV, CV0, CV15 and  
364 CV30 for initial paracetamol concentrations of 10, 20 and 40 mg L<sup>-1</sup>. While CV took almost 3  
365 days to equilibrate, CV15 and CV30 reached equilibrium in 1h at  $C_0 = 10$  mg L<sup>-1</sup> and 5 h at  
366  $C_0 = 40$  mg L<sup>-1</sup>. CV0 reached equilibrium in about 5h at  $C_0 = 10$  mg L<sup>-1</sup> and 12h at  $C_0 = 40$   
367 mg L<sup>-1</sup>. For the three ACs (CV0, CV15 and CV30), the removal of paracetamol at equilibrium  
368 was complete for the three concentrations tested. The experimental kinetic data were best  
369 fitted by the pseudo-second order kinetic model.

370 Figure 6

371 Table SI 5 shows the kinetic parameters derived from the application of PFO and PSO  
372 models, and the corresponding determination coefficients  $R^2$ . For the three concentrations of  
373 paracetamol tested, a longer activation time had a positive effect on the initial ( $h$ ) and global  
374 ( $k_1$  and  $k_2$ ) adsorption rates, and reduction of the adsorption half-time ( $t_{1/2}$ ), i.e., the time  
375 required to reach half of the paracetamol uptake at equilibrium. For example,  $t_{1/2}$  at the  
376 highest initial concentration (40 mg L<sup>-1</sup>) for CV15 and CV30 was 6 minutes while it was 282

377 min for CV. Then, it can be concluded that the adsorption process of paracetamol is faster  
378 with activation. Given the dimensions of the paracetamol molecule (0.46 nm and 0.66 nm for  
379 monomer and dimer, respectively), micropores are known to be the active sites with the  
380 highest adsorption potential for its removal from the liquid phase (Mestre et al., 2009). Thus,  
381 a higher volume of micro- and mesopores and a wider micropore size distribution should  
382 allow a faster diffusion of paracetamol molecules in the materials.

383 The initial concentration of paracetamol did not show a marked effect on the PFO constant.  
384 However, the parameter  $k_2$  decreased with the increase in  $C_0$ , in agreement with previous  
385 studies of adsorption of diuron (Al Bahri et al., 2016) or ibuprofen (Mestre et al., 2007).

386 Regarding the removal efficiency, there was no significant difference between the ACs for  
387 all the concentrations tested (removal between 96 and 99%). For low initial concentrations of  
388 paracetamol ( $10 \text{ mg L}^{-1}$ ), the CV removed as much paracetamol as ACs at equilibrium, but its  
389 performance decreased with the increase in  $C_0$ . This is an interesting result, given that this  
390 type of pollutant is present at low concentrations in the environment. Since the production of  
391 CV is an easy and reproducible process, which does not require any exceptional equipment, it  
392 is a promising material to continue exploring in difficult economic contexts.

### 393 *3.2.2 Paracetamol equilibrium adsorption studies*

394 The paracetamol adsorption isotherms displayed in Figure 7 suggest that the adsorption  
395 mechanisms of the original carbon (CV) and the activated carbon CV15 were the same, as  
396 both were type II (Brunauer et al., 1940). The isotherm obtained for CV15 has two defined  
397 regions: in the first, a steep initial rise that approaches a plateau is observed and, in the second  
398 region, an upward curvature is recorded for higher equilibrium paracetamol concentrations.  
399 The former phenomenon is related to the formation of a complete monolayer, while the latter  
400 is explained by multilayer or aggregate formation at the interface at high coverage (Girods et

401 al., 2009). The formation of multilayers could be related to the characteristics of the adsorbent  
402 surface and to the pH of the medium, which could affect the interactions between the solvent,  
403 the adsorbate and the adsorbent (Al Bahri et al., 2016). This type of isotherm has also been  
404 reported by Terzyk and Rychlicki (Terzyk and Rychlicki, 2000) for some chemically ACs  
405 when removing paracetamol at similar concentrations, but this is not the usual behaviour  
406 reported in the literature concerning paracetamol adsorption. However, it has been also  
407 observed for other pollutants such as phenol (Girods et al., 2009), cationic dyes (Cotoruelo et  
408 al., 2011) and diuron (Al Bahri et al., 2016). Figure 7a shows a higher paracetamol uptake at  
409 20°C compared to that determined at 30°C, which could be related to the experimental  
410 uncertainty (the error bars of the two temperatures indeed overlap), as well as to small uptake  
411 differences between these two fairly close temperatures.

412 Figure 7

413 Langmuir, Freundlich and Sips models were fitted to the data corresponding to CV and  
414 CV15 samples (see Table SI 6 and Figures SI 10 and SI 11). In addition, the Langmuir and  
415 Freundlich models were applied to the monolayer region only (see Table SI 7 and Figure SI  
416 8). This approach gave results different from those obtained when applied to the entire range  
417 of equilibrium experimental data. Since the isotherms were type II, multilayer adsorption may  
418 be better described by applying the BET equation in the liquid phase (Brunauer et al., 1938).  
419 Table SI 9 summarises the parameters derived from this model.

420 The monolayer adsorption capacities  $q_m$  derived from the application of the BET model  
421 were equal to the values obtained when the Langmuir model was applied to the monolayer  
422 region. The values obtained were in the range of 14.4 to 14.9 mg g<sup>-1</sup> and 88.1 to 98.2 mg g<sup>-1</sup>  
423 for CV and CV15, respectively. In addition, the ratios of the  $K_{BET}$  and  $C_s$  parameters were  
424 very close to the values of  $K_L$  of the monolayer region. This proximity of the parameters

425 means that at low concentration, the two models converge towards a very similar value of  
426 Henry's constant.

427 As far as the effect of temperature is concerned, there is no clear trend. The calculated  
428 parameters, such as the equilibrium constant  $K_L$  and the monolayer capacity  $q_m$  of the  
429 Langmuir equation, do not change gradually with increasing temperature. Contrasting results  
430 have been reported in literature. Consistent with our study, some authors ((Baccar et al., 2012)  
431 and (Mestre et al., 2007)) did not notice any effect of temperature on the removal of  
432 pharmaceutical products, among them ibuprofen and diclofenac. More specifically on  
433 paracetamol, while García-Mateos et al. (García-Mateos et al., 2015) reported an exothermic  
434 nature of the adsorption process (i.e., the uptake decreased with temperature), others ((Terzyk  
435 and Rychlicki, 2000) and (Cotoruelo et al., 2011)) observed an endothermic behaviour (i.e.,  
436 the uptake increased with temperature ). Moreover, Villaescusa et al. (Villaescusa et al., 2011)  
437 reported similar sorption capacity when the temperature was maintained in the range of 5–  
438 20°C, but a slight increase in sorption was observed when the temperature was increased to  
439 25–30°C.

### 440 *3.3 Comparison with data from the literature*

441 Figure 8 collects information related to paracetamol removal with different types of  
442 activated carbons and modified carbons reported in the literature (Cabrita et al., 2010;  
443 Cotoruelo et al., 2011; Galhetas et al., 2014a, 2014b; García-Mateos et al., 2015; Mestre et al.,  
444 2015) and in the present study. Comparison with the literature is sometimes difficult because  
445 experimental variables chosen for materials synthesis and removal assays differ considerably  
446 from one study to another. For instance, the paracetamol concentrations tested here are  
447 significantly lower, but more realistic, than those used in other articles, whereas they have a  
448 very high influence on the adsorption capacities obtained in this work.

449

## Figure 8

450 There is a trend ( $R^2 = 0.78$ ) that suggests that the higher the surface area, the higher the  
451 maximum paracetamol removal capacity ( $q_m$ ). As mentioned in many articles, surface  
452 chemistry also influences the removal capacity, and different activation processes and/or  
453 heteroatom doping can introduce changes in the surface functionalities of the ACs. Hence, the  
454 surface functional groups and the net surface charge might explain the variability remaining  
455 unexplained in the material performance.

456

### 457 **4. Conclusion**

458 Four microporous activated carbons were obtained from a biochar precursor, called CV,  
459 produced with Eucalyptus pruning residues charred in a simple and low-cost device, a Kon-  
460 Tiki kiln. Additional  $\text{CO}_2$  activation significantly enhanced the specific surface area, the total  
461 pore volume and the micropore volume.

462 The equilibrium paracetamol (PC) adsorption was reached at 5h for the activated carbons  
463 and at 3 days for their precursor at the highest initial paracetamol concentration tested, and a  
464 pseudo-second order model suitably fitted the experimental data. The textural characterisation  
465 suggested an opening and widening of micropores and a development of mesopores with  $\text{CO}_2$   
466 activation, which favoured the diffusion of paracetamol molecules in the material.

467 At low concentrations, which are the most realistic for this type of contaminants, CV had a  
468 very high removal efficiency, similar to those of the activated carbons tested ( $> 95\%$ ). A  
469 simple adjustment (i.e., an increase) in the solid / liquid ratio might be enough to reduce the  
470 time for the efficient treatment of water in vulnerable communities with such inexpensive  
471 carbon material.

472 Concerning paracetamol uptake at equilibrium, CV and CV15 showed a favourable  
473 adsorption and the corresponding isotherms suggested the formation of paracetamol  
474 multilayers. The equilibrium adsorption capacities of CV15, whether for monolayer or  
475 multilayer adsorption, were about 5 times higher than for CV. This has been attributed to the  
476 more developed textural properties of CV15.

477

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482

483 **References**

- 484 Acosta, R., Fierro, V., Martinez de Yuso, A., Nabarlatz, D., Celzard, A., 2016. Tetracycline  
485 adsorption onto activated carbons produced by KOH activation of tyre pyrolysis char.  
486 *Chemosphere* 149, 168–176. <https://doi.org/10.1016/j.chemosphere.2016.01.093>
- 487 Al Bahri, M., Calvo, L., Gilarranz, M.A., Rodriguez, J.J., 2016. Diuron Multilayer Adsorption  
488 on Activated Carbon from CO<sub>2</sub> Activation of Grape Seeds. *Chem. Eng. Commun.* 203,  
489 103–113. <https://doi.org/10.1080/00986445.2014.934447>
- 490 Baccar, R., Sarrà, M., Bouzid, J., Feki, M., Blánquez, P., 2012. Removal of pharmaceutical  
491 compounds by activated carbon prepared from agricultural by-product. *Chem. Eng. J.*  
492 211–212, 310–317. <https://doi.org/10.1016/j.cej.2012.09.099>
- 493 Basta, A.H., Fierro, V., El-Saied, H., Celzard, A., 2009. 2-Steps KOH activation of rice straw:  
494 An efficient method for preparing high-performance activated carbons. *Bioresour.*  
495 *Technol.* 100, 3941–3947. <https://doi.org/10.1016/j.biortech.2009.02.028>
- 496 Boudrahem, N., Delpeux-Ouldriane, S., Khenniche, L., Boudrahem, F., Aissani-Benissad, F.,  
497 Gineys, M., 2017. Single and mixture adsorption of clofibric acid, tetracycline and  
498 paracetamol onto Activated carbon developed from cotton cloth residue. *Process Saf.*  
499 *Environ. Prot.* 111, 544–559. <https://doi.org/10.1016/j.psep.2017.08.025>
- 500 Bound, J.P., Voulvoulis, N., 2006. Predicted and measured concentrations for selected  
501 pharmaceuticals in UK rivers: Implications for risk assessment. *Water Res.* 40, 2885–  
502 2892. <https://doi.org/10.1016/j.watres.2006.05.036>
- 503 Brunauer, S., Deming, L.S., Deming, W.E., Teller, E., 1940. On a Theory of the van der  
504 Waals Adsorption of Gases. *J. Am. Chem. Soc.* 62, 1723–1732.  
505 <https://doi.org/10.1021/ja01864a025>



506 Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of Gases in Multimolecular Layers.  
507 J. Am. Chem. Soc. 60, 309–319. <https://doi.org/10.1021/ja01269a023>

508 Cabrita, I., Ruiz, B., Mestre, A.S., Fonseca, I.M., Carvalho, A.P., Ania, C.O., 2010. Removal  
509 of an Analgesic Using Activated Carbons Prepared From. Chem. Eng. J. 163, 1–28.  
510 <https://doi.org/10.1016/j.cej.2010.07.058>

511 Carrott, P.J.M., Nabais, J.M.V., Ribeiro Carrott, M.M.L., Menéndez, J.A., 2001. Thermal  
512 treatments of activated carbon fibres using a microwave furnace. Microporous  
513 Mesoporous Mater. 47, 243–252. [https://doi.org/10.1016/S1387-1811\(01\)00384-5](https://doi.org/10.1016/S1387-1811(01)00384-5)

514 Cornelissen, G., Pandit, N.R., Taylor, P., Pandit, B.H., Sparrevik, M., Schmidt, H.P., 2016.  
515 Emissions and char quality of flame-curtain “Kon Tiki” kilns for farmer-scale  
516 charcoal/biochar production. PLoS One 11, 1–16.  
517 <https://doi.org/10.1371/journal.pone.0154617>

518 Correia, B., Freitas, R., Figueira, E., Soares, A.M.V.M., Nunes, B., 2016. Oxidative effects of  
519 the pharmaceutical drug paracetamol on the edible clam *Ruditapes philippinarum* under  
520 different salinities. Comp. Biochem. Physiol. Part - C Toxicol. Pharmacol. 179, 116–  
521 124. <https://doi.org/10.1016/j.cbpc.2015.09.006>

522 Cotoruelo, L.M., Marqués, M.D., Leiva, A., Rodríguez-Mirasol, J., Cordero, T., 2011.  
523 Adsorption of oxygen-containing aromatics used in petrochemical, pharmaceutical and  
524 food industries by means of lignin based active carbons. Adsorption 17, 539–550.  
525 <https://doi.org/10.1007/s10450-010-9319-x>

526 Daughton, C.G., Ternes, T.A., 1999. Pharmaceuticals and Personal Care Products in the  
527 Environment : Agents of Subtle Change? Environ. Health Perspect. 107, 907–938.

528 Dordio, A. V., Estêvão Candeias, A.J., Pinto, A.P., Teixeira da Costa, C., Palace Carvalho,

529 A.J., 2009. Preliminary media screening for application in the removal of clofibric acid,  
530 carbamazepine and ibuprofen by SSF-constructed wetlands. *Ecol. Eng.* 35, 290–302.  
531 <https://doi.org/10.1016/j.ecoleng.2008.02.014>

532 Dubinin, M.M., 1989. Fundamentals of the theory of adsorption in micropores of carbon  
533 adsorbents: Characteristics of their adsorption properties and microporous structures.  
534 *Carbon N. Y.* 27, 457–467. [https://doi.org/10.1016/0008-6223\(89\)90078-X](https://doi.org/10.1016/0008-6223(89)90078-X)

535 Fierro, V., Muñiz, G., Basta, A.H., El-Saied, H., Celzard, A., 2010. Rice straw as precursor of  
536 activated carbons: Activation with ortho-phosphoric acid. *J. Hazard. Mater.* 181, 27–34.  
537 <https://doi.org/10.1016/j.jhazmat.2010.04.062>

538 Fierro, V., Torné-Fernández, V., Celzard, A., 2006. Kraft lignin as a precursor for  
539 microporous activated carbons prepared by impregnation with ortho-phosphoric acid:  
540 Synthesis and textural characterisation. *Microporous Mesoporous Mater.* 92, 243–250.  
541 <https://doi.org/10.1016/j.micromeso.2006.01.013>

542 Fuwape, J.A., 1993. Charcoal and fuel value of agroforestry tree crops. *Agrofor. Syst.* 22,  
543 175–179. <https://doi.org/10.1007/BF00705232>

544 Galhetas, M., Mestre, A.S., Pinto, M.L., Gulyurtlu, I., Lopes, H., Carvalho, A.P., 2014a.  
545 Carbon-based materials prepared from pine gasification residues for acetaminophen  
546 adsorption. *Chem. Eng. J.* 240, 344–351. <https://doi.org/10.1016/j.cej.2013.11.067>

547 Galhetas, M., Mestre, A.S., Pinto, M.L., Gulyurtlu, I., Lopes, H., Carvalho, A.P., 2014b.  
548 Chars from gasification of coal and pine activated with K<sub>2</sub>CO<sub>3</sub>: Acetaminophen and  
549 caffeine adsorption from aqueous solutions. *J. Colloid Interface Sci.* 433, 94–103.  
550 <https://doi.org/10.1016/j.jcis.2014.06.043>

551 Gaqa, S., Mamphweli, S., Katwire, D., Meyer, E., 2014. The Properties and Suitability of

552 Various Biomass/Coal Blends for Co-Gasification Purposes. *J. Sustain. Bioenergy Syst.*  
553 04, 175–182. <https://doi.org/10.4236/jsbs.2014.43016>

554 García-Mateos, F.J., Ruiz-Rosas, R., Marqués, M.D., Cotoruelo, L.M., Rodríguez-Mirasol, J.,  
555 Cordero, T., 2015. Removal of paracetamol on biomass-derived activated carbon:  
556 Modeling the fixed bed breakthrough curves using batch adsorption experiments. *Chem.*  
557 *Eng. J.* 279, 18–30. <https://doi.org/10.1016/j.cej.2015.04.144>

558 Girods, P., Dufour, A., Fierro, V., Rogaume, Y., Rogaume, C., Zoulalian, A., Celzard, A.,  
559 2009. Activated carbons prepared from wood particleboard wastes: Characterisation and  
560 phenol adsorption capacities. *J. Hazard. Mater.* 166, 491–501.  
561 <https://doi.org/10.1016/j.jhazmat.2008.11.047>

562 Girón, R.P., Suárez-Ruiz, I., Ruiz, B., Fuente, E., Gil, R.R., 2012. Fly ash from the  
563 combustion of forest biomass (*Eucalyptus globulus* bark): Composition and  
564 physicochemical properties. *Energy and Fuels* 26, 1540–1556.  
565 <https://doi.org/10.1021/ef201503u>

566 Gros, M., Petrović, M., Barceló, D., 2006. Development of a multi-residue analytical  
567 methodology based on liquid chromatography-tandem mass spectrometry (LC-MS/MS)  
568 for screening and trace level determination of pharmaceuticals in surface and  
569 wastewaters. *Talanta* 70, 678–690. <https://doi.org/10.1016/j.talanta.2006.05.024>

570 Heidari, A., Stahl, R., Younesi, H., Rashidi, A., Troeger, N., Ghoreyshi, A.A., 2014. Effect of  
571 process conditions on product yield and composition of fast pyrolysis of *Eucalyptus*  
572 *grandis* in fluidized bed reactor. *J. Ind. Eng. Chem.* 20, 2594–2602.  
573 <https://doi.org/10.1016/j.jiec.2013.10.046>

574 Ho, Y.S., McKay, G., 1999. Pseudo-second order model for sorption processes. *Process*

575 Biochem. 34, 451–465.

576 Ibarra, J. V., Moliner, R., Palacios, J.M., 1991. Catalytic effects of zinc chloride in the  
577 pyrolysis of Spanish high sulphur coals. *Fuel* 70, 727–732.

578 Jagiello, J., 1994. Stable Numerical Solution of the Adsorption Integral Equation Using  
579 Splines. *Langmuir* 10, 2778–2785. <https://doi.org/10.1021/la00020a045>

580 Jagiello, J., Badosz, T., Putyera, K., Schwarz, J., 1995. Determination of Proton Affinity  
581 Distributions for Chemical Systems in Aqueous Environments Using a Stable Numerical  
582 Solution of the Adsorption Integral Equation. *J. Colloid Interface Sci.* 172, 341–346.  
583 <https://doi.org/https://doi.org/10.1006/jcis.1995.1262>

584 Khanna, P.K., Raison, R.J., Falkiner, R.A., 1994. Chemical properties of ash derived from  
585 Eucalyptus litter and its effects on forest soils. *For. Ecol. Manage.* 66, 107–125.  
586 [https://doi.org/10.1016/0378-1127\(94\)90151-1](https://doi.org/10.1016/0378-1127(94)90151-1)

587 Khider, T.O., Elsaki, O.T., 2012. Heat Value of Four Hardwood Species from. *J. For. Prod.*  
588 *Ind.* 1, 5–9.

589 Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B.,  
590 Buxton, H.T., 2002. Pharmaceuticals, hormones, and other organic wastewater  
591 contaminants in U.S. streams, 1999-2000: A national reconnaissance. *Environ. Sci.*  
592 *Technol.* 36, 1202–1211. <https://doi.org/10.1021/es011055j>

593 Kumar, R., Pandey, K.K., Chandrashekar, N., Mohan, S., 2010. Effect of tree-age on calorific  
594 value and other fuel properties of Eucalyptus hybrid. *J. For. Res.* 21, 514–516.  
595 <https://doi.org/10.1007/s11676-010-0108-x>

596 Lagergren, S., 1898. Zur theorie der sogenannten adsorption gelöster stoffe, *Kungliga*

597 Svenska Vetenskapsakademiens. Handlingar 24, 1–39.

598 Lin, Y.R., Teng, H., 2002. Mesoporous carbons from waste tire char and their application in  
599 wastewater discoloration. *Microporous Mesoporous Mater.* 54, 167–174.  
600 [https://doi.org/10.1016/S1387-1811\(02\)00380-3](https://doi.org/10.1016/S1387-1811(02)00380-3)

601 Lladó, J., Lao-Luque, C., Ruiz, B., Fuente, E., Solé-Sardans, M., Dorado, A.D., 2015. Role of  
602 activated carbon properties in atrazine and paracetamol adsorption equilibrium and  
603 kinetics. *Process Saf. Environ. Prot.* 95, 51–59.  
604 <https://doi.org/10.1016/j.psep.2015.02.013>

605 Marques, S.C.R., Marcuzzo, J.M., Baldan, M.R., Mestre, A.S., Carvalho, A.P., 2017.  
606 Pharmaceuticals removal by activated carbons: Role of morphology on cyclic thermal  
607 regeneration. *Chem. Eng. J.* 321, 233–244. <https://doi.org/10.1016/j.cej.2017.03.101>

608 Mestre, A.S., Bexiga, A.S., Proença, M., Andrade, M., Pinto, M.L., Matos, I., Fonseca, I.M.,  
609 Carvalho, A.P., 2011. Activated carbons from sisal waste by chemical activation with K  
610 2CO 3: Kinetics of paracetamol and ibuprofen removal from aqueous solution.  
611 *Bioresour. Technol.* 102, 8253–8260. <https://doi.org/10.1016/j.biortech.2011.06.024>

612 Mestre, A.S., Pires, J., Nogueira, J.M.F., Carvalho, A.P., 2007. Activated carbons for the  
613 adsorption of ibuprofen. *Carbon N. Y.* 45, 1979–1988.  
614 <https://doi.org/10.1016/j.carbon.2007.06.005>

615 Mestre, A.S., Pires, J., Nogueira, J.M.F., Parra, J.B., Carvalho, A.P., Ania, C.O., 2009. Waste-  
616 derived activated carbons for removal of ibuprofen from solution: Role of surface  
617 chemistry and pore structure. *Bioresour. Technol.* 100, 1720–1726.  
618 <https://doi.org/10.1016/j.biortech.2008.09.039>

619 Mestre, A.S., Tyszko, E., Andrade, M.A., Galhetas, M., Freire, C., Carvalho, A.P., 2015.

620 Sustainable activated carbons prepared from a sucrose-derived hydrochar: Remarkable  
621 adsorbents for pharmaceutical compounds. *RSC Adv.* 5, 19696–19707.  
622 <https://doi.org/10.1039/c4ra14495c>

623 Mullen, C.A., Boateng, A.A., Goldberg, N.M., Lima, I.M., Laird, D.A., Hicks, K.B., 2010.  
624 Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis. *Biomass*  
625 *and Bioenergy* 34, 67–74. <https://doi.org/10.1016/j.biombioe.2009.09.012>

626 Pandit, N.R., Mulder, J., Hale, S.E., Schmidt, H.P., Cornelissen, G., 2017. Biochar from “Kon  
627 Tiki” flame curtain and other kilns: Effects of nutrient enrichment and kiln type on crop  
628 yield and soil chemistry. *PLoS One* 12, 1–12.  
629 <https://doi.org/10.1371/journal.pone.0176378>

630 Rodríguez-Reinoso, F., Molina-Sabio, M., González, M.T., 1995. The use of steam and CO<sub>2</sub>  
631 as activating agents in the preparation of activated carbons. *Carbon N. Y.* 33, 15–23.  
632 [https://doi.org/10.1016/0008-6223\(94\)00100-E](https://doi.org/10.1016/0008-6223(94)00100-E)

633 Ruiz, B., Cabrita, I., Mestre, A.S., Parra, J.B., Pires, J., Carvalho, A.P., Ania, C.O., 2010.  
634 Surface heterogeneity effects of activated carbons on the kinetics of paracetamol removal  
635 from aqueous solution. *Appl. Surf. Sci.* 256, 5171–5175.  
636 <https://doi.org/10.1016/j.apsusc.2009.12.086>

637 Schaefer, S., Fierro, V., Izquierdo, M.T., Celzard, A., 2016. Assessment of hydrogen storage  
638 in activated carbons produced from hydrothermally treated organic materials. *Int. J.*  
639 *Hydrogen Energy* 41, 12146–12156. <https://doi.org/10.1016/j.ijhydene.2016.05.086>

640 Schmidt, H.-P., Taylor, P., 2014. Kon-Tiki - the democratization of biochar production  
641 [WWW Document]. *Biochar J.*

642 Selmi, T., Sanchez-Sanchez, A., Gadonneix, P., Jagiello, J., Seffen, M., Sammouda, H.,

643 Celzard, A., Fierro, V., 2018. Tetracycline removal with activated carbons produced by  
644 hydrothermal carbonisation of *Agave americana* fibres and mimosa tannin. *Ind. Crops*  
645 *Prod.* 115, 146–157. <https://doi.org/10.1016/j.indcrop.2018.02.005>

646 Seredych, M., Biggs, M.J., Bandosz, T.J., 2015. Oxygen reduction on chemically  
647 heterogeneous iron-containing nanoporous carbon: The effects of specific surface  
648 functionalities. *Microporous Mesoporous Mater.* 221, 137–149.  
649 <https://doi.org/10.1016/j.micromeso.2015.09.032>

650 Spessato, L., Cazetta, A.L., Melo, S., Pezoti, O., Tami, J., Ronix, A., Fonseca, J.M., Martins,  
651 A.F., Silva, T.L., Almeida, V.C., 2020. Synthesis of superparamagnetic activated carbon  
652 for paracetamol removal from aqueous solution. *J. Mol. Liq.* 300.  
653 <https://doi.org/10.1016/j.molliq.2019.112282>

654 Stoeckli, F., Guillot, A., Hugli-Cleary, D., Slassi, A.M., 2000. Pore size distributions of active  
655 carbons assessed by different techniques. *Carbon N. Y.* 38, 938–941.  
656 [https://doi.org/10.1016/s0008-6223\(00\)00057-9](https://doi.org/10.1016/s0008-6223(00)00057-9)

657 Szczurek, A., Amaral-Labat, G., Fierro, V., Pizzi, A., Celzard, A., 2014. Chemical activation  
658 of tannin-based hydrogels by soaking in KOH and NaOH solutions. *Microporous*  
659 *Mesoporous Mater.* 196, 8–17. <https://doi.org/10.1016/j.micromeso.2014.04.051>

660 Terzyk, A.P., 2001. The influence of activated carbon surface chemical composition on the  
661 adsorption of acetaminophen (paracetamol) in vitro. Part II. TG, FTIR, and XPS analysis  
662 of carbons and the temperature dependence of adsorption kinetics at the neutral pH.  
663 *Colloids Surfaces A Physicochem. Eng. Asp.* 177, 23–45. [https://doi.org/10.1016/S0927-](https://doi.org/10.1016/S0927-7757(00)00594-X)  
664 [7757\(00\)00594-X](https://doi.org/10.1016/S0927-7757(00)00594-X)

665 Terzyk, A.P., Rychlicki, G., 2000. The influence of activated carbon surface chemical

666 composition on the adsorption of acetaminophen (paracetamol) in vitro: The temperature  
667 dependence of adsorption at the neutral pH. *Colloids Surfaces A Physicochem. Eng.*  
668 *Asp.* 163, 135–150. [https://doi.org/10.1016/S0927-7757\(99\)00298-8](https://doi.org/10.1016/S0927-7757(99)00298-8)

669 Terzyk, A.P., Rychlicki, G., Biniak, S., Łukaszewicz, J.P., 2003. New correlations between  
670 the composition of the surface layer of carbon and its physicochemical properties  
671 exposed while paracetamol is adsorbed at different temperatures and pH. *J. Colloid*  
672 *Interface Sci.* 257, 13–30. [https://doi.org/10.1016/S0021-9797\(02\)00032-2](https://doi.org/10.1016/S0021-9797(02)00032-2)

673 Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J.P., Rodriguez-Reinoso, F., Rouquerol,  
674 J., Sing, K.S.W., 2015. Physisorption of gases, with special reference to the evaluation of  
675 surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* 87,  
676 1051–1069. <https://doi.org/10.1515/pac-2014-1117>

677 Villaescusa, I., Fiol, N., Poch, J., Bianchi, A., Bazzicalupi, C., 2011. Mechanism of  
678 paracetamol removal by vegetable wastes: The contribution of  $\pi$ - $\pi$  interactions,  
679 hydrogen bonding and hydrophobic effect. *Desalination* 270, 135–142.  
680 <https://doi.org/10.1016/j.desal.2010.11.037>

681 WHO, 2004. *Guidelines for Drinking-water Quality*, 3rd ed. WHO, Geneva.

682 Wiegel, S., Aulinger, A., Brockmeyer, R., Harms, H., Löffler, J., Reincke, H., Schmidt, R.,  
683 Stachel, B., Von Tümpling, W., Wanke, A., 2004. Pharmaceuticals in the river Elbe and  
684 its tributaries. *Chemosphere* 57, 107–126.  
685 <https://doi.org/10.1016/j.chemosphere.2004.05.017>

686 Wu, S., Zhang, L., Chen, J., 2012. Paracetamol in the environment and its degradation by  
687 microorganisms. *Appl. Microbiol. Biotechnol.* 96, 875–884.  
688 <https://doi.org/10.1007/s00253-012-4414-4>



689 Zhang, T., Walawender, W.P., Fan, L.T., Fan, M., Daugaard, D., Brown, R.C., 2004.  
690 Preparation of activated carbon from forest and agricultural residues through CO<sub>2</sub>  
691 activation. Chem. Eng. J. 105, 53–59. <https://doi.org/10.1016/j.cej.2004.06.011>  
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693 **Captions of the Figures**

694 **Figure 1.** (a) SEM images of CV (500 ×, left) and CV30 (200 ×, right); (b) Photos of the  
695 samples showing the increase in ash content with activation time; (c) Elemental mapping by  
696 SEM-EDX of samples CV, CV0 and CV30.

697 **Figure 2.** Adsorption-desorption isotherms of (a) N<sub>2</sub> at -196°C and (b) CO<sub>2</sub> at 0°C; (c) fits of  
698 the isotherms by the NLDFT for CV30; and (d) corresponding pore size distributions.

699 **Figure 3.** Changes of pore texture parameters as function of the burn-off: (a) surface areas  
700  $A_{\text{BET}}$ ,  $A_{\text{TOTAL}}$ , and  $S_{\text{NLDFT}}$ ; and (b) pore volumes (total and micropore) and average pore sizes.

701 **Figure 4.** Pore size distribution in the ranges of mesopores and macropores obtained by  
702 mercury intrusion: (a) differential; and (b) cumulative Hg intrusion volumes.

703 **Figure 5.** Distribution of functional groups as a function of  $pK_a$ , for CV (blue) and CV15  
704 (light brown) samples.

705 **Figure 6.** Fits of the PFO and PSO models to the experimental data of paracetamol adsorption  
706 kinetics on CV, CV0, CV15 and CV30 at 30°C, with three different paracetamol initial  
707 concentrations (10, 20 and 40 mg L<sup>-1</sup>).

708 **Figure 7.** Experimental paracetamol adsorption isotherms at 20°C (red), 30°C (blue) and  
709 40°C (green) for: (a) CV; and (b) CV15 samples. The symbols correspond to experimental  
710 data whereas the lines represent the fits using the BET isotherm model.

711 **Figure 8.** Maximum paracetamol adsorption capacities of activated carbons (obtained in  
712 similar experimental conditions) as a function of their BET surface area (1- Mestre et al,  
713 2015; 2- Galhetas et al, 2014a; 3- Galhetas et al, 2014b; 4- Cotoruelo et al, 2011; 5- Cabrita et  
714 al, 2010; 6- Spessato et al., 2020; 7- Lladó et al., 2015 and 8- Marques et al., 2017).

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717 **Paracetamol removal by Kon-Tiki kiln-derived biochar and activated carbons**

718 Bursztyn Fuentes et al.

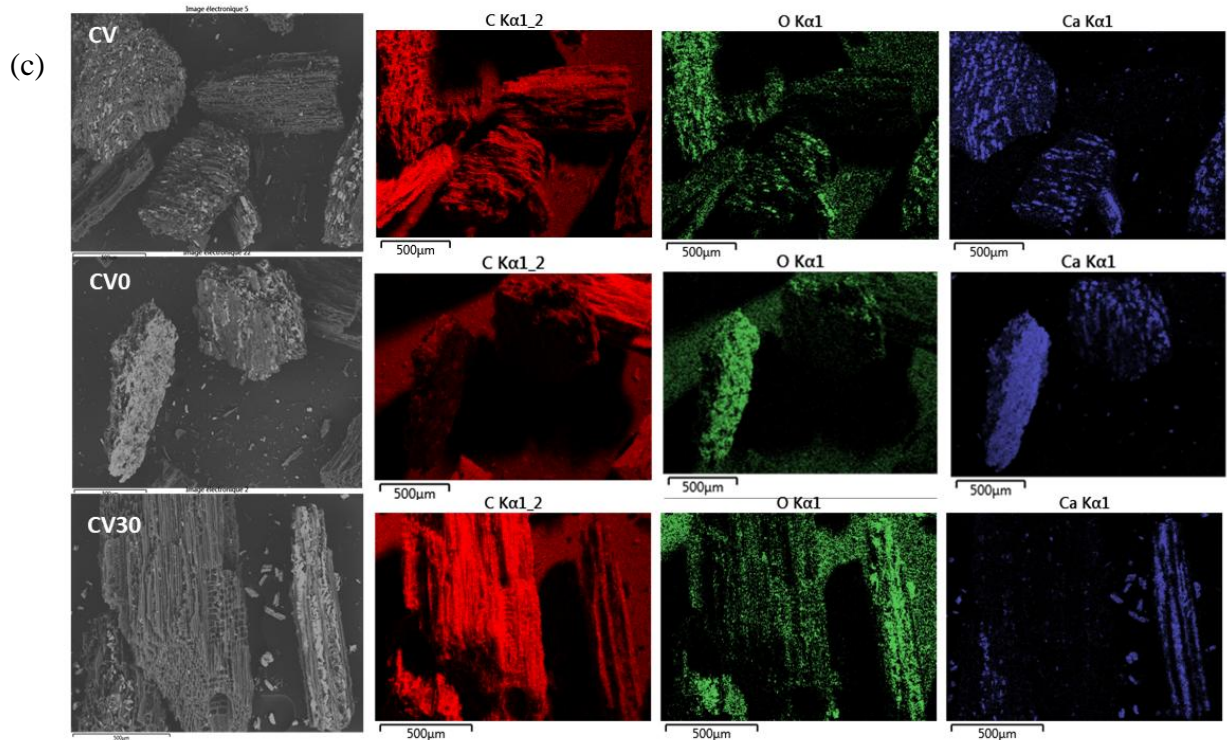
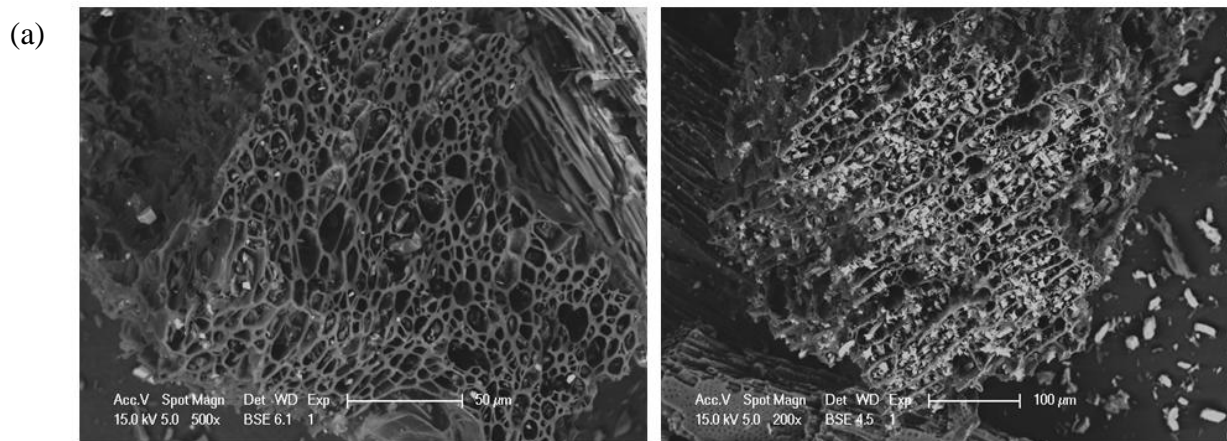
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Figure 1



726 **Paracetamol removal by Kon-Tiki kiln-derived biochar and activated carbons**

727 Bursztyn Fuentes et al.

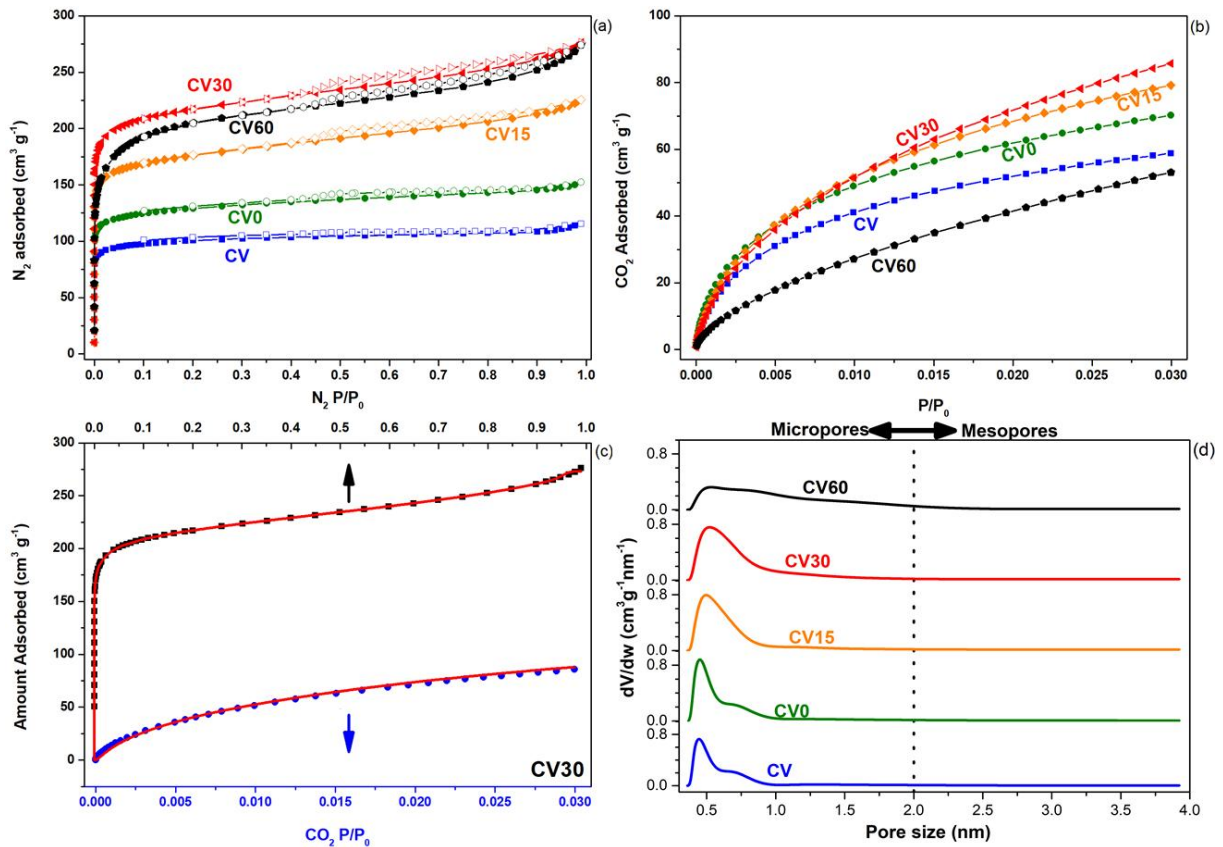
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Figure 2



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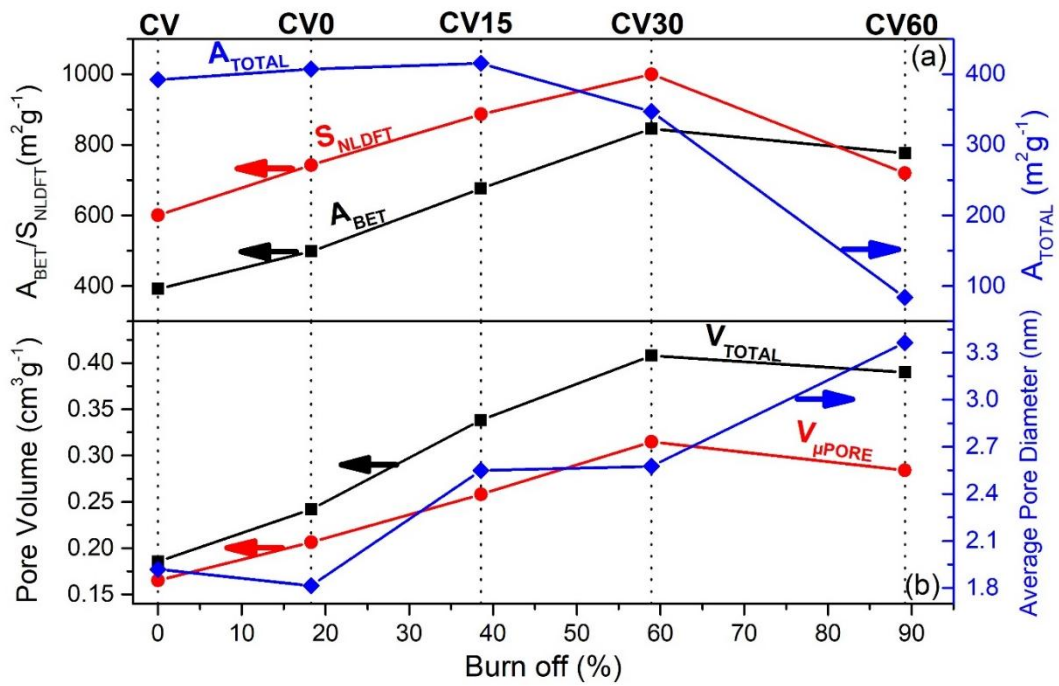
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Figure 3



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757 Bursztyn Fuentes et al.

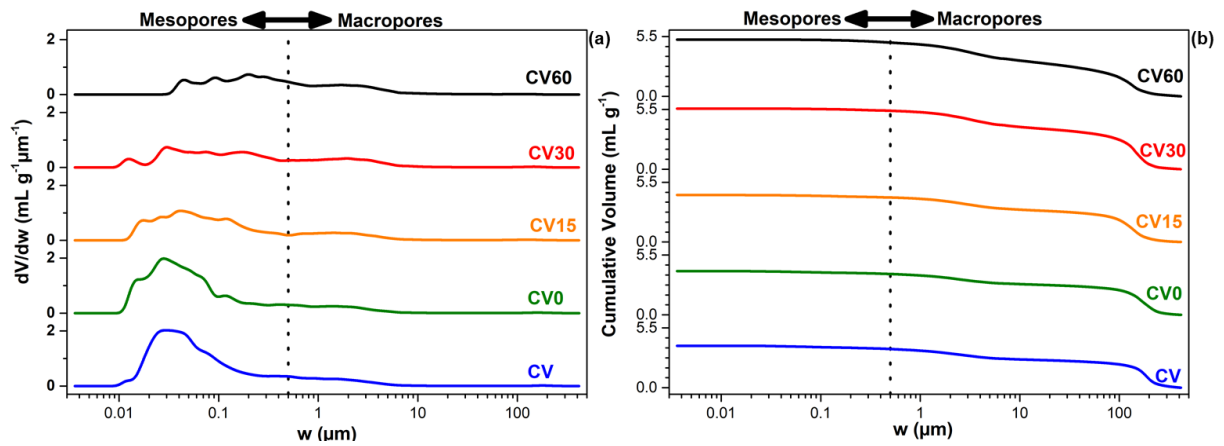
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Figure 4



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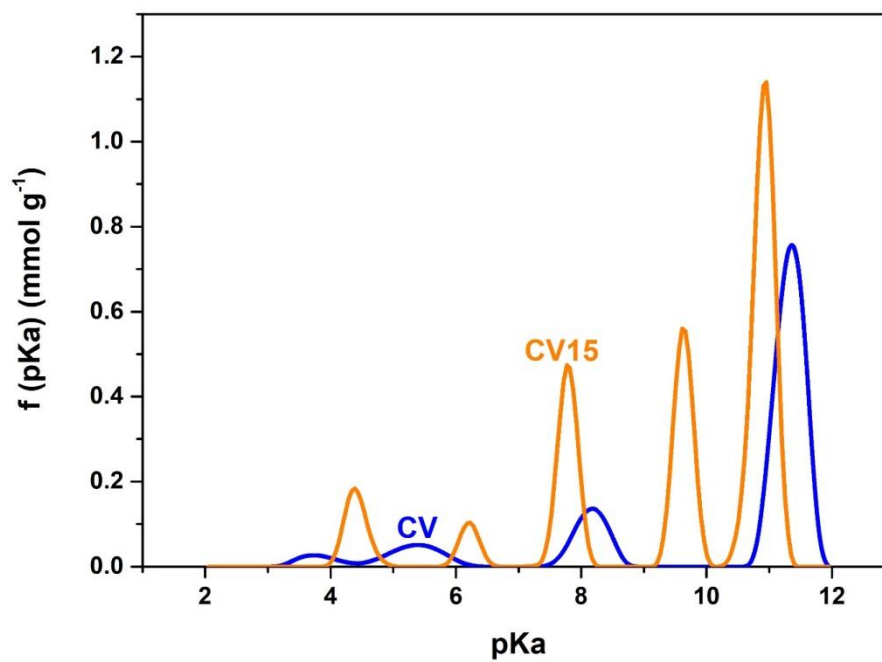
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Figure 5



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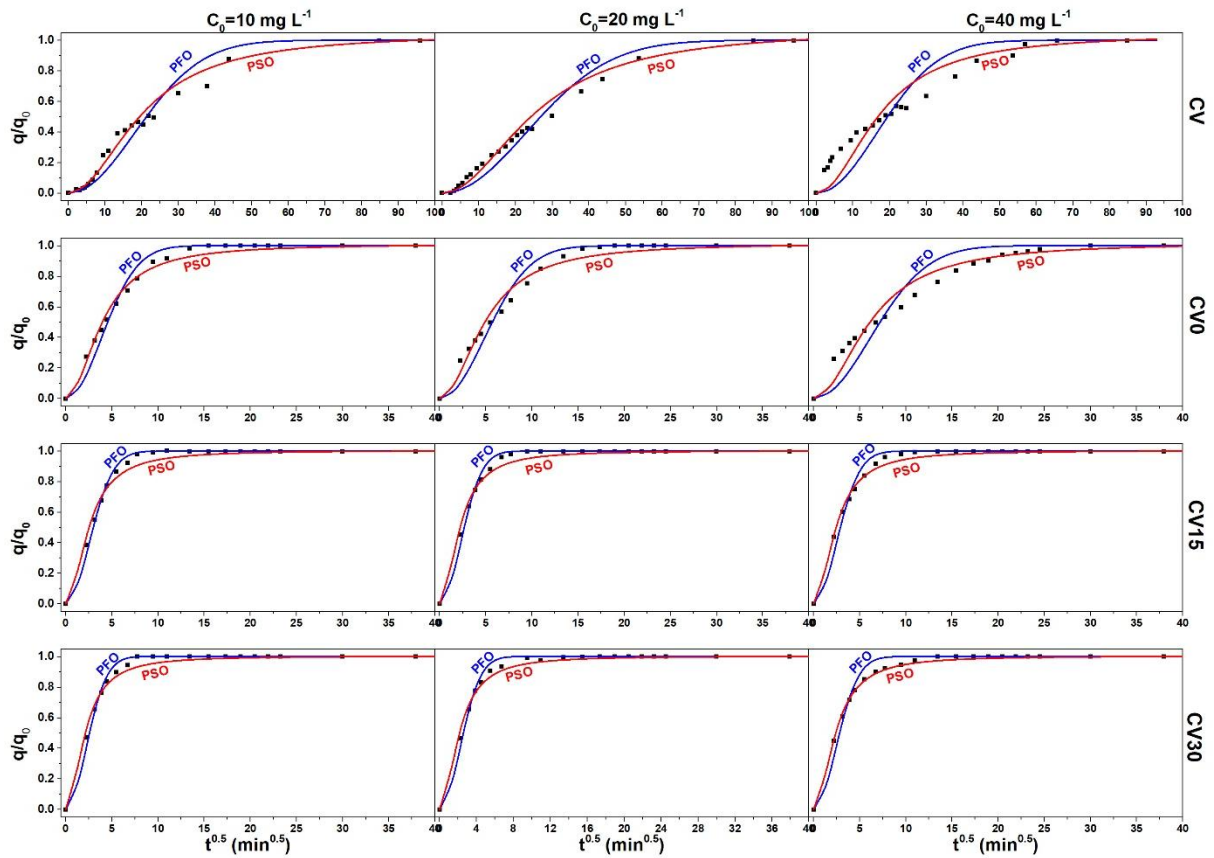
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Figure 6



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808 **Paracetamol removal by Kon-Tiki kiln-derived biochar and activated carbons**

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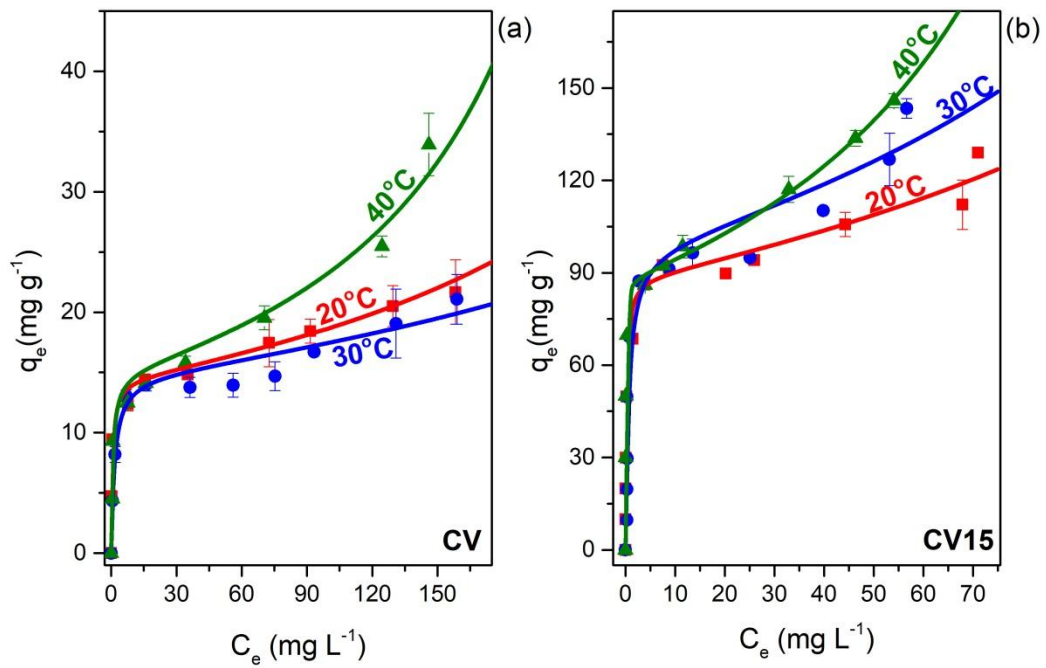
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Figure 7



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825 **Paracetamol removal by Kon-Tiki kiln-derived biochar and activated carbons**

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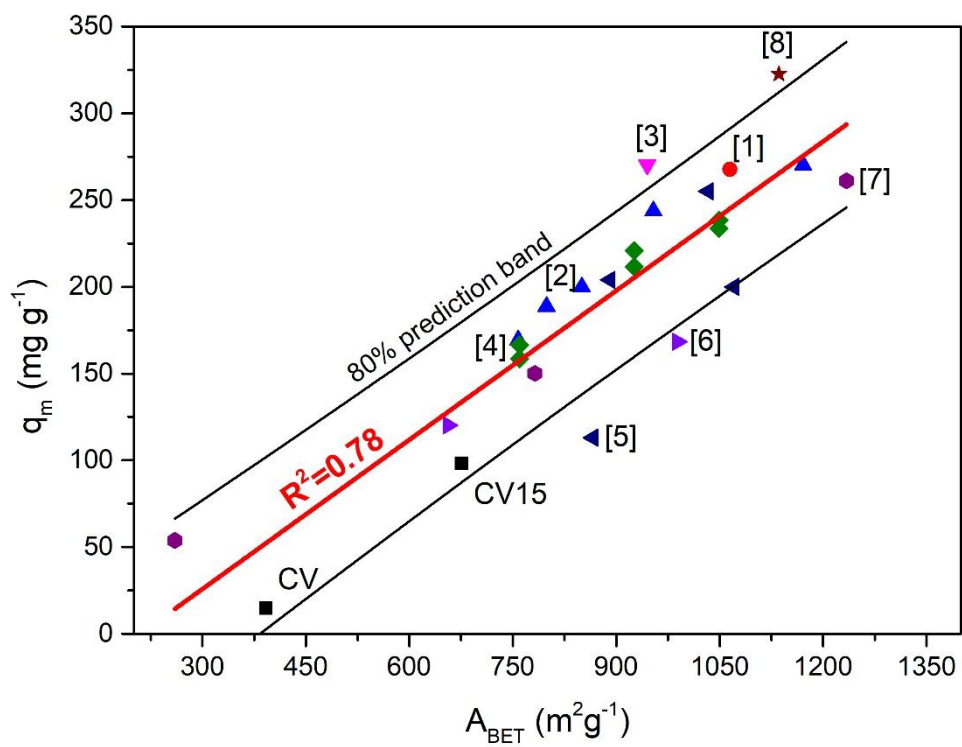
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Figure 8



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