Upcycling spent brewery grains through the production of carbon adsorbents –
application to the removal of carbamazepine from water

Andreia F. C. Sousa\textsuperscript{a}, María Victoria Gil\textsuperscript{b}, Vânia Calisto\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a}Department of Chemistry and CESAM (Centre for Environmental and Marine Studies),
University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal

\textsuperscript{b}Instituto Nacional del Carbón, INCAR-CSIC, Calle Francisco Pintado Fe 26, 33011
Oviedo, Spain

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

Spent brewery grains, a by-product of the brewing process, were used as precursor of biochars and activated carbons to be applied to the removal of pharmaceuticals from water. Biochars were obtained by pyrolysis of the raw materials, while activated carbons were produced by adding a previous chemical activation step. The influence of using different precursors (from distinct fermentation processes), activating agents (potassium hydroxide, sodium hydroxide and phosphoric acid), pyrolysis temperatures, and residence times was assessed. The adsorbents were physicochemically characterized and applied to the removal of the antiepileptic carbamazepine from water. Potassium hydroxide activation produced the materials with the most promising properties and adsorptive removals, with specific surface areas up to 1120 m² g⁻¹ and maximum adsorption capacities up to 190 ± 27 mg g⁻¹ in ultrapure water. The adsorption capacity suffered a reduction of <70% in wastewater, allowing to evaluate the impact of realistic matrices on the efficiency of the materials.

Keywords

Brewery wastes; Pyrolysis; Chemical activation; Activated carbon; Pharmaceuticals; Wastewater treatment.
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).
However, considering that the efficient reuse of this agro-industrial waste can be important, not only from the perspective of the brewer who can benefit from the valorization of this by-product, but also from an environmental point of view, the study of alternative SBG applications is highly desirable (Barrozo et al., 2019). In this context, comes up the possibility of using SBG to produce adsorbent materials aiming at the adsorptive removal of water micro-contaminants, such as pharmaceuticals.

In the last years, a few studies have reported the possibility to use raw and processed SBG as adsorbent to remove contaminants from water. To the best of the authors’ knowledge, the application of SBG to the removal of pharmaceuticals from water has not been so far reported in literature. However, some examples of the application of this material to the removal of other organic pollutants, such as dyes used in paper and textile industries (Fontana et al., 2016; Silva et al., 2004), or inorganic pollutants, such as metals (Ferraz et al., 2005; Wierzba and Andrzej, 2019), from water can be found in literature. Concerning organic contaminants, Silva et al. (2004) studied the removal of acid orange 7, a dye currently used in paper and textile industries, by SBG in aqueous solutions (Silva et al., 2004). The results showed high levels of color removal (above 90%, for an initial dye concentration of 60 mg L\(^{-1}\)), with low contact times between adsorbent and dye (less than 1 h), attaining a maximum adsorption capacity of ~30.5 mg g\(^{-1}\), at 30 °C. The reported removal capacity was obtained using the SBG in its raw form, i.e., without any previous treatments such as milling and/or sieving, incineration or chemical modification. Gonçalves et al. (2017) used SBG to produce bio-oil and a granular AC via pyrolysis and CO\(_2\) activation (Gonçalves et al., 2017). In the production of the AC by these authors, the effect of the activation time on 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$_3$PO$_4$; 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%),
sodium hydroxide (EKA pellets, pure). The ultrapure water was obtained from a Milli-Q Millipore system (Milli-Q plus 185).

2.2. Production of carbon adsorbents

To produce the adsorbent materials, SBG from the brewery Faustino Microcervejeira, Lda (Aveiro, Portugal) was used as precursor. In order to evaluate the effect of using SBG arising from different types of fermentation on the properties of the produced materials, two different residues were collected: SBG from the production of Barleywine (BW), a type of beer that has a high fermentation, and SBG from the production of Pilsener (PL), beer that has a low fermentation process. After collection, the SBG was dried at room temperature for several days, followed by a 24 h period at 104 °C in an oven, to eliminate the moisture. Then, it was grinded with a blade mill and stored dry until use. The adsorbents were produced by pyrolysis of BW and PL in a furnace muffle (Nüve, series MF 106, Turkey) under inert environment (nitrogen flow), at different temperatures (heating rate of 10 °C min⁻¹) and residence times, and with (AC) or without (biochar) a previous activation process, as detailed below. The yield of production (η) of all carbon adsorbents produced was calculated by Eq. (1):

\[ \eta(\%) = \left( \frac{\text{final mass of carbon adsorbent (g)}}{\text{mass of precursor (g)}} \right) \times 100 \]  

2.2.1. Preparation of biochar

The raw SBG was weighed in porcelain crucibles and carbonized at 600 °C and 800 °C, using residence times of 60 and 150 min. Accordingly, BW was pyrolyzed under such conditions, resulting in the following materials: BC-BW-600-60, BC-BW-600-150, BC-BW-800-60, and BC-BW-800-150. Preliminary tests carried out with
these materials indicated that pyrolysis at 600 °C, 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 °C) was used for PL, i.e., it was treated at 800 °C 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 °C for 150 min. The chemical agents used for activation were KOH, NaOH and H$_3$PO$_4$ 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$_3$PO$_4$, 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
materials were obtained: KOH-BW-800-150, NaOH-BW-800-150, H$_3$PO$_4$-BW-800-150, KOH-PL-800-150, NaOH-PL-800-150 and H$_3$PO$_4$-PL-800-150.

2.3. Characterization of precursors and carbon adsorbents

The precursors (PL and BW) and the obtained materials were characterized by the following techniques: total organic carbon, proximate analysis, Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR), point of zero charge, determination of carbons' functional groups by back-titration, $S_{BET}$ and scanning electron microscopy (SEM). A detailed description of the procedures used can be found in the Supplementary Material (SM).

2.4. Batch adsorption experiments

In order to test the adsorptive performance of the produced materials for the removal of CBZ from water, adsorption experiments were made under shaking and batch conditions. In a first analysis of the produced biochars and ACs, some preliminary adsorption tests were carried out in order to select the most promising materials that will be subjected to a deeper analysis (kinetic and isothermal studies). For these tests, CBZ solutions with an initial concentration ($C_i$) of 5 mg L$^{-1}$ were prepared in ultrapure water. Subsequently, these solutions were placed in polypropylene tubes containing a known mass of adsorbent (varying from 25 to 1000 mg L$^{-1}$ for biochars and 25 to 50 mg L$^{-1}$ for ACs) and shaken in an overhead shaker (Heidolph, Reax 2) at 80 rpm for 24 h and under controlled temperature (25.0 °C ± 0.1 °C). Based on the adsorption percentages resulting from these experiments, the materials with the best adsorptive properties were selected for further studies, as described in sections 2.4.1 and 2.4.2.
Generally, all studies (preliminary, kinetic and equilibrium) were performed in triplicate. Each experiment included a control (CBZ solution without the adsorbent) that was used as reference for the calculation of adsorption percentages after the contact time between the solution and the material. After stirring under specific conditions, sample aliquots were filtered through 0.22 μm PVDF filters (Whatman) and analyzed by Micellar Electrokinetic Chromatography, in order to determine the remaining pharmaceutical concentration, as described in section 2.6.

2.4.1. Adsorption kinetics

To study the adsorption kinetics of CBZ onto the selected carbons (KOH-BW-800-150 and KOH-PL-800-150), a fixed dose of the carbon adsorbent (mg L\(^{-1}\)) was placed in tubes and put in contact with 45 mL of 5 mg L\(^{-1}\) of two aqueous solutions of CBZ (prepared in ultrapure water and wastewater, respectively). The concentrations of both KOH-BW-800-150 and KOH-PL-800-150 were 15 mg L\(^{-1}\) and 40 mg L\(^{-1}\) in ultrapure water and wastewater, respectively. The solutions were shaken for different time intervals between 5 and 240 min for ultrapure water, and 15 and 1860 min for wastewater. A minimum of six time intervals were considered for each system and the dose of carbon material was selected in order to obtain a significant adsorption percentage but, simultaneously, to avoid CBZ removals close to 100% which would difficult the analytical determination of the remaining CBZ concentration. The adsorbed concentration of CBZ onto each AC at time \(t\), \(q_t\) (mg g\(^{-1}\)), was calculated by Eq. (2). The experimental data were fitted by pseudo-first-order model (Lagergren, 1898) and pseudo-second-order model (Ho et al., 2000), presented in Eqs. (3) and (4), respectively, in order to determine the kinetic parameters of each system.
where $C_i$ (mg L$^{-1}$) is the initial concentration of pharmaceutical, $C_t$ (mg L$^{-1}$) is the concentration of pharmaceutical in solution at time $t$, $V$ (L) is the volume of solution, $m$ is the mass of adsorbent (g), $q_e$ refers to the amount of adsorbate per unit mass of adsorbent at equilibrium (mg g$^{-1}$), $k_1$ is the pseudo-first order rate constant (min$^{-1}$) and $k_2$ is the pseudo-second order rate constant (g mg$^{-1}$ min$^{-1}$). Non-linear fittings were performed using GraphPad Prism, version 5.

2.4.2. Adsorption equilibrium

For the determination of the adsorption isotherms, the experiments were performed using the shaking time needed to attain the equilibrium, as determined in section 2.4.1, and varying the concentration of carbon adsorbents while keeping the initial concentration of the CBZ constant (5 mg L$^{-1}$). These experiments allow to calculate the adsorption capacity of the materials. Briefly, 50 mL of a 5 mg L$^{-1}$ aqueous solution of CBZ was added at different doses of each carbon. For ultrapure water, the dose of KOH-BW-800-150 and KOH-PL-800-150 varied between 12.5-30 mg L$^{-1}$ and 20-40 mg L$^{-1}$, respectively; and for wastewater, it varied between 35-90 mg L$^{-1}$ and 25-70 mg L$^{-1}$, respectively. A minimum of six concentrations were considered for each system. The adsorbed concentration of CBZ onto each AC at the equilibrium, $q_e$ (mg g$^{-1}$), was calculated by Eq. (5). The experimental data were fitted by Langmuir (Langmuir, 1916) and Freundlich (Freundlich, 1906) isotherm models.
(Eqs. (6) and (7), respectively) in order to determine the equilibrium parameters of the systems. Non-linear fittings were performed using GraphPad Prism, version 5.

\[ q_e = \frac{(C_e - C_0)^y}{m} \]  
\[ q_e = \frac{q_m \times K_L \times C_e}{1 + K_L \times C_e} \]  
\[ q_e = K_F \times C_e^{(1/N)} \]

where \( C_e \) (mg L\(^{-1}\)) is the concentration of CBZ in solution at the equilibrium, \( q_m \) is the maximum adsorption capacity of each material towards CBZ (mg g\(^{-1}\)), \( K_L \) is the Langmuir equilibrium constant (L mg\(^{-1}\)), \( K_F \) is the Freundlich equilibrium constant (mg g\(^{-1}\) (L mg\(^{-1}\))\(^{1/N}\)), \( N \) are the degrees of non-linearity, and all the other variables are defined as in Eqs. (2), (3) and (4).

2.5. Wastewater sampling

Wastewater was collected in June 2019 in a local Sewage Treatment Plant (Aveiro, Portugal) and it corresponds to the final effluent, after the biological treatment, as discharged into receiving waters (~3.3 km away from the coast, into the Atlantic Ocean). Immediately after collection in order to remove suspended organic matter, it was filtered through cellulose Supor-450 membrane disc filters 0.45 μm with a vacuum system. After filtration, the samples were stored in the dark at 4 °C and used within no longer than 15 days. The collected effluent was characterized by measuring conductivity (WTW meter), pH (pH/mV/°C meter pHemenenal® pH 1100L, VWR) and dissolved organic carbon content (TOC-VCPH Shimadzu). The pH, conductivity and dissolved organic carbon were 8.42, 2.78 ms cm\(^{-1}\) and 18.0 ± 0.8 mg L\(^{-1}\), respectively.

2.6. Pharmaceutical’s quantification
The quantification of CBZ was performed by Micellar Electrokinetic Chromatography using a Beckman P/ACE MDQ instrument (Fullerton, CA, USA), equipped with a UV-Vis detection system, controlled by the software 32 Karat, according to the procedure described by Calisto et al. (Calisto et al., 2011), with minor modifications. Briefly, a coated silica capillary with 30 cm to the detection window was used and the electrophoretic separation was performed at 25 °C and 25 kV, during 4.5 min runs. Ethylvanillin was used as internal standard and sodium tetraborate was used to obtain higher repeatability and better peak shape and resolution. Both were spiked to all samples and standard solutions at final concentrations of 3.34 mg L\(^{-1}\) and 10 mM, respectively. Detection of CBZ was monitored at 214 nm and the separation buffer consisted of 15 mM of sodium tetraborate and 20 mM of sodium dodecyl sulphate. The calibration curve was determined for a concentration range between 0.25 and 5 mg L\(^{-1}\). All the analyses were performed in triplicate.

3. Results and discussion

3.1. Yield of the adsorbents’ production

After the production (pyrolysis and washing) of the adsorbent materials, the production yield was calculated. A considerable difference between the values obtained for the biochars and for the ACs was observed. Briefly, the yields obtained were around 30 % for all biochars; 13 % for BW and PL KOH-ACs; 11 and 4 % for BW and PL NaOH-ACs, respectively; and around 51 % for BW and PL H\(_3\)PO\(_4\)-ACs. In general, the washing step was an inevitable cause for material losses, due to the removal of the inorganic fraction. The low production yields obtained for the KOH-ACs and NaOH-ACs (in opposition to the ones obtained for biochars and H\(_3\)PO\(_4\)-ACs) can be due to a
higher loss of volatile organic matter caused by the reaction with the alkali bases. On the other hand, for H$_3$PO$_4$-ACs, the product yield increased comparatively to biochars. According to Molina-Sabio et al. (1995), the high yield of H$_3$PO$_4$-ACs can be due to the formation of largest structural units by the reaction between this activating agent and the lignocellulosic precursor which do not escape as volatile matter during pyrolysis. This leads to a final material with higher density, most likely due to the generation of phosphate or polyphosphate structures (Hunsom and Autthanit, 2013), contributing to increase the product yield.

3.2. Physical and chemical characterization

The results concerning total organic carbon determination are presented in Table S1 of SM. Both precursors present a high value of total organic carbon (48.5 ± 0.6% and 48.2 ± 0.2% for BW and PL, respectively) and very low inorganic carbon contents (< limit of detection), corroborating that these residues constitute a promising raw material for the production of carbon adsorbents. Comparing the total organic carbon content values of the carbon adsorbents with those of the precursors, the increase for biochars and ACs is clear (~30 %), except for H$_3$PO$_4$-BW-800-150 and H$_3$PO$_4$-PL-800-150, for which total organic carbon remained similar to the precursor.

The thermogravimetric analyses of the raw materials (BW and PL) and the resulting KOH-ACs are depicted in Fig. S1 of SM, while the corresponding proximate analyses, reported on a dry basis, are depicted in Table 1. The results showed that BW and PL have similar characteristics, i.e., low ash contents and high volatile matter and fixed carbon contents. According to Fig. S1, a pronounced thermal decomposition of the precursors began at approximately 200 °C. However, BW and PL have three stages of
mass loss during the pyrolysis process, corresponding to derivative thermogravimetric
peaks at 84, 295 and 352 °C and 83, 283 and 351 °C, respectively. Initially, the
derivative thermogravimetric curve shows a peak (~80 °C) corresponding to the mass
loss derived from water evaporation (Mahmood et al., 2017; Oliveira et al., 2018). The
major weight loss was observed in the temperature range of 200-500 °C, which is due to
the thermal decomposition of the main SBG constituents (cellulose, hemicellulose and
lignin) (Mahmood et al., 2017). At ~500 °C the breakdown of lignocellulosic
material was finished, and no further weight loss was observed. This indicates that the
basic structure of carbon is expected to have been formed at 500 °C, which should be
considered as the lowest carbonization temperature for AC production from SBG. The
tested pyrolysis temperatures were 600 and 800 °C, since higher temperatures usually
translate into a higher development of microporosity, which is advantageous for
adsorbents with superior adsorption capacity (Calisto et al., 2014). For KOH-ACs, the
volatile matter content is much lower than that of the raw materials. On the other hand,
an increase (approximately four times higher) in the fixed carbon content was observed.
In fact, the ratio between the volatile matter and fixed carbon percentages for KOH-ACs
suffered a substantial decrease compared to the raw materials, indicating an extensive
volatile matter release with the increase of the non-volatile carbon fraction, which are
two factors that positively contribute to the formation of a carbon rich and highly
porous adsorbent (Calisto et al., 2014). The high fixed carbon content is consistent with
the total organic carbon determination. Moreover, the low ash content (below 15%) is
also in accordance with the low inorganic carbon content of the samples.

Regarding FTIR-ATR analyses, the spectra of the BW, PL and of the produced
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...
carboxyl and total basic groups, were obtained by back titrations (Table 2). Low point of zero charge is directly connected with the presence of high concentrations of the carboxyl groups; on the other hand, higher point of zero charge is linked to a higher concentration of total basic groups and lower concentration of carboxyl groups. The point of zero charge determined for KOH-BW-800-150 and KOH-PL-800-150 is neutral or slightly basic, respectively, which is in line with the very similar concentrations obtained for the two functional groups for both materials.

For the study of the textural features of the materials, nitrogen adsorption isotherms and SEM were used as characterization techniques. The results of $S_{BET}$ and the textural characterization of all the produced carbon adsorbents are presented in Table 3. PL-based carbons presented slightly higher $S_{BET}$ compared with BW-based carbons produced under the same conditions. This fact may be explained by the relative higher content of volatile matter in PL in comparison with BW. KOH-BW-800-150 and KOH-PL-800-150 were the materials with the highest $S_{BET}$, 1090 and 1120 m$^2$ g$^{-1}$, respectively. On the other hand, the ACs obtained with NaOH and H$_3$PO$_4$ chemical activation resulted in much lower $S_{BET}$, more comparable with the values obtained for the biochars than with the KOH-based ACs. The same conclusion is valid for total pore volume ($V_p$) and micropore volume ($W_0$) values, which will certainly influence the adsorptive capacity of these materials. This comparison is particularly interesting in the case of the materials resulting from KOH and NaOH chemical activation: the activating agents are of similar nature, both alkali hydroxides, but the results are drastically different for the two alkali metals, indicating that potassium has a determinant influence in the development of the microporosity.
A comparison of the $S_{\text{BET}}$ values obtained by other literature studies using precursors with similar nature reveals that the results presented in this manuscript are quite interesting. There are some works that use SGB in its raw form, as that described by Fontana et al. (Fontana et al., 2016), who only dried, crushed and sieved the raw material, and they obtained a $S_{\text{BET}}$ of 0.8246 m$^2$ g$^{-1}$. In what concerns materials resulting from chemical activation, most authors initially carbonize the previously dried SBG and then activate the resultant carbon material, adopting a two-step activation instead of the one-step procedure applied in the present manuscript. The study of Olajire et al. (Olajire et al., 2017) is an example of such cases, where dry SBG was carbonized at 300 °C during 30 minutes and subsequently activated with $\text{H}_3\text{PO}_4$ and subjected to a second carbonization at 300 °C during 1h. The resultant carbon presented a $S_{\text{BET}}$ of 412 m$^2$ g$^{-1}$ (Olajire et al., 2017). Also, a comparison of the materials described in this study with some commercially available ACs show that KOH-BW-800-150 and KOH-PL-800-150 presented higher $S_{\text{BET}}$. For example the commercial AC, PULSORB FG4 (PBFG4) and Norit (SAE SUPER 8003.6) (applied by Calisto et al. (Calisto et al., 2014) and Silva et al. (Silva et al., 2019), respectively) have a $S_{\text{BET}}$ of 848 and 996 m$^2$ g$^{-1}$, respectively, indicating that the produced materials have very promising properties to be used as adsorbents.

Fig. 1 shows the SEM images of both precursors and some examples of BW and PL-based carbons. The images show a gradual difference between the surface morphology of the precursors, the biochars and of the KOH-ACs. In comparison to ACs, the structure of biochars is more homogeneous, with some degree of destruction of the original structure and a few pores can be observed (as confirmed by $S_{\text{BET}}$ analysis). On the other hand, the structure of the KOH-AC is a much rougher surface.
(particularly, for PL-materials) with a well-developed porosity. The highly porous
structure is in accordance with a higher surface area, as can be confirmed by the results
of \( S_{\text{BET}} \), \( V_p \) and \( W_0 \) (Table 3). Other SEM images of the biochars and KOH-AC are
presented in Figs. S4 and S5 of SM, respectively, at different magnifications.

3.3. Batch adsorption experiments

Preliminary tests were performed to evaluate the adsorptive removal of CBZ
from water by all the produced carbons, allowing to identify the most promising
materials. For the biochars, a considerable range of carbon dosages (between 25 and
1000 mg L\(^{-1}\)) was tested. The results showed a negligible CBZ adsorption, even at
materials’ dose as high as 1000 mg L\(^{-1}\) (data not shown). This performance is in
accordance with the very low \( S_{\text{BET}} \) obtained for the non-activated carbons. Therefore,
kinetic and equilibrium studies were not performed with biochars.

On the other hand, the ACs revealed much more interesting results, even at
much lower carbon doses (25 and 50 mg L\(^{-1}\)) as evidenced by the data depicted in Table
S2 of SM. The ACs with the best adsorptive performance to remove CBZ (\( C_i = 5 \text{ mg L}^{-1} \))
from aqueous solutions were KOH-BW-800-150 and KOH-PL-800-150, with
adsorption percentages of 88 ± 11\% and 85 ± 7\%, respectively, using only 25 mg L\(^{-1}\) of
material. The others ACs were not able to satisfactorily adsorb CBZ at the tested doses,
with removal percentages below 15 ± 6\%, using 50 mg L\(^{-1}\) of material. Better removal
percentages for the KOH-ACs are certainly related with their \( S_{\text{BET}} \), \( V_p \) and \( W_0 \), which are
much higher than those obtained for NAOH-ACs and H\(_3\)PO\(_4\)-ACs (Table 3). Based on
these results, the two KOH-ACs (KOH-BW-800-150 and KOH-PL-800-150) were
selected to perform kinetic and equilibrium studies. For this purpose, both ultrapure
water and wastewater were used as test matrices, in order to evaluate the adsorptive behavior of the materials under more realistic and representative conditions.

3.3.1. Adsorption kinetics

The amount of CBZ adsorbed onto KOH-BW-800-150 and KOH-PL-800-150 at time $t (q_t, \text{mg g}^{-1})$ versus time, as well as the fittings of the experimental data to pseudo-first and second orders kinetic models (Eqs. (3) and (4), respectively) are represented in Fig. 2. The fitting parameters are summarized in Table 4. Generally, the pseudo-second-order model was the model that best fitted the experimental data, with determination coefficients ($r^2$) ranging from 0.974 to 0.985 (except for KOH-BW-800-150 in ultrapure water). The adequacy of the pseudo-second-order model to describe the adsorption of CBZ onto carbon adsorbents was in line with the results previously reported in several literature studies, where this model was the one presenting the most satisfactory fittings to the experimental data (Calisto et al., 2017, 2015; Chen et al., 2017; Oliveira et al., 2018; Silva et al., 2019; To et al., 2017).

Considering the adsorption of CBZ onto KOH-BW-800-150 and KOH-PL-800-150, it can be verified that the observed adsorption rates ($k_2$) determined by the pseudo-second-order model indicated that no major differences can be found for the adsorption kinetics for both materials and both matrices. All the systems attained adsorption equilibrium after 120 to 240 min of contact between the adsorbent and CBZ. Overall, and considering that equilibrium is quickly reached, both SBG-based carbons are kinetically adequate for wastewater treatment, combining quick kinetics with no significant matrix interferences (that could have been possibly observed due to the
compositional complexity of the Sewage Treatment Plant’s effluent) in the time needed
to attain equilibrium.

3.3.2. Adsorption equilibrium

The adsorption isotherms, represented as the amount of CBZ adsorbed onto
KOH-BW-800-150 and KOH-PL-800-150 at equilibrium ($q_e$, mg g$^{-1}$) versus the amount
of pharmaceutical remaining in solution ($C_e$, mg L$^{-1}$), are shown in Fig. 3. The fitting
parameters obtained for the experimental data using Langmuir and Freundlich isotherm
models (Eqs. (6) and (7), respectively) are summarized in Table 4. The Langmuir-
Freundlich equilibrium model (Sips, 1948) has also been tested for fitting the
experimental data. However, the determination of the Langmuir-Freundlich adsorption
parameters was ambiguous for all systems, and thus it was not considered in this
discussion.

According to the results obtained for the $r^2$, ranging from 0.953 to 0.983, the
equilibrium experimental data are satisfactorily described by the Langmuir model, for
both matrices and materials. As evidenced in Fig. 3 and confirmed by the adsorption
parameters depicted in Table 4, it was possible to conclude that the Langmuir maximum
adsorption capacity ($q_m$) for KOH-BW-800-150 and KOH-PL-800-150, was
significantly higher in ultrapure water than in wastewater. The $q_m$ in wastewater
decreased ~70 and ~60% for KOH-BW-800-150 and KOH-PL-800-150, respectively.
This can be due to the complex chemical composition of the wastewater, which contains
organic and inorganic components, such as dissolved organic matter, that can compete
for the adsorption sites of the carbons and, consequently, hamper the access to the pores
of the adsorbents (Oliveira et al., 2018; Silva et al., 2019). These results reinforce that,
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
activation procedures to attain efficiencies comparable to commercially available options. On the other hand, ACs produced from industrial or agricultural wastes present significantly higher performances than biochars and similar to the results obtained for AC produced from SBG (up to 190 mg g\(^{-1}\)), varying from 93 mg g\(^{-1}\) (Oliveira et al., 2018) to 335 mg g\(^{-1}\) (Torrellas et al., 2015). While the evaluation of the materials’ adsorptive capacity in ultrapure or distilled water is always considered in the literature, fewer works were carried out in real matrices, namely wastewater. In these cases, and considering CBZ in particular, some studies reported that the adsorptive removal remained almost unchanged (Silva et al., 2019) while others observed a significant decrease in the ability to remove the target pollutant (Oliveira et al., 2018), as verified for the AC described in the present work. In this context, further research needs to be done to improve the adsorptive performance of the adsorbent materials at conditions representative of the target application, where the competition with dissolved organic matter and other organic and inorganic compounds could be determinant. The modification of the adsorbent surface by chemical functionalization could be a possible way to improve the affinity of the materials towards specific pharmaceuticals.

Overall, considering the large-scale production all over the world and the sustainable nature of the precursor used in the production of adsorbents, the results presented in this study indicate that SBG is a viable AC precursor that might be successfully applied to the removal of pharmaceuticals from water. Nevertheless, it should be highlighted that the sustainability of the whole process can be hampered by the use of high temperatures and pyrolysis times combined with high proportions of activating agents, which are required for obtaining materials with adequate properties 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.
Acknowledgments

Thanks are due for the financial support to CESAM (UID/AMB/50017/2019), to FCT/MEC through national funds, and the co-funding by the FEDER, within the PT2020 Partnership Agreement and Compete 2020. Vânia Calisto is thankful to FCT for the Scientific Employment Stimulus Program (CEECIND/00007/2017), while Maria V. Gil acknowledges support from a Ramón y Cajal grant (RYC-2017-21937) of the Spanish government, co-financed by the European Social Fund (ESF). The authors would like to thank Valdemar Esteves, Marta Otero and Guilaine Jaria for the helpful scientific discussions. Milton Fontes and workers of Aveiro’s Sewage Treatment Plant (Águas do Centro Litoral) are gratefully acknowledged for assistance on the effluent sampling campaigns. The authors also thank Faustino Microcervejeira, Lda. (Aveiro, Portugal) and its head brewer Gonçalo Faustino for kindly providing the brewing residues used in this work.

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
Barrozo, M.A.S., Borel, L.D., Lira, T.S., Ataíde, C.H., 2019. Fluid dynamics analysis and pyrolysis of brewer’s spent grain in a spouted bed reactor. Particuology 42, 199–207. doi:10.1016/j.partic.2018.06.001

Borel, L.D., Lira, T.S., Ribeiro, J.A., Ataíde, C.H., Barrozo, M.A.S., 2018. Pyrolysis of brewer’s spent grain: Kinetic study and products identification. Ind. Crops Prod. 121, 388–395. doi:10.1016/j.indcrop.2018.05.051

Calisto, V., Domingues, M.R.M., Erny, G.L., Esteves, V.I., 2011. Direct photodegradation of carbamazepine followed by micellar electrokinetic chromatography and mass spectrometry. Water Res. 45, 1095–1104. doi:10.1016/j.watres.2010.10.037

Calisto, V., Ferreira, C.I.A., Oliveira, J.A.B.P., Otero, M., Esteves, V.I., 2015. Adsorptive removal of pharmaceuticals from water by commercial and waste-based carbons. J. Environ. Manage. 152. doi:10.1016/j.jenvman.2015.01.019

Calisto, V., Ferreira, C.I.A., Santos, S.M., Gil, M.V., Otero, M., Esteves, V.I., 2014. Production of adsorbents by pyrolysis of paper mill sludge and application on the removal of citalopram from water. Bioresour. Technol. 166, 335–344. doi:http://dx.doi.org/10.1016/j.biortech.2014.05.047

Calisto, V., Jaria, G., Silva, C.P., Ferreira, C.I.A., Otero, M., Esteves, V.I., 2017. Single and multi-component adsorption of psychiatric pharmaceuticals onto alternative and commercial carbons. J. Environ. Manage. 192, 15–24.

Chen, D., Xie, S., Chen, C., Quan, H., Hua, L., Luo, X., Guo, L., 2017. Activated biochar derived from pomelo peel as a high-capacity sorbent for removal of carbamazepine from aqueous solution. RSC Adv. 7, 54969–54979. doi:10.1039/C7RA10805B
Clara, M., Strenn, B., Kreuzinger, N., 2004. Carbamazepine as a possible anthropogenic marker in the aquatic environment: investigations on the behaviour of carbamazepine in wastewater treatment and during groundwater infiltration. Water Res. 38, 947–954.

Coates, J., 2000. Interpretation of Infrared Spectra - A Practical Approach, in: Meyers, R.A. (Ed.), Encyclopedia of Analytical Chemistry. John Wiley & Sons Ltd, Chichester, pp. 10815–10837.

Delgado, N., Capparelli, A., Navarro, A., Marino, D., 2019. Pharmaceutical emerging pollutants removal from water using powdered activated carbon: Study of kinetics and adsorption equilibrium. J. Environ. Manage. 236, 301–308. doi:10.1016/J.JENVMAN.2019.01.116

Fekadu, S., Alemayehu, E., Dewil, R., Van der Bruggen, B., 2019. Pharmaceuticals in freshwater aquatic environments: A comparison of the African and European challenge. Sci. Total Environ. 654, 324–337. doi:10.1016/J.SCITOTENV.2018.11.072

Ferraz, A.I., Tavares, M.T., Teixeira, J.A., 2005. Sorption of Cr (III) from aqueous solutions by spent brewery grain. CHEMPOR 2005 - 9th Int. Chem. Eng. Conf. s.n.

Fontana, I.B., Peterson, M., Cechinel, M.A.P., 2018. Application of brewing waste as biosorbent for the removal of metallic ions present in groundwater and surface waters from coal regions. J. Environ. Chem. Eng. 6, 660–670. doi:10.1016/J.JECE.2018.01.005

Fontana, K.B., Chaves, E.S., Sanchez, J.D.S., Watanabe, E.R.L.R., Pietrobelli, J.M.T.A., Lenzi, G.G., 2016. Textile dye removal from aqueous solutions by malt
Gonçalves, G. da C., Nakamura, P.K., Furtado, D.F., Veit, M.T., 2017. Utilization of brewery residues to produce granular activated carbon and bio-oil. J. Clean. Prod. 168, 908–916. doi:10.1016/J.JCLEPRO.2017.09.089

Hunsom, M., Autthanit, C., 2013. Adsorptive purification of crude glycerol by sewage sludge-derived activated carbon prepared by chemical activation with H3PO4, K2CO3 and KOH. Chem. Eng. J. 229, 334–343. doi:10.1016/j.cej.2013.05.120

Jaria, G., Calisto, V., Silva, C.P., Gil, M.V., Otero, M., Esteves, V.I., 2019. Obtaining granular activated carbon from paper mill sludge – A challenge for application in the removal of pharmaceuticals from wastewater. Sci. Total Environ. 653, 393–400. doi:10.1016/J.SCITOTENV.2018.10.346

Jaria, G., Silva, C.P., Ferreira, C.I.A., Otero, M., Calisto, V., 2017. Sludge from paper mill effluent treatment as raw material to produce carbon adsorbents: An alternative waste management strategy. J. Environ. Manage. 188, 203–211.

Jelic, A., Gros, M., Ginebreda, A., Cespedes-Sánchez, R., Ventura, F., Petrovic, M., Barcelo, D., 2011. Occurrence, partition and removal of pharmaceuticals in sewage
water and sludge during wastewater treatment. Water Res. 45, 1165–1176. doi:10.1016/j.watres.2010.11.010

Jones, O.A., Voulvoulis, N., Lester, J.N., 2002. Aquatic environmental assessment of the top 25 English prescription pharmaceuticals. Water Res. 36, 5013–5022.

Lagergren, S., 1898. About the Theory of So-called Adsorption of Soluble Substances. K. Sven. Vetenskapsakademiens 24, 1–39.

Langmuir, I., 1916. The constitution and fundamental properties of solids and liquids. J. Am. Chem. Soc. 38, 2221–2295. Doi:10.1021/ja02268a002

Li, W.C.C., 2014. Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil. Environ. Pollut. 187, 193–201. doi:10.1016/j.envpol.2014.01.015

Mahmood, T., Ali, R., Naeem, A., Hamayun, M., Aslam, M., 2017. Potential of used Camellia sinensis leaves as precursor for activated carbon preparation by chemical activation with H3PO4; optimization using response surface methodology. Process Saf. Environ. Prot. 109, 548–563. doi:10.1016/j.psep.2017.04.024

Molina-Sabio, M., Rodríguez-Reinoso, F., Caturla, F., Sellés, M.J., 1995. Porosity in granular carbons activated with phosphoric acid. Carbon N. Y. 33, 1105–1113. doi:https://doi.org/10.1016/0008-6223(95)00059-M

Nielsen, L., Zhang, P., Bandosz, T.J., 2015. Adsorption of carbamazepine on sludge/fish waste derived adsorbents: Effect of surface chemistry and texture. Chem. Eng. J. 267, 170–181. doi:10.1016/J.CEJ.2014.12.113

Olajire, A., Abidemi, J., Lateef, A., Benson, N.U., 2017. Adsorptive desulphurization of model oil by Ag nanoparticles-modified activated carbon prepared from brewer’s spent grains. J. Environ. Chem. Eng. 5, 147–159. doi:10.1016/j.jece.2016.11.033
Oliveira, G., Calisto, V., Santos, S.M., Otero, M., Esteves, V.I., 2018. Paper pulp-based adsorbents for the removal of pharmaceuticals from wastewater: A novel approach towards diversification 631–632, 1018–1028.

Olszewski, M.P., Arauzo, P.J., Wądrzyk, M., Kruse, A., 2019. Py-GC-MS of hydrochars produced from brewer’s spent grains. J. Anal. Appl. Pyrolysis 140, 255–263. doi:10.1016/j.jaap.2019.04.002

Silva, C.P., Jaria, G., Otero, M., Esteves, V.I., Calisto, V., 2019. Adsorption of pharmaceuticals from biologically treated municipal wastewater using paper mill sludge-based activated carbon. Environ. Sci. Pollut. Res. 26, 13173–13184. doi:10.1007/s11356-019-04823-w

Silva, J.P., Sousa, S., Rodrigues, J., Antunes, H., Porter, J., Gonçalves, I., Ferreira-Dias, S., 2004. Adsorption of acid orange 7 dye in aqueous solutions by spent brewery grains. Sep. Purif. Technol. 40, 309–315. doi:10.1016/j.seppur.2004.03.010

Sips, R., 1948. On the structure of a catalyst surface. J. Chem. Phys. 16, 490–495. doi:10.1063/1.1746922

To, M.-H., Hadi, P., Hui, C.-W., Lin, C.S.K., McKay, G., 2017. Mechanistic study of atenolol, acebutolol and carbamazepine adsorption on waste biomass derived activated carbon. J. Mol. Liq. 241, 386–398. doi:10.1016/J.MOLLIQ.2017.05.037

Torrellas, S.Á., García Lovera, R., Escalona, N., Sepúlveda, C., Sotelo, J.L., García, J., 2015. Chemical-activated carbons from peach stones for the adsorption of emerging contaminants in aqueous solutions. Chem. Eng. J. 279, 788–798.

Tran, N.H., Reinhard, M., Gin, K.Y.-H., 2018. Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions-a review. Water Res. 133, 182–207. doi:10.1016/J.WATRES.2017.12.029
Vanreppelen, K., Vanderheyden, S., Kuppens, T., Schreurs, S., Yperman, J., Carleer, R., 2014. Activated carbon from pyrolysis of brewer’s spent grain: Production and adsorption properties. Waste Manag. Res. 32, 634–645. doi:10.1177/0734242X14538306

Wierzba, S., Andrzej, K., 2019. Heavy metal sorption in biosorbents - Using spent grain from the brewing industry. J. Clean. Prod. 225, 112–120. doi:10.1016/j.jclepro.2019.03.286

Wierzba, S., Rajfur, M., Nabrdalik, M., Kłos, A., 2019. Assessment of the influence of counter ions on biosorption of copper cations in brewer’s spent grain - Waste product generated during beer brewing process. Microchem. J. 145, 196–203. doi:10.1016/j.microc.2018.10.040
**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 (wt%, dry basis) | Volatile matter (VM) | Fixed carbon (FC) | Ash  | VM/FC |
|------------------|---------------------------|----------------------|-------------------|------|-------|
| 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 ($S_{\text{BET}}$); total pore volume ($V_p$); micropore volume ($W_0$); and average micropore width (L).

| Material          | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | $V_p$ (cm$^3$ g$^{-1}$) | $W_0$ (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 1\(^{st}\) 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 2\(^{nd}\) 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                        | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | Equilibrium experimental conditions$^1$ | Maximum adsorption capacity$^2$ (mg g$^{-1}$) | Reference                     |
|---------------------------------|----------------------------------|----------------------------------------|-----------------------------------------------|--------------------------------|
| Commercial AC (PBFG4)           | 848                              | $T = 25 \, ^\circ C; C_0 = 5 \, \text{mg L}^{-1}$ | 116 (ultrapure water)                          | (Calisto et al. 2015)         |
| Comercial AC (Norit)            | 996                              | $T = 25 \, ^\circ C; C_0 = 5 \, \text{mg L}^{-1}$ | 174 (ultrapure water); 160 (wastewater, pH 7.7 - 7.9) | (Silva et al. 2019)           |
| Commercial AC from vegetable origin | 1328              | $T = 25 \, ^\circ C; C_0 = 10 - 40 \, \text{mg L}^{-1}$ | 242 (distilled water, pH ~6)                  | (Delgado et al. 2019)         |
| Biochar from paper mill sludge  | 414                              | $T = 25 \, ^\circ C; C_0 = 5 \, \text{mg L}^{-1}$ | 17.4 (ultrapure water, converted from µmol g$^{-1}$) | (Calisto et al. 2017)         |
| Carbonized sewage sludge+fish waste | 34 - 101            | $T = 30 \, ^\circ C; C_0 = 1 - 100 \, \text{mg L}^{-1}$ | 4.9 – 37.2 (Sips isotherm)                     | (Nielsen et al. 2015)         |
| AC from bleached paper pulp     | 768 - 965                       | $T = 25 \, ^\circ C; C_0 = 5 \, \text{mg L}^{-1}$ | 57 – 93 (ultrapure water); 29.9 - 80 (wastewater, pH 7.8) | (Oliveira et al. 2018)        |
| AC from paper mill sludge       | 1627                             | $T = 25 \, ^\circ C; C_0 = 5 \, \text{mg L}^{-1}$ | 212 (ultrapure water); 209 (wastewater, pH 7.7 - 7.9) | (Silva et al. 2019)           |
| AC from palm kernel shell       | 711.5                            | $T = 25 \, ^\circ C; C_0 = 100 – 250 \, \text{mg L}^{-1}$ | 208 (ultrapure water, pH 7, converted from mmol g$^{-1}$) | (To et al. 2017)              |
| AC from peach stones            | 959 - 1216                       | $T = 30 \, ^\circ C; C_0 = 100 \, \text{mg L}^{-1}$ | 335 (ultrapure water)                          | (Torrellas et al. 2015)       |
| AC from pomelo peel             | 198.0 – 904.1                   | $T = 25 \, ^\circ C; C_0 = 10 – 100 \, \text{mg L}^{-1}$ | 80.64 - 286.5 (ultrapure water)               | (Chen et al. 2017)            |
| AC from spent brewery grains    | 1090-1120                       | $T = 25 \, ^\circ C; C_0 = 5 \, \text{mg L}^{-1}$ | 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.
