

1 **How does phosphoric acid interact with cherry stones? A discussion on**
2 **overlooked aspects of chemical activation**

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15
16 **Abstract**

17 The fabrication of activated carbon (AC) is widely carried out by the so-called chemical
18 activation method, in which the biomass substratum is put in touch with an
19 impregnating chemical agent prior to the carbonization stage. Even though this
20 methodology is known for a long time, there are many features that are still poorly
21 understood, particularly those regarding the details of the underlying mechanisms
22 implied during the interaction of the activating agent with the precursor, eventually
23 leading to the development of AC. Previous research conducted in the laboratories dealt
24 with the use of cherry stones (CS) and phosphoric acid, towards ACs with tailored
25 porous structures, finding out that the experimental variables of the impregnation stage

26 were crucial for their eventual characteristics. Thus, the results obtained at that time
27 deserved further discussion, with the aim at unraveling the true nature of those findings.
28 With such purpose, we herein deepen into the use of CS and H₃PO₄ in non-conventional
29 impregnation methodologies, performed in the previous works. Four series of H₃PO₄-
30 impregnated products were prepared in a previous research, using a wide range of
31 impregnation strategies, aiming at controlling the loading of H₃PO₄ on the
32 lignocellulosic substratum. Herein, by only staring at the mass uptake upon
33 impregnation and subsequent drying, it was possible to link the uptake with the
34 chemical changes of H₃PO₄ in agreement with essential chemistry knowledge. Mass
35 gain is strongly dependent on the impregnation method, and interesting insights arise on
36 the basis of the mass changes of CS after impregnation.

37

38 **1. Introduction**

39 Lignocellulosic biomass includes materials such as agricultural residues, forestry
40 residues, portions of municipal solid waste, and various industrial wastes (Palonen et al.
41 2004). It is a low cost and abundant resource with a great potential to support large-
42 scale production of fuels and chemicals. Valuable materials such as activated carbon
43 (AC) can also be prepared from lignocellulosic biomass (Danish and Ahmad 2018). AC
44 is a synthetic kind of porous material that possesses high adsorption ability thereby
45 being an extremely versatile adsorbent of gases, vapours, and chemical species in
46 solution (Danish et al. 2017). Because of its adsorption properties, AC is used as
47 adsorbent, catalyst and support for catalysts (Tsoncheva et al. 2018). AC is usually
48 prepared by one of the well-known two-stage methods of physical or chemical
49 activation. In the chemical method, the selected precursor is usually impregnated with
50 an activating agent in the first place, such as H₃PO₄ in aqueous solution, and the

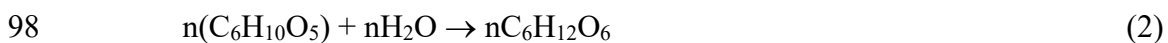
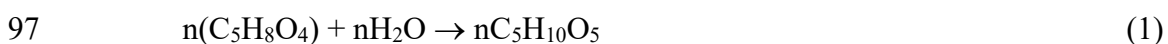
51 resulting product is then carbonized under specific heating conditions (Danish et al.
52 2014). Frequently, impregnation is carried out in two successive steps of soaking and
53 drying by heating below and above the boiling point of water, respectively. In the
54 impregnation stage, H₃PO₄ interacts chemically and physically with the precursor and as
55 a result changes occur in the chemical composition of the system which will influence
56 not only the impregnation process but also the subsequent carbonization, and ultimately
57 the porous structure of the final product.

58 The principal biopolymeric components of lignocellulosic biomass are
59 hemicelluloses, cellulose and lignin. In addition, it contains extractives (i.e. oils, fats,
60 etc.) and trace amounts of inorganic compounds and metal ions (Horvath et al. 2010).
61 Hemicelluloses are mixtures of polysaccharides synthesized in wood almost entirely
62 from glucose, mannose, galactose, xilose, arabinose, 4-*O* methylglucuronic acid, and
63 galactoronic acid residues (Pettersen 1984). Structurally, xylose, mannose and galactose
64 are found as monomeric fragments in the hemicellulose backbone chain, and arabinose,
65 galactose, and 4-*O*-methyl-d-glucuronic acid in hemicellulose side chains (Pettersen
66 1984). Cellulose is the main constituent of plant cell wall conferring structural support.
67 It is a glucan polymer consisting of long, linear parallel chains of 1,4-β-bonded
68 anhydroglucose units. The molecular chains pack in layers that are held together by
69 weak van der Waals forces (Pettersen 1984). In cellulose chains, hydroxyl groups form
70 intra- and intermolecular hydrogen bonds, as displayed in Figure 1a (Pettersen 1984;
71 Negahdar et al. 2016), as displayed in Figure 1a. Chemically, lignin is a phenolic
72 substance derived mainly from three alcohols with a different degree of methoxylation
73 (i.e., coniferyl, sinapyl and p-coumaryl alcohols), which are connected with different
74 types of ethers and carbon-carbon bonds (Boerjan et al. 2003).

75 On the other hand, lignocellulosic biomass includes fruit stones that possess a
76 hardened endocarp are called drupes. These fruit stones are formed by lignification of
77 the fruit endocarp layer (Dardick et al. 2010). Lignification is the process of producing
78 the lignin polymer from lignin monomers via enzymatic oxidative reactions aided by
79 peroxidases and laccases. Previous studies indicate that lignification begins in the
80 second stage of fruit development until maturity. Furthermore, the biochemical analysis
81 of a wide series of drupes has shown that they contain nearly twice as much lignin as
82 wood (Dardick and Callahan 2014). Chemical structures for hemicelluloses and lignin
83 have frequently been reported before in the literature (Pettersen 1984, Jagtoyen and
84 Derbyshire 1998, Chávez-Sifontes and Domine 2013, Oinoen et al. 2015, Baipai 2016,
85 Negahdar et al. 2016).

86 Among the above mentioned biopolymers, hemicelluloses are not crystalline,
87 soluble in alkali and easily hydrolyzed by acids. The solubility of cellulose is hindered
88 as it is covalently, intimately associated with lignin and hemicelluloses (Pettersen
89 1984). Since the cellulose structure consists of crystalline and amorphous domains
90 (Pettersen 1984), the crystalline one constituting the major proportion, only a minor
91 portion of this biopolymer is soluble in substances such as acids. As far as lignin is
92 concerned, partial digestion by acid action occurs (Jagtoyen and Derbyshire 1998). By
93 acid-catalyzed hydrolysis, hemicellulose chains eventually convert into five and six
94 carbon sugars and cellulose chains into six carbon sugar (glucose) by Reactions (1) and
95 (2) (Wyman 2013; Satarn et al. 2014):

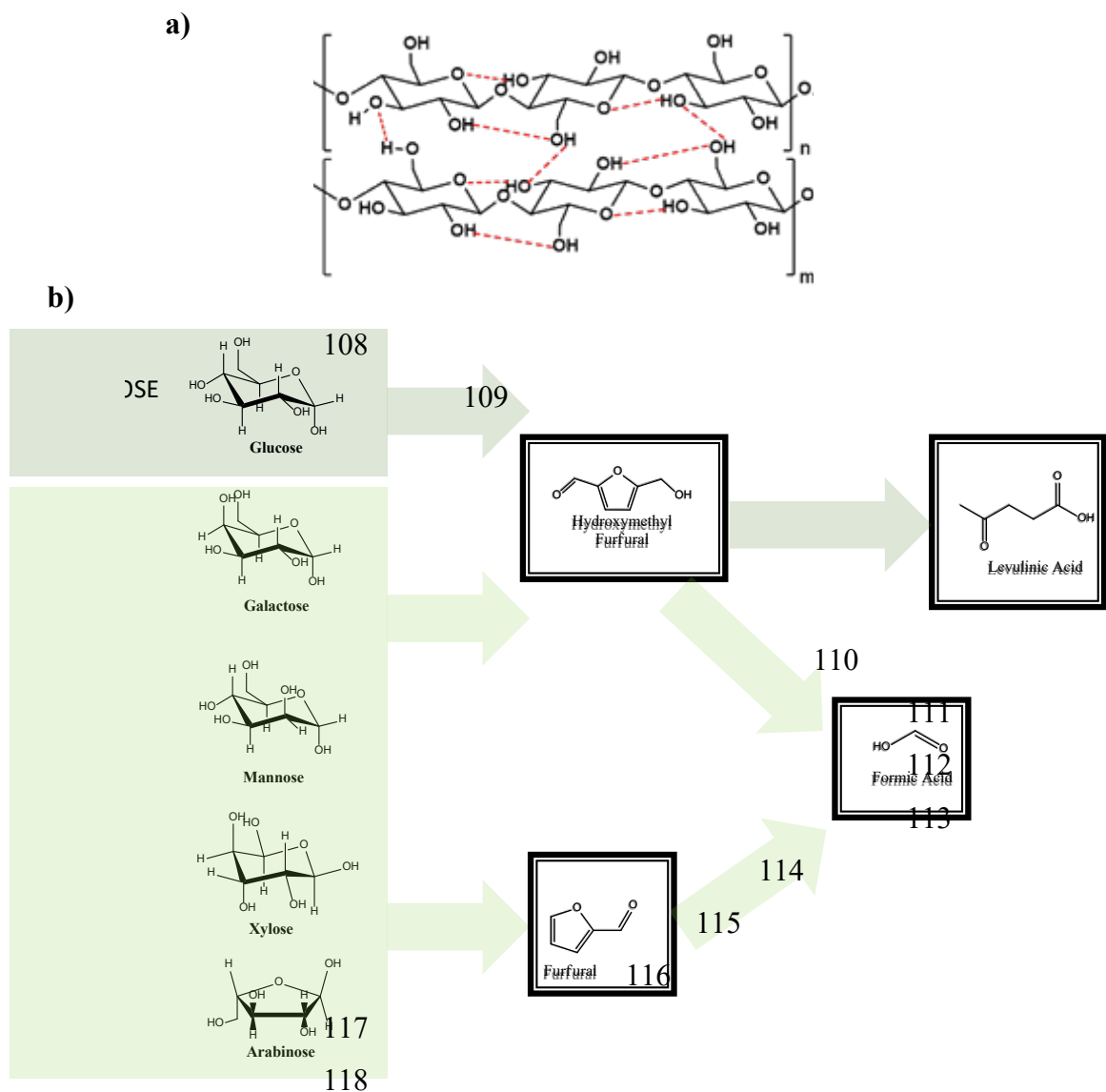
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100 and resulting monosaccharides may undergo dehydration and transform into furan ring
 101 containing compounds such as furfural and hydroxymethylfurfural (HMF), as shown in
 102 Fig. 1b (Ek et al. 2009).

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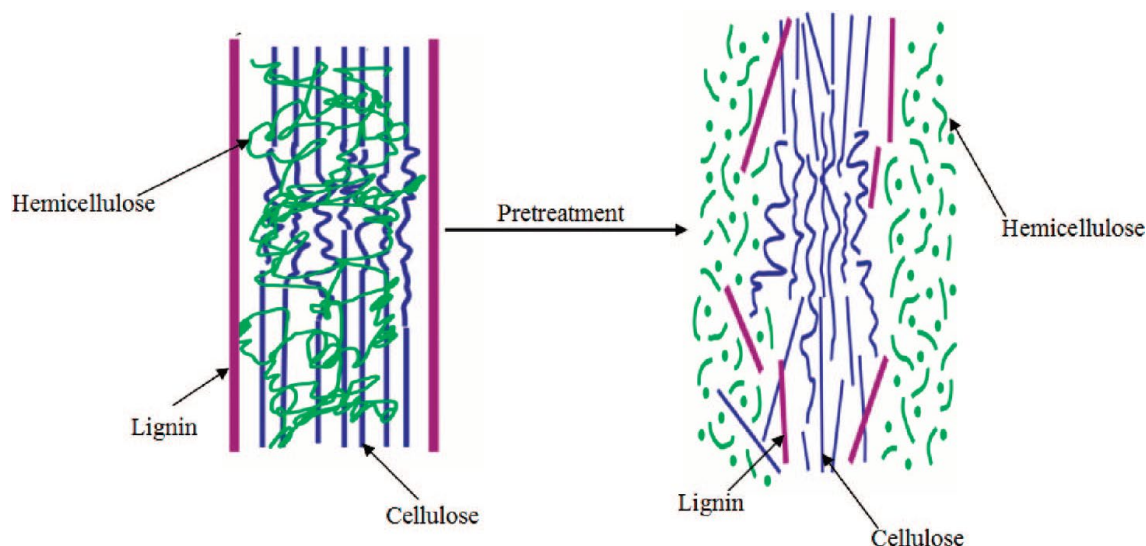


119 Fig. 1. a) Representation of the structure and intramolecular hydrogen bonding of
 120 cellylose, b) Chemical changes produced as a result of the hydrolysis of cellulose and
 121 hemicelluloses.

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124 When H_3PO_4 is specifically used in the treatment of lignocellulosic materials,
 125 the hydrolysis of hemicelluloses and cellulose is more or less severe depending on the
 126 acid concentration (Nguyen et al. 2009; Agbor et al. 2011). With 1-10 % H_3PO_4 under

127 mild heating conditions, hydrolysis mainly concerns the hemicellulosic fraction as the
128 cellulosic fraction is not affected to an appreciable extent (Gómez et al. 2004, 2006).
129 However, anhydrous H_3PO_4 is an excellent direct solvent for cellulose. The dissolving
130 power of this acid is very strong with dissolution occurring within a few minutes. As a
131 result, even 38% (w/w) cellulose solutions can be prepared (Boerstoel et al. 2001). After
132 the acid hydrolysis, the extraction of lignin can be performed from the residual liquid
133 and solid phases (Horvath 2006; Tsubota et al. 2015). Figure 2 depicts the changes
134 originated in the structure of biomass by acid treatment (Hsu et al. 1980; Kumar et al.
135 2009). The residual liquid from the hydrolysis of sugar cane bagasse with dilute H_3PO_4
136 is constituted of sugars (xylose, glucose and arabinose), products of decomposition of
137 the hemicelluloses (such as oligomers from the polymers and acetic acid generated from
138 the hydrolysis of acetyl groups linked to sugars) and of the monosaccharides released
139 (such as furfural, product of dehydration of pentoses, and HMF, and products of
140 dehydration of hexoses). In the concentration of the mixture obtained by evaporation
141 not only water but also small amounts of reaction products (e.g. growth inhibitors such
142 as acetic acid, furfural and HMF) are removed (Gómez et al. 2004, 2006; citations
143 therein). Using dilute H_3PO_4 in the treatment of commercial cellulose prior to heating at
144 high temperature Dobele et al. (2003) concluded that the extent to which
145 levoglucosenone is formed depends on the cellulose crystallinity and the degree of
146 dehydration. With concentrated acids, however, the dissolution leads to a hydrolytic
147 cleavage of the cellulose chains, and the cellulose molecules are transformed to
148 derivatives, such as esters (Horvath 2006).
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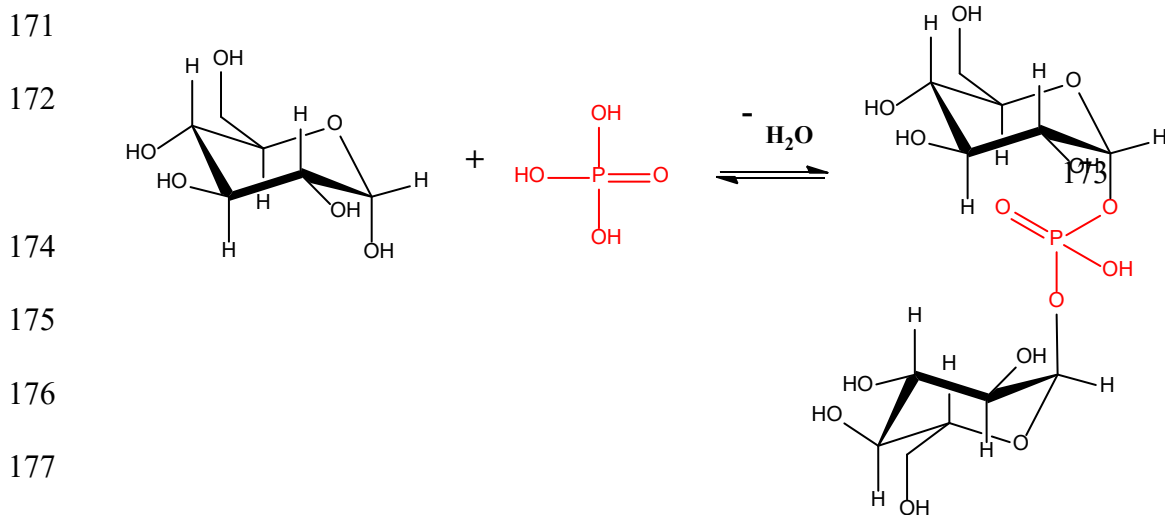
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152 Fig. 2. General overview experienced by lignocellulosic biomass upon treatment
 153 with acids. Reprinted with permission from reference (Kumar et al. 2009). American
 154 Chemical Society © 2009.

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157 Another process variable with influence on the chemical changes produced in
 158 lignocellulosic materials by treatment with H_3PO_4 solution is the soaking temperature
 159 (Solum et al. 1995). The reaction of white oak wood with 30% H_3PO_4 at low
 160 temperatures between 50 and 170 °C principally promotes dehydration and also
 161 chemical changes such as loss of carboxyl and methyl groups from hemicelluloses,
 162 formation of ketone groups (possibly by the formation of levoglucosenone) and ester
 163 groups from amorphous cellulose, the formation of phosphate esters (see Fig. 3;
 164 Jagtoyen and Derbyshire 1998), initiation of crosslinking reactions, development of
 165 aromaticity and loss of aliphatic, carboxyl and carbonyl groups, and significant
 166 alteration of the lignin structure. When heating at high temperatures, the H_3PO_4 was
 167 found to promote an expansion of the wood structure above the range of 250-450 °C
 168 with an associated development of porosity and creation of an extensive surface area.
 169 Above 450 °C, a secondary dimensional contraction paralleled the reduction in porosity
 170 (Solum et al. 1995).



178 Fig. 3. Reaction of phosphoric acid (red) with glucose units (contained in
 179 cellulose) giving rise to phosphate ester bonds, at low temperatures.
 180

181

182 When H_3PO_4 alone is heat-treated, pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$),
 183 metaphosphoric acid (HPO_3) and phosphorus pentoxide (P_2O_5) are successively formed
 184 as temperature rises. However, the heat treatment of a lignocellulosic material (e.g.
 185 yellow poplar) with such a chemically modified H_3PO_4 gives rise to the formation of
 186 ester linkages with $-\text{OH}$ groups on cellulose at temperatures below $200\text{ }^\circ\text{C}$, attachment
 187 of small polyaromatic units mostly by phosphate and polyphosphate bridges at $280\text{ }^\circ\text{C}$,
 188 and scission of P-O-C bonds at higher temperatures (Jagtoyen and Derbyshire 1998).
 189 These chemical changes involving phosphorus acids are accompanied by the formation
 190 of crosslinks between the polymer chains, occurrence of cyclization and condensation
 191 reactions leading to an increase in aromaticity and in the size of the polyaromatic unit,
 192 and cleavage of crosslinks leading to a very extensive growth of the size of the aromatic
 193 units (Jagtoyen and Derbyshire 1998). With H_3PO_4 -impregnated cherry stones, a great
 194 increase in weight loss was observed between 625 and $900\text{ }^\circ\text{C}$ as compared to the
 195 starting material, this being connected with the gasification of carbon atoms by P_2O_5

196 and thermal decomposition of polyphosphoric acids with the formation, in both
197 instances, of white phosphorus (P_4) as a reaction product (Olivares-Marín et al. 2006).

198 With a view to preparing AC with a tailored porous structure, several
199 impregnation strategies of a lignocellulosic material such as cherry stones, CS (i.e. an
200 agro-industrial by-product generated in abundance in a large number of European
201 countries like Turkey, Italy and Spain), were devised and the associated mass changes
202 have been reported before (González-Domínguez et al. 2011, 2017). Such strategies not
203 only included the use of H_3PO_4 solutions of different concentrations but also of further
204 diluted or over-concentrated H_3PO_4 solutions, and also the use of thermally modified
205 CS. In other strategies, impregnation is effected in a single impregnation step, instead of
206 in two steps (impregnation and drying) as in the usual method, and the filtered residues
207 are either washed with distilled water or reused as the impregnation solution. The
208 present study aims at unravelling the underlying mechanisms ruling the impregnation
209 process in agreement with physical and chemical changes undergone by the H_3PO_4
210 impregnation solution and lignocellulosic substratum after soaking and drying steps.

211

212 **2. Experimental**

213

214 *2.1. Materials and Methods*

215 Cherry stones (CS) from Valle del Jerte (province of Cáceres, Spain) were used
216 as the AC precursor. As-received, CS was first air dried and then milled and sieved, the
217 particle size between 1 and 2 mm being chosen. Data of the chemical analyses obtained
218 for CS are compiled in Table 1 (Durán-Valle et al. 2005). The lignocellulosic
219 composition of CS is: hemicelluloses 14.7%; cellulose 29.4%; lignin 30.7%, and its
220 empirical formula is $CH_{1.52}O_{0.62}N_{0.006}$ (González et al. 2003). For comparison purposes,

221 biopolymer compositions for other fruit stones and for lignocellulosic materials such as
 222 wood, are compiled in Table 2. The elsewhere reported thermogravimetric analysis of
 223 CS (Olivares-Marin et al. 2006) in inert atmosphere (under a N₂ flow) showed two
 224 weight loss effects between 30-200 °C and 200-300 °C. The former with a mass loss of
 225 8.28 wt.% was associated with the release of moisture and a small fraction of volatile
 226 components from CS. The latter with a mass loss of 17.93 wt.% was ascribed to the
 227 thermal decomposition of less stable chemical constituents of CS (Olivares-Marin et al.
 228 2006), chiefly hemicelluloses (Baquero et al. 2003; Carvalho et al. 2002; Girgis and
 229 Ishak 1999; Himmel et al. 2007; Lim et al. 2010; Mantanis et al. 1994; Stamm 1934,
 230 1964; Yang et al. 2007). After sizing, CS were cleaned and conditioned by soaking
 231 overnight in diluted sulphuric acid (5% v/v), thoroughly rinsed with distilled water
 232 (until neutral pH), and oven-dried at 120°C for 24 h.

233 **Table 1:** Chemical analyses of CS

234

235	Ultimate	wt. %	Proximate	wt. %
236	Carbon	49.00	Moisture	5.41
237	Hydrogen	6.37	Volatile matter	71.72
238	Nitrogen	0.24	Ashes	0.24
239	Oxygen	44.15	Fixed carbon	22.63
240				
241				
242				

243 **Table 2:** Biopolymer composition of lignocellulosic materials (wt.%)

Scientific Name	Description	Hemicelluloses	Cellulose	Lignin	Reference
<i>Prunus avium</i>	Cherry stones	14.7	29.4	30.7	(González et al. 2003)
<i>Olea europea</i>	Olive stones*	21.9	31.9	26.5	(Heredia et al. 1987)
<i>Phoenix dactylifera</i>	Date stones	18	42	11	(Bouchelta et al. 2008)
<i>Populus tremuloides</i>	Aspen wood	20 - 35	40 - 50	15 - 30	(Horvath 2006)
	Tree wood	65 - 75		18 - 35	(Pettersen 1984)
	Forestry waste	20 - 35	35 - 50	15 - 25	(Wyman 1994)

244 * On a dry basis scale.

245

246 Commercial H₃PO₄ reagent grade (85% PA-ACS-ISO, Panreac) was used.

247 Because of its very polar character, the H₃PO₄ molecule is highly soluble in water, i.e.

248 548 g H₃PO₄/100 g H₂O at 25 °C (Lide 2005). It behaves like a tribasic acid, K₁ being

249 $7.11 \cdot 10^{-3}$ at 25 °C (Greenwood and Earnshaw 1989). K₁ decreases with temperature as

250 concentration increases. H₃PO₄ tends to bond by intermolecular hydrogen bridges,

251 aggregation and condensation. As a last resort polyphosphoric acids of general formula

252 H_{n+2}P_nO_{3n+1}, with *n* up to 17, are formed as a complex mixture of linear molecules of

253 various chain lengths (Toy 1973). The P₂O₅ concentrations to which orthophosphoric,

254 pyrophosphoric and polyphosphoric acid correspond are 72.4, 79.6 and 84.0 wt.%,

255 respectively, whereas compositions in between the first and the second concentrations

256 are referred to as superphosphoric acid (Boerstoel et al. 2001). The formation of

257 molecular aggregates in the solution gives rise to an increase in viscosity, decrease in

258 vapor pressure, and increase in boiling point with the rise in concentration. As a guide,

259 viscosity (c_p) at 20 °C is 2.6 for 30 wt.% H₃PO₄ solution and 47.0 for 85 wt.% H₃PO₄

260 solution. The vapor pressure (mm Hg) at 25 °C is 21.19 for 29.80 wt.% H₃PO₄ solution

261 and 3.86 for 80.14 wt.% H₃PO₄ solution (Greenwood and Earnshaw 1989). Finally,

262 boiling point ranges between 100.2 and 108.0 °C for 10-50 wt.% H₃PO₄ solution and is

263 150 °C for the 85 wt.% H₃PO₄ solution (Toy 1973).

264 N₂ adsorption isotherms were measured in Autosorb-1 (Quantachrome) instrument, and

265 the surface area was determined as reported in González-Domínguez et al. (2017).

266 X-ray photoelectron spectroscopy (XPS) measurements were carried out in a K-Alpha

267 Thermo Scientific equipment under high vacuum conditions ($2 \cdot 10^{-7}$ mbar). A

268 monochromatic radiation of 1486.68 eV (Al K_α line) was used to irradiate samples

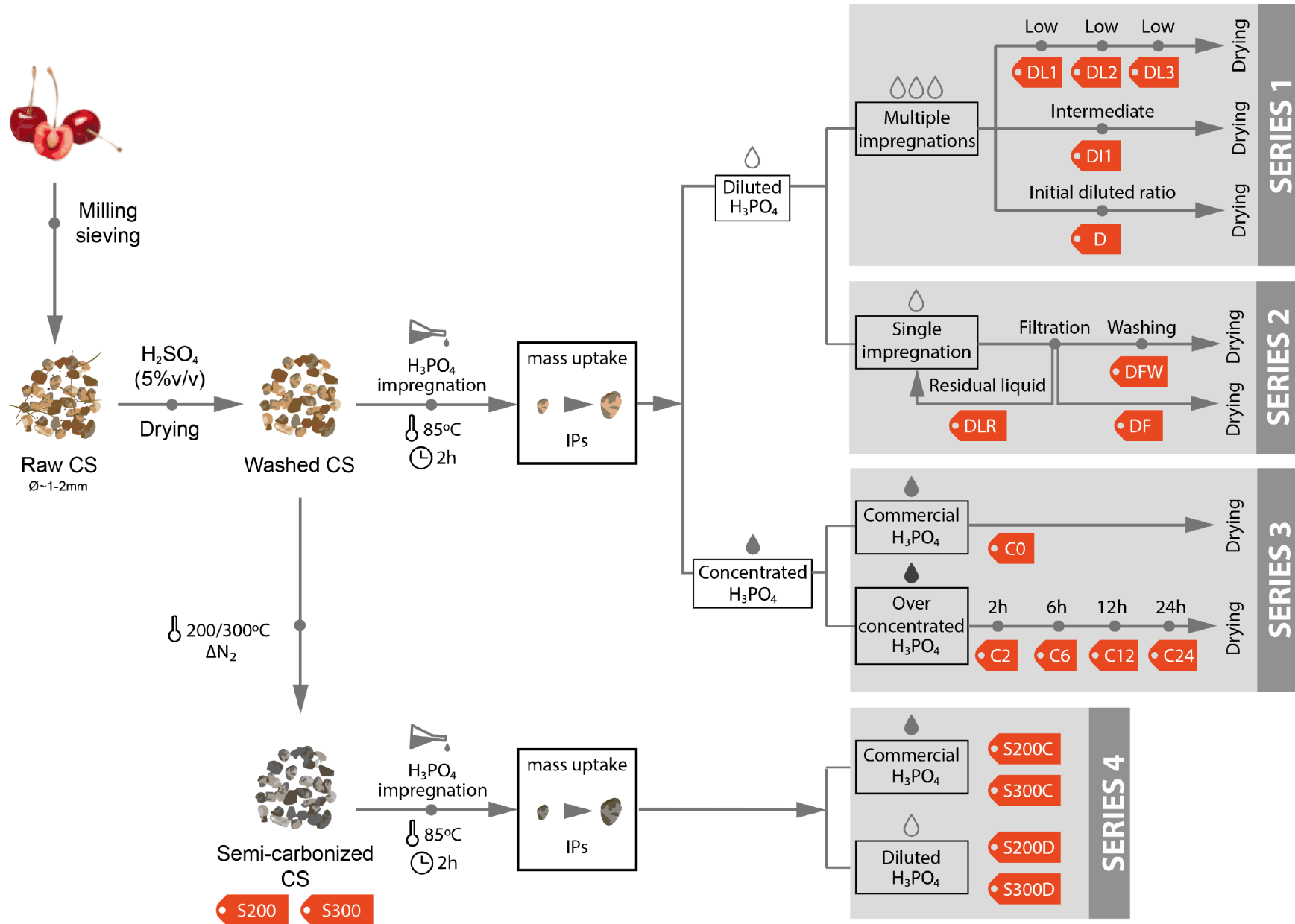
269 perpendicularly at 12 kV. Additionally, a flood gun device (working at 4.2 mA)
270 compensated for the load losses. The register settings were established as 50 ms
271 accumulation time for each step in all cases. Survey spectra were recorded by 1eV
272 energy steps and 20 scans.

273

274 *2.2. Impregnation strategies*

275 Scheme 1 fully depicts the whole scenario undergone to carry out impregnation
276 of CS with phosphoric acid. Two H₃PO₄ solutions were used as stocks. One was a
277 diluted (D) solution and the other was a concentrated (C) solution, and contained 16 g
278 H₃PO₄/100 mL water and 144.5 g H₃PO₄/100 mL water, respectively. In fact,
279 commercial H₃PO₄ without further dilution was used as C. Solutions of the same
280 H₃PO₄ concentrations were also used in a previous study (Olivares-Marín et al. 2006).
281 In a typical impregnation experiment, as described in more detail elsewhere (González-
282 Domínguez et al. 2011), 100 mL of H₃PO₄ solution were first brought into contact with
283 about 25 g of CS in a beaker and the system, under steady magnetic stirring, was heated
284 at 85 °C for 2 h. To prevent unwanted solvent losses by evaporation, the beaker was
285 maintained sealed with a latex film throughout the entire process. Then, the resulting
286 liquid/solid mixture was oven-dried at 120 °C for 24 h. For the sake of brevity, the first
287 and second impregnation treatments are referred to as FIT and SIT hereafter. As a
288 whole, four series of impregnated products (IPs) were prepared (see Table 3 and
289 Scheme 1).

Scheme 1. General preparation process of H₃PO₄-impregnated CS



184 **Table 3:** Experimental conditions, sample nomenclature and mass changes upon
 185 impregnation (reproduced with permission from (González-Domínguez et al. 2011), ©
 186 Elsevier 2011).

[H ₃ PO ₄] g/100 mL	t/h	NI	Filtering	Washing	T/°C	IP codes	Series	Δm/g
16						D	1	7.30
5.33						DL1		1.20
5.33		2				DL2		1.85
10.66						DI1		4.43
5.33		3				DL3		2.30
16			Yes			DF	2	1.34
16			Yes	Yes		DFW		0.48
n-d						DRL		n-d
144.5	0					C0	3	135.54
	2					C2		143.20
	6					C6		126.29
	12					C12		127.45
	24					C24		134.96
16					200	S200D	4	9.09
16					300	S300D		15.04
144.5					200	S200C		132.80
144.5					300	S300C		94.36

187 *Abbreviations: n-d, not determined; t, oven-drying time; NI, number of successive*
 188 *impregnations; T, semi-carbonization temperature.*

189 *IP codes: D, dilute solution; L, low concentration; I, intermediate concentration; F,*
 190 *filtration; FW, filtration and washing; RL, residual liquid; C, concentrated solution; S,*
 191 *semi-carbonized product.*

192
 193

194 • Series 1: Since dilute H₃PO₄ catalyzes the hydrolysis of hemicelluloses, this series of
 195 IPs was prepared by further diluting D and by effecting the FIT and SIT only once with
 196 the starting D (16 g/100mL) and with two more diluted H₃PO₄ solutions, namely 5.33
 197 g/100mL (DL1) and 10.66 g/100mL (DI1). Using the most diluted solution (i.e. that
 198 used in the preparation of DL1), the impregnation process was also carried out
 199 successively twice or three times with identical aliquots (DL2, DL3). In this way, the
 200 eventual amount of H₃PO₄ used in the various impregnation treatments was the same for
 201 DL2 and DI1 and for DL3 and D. Accordingly, not only CS but also previously H₃PO₄-
 202 impregnated CS were used in the impregnation treatments.

203 • Series 2 was also prepared with D. However, unlike in the preparation of series 1,
204 after the FIT the supernatant liquid was filtered (DF), the residual solid was thoroughly
205 washed with distilled water (DFW) or the filtrate was used as the impregnation solution
206 for a fresh sample of CS (DRL). The preparation of DRL was intended not only as a
207 different impregnation strategy concerning the dilution of H₃PO₄ but also to obtain
208 information on the feasibility of recycling.

209 • For Series 3, C was oven-dried at 120 °C for 2-24 h before its use in the FIT of CS.
210 This impregnation strategy was devised by taking into account the possible dependence
211 on the concentration of the physical and chemical state of H₃PO₄ in the impregnation
212 solution.

213 • Regarding Series 4, CS were first heat-treated at 200 or 300 °C for 2 h in N₂ (flow =
214 100 mL/min) and the resulting chars (semi-carbonized CS), which are designated S200
215 and S300, were then impregnated with D and C. This strategy concerned the influence
216 of composition of the lignocellulosic substratum on impregnation. The impregnation
217 methods are summarized in Table 3, which also includes mass data and sample codes.
218 To the authors' knowledge, this is the first time such methods are used in the
219 impregnation of lignocelulosic materials with H₃PO₄. As a guide, see references
220 (Molina-Sabio et al. 1995; Stamm 1934) for comparison purposes.

221

222 **3. Results and discussion**

223 *3.1. Mass changes*

224 The mass increase produced by impregnation of CS and CS chars with H₃PO₄
225 solution was calculated through Expression (1)

$$226 \quad \Delta m = m_f - m_0 \quad (1)$$

227 where m_0 and m_f are the initial and final mass of sample, and Δm the mass of H_3PO_4
228 loaded into the CS. Therefore, m_f represents the neat mass change associated not only
229 with the loading of activating agent on CS and CS chars but also with physical and
230 chemical processes which likely occurred during the impregnation process (i.e.
231 solubilisation, hydrolysis, other chemical reactions, and so on) with involvement of the
232 lignocellulosic material (Baquero et al. 2003; Lim et al. 2010). The aforesaid processes
233 only caused mass decrease that influenced m_f provided that the resulting products,
234 because of their volatility, were released from the medium during any of the
235 impregnation treatments. The obtained Δm values have previously been reported
236 (González-Domínguez et al. 2011, 2017) and are collected in Table 3. In brief, it was
237 shown that Δm :

- 238 • Markedly decreases with the dilution of the dilute solution (IPs DL1, DI1 and D).
- 239 • Significantly decreases when the impregnation process was effected more than once
240 with aliquots (IPs DL1, DL2 and DL3). As a guide, for D0 and DL3 (i.e. both IPs
241 prepared using the same amount of H_3PO_4), the percentage of H_3PO_4 loading is 45.6
242 and 33.4 (as obtained from $\Sigma\Delta m$), respectively.
- 243 • Greatly decreases for the IPs prepared by removing the filtrate and by further washing
244 the resulting product with distilled water. Δm is approximately five- and fifteen-fold for
245 D0 that for DF and DFW, respectively.
- 246 • Noticeably increases for DRL. For this IP Δm is 10.9 g, which is therefore
247 pronouncedly higher than 7.3 g for D0. By taking 1.34 g as the amount of H_3PO_4 loaded
248 on CS in the FIT (i.e. the same as in the preparation of DF), the surplus of substance
249 remaining in the filtrate was 14.66 g. Then, it follows that Δm was higher when the
250 filtrate was used as the impregnation solution, in spite of the fact that the presence of
251 H_3PO_4 in the filtrate was smaller than in D (i.e. 14.66 g as compared to 16 g).

252 • Increases with the concentration of the impregnation solution, as seen above, but
253 especially when C was used. The percentage of H₃PO₄ loading is as high as 93.8 for C0
254 whereas for D it is 45.6.

255 • Varies rather irregularly with time of the previous oven-drying of C at 120 °C.
256 Clearly, loading was only significantly promoted when oven-drying for the shortest
257 time of 2 h. For longer times, as compared to C0 (i.e. the IP prepared without prior
258 oven-drying), it first significantly decreases and then remains almost unchanged.

259 • Is also strongly dependent on whether CS or CS chars were used as the substratum in
260 the impregnation with H₃PO₄. Δm is higher for the CS chars, in particular for S300, than
261 for CS, provided that D was used. For C, however, Δm is slightly lower for S200C than
262 for C0. In the case of S300C, drying was not completely achieved after the SIT and
263 therefore, Δm could not be obtained Δm (González-Domínguez et al. 2011).

264

265 3.2. Insights into the impregnation mechanisms

266

267 3.2.1. Impregnation with dilute H₃PO₄ solution- by further dilution

268 The obtained values of Δm for DL1, DI1 and D0 (Table 3) point out a noticeably
269 increased reluctance of H₃PO₄ to its loading on CS with the successive dilution of the
270 impregnation solution. As a tentative, it may be accounted for by thoroughly examining
271 the effects on the composition of the solution associated with the impregnation process
272 throughout which CS swelling and shrinkage occurred, as follows. The CS constituent
273 biopolymers (cellulose, hemicellulose and lignin) contain oxygen functional groups
274 which are hydrophilic in nature and may attract water molecules through hydrogen
275 bonding, although some groups such as glycosidic bridges and ethers may not have this
276 high capability. Anyways, the material should start swelling in a single phase uniform

277 (homogeneous) system such as the H_3PO_4 solution as soon as contact was established
278 between the solid/liquid phases in the FIT. Certainly, such oxygen groups should be
279 necessarily accessible to water as swelling occurs. In this connection, it is pertinent to
280 note that lignocellulosic materials are inherently recalcitrant to chemicals and enzymes
281 due to a wide series of natural factors (Himmel et al. 2007). Further, a characteristic of
282 the swelling process is the anisotropy. For lignocellulosic materials such as woods,
283 swelling varies by tangential (i.e. in the direction of the annual growth rings)>> radial
284 >> longitudinal (Stamm 1964). Other factors with influence on the swelling process are
285 related to the composition, solvent, and heat treatment temperature. The various
286 biopolymers of lignocellulosic materials participate unevenly in the swelling process.
287 Thus, hemicelluloses are the most hygroscopic polymer in cell walls, followed by lignin
288 and finally cellulose, in particular crystalline cellulose (Himmel et al. 2007). Swelling is
289 significantly enhanced by the removal of extractives by the action of solvents (Mantanis
290 et al. 1994). Solvents such as water with a great ability to bind by strong hydrogen
291 bonding possess a large swelling capacity (Mantanis et al. 1994; Stamm 1964), the
292 process being then very favourable. This process is extremely fast even at room
293 temperature and significantly increases its rate at higher temperatures. At 100 °C, the
294 rate of swelling tremendously increases. However, the maximum swelling only
295 increases slightly as the temperature increases. As a result of swelling, the material
296 expands until the cell wall becomes saturated with water (fiber saturation point) (Stamm
297 1964). For all wood species, this point is reached for the moisture content of
298 approximately 30% (1957). Moisture beyond the fiber saturation point is free water and
299 does not contribute to further expansion (Mantanis et al. 1994).

300 Insofar as CS swelled and expanded, the diffusion of H_3PO_4 in CS would be
301 easier and this should enable the H_3PO_4 molecule to compete with the water molecule

302 for oxygen functional groups of CS biopolymers to bind by hydrogen bonding. In fact,
303 the hydrogen bonding potential of the H_3PO_4 molecule is even larger than for the water
304 molecule. In crystalline state, each H_3PO_4 molecule is linked to six others by hydrogen
305 bonds and extensive hydrogen bonding persists on fusion (Greenwood and Earnshaw
306 1989). In aqueous solution, such a potential may be even more effective than for other
307 aggregation states of matter on account of the absence of steric hindrance to bind to
308 water molecules. Nevertheless, competition should be unfavorable for H_3PO_4 because of
309 the lower polarity of the O-H bond for H_3PO_4 . Dissociated H_3PO_4 should be able to
310 form stronger hydrogen bonding than the neutral molecule, owing to the involvement of
311 the negatively charged H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} ions. However, H_3PO_4 in aqueous
312 solution is poorly dissociated and to a lesser degree when heating above room
313 temperature. Since the FIT was performed at 85 °C, the thermal agitation of the system
314 is another factor that should also handicap the involvement of the H_3PO_4 molecule in
315 hydrogen bonding in the bulk of the solution and with oxygen groups of CS. The effect
316 would be weaker than for the water molecule which binds more strongly by hydrogen
317 bonding than the H_3PO_4 molecule. In any event, it should be noted here that even in the
318 case of water in the liquid state, the fluctuating molecular aggregates are continuously
319 changing by effect of the thermal agitation on hydrogen bonding (Doménech 1998). In
320 brief, the extensive hydrogen bonding of H_3PO_4 in the bulk of the solution and its
321 weaker hydrogen bonding to oxygen groups of CS as compared to water together with
322 the thermal agitation of the system would contribute to stabilize H_3PO_4 in the bulk of
323 solution rather than in the loaded state, this rendering the loading process of H_3PO_4
324 difficult in the FIT.

325 In the SIT, which was carried out by oven-heating at 120 °C for 24 h, the
326 vaporization of water from the supernatant in contact with the lignocellulosic

327 substratum and also of indigenous water of CS (i.e. free water, linked water and water
328 of constitution) occurred. Water rather than H_3PO_4 should preferably vaporize in
329 accordance with the markedly lower boiling point of water than of H_3PO_4 . Concomitant
330 with the process of water vaporization, H_3PO_4 should become progressively more
331 concentrated in the transient liquid in contact with CS. However, simultaneous to its
332 concentration, H_3PO_4 should be loaded on CS, this being then a tending factor to lower
333 the concentration of H_3PO_4 in the aforesaid liquid. Thus, in brief, the processes of
334 vaporization, concentration, and loading were time-dependent and interdependent with
335 each other. As a result of vaporization and concentration, the boiling point increased
336 and vapour pressure decreased with the course of time. That is to say, the tendency of
337 the liquid to vaporize was progressively smaller with time. Furthermore, owing to its
338 dependence on concentration, the boiling point was first below (i.e. $> 100\text{ }^\circ\text{C}$; as a
339 guide, for 10 wt% H_3PO_4 solution is $100.2\text{ }^\circ\text{C}$ (Toy 1973) and then above $120\text{ }^\circ\text{C}$.
340 Accordingly, the liquid first boiled and then evaporated. Since the mass of liquid taking
341 part in the vaporization process was different in both instances (i.e. the process occurred
342 within the entire mass of the liquid and only on its surface, respectively), it should
343 influence the degree of thermal agitation in the system and the kinetics of the
344 vaporization process, which was first faster and then progressively slower. As a result,
345 the aggregation of H_3PO_4 units by hydrogen bonding during the evaporation process
346 would be promoted not only on account of the concentration rise but also, from a given
347 oven-drying time on, because of a lesser agitation in the system. Aggregation should
348 originate a stability gain against evaporation and for the loaded state as it should
349 propitiate the loading of large size units which would be able to interact simultaneously
350 with a larger number of active sites of the lignocellulosic substratum.

351 Another factor that likely contributed to stabilize H_3PO_4 in the loaded state was the
352 shrinkage undergone by the swollen CS in the SIT. Swelling is a reversible process and
353 a given material shrinks as it loses moisture (Mantanis et al. 1994). Shrinking occurs
354 only at moisture content values below the above-mentioned fiber-saturation point.
355 Furthermore, shrinkage is proportional to the amount of moisture lost below such a
356 point (1954). Therefore, shrinkage only commenced after a great proportion of moisture
357 had been removed from the swollen CS by evaporation. Of course, water should have
358 also been vaporized before from the bulk of the transient liquid. Regarding H_3PO_4 , since
359 the un-evaporated amount of it still remaining in the system was too small (i.e. much
360 more than that of CS) to form a two-dimensional liquid on the surface of CS, it should
361 be found therefore up-taken in CS. On going on oven-heating, H_3PO_4 to some extent
362 might also be removed from CS, although the process should be less favourable than for
363 water as the vapour pressure is lower for H_3PO_4 . Besides, a greater availability of active
364 sites by moisture loss would enable H_3PO_4 to further bind to CS. Further, the volume
365 contraction should hinder the release of H_3PO_4 from CS, particularly with the increase
366 in the degree of H_3PO_4 aggregation in the up-taken state. The presence of H_3PO_4 in CS
367 may diminish its shrinkage, similarly to for inorganic salts (Stamm 1934).

368 From the above statements it follows that the aggregation of H_3PO_4 would have
369 been a key factor with regard to its stabilization against evaporation from the transient
370 impregnating liquid and, after its loading on CS, from the up-taken state and therefore
371 to its eventual neat loading on CS during the SIT long. However, since the impregnation
372 of CS was effected with dilute H_3PO_4 solutions, it is likely that aggregation was
373 significantly restricted by an insufficient presence of H_3PO_4 . In addition, the thermal
374 agitation of the system was opposed to aggregation. These two factors, in particular the
375 former, should play a decisive role on H_3PO_4 , which would tend to evaporate instead of

376 becoming loaded on CS, which would be in line with the observed variation of Σm with
377 the degree of dilution of the impregnation solution. In short, depending on whether the
378 concentration of the initial H_3PO_4 solution was lower or higher the process of either
379 vaporization or loading was more dominant in the SIT.

380

381 *3.2.2. Impregnation with dilute H_3PO_4 solution - step-by-step*

382 The significantly smaller loading of H_3PO_4 when the impregnation process was
383 effected by successively repeating it (DL1, DL2, DL3) as compared to the single
384 impregnation process strategy (DL1, DI1, D0) indicates that the H_3PO_4 -impregnated
385 product resulting from a previous impregnation process (consisting of both soaking and
386 drying steps) became passivated to its further impregnation with a fresh aliquot. This is
387 ascribable to changes produced in the chemical composition of CS as a result of the
388 previous impregnation process, namely the lixiviation of soluble fractions and the
389 hydrogen bonding between H_3PO_4 and polar oxygen species in CS. Such a composition
390 should mainly be affected during the SIT as H_3PO_4 concentrated in the transient liquid
391 in contact with CS, and as a result, its reactivity against CS structural biopolymers
392 should increase, as evidenced by previously reported results. Thus, hemicelluloses are
393 readily soluble in water (Horvath 2006). Extractives are also removed by the action of a
394 polar solvent such as cold and hot water (Vassilev et al. 2012). From the chemical
395 standpoint, H_3PO_4 may act as a reactant or as a catalyst. As is well known, the H_3PO_4
396 molecule may condensate with one or more surface hydroxyl groups of metal oxides
397 giving one or more water molecules. Dilute H_3PO_4 at moderate temperature (i.e.
398 typically 1-10 wt.% and 100-150 °C; Lenihan et al. 2011) catalyzes the hydrolysis of the
399 hemicellulose fraction. However, it does not attack the cellulosic fraction to an
400 appreciable extent (Gómez et al. 2006).

401

402 *3.2.3. Impregnation with dilute H₃PO₄ solution - by filtering and washing*

403 From the very high sensitivity of the loading of H₃PO₄ on CS to the removal of
404 the supernatant liquid after the FIT of CS with the dilute H₃PO₄ solution and to the
405 washing of the residual product with distilled water, it is evident in turn not only that the
406 activating agent was scarcely prone to become loaded on the lignocellulosic substratum
407 in such a step of the impregnation process but also that the fraction of H₃PO₄ that
408 achieved it to a large extent was susceptible to be removed from the previously loaded
409 state by the washing action of water. From these results, it is evident that the interaction
410 of the substratum with H₃PO₄ was weak and that loading was then a reversible process.
411 On the other hand, these results prove that in the impregnation process most loading of
412 activating agent occurred during the SIT. It is likely that, after this impregnation step,
413 organic matter leached out before from CS by physico-chemical action of the dilute
414 H₃PO₄ solution (i.e. mostly hemicelluloses and extractives) was found either dissolved
415 in the residual liquid or simply deposited on CS, being then easily removed during the
416 filtration and washing operations and thus, also causing mass decrease.

417

418 *3.2.4. Impregnation with dilute H₃PO₄ solution - using the filtrate as an*
419 *impregnating solution*

420 The enhanced mass increase produced when the impregnation of CS was
421 performed using the filtrate obtained after the FIT as the impregnation solution was at
422 first surprising. Because of the presence in such a liquid of not only H₃PO₄ remaining in
423 excess after the previous FIT of a CS specimen but also of organic matter coming from
424 CS, it was expected that the effects of the impregnation solution (i.e. filtrate) on
425 biopolymers of a fresh CS specimen, due to processes of hydrolysis, catalysis, and so

426 on, would have been mitigated. However, when studying the hydrolysis of sugar cane
427 bagasse (SCB) using H_3PO_4 at the ratios of H_3PO_4 to SCB of 2, 4 and 6 % and heating
428 at 122 °C for 0-300 min (i.e. the reactant ratios are much lower and the treatment times
429 are much shorter than for the present study), it was found by Gámez et al. (2006) that
430 the solubilised fraction (SF) is a function of both the H_3PO_4 /SCB ratio and treatment
431 time. Thus, SF as a rule increases as both variables of the hydrolysis process increase.
432 However, for high reactant ratios and long treatment times SF markedly decreases.
433 From these results it becomes apparent that a stronger solubilisation effect at shorter
434 times to a great extent inhibits the process at longer times. It was also stated by the same
435 authors that in the operation of concentration of the hydrolysates by evaporation,
436 besides water, small amounts of growth inhibitors such as acetic acid, furfural and
437 hydroxymethylfurfural are removed (Gámez et al. 2006; Martínez et al. 2002 and
438 citations therein). Accordingly, it seems that to the mass increase produced when the
439 filtrate was used as the impregnation solution contributes the loading of not only H_3PO_4
440 but also of organic matter. The organic fraction may make up of products arising from
441 physico-chemical interactions of H_2O and H_3PO_4 with CS biopolymers in both FITs and
442 in the SIT which did not undergo evaporation during the SIT and that remained loaded,
443 perhaps simply deposited, on CS after the SIT.

444

445 3.2.5. Impregnation with concentrated H_3PO_4 solution – using commercial H_3PO_4

446 From the very high Δm obtained for C0 (i.e. the mass loss was as low as 20 wt.%
447 and it should be further taken into account the probable loss of indigenous water of CS
448 during the SIT) than for D0 it is evident the high tendency exhibited by H_3PO_4 to the
449 loading on CS, as an opposing effect to its removal by evaporation, during the
450 impregnation process, which consisted of the FIT and SIT.

451 In the FIT, it is likely that the swelling of CS in the H₃PO₄ solution was a very
452 important factor in connection with the loading process of H₃PO₄. Swelling was
453 accompanied by an increase in the pore size and accessible surface area of CS (Stone et
454 al. 1969), which should facilitate the diffusion of H₃PO₄ in CS and enhance the uptake
455 of H₃PO₄. Using cotton linters and 72.0 to 78.8% H₃PO₄ solutions at 2 °C, it was
456 observed earlier that they were swollen to an increasing extent with increasing
457 concentration of the acid solution. The swelling increase was especially sensitive only
458 for the most concentrated acid solutions. As a result of swelling, the surface area of the
459 cellulose gel was accessible to a molecule of 40 Å diameter (Stone et al. 1969). On the
460 basis of the higher concentration of the H₃PO₄ solution used in the impregnation of CS
461 (85 wt.% instead of 78.8 wt.% at most) and of the higher temperature of the swelling
462 system (i.e. 85 °C instead of 25°C), it may be speculated that the degree of swelling of
463 CS in such a solution was large, and that the swollen material was then internally
464 accessible even to large size molecular aggregates of H₃PO₄ present in the solution.
465 After swelling, H₃PO₄ should interact physico-chemically with chemical constituents of
466 CS. In relation to mass balance, the changes produced in the basic structural
467 components of CS are of particular relevance in the present study.

468 Because of its fibrous structure and the strong hydrogen bonds, cellulose is insoluble
469 in most solvents (Horvath 2006), including water and most common organic liquids
470 (Swatloski et al. 2002). However, it can be directly dissolved in concentrated acids, for
471 example, H₃PO₄, which possess higher reactivity toward hydrogen bonds than the dilute
472 acids (Harris and Lang 1947) and that disrupt such bonds in the cellulose chain and
473 convert it to an amorphous state. The de-crystallized cellulose forms a homogeneous gel
474 without the acid, which allows hydrolysis reactions (Orozco et al. 2007). The
475 dissolution of cellulose leads to hydrolytic cleavage of its chains, and the cellulose

476 molecules are transformed to derivatives, such as esters (Horvath 2006). The interaction
477 of mineral acids with polysaccharides proceeds via protonation of the oxygen atom on
478 glycosidic bonds, stabilization of the pyranosyl cation by mesomerism, formation of
479 oxonium ions by water addition, and stabilization of it by hydrogen splitting (Dobele et
480 al. 2003 and references therein).

481 Regarding lignin, this biopolymer has a very low solubility in most solvents. If a
482 solvent dissolves cellulose, then it is more likely that it also dissolves hemicelluloses
483 and lignin. If lignin is bonded to carbohydrates, it requires chemical degradation for
484 solution (Horvath 2006). Thus, there is no known method for isolating unaltered lignin
485 from plant cell walls, and chemical (or biochemical) degradation methods produce low
486 molecular weight products in modest yields only (Kilpelainen et al. 2007).
487 Nevertheless, Fierro et al. (2005) pointed out that the reaction of kraft lignin with 85
488 wt.% H_3PO_4 aqueous solution starts at room temperature as soon as they are mixed
489 since the temperature of the sample increases immediately. This observation was in
490 agreement with Lai (1991) who reported that cleavage of aryl ether bonds is
491 accompanied by dehydration, degradation and condensation reactions together with
492 formation of ketones by hydrolysis of ether linkages at low temperatures. According to
493 Jagtoyen and Derbyshire (1998), the reaction of wood with 28 wt.% H_3PO_4 solution
494 probably begins at temperatures as low as 50-100 °C first with the attack of
495 hemicellulose and lignin. Loss of carboxyl and methyl groups from hemicelluloses even
496 at 50 °C and changes in lignin composition occurred.

497 In the light of the above statements it is clear that under the soaking conditions of
498 CS with the concentrated H_3PO_4 solution not only hemicelluloses (and extractives), as
499 described above, but also cellulose and lignin were susceptible to interact physico-
500 chemically with H_3PO_4 . Probably, the action of this acid during the FIT was controlled

501 by the accessibility of the CS biopolymers, which will depend on factors such as the
502 swelling process and chemical structure of CS. In the first place, it is worth underlining
503 again here that a characteristic of the swelling of lignocellulosic materials is its
504 anisotropy, which is important as the degree of swelling should determine the internal
505 surface area of contact between the solid and liquid phases. Furthermore, composition
506 changes produced as a result of such a process would further increase the accessible
507 porosity. This was associated with the removal of hemicelluloses by Grethlein (1985).
508 However, it was also stated that the attack first of the hemicellulose and lignin by
509 H_3PO_4 was due to an easier access to these biopolymers than to the crystalline cellulose
510 (Jagtøyen and Derbyshire 1998). Therefore, the acid treatment to some extent may strip
511 hemicelluloses and lignin. For cellulose, ordered regions and highly disordered regions
512 exist alternatively in its fibrils (Ho et al. 2011). A limited swelling of the amorphous
513 cellulose (i.e. dependent on the hydrogen bonding strength and molecular size of the
514 solvent) would not cause intercrystalline swelling (Horvath 2006). Neither water nor
515 other small molecules can penetrate the very tight crystallites. Out of the main
516 biopolymers of lignocellulosic materials, cellulose is therefore the most recalcitrant one.

517 In the SIT, an important factor related to the thermal stabilization and loading
518 process of H_3PO_4 was likely the degree of association of H_3PO_4 in the transient
519 impregnating liquid before its loading on CS. As compared to the initial concentrated
520 solution, a further aggregation of H_3PO_4 in the aforesaid liquid was possible, provided
521 that the kinetics of the evaporation process for water was faster than that of the loading
522 process for H_3PO_4 as it should result in a concentration increase. Because of the
523 influence of concentration on physical properties such as viscosity, boiling point, and
524 vapour pressure, it would enable smaller H_3PO_4 aggregates to become closer and to
525 interact slower during longer by cohesive forces. Eventually, a viscous syrupy liquid

526 may be formed as the amount of H_3PO_4 contained in the impregnation solution (i.e.
527 144.5 g in 100 mL of solution) was much larger than that of CS (i.e. 25 g). Since CS can
528 be regarded as a high energy solid, as the bonds between atoms of its constituent
529 chemical elements are very strong, such a liquid should achieve complete wetting with
530 its surface. Of course, adhesion should be strong and/or extensive enough to the loading
531 process was feasible from the thermodynamic standpoint. Loading would prevent
532 H_3PO_4 from evaporation, with the consequent mass increase of IPs. However, loading
533 may be hindered as a result of textural changes produced in the material because of
534 drying (i.e. hornification is the term used in the paper industry to describe such
535 changes). Thus, when wood pulp was dried by various methods it was found by
536 Esteghlalian et al. (2001) that it significantly reduced the population of larger pores and
537 that the partial closure of larger pores created a larger number of smaller pores. These
538 textural effects may render the diffusion of H_3PO_4 in CS porosity difficult and its
539 evaporation from the liquid state easier than from the loaded state, which would become
540 stabilized against evaporation.

541 After wetting, if H_3PO_4 were found in liquid state, it would dissolve cellulose,
542 which may be hydrophobic or hydrophilic in nature. In fact, it was previously reported
543 that anhydrous phosphoric acid (i.e. with a P_2O_5 concentration above 74%,
544 superphosphoric acid) is an excellent direct solvent for cellulose (Boerstael et al. 2001).
545 Furthermore, by treating the cell walls chemically, it is possible to isolate smaller or
546 wider cellulose fibril aggregates. Since cellulose fibers are commonly negatively
547 charged due to the presence of $-O^-$ and $-COO^-$ groups, which arise from deprotonation
548 of alcohol and small amounts of carboxylic acid groups respectively (Ho et al. 2011),
549 and H_3PO_4 in liquid state undergoes extensive self-ionization (Greenwood and Earnshaw
550 1989), the formation of sorts of ion pairs in the suspension would further contribute to

551 stabilize the cellulose aggregates in the impregnation system. In addition, the
552 stabilization of lixiviated organic matter by hydrophobic interactions occurring either in
553 the bulk of the suspension or with the remaining un-attacked fraction of the
554 lignocellulosic substratum should not be ruled out. In this connection, it should be
555 recalled here that hydrophobic compounds commonly possess a long hydrocarbon chain
556 with little reactive functional groups or its ionic charge is screened. Finally, because a
557 high molecular weight, aforesaid aggregates should have a low tendency to vaporize. In
558 short, they should be prone to remain in the system after the SIT, contributing to the
559 final mass of IP.

560

561 *3.2.6. Impregnation with concentrated H₃PO₄ solution – using H₃PO₄ after oven-* 562 *drying*

563 When the concentrated H₃PO₄ solution was oven-dried for 2-24 h prior to the use in
564 the impregnation process of CS, the variation of Δm was noticeably irregular and
565 sometimes more significant (see data in Table 3). After oven-drying such a solution
566 itself, it was observed that its volume reduction was strongly time-dependent. It was
567 practically inappreciable for 2 and 24 h and approximately 10 vol.% for 12 h (instead of
568 as low as 10 vol.% at most, as previously erroneously reported; González-Domínguez et
569 al. 2011). Although it was expected that the volume reduction was slight because of the
570 high concentration of the H₃PO₄ solution (i.e. the content of P₂O₅ in a 85 wt.% H₃PO₄
571 solution is 61.55 wt.%; Toy 1973), it is exceedingly smaller in some instances, as for the
572 heating time of 24 h. Since the 85 wt.% solution H₃PO₄ must contain the dimeric
573 species (H₃PO₄)₂ (i.e. two acid molecules associated via hydrogen bonding) (Wertz and
574 Cook 1985), the degree of H₃PO₄ aggregation and the loss of water by evaporation
575 should increase with heat treatment time. During the FIT of CS with the resulting

576 H₃PO₄ concentrated solutions, the stirring of the heterogeneous mixture became more
577 difficult. Furthermore, solidification occurred practically at the end of the FIT for C12
578 and the formation of a solid phase on the surface of a very viscous liquid was easily
579 visible for C24. After the SIT of the residual heterogeneous mixture, which was made
580 up of a solid and a more or less viscous liquid, a sponge-like compact mass was
581 obtained, the appearance of which being quite different from that of Series 1 and 2 IPs.
582 From these observations it is clear that the previous oven-drying of the H₃PO₄ solution
583 markedly influenced the physical properties of the liquid in contact with CS during the
584 SIT. As compared to the impregnation treatment with the non oven-dried solution, it
585 was expected that as a result of water vaporization during the previous heating a more
586 concentrated solution of H₃PO₄ was longer in contact with the substrate during the SIT
587 and that this would influence the degree of H₃PO₄ aggregation and the size of the
588 aggregates loaded on CS. The occurrence of changes in the chemical composition of
589 H₃PO₄ should not be ruled out on account of the concentration increase. Nevertheless,
590 in this connection it should be borne in mind, however, that impregnation was carried
591 out by heating at 85 and 120 °C in the successive steps of the impregnation process and
592 that the formation of the dimer H₄P₂O₇ by condensation reactions involving H₃PO₄
593 occurs at temperatures as high as 213 °C (Platanov 2000) and 240 °C (Sharpe 1989).

594

595 *3.2.7. Using CS chars as the feedstock*

596 The Δm increase for S200D and for S300D (i.e. both IPs prepared with the dilute
597 H₃PO₄ solution) is ascribable to porosity development in CS as a result of the charring
598 process as it should favour the diffusion of the impregnation solution in the chars and
599 hence, the loading of H₃PO₄. Porosity was created due to the loss mainly of water at 200
600 °C and of water and hemicelluloses at 300 °C (Liu et al. 2011; Yang et al. 2007).

601 Therefore, the thermal effect on the texture of CS embraced the entire mass of CS. In
602 this respect, it was different from that of swelling as this process is characterized by its
603 anisotropy. In accordance with the Δm values, the textural effect on the loading of
604 H_3PO_4 was markedly stronger for S300D than for S200D, as expected, since the mass
605 loss produced by dehydration and partial devolatilization of CS was higher when
606 charring at 300 °C. In addition, the size of chemical species removed from CS was
607 different at both charring temperatures, which should influence the porosity distribution
608 and accessibility in the charred products and as a last resort the loading process.

609 S200C and S300C were prepared with the commercial concentrated H_3PO_4 solution.
610 For S200C, as compared to C0, the Δm values indicate that loading slightly decreased.
611 In the case of S300C, however, a certain amount of readily visible liquid remained after
612 oven-drying at 120 °C for 24 h in the SIT. Such a liquid was separated by filtration and
613 the residual impregnated product was oven-dried again. Clearly, these results advocate
614 for a restricted diffusion of H_3PO_4 in the chars. Likely, it was due to the presence of
615 narrow pores in the chars and of large H_3PO_4 molecular aggregates in the impregnation
616 solution. The size of the pores would be determined not only by the size of the matter
617 affected by dehydration and devolatilization processes of CS and by its distribution in
618 the bulk of the mass of CS but also by another concurrent thermal effect of mass
619 contraction. This would be responsible for a further porosity shrinkage which rendered
620 its access more difficult. Surely, it also decreased the degree of swelling of the chars in
621 the impregnation solution and as a last resort the loading of H_3PO_4 . In part, **as least**,
622 loading should be mechanical instead of by a physical or chemical process. On the other
623 hand, the stronger unfavourable effect for S300 is attributable to a more limited
624 swelling of this char than of S200 in the impregnation solution. It should prevent H_3PO_4
625 from accessing biopolymers still remaining in the char and thereby from becoming

626 stabilized in the loaded state. Despite this, H₃PO₄ remained in the system saturating the
 627 char, as expected. Thus, 120 °C is a temperature well below the boiling point of H₃PO₄
 628 (Brown and Whitt 1952) and at this temperature, H₃PO₄ possesses a low vapour
 629 pressure, and therefore, it must evaporate slowly.

630

631 3.3. Implications in the AC development and composition

632 By subjecting to thermal treatment to all the aforesaid IPs (at 500°C for 2h), a wide
 633 range of activated carbons can be prepared (González-Domínguez et al. 2017). As seen
 634 in Table 4 and Figure 4, high concentrations of the H₃PO₄ activating agent usually
 635 produce high specific surface areas (~ 1500 m² g⁻¹), while lower H₃PO₄ amounts create
 636 narrower pores and more homogeneous pore size distributions. The efficiency of the
 637 activation process can be improved through the control of the thoroughly described
 638 impregnation variables:

639

640 **Table 4:** Surface characterization of the AC derived from the IPs described in the
 641 present work. B.E.T. surface area (González-Domínguez et al. 2017) and chemical
 642 surface composition obtained by XPS.
 643

AC sample	S _{BET} (m ² /g)	Surface at. %			
		%C	%N	%O	%P
DA	640	80.5	2.0	15.2	2.0
DL1A	123	84.9	1.4	11.4	2.3
DL2A	512	86.1	0.5	10.9	2.5
DI1A	351	82.3	1.1	13.9	2.8
DL3A	837	82.6	1.7	13.1	2.6
DFA	134	84.5	1.5	11.9	2.2
DFWA	337	87.3	2.3	10.4	~ 0

DRLA	791	82.8	1.9	12.9	2.3
C0A	1491	91.2	~ 0	6.7	2.1
C2A	1203	88.2	~ 0	8.8	2.9
C6A	1441	90.1	~ 0	7.6	2.3
C12A	1440	90.8	~ 0	7.0	2.2
C24A	1438	87.3	~ 0	9.8	2.9
S200DA	660	85.8	~ 0	11.6	2.6
S300DA	330	82.7	1.2	12.4	2.9
S200CA	1489	85.7	~ 0	10.8	3.5
S300CA	596	75.1	0.9	17.7	2.9

644

645

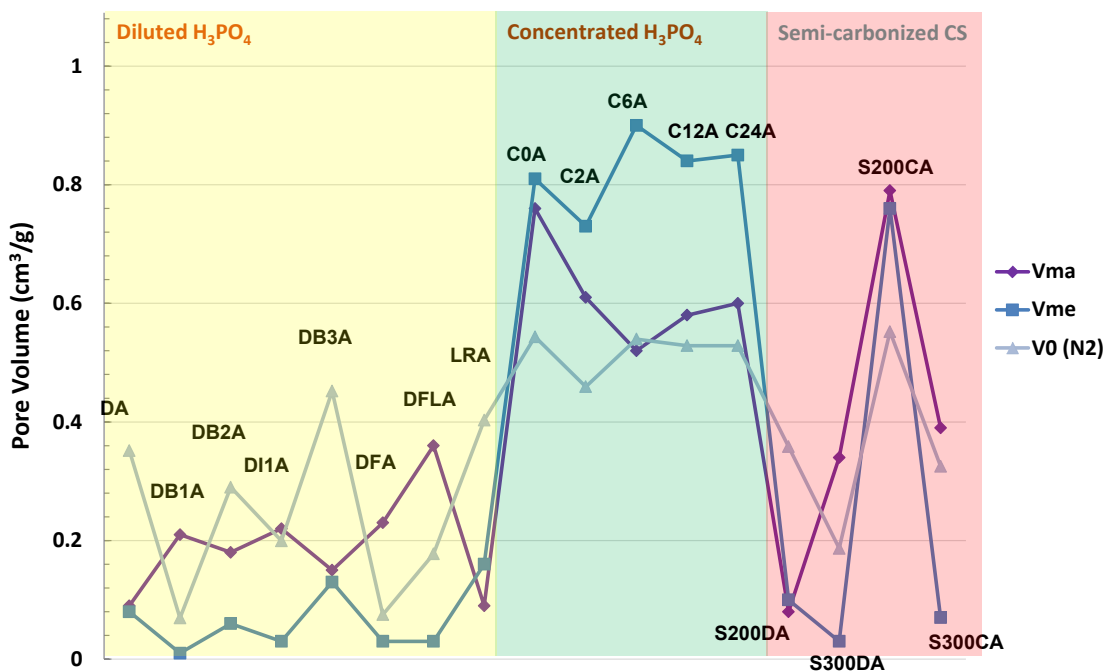
646 • Number of impregnation steps: porosity development increases when the
647 impregnation is performed in several steps with dilute solutions, instead of only one
648 impregnation with an identical amount of H₃PO₄. Similarly, super-concentrating the
649 commercial H₃PO₄ solution does not lead to further increases in the porosity.

650 • Reutilization of the H₃PO₄ solution: two activated carbons (337 and 791 m² g⁻¹) can
651 be prepared with the same H₃PO₄ amount that is needed for the preparation of only
652 one adsorbent (640 m² g⁻¹) by direct impregnation.

653 • From activation experiments starting with semi-carbonized CS, it has been
654 recognized that biopolymer components decomposed at 300 °C play a key role in the
655 activation mechanism with H₃PO₄.

656 • As regards the surface chemical composition, the series of AC which underwent
657 impregnation with diluted H₃PO₄ solutions present a C/O ratio in the range of 5 – 8,
658 while concentrated impregnation solutions give rise to a C/O ratio in the range of 10

659 – 14. Nitrogen contents also differ significantly from one case to the other, being
 660 almost inexistent for ACs impregnated with concentrated H_3PO_4 solutions.
 661 Surprisingly, the phosphorus content seems to be practically unaltered in all cases.
 662 Further, the effect of semi-carbonization is also visible.
 663 The operational strategies studied in this work can be applied to the efficient preparation
 664 of activated carbons with tailored porosities and surface chemistries for specific
 665 applications, according to the underlying chemical processes occurring between H_3PO_4
 666 and biomass.
 667



668
 669 **Fig. 4.** Compendium of pore volumes of the different AC samples obtained after
 670 carbonization of the IPs described in the present paper. $V_{0(N_2)}$ = micropores by nitrogen
 671 adsorption; V_{me} = mesopores by mercury porosimetry; V_{ma} = macropores by mercury
 672 porosimetry. (González-Domínguez et al. 2017).
 673

674

675 4. Conclusion

676 A wide series of non-conventional strategies was used in the impregnation of CS
 677 with H_3PO_4 in aqueous solution (González-Domínguez et al. 2011, 2017). In this

678 technical report, the results previously collected from such experiments are
679 comprehensively discussed and linked to essential chemistry knowledge, eventually
680 drawing potentially interesting information. The mass changes were evaluated and
681 tentatively accounted for, in general, by considering them dependent on the
682 concentration of the H₃PO₄ solution and its chemical and physical properties, their
683 evolution along de impregnation process and influence on the degree of association and
684 loading of H₃PO₄, in connection with the biopolymer composition of the lignocellulosic
685 substratum and with its wetting, swelling and/or shrinkage. Valuable information is
686 inferred with a view to setting up experimental methods that may pave the way towards
687 a controlled interaction of H₃PO₄ with the feedstock and as a last resort preparation of
688 activated carbon with tailored textural properties to be used with specific ends. In
689 summary, by using dilute H₃PO₄ solutions in the impregnation stage, one can obtain a
690 higher porosity development in ACs by successive steps with lower H₃PO₄
691 concentration, rather than in a single step with a more concentrated acid. The
692 reutilization of H₃PO₄ is feasible, and provides a means to fabricate ACs with lower
693 reagents consumption and good properties. Finally, the use of concentrated H₃PO₄
694 solutions or CS chars as the feedstock can be advantageous for obtaining ACs with high
695 porosity.

696

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701

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