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Highly microporous activated carbons derived from biocollagenic wastes of the leather industry as adsorbents of aromatic organic pollutants in water

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Graphical abstract

Highlights

- Valorisation of biocollagenic wastes from tanning industry
- The activated carbons present specific surface area ($S_{BET}$) of up to 1664 m$^2$ g$^{-1}$
- The adsorbents are mainly microporous with micropore volumes up to 0.536 cm$^3$ g$^{-1}$
- Superior performance for adsorption of benzaldehyde ($q_{max}$: 3.77 mmol g$^{-1}$ adsorbent)
- Acetanilide, aniline and benzoic acid were affected by nitrogen content on AC

Abstract

Leather industries generate large amounts of biocollagenic wastes that need to be processed. Moreover, the presence of aromatic organic pollutants produced by different industries (pharmaceutical, food, perfume,...) is increasing in surface and groundwater and this is seriously affecting the environment. The purpose of this study is to use biocollagenic wastes (shavings, trimmings and buffing dust) and their pyrolyzed products as bioprecursors of activated carbons for future waste water applications. Activated carbons were prepared by KOH and K$_2$CO$_3$ chemical activation at different temperatures. The characteristics of the precursors and the influence of the activating temperature and activating agent on the process were studied and discussed. The obtained materials and two commercial activated carbons (WAC and YAO) were used as adsorbents to remove the following aromatic organic pollutants from the water: acetanilide, aniline, benzaldehyde, benzoic acid, methyl benzoate and phenol. The results obtained show that an increase in the activating temperature led to a higher textural development in the adsorbents. The best activated carbons were obtained by means of KOH chemical activation resulting in $S_{BET}$ and $V_{TOT}$ values of up to 1664 m$^2$ g$^{-1}$ and 0.735 cm$^3$ g$^{-1}$
respectively. All the adsorbents were predominantly microporous with a certain degree of mesoporosity and a significant amount of nitrogen (up to 3%). The main adsorption mechanism proposed for the different organic pollutants was dispersive interaction influenced by a hydrogen mechanism. Moreover, an increase in the nitrogen content of the adsorbents decreased the adsorption capacity of acetanilide, benzoic acid and aniline, whereas electrostatic influences reduced the adsorption capacity of benzoic acid.

**Keywords:** Activated-carbon, biocollagenic-materials, organic-pollutants, waste-water, adsorption

### 1. Introduction

One of the most important industries in Spain is the production of textiles, leather goods and shoes, representing about 4.7% of the total economic production of Spain. The leather production process is divided into different steps in which the raw material is treated (skinning, curing, beamhouse operations, tanning, drying,...). In the tanning process the putrescent skins of animals are treated so that they are converted into non-biodegradable leather by means vegetable (tannins) or mineral (chromium salts) methods. The leather-making process generates substantial quantities of solid and liquid wastes (hides and skins, fats, shavings and trimmings, buffing dust, process effluents, sludge,...). The most common way to manage most of the solid wastes is by disposing of them on landfill sites or by incineration. However, these methods have disadvantages such as the cost of process, the production of dioxins and ash, etc. The vegetable tanning industry generates solid wastes with high tannin and collagen content and free of hazardous matter such as heavy metals. This kind of vegetable-tanned leather waste can be regarded as a mixture of animal and vegetable biomass. One of the ways of taking advantage of these wastes originated from the vegetable tanning industry could be the production of activated carbons (ACs), due to the high demand for these adsorbents and the possible introduction of stricter environmental regulations. The main raw materials used to prepare activated carbons are peat and coals of different rank. In order to reduce the total cost, efforts are being made to produce low-cost alternatives from waste precursors (sewage sludge [1, 2], macroalgalge wastes [3], linseed [4], ...). Similarly, the use of biocollagenic wastes of vegetable tanning could result in a decrease in total cost production of activated carbon.
(considered as a high value-added product) and contribute to an improvement of the environment.

There is little information available in the literature about the use of leather wastes as bioprecursors of activated carbon. Most of them are subjected to physical activation with carbon dioxide or steam [5, 6]. Kong [5, 7] carried out chemical activation with $\text{H}_2\text{P}_2\text{O}_7$ in a microwave furnace and obtained activated carbons with a specific surface area ($S_{\text{BET}}$) of between 200 and 500 m$^2$ g$^{-1}$. Gil et al. [48] introduced a previous pyrolysis step in the alkaline activation of biocollagenic wastes and obtained highly microporous activated carbons.

A lot of companies use aromatic compounds (phenol, aniline, acetanilide, ...) in their synthesis process (pharmaceutical, pesticides, food, ...). Sometimes, these compounds are emitted via water effluents which can represent a serious problem for the environment. Sometimes, due their pleasant odour properties, these compounds can be recovered to improve the quality of the final product (as in the case of benzaldehyde in coffee production) [9]. An effective way to eliminate these organic compounds or to recover them from effluents could be to introduce an adsorption step with activated carbon or other adsorbents (multiwalled carbon nanotube [10], and composite [11]) during the cleaning process of water or in the production process.

The adsorption capacity of an activated carbon depends on its physical and chemical characteristics (pore size, functional groups, ...) and the characteristics of the adsorbate (size, hydrophobicity, ...) [12]. The presence of functional groups on the surface of the activated carbon can affect the dispersion interactions between the aromatic rings of the graphene layers of activated carbons and the aromatic rings of the molecules. Moreover, the presence of water can enhance or decrease the adsorption of organic molecules due to hydrogen bonding [13-15].

The aim of the present study is to obtain ACs from biocollagenic wastes and a char able to efficiently remove aromatic organic pollutants from water. The ACs are prepared by chemical activation using KOH and $\text{K}_2\text{CO}_3$ at different activating temperatures. Variables such as activation temperature, activating agent and type of precursor are studied and discussed in order to determine their influence on the activation process. The eight ACs obtained are used in environmental applications in aqueous phase. In addition, two
commercial activated carbons, WAC and YAO, are selected for comparison purposes. The ACs are characterized on the basis of elemental composition, surface analysis (FTIR) and textural analysis for the purpose of establishing the factors involved in the adsorption of the six selected aromatic compounds: acetanilide, aniline, benzaldehyde, benzoic acid, methyl benzoate and phenol.

2. Materials and methods

2.1. Materials

A mixture of biocollagenic wastes (shavings, trimmings and buffing dust), originated from the vegetable tanning industry, labelled BCT was used as biomaterial to obtain the ACs. The proportions of this mixture were generated and homogenized as in the leather industry (84% shavings, 15% trimmings and 1% buffing dust). The sampling and the treatment of the samples has been aimed and discussed in a recent work [16].

BCT was subjected to a pyrolysis process and the resulting char, named BCTP, was also used as bioprecursor of the activated carbons. The pyrolysis conditions for BCT were selected on the basis of a previous work on pyrolysis [16] in which the potential energy of the fractions generated (char, condensable and gas fraction) was studied.

The ACs were obtained by means of conventional chemical activation in a horizontonal electrical furnace (Carbolite CTF 12/65/550). The bioprecursors, BCT and BCTP, were activated at activating agent/precursor mass ratios of 0.33:1 and 1:1, respectively, with KOH and K$_2$CO$_3$. Moreover, all the activations were carried out at two different temperatures (750 and 900 °C) obtaining eight ACs (Table 1)

Table 1

After chemical activation the samples were washed in order to remove the activating agent residues and any inorganic matter blocking the porosity with hydrochloric (5 M) and then rinsed with deionised water (milli-Q). Two commercial ACs, YAO and WAC supplied by Eurocarb, were chosen for their organic origin (coconut and wood, respectively) for comparison purposes. Both ACs were activated with steam and are known to be good products for the adsorption of aromatic organic pollutants on water.
2.2. Chemical and textural characterization

The ACs obtained were characterized from their ultimate analysis and ashes. The ash content was determined according to method described in norm ISO 1171 [17]. The ultimate analysis was carried out on a LECO CHN-2000 and a LECO Sulphur Determination S-144-DR, and the oxygen content was determined with elemental microanalysis with automated equipment LECO VTF-900.

FTIR technique was applied in order to determine the main functional groups on the surface of the activated carbons. For this purpose spectra were determined between 4000 and 400 cm\(^{-1}\) using an FTIR spectroscope (Nicolet 8700 Fourier Transform Infrared Spectrometer with DGTS Detector).

The texture of the different activated carbons was characterized from \(\text{N}_2\) adsorption isotherms at -196 °C, in a conventional volumetric apparatus (ASAP 2420 from Micrometics). Before each experiment, the samples were outgassed under vacuum at 120 °C for overnight to remove any adsorbed moisture and/or gases. The isotherms were used to calculate the specific surface area (\(S_{\text{BET}}\)) and total pore volume, (\(V_{\text{TOT}}\)), at a relative pressure of 0.95 in addition to the pore size distribution. The pore size distribution (PSD) was evaluated using the density functional theory (DFT), assuming slit-shape pore geometry. The surface morphology of the different activated carbons was examined using a scanning electron microscope (FEI, Quanta FEG 650 Model) equipped with an Energy-Dispersive X-ray analyzing system (Ametek-EDAX, Apollo X detector).

2.3. Adsorbates

The six evaluated organic pollutants were acetanilide (CAS 183-44-4, Spain), aniline (CAS 62-53-2, 99%, Scharlau, Spain), benzaldehyde (CAS 100-52-7, 99%, Panreac, Spain), benzoic acid (CAS 65-85-0, 99%, Scharlau, Spain), methyl benzoate (CAS 93-58-3, 98%, Panreac, Spain) and phenol (CAS 108-95-2, 98.5%, Panreac, Spain). The physico-chemical properties of these compounds (pKa, solubility, molecular weight, hydrophobicity, molecular size,...) [18] are shown in Supplementary information (SI) Table SI 1. The molecule dimensions (the closest fitting “box” around the molecule), surface areas (grid and approximate) and volume were calculated using Hyperchem 8.0
Different stock solutions of each compound (100 mg L\(^{-1}\)) were prepared with ultra-pure water obtained from Milli-Q purification systems (Millipore academics). From these solutions, samples for calibration and sorption experiments were obtained by dilution with ultra-pure water (Milli-Q).

### 2.4. Adsorption assays

For the equilibrium adsorption studies, 10 mg of adsorbent was added to 50 mL of different organic compound solutions with various concentrations (5-100 mg L\(^{-1}\)). The mixtures were stirred at 25ºC on a multipoint agitation plate. After 24 hours, samples were taken and filtered through a cellulose acetate filter (0.45 μm diameter pore) and the remaining concentrations of adsorbates were analyzed in a UV/Vis-visible spectrophotometer (Lambda 25 PerkingElmer) at the corresponding wavelength of each compound (Table SI 1). The pollutant uptake, \( q \), was determined using the formula:

\[
q = \frac{(C_0 - C_f)V}{W}
\]  

where \( q \) is the amount (mmol g\(^{-1}\)) of organic compounds adsorbed, \( C_0 \) and \( C_f \) are the initial and final concentration (mg L\(^{-1}\)), respectively, \( V \) is the volume (L) of the adsorbate solution and \( W \) is the weight (g) of the activated carbon used.

### 2.5. Adsorption modelling

The experimental results were fitted to two parameter isotherm models: Langmuir (Eq. 2) and Freundlich (Eq. 3) [20]

\[
q_e = \frac{q_{\text{max}}K_L C_e}{1 + K_L C_e}
\]  

\[
q_e = K_f C_e^{1/n}
\]

where \( q_e \) (mmol g\(^{-1}\)) is the amount of compound adsorbed per mass of unit carbon, \( C_e \) (mmol L\(^{-1}\)) is the organic compound concentration at equilibrium, \( q_{\text{max}} \) (mmol g\(^{-1}\)) is the
maximum adsorption capacity, $K_L$ (L mmol$^{-1}$) is a constant related to the affinity between the pollutant and the adsorbent, $K_f$ ((mmol g$^{-1}$) (L mmol$^{-1}$)$^{1/n}$) is the Freundlich sorption constant and $n$ is a constant related to the intensity of the adsorption.

The parameter estimation of the different isotherms was solved using MATLAB software and minimizing the objective function (OF) given in equation (4) [19].

$$OF = \sqrt{\sum_{i=1}^{N} [q(P_1, P_2) - q^*]^2} \quad (4)$$

where $N$ is the number of measurements performed, $q^*$ is the experimental solute uptake, $q (P_1, P_2)$ is the uptake predicted by the model, $P_1$ and $P_2$ are the different estimated parameters. In the case of the Langmuir model, the parameters are $q_{\text{max}}$ and $K_L$, and for Freundlich $K_f$ and $n$.

3. Results and discussion

3.1. Chemical and surface analysis of the activated carbons

The chemical composition of the bioprecursors, BCT and BCTP, was studied in previous work [16]. Their high carbon and low ash content make these biomaterials a very suitable bioprecursor for obtaining ACs.

Overall, the ACs obtained have a high carbon content, (82-94 %), and a low ash content, (0.8-5.5%). These values are similar to, or better than, those of the commercial ACs (carbon content: 86-91 %; ash content: 4.9-8.4 %), Table 2.

Table 2

There are slight differences in the chemical compositions of the ACs based on the bioprecursor type; and so, the adsorbents derived from BCT are characterized by a carbon content of approx. 82-87% an oxygen content of 8 to 12% and an acid pH (3.6). In contrast ACs from BCTP have a higher carbon content (>90%), an oxygen content between 3.5-10 % and acid pH (4-6), except in the case of the G sample. WAC and YAO, activated with steam, showed a basic pH of approx. 10.5. According to Montes-Morán [21], the presence of ashes is one of the factors leading to the basicity of the activated carbons.
An important experimental variable that has a significant influence on the chemical properties of the ACs is the activation temperature. The activated carbon B presents a lower carbon and higher oxygen content than the adsorbent material obtained at 750 ºC (A sample), Table 2. This result is in disagreement with the other materials of this study where an increase in the temperature entails an increase in carbon content and a decrease in oxygen content. It can also be seen noticed that an increase in temperature leads to a much higher ash content in sample B (5.5 %) than A (1.68%). Although, in general, an increase in the activation temperature entails an increase in the ash content, when KOH is used as activating agent, and BCT as bioprecursor, the increase in the ash content is much higher. Ferrera-Lorenzo [3] studied the effect of some of the experimental variables of KOH activation on the chemical and textural properties of macroalgae waste-based ACs and observed that the most suitable temperature without any pyrolyzed wastes was 750 ºC. The ACs from BTCP show an increase of up to 20% in the carbon content with the increase in the activation temperature while nitrogen content decreases more than 52% (Table 2). The chemical composition evolution of these materials (E, F and BCTP activated carbons (C, D, G, H)) is similar to that observed by Tsai [22] in their work on the activation of agricultural wastes using KOH and K$_2$CO$_3$.

The activated carbons were also characterized by infrared spectroscopy in order to get information about the main functional groups on the activated carbons surface. The different IR spectra are shown in Fig. 1, Fig SI 4 and Fig SI 6.

**Figure 1**

The main bands presented in the eight ACs are a broad band in the 3500- 3000 cm$^{-1}$ region which two peaks can be differentiated, the OH stretching vibration (3500-3200) and NH$_2$ and/or NH (3500-3300 and 3200-3000) [23]. The hydroxyl function could belong to an alcohol, phenol or carboxylic group while NH could belong to amine or amide group. The NH band (3200-3000) is considerable more intense in B than the rest of activated carbons, and the hydroxyl group (3500-3200) has more importance in C. The two closest bands at 2910 and 2850 cm$^{-1}$ correspond to asymmetric and symmetric C-H stretching vibrations of aliphatic groups (CH$_3$ CH$_2$). These bands are more intense in the AC from low activation temperature, suggesting that an increase of temperature decrease the functional groups on the surface. Another important peak is at approximately 1750 cm$^{-1}$. 
characteristic of the stretching vibration of the carboxylic group (C=O). The band at the 1585 cm\(^{-1}\) region can be due to C=O stretching vibrations in sp\(^2\) hybridized carbons in polyaromatic rings, or it can also be –NH bending vibration. This band is stronger in the activated carbons A and B. The presence of the group C-N can be shown at approximately 1400 cm\(^{-1}\). Furthermore, A strong band at 1120 cm\(^{-1}\) (1223, 1150-70 cm\(^{-1}\)) correspond to asymmetric C-O-C extension vibrations (or C-O, alkoxy or acyl). The last common band in all AC is approximately at 620 cm\(^{-1}\) that it could be CH bending vibration or OH vibration “out of plane” [23]

However, there are more significant differences among the different activated carbon. A common peak between high temperature activated carbons (900ºC) is at 2085 cm\(^{-1}\). It could be due to the formation of (C\(\equiv\)N). Moreover, other close and weak bands are observed at 2290-70 cm\(^{-1}\) (C\(\equiv\)N\(\rightarrow\)O; [23], activated carbon B Fig 1). According to Fuente et al [24], cyanides can be formed during chemical activation with hydroxides when it is used precursors with nitrogen content. The reduction of the species H\(_2\) and metallic K formed during the KOH carbon activation process could promote the transformation of structural nitrogen to cyanides. As can be seen in the FTIR of the precursors BCT and BCTP (Fig SI 3 and Fig SI 5), there are absence of the different peaks between 2400 and 2000 cm\(^{-1}\). Suggesting that after activation at higher temperature, the formation of cyanides can be possible due to the presence of nitrogen in the precursor.

Finally, activated carbon C shows more bands from 1509 to 1000 cm\(^{-1}\). These bands can be related to phenolic groups. According to Fuente et al [25], C-O-H deformation with simultaneous carbon ring vibrations can be found between 1420-1480 cm\(^{-1}\) which a band at 1460 cm\(^{-1}\) is typical of oxidized carbons (O-H deformation in carboxyl groups). Moreover, in the region from 1000 to 1200 cm\(^{-1}\) is found C-O stretching and C-O-H bending vibrations.

### 3.2. Textural analyses of activated carbons

The nitrogen adsorption isotherms at -196 °C of the activated carbons are shown in Fig. SI 1. In addition, Table 3 shows the data corresponding to the textural parameters (\(S_{\text{BET}}\), \(V_{\text{TOT}}\) and the PSD).

Table 3
The ACs obtained from BCT and BCTP (Fig. SI 1a, 1b) show hybrid adsorption isotherms of type I-IV according to the IUPAC classification [26]. Moreover, the N$_2$ isotherms of these ACs display a wide hysteresis loop of type H4 [27], indicating the presence of mesopores of small diameter. The N$_2$ isotherm of YAO (Fig. SI 1c) is mainly of type I with a narrow knee at low relative pressures (p/p$_0$ <0.1), indicating a micropore structure. In the case of WAC (Fig. SI 1c), the nitrogen isotherm is of type I-IV and it is distinguished from that of the biocollagenic activated carbons by its steep slope at a relative pressure of from 0.1 to 1, suggesting a high degree of mesoporosity.

Generally speaking the ACs obtained are highly microporous adsorbents with a S$_{BET}$ between 838-1664 m$^2$ g$^{-1}$ and a V$_{TOT}$ between 0.390-0.735 cm$^3$ g$^{-1}$. These results are similar to, or better than, those of the commercial ACs, Table 3.

An important factor to be taken into account is the effect of the activating agent upon the textural properties of ACs. In general, the adsorbent materials obtained with KOH present a higher (A,C and D) or similar (B) adsorption capacity, S$_{BET}$ and V$_{TOT}$ than the corresponding ACs obtained with K$_2$CO$_3$ (E,F,G and H ), Fig. SI 1. and Table 3. The adsorbent materials with the highest textural development are A and D. These samples have a S$_{BET}$ of 1602 and 1664 m$^2$ g$^{-1}$, respectively. A difference of more than 11.5% of S$_{BET}$ was achieved using KOH with respect to K$_2$CO$_3$ (the exception being between the B and F activated carbons). This difference is more remarkable at low temperature of activation (22-27%).

The activating agent is one of the variables that most affects the textural properties of the adsorbents obtained so various authors have studied the reactions that take place between alkaline hydroxides and the carbonaceous material [28, 29]. At lower activation temperatures with KOH (<750 ºC), various secondary reactions may occur, that favour the formation of CO$_2$. According to Marsh [30] the formation of CO$_2$ may lead to physical activation on the carbonaceous structure which would enhance the development of porosity. On the other hand, when the activation temperature increases to over 891 ºC the potassium oxide formed in the presence of CO$_2$ generates more K$_2$CO$_3$ that reacts with the carbonaceous structure. These reactions cause an increase in the formation of metallic potassium which is introduced into the carbonaceous material. As a result the carbon particles disintegrate into powders [30], reducing the ultramicroporosity, the carbon,
nitrogen and sulphur content and increasing the ashes, as it can be happened in sample B (Table 3.).

In the activation with $\text{K}_2\text{CO}_3$, moderate activation temperatures (<891°C) give rise to low reactions with the carbonaceous structure. When the activation temperature exceeds 891°C, the potassium carbonate may decompose to produce CO$_2$. This may enhance the chemical-physical activation of the carbonaceous material, increasing the amount of micropores.

Another effect that must be taken into account is that of the activating temperature. In general, an increase in the activation temperature supposed an increase in the adsorption capacity, with the exception of A and B materials. The isotherms of the adsorbents materials at 750 °C (A, C, E and G) display a narrow knee at low relative pressures ($p/p^0 <0.1$) while in the case of the materials obtained at 900 °C (B, D, F and H) the knee is broader ($p/p^0 <0.2$), especially in the ACs derived from BCT (B and F), suggesting the presence of wide micropores in these materials, Fig. SI 1a, 1b.

Furthermore, an increase in the activation temperature leads to an increase in the $S_{\text{BET}}$ which is especially high in the case of the bioprecursor BCTP. In this case, D and H adsorbents have a $S_{\text{BET}}$ of 1664 and 1465 m$^2$ g$^{-1}$ respectively which represents an increase greater than 500 m$^2$ g$^{-1}$ with respect to the materials obtained at 750 °C, Table 3. In the activated carbons obtained from BCT the same trend can be observed as in adsorbents E and F, although in this case the variation in $S_{\text{BET}}$ is moderate (an increase of 200 m$^2$ g$^{-1}$ approx.). Sample B remains an exception to this behaviour. which shows a lower $S_{\text{BET}}$ (1421 m$^2$ g$^{-1}$) than A (a decrease of 200 m$^2$ g$^{-1}$ approx.).

On the other hand, the adsorbents with the best textural development are obtained when BCT is used as bioprecursor except when KOH is used as activating agent at high temperature (900 °C).

Fig. 2 shows the proportions (in terms of percentages) of micro-mesoporosity volume distribution. From the results it can be observed that all of the adsorbents are microporous materials with a low contribution of mesoporosity. The ACs from BCT show a well developed microporosity emphasising the high percentage of supermicropore structure while the adsorbents obtained from BCTP is noteworthy the high percentage of ultramicropores.
In Fig. SI 2, it can be seen that the pore diameter becomes wider with increasing activation temperature. This is particularly noticeable in materials obtained from BCT (from approx. 1.5 nm to 3 nm in the case of A and B). Furthermore with the increase in temperature, the ultramicroporosity decreases drastically. This behaviour has been reported in several works on activation with different biomass wastes [3, 31]. It seems that severe temperature conditions with KOH as activating agent can destroy ultramicroporosity in favour of the development of wider pores. There is only one exception to this behaviour and it occurs when BCTP is used as bioprecursor and K$_2$CO$_3$ as activating agent. In this case, an increase in activation temperature entails an increase in the ultramicropore volume. On the other hand, in agreement with other authors [3, 31], there is an enhancement in the development of supermicroporosity with the increase in activation temperature, which is especially noteworthy in sample H (0.219 cm$^3$ g$^{-1}$) when compared to sample G (0.046 cm$^3$ g$^{-1}$).

As regards the commercial ACs, YAO has a higher $S_{BET}$ than WAC and also a higher of microporosity volume ($V_{tot\, mi} = 0.357$ cm$^3$ g$^{-1}$ versus to 0.248 cm$^3$ g$^{-1}$), whereas WAC presents a higher mesoporosity ($WAC\, V_{me} = 0.285$ cm$^3$ g$^{-1}$ v.s. YAO $V_{me} = 0.020$ cm$^3$ g$^{-1}$), Table 3. and Fig. SI 2.

Table 4 shows the comparison of two ACs (A and D) of the present work with other activated carbons from different biowastes. As can be seen, the use of KOH or K$_2$CO$_3$ produce higher microporous activated carbons with a higher BET respect than activated carbons obtained with ZnCl$_2$, H$_3$PO$_4$ and steam at similar conditions. Furthermore, depending on the biowaste used (algae meal [3], rice husk [32], mombine fruit stone [33]), the total pore volume obtained is higher than the activated carbons of this work.

3.3 SEM

Fig. 3. shows the SEM photographs of the ACs obtained at several magnifications. The initial collagen structure of the original skin [16] was destroyed during the activation with
KOH or K$_2$CO$_3$. On the other hand, some of the macropore structure of the original pyrolysed bioprecursor was maintained after chemical activation, as shown in Fig. 3h.

Figure 3
The ACs from BCT obtained with KOH (Fig 3a and Fig. 3b) show a rough surface with some smooth and fine parts. When activation was carried out at 900 ºC (Fig. 3b), the aggressive conditions intensified the rough surface. In the case of pyrolysed materials activated with KOH (Fig. 3c and Fig. 3d), the resulting surface was completely smooth and more macroporosity developed compared to the activated carbons that had not been previously pyrolysed (Fig. 3a and Fig. 3b). This behaviour was similar to obtained with algae pyrolysed and non pyrolysed activated carbons [3]. On the other hand a lot of irregular cavities were observed in the activation of acacia seed shells at 900 ºC [38], suggesting that at this temperature and depending on the biowaste used, the structure can be more degraded.

ACs chemically activated with K$_2$CO$_3$ showed a higher development of macroporosity at the different temperatures possibly due to the chemical and physical activation originating from the degradation of carbonates to carbon dioxide at 900 ºC (Fig 3e, 3f, 3g, 3h.). The four activated carbons show a fine surface, and the collagenous structure of the raw material [16] having been destroyed at both temperatures (750 and 900 ºC).

3.4. Adsorption studies and modelling

The adsorption isotherms of the six pollutants for the ACs are shown in Fig. 4, Fig. SI 7 and Fig. SI 8

Figure 4
According to Giles’ classification [39, 40], the methyl benzoate isotherms corresponding to biocollagenic ACs can be classified as being of type H, which means that these adsorbents have a strong affinity for this ester. The isotherms corresponding to benzaldehyde, acid benzoic, acetanilide, aniline and phenol are types L (group 2) for most of the ACs indicating a weaker affinity for these compounds. In the case of the adsorption of benzaldehyde onto the activated carbons A, E and F, the isotherm may be type L, group 3. This group is characterized by a plateau (an initial monolayer) and then a rise that may represent the start of a second layer.
The adsorption isotherm of phenol on activated carbon C is type L, group 4 where a second layer has already formed. WAC shows an isotherm of type S group 2 for benzoic acid (Fig SI 4). It can be seen that on the S curve the slope at first increases with the concentration, because in cooperative adsorption, the number of sites capable of retaining a solute increases [39]. The S curve suggests strong competition between the water molecules and, in this case, benzoic acid when present in low concentrations.

The experimental data were fitted to Langmuir and Freundlich models. Tables SI 2-7 show the constants obtained and the objective function (OF) values for the two models.

In the case of the minimum OF values, the Langmuir equation provides a better description of acetanilide, aniline and benzoic acid in most of the AC, indicating the formation of a monolayer, whereas the Freundlich model explains the adsorption of benzaldehyde and methyl benzoate better. Which of the two models best describes phenol depends on the AC used.

The highest maximum adsorption ($q_{\text{max}}$) (Table SI 2-7) and the best adsorption equilibrium constant ($K_L$) for the different organic compounds (except for benzoic acid and phenol) is provided by the adsorbent D. The high $K_L$ value of methyl benzoate reflects its high affinity for all the ACs used in this work. The Freundlich parameter $n$, indicates that adsorption is favourable for all the ACs and six organic compounds because this value is between 1 and 10 [19].

3.4.1. Effect of the nature of the adsorbate

The adsorption selectivity of the aromatic organic compounds on the ACs follows the order: methyl benzoate> benzaldehyde> benzoic acid> acetanilide (except in the case of activated carbons G, YAO and WAC)> aniline≈phenol. This order is compared with the physical-chemical properties of the compounds (Table SI 1.) in order to establish which properties would have the greatest influence on adsorption.

It is clear from the results that molecular weight and size, solubility and the coefficient $\log K_{ow}$ and pKa do not play a dominant role in the adsorption of these organic molecules. For example, benzaldehyde (smaller dimensions, weight and volume, higher solubility) is more early adsorbed than acetanilide and benzoic acid. Moreover, the adsorption of
acetanilide was favoured with respect to that of phenol ($\log K_{ow}$ phenol $> \log K_{ow}$ acetanilide), and also the adsorption of benzaldehyde with respect to that of benzoic acid.

The mechanism of dispersive/repulsive interactions (donor-acceptor mechanism, $\pi$-$\pi$ EDA interactions [41]) deserves serious considerations. According to our results, the chemical substituent in the aromatic molecule seems to play an important role in adsorption. The -OH, -NH$_2$ and –NHCOR groups act as electron donating while –COOH, -CHO and –COOR groups act as electron withdrawing (acceptor) to the aromatic ring. Donator groups which have unshared pairs of electrons, activate the aromatic ring because the resonance effect is stronger than the inductive effect, moving the electron towards to the ring. On the other hand, withdrawing groups deactivate the ring due to an inductive effect in the presence of an electronegative atom that withdraws the electrons from the ring. In the present work compounds with withdrawing groups (benzoic acid, methyl benzoate and benzaldehyde) are more readily adsorbed than those with donating groups (phenol, aniline and acetanilide) on all the ACs except on G. This behaviour suggest the dispersion effects due to the electron donating and withdrawing groups are the main interaction between the organic molecules and the ACs, although other properties may also play a secondary role.

3.4.2 Effect of the pore distribution and carbon surface chemistry

To assess the influence of pore size distribution on the adsorption of organic compounds, the maximum adsorption capacities ($q_{max}$) for each compound were correlated with the ultramicropore, total micropore, pH and ashes values of the activated carbons (Table SI8.). Moreover, $q_{max}$ values were normalized with respect to the pore volumes (ultramicropore and total micropore) to observe the influence of the oxygen and nitrogen contents of the biocollagenic ACs (Table SI9 and Table SI10).

The maximum adsorption capacities show a good linear correlation with the total micropore volume values for acetanilide, aniline, benzaldehyde, methyl benzoate and phenol ($r > 0.6365$). It suggests that the adsorption of these compounds occurs predominantly in pores smaller than 2 nm. There is no correlation between the maximum adsorption capacities of benzoic acid with the total micropore volume ($r=0.1355$) but a good correlation was observed with the pH ($r = 0.7703$), suggesting that electrostatic
interactions of the benzoates play a higher interactive role than dispersive interactions on the activated carbons. Fig. 5 shows an increasing trend in the adsorption of benzoic acid with the increase in pH and the micropore volumes. As can be seen activated carbons G and WAC show similar micropore structure (Table 3) but differ on the oxygen and nitrogen groups and pH. WAC is a basic AC, when it is neutral solution, the pH$_{sol}$ is lower than pH$_{AC}$ so the basic sites on the surface of the ACs combine with protons from the medium, resulting in a positively charged surface. On the other hand, G is acid (ph ≈ 4). In a neutral medium where pH$_{sol}$ > pH$_{AC}$, acid sites on the carbon surface will dissociate, making the surface of the carbon negative. According to Menendez-Diaz [42] the adsorption of anions will be enhanced on a positively charged surface, whereas in acidic carbons the adsorption of basic compounds will be favoured. In this study, at high concentrations the adsorption of benzoic acid was enhanced on WAC.

Figure 5

Furthermore, it seems that an increase in the nitrogen content produces a decrease in the adsorption of benzoic acid on the biocollagenic ACs ($r$= -0.9225, Table SI9). It suggests that the nitrogen content of the biocollagenic ACs has a slightly acidic nature (as could be the cyanide group, Fig. 1) that increases the negative charge or the polarity of the ACs.

As regards the adsorption of benzaldehyde, this may be affected by the presence of oxygen on the activated carbon. According to the results of this study, the greater the oxygen content of the activated carbon, the greater the adsorption of benzaldehyde (moderate correlation $r$ = 0.6420). These results agree with those of Duman and Ayranci [43] who studied the adsorption of benzaldehyde in an activated carbon cloth from a phenolic polymer fibre with an oxygen content of approximately 4.5%. Their study concluded that benzaldehyde adsorption involved mainly hydrogen bonding and dispersion interactions but no repulsion. In this study, the presence of phenolic (OH groups, Fig. 1) can enhance the hydrogen bonding between the surface of activated carbons and the –CHO group of benzaldehyde. In accordance with that, methyl benzoate may also be governed by dispersion interactions (due to its withdrawing group) and by hydrogen bonding. Furthermore, methyl benzoate shows the highest linear correlation between the maximum adsorption capacity and the total micropore volume ($r$=0.9276, Table A7) and a very low correlation with oxygen and nitrogen at total micropore volume (Table A9), suggesting that physical adsorption might also be playing a role. The physical
adsorption mechanism consists of pore filling and a stronger binding of the adsorbate [44].

As can be seen from the high correlation (r= -0.9385) in Fig. 6, the adsorption of acetonilide is negatively influenced by the nitrogen content in the biocollagenic ACs. According to Terzyk [14, 15], the adsorption of acetonilide takes place in the smallest micropores. It can be influenced by the surface polarity of the activating carbon (carboxylic, phenolic and basic groups) because water competes with acetonilide for the same active sites. Physical adsorption may also take place via micropore filling. In this study, the presence of OH and NH groups on the surface of ACs (Fig 1), and an increase in nitrogen content may favour the adsorption of water.

Figure 5 6

In the case of aniline and phenol, the adsorption of both compounds is lower than that of the deactivating group molecules. Moreover, there is lower correlation between the adsorption capacity and the oxygen or/nitrogen contents of the biocollagenic activated carbons (r < 0.5). This suggests that the high heterogeneity on the surface of ACs (Phenolic (-OH), amine (-NH), carboxylic (C=O), cyanide (CΞN), sulphur,...) does not show such a clear tendency in the adsorption of aniline and phenol. Several authors [13, 45, 46] have studied the adsorption of one or both compounds on aqueous media. According to Faira [45], the adsorption of aniline occurred mainly through dispersive interactions and the presence of oxygen groups (at high pH) enhanced the electronic density and adsorption on activated carbons. Franz [13] observed that aniline and phenol adsorption was influenced by dispersive/repulsive interactions with the aromatic ring and hydrogen bonding. In the case of aniline, the presence of oxygen groups increased adsorption while in the presence of nitrogen groups adsorption was lower. On the other hand, the adsorption of phenol the opposite effects were observed. These difference findings were due to the effect of water adsorption and the hydrogen bonding mechanism. In this study, these differences and effects can be observed on activated carbons A and D which present similar textural properties (S_{BET} ≈ 1600 m² g⁻¹) and different oxygen and nitrogen content (Table 2). The adsorption of phenol and aniline were significantly reduced on A (1.60 and 2 mmol g⁻¹, respectively Fig. 4), which show high oxygen content, respect on D (2.25 and 2.40 mmol g⁻¹, respectively Fig. 4). The presence of more phenolic
groups on A could reduce the adsorption of phenol about a 25% (respect D) by means of hydrogen bonding interactions. The reduction is low in the case of the adsorption of aniline (approx. 15%) suggesting that the phenolic groups could enhance the adsorption of aniline in front of the water. Finally, Lorenc-Grabowska [46] discussed three different adsorption mechanisms (π-π dispersion interaction, electron donor-acceptor and hydrogen bonding) for the adsorption of phenol on nitrogen-enriched ACs. They concluded that π-π dispersion interaction took place via the filling of small micropores, with the electron donor-acceptor exchange taking place between the nitrogen electron donor groups (pyridinic) and phenol acting as acceptor in the micropores and mesopores, and no hydrogen bonding occurring between phenol and nitrogen groups.

On the basis of the results of the present work and the above discussion, it can be concluded that the main mechanism influencing the adsorption of the organic molecules is that of dispersive/repulsion interaction between the aromatic rings of molecules and aromatic rings in the ACs. Nevertheless, other features may affect the main mechanism, such as electrostatic interaction (as in the case of benzoic acid), and the hydrogen bonding mechanism that enhances the adsorption of water, thereby affecting the adsorption of the organic molecules due to the presence of different functional groups on the surface of the ACs (OH, NH, C=O, ...).

4. Conclusions

Activated carbons were obtained from biocollagenic wastes by means of chemical activation with alkaline agents (KOH and K₂CO₃). The effect of the activation temperature, chemical agent and type of bioprecursor (pyrolysed and non pyrolysed) was analysed and the main conclusions were:

- The adsorbents prepared from non-pyrolysed biocollagenic materials were characterized by a supermicroporous structure and a low degree of mesoporosity. On the other hand, ultramicroporosity was more developed in pyrolysed ACs.

- Activation at 900 ºC with KOH reduced the performance of the ACs due to the formation of a greater quantity of ashes but their textural properties were similar to those activated at 750 ºC.
Activated carbons from biocollagenic wastes contained a large quantity of nitrogen (1.4 to 2.5% approx.) and oxygen (3.5 to 12% approx) due to their animal origin.

Dispersion/repulsive interactions between aromatic molecule rings and those on the surface of the activated carbons were found to be the main factor controlling the adsorption process of the aromatic pollutants. However, hydrogen bonding might also have influenced the adsorption of the organic compounds.

The increase in nitrogen content and nitrogen surface groups had a negative influence on the adsorption of acetanilide, aniline and benzoic acid and favoured the adsorption of phenol. On the other hand, the presence of oxygen functional groups decreased the adsorption of phenol and favoured the adsorption of benzaldehyde.

Electrostatic interactions acted against the adsorption of benzoic acid onto the acidic biocollagenic waste ACs, and favoured its adsorption on basic commercial ACs.

**Acknowledgements**

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References


[27] K.S.W. Sing, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Provisional), Pure Appl. Chem. 54 (1982) 2201-2218.


Figure captions

**Figure 1** IR spectra of activated carbons A, B, C, and D. a) Spectra of A and B (4000-400 cm⁻¹), b) Partial spectra of B (2400-2000 cm⁻¹), c) Spectra of C and D (4000-400 cm⁻¹), d) Spectra of C and D (1800-1200 cm⁻¹)
Figure 2 Pore percentages of the leather wastes activated carbons
Figure 3 Scanning electron microscopic (SEM) of the activate carbons obtained at 500x and 5000x a) A, b) B, c) C, d) D, e) E, f) F, g) G and h) H
Figure 4 Aromatic compounds adsorption onto the KOH activated carbons a) A, b) B, c) C and d) D.
Figure 5 Trend of the benzoic acid adsorption versus total micropore volume and the pH of the activated carbons
Figure 6 Relation between the $q_{\text{max}}$ of acetanilide/Volume of ultramicropororosity with respect to the nitrogen content of the activated carbons.
Table 1 Activation process characteristics and simplified annotation of the activated carbons

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>Bioprecursor</th>
<th>Chemical agent</th>
<th>Activating ratio (Agent/precursor)</th>
<th>Activating temperature (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>BCT</td>
<td>KOH</td>
<td>0.33:1</td>
<td>750</td>
</tr>
<tr>
<td>B</td>
<td>BCT</td>
<td>KOH</td>
<td>0.33:1</td>
<td>900</td>
</tr>
<tr>
<td>C</td>
<td>BCTP</td>
<td>KOH</td>
<td>1:1</td>
<td>750</td>
</tr>
<tr>
<td>D</td>
<td>BCTP</td>
<td>KOH</td>
<td>1:1</td>
<td>900</td>
</tr>
<tr>
<td>E</td>
<td>BCT</td>
<td>K₂CO₃</td>
<td>0.33:1</td>
<td>750</td>
</tr>
<tr>
<td>F</td>
<td>BCT</td>
<td>K₂CO₃</td>
<td>0.33:1</td>
<td>900</td>
</tr>
<tr>
<td>G</td>
<td>BCTP</td>
<td>K₂CO₃</td>
<td>1:1</td>
<td>750</td>
</tr>
<tr>
<td>H</td>
<td>BCTP</td>
<td>K₂CO₃</td>
<td>1:1</td>
<td>900</td>
</tr>
</tbody>
</table>
Table 2. Chemical characterization of the activated carbons

<table>
<thead>
<tr>
<th>Material</th>
<th>Moisture (%)</th>
<th>Ash (%)*</th>
<th>C (%)*</th>
<th>H (%)*</th>
<th>N (%)*</th>
<th>S (%)*</th>
<th>O (%)*</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH ACs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>4.04</td>
<td>1.68</td>
<td>87.44</td>
<td>-</td>
<td>2.52</td>
<td>2.00</td>
<td>7.79</td>
<td>3.60</td>
</tr>
<tr>
<td>B</td>
<td>4.99</td>
<td>5.50</td>
<td>82.43</td>
<td>0.38</td>
<td>2.13</td>
<td>1.78</td>
<td>8.96</td>
<td>3.70</td>
</tr>
<tr>
<td>C</td>
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<td>90.61</td>
<td>0.38</td>
<td>2.60</td>
<td>0.80</td>
<td>6.79</td>
<td>4.10</td>
</tr>
<tr>
<td>D</td>
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<td>1.29</td>
<td>93.93</td>
<td>0.28</td>
<td>1.38</td>
<td>0.52</td>
<td>3.46</td>
<td>5.60</td>
</tr>
<tr>
<td>K₂CO₃ ACs</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1.27</td>
<td>11.91</td>
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</tr>
<tr>
<td>F</td>
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<td>85.43</td>
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<td>1.52</td>
<td>1.81</td>
<td>9.68</td>
<td>3.60</td>
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<tr>
<td>G</td>
<td>1.66</td>
<td>3.21</td>
<td>83.45</td>
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<td>2.93</td>
<td>1.07</td>
<td>10.11</td>
<td>4.00</td>
</tr>
<tr>
<td>H</td>
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<td>2.40</td>
<td>92.71</td>
<td>0.33</td>
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<td>0.62</td>
<td>4.25</td>
<td>6.30</td>
</tr>
<tr>
<td>Commercial AC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YAO</td>
<td>4.25</td>
<td>4.87</td>
<td>90.92</td>
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<td>0.78</td>
<td>0.13</td>
<td>4.61</td>
<td>10.40</td>
</tr>
<tr>
<td>WAC</td>
<td>13.39</td>
<td>8.36</td>
<td>86.84</td>
<td>0.70</td>
<td>0.52</td>
<td>0.09</td>
<td>5.46</td>
<td>10.60</td>
</tr>
</tbody>
</table>

*Dry base
Table 3. Textural properties of the different activated carbons

<table>
<thead>
<tr>
<th>Material</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$V_{\text{tot at } p/p^0=0.95}$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{\text{umi}}$ (cm$^3$ g$^{-1}$)*</th>
<th>$V_{\text{smi}}$ (cm$^3$ g$^{-1}$)*</th>
<th>$V_{\text{tot mi}}$ (cm$^3$ g$^{-1}$)*</th>
<th>$V_{\text{me}}$ (cm$^3$ g$^{-1}$)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH ACs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>1602</td>
<td>0.695</td>
<td>0.249</td>
<td>0.264</td>
<td>0.513</td>
<td>0.021</td>
</tr>
<tr>
<td>B</td>
<td>1421</td>
<td>0.675</td>
<td>0.176</td>
<td>0.260</td>
<td>0.436</td>
<td>0.088</td>
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<td>C</td>
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<td>0.249</td>
<td>0.126</td>
<td>0.375</td>
<td>0.040</td>
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<td>D</td>
<td>1664</td>
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<td>0.243</td>
<td>0.293</td>
<td>0.536</td>
<td>0.022</td>
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<tr>
<td>K$_2$CO$_3$ ACs</td>
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<td></td>
<td></td>
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<tr>
<td>E</td>
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<td>0.233</td>
<td>0.156</td>
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<td>0.035</td>
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<td>F</td>
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<td>0.262</td>
<td>0.455</td>
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<tr>
<td>G</td>
<td>838</td>
<td>0.390</td>
<td>0.214</td>
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<td>0.260</td>
<td>0.042</td>
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<tr>
<td>H</td>
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<td>0.219</td>
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<td>0.044</td>
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<td>Commercial ACs</td>
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<tr>
<td>YAO</td>
<td>1092</td>
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<td>0.162</td>
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<td>0.020</td>
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<tr>
<td>WAC</td>
<td>893</td>
<td>0.540</td>
<td>0.137</td>
<td>0.111</td>
<td>0.248</td>
<td>0.285</td>
</tr>
</tbody>
</table>

* determined by DFT

$V_{\text{umi}}$ = Volume of ultramicropores; $V_{\text{smi}}$ = Volume of supermicropore; $V_{\text{tot mi}}$ = Volume of total micropores; $V_{\text{me}}$ = Volume of mesopores
Table 4 Comparison of different activated carbons from biowastes of present work with other literature data

<table>
<thead>
<tr>
<th>Biowaste</th>
<th>Activation agent</th>
<th>T (º C)</th>
<th>BET (m²/g)</th>
<th>Vtotal</th>
<th>Vmicro</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algae meal waste</td>
<td>KOH</td>
<td>750</td>
<td>1982</td>
<td>0.914</td>
<td>0.412</td>
<td>[3]</td>
</tr>
<tr>
<td>Waste corn cob</td>
<td>KOH</td>
<td>750</td>
<td>1004</td>
<td>0.49</td>
<td>-</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td>K2CO3</td>
<td>800</td>
<td>1541</td>
<td>0.74</td>
<td>-</td>
<td>[22]</td>
</tr>
<tr>
<td>Leather wastes</td>
<td>Steam</td>
<td>750</td>
<td>421</td>
<td>0.326</td>
<td>0.184</td>
<td>[7]</td>
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<tr>
<td>Rice husk</td>
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<td>900</td>
<td>3044</td>
<td>2.25</td>
<td>0.775</td>
<td>[32]</td>
</tr>
<tr>
<td>Mombine fruit sotnes</td>
<td>KOH</td>
<td>700</td>
<td>2290</td>
<td>1.0729</td>
<td>0.9245</td>
<td>[33]</td>
</tr>
<tr>
<td>Coffee residue</td>
<td>ZnCl₂</td>
<td>600</td>
<td>810</td>
<td>0.484</td>
<td>0.339</td>
<td>[34]</td>
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<tr>
<td>Bamboo waste</td>
<td>H3PO4 + K2CO3</td>
<td>750</td>
<td>2237</td>
<td>1.13</td>
<td>1.03</td>
<td>[35]</td>
</tr>
<tr>
<td>Peach stone</td>
<td>H3PO₄</td>
<td>435</td>
<td>1216</td>
<td>0.81</td>
<td>0.25</td>
<td>[36]</td>
</tr>
<tr>
<td>Nut shells</td>
<td>ZnCl₂</td>
<td>400</td>
<td>1478</td>
<td>0.973</td>
<td>0.356</td>
<td>[37]</td>
</tr>
<tr>
<td>Deffated grape seeds carbonized</td>
<td>KOH</td>
<td>750</td>
<td>1169</td>
<td>0.458</td>
<td>0.379</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td>KOH</td>
<td>900</td>
<td>1604</td>
<td>0.672</td>
<td>0.522</td>
<td>[38]</td>
</tr>
<tr>
<td>Accacia seed shells carbonized</td>
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<td>900</td>
<td>1684</td>
<td>0.716</td>
<td>0.539</td>
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<td>750</td>
<td>1602</td>
<td>0.695</td>
<td>0.513</td>
<td>This work</td>
</tr>
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<td>K2CO3</td>
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