1 **Upcycling spent brewery grains through the production of carbon adsorbents –**

2 **application to the removal of carbamazepine from water**

3 *Andreia F. C. Sousa[a], María Victoria Gil[b], Vânia Calisto[a]**

4 [a]Department of Chemistry and CESAM (Centre for Environmental and Marine Studies),

5 University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal

6 [b]Instituto Nacional del Carbón, INCAR-CSIC, Calle Francisco Pintado Fe 26, 33011

7 Oviedo, Spain

8 *Corresponding author: vania.calisto@ua.pt*

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

Abstract

24

25   Spent brewery grains, a by-product of the brewing process, were used as

26 precursor of *biochars* and activated carbons to be applied to the removal of

27 pharmaceuticals from water. *Biochars* were obtained by pyrolysis of the raw materials,

28 while activated carbons were produced by adding a previous chemical activation step.

29 The influence of using different precursors (from distinct fermentation processes),

30 activating agents (potassium hydroxide, sodium hydroxide and phosphoric acid),

31 pyrolysis temperatures, and residence times was assessed. The adsorbents were

32 physicochemically characterized and applied to the removal of the antiepileptic

33 carbamazepine from water. Potassium hydroxide activation produced the materials with

34 the most promising properties and adsorptive removals, with specific surface areas up to

35 $1120 \ \text{m}^2 \ \text{g}^{-1}$ and maximum adsorption capacities up to $190 \pm 27 \ \text{mg} \ \text{g}^{-1}$ in ultrapure

36 water. The adsorption capacity suffered a reduction of <70% in wastewater, allowing to

37 evaluate the impact of realistic matrices on the efficiency of the materials.

38

39 **Keywords**

40 Brewery wastes; Pyrolysis; Chemical activation; Activated carbon; Pharmaceuticals;

41 Wastewater treatment.

42

43

44

45

46

47

1. Introduction

The use of agricultural and industrial wastes to produce added-value materials is an interesting possibility to reduce the negative impacts of agro-industrial processes, and to reintroduce end-of-life residues into the productive chain (Borel et al., 2018; Jaria et al., 2019). These wastes, usually available in large amounts, can be an alternative to non-renewable sources for being utilized as precursors of carbon materials, such as activated carbons (ACs), to be applied in water purification systems (Azargohar and Dalai, 2008). AC is a carbonaceous material with high adsorption capacity towards a vast number of compounds, such as pharmaceuticals (Jaria et al., 2019). The key properties associated to an AC with high adsorption capacities include high specific surface area (S_{BET}) and microporosity, as well as high carbon and low ash contents (Jaria et al., 2015). For these reasons, agro-industrial lignocellulosic residues, which have low inorganic and relatively high volatile contents, are considered good precursors of AC (Azargohar and Dalai, 2008).

Spent brewery grains (SBG) are lignocellulosic wastes which constitute a major by-product of the brewing process, representing around 85% of the total wastes generated by the brewing industry (Borel et al., 2018; Vanreppelen et al., 2014). This material consists of the remains from the barley malt after the mashing process (Barrozo et al., 2019), and their properties depend on the type of used barley and the brewing technology (Olszewski et al., 2019). Nevertheless, their main polysaccharides are generally hemicellulose (mainly arabinoxylane), and cellulose, while lignin and a considerable amount of proteins and lipids are also part of the typical reported composition of SBG (Olszewski et al., 2019; Wierzba et al., 2019). To date, SBG has primarily been used as animal feed (Gonçalves et al., 2017; Vanreppelen et al., 2014).

3

72   However, considering that the efficient reuse of this agro-industrial waste can be

73   important, not only from the perspective of the brewer who can benefit from the

74   valorization of this by-product, but also from an environmental point of view, the study

75   of alternative SBG applications is highly desirable (Barrozo et al., 2019). In this

76   context, comes up the possibility of using SBG to produce adsorbent materials aiming at

77   the adsorptive removal of water micro-contaminants, such as pharmaceuticals.

78   In the last years, a few studies have reported the possibility to use raw and

79   processed SBG as adsorbent to remove contaminants from water. To the best of the

80   authors' knowledge, the application of SBG to the removal of pharmaceuticals from

81   water has not been so far reported in literature. However, some examples of the

82   application of this material to the removal of other organic pollutants, such as dyes used

83   in paper and textile industries (Fontana et al., 2016; Silva et al., 2004), or inorganic

84   pollutants, such as metals (Ferraz et al., 2005; Wierzba and Andrzej, 2019), from water

85   can be found in literature. Concerning organic contaminants, Silva et al. (2004) studied

86   the removal of acid orange 7, a dye currently used in paper and textile industries, by

87   SBG in aqueous solutions (Silva et al., 2004). The results showed high levels of color

88   removal (above 90%, for an initial dye concentration of 60 mg L^{-1}), with low contact

89   times between adsorbent and dye (less than 1 h), attaining a maximum adsorption

90   capacity of ~30.5 mg g^{-1}, at 30 ºC. The reported removal capacity was obtained using

91   the SBG in its raw form, i.e., without any previous treatments such as milling and/or

92   sieving, incineration or chemical modification. Gonçalves et al. (2017) used SBG to

93   produce bio-oil and a granular AC via pyrolysis and CO_2 activation (Gonçalves et al.,

94   2017). In the production of the AC by these authors, the effect of the activation time on

95   some properties, including S_{BET}, was investigated. The adsorptive properties of AC were

evaluated by the determination of the iodine number and methylene blue discoloration. The authors concluded that the S_{BET}, iodine number and methylene blue adsorption onto the AC increased as activation time increased. Therefore, six hours of activation resulted in an AC with S_{BET} of 617.4 m^2 g^{-1}, an iodine number of 490.1 mg g^{-1} and an excellent adsorption of methylene blue (99.97 % for an initial concentration of 200 mg L^{-1} of methylene blue and granular AC dosage of 10 000 mg L^{-1}). Ferraz et al. (2005) in a study for Cr (III) adsorption also used SBG as adsorbent, obtaining a maximum adsorption capacity of 17.84 mg g^{-1} at pH 5.0 (Ferraz et al., 2005). As in the study carried out by Silva et al. (2004), this work also reported a good removal capacity of Cr (III) using the SBG in its raw form.

Considering the above-mentioned studies and the high availability of SBG for its large-scale application, the use of this biomass as sorbent for the removal of pharmaceuticals from contaminated water could be a sustainable solution for the valorization of this residue, upcycling it through its transformation into an added-value product. The main objective of this work consists of using SBG as a precursor of *biochar* and AC. SBG obtained from two different types of brewing processes was selected to evaluate the impact of the fermentation on the properties of the resulting adsorbents. The produced materials were physical and chemically characterized and subsequently tested as adsorbents to remove the antiepileptic pharmaceutical carbamazepine (CBZ) from aqueous solutions. CBZ was selected due to its relevance as environmental microcontaminant. It is one of the most frequently detected pharmaceuticals in the aquatic environment (Fekadu et al., 2019; Li, 2014; Tran et al., 2018), most possibly as a consequence of being highly recalcitrant to conventional wastewater treatments (Jelic et al., 2011). For these reasons, CBZ has been proposed by

several authors as a valid marker of anthropogenic pollution (Bahlmann et al., 2012; Clara et al., 2004). This pharmaceutical (M_w 236.27 g mol^{-1}) is neutral over the range of environmentally relevant pH (pKa of 13.9, related to the deprotonation of the $-NH_2$ group of CBZ) (Jones et al., 2002) and has a relatively low water solubility (18 mg L^{-1} at 25 ºC, with a log K_{ow} of 2.45) (Aga, 2008). The materials produced in this work with the best performance for the adsorption of CBZ, selected after a battery of preliminary tests, were subjected to kinetic and isothermal studies both in ultrapure water and wastewater (final effluent collected at a Sewage Treatment Plant), in order to confirm their adequacy for the target application.

2. Material and methods

2.1. Chemicals

The reagents used for the activation process during the production of AC were potassium hydroxide (KOH; EKA pellets, ≥86%), sodium hydroxide (NaOH; EKA pellets, pure) and phosphoric acid (H_3PO_4; Acros Organics, 85%). For washing the produced materials, hydrochloric acid (HCl; AnalaR NORMAPUR, 37%) was used. CBZ (Sigma-Aldrich, 99%) was the pharmaceutical used for the adsorption experiments, where CBZ aqueous solutions were prepared both in ultrapure water and in wastewater. For the analytical quantification of CBZ by Micellar Electrokinetic Chromatography (as described in section 2.6), all the chemicals used were of analytical grade: sodium dodecylsulphate (SDS, Sigma Aldrich, 99%), hexadimethrine bromide (polybrene, Sigma Aldrich, ≥95%), sodium chloride (José Manuel dos Santos, 99.5%), ethylvanillin (Sigma Aldrich, 99%), sodium tetraborate (Riedel-de-Haën, 99.5%),

143 sodium hydroxide (EKA pellets, pure). The ultrapure water was obtained from a Milli-

144 Q Millipore system (Milli-Q plus 185).

145

146 **2.2.   Production of carbon adsorbents**

147   To produce the adsorbent materials, SBG from the brewery Faustino

148 Microcervejeira, Lda (Aveiro, Portugal) was used as precursor. In order to evaluate the

149 effect of using SBG arising from different types of fermentation on the properties of the

150 produced materials, two different residues were collected: SBG from the production of

151 Barleywine (BW), a type of beer that has a high fermentation, and SBG from the

152 production of Pilsener (PL), beer that has a low fermentation process. After collection,

153 the SBG was dried at room temperature for several days, followed by a 24 h period at

154 104 ºC in an oven, to eliminate the moisture. Then, it was grinded with a blade mill and

155 stored dry until use. The adsorbents were produced by pyrolysis of BW and PL in a

156 furnace muffle (Nüve, series MF 106, Turkey) under inert environment (nitrogen flow),

157 at different temperatures (heating rate of 10 °C min^{-1}) and residence times, and with

158 (AC) or without (*biochar*) a previous activation process, as detailed below. The yield of

159 production (η) of all carbon adsorbents produced was calculated by Eq. (1):

160 $$\eta(\%) = \frac{final\ mass\ of\ carbon\ adsorbent\ (g)}{mass\ of\ precursor\ (g)} \times 100 \qquad (1)$$

161

162 2.2.1. Preparation of *biochar*

163   The raw SBG was weighed in porcelain crucibles and carbonized at 600 ºC and

164 800 °C, using residence times of 60 and 150 min. Accordingly, BW was pyrolyzed

165 under such conditions, resulting in the following materials: BC-BW-600-60, BC-BW-

166 600-150, BC-BW-800-60, and BC-BW-800-150. Preliminary tests carried out with

these materials indicated that pyrolysis at 600 ºC, without chemical activation, did not

result in materials with interesting properties for the adsorptive removal of organic

contaminants. For this reason, only the higher temperature (800 ºC) was used for PL,

i.e., it was treated at 800 ºC for 60 min and 150 min, giving the BC-PL-800-60 and BC-

PL-800-150 materials. After pyrolysis, the materials were washed with a 0.5 M solution

of HCl for the removal of ashes and other inorganic content. For this purpose, for each

10 g of material ~200 mL of 0.5 M HCl were added; the materials were immersed in the

acid solution for 1 h and subsequently vacuum filtered and washed with distilled water

until the washing leachate reached neutral pH (e.g. ~200 mL of distilled water for each

10 g of AC activated with alkaline agents or up to a few liters for acid activated

materials). Finally, the material was oven dried at 104 °C for 24 h and separated by

grain size. The granulometry used in the adsorption tests was below 0.18 mm.

2.2.2. Preparation of activated carbon

Different types of AC were prepared by chemical activation of SBG, followed

by carbonization at 800 ºC for 150 min. The chemical agents used for activation

were KOH, NaOH and H_3PO_4 in a ratio precursor:activating agent of 1:1 (*w/w*). For the

materials activated with KOH and NaOH, the solid activating agent was dissolved in

distilled water in a proportion activating agent:water of 3:10 (*w/v*), whereas for the

activation with H_3PO_4, the activating agent was diluted in a ratio activating agent:water

of 1:3 (*v/v*). In both cases, SBG was impregnated for 1 h with the activating agent

solution, using an ultrasonic bath. The resulting slurry was then dried at room

temperature. Then, the materials were pyrolyzed and subjected to washing and sieving

under the same conditions as those described for the *biochar* (section 2.2.1). Six AC

191 materials were obtained: KOH-BW-800-150, NaOH-BW-800-150, H_3PO_4-BW-800-

192 150, KOH-PL-800-150, NaOH-PL-800-150 and H_3PO_4-PL-800-150.

193

194 **2.3.   Characterization of precursors and carbon adsorbents**

195   The precursors (PL and BW) and the obtained materials were characterized by

196 the following techniques: total organic carbon, proximate analysis, Fourier transform

197 infrared spectroscopy with attenuated total reflectance (FTIR-ATR), point of zero

198 charge, determination of carbons' functional groups by back-titration, S_{BET} and scanning

199 electron microscopy (SEM). A detailed description of the procedures used can be found

200 in the Supplementary Material (SM).

201
202 **2.4.   Batch adsorption experiments**

203   In order to test the adsorptive performance of the produced materials for the

204 removal of CBZ from water, adsorption experiments were made under shaking and

205 batch conditions. In a first analysis of the produced *biochars* and ACs, some

206 preliminary adsorption tests were carried out in order to select the most promising

207 materials that will be subjected to a deeper analysis (kinetic and isothermal studies). For

208 these tests, CBZ solutions with an initial concentration (C_i) of 5 mg L^{-1} were prepared

209 in ultrapure water. Subsequently, these solutions were placed in polypropylene tubes

210 containing a known mass of adsorbent (varying from 25 to 1000 mg L^{-1} for *biochars*

211 and 25 to 50 mg L^{-1} for ACs) and shaken in an overhead shaker (Heidolph, Reax 2) at

212 80 rpm for 24 h and under controlled temperature (25.0 ºC ± 0.1 ºC). Based on the

213 adsorption percentages resulting from these experiments, the materials with the best

214 adsorptive properties were selected for further studies, as described in sections 2.4.1 and

215 2.4.2.

216   Generally, all studies (preliminary, kinetic and equilibrium) were performed in

217   triplicate. Each experiment included a control (CBZ solution without the adsorbent) that

218   was used as reference for the calculation of adsorption percentages after the contact

219   time between the solution and the material. After stirring under specific conditions,

220   sample aliquots were filtered through 0.22 μm PVDF filters (Whatman) and analyzed by

221   Micellar Electrokinetic Chromatography, in order to determine the remaining

222   pharmaceutical concentration, as described in section 2.6.

223

224   2.4.1.   Adsorption kinetics

225   To study the adsorption kinetics of CBZ onto the selected carbons (KOH-BW-

226   800-150 and KOH-PL-800-150), a fixed dose of the carbon adsorbent (mg L^{-1}) was

227   placed in tubes and put in contact with 45 mL of 5 mg L^{-1} of two aqueous solutions of

228   CBZ (prepared in ultrapure water and wastewater, respectively). The concentrations of

229   both KOH-BW-800-150 and KOH-PL-800-150 were 15 mg L^{-1} and 40 mg L^{-1} in

230   ultrapure water and wastewater, respectively. The solutions were shaken for different

231   time intervals between 5 and 240 min for ultrapure water, and 15 and 1860 min for

232   wastewater. A minimum of six time intervals were considered for each system and the

233   dose of carbon material was selected in order to obtain a significant adsorption

234   percentage but, simultaneously, to avoid CBZ removals close to 100% which would

235   difficult the analytical determination of the remaining CBZ concentration. The adsorbed

236   concentration of CBZ onto each AC at time t, q_t (mg g^{-1}), was calculated by Eq. (2). The

237   experimental data were fitted by pseudo-first-order model (Lagergren, 1898) and

238   pseudo-second-order model (Ho et al., 2000), presented in Eqs. (3) and (4), respectively,

239   in order to determine the kinetic parameters of each system.

240 $$q_t = \frac{(C_i - C_t)V}{m} \tag{2}$$

241 $$q_t = q_e(1 - e^{-k_1 t}) \tag{3}$$

242 $$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \tag{4}$$

243 where C_i (mg L^{-1}) is the initial concentration of pharmaceutical, C_t (mg L^{-1}) is the

244 concentration of pharmaceutical in solution at time t, V (L) is the volume of solution,

245 m is the mass of adsorbent (g), q_e refers to the amount of adsorbate per unit mass of

246 adsorbent at equilibrium (mg g^{-1}), k_1 is the pseudo-first order rate constant (min^{-1}) and

247 k_2 is the pseudo-second order rate constant (g mg^{-1} min^{-1}). Non-linear fittings were

248 performed using GraphPad Prism, version 5.

249

250   2.4.2. Adsorption equilibrium

251   For the determination of the adsorption isotherms, the experiments were

252 performed using the shaking time needed to attain the equilibrium, as determined in

253 section 2.4.1, and varying the concentration of carbon adsorbents while keeping the

254 initial concentration of the CBZ constant (5 mg L^{-1}). These experiments allow to

255 calculate the adsorption capacity of the materials. Briefly, 50 mL of a 5 mg L^{-1} aqueous

256 solution of CBZ was added at different doses of each carbon. For ultrapure water, the

257 dose of KOH-BW-800-150 and KOH-PL-800-150 varied between 12.5-30 mg L^{-1} and

258 20-40 mg L^{-1}, respectively; and for wastewater, it varied between 35-90 mg L^{-1} and 25-

259 70 mg L^{-1}, respectively. A minimum of six concentrations were considered for each

260 system. The adsorbed concentration of CBZ onto each AC at the

261 equilibrium, q_e (mg g^{-1}), was calculated by Eq. (5). The experimental data were fitted

262 by Langmuir (Langmuir, 1916) and Freundlich (Freundlich, 1906) isotherm models

263   (Eqs. (6) and (7), respectively) in order to determine the equilibrium parameters of the

264   systems. Non-linear fittings were performed using GraphPad Prism, version 5.

265   $q_e = \frac{(C_i - C_e)V}{m}$ (5)

266   $q_e = \frac{q_m \times K_L \times C_e}{1 + K_L \times C_e}$ (6)

267   $q_e = K_F \times C_e^{(1/N)}$ (7)

268   where C_e (mg L^{-1}) is the concentration of CBZ in solution at the equilibrium, q_m is the

269   maximum adsorption capacity of each material towards CBZ (mg g^{-1}), K_L is the

270   Langmuir equilibrium constant (L mg^{-1}), K_F is the Freundlich equilibrium constant (mg

271   g^{-1} (L mg^{-1})$^{1/N}$), N are the degrees of non-linearity, and all the other variables are

272   defined as in Eqs. (2), (3) and (4).

273

274   **2.5.**   **Wastewater sampling**

275   Wastewater was collected in June 2019 in a local Sewage Treatment Plant

276   (Aveiro, Portugal) and it corresponds to the final effluent, after the biological treatment,

277   as discharged into receiving waters (~3.3 km away from the coast, into the Atlantic

278   Ocean). Immediately after collection in order to remove suspended organic matter, it

279   was filtered through cellulose Supor-450 membrane disc filters 0.45 µm with a vacuum

280   system. After filtration, the samples were stored in the dark at 4 °C and used within no

281   longer than 15 days. The collected effluent was characterized by measuring conductivity

282   (WTW meter), pH (pH/mV/°C meter pHenomenal® pH 1100L, VWR) and dissolved

283   organic carbon content (TOC-VCPH Shimadzu). The pH, conductivity and dissolved

284   organic carbon were 8.42, 2.78 ms cm^{-1} and 18.0 ± 0.8 mg L^{-1}, respectively.

285

286   **2.6.**   **Pharmaceutical's quantification**

287   The quantification of CBZ was performed by Micellar Electrokinetic

288   Chromatography using a Beckman P/ACE MDQ instrument (Fullerton, CA, USA),

289   equipped with a UV-Vis detection system, controlled by the software 32 Karat,

290   according to the procedure described by Calisto et al. (Calisto et al., 2011), with minor

291   modifications. Briefly, a coated silica capillary with 30 cm to the detection window was

292   used and the electrophoretic separation was performed at 25 °C and 25 kV, during

293   4.5 min runs. Ethylvanillin was used as internal standard and sodium tetraborate was

294   used to obtain higher repeatability and better peak shape and resolution. Both were

295   spiked to all samples and standard solutions at final concentrations of 3.34 mg L^{-1} and

296   10 mM, respectively. Detection of CBZ was monitored at 214 nm and the separation

297   buffer consisted of 15 mM of sodium tetraborate and 20 mM of sodium

298   dodecyl sulphate. The calibration curve was determined for a concentration range

299   between 0.25 and 5 mg L^{-1}. All the analyses were performed in triplicate.

300

301   **3. Results and discussion**

302   **3.1. Yield of the adsorbents' production**

303   After the production (pyrolysis and washing) of the adsorbent materials, the

304   production yield was calculated. A considerable difference between the values obtained

305   for the *biochars* and for the ACs was observed. Briefly, the yields obtained were around

306   30 % for all *biochars*; 13 % for BW and PL KOH-ACs; 11 and 4 % for BW and PL

307   NaOH-ACs, respectively; and around 51 % for BW and PL H$_3$PO$_4$-ACs. In general, the

308   washing step was an inevitable cause for material losses, due to the removal of the

309   inorganic fraction. The low production yields obtained for the KOH-ACs and NaOH-

310   ACs (in opposition to the ones obtained for *biochars* and H$_3$PO$_4$-ACs) can be due to a

311 higher loss of volatile organic matter caused by the reaction with the alkali bases. On

312 the other hand, for H_3PO_4-ACs, the product yield increased comparatively to *biochars.*

313 According to Molina-Sabio et al. (1995), the high yield of H_3PO_4-ACs can be due to the

314 formation of largest structural units by the reaction between this activating agent and the

315 lignocellulosic precursor which do not escape as volatile matter during pyrolysis. This

316 leads to a final material with higher density, most likely due to the generation of

317 phosphate or polyphosphate structures (Hunsom and Autthanit, 2013), contributing to

318 increase the product yield.

319

320 **3.2. Physical and chemical characterization**

321 The results concerning total organic carbon determination are presented in Table

322 S1 of SM. Both precursors present a high value of total organic carbon (48.5 ± 0.6%

323 and 48.2 ± 0.2% for BW and PL, respectively) and very low inorganic carbon contents

324 (< limit of detection), corroborating that these residues constitute a promising raw

325 material for the production of carbon adsorbents. Comparing the total organic carbon

326 content values of the carbon adsorbents with those of the precursors, the increase for

327 *biochars* and ACs is clear (~30 %), except for H_3PO_4-BW-800-150 and H_3PO_4-PL-800-

328 150, for which total organic carbon remained similar to the precursor.

329 The thermogravimetric analyses of the raw materials (BW and PL) and the

330 resulting KOH-ACs are depicted in Fig. S1 of SM, while the corresponding proximate

331 analyses, reported on a dry basis, are depicted in Table 1. The results showed that BW

332 and PL have similar characteristics, i.e., low ash contents and high volatile matter and

333 fixed carbon contents. According to Fig. S1, a pronounced thermal decomposition of the

334 precursors began at approximately 200 °C. However, BW and PL have three stages of

335   mass loss during the pyrolysis process, corresponding to derivative thermogravimetric

336   peaks at 84, 295 and 352 °C and 83, 283 and 351 °C, respectively. Initially, the

337   derivative thermogravimetric curve shows a peak (~80 ºC) corresponding to the mass

338   loss derived from water evaporation (Mahmood et al., 2017; Oliveira et al., 2018). The

339   major weight loss was observed in the temperature range of 200-500 °C, which is due to

340   the thermal decomposition of the main SBG constituents (cellulose, hemicellulose and

341   lignin) (Mahmood et al., 2017). At ~500 °C the breakdown of lignocellulosic

342   material was finished, and no further weight loss was observed. This indicates that the

343   basic structure of carbon is expected to have been formed at 500 ºC, which should be

344   considered as the lowest carbonization temperature for AC production from SBG. The

345   tested pyrolysis temperatures were 600 and 800 ºC, since higher temperatures usually

346   translate into a higher development of microporosity, which is advantageous for

347   adsorbents with superior adsorption capacity (Calisto et al., 2014). For KOH-ACs, the

348   volatile matter content is much lower than that of the raw materials. On the other hand,

349   an increase (approximately four times higher) in the fixed carbon content was observed.

350   In fact, the ratio between the volatile matter and fixed carbon percentages for KOH-ACs

351   suffered a substantial decrease compared to the raw materials, indicating an extensive

352   volatile matter release with the increase of the non-volatile carbon fraction, which are

353   two factors that positively contribute to the formation of a carbon rich and highly

354   porous adsorbent (Calisto et al., 2014). The high fixed carbon content is consistent with

355   the total organic carbon determination. Moreover, the low ash content (below 15%) is

356   also in accordance with the low inorganic carbon content of the samples.

357   Regarding FTIR-ATR analyses, the spectra of the BW, PL and of the produced

358   carbon adsorbents are presented in Fig. S2 of SM, allowing to identify the major

functional groups. The results show that the precursor materials (both BW and PL) have

a much more complex chemical composition than the produced carbon adsorbents. The

spectra of BW and PL present several typical bands of cellulose. The bands between

2935–2915, 2865–2845 and 2880–2860 cm^{-1} correspond to vibrations of the C−H

stretch in asymmetric and symmetric aliphatic chains (−CH_2 and −CH_3, respectively)

(Coates, 2000), which may belong to cellulose, lignin or hemicellulose (Fontana et al.,

2018). In both cases, these bands disappeared in ACs, however, they are still noted in

the BC-BW-800-150 and BC-PL-800-150. The peak at 1743 cm^{-1}, found in spectra of

PL, corresponds to the vibration of the stretching of the carbonyl group (C=O) in

ketones, ethers, aldehydes and carboxylic acids. In the FTIR spectra of BW and PL-

based *biochars* (BC-BW-800-60, BC-BW-800-150, BC-PL-800-60 and BC-PL-800-

150), the typical bands of cellulose disappeared. This fact showed that there was a

considerable degradation of the main functional groups of BW and PL after pyrolysis,

even without activation. Additionally, for spectra of the BW, PL and respective ACs,

several peaks are present between 1650 and 1150 cm^{-1}. These peaks can be associated

to the cellulosic ethers (C−O−C bonds) (~1150 cm^{-1}) (Coates, 2000), to the C−O

stretching in carbonyl group (~1238 cm^{-1}) (Coates, 2000), to the C−H bending

vibrations (~1300 cm^{-1}) (Fontana et al., 2018; Jaria et al., 2017), and to the carbonyl

group in aromatic rings (~1641 cm^{-1}) (Calisto et al., 2014; Coates, 2000) found in lignin

(Fontana et al., 2018). The groups identified in the FTIR spectra of the BW and PL are

in agreement with the brewing waste composition, which is rich in cellulose

hemicellulose, lignin and proteins (Olszewski et al., 2019; Wierzba et al., 2019).

The point of zero charge (Table 2 and Fig. S3 of SM) was determined in order to

know the net charge of the ACs. The concentrations of some functional groups, namely

383   carboxyl and total basic groups, were obtained by back titrations (Table 2). Low point

384   of zero charge is directly connected with the presence of high concentrations of the

385   carboxyl groups; on the other hand, higher point of zero charge is linked to a higher

386   concentration of total basic groups and lower concentration of carboxyl groups. The

387   point of zero charge determined for KOH-BW-800-150 and KOH-PL-800-150 is

388   neutral or slightly basic, respectively, which is in line with the very similar

389   concentrations obtained for the two functional groups for both materials.

390   For the study of the textural features of the materials, nitrogen adsorption

391   isotherms and SEM were used as characterization techniques. The results of S_{BET} and

392   the textural characterization of all the produced carbon adsorbents are presented in

393   Table 3. PL-based carbons presented slightly higher S_{BET} compared with BW-based

394   carbons produced under the same conditions. This fact may be explained by the relative

395   higher content of volatile matter in PL in comparison with BW. KOH-BW-800-150 and

396   KOH-PL-800-150 were the materials with the highest S_{BET}, 1090 and 1120 $m^2\ g^{-1}$,

397   respectively. On the other hand, the ACs obtained with NaOH and H_3PO_4 chemical

398   activation resulted in much lower $S_{BET},$ more comparable with the values obtained for

399   the *biochars* than with the KOH-based ACs. The same conclusion is valid for total pore

400   volume (V_p) and micropore volume (W_0) values, which will certainly influence the

401   adsorptive capacity of these materials. This comparison is particularly interesting in the

402   case of the materials resulting from KOH and NaOH chemical activation: the activating

403   agents are of similar nature, both alkali hydroxides, but the results are drastically

404   different for the two alkali metals, indicating that potassium has a determinant influence

405   in the development of the microporosity.

406   A comparison of the S_{BET} values obtained by other literature studies using

407   precursors with similar nature reveals that the results presented in this manuscript are

408   quite interesting. There are some works that use SGB in its raw form, as that described

409   by Fontana et al. (Fontana et al., 2016), who only dried, crushed and sieved the raw

410   material, and they obtained a S_{BET} of 0.8246 m² g^{-1}. In what concerns materials resulting

411   from chemical activation, most authors initially carbonize the previously dried SBG and

412   then activate the resultant carbon material, adopting a two-step activation instead of the

413   one-step procedure applied in the present manuscript. The study of Olajire et al. (2017)

414   is an example of such cases, where dry SBG was carbonized at 300 °C during 30

415   minutes and subsequently activated with H_3PO_4 and subjected to a second carbonization

416   at 300 °C during 1h. The resultant carbon presented a S_{BET} of 412 m² g^{-1} (Olajire et al.,

417   2017). Also, a comparison of the materials described in this study with some

418   commercially available ACs show that KOH-BW-800-150 and KOH-PL-800-150

419   presented higher S_{BET}. For example the commercial AC, PULSORB FG4 (PBFG4) and

420   Norit (SAE SUPER 8003.6) (applied by Calisto et al. (Calisto et al., 2014) and Silva et

421   al. (Silva et al., 2019), respectively) have a S_{BET} of 848 and 996 m² g^{-1}, respectively,

422   indicating that the produced materials have very promising properties to be used as

423   adsorbents.

424   Fig. 1 shows the SEM images of both precursors and some examples of BW and

425   PL-based carbons. The images show a gradual difference between the surface

426   morphology of the precursors, the *biochars* and of the KOH-ACs. In comparison to

427   ACs, the structure of *biochars* is more homogeneous, with some degree of destruction

428   of the original structure and a few pores can be observed (as confirmed by S_{BET}

429   analysis). On the other hand, the structure of the KOH-AC is a much rougher surface

430   (particularly, for PL-materials) with a well-developed porosity. The highly porous

431   structure is in accordance with a higher surface area, as can be confirmed by the results

432   of S_{BET}, V_p and W_0 (Table 3). Other SEM images of the *biochars* and KOH-AC are

433   presented in Figs. S4 and S5 of SM, respectively, at different magnifications.

434

435   **3.3. Batch adsorption experiments**

436   Preliminary tests were performed to evaluate the adsorptive removal of CBZ

437   from water by all the produced carbons, allowing to identify the most promising

438   materials. For the *biochars*, a considerable range of carbon dosages (between 25 and

439   1000 mg L^{-1}) was tested. The results showed a negligible CBZ adsorption, even at

440   materials' dose as high as 1000 mg L^{-1} (data not shown). This performance is in

441   accordance with the very low S_{BET} obtained for the non-activated carbons. Therefore,

442   kinetic and equilibrium studies were not performed with *biochars*.

443   On the other hand, the ACs revealed much more interesting results, even at

444   much lower carbon doses (25 and 50 mg L^{-1}) as evidenced by the data depicted in Table

445   S2 of SM. The ACs with the best adsorptive performance to remove CBZ (C_i = 5 mg L^{-}

446   ^{1}) from aqueous solutions were KOH-BW-800-150 and KOH-PL-800-150, with

447   adsorption percentages of 88 ± 11% and 85 ± 7%, respectively, using only 25 mg L^{-1} of

448   material. The others ACs were not able to satisfactorily adsorb CBZ at the tested doses,

449   with removal percentages below 15 ± 6%, using 50 mg L^{-1} of material. Better removal

450   percentages for the KOH-ACs are certainty related with their S_{BET}, V_p and W_0, which are

451   much higher than those obtained for NAOH-ACs and H_3PO_4-ACs (Table 3). Based on

452   these results, the two KOH-ACs (KOH-BW-800-150 and KOH-PL-800-150) were

453   selected to perform kinetic and equilibrium studies. For this purpose, both ultrapure

454   water and wastewater were used as test matrices, in order to evaluate the adsorptive

455   behavior of the materials under more realistic and representative conditions.

456

457   3.3.1. Adsorption kinetics

458   The amount of CBZ adsorbed onto KOH-BW-800-150 and KOH-PL-800-150 at

459   time t (q_t, mg g^{-1}) *versus* time, as well as the fittings of the experimental data to pseudo-

460   first and second orders kinetic models (Eqs. (3) and (4), respectively) are represented in

461   Fig. 2. The fitting parameters are summarized in Table 4. Generally, the pseudo-second-

462   order model was the model that best fitted the experimental data, with determination

463   coefficients (r^2) ranging from 0.974 to 0.985 (except for KOH-BW-800-150 in ultrapure

464   water). The adequacy of the pseudo-second-order model to describe the adsorption of

465   CBZ onto carbon adsorbents was in line with the results previously reported in several

466   literature studies, where this model was the one presenting the most satisfactory fittings

467   to the experimental data (Calisto et al., 2017, 2015; Chen et al., 2017; Oliveira et al.,

468   2018; Silva et al., 2019; To et al., 2017).

469   Considering the adsorption of CBZ onto KOH-BW-800-150 and KOH-PL-800-

470   150, it can be verified that the observed adsorption rates (k_2) determined by the pseudo-

471   second-order model indicated that no major differences can be found for the adsorption

472   kinetics for both materials and both matrices. All the systems attained adsorption

473   equilibrium after 120 to 240 min of contact between the adsorbent and CBZ. Overall,

474   and considering that equilibrium is quickly reached, both SBG-based carbons are

475   kinetically adequate for wastewater treatment, combining quick kinetics with no

476   significant matrix interferences (that could have been possibly observed due to the

477   compositional complexity of the Sewage Treatment Plant's effluent) in the time needed

478   to attain equilibrium.

479

480   3.3.2. Adsorption equilibrium

481   The adsorption isotherms, represented as the amount of CBZ adsorbed onto

482   KOH-BW-800-150 and KOH-PL-800-150 at equilibrium (q_e, mg g^{-1}) *versus* the amount

483   of pharmaceutical remaining in solution (C_e, mg L^{-1}), are shown in Fig. 3. The fitting

484   parameters obtained for the experimental data using Langmuir and Freundlich isotherm

485   models (Eqs. (6) and (7), respectively) are summarized in Table 4. The Langmuir-

486   Freundlich equilibrium model (Sips, 1948) has also been tested for fitting the

487   experimental data. However, the determination of the Langmuir-Freundlich adsorption

488   parameters was ambiguous for all systems, and thus it was not considered in this

489   discussion.

490   According to the results obtained for the r^2, ranging from 0.953 to 0.983, the

491   equilibrium experimental data are satisfactorily described by the Langmuir model, for

492   both matrices and materials. As evidenced in Fig. 3 and confirmed by the adsorption

493   parameters depicted in Table 4, it was possible to conclude that the Langmuir maximum

494   adsorption capacity (q_m) for KOH-BW-800-150 and KOH-PL-800-150, was

495   significantly higher in ultrapure water than in wastewater. The q_m in wastewater

496   decreased ~70 and ~60% for KOH-BW-800-150 and KOH-PL-800-150, respectively.

497   This can be due to the complex chemical composition of the wastewater, which contains

498   organic and inorganic components, such as dissolved organic matter, that can compete

499   for the adsorption sites of the carbons and, consequently, hamper the access to the pores

500   of the adsorbents (Oliveira et al., 2018; Silva et al., 2019). These results reinforce that,

501   despite the relevance of a first evaluation of the adsorptive capacity of the materials in

ultrapure water, tests using real wastewater are of utmost importance to predict the

behavior of the adsorbents under conditions as close as possible to their real application.

A comparison between KOH-BW-800-150 and KOH-PL-800-150 reveals that

these two materials have a similar q_m (190 ± 27 and 178 ± 10, respectively), in ultrapure

water. In wastewater the q_m was slightly lower for KOH-BW-800-150 than for KOH-

PL-800-150 (57.4 ± 1.6 and 76.0 ± 1.5, respectively). Still, the performance of the

materials is very similar with no major differences between them, highlighting that SBG

resulting from different fermentation levels do not result in adsorbents materials with

significantly distinct adsorptive properties for the systems considered in the present

study.

The removal of CBZ from both ultrapure water and wastewater through

adsorption onto commercial or waste-based carbon adsorbents has been addressed in the

literature by several authors. Table 5 presents some examples of relevant studies from

the last 5 years, allowing for a comparative evaluation of the performance of the

materials depicted in the present study. Along with the maximum adsorption capacity

towards CBZ, S_{BET} of the materials was also presented as it is considered a key property

of the adsorbents. The results here obtained are comparable to the performances

observed for commercial ACs, which attained q_m between 116 mg g^{-1} (Calisto et al.,

2015) and 242 mg g^{-1} (Delgado et al., 2019) in ultrapure pure or distilled water. This is a

good indication of the satisfactory removal efficiencies of the materials derived from

SBG chemical activation and pyrolysis. When compared with other waste-based

adsorbents, *biochars* produced by carbonization with no activation agents have

significantly lower performances (Calisto et al., 2017; Nielsen et al., 2015), as it was

also verified for the *biochars* produced from SBG, corroborating the need of such

526   activation procedures to attain efficiencies comparable to commercially available

527   options. On the other hand, ACs produced from industrial or agricultural wastes present

528   significantly higher performances than *biochars* and similar to the results obtained for

529   AC produced from SBG (up to 190 mg g^{-1}), varying from 93 mg g^{-1} (Oliveira et al.,

530   2018) to 335 mg g^{-1} (Torrellas et al., 2015). While the evaluation of the materials'

531   adsorptive capacity in ultrapure or distilled water is always considered in the literature,

532   fewer works were carried out in real matrices, namely wastewater. In these cases, and

533   considering CBZ in particular, some studies reported that the adsorptive removal

534   remained almost unchanged (Silva et al., 2019) while others observed a significant

535   decrease in the ability to remove the target pollutant (Oliveira et al., 2018), as verified

536   for the AC described in the present work. In this context, further research needs to be

537   done to improve the adsorptive performance of the adsorbent materials at conditions

538   representative of the target application, where the competition with dissolved organic

539   matter and other organic and inorganic compounds could be determinant. The

540   modification of the adsorbent surface by chemical functionalization could be a possible

541   way to improve the affinity of the materials towards specific pharmaceuticals.

542   Overall, considering the large-scale production all over the world and the

543   sustainable nature of the precursor used in the production of adsorbents, the results

544   presented in this study indicate that SBG is a viable AC precursor that might be

545   successfully applied to the removal of pharmaceuticals from water. Nevertheless, it

546   should be highlighted that the sustainability of the whole process can be hampered by

547   the use of high temperatures and pyrolysis times combined with high proportions of

548   activating agents, which are required for obtaining materials with adequate properties

549   for increased adsorptive performances. In this sense, further research should be carried

out to investigate the conversion of SBG into AC using milder conditions by applying,

for instance, alternative heating technologies, such as microwave-induced pyrolysis.

Moreover, the produced adsorbents are in powdered form, which might hinder their

affordable applicability in Sewage Treatment Plants due to the need of introducing an

additional step aimed at separating the treated aqueous phase from the powdered AC.

This might be overcome by (i) testing the introduction of magnetic properties in the

produced AC, and (ii) testing the performance of SBG-derived granular materials. In

fact, the applied production process allows to obtain higher particle sizes (granular AC)

without the need of any extra step (such as the addition of agglomeration agents).

4. Conclusions

The chemical activation of SBG was fundamental to obtain high-efficiency

adsorbents, being KOH-ACs the materials with the most interesting physicochemical

characteristics and the best adsorptive performance towards CBZ. Moreover, using as

precursor SBG from different types of fermentation does not influence the adsorbents'

properties. Adsorption studies in Sewage Treatment Plant´s wastewater allowed to

verify a decrease in the performance of the materials, in comparison to ultrapure water,

highlighting the importance of using realistic matrices as model systems. This study

represents a step forward in the utilization of SBG for ACs production, enabling its

application to the effective adsorption of pharmaceuticals.

Supplementary Materials

E-supplementary data of this work can be found in online version of the paper.

References

Aga, D.S., 2008. Fate of pharmaceuticals in the environment and in water treatment systems.

Azargohar, R., Dalai, A.K., 2008. Steam and KOH activation of biochar: Experimental and modeling studies. Microporous Mesoporous Mater. 110, 413–421. doi:10.1016/j.micromeso.2007.06.047

Bahlmann, A., Carvalho, J.J., Weller, M.G., Panne, U., Schneider, R.J., 2012. Immunoassays as high-throughput tools: Monitoring spatial and temporal variations of carbamazepine, caffeine and cetirizine in surface and wastewaters. Chemosphere 89, 1278–1286. doi:10.1016/j.chemosphere.2012.05.020

598   Barrozo, M.A.S., Borel, L.D., Lira, T.S., Ataíde, C.H., 2019. Fluid dynamics analysis

599   and pyrolysis of brewer's spent grain in a spouted bed reactor. Particuology 42,

600   199–207. doi:10.1016/j.partic.2018.06.001

601   Borel, L.D., Lira, T.S., Ribeiro, J.A., Ataíde, C.H., Barrozo, M.A.S., 2018. Pyrolysis of

602   brewer's spent grain: Kinetic study and products identification. Ind. Crops Prod.

603   121, 388–395. doi:10.1016/j.indcrop.2018.05.051

604   Calisto, V., Domingues, M.R.M., Erny, G.L., Esteves, V.I., 2011. Direct

605   photodegradation of carbamazepine followed by micellar electrokinetic

606   chromatography and mass spectrometry. Water Res. 45, 1095–1104.

607   doi:10.1016/j.watres.2010.10.037

608   Calisto, V., Ferreira, C.I.A., Oliveira, J.A.B.P., Otero, M., Esteves, V.I., 2015.

609   Adsorptive removal of pharmaceuticals from water by commercial and waste-

610   based carbons. J. Environ. Manage. 152. doi:10.1016/j.jenvman.2015.01.019

611   Calisto, V., Ferreira, C.I.A., Santos, S.M., Gil, M.V., Otero, M., Esteves, V.I., 2014.

612   Production of adsorbents by pyrolysis of paper mill sludge and application on the

613   removal of citalopram from water. Bioresour. Technol. 166, 335–344.

614   doi:http://dx.doi.org/10.1016/j.biortech.2014.05.047

615   Calisto, V., Jaria, G., Silva, C.P., Ferreira, C.I.A., Otero, M., Esteves, V.I., 2017. Single

616   and multi-component adsorption of psychiatric pharmaceuticals onto alternative

617   and commercial carbons. J. Environ. Manage. 192, 15–24.

618   Chen, D., Xie, S., Chen, C., Quan, H., Hua, L., Luo, X., Guo, L., 2017. Activated

619   biochar derived from pomelo peel as a high-capacity sorbent for removal of

620   carbamazepine from aqueous solution. RSC Adv. 7, 54969–54979.

621   doi:10.1039/C7RA10805B

622   Clara, M., Strenn, B., Kreuzinger, N., 2004. Carbamazepine as a possible anthropogenic

623   marker in the aquatic environment: investigations on the behaviour of

624   carbamazepine in wastewater treatment and during groundwater infiltration. Water

625   Res. 38, 947–954.

626   Coates, J., 2000. Interpretation of Infrared Spectra - A Practical Approach, in: Meyers,

627   R.A. (Ed.), Encyclopedia of Analytical Chemistry. John Wiley & Sons Ltd,

628   Chichester, pp. 10815–10837.

629   Delgado, N., Capparelli, A., Navarro, A., Marino, D., 2019. Pharmaceutical emerging

630   pollutants removal from water using powdered activated carbon: Study of kinetics

631   and adsorption equilibrium. J. Environ. Manage. 236, 301–308.

632   doi:10.1016/J.JENVMAN.2019.01.116

633   Fekadu, S., Alemayehu, E., Dewil, R., Van der Bruggen, B., 2019. Pharmaceuticals in

634   freshwater aquatic environments: A comparison of the African and European

635   challenge. Sci. Total Environ. 654, 324–337.

636   doi:10.1016/J.SCITOTENV.2018.11.072

637   Ferraz, A.I., Tavares, M.T., Teixeira, J.A., 2005. Sorption of Cr (III) from aqueous

638   solutions by spent brewery grain. CHEMPOR 2005 - 9th Int. Chem. Eng. Conf.

639   s.n.

640   Fontana, I.B., Peterson, M., Cechinel, M.A.P., 2018. Application of brewing waste as

641   biosorbent for the removal of metallic ions present in groundwater and surface

642   waters from coal regions. J. Environ. Chem. Eng. 6, 660–670.

643   doi:10.1016/J.JECE.2018.01.005

644   Fontana, K.B., Chaves, E.S., Sanchez, J.D.S., Watanabe, E.R.L.R., Pietrobelli,

645   J.M.T.A., Lenzi, G.G., 2016. Textile dye removal from aqueous solutions by malt

646   bagasse: Isotherm, kinetic and thermodynamic studies. Ecotoxicol. Environ. Saf.

647   124, 329–336. doi:10.1016/j.ecoenv.2015.11.012

648   Freundlich, H., 1906. Over the adsorption in solution. J. Phys. Chem. 18, 385–470.

649   Gonçalves, G. da C., Nakamura, P.K., Furtado, D.F., Veit, M.T., 2017. Utilization of

650   brewery residues to produces granular activated carbon and bio-oil. J. Clean. Prod.

651   168, 908–916. doi:10.1016/J.JCLEPRO.2017.09.089

652   Ho, Y.S., McKay, G., Wase, D.A.J., Forster, C.F., 2000. Study of the sorption of

653   divalent metal ions on to peat. Adsorpt. Sci. Technol. 18, 639–650.

654   doi:10.1260/0263617001493693

655   Hunsom, M., Autthanit, C., 2013. Adsorptive purification of crude glycerol by sewage

656   sludge-derived activated carbon prepared by chemical activation with H_3PO_4 ,

657   K_2CO_3 and KOH. Chem. Eng. J. 229, 334–343. doi:10.1016/j.cej.2013.05.120

658   Jaria, G., Calisto, V., Gil, M.V., Otero, M., Esteves, V.I., 2015. Removal of fluoxetine

659   from water by adsorbent materials produced from paper mill sludge. J. Colloid

660   Interface Sci. 448, 32–40. doi:http://dx.doi.org/10.1016/j.jcis.2015.02.002

661   Jaria, G., Calisto, V., Silva, C.P., Gil, M.V., Otero, M., Esteves, V.I., 2019. Obtaining

662   granular activated carbon from paper mill sludge – A challenge for application in

663   the removal of pharmaceuticals from wastewater. Sci. Total Environ. 653, 393–

664   400. doi:10.1016/J.SCITOTENV.2018.10.346

665   Jaria, G., Silva, C.P., Ferreira, C.I.A., Otero, M., Calisto, V., 2017. Sludge from paper

666   mill effluent treatment as raw material to produce carbon adsorbents: An

667   alternative waste management strategy. J. Environ. Manage. 188, 203–211.

668   Jelic, A., Gros, M., Ginebreda, A., Cespedes-Sánchez, R., Ventura, F., Petrovic, M.,

669   Barcelo, D., 2011. Occurrence, partition and removal of pharmaceuticals in sewage

670   water and sludge during wastewater treatment. Water Res. 45, 1165–1176.

671   doi:10.1016/j.watres.2010.11.010

672   Jones, O.A., Voulvoulis, N., Lester, J.N., 2002. Aquatic environmental assessment of

673   the top 25 English prescription pharmaceuticals. Water Res. 36, 5013–5022.

674   Lagergren, S., 1898. About the Theory of So-called Adsorption of Soluble Substances.

675   K. Sven. Vetenskapsakademiens 24, 1–39.

676   Langmuir, I., 1916. The constitution and fundamental properties of solids and liquids. J.

677   Am. Chem. Soc. 38, 2221–2295. Doi:10.1021/ja02268a002

678   Li, W.C.C., 2014. Occurrence, sources, and fate of pharmaceuticals in aquatic

679   environment and soil. Environ. Pollut. 187, 193–201.

680   doi:10.1016/j.envpol.2014.01.015

681   Mahmood, T., Ali, R., Naeem, A., Hamayun, M., Aslam, M., 2017. Potential of used

682   Camellia sinensis leaves as precursor for activated carbon preparation by chemical

683   activation with H3PO4; optimization using response surface methodology. Process

684   Saf. Environ. Prot. 109, 548–563. doi:10.1016/j.psep.2017.04.024

685   Molina-Sabio, M., Rodríguez-Reinoso, F., Caturla, F., Sellés, M.J., 1995. Porosity in

686   granular carbons activated with phosphoric acid. Carbon N. Y. 33, 1105–1113.

687   doi:https://doi.org/10.1016/0008-6223(95)00059-M

688   Nielsen, L., Zhang, P., Bandosz, T.J., 2015. Adsorption of carbamazepine on

689   sludge/fish waste derived adsorbents: Effect of surface chemistry and texture.

690   Chem. Eng. J. 267, 170–181. doi:10.1016/J.CEJ.2014.12.113

691   Olajire, A., Abidemi, J., Lateef, A., Benson, N.U., 2017. Adsorptive desulphurization of

692   model oil by Ag nanoparticles-modified activated carbon prepared from brewer's

693   spent grains. J. Environ. Chem. Eng. 5, 147–159. doi:10.1016/j.jece.2016.11.033

694   Oliveira, G., Calisto, V., Santos, S.M., Otero, M., Esteves, V.I., 2018. Paper pulp-based

695   adsorbents for the removal of pharmaceuticals from wastewater: A novel approach

696   towards diversification 631–632, 1018–1028.

697   Olszewski, M.P., Arauzo, P.J., Wądrzyk, M., Kruse, A., 2019. Py-GC-MS of

698   hydrochars produced from brewer's spent grains. J. Anal. Appl. Pyrolysis 140,

699   255–263. doi:10.1016/j.jaap.2019.04.002

700   Silva, C.P., Jaria, G., Otero, M., Esteves, V.I., Calisto, V., 2019. Adsorption of

701   pharmaceuticals from biologically treated municipal wastewater using paper mill

702   sludge-based activated carbon. Environ. Sci. Pollut. Res. 26, 13173–13184.

703   doi:10.1007/s11356-019-04823-w

704   Silva, J.P., Sousa, S., Rodrigues, J., Antunes, H., Porter, J., Gonçalves, I., Ferreira-Dias,

705   S., 2004. Adsorption of acid orange 7 dye in aqueous solutions by spent brewery

706   grains. Sep. Purif. Technol. 40, 309–315. doi:10.1016/j.seppur.2004.03.010

707   Sips, R., 1948. On the structure of a catalyst surface. J. Chem. Phys. 16, 490–495.

708   doi:10.1063/1.1746922

709   To, M.-H., Hadi, P., Hui, C.-W., Lin, C.S.K., McKay, G., 2017. Mechanistic study of

710   atenolol, acebutolol and carbamazepine adsorption on waste biomass derived

711   activated carbon. J. Mol. Liq. 241, 386–398. doi:10.1016/J.MOLLIQ.2017.05.037

712   Torrellas, S.Á., García Lovera, R., Escalona, N., Sepúlveda, C., Sotelo, J.L., García, J.,

713   2015. Chemical-activated carbons from peach stones for the adsorption of

714   emerging contaminants in aqueous solutions. Chem. Eng. J. 279, 788–798.

715   Tran, N.H., Reinhard, M., Gin, K.Y.-H., 2018. Occurrence and fate of emerging

716   contaminants in municipal wastewater treatment plants from different geographical

717   regions-a review. Water Res. 133, 182–207. doi:10.1016/J.WATRES.2017.12.029

718 Vanreppelen, K., Vanderheyden, S., Kuppens, T., Schreurs, S., Yperman, J., Carleer, R.,

719   2014. Activated carbon from pyrolysis of brewer's spent grain: Production and

720   adsorption properties. Waste Manag. Res. 32, 634–645.

721   doi:10.1177/0734242X14538306

722 Wierzba, S., Andrzej, K., 2019. Heavy metal sorption in biosorbents - Using spent grain

723   from the brewing industry. J. Clean. Prod. 225, 112–120.

724   doi:10.1016/j.jclepro.2019.03.286

725 Wierzba, S., Rajfur, M., Nabrdalik, M., Kłos, A., 2019. Assessment of the influence of

726   counter ions on biosorption of copper cations in brewer's spent grain - Waste

727   product generated during beer brewing process. Microchem. J. 145, 196–203.

728   doi:10.1016/j.microc.2018.10.040

729

Table 1. Proximate analyses for precursors (BW and PL) and activated carbons produced by chemical activation with KOH (KOH-BW-800-150 and KOH-PL-800-150)

Material	Moisture	Volatile matter (VM)	Fixed carbon (FC)	Ash	VM/FC
		(*wt*%, dry basis)			
BW	3.34	74.08	21.95	3.97	3.38
PL	2.86	75.75	19.30	4.95	3.93
KOH-BW-800-150	24.71	12.43	83.12	4.45	0.15
KOH-PL-800-150	22.90	8.24	78.00	13.76	0.11

Table 2. Point of zero charge and amount of carboxyl and total basic functional groups of KOH-BW-800-150 and KOH-PL-800-150 determined by back titration

Material	Functional groups (mmol g^{-1})		Point of zero charge
	Carboxylic acids	Basic groups (Total)	
KOH-BW-800-150	2.27	2.29	6.9
KOH-PL-800-150	2.28	2.56	8.0

Table 3. Textural characterization of all the produced carbon adsorbents – specific surface area (S_{BET}); total pore volume (V_p); micropore volume (W_0); and average micropore width (L).

Material	S_{BET} (m^2 g^{-1})	V_p (cm^3 g^{-1})	*Dubinin-Astakhov* (DA)	
			W_0 (cm^3 g^{-1})	L (nm)
BC-BW-800-60	3	0.01	0.001	1.79
BC-BW-800-150	3	0.01	0.001	1.77
KOH-BW-800-150	1090	0.55	0.44	1.48
NaOH-BW-800-150	18	0.02	0.01	1.95
H$_3$PO$_4$-BW-800-150	14	0.02	0.01	1.86
BC-PL-800-60	4	0.02	0.002	1.91
BC-PL-800-150	5	0.02	0.002	1.82
KOH-PL-800-150	1120	0.60	0.46	1.49
NaOH-PL-800-150	267	0.54	0.12	1.73
H$_3$PO$_4$-PL-800-150	29	0.05	0.02	2.04

Table 4. Fitting parameters of pseudo-first and pseudo-second order kinetic models, and of Langmuir and Freundlich equilibrium models, to the experimental data

		Ultrapure water		Wastewater	
		KOH-BW-800-150	KOH-PL-800-150	KOH-BW-800-150	KOH-PL-800-150
Kinetic models					
Pseudo 1st order	q_e (mg g^{-1})	179 ± 4	182 ± 9	45 ± 3	59 ± 4
	k_1 (min^{-1})	0.066 ±0.006	0.09 ± 0.02	0.024 ± 0.005	0.037 ± 0.009
	r^2	0.993	0.959	0.948	0.933
	$n*$	7	7	7	7
Pseudo 2nd order	q_e (mg g^{-1})	199 ± 11	201 ± 7	51 ± 3	64 ± 2
	k_2 (mg g^{-1} min)	0.0004 ± 0.0001	0.0006 ± 0.0001	0.0005 ± 0.0001	0.0009 ± 0.0002
	r^2	0.974	0.985	0.979	0.974
	$n*$	7	7	7	7
Equilibrium adsorption models					
Langmuir	q_m (mg g^{-1})	190 ± 27	178 ± 10	57.4 ± 1.6	76.0 ± 1.5
	K_L (L mg^{-1})	3 ± 2	6 ± 2	36 ± 21	60 ± 25
	r^2	0.953	0.966	0.973	0.983
	$n*$	6	9	9	9
Freundlich	K_F (mg g^{-1} (mg L^{-1})$^{-N}$)	144 ± 12	151 ± 4	55.0 ± 1.3	73.4 ± 1.4
	N	7 ± 5	5.3 ± 1.6	32 ± 25	25 ± 12
	r^2	0.944	0.959	0.966	0.979
	$n*$	6	9	9	9

* n is the number of data points used in the fitting.

Table 5. Examples of literature studies reporting the adsorptive removal of carbamazepine using commercial or waste-based carbon adsorbents

Adsorbent	S_{BET} (m² g⁻¹)	Equilibrium experimental conditions[1]	Maximum adsorption capacity[2] (mg g⁻¹)	Reference
Commercial AC (PBFG4)	848	T = 25 ºC; C_0 = 5 mg L⁻¹	116 (ultrapure water)	(Calisto et al. 2015)
Comercial AC (Norit)	996	T = 25 ºC; C_0 = 5 mg L⁻¹	174 (ultrapure water); 160 (wastewater, pH 7.7 - 7.9)	(Silva et al. 2019)
Commercial AC from vegetable origin	1328	T = 25 ºC; C_0 = 10 - 40 mg L⁻¹	242 (distilled water, pH ~6)	(Delgado et al. 2019)
Biochar from paper mill sludge	414	T = 25 ºC; C_0 = 5 mg L⁻¹	17.4 (ultrapure water, converted from µmol g⁻¹)	(Calisto et al. 2017)
Carbonized sewage sludge+fish waste	34 - 101	T = 30 ºC; C_0 = 1 – 100 mg L⁻¹	4.9 – 37.2 (Sips isotherm)	(Nielsen et al. 2015)
AC from bleached paper pulp	768 - 965	T = 25 ºC; C_0 = 5 mg L⁻¹	57 - 93 (ultrapure water); 29.9 - 80 (wastewater, pH 7.8)	(Oliveira et al. 2018)
AC from paper mill sludge	1627	T = 25 ºC; C_0 = 5 mg L⁻¹	212 (ultrapure water); 209 (wastewater, pH 7.7 - 7.9)	(Silva et al. 2019)
AC from palm kernel shell	711.5	T = 25 ºC; C_0 = 100 – 250 mg L⁻¹	208 (ultrapure water, pH 7, converted from mmol g⁻¹)	(To et al. 2017)
AC from peach stones	959 - 1216	T = 30 ºC; C_0 = 100 mg L⁻¹	335 (ultrapure water)	(Torrellas et al. 2015)
AC from pomelo peel	198.0 – 904.1	T = 25 ºC; C_0 = 10 – 100 mg L⁻¹	80.64 - 286.5 (ultrapure water)	(Chen et al. 2017)
AC from spent brewery grains	1090-1120	T = 25 ºC; C_0 = 5 mg L⁻¹	178 - 190 (ultrapure water); 57.4 – 76.0 (wastewater, pH 8.4)	This study

[1] C_0 – carbamazepine initial concentration

[2] Maximum adsorption capacity determined by fitting the experimental data with the Langmuir isotherm model, unless stated otherwise

Fig. 1. SEM images of precursors (BW, PL), *biochars* (BC-BW-800-150, BC-PL-800-150) and AC (KOH-BW-800-150 and KOH-PL-800-150) at different magnifications

Fig. 2. Kinetic fittings for experimental data for KOH-BW-800-150 in a) ultrapure water and b) wastewater; and for KOH-PL-800-150 in c) ultrapure water and d) wastewater. The results were fitted to pseudo-first (solid lines) and pseudo-second (dashed lines) order kinetic models. Each point (± standard deviation) is the average of three replicates. Note that x and y-axis scales are not the same in all graphs to allow a better visualization of the results

Fig. 3. Fittings for the isotherms experimental data for KOH-BW-800-150 in a) ultrapure water and b) wastewater; and for KOH-PL-800-150 in c) ultrapure water and d) wastewater. The results were fitted to Langmuir (solid lines) and Freundlich (dashed lines) equilibrium models. Each point (± standard deviation) is the average of three replicates. Note that x and y-axis scales are not the same in all graphs to allow a better visualization of the results

3 000 ×

500 ×

PL

3 000 ×

500 ×

BW

10 000 ×

3 000 ×

BC-PL-800-150

10 000 ×

3 000 ×

BC-BW-800-150

20 000 ×

10 000 ×

KOH-PL-800-150

20 000×

10 000 ×

KOH-BW-800-150