

1 Mechanochemical and chemical activation of lignocellulosic material to
2 prepare powdered activated carbons for adsorption applications

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29 **Abstract**

30 This work presents a solvent-free mechanochemical approach toward controlled
31 preparation of powdered activated carbons from lignocellulosic residue (horse chestnut
32 shell, CS). The physicochemical changes of the biomass during mechanochemical and
33 chemical activation with K_2CO_3 and the properties of the final materials obtained after
34 pyrolysis at 700 °C have been investigated by means of thermogravimetric analysis (TG-
35 DTG), scanning electron microscopy (SEM), X-ray diffraction (XRD), N_2 adsorption-
36 desorption, infrared and micro-Raman spectroscopy. The results indicated that the
37 mechanochemical activation is superior to the traditional chemical activation in terms of
38 specific surface area, pore development and the degree of structural order of the activated
39 carbons. Furthermore, it has been observed that the later parameters depend on the
40 milling time and the maximal BET surface area ($1040 \text{ m}^2/\text{g}$) and total pore volume (1.01
41 cm^3/g) of the resulting mesoporous material can be obtained after 3h milling of the raw
42 material/ K_2CO_3 mixture. In addition, malachite green oxalate (MGO) adsorption
43 capacities of the carbons were also examined and adsorption uptake up to 250 mg/g is
44 observed. This study demonstrates the potential use of CS as a precursor in the
45 preparation of activated carbon for adsorption applications and opens up new ways for
46 activation of lignocellulosic materials under ball-milling conditions.

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50 **Keywords:** activated carbon; lignocellulosic residue; mechanochemical activation;
51 chemical activation; microstructure; adsorption

52 **1. Introduction**

53 The preparation of activated carbons (ACs) with appropriate structural and chemical
54 properties has gained much attention over the last decades (Marsh and Rodríguez
55 Reinoso, 2006). Due to their highly developed internal surface area, porous structure and
56 high degree of surface reactivity, ACs are widely used as adsorbents in a variety of
57 industrial fields for water purification, gas separation and catalysis [1-3]. Furthermore,
58 porous carbon materials play an important role in numerous emergent applications such
59 as storage of electrical energy in supercapacitors [4], immobilization and separation of
60 large biomolecules [5], CO₂ capture [6] and hydrogen storage [7]. Activated carbon can
61 be produced from a wide range of carbonaceous precursors such as bituminous coal,
62 wood, coconut shell, peat, petroleum pitch, and polymers [8]. Among all the precursors,
63 lignocellulosic residues have received an increasing attention due to their low-cost,
64 renewability and wide prevalence [9]. A huge number of lignocellulosic biomass based
65 ACs such as bamboo [10], cherry stones [11], rice husk and bagasse [12], coffee endocarp
66 [13], potato peels [14] and peanut shells [15] have been reported.

67 There are two methods for preparing activated carbon – physical and chemical
68 activation. The physical activation consists of the pyrolysis of the carbonaceous
69 precursor and gasification of the char at high temperatures. In chemical activation (also
70 called wet oxidation) process, the raw material is first impregnated by strongly reacting
71 chemicals such as ZnCl₂, H₂SO₄, NaOH, KOH, K₂CO₃, K₂HPO₄ or H₃PO₄, followed by
72 thermal activation in an inert atmosphere. In the latter method, the dehydrating effect of
73 the used activating agents hinders the formation of tar which lead to higher AC yield and
74 to lower activation temperature than those reported for the physical activation [16]. In

75 addition, ACs obtained by chemical activation demonstrate higher surface area and better
76 developed mesoporosity than physical activation [17].

77 Mechanochemical activation of the precursors can be considered as another
78 method for fabrication of AC. Ball-milling has proved to be effective for preparing
79 ceramic powders [18] and nanomaterials [19], for conducting solvent-free organic
80 reactions [20] and for degradation of waste materials [21]. Mechanochemistry offers
81 several benefits over traditional solvent-based protocols like simplicity, mild/short
82 reaction conditions, ease of scale-up and the ability to synthesize metastable phases [22].
83 Performing reactions without the need of solvents is advantageous, as it is eco-friendly
84 and low-cost process. Nevertheless, as far as we know, this technique has rarely been
85 applied for the activation of carbonaceous precursors in preparation of AC powders.

86 In this study, we investigate the potential of mechanochemical treatment of
87 lignocellulosic biomass/activating agent mixtures under solvent-free conditions as an
88 alternative route for preparation of AC. Horse chestnut shell was chosen as a renewable
89 carbon resource. Horse chestnut (*Aesculus hippocastanum*) is a deciduous tree native to
90 the Balkan Peninsula, but grow throughout the Northern Hemisphere [23]. Horse
91 chestnut is one of the most attractive ornamental trees and is planted widely in parks and
92 gardens in both urban and rural areas in Europe, e.g. at least 20 000 horse chestnut trees
93 grow in Vienna and its environs [23]. Although the dried ripe seeds of the tree are of
94 medicinal interest, the horse chestnut shell has no significant industrial and commercial
95 use. Because of the prevalence of the species, horse chestnut shell can be considered as
96 an inexpensive raw material in AC fabrication.

97 The main goal of the present work is to determine the effects of the solid state
98 mechanochemical activation of chestnut shell in the presence of K_2CO_3 on the

99 physicochemical characteristics and adsorption properties of the as-prepared ACs in
100 comparison to the traditional chemical activation method. In the first part of the paper,
101 the structural and compositional transformations in the course of ball-mill-based
102 mechanochemical activation of horse chestnut shells in the presence of K_2CO_3 are
103 examined. The mechanochemically obtained precursors have been heated at 700 °C in
104 order to obtain porous carbons and their morphological, structural and textural features
105 are reported in the second part of the paper. The prepared materials have also been tested
106 in the adsorption of malachite green oxalate from aqueous solution at room temperature
107 (25 °C). For the sake of comparison, AC prepared by traditional chemical activation
108 method *via* impregnation of the raw material with K_2CO_3 is also assayed.

109

110 **2. Experimental**

111 *2.1. Materials*

112 Horse chestnut (*Aesculus hippocastanum*) seeds were collected from a park region in
113 Sofia, washed thoroughly with distilled water, dried at room temperature and peeled to
114 get the shells off. The shells were washed once again, dried at 110 °C for 6 h, crushed
115 and sieved. Fraction with particle size of 1–1.7 mm was used in the rest of our work
116 (denoted as CS). For the characterization of CS proximate and elemental analyses were
117 performed. Moisture, volatile matter, fixed carbon and ash contents of the raw material
118 were determined according to the ASTM standard methods. Elemental analyses were
119 performed with Carlo Erba 1106 combustion elemental analyzer. Sulfur content was
120 determined by Eshka method. The proximate, ultimate and component analyses of CS
121 sample are shown in Table 1.

122 In order to obtain mechanically activated precursors, the raw material (CS) was
123 mixed with K_2CO_3 at the K_2CO_3/CS mass ratio of 1:1 and the mixture was milled in a
124 planetary ball mill Pulverisette 5 (Fritsch) at 550 rpm with the ball-to-powder mass ratio
125 of 10:1. Before the experiments, potassium carbonate (>99 %, Fisher Chemical) was
126 dehydrated at 120 °C overnight. The samples (denoted as CSK-*t*) were treated for 1, 2, 3
127 and 4 hours (*t*). CS powder was also milled at the same conditions for the same times
128 (samples named CS-*t*). For traditional wet oxidation, CS powder was kneaded with
129 saturated aqueous solution of K_2CO_3 (K_2CO_3/CS mass ratio of 1:1) at room temperature
130 and the mixture was then dried at 110 °C for 6 hours. The obtained impregnated sample
131 is denoted as CSK-W. The carbonization of CSK-*t* and CSK-W samples was performed
132 in a conventional horizontal furnace at 700 °C in nitrogen flow. In each run the activation
133 temperature was reached at a 10 °C/min heating rate and maintained for 1 h. The resulting
134 carbons were washed with doubly distilled water till neutral pH and dried at 110 °C
135 overnight. The activated carbons prepared from CSK-*t* precursors are denoted as AC-*t*
136 and from CSK-W as AC-W.

137 2.2. Methods

138 The thermal behavior of CS, CS-*t*, CSK-*t* and CSK-W samples were studied by
139 thermogravimetry (TG) and derivative thermogravimetry (DTG) in nitrogen atmosphere,
140 using Perkin-Elmer TGS-2 thermobalance. The total weight losses of the samples were
141 determined from the corresponding TG curves at the final heating temperature of 700 °C.
142 Powder X-ray diffraction (XRD) patterns of the samples were recorded at room
143 temperature on the Bruker D8 Advance diffractometer using $CuK\alpha$ radiation. The
144 morphology and the microstructure of CS, CS-*t*, CSK-*t*, AC-*t* and AC-W were analyzed
145 by scanning electron microscopy (SEM, JEOL 5510) applying gold coating before the

146 observation. The Fourier transform infrared (FTIR) spectra (KBr pellets) of the studied
147 samples were recorded between 4000 and 400 cm^{-1} by using Nicolet 6790 FT-IR
148 (Thermo Scientific) spectrometer.

149 Raman spectra of AC-*t* and AC-W samples were measured using micro-Raman
150 spectrometer HR 800 (Jobin Yvon). The grating utilized is 600 gr/mm. The excitation is
151 provided by the built-in He-Ne laser, at 632.8 nm. The laser intensity on the sample was
152 less than 0.06 mW and the spectral accuracy achieved is better than 1 cm^{-1} . Each
153 spectrum is an average of 5 spectra, obtained from 5 different points from the sample
154 with objective x50.

155 The texture characteristics of activated carbons were determined by low-
156 temperature (77.4 K) nitrogen adsorption in a Quantachrome Instruments NOVA 1200e
157 apparatus. The nitrogen adsorption–desorption isotherms were analyzed to evaluate the
158 following parameters: the specific surface areas (S_{BET}) were determined on the basis of
159 the BET equation, the total pore volume (V_t) was estimated in accordance with the
160 Gurvich rule at a relative pressure close to 0.99. The volume of the micropores (V_{MIC})
161 and specific surface area connected to micropores (S_{MIC}), as well as the external specific
162 surface area (S_{EXT}) were evaluated according to V-t-method. Additionally, the pore-size
163 distributions were calculated by DFT method using slit pore, NLDFT (nonlocal density
164 functional theory) equilibrium model. All samples were outgassed for 16 h in vacuum at
165 120 °C before the measurements.

166 Batch adsorption experiments were carried out by agitating 0.04 g of AC-*t* and AC-
167 W in 125 mL (100 mgL^{-1}) of malachite green oxalate (MGO, $\text{C}_{48}\text{H}_{50}\text{N}_4\text{O}_4 \cdot 2\text{C}_2\text{H}_2\text{O}_4$, 90%
168 dye content, Aldrich) aqueous solutions in an incubator at 25 °C for 72 h to ensure that

169 the adsorption equilibrium is reached. The adsorbed amounts were then calculated from
170 the difference between the initial and equilibrium concentration of the dye, as determined
171 with UV-Vis absorption spectroscopy (Evolution 300 Thermo Scientific
172 Spectrophotometer).

173

174 **3. Results and discussion**

175 *3.1. Mechanochemical treatment vs impregnation of raw biomass*

176 *3.1.1. TG-DTG*

177 The TG and corresponding derivative (DTG) curves for the raw material (CS), CSK-*t*
178 and CSK-W samples are compared in Fig 1a, b. The TG curve of CS reveals a total loss
179 of 62.7% at 700 °C. As shown, the DTG curve exhibits three main decomposition steps
180 at 74, 250 and 317 °C, and above this temperature a gradual weight loss is observed.
181 Based on the literature survey on the pyrolysis of lignocellulosics [25], the
182 decomposition of CS starts with desorption of the adsorbed water, followed by the
183 decomposition of hemicellulose (180-285 °C) and of cellulose in the range 275-365 °C.
184 Lignin is the last component to decompose, over a temperature range of 365-500 °C. As
185 can be seen, the milling of the raw material in the presence of K₂CO₃ has a significant
186 effect on the thermal decomposition of the horse chestnut shell. First, the weight loss
187 decreases gradually with increasing milling time (44.8% for CSK-1 and 37.2% for CSK-
188 4). Second, the pyrolysis of lignocellulose occurs at lower temperatures (main DTG
189 peaks at 260 °C and 269 °C for CSK-1 and CSK-2, 3, 4, respectively) in one step over a
190 broad temperature range between 160 °C and 400 °C. Undoubtedly, these effects are due
191 to the fact that K₂CO₃ promotes dehydration and oxidation of CS at lower temperature
192 and accelerates the carbonization. These results are similar to those reported by Horikawa

193 et al. [10] on the TG behavior of K₂CO₃-impregnated bamboo. For the sake of
194 comparison, thermogravimetric analysis of CS-1 and CS-4 samples has also been
195 performed and the resulting curves are shown in Fig. 1c, d. As shown, TG-DTG profiles
196 are very similar to that of CS and, furthermore, the weight loss do not change with milling
197 time. The only difference between the curves in Fig. 1d is the shift to lower temperatures
198 of the DTG peaks of lignocellulose components with increasing milling time. One can
199 explain the observed decrease of decomposition temperatures with variations in particle
200 size between samples, i.e. decreasing the particle size as a result of milling (see below)
201 decreases the starting and peak temperatures in TG-DTG curves.

202 The thermogravimetric data for CSK-W sample are shown as inserts in Fig. 1.
203 The TG curve of CSK-W reveals a total loss of 39.5 %. Similar to CSK-*t* data, the main
204 DTG step occurs at lower temperature than for CS, indicating the influence of
205 impregnated K₂CO₃ on the pyrolysis of CS. In addition, the DTG curves of CSK-*t* and
206 CSK-W exhibit decomposition steps around 130 °C and at 171 °C, respectively. We
207 tentatively attribute these events to the decomposition of potassium compounds formed
208 during the milling/impregnation processes.

209 3.1.2. FTIR

210 FTIR spectroscopy was used to determine the changes that occur in the chemical
211 composition of the biomass during mechanochemical and impregnation treatments.
212 Selected FTIR spectra are reported in Fig. 2a. The spectrum of CS is very similar to the
213 FTIR spectra of sweet chestnut (*Castanea sativa*) and Chinese chestnut (*Castanea*
214 *mollissima*) shells reported recently [26,27]. The broad band observed at 3420 cm⁻¹
215 indicates the existence of free and intermolecular bonded hydroxyl groups. The band at

216 2922 cm^{-1} and its shoulder at 2859 cm^{-1} are attributed to the C–H stretching and bending
217 vibrations, respectively. The peak around 1735 cm^{-1} is typical for hemicellulose and
218 shows the carbonyl (C=O) stretching vibration of ketons, aldehydes or carboxylic groups.
219 The bands at 1613 cm^{-1} and 1520 cm^{-1} indicate aromatic skeleton vibrations of lignin
220 fraction. The bands at 1445 cm^{-1} and 1282 cm^{-1} are due to the aliphatic part of lignin and
221 to C–O–C stretching in ethers, respectively. The peaks in the region of 1108 to 1010 cm^{-1}
222 represent the C-O stretch band and deformation bands in lignin, cellulose and
223 hemicellulose. As can be seen from the FTIR spectra presented in Fig. 2a,
224 mechanochemical treatment introduces substantial changes in the spectrum of CS. The
225 peak at 1735 cm^{-1} is absent in the spectrum of CSK-1 which indicates that most of the
226 hemicellulose was removed during the first hour of milling. Furthermore, the peaks at
227 1613 cm^{-1} , 1520 cm^{-1} , 1445 cm^{-1} and at around 1057 cm^{-1} decrease significantly and even
228 disappear in CSK-4 and CSK-W spectra. Thus, it appears that during the ball-milling
229 process, K_2CO_3 interacts with CS and as a result considerable deconstruction of
230 lignocellulosic biomass matrix takes place. This conclusion is strongly supported by the
231 absence of any significant changes in the FTIR spectrum of CS after milling for the same
232 times without K_2CO_3 (see Fig. 2b). Similar changes occur during wet impregnation of
233 CS, as indicated in the FTIR spectrum of CSK-W. Meanwhile, additional peaks appear
234 in the spectra of K_2CO_3 -treated materials. Two large bands at *ca.* 1650 cm^{-1} and at *ca.*
235 1410 cm^{-1} can be observed in the CSK-4 and CSK-W spectra. They are attributed to C=O
236 and C–O vibrations in the carbonate group, respectively [28]. According to the literature,
237 the band at 830 cm^{-1} is characteristic of KHCO_3 , while the band at 670 cm^{-1} is due to the
238 presence of K_2CO_3 [28].

239 3.1.3. SEM

240 The morphological changes during mechanochemical treatment of CS and CSK
241 have been assessed by SEM. Fig.3a, b reveals that in the course of the milling process a
242 gradual fracturing and size reduction of the CS particles occur. Thus, after 4h milling
243 only individual grains and aggregates smaller than about 5 μm are detected. In contrast
244 to the CS-*t*, SEM images from CSK-1 and CSK-4 (Fig. 3c, d) show that after 1h milling
245 a reduction of particle size occurs but with increasing milling time a process of particles
246 consolidation takes place and the image of CSK-4 reveals the presence of particles larger
247 than 5 μm .

248 3.1.4. XRD

249 In order to gain additional insights into the chemical composition of CSK-*t* and
250 CSK-W samples, XRD measurements have been performed. XRD patterns of CS,
251 starting K_2CO_3 , CSK-*t* and CSK-W are compared in Fig. 3e. The X-ray diffractogram of
252 CS shows two broad peaks at $2\theta=15.2^\circ$ and $2\theta=22.5^\circ$, which are consistent with cellulose
253 I lattice [29]. As shown, these peaks are not detected in the XRD pattern of the CS/ K_2CO_3
254 mixture after 1h milling. Another important observation is that the diffraction peaks of
255 K_2CO_3 are not identified in the patterns of CSK-*t* and, furthermore, a gradual change in
256 the phase composition with milling time occurs. Namely, XRD analysis of CSK-1 shows
257 the presence of KHCO_3 and $\text{K}_4\text{H}_2(\text{CO}_3)_3 \cdot 1.5\text{H}_2\text{O}$, but with increasing milling time the
258 peaks of $\text{K}_4\text{H}_2(\text{CO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ diminish while the intensities of XRD diffraction peaks of
259 KHCO_3 increase. Finally, the pattern of CSK-4 shows only the diffraction maxima of
260 KHCO_3 phase. Obviously, hydration and carbonation of K_2CO_3 occur in the course of
261 CS treatment. This fact is not surprising taking into account that K_2CO_3 is a well-known
262 chemisorbent, which reacts with atmospheric CO_2 in the presence of water vapor forming
263 KHCO_3 . It has been reported that the mixed potassium carbonate–hydrocarbonate phase

264 $K_4H_2(CO_3)_3 \cdot 1.5H_2O$ is a by-product of K_2CO_3 carbonation in wet atmosphere [30]. The
265 rate of $K_2CO_3 \rightarrow KHCO_3$ conversion increases with increasing milling time and this
266 result can be due to the increased sorption activity of potassium-containing species
267 towards ambient air. One can also safely assume that the K_2CO_3 conversion is accelerated
268 due to additional amounts of CO_2 and H_2O released in the milling vessel as a result of
269 lignocellulose degradation.

270 The results presented above clearly indicate that ball-milling of CS in the presence
271 of K_2CO_3 leads to the substantial degradation of lignocellulosic material. The latter
272 accelerates the carbonization of CS and leads to higher carbon yield. In this respect, the
273 mechanically-driven chemical changes in CS after 2h milling are comparable to those
274 obtained during chemical activation. Part of K_2CO_3 in the CSK-*t* is converted to
275 $K_4H_2(CO_3)_3 \cdot 1.5H_2O$ and $KHCO_3$ as a result of hydration and carbonation processes. The
276 weight loss observed in TG-DTG curves of CSK-*t* and CSK-W in 100-200 °C range can
277 be attributed to the dehydration of these phases.

278 3.2. Characterization of activated carbons

279 3.2.1. SEM

280 SEM examinations shown in Fig. 4 revealed that after pyrolysis of CSK-*t* at 700 °C a
281 significant amount of pores were developed on the surfaces of the biochars. The SEM
282 image of the raw material displays a smooth surface, with relatively large cracks. SEM
283 micrograph of AC-1 shows a wrinkled surface with circularly shaped macropores with
284 sizes between 0.06 μm and 0.2 μm . SEM images of AC-2, 3, 4 at the same magnification
285 reveal a progressive development of smooth surfaces, riddled with homogenously
286 distributed macropores. These pores were resulted from the evaporation and release of

287 organic matter of the raw material, leaving the surface of resultant AC smooth and
288 porous. The average macropore diameter for AC-2 and AC-3 is estimated to be about 60
289 nm. Interestingly, SEM micrograph of AC-4 indicates a small increase in pore size
290 (average pore diameter of about 100 nm). There is a distinct difference in the surface
291 morphology of AC-W compared to the AC-*t* samples. SEM image of AC-W (see Fig. 4)
292 shows that the morphology of the product is nondescript and quite irregular.

293 3.2.2. Nitrogen adsorption-desorption

294 Nitrogen adsorption-desorption isotherms and the pore size distributions (PSDs) of
295 the AC-*t* and AC-W samples are given in Fig. 5 with the related textural parameters
296 modelled from the adsorption data summarized in Table 2. In accordance to IUPAC
297 classifications, all isotherms show type-IV adsorption with a typical hysteresis loops in
298 the relative pressure range of 0.4–0.99, indicating a mesoporous structure. However, the
299 curves of AC-1 and AC-W differ noticeably from those of AC-2, 3, 4 in terms of shape
300 and N₂ adsorption amount. The uniformity and dimension of mesopores can be directly
301 evaluated by their PSDs (Fig. 5). AC-2, AC-3 and AC-4 samples yield a narrow pore size
302 distribution with a distinct peak centered at 3.8 nm and a shoulder at about 4.8 nm. AC-
303 1 and AC-W show wider PSD with mesopores larger than 5 nm. Mechanochemical
304 activation results in higher surface areas and benefits the formation of pores according to
305 the parameters in Table 2. It can be seen that the S_{BET} of AC-W exhibits the lowest value
306 compared to other carbons and also that the S_{BET} of AC-*t* samples first increases with
307 milling time, going from 903 m²g⁻¹ for AC-1 to 1040 m²g⁻¹ for AC-3, and then slightly
308 decreases to 1023 m²g⁻¹ for AC-4. S_{EXT} and D_p follow similar trends, showing highest
309 values for AC-3, while S_{MIC} , V_t and V_{MIC} increase almost linearly with increasing milling
310 time. Values reported in Table 2 indicate that the porous architecture of AC-*t* samples

311 can be tuned by varying milling time. It appears that milling times between 3 and 4h are
312 most potentially effective in producing AC with the highest values of S_{BET} , V_t and V_{MIC} .

313 3.2.3. FTIR

314 The infrared spectra of all studied ACs show very similar band profiles. Fig. 6a
315 displays a selection of FTIR spectra corresponding to AC-1, AC-4 and AC-W. As one
316 can see, the number of absorption bands is significantly reduced compared to the
317 spectrum of the neat material shown in Fig. 2a. This result suggests that many weak
318 bonds of CS were broken in the carbonization and activation conditions. After
319 carbonization treatment only absorption bands at 3426 cm^{-1} (OH stretching), around
320 3230 cm^{-1} (aromatic C–H stretching), between $3000\text{--}2800\text{ cm}^{-1}$ (asymmetric and
321 symmetric C–H stretching), 1610 cm^{-1} (C=C ring stretching in a large aromatic skeleton
322 in activated carbons) and between $1200\text{--}1000\text{ cm}^{-1}$ (C–O stretching) are detected. The
323 peaks assigned to several O-functionalities (C=O, CO–O, C–OH, C–O–C) in the
324 spectrum of CS (see Fig. 2) are completely absent in the spectra of ACs. Thus, FTIR
325 results indicate that the ACs prepared at $700\text{ }^\circ\text{C}$ are relatively poor in surface functional
326 groups, irrespective of the conducted activation scheme (mechanochemical vs chemical
327 activation).

328 3.2.4. XRD

329 XRD patterns of the ACs are shown in Fig. 6b. As can be seen, AC-*t* samples
330 exhibit practically identical profiles with two broad peaks corresponding to $2\theta=25.9^\circ$ and
331 42.7° , which are assigned to reflections from the (002) and (01) planes of turbostratic
332 carbon structures in ACs [31]. Apparently, the diffraction peaks in the pattern of AC-W
333 are shifted to lower 2θ angles (24.9° and 41.8° , respectively). Using the Bragg law, the

334 interlayer spacings d_{002} calculated for AC-*t* and AC-W are 0.344 and 0.357 nm,
335 respectively. The d_{002} value of AC-*t* is closer to the ideal graphite spacing (0.335 nm) and
336 demonstrates that the mechanochemical activation brings the graphitic planes of the final
337 material closer than the wet oxidation scheme.

338 3.2.5. Raman spectroscopy

339 To elucidate in more detail the material microstructure of AC powders, micro-
340 Raman spectroscopy analysis was undertaken on AC-*t* and AC-W samples, as shown in
341 Fig. 7a. The presented Raman spectra are very similar, containing two broad and
342 overlapping bands. The decomposition analysis of the spectra was performed by using
343 four Gaussian peak shapes on top of a straight baseline as proposed by Shimodaira and
344 Masui [32] for Raman spectra of ACs. The peaks at $\sim 1598 \text{ cm}^{-1}$ (G1 band) and at ~ 1335
345 cm^{-1} (D1 band) are assigned to the graphitic structure of the activated carbon, since such
346 vibrations are analogous to the G (E_{2g} in-plane vibration mode) and D (A_{1g} in-plane
347 breathing mode) vibrations exhibited in the spectra of the basal plane of polycrystalline
348 graphite [33,34]. The G2 ($\sim 1520 \text{ cm}^{-1}$) and D2 ($\sim 1190 \text{ cm}^{-1}$) components are ascribed to
349 the amorphous structure of the AC (or sp² clusters), according to similarities among the
350 broad peaks exhibited in the spectra of amorphous carbon (a-C) films [35]. Calculated
351 fitting parameters for AC-*t* and AC-W such as peak center and full width at the half
352 maximum (FWHM) are listed in Table 3. A plot between peak center and FWHM is
353 shown in Fig. 7b in order to verify the behavior of the Gaussian parameters. As shown,
354 G1, G2 and D1 positions and widths are stable for all AC-*t* samples and only the points
355 for D2 peak are scattered. Noticeably, G2 and D1 points of AC-W are located downwards
356 and upwards, respectively, from the AC-*t* domains. This result suggests that AC-*t*
357 samples have similar microstructural characteristics and they are different from those of

358 the chemically activated carbon. The latter conclusion is in accord with the calculated
359 integrated intensity ratio $I(D1)/I(G1)$ (Table 3). The relative Raman intensity of the D1
360 and G1 bands is a measure of the degree of graphitization of the material, so that the
361 graphitization degree is higher as $I(D1)/I(G1)$ approaches zero [36]. It can be seen that
362 the $I(D1)/I(G1)$ value of AC-W (5.14) is noticeably higher than for AC- t samples. Thus,
363 the spectral data and fitting may suggest that AC-W has a less crystalline character than
364 the mechanochemically activated carbons. Additionally, the $I(D1)/I(G1)$ value for AC- t
365 samples decreases with increasing t (the ratio goes from 3.69 for AC-1 through 3.44 for
366 AC-2, 3 to 3.10 for AC-4), so suggesting that milling time is beneficial for the growth of
367 ordered graphitic domains.

368 3.2.6. MGO adsorption

369 Finally, the obtained ACs were tested in the liquid phase adsorption of MGO and
370 the adsorption capacities at equilibrium are compared in Fig. 8a. Although several
371 countries have banned using Malachite Green due to carcinogenic, genotoxic, mutagenic,
372 and teratogenic properties [37], it is still being used in fish farming industry and for
373 dyeing silk, wool, jute, leather and cotton because of its low-cost and availability [37].
374 Thus, there is a constant need of developing novel cost-effective adsorbents for MGO
375 removal. The adsorption uptake of MGO on AC-3,4, AC-2, AC-1 and AC-W are 250,
376 217, 200 and 185 mg/g, respectively, and follows an order of AC-4, AC-3>AC-2>AC-
377 1>AC-W. These values are higher than the reported adsorption capacity of commercial
378 activated carbon (8.27 mg/g) [38] and are comparable with adsorption capacity of
379 groundnut shell based activated carbon (222.2 mg/g) [39]. Noticeably, the order of
380 adsorption capacity of ACs coincides with the order of S_{BET} (see Table 1). Fig. 8b shows
381 the adsorption capacity normalized by the S_{BET} of the ACs and the MGO uptake is in

382 order of AC-W>AC-4, AC-3>AC-2, AC-1. Thus, it appears that the surface area is
383 important, but not the only factor to determine the adsorption capacity of the ACs. As
384 AC-*t* and AC-W exhibit similar surface functionalization (see FTIR spectra in Fig. 6a) it
385 can be assumed that the concentration of functional groups is not the reason for the
386 highest normalized adsorption of AC-W. We suppose that the later could be due to the
387 highest average pore width (4.6 nm) and lower graphitization degree of the material. The
388 first factor is beneficial for MGO to penetrate into the micro-mesopores of AC-W
389 compared to the AC-*t* samples. It has been reported that for adsorbents with small pore
390 widths pore blockage may occur due to the aggregation of voluminous molecules, such
391 as dyes, in the pore orifice [40]. Thus, the full surface area of the adsorbent cannot be
392 exploited and the adsorption uptake is reduced. The lower graphitization degree of AC-
393 W gives rise to a more hydrophilic surface for the incursion of aqueous phase and favors
394 interactions with MGO. Undoubtedly, the adsorption performance of the CS-derived AC
395 powders can be further improved. Additional studies on the effects of key process
396 parameters such as CS/K₂CO₃ mass ratio, carbonization temperature and retention time
397 on the physicochemical properties of the final materials are needed in order to provide
398 the most favorable conditions for the AC-*t* and AC-W fabrication. Furthermore, high-
399 energy ball milling is a complex process and optimization of a number of variables such
400 as milling container, milling speed, milling time, type, size and size distribution of the
401 grinding medium, ball-to-powder mass ratio and milling atmosphere [41,42] is also
402 possible in order to define the most effective settings for the preparation of CSK
403 precursor.

404 The results presented above clearly indicate the feasibility to adjust S_{BET} , pore texture
405 and microstructural characteristics of the obtained AC powders by milling time as an

406 important process parameter. Obviously, the dry mechanochemical conditions promote
407 reactions between the biomass and the activating agent. The latter is advantageous in the
408 carbonization step when formation of pores and ordering of the graphitic structure occur.
409 Moreover, mechanochemical activation is more effective in developing homogeneous
410 mesoporosity in the final material than the traditional chemical activation. For AC-*t* the
411 S_{BET} of the samples dictates the MGO uptake, while the pore width and lower
412 graphitization degree of AC-W appear profitable for its adsorption properties. Although
413 the present study is devoted to ACs prepared from chestnut shell as a raw material, the
414 experimental details and results can be extended to other lignocellulosic residues. Based
415 on our results, it is reasonable to expect improved textural properties of ACs prepared
416 *via* mechanochemical route from lignocellulosic materials already utilized for AC
417 fabrication by chemical activation with K_2CO_3 .

418

419 **4. Conclusions**

420 A series of powdered activated carbons were prepared from horse chestnut shell using
421 K_2CO_3 as an activating agent under solvent-free mechanochemical and traditional
422 chemical conditions. After carbonization at 700 °C, predominantly mesoporous carbons
423 were obtained and the BET analysis yielded specific areas over the plausible range for
424 commercial activated carbons (500-1500 cm^2/g) [43]. The results imply that the
425 mechanochemical activation is superior to the chemical activation in terms of specific
426 surface area, pore development and the degree of structural order of the activated
427 carbons. Furthermore, the textural and microstructural characteristics of the
428 mechanochemically activated carbons can be tailored by varying the milling time. The

429 high surface areas of the mechanochemically obtained carbons are reflected in the
430 observed adsorption capacity for Malachite Green Oxalate up to 250 mg/g. It has been
431 revealed that the highest average pore width and lower graphitization degree of the
432 chemically activated material are also beneficial for the dye uptake.

433 This study has shown that the horse chestnut shells could be used as a raw material
434 for preparation of activated carbon for adsorption applications. In addition, it has been
435 demonstrated that high energy ball milling can be considered as a viable method for
436 activation of lignocellulosic materials.

437 **Acknowledgement**

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553 **Figure captions**

554 **Fig. 1.** TG and DTG curves of (a, b) CS, CSK-*t* and CSK-W (inserts) and (c, d) CS, CS-
 555 1 and CS-4.

556 **Fig. 2.** FTIR spectra of (a) CS, CSK-1, CSK-4 and CSK-W and (b) CS, CS-1 and CS-4.

557 **Fig. 3.** SEM images of (a) CS-1, (b) CS-4, (c) CSK-1 and (d) CSK-4. (e) XRD patterns
 558 of CS, anhydrous K_2CO_3 , CSK-*t* and CSK-W. Crystalline phases: *— K_2CO_3 , ○—
 559 $K_4H_2(CO_3)_3 \cdot 1.5H_2O$ (ICDD PDF-2 #20-0886) and ●— $KHCO_3$ (ICDD PDF-2 #12-0292).

560 **Fig. 4.** SEM images of CS, AC-*t* and AC-W. The inserts show higher magnification
 561 images.

562 **Fig. 5.** Nitrogen adsorption-desorption isotherms and pore size distributions obtained by
 563 DFT method of AC-*t* and AC-W.

564 **Fig. 6.** (a) FTIR spectra of AC-1, AC-4 and AC-W. (b) XRD patterns of AC-*t* and AC-
 565 W.

566 **Fig. 7.** (a) Raman spectra with fitting results for AC-*t* and AC-W. (b) Plots of Raman
 567 shift versus the FWHM obtained by peak deconvolution. The excitation wavelength is
 568 632.8 nm, provided by a He-Ne laser.

569 **Fig. 8.** (a) Adsorption capacities and (b) surface area normalized adsorption capacities
570 of MG at equilibrium (25 °C).

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