Sustainable thermochemical single-step process to obtain Magnetic Activated Carbons from chestnut industrial wastes

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ABSTRACT

A novel thermochemical process based on a single step was optimized to obtain magnetic activated carbons from an industrial biomass waste. Anhydrous iron chloride was used as an activating agent and mixed directly with the chestnut shell waste. The effect of the activation temperature (220-800°C) on the chemical, morphological, textural and magnetic properties of the materials was studied.

The results demonstrated the presence of different iron compounds depending on the activation temperature set, as well as their influence on morphological and textural development of the magnetic activated carbons (BET specific surface area, S_{BET} , up to 568 m²g⁻¹, total pore volume, V_{TOT} , up to 0.294 cm³g⁻¹ *versus* to 1 m²g⁻¹ and 0.007 cm³g⁻¹, respectively, for the raw biomass waste). The techniques employed, especially Mössbauer spectroscopy showed relative contributions of the different iron compounds (magnetite, maghemite, metallic iron...) in the materials. The higher activation temperature (800 °C) favoured the formation of metal Fe and iron carbide. Additionally, the magnetic properties measured by Vibrating Sample Magnetometry, VSM, confirmed the coexistence of different ferromagnetic phases being the remanent magnetization, M_{R} , (up to 3.88 emu/g) and coercivity, H_{c} , (up to 140 Oe), larger as activation temperature increases. A higher activation temperature favoured the development and evolution towards other iron compounds, while at low temperature, 220 °C, the presence of these compounds were null and their behaviour resembling the results obtained for the original biomass waste.

KEYWORDS: Biomass, Chestnut industrial waste, Food industry, Magnetic activated carbon (MAC), Sustainable activation, One-step chemical activation, Vibrating Sample Magnetometer (VSM)

▪ INTRODUCTION

In recent years, environmental contamination in air, soil and water has become a serious problem and the introduction of stricter environmental regulations promotes the search for solutions developing new techniques and materials to face them. An alternative increasingly demanded materials are activated carbons (ACs), due to their appropriate characteristics as adsorbents to remove pollutants¹.

The preparation of this kind of materials can be done from very diverse precursors, the most used are wood, peat and coals, although during the last years those obtained from biomass wastes have been investigated more frequently with good and promising results²⁻⁷.

The production of ACs from biomass wastes result into a low-cost materials and friendly to the environment to retain mercury⁵, to remove volatile organic compounds (VOCs)³ or for the wastewater treatment to remove hazardous pollutants such as heavy metals, dyes^{2, 7} and pharmaceutical and personal care products (PPCPs)⁷⁻⁹ and others as phenolic compounds⁷. Activated carbons from biomass wastes can be also highly suitable for CO₂ capture⁶ due the gas storage capacities of the biomass based activated carbons².

Search for novel sources to produce ecofriendly low-cost activated carbons and their multiple environmental applications as well as the increasing interest in the improvement of their characteristics and effectiveness as adsorbents and catalytic supports have resulted in the obtaining of Magnetic Activated Carbons (MACs)¹⁰⁻¹⁴, a class of carbonaceous materials with an undeniable adsorption capacity and magnetic properties. Currently, the use of natural precursors such as biomass wastes is an

emerging and important low-cost sustainable alternative and natural precursor^{12, 15} to make MACs.

MACs have great potential applications in several areas such as environment, bioscience and medicine¹⁶. In the environmental technology, MACs can be used as adsorbents for the removal of traditional and emerging pollutants from liquid effluents^{7, 17-19}. An interesting property of MACs is that these materials, once the adsorbent properties have been exhausted, they can be easily separated from complex systems by using an external magnetic field. Furthermore, the MACs regeneration can be performed by advanced oxidation processes (AOPs) using H₂O₂ and the iron compounds contained within MACs (Fenton reaction). Some of these materials have also very good catalytic properties so they can be used in various industrial processes^{14, 20}. In the biosciences and medicine area an important property of MACs is that these materials can be targeted to a desired place using an external magnetic field¹⁶.

The transformation of an activated carbon into magnetic derivatives is being studied using various methods for its preparation^{16, 21}: chemical precipitation²²⁻²³, high temperature treatment^{18, 24}; or encapsulation²⁵. On the other hand, a MAC can be developed from a biomass through a chemical activation process with a previous pyrolysis step of the precursor²⁶ or without it^{12, 17}. In these cases, the precursor (biomass or pyrolyzed biomass) gets in touch with the activating agent (iron salt) usually by impregnation^{12, 17}, and then the activation process is carried out.

The biomass wastes usually employed are from different origins and nature^{12, 17, 26-27}. This work is focused on chestnut shell wastes (CH) due its suitable characteristics²⁸, important industrial waste role and barely studied in this field.

Chestnut is the fruit of the chestnut tree, *Castanea Sativa*. Nowadays, world chestnut production is estimated on 2 Mt²⁹ while in 60's years of XX Century it was around 600 kt. Approximately, 10% of the fruit corresponds to the peel, which generates a large amount of waste. The production is based in two main regions: Europe and Asia, although there are other emerging countries producers (Australia, Chile or USA). In Europe is mainly produced in the south part of the continent but Turkey is the biggest European producer with 60 kt³⁰. Likewise, there is a well-developed agro-food industry in Europe that needs a constantly quantity of chestnuts to support their fresh consumption and transformation: marron glacé, candied products, etc.³⁰ Despite this, few studies are involved in CH and their applications as activated carbons^{28, 31} and it is practically null in terms of MACs, although recently, at Esra Altintig et al. work³², bio-based magnetic activated carbon from this waste resulted as a potential sorbents for effective removal of malachite green from wastewaters.

The present work introduces several novel aspects in MACs preparation that have not been studied in other works with any biomass before. The contact, between the CH and the activating agent will not be carried out by impregnation (more usual method), but by physical mixture in solid state. On the other hand, an only one-step thermochemical activation process turning it much more optimal, sustainable and economical.

In this research work, considering a scenario of circular economy, is raised to advance in the use of industrial biomass wastes by transforming them into carbonaceous adsorbent materials with magnetic and or catalytic properties. The specific challenges are focused on the optimization of the experimental conditions for the chemical activation process and the effects on the development of chemical, morphological,

textural and magnetic properties in magnetic activated carbons (MACs). In general, the major goal of this study is to develop an experimental methodology of novel chemical activation that allows the management and sustainable valorization of a raw biomass industrial waste and its transformation into MACs.

▪ EXPERIMENTAL SECTION

Industrial biomass waste. A chestnut shell waste (CH) was used as raw material in the preparation of Magnetic Activation Carbons (MACs). CH is an industrial food-waste generated from the peeling process in the preparation of candied products (i.e. marron-glacé, chestnut jam, etc...). It was supplied by an industry located in El Bierzo-León, in the north of Spain.

Preparation of Magnetic Activated Carbons (MACs). CH waste was grounded and crushed to a fine particle size (< 3 mm) to favor the physical mixing with the activating agent and the process of chemical activation. The activating agent used is anhydrous FeCl_3 in powder form and appropriate doses. The FeCl_3 -biomass waste mixtures were prepared in a glove box and the physical mixing was done manually. Given the above conditions, the mixture is produced quickly and homogeneously.

Magnetic activated carbons were obtained using a novel single-step thermochemical process based on the direct physical mixture of the raw CH and the anhydrous FeCl_3 . The proposed single-step process, without a previous pyrolysis step as it is a common method used in other studies^{10, 12, 33}. It mainly differs in two aspects: (1) the activating agent used is an anhydrous iron salt instance of a hydrated iron salt; and (2) no impregnation step of the carbon source with the chemical activation agent is required.

The activating agent and the crushed biomass waste were physically mixed and the optimum ratio was 0.5:1 w/w. The small particle size of the CH facilitates the mixing process with the activating agent in also powder form. This preparation of the starting materials saves time and favors a more sustainable process without an impregnation step.

The chemical activation process was carried out in a conventional tubular furnace, Carbolite CTF 12/65//550, at a heating rate of 5 °C min⁻¹ from ambient to six different final temperatures: 220, 400, 500, 600, 700 and 800 °C and the desired final temperature was maintained for 60 min under a constant N₂ flow rate of 150 ml/min. These variables were selected on the basis of previous studies in our research group^{3, 6, 28}.

After thermochemical process, MACs were washed to remove products that could be blocking the porosity. Samples were repetitively washed with deionized water (Milli-Q) until the washing water reached a constant pH and finally, they were dried at 105 °C and then in a vacuum stove at 60 °C.

Characterization of the materials. The chemical characterization of the samples consisted of moisture and ash determination and elemental composition. The moisture of the sample was obtained following the UNE 33002 standard procedure, on the basis of the weight loss at 105 °C over a period of 1 h. The ash content was determined by calcination at 815 °C for 1 h in presence of oxygen, according to the UNE 32004 standard procedure. The elemental analysis was carried out using a LECO CHN-2000 for C, H and N (ASTM D-5773) and a LECO S-144 DR (ASTM D-5016) for sulphur.

The inorganic composition of CH, was determined by inductively coupled plasma and mass spectrometry (ICP-MS). For this analysis the chestnut shell ashes were digested in

a microwave oven with a mixture of nitric and hydrochloric acids. An Agilent 7700x ICP-MS equipment was used for the elemental analysis.

X-ray diffraction (XRD) measurements were carried out in a Bruker D8 Advance diffractometer equipped with a graphite monochromator and an internal silicon powder pattern was used as reference material. The equipment was connected to a CuK α radiation source. The diffraction data were collected by step scanning using a step size of 0.02° and a step-time of 3 s. The scan range 2 θ was from 5° to 80°.

Fourier-Transform infrared (FTIR) spectra were collected on a Nicolet IR 8700 spectrophotometer fitted with a deuterated triglycerine sulphate (DTGS) detector. All spectra were obtained in the mid-IR region, 4000-400 cm⁻¹, in the transmission mode by co-adding 128 scans at a resolution of 4 cm⁻¹. The spectra were recorded using KBr standard pellets.

Raman spectroscopy analysis was performed to compliment the results from FTIR. The Raman spectra were obtained using a JYV-Jobin Yvon spectrometer LabRam HR UV 800 model with an Olympus confocal microscope BXFM-ILHS using DPSS laser model CDPS532M: 532 nm diode laser. CCD detector and working conditions: grating 950 l / mm, objective x100, hole 200, spectral interval analyzed (120-1850 cm⁻¹ and 120-800 cm⁻¹), 4 accumulations / 35 sg each and calibration with silicon plate at 520.80 cm⁻¹.

Mössbauer spectra were recorded at room temperature (RT) in the transmission mode using a constant acceleration spectrometer equipped with a ⁵⁷Co(Rh) source. The samples were prepared to give an effective absorber thickness of 5 mg of natural iron per cm². The velocity scale was calibrated using a 6 μ m thick α -iron foil and the isomer shifts were referred to the centroid of the spectrum of α -iron at RT. The spectra were

computer-fitted using the usual constraints of equal area and width for the two lines of a doublet and equal width and areas in the ratio 3:2:1:1:2:3 for the six lines of a doublet. The relative concentrations of each iron species were obtained from their relative areas assuming equal recoil-free fractions at RT for all the spectral components.

The morphological properties of the MACs were examined using a scanning electron microscope (ZEISS Model DMS-942) equipped with an energy-dispersive X-ray analysis system (Link-Isis II), SEM-EDX. To decrease the charging of the samples and to improve the SEM pictures the samples were covered with iridium prior to SEM examination.

The true density of MACs was obtained by helium pycnometry on a Micromeritics AccuPyc 1330 pycnometer. The textural properties of the materials were characterized from N₂ adsorption isotherms at -196 °C in a Micromeritics ASAP 2420 system and CO₂ adsorption isotherms at 0 °C on a Quantachrome NOVA 4000 model instrument.

Before helium pycnometry, N₂ and CO₂ adsorption, the samples were outgassed under vacuum at 120 °C overnight to remove any adsorbed moisture and/or gases.

A vibrating sample magnetometer, VSM, (Microsense EV-9) was used to measure magnetic properties by means of the M(H) magnetization hysteresis curve in the field range from -20 to 20 kOe at RT. In order to perform measurements, about 50 mg of every powder sample were compacted and encapsulated into a 70 mm³ acrylic cup which is firmly stuck to an 8 mm Pyrex transverse rod by means double side Scotch® tape.

▪ RESULTS AND DISCUSSION

Chemical Characterization. [Table 1](#) shows the ultimate analysis of the CH and MACs together with the ash and iron contents. The final pHs of the MACs after washing several times with deionized water (Milli-Q) until a constant value of washing water pH was reached, are also presented in [Table 1](#).

Information about the molecular structure reveals that the carbon percentage (50.27%, db) associated with low ash and sulphur values made CH as a suitable precursor of MACs. Such key characteristics are preferred in the production of ACs^{3, 6, 34}. It is also important to point out that the chemical composition of chestnut shells depend on the variety and where they come from. However, the chemical composition of the CH in this study is consistent with the wastes used by other authors to obtain ACs^{28, 33}.

The activation temperature has a remarkable influence in the chemical composition of the MACs, [Table 1](#). These materials have high carbon content (67-70%, db), except in the sample at the lowest temperature of 220 °C (58.9%, db), although this content is always superior to that presented in the CH sample (50.27 %,db). The hydrogen content varies from 5.30% in CH to as low as 0.98% for the MAC at the highest temperature. Minor elements, S and N, in the raw CH do not follow a general pattern in the MACs. The results of the iron content present in MACs, as determined by ICP-MS, increases progressively with an increase in the activation temperature from 0.55 % in CH, only 1.06% in MAC obtained at 220 °C and finally up to 23.46 % in MAC obtained at 800°C. A similar trend was found in the MAC prepared from the lignin hydrochar derived from eucalyptus at 700 °C and 800 °C¹³. The amount of ashes also increases with the activation temperature in these materials (up to 34.5% in sample at 800 °C versus 0.9% in the raw material biowaste) due to the iron incorporation into the MACs, [Table 1](#).

Usually, the resulting material after a chemical activation was washed using HCl and repetitive washes with deionized water (Milli-Q), to eliminate the traces of activating agent and other products that could be blocked the porosity of the material obtained. In this work the materials obtained were washed exclusively with water because the hydrolysis of certain species of iron already generate the acidity in the wash. With this procedure, the process of obtaining MACs becomes more sustainable.

Table 1. Ash content and chemical composition of the precursor (CH) and the magnetic activated carbons (MACs) at different temperatures.

SAMPLE	T(°C)	Mass fraction (%) db						Fe (wt%)	pH
		Ash	C	H	N	S	O		
CH		0.87	50.27	5.30	0.52	0.02	43.02	0.55	---
MAC-220	220	2.00	58.90	3.59	0.48	---	35.03	1.06	4.0
MAC-400	400	12.94	67.84	2.46	0.55	0.13	16.08	9.45	2.3
MAC-500	500	16.00	66.86	2.69	0.81	0.08	13.56	8.80	2.8
MAC-600	600	22.00	70.38	2.05	0.90	0.05	4.62	11.17	3.0
MAC-700	700	25.25	68.44	1.48	0.83	0.04	3.96	16.69	3.5
MAC-800	800	29.12	67.82	0.98	0.93	----	1.15	23.46	5.2

*The O was calculated by difference

Figure 1 represents the XRD diffractograms corresponding to CH and MACs obtained at different temperatures. In the raw material (CH) and in the sample activated at the lowest temperate of 220 °C (MAC-220) only broad humps between 10 to 30° at 2θ are observed in these two samples could be assigned to the amorphous carbon³².

However the patterns of samples obtained at activation temperature equal or greater than 400 °C showed well-resolved peaks at 2θ values around 18.32°, 30.13°, 35.49°, 37.07°, 43.10°, 53.49°, 57.01° and 62.60°. These Bragg peaks are indexed to (111), (220), (311), (222), (400), (422), (511) and (440) reflections of magnetite, Fe₃O₄, with a face-centered cubic (fcc) structure (PDF-2 card no. 01-08-0691). Besides that, a low-

intensity peak at $2\theta=44.71^\circ$ is also found, and it is very likely to be related to the most intensity reflection (110) of metallic iron, Fe (PDF-2 card no. 01-09-7194).

These peaks are similar to those found by other authors who have used different precursors and methodologies in the obtention of MACs^{19, 26, 32, 35-36}, where the formation of crystalline magnetite was also confirmed by XRD. Nevertheless, the identification of magnetite and maghemite phases by XRD is quite intricate, because both phases possess similar spinel structure with almost identical lattice parameters³⁷. Moreover, in Shengli Zhang et al. research the effect of high activation temperature (above 650 °C) on the MACs led to crystal structure transformation of Fe_3O_4 to produce well-crystallized Fe and at 700-800 °C several Fe_3C peaks appeared²⁶.

Figure 1 X-ray diffraction (XRD) of the CH and MACs obtained at different temperatures.

Bragg peak positions are indicated on the top of the figure for the different Fe_3O_4 and Fe crystal structures.

FTIR spectra of the evolution of structural features of CH and MACs are shown in **Figure 2**. Additionally, to help in the location of the main absorption bands of magnetite, its spectrum is also displayed in **Figure 2**. The spectrum of CH is characterized by features common to lignocellulosic biomass and the assignments of

main absorption bands corresponding to different functional groups are also depicted in **Figure 2** based on previous studies³⁸.

The FTIR results show that the raw CH suffers some chemical changes which are linked to the activation temperature. Obviously, the MAC activated at 220 °C has the most recognizable absorption bands attributed to the raw CH and the most significant changes at the lowest temperature are due to the loss of the less thermally stable functional groups which leads to the release of relatively low molecular weight substances. In comparison with CH, it can be clearly observed that the absorbance characteristics assigned to the oxygen-containing groups are more affected. These chemical changes are linked to a decrease in the strong band due to the stretching vibration of hydrogen bonded O-H around 3400 cm^{-1} ($\nu\text{O-H}$), a slight decrease in carbonyl groups at 1740 cm^{-1} ($\nu\text{C=O}$) and C-O bonds in the range $1300\text{--}1000\text{ cm}^{-1}$ ($\nu\text{C-O}$) together with a decrease in the stretching and deformation vibrations of C-H bonds in aliphatic groups ($3000\text{--}2800\text{ cm}^{-1}$ and $1475\text{--}1350\text{ cm}^{-1}$, respectively). For the MACs series with the increase of activation temperature from 220 to 800 °C, the structural organic components, polysaccharides and lignin, occurs in abrupt changes which are reflected in the variation of intensity, location and shape of the absorption bands. As temperature increases there is almost complete loss of C=O functionalities (1740 cm^{-1}) and the formation of new components in MACs. A gradually deoxygenation of the precursor and, consequently of the MACs, occurs as the activation temperature increases, becoming deeper at the highest temperature. This is in line with less H, less O, and more C in the elemental composition (**Table 1**). Likewise, some absorption bands below 900 cm^{-1} appear which are presented in the magnetite spectrum, **Figure 2**. Especially remarkable is the intense band at approximately 575 cm^{-1} assigned to Fe-O in iron oxide and in the magnetic substances, suggesting the presence of iron

oxide and magnetite³⁹⁻⁴⁰. The MACs obtained at 400, 500, 600, 700 and 800 °C presented two characteristic bands at 565 and 450 cm⁻¹, being the absorption band at 565 cm⁻¹ the most significant at temperatures of 700 and 800 °C. These absorption bands are similar to those found in the Ying-Sing works⁴¹⁻⁴² where they are attributable to the formation of hematite (α -Fe₂O₃) and the IR spectral analysis reveals that the magnetite is converted to, α -Fe₂O₃ at 500 °C and above⁴¹. In **Figure 2**, at 700 and 800 °C a shoulder over 655 cm⁻¹ is appreciated in the band at 565 cm⁻¹ and is similar as that found in magnetite-Fe₃O₄ in previous investigations, while the distinct high-frequency shoulder at 635 cm⁻¹ is close to that of maghemite, γ -FeO₃⁴³. Further on, **Table 2** and **Figure 4** reflect the results provided by the Mössbauer spectroscopy where for MACs obtained at 700 and 800 °C the presence of γ -FeO₃ is confirmed.

Figure 2. FTIR spectra of the CH, the MACs obtained at different temperatures and the magnetite.

The structure features of the carbon layer in the CH and CH-based MACs were detected by Raman spectroscopy. In [Figure 3](#) two Raman characteristic peaks in the carbonaceous materials are observed in the MACs obtained: Peak at 1350 cm^{-1} which is induced by structural defects associated with graphitic disorder⁴⁴ (D-band) and the second one at 1580 cm^{-1} which corresponds to in-plane vibrations of sp^2 -bonded carbon atoms observed for graphite crystals⁴⁵ (G-band). The peak appearing at 1300 cm^{-1} in the magnetite spectrum, [Figure 3](#), contributed to the widening to the D-band presented in the CH based-MACs. None of these peaks are observed in the case of the

raw material. In the MAC obtained at 220 °C the D-band was not completely developed and seems to be a shoulder of the G-band. They are very closely and the D-band is lower and less defined. This effect also happens in Rufford et al. research⁴⁶, where the intensity of the D peak of the samples treated at 300 °C is lower than that of the MACs obtained at 900 °C. Also, in the Gong et al. work¹⁷, Raman bands peaks for MACs obtained at 400 °C were not well-defined, due to the incomplete carbonization as a consequence of the low activation temperature. Furthermore, the structural disorder reflected in the Raman D-band at higher temperatures could indicate the increase of the microporosity in the material⁴⁶.

The Raman spectra of MACs obtained from 400 °C to 800 °C showed small peaks that were detected at 223, 287, 402 and 599 and 637 cm^{-1} and they are very similar to those presented in the magnetite spectrum, **Figure 3**. This magnetite spectrum resembles that which appears in the Alvear et al. work⁴⁷.

The raw material and the sample MAC-220 did not present these peaks and their spectra were very similar in this range. Besides these bands showed more intensity depending on which areas of the material are illuminated: magnetite crystals or carbonaceous material. These peaks indicated the presence of magnetite and iron oxides^{40, 48}. In MACs obtained at 700 and 800 °C seems to decrease the intensity of the characteristic peaks of the magnetite, due to the evolution of the magnetic species presented in those materials towards other iron species as it was indicated by the Mössbauer analysis in the **Table 2** and **Figure 4**.

It is worth nothing that Raman is used in this work to support other more common techniques employed in the study of MACs.

Figure 3. Raman spectra of the CH, the MACs obtained at different temperatures and the magnetite.

A deeper analysis of the iron species is performed by Mössbauer spectroscopy. [Figure 4](#) shows the Mössbauer spectra recorded for all the samples considered in this paper. The spectrum corresponding to sample MAC-220 is characterized by a very low

absorption resulting from its very small iron concentration (**Table 1**). The spectrum consists in a single paramagnetic doublet with Mössbauer parameters ($\delta=0.37 \text{ mms}^{-1}$; $\Delta=0.85 \text{ mms}^{-1}$) which are typical of Fe^{3+} in distorted oxygen octahedral coordination and probably arises from the presence of small particle Fe^{3+} -containing oxides⁴⁹. The spectrum has very broad lines what is compatible with the occurrence of a multiplicity (distribution) of Fe^{3+} ions in slightly different distorted octahedral environments. The result is compatible with the presence of chemical inhomogeneities/ disorder in the sample and correlates well with its XRD data (**Figure 1**) which only show a broad background with no evident diffraction reflections.

The spectra recorded for samples MAC-400, MAC-500 and MAC-600 contain two sextets and a paramagnetic Fe^{3+} doublet. The Mössbauer parameters of the two sextets ($\delta_A=0.30 \text{ mms}^{-1}$; $2\varepsilon_A=0.02 \text{ mms}^{-1}$; $H_A=48.6 \text{ T}$; $\delta_B=0.66 \text{ mms}^{-1}$; $2\varepsilon_B=-0.01 \text{ mms}^{-1}$; $H_B=45.2 \text{ T}$) are characteristic of the Fe^{3+} tetrahedral (A) and $\text{Fe}^{2.5+}$ octahedral (B) sites of magnetite (Fe_3O_4)⁴⁹ while the parameters of the doublet are very close to those observed for the doublet of the first sample and, therefore, it can be associated with the presence of superparamagnetic Fe^{3+} containing oxides. The B/A sextet area ratio is around 1.0 what indicates that magnetite is non-stoichiometric. The relative contributions of these two iron species vary from sample to sample, their respective percentages being collected in **Table 2**.

The spectrum corresponding to sample MAC-700 is rather more complex. The spectrum also contains magnetite and paramagnetic components but in addition to those it has a maghemite ($\gamma\text{-Fe}_2\text{O}_3$) contribution ($\delta=0.31 \text{ mms}^{-1}$; $2\varepsilon_A=0.02 \text{ mms}^{-1}$; $H_A=49.8 \text{ T}$) and two other broad, minor magnetic contributions which have a more difficult assignment on the basis of their Mössbauer parameters ($\delta=0.41 \text{ mms}^{-1}$; $2\varepsilon_A=0.08 \text{ mms}^{-1}$; $H_A=42.1$

T and $\delta=0.37 \text{ mms}^{-1}$; $2\varepsilon_A=-0.10 \text{ mms}^{-1}$; $H_A=32.7 \text{ T}$). Since their isomer shifts are characteristic of Fe^{3+} and they have relatively low hyperfine magnetic field values they could be associated with nanophasic iron oxides. **Table 2** collects the relative contributions of each iron phase to this sample.

Finally, the spectrum recorded from MAC-800 is, by far, the most complex of all the samples. It contains non-stoichiometric magnetite, maghemite, a small paramagnetic Fe^{3+} contribution, a component assignable to a nanophasic iron oxide, metallic iron ($\delta=0.00 \text{ mms}^{-1}$; $2\varepsilon_A=0.00 \text{ mms}^{-1}$; $H_A=33.0 \text{ T}$) and the iron carbide, Fe_3C , cementite ($\delta=0.17 \text{ mms}^{-1}$; $2\varepsilon_A=0.00 \text{ mms}^{-1}$; $H_A=20.8 \text{ T}$)⁵⁰. The relative concentrations of each species are collected in **Table 2**.

Table 2. Relative contributions of the different iron phases identified by Mössbauer spectroscopy.

Sample	Relative spectral area (%)						
	Paramagnetic Fe^{3+}	Fe_3O_4	$\gamma\text{-Fe}_2\text{O}_3$	Nanophasic Fe^{3+} oxide	Nanophasic Fe^{3+} oxide	Metallic iron	Fe_3C
MAC-220	100	---	---	---	---	---	---
MAC-400	45	55	---	---	---	---	---
MAC-500	23	77	---	---	---	---	---
MAC-600	33	67	---	---	---	---	---
MAC-700	23	39	18	8	12	---	---
MAC-800	4	39	10	7	---	30	10

Figure 4. Room temperature Mössbauer spectra recorded from (a) MAC-220, (b) MAC-400, (c) MAC-500, (d) MAC-600, (e) MAC-700 and (f) MAC-800.

Morphology and Structure of the materials. Some SEM photographs taken at different magnifications of the raw material (CH) and the chestnut shell wastes-based magnetic activated carbons are shown in [Figure 5](#). Pictures corresponding to MACs

present significant differences or similarities in their morphology between them and with the raw material depending on the temperature.

SEM observations of the CH raw biomass reveals the presence of irregularly-shaped, compact and hard particles with fibrous material (**Figure 5 a**). When a soft activation at 220 °C is applied, the MAC obtained did not present any appreciable singularity except the appearance of some holes or cavities in the surface. This effect is better appreciated in the Oliveira et al. study¹⁰ where the MACs obtained from coffee husks by impregnation with ferric chloride presented surface craters with thinner walls in the materials activated at 280 °C and probably favored by the presence of iron species in their preparation.

In the present work, MACs prepared at temperatures greater or equal than 400 °C showed cavities and channels more developed and more numerous than in MAC obtained at 220 °C indicating the generation of porosity although some of these pores could be occupied or blocked by the iron compounds formed.

In the EDX analysis of the sample MAC-220, **Figure 5 b**) the iron atomic percentage indicated was insignificant (<0.1%) and no iron compounds were observed. On the other hand, the carbon atomic percentage in this material remained high (72.46%) as the studied area showed. These results are in line with those obtained in the elemental analysis of this material (**Table 1**) which presented a carbon content of 58.90% and Fe of 1.06%.

At temperatures greater or equal than 400 °C, cavities and channels more developed and more numerous were visible in the obtained MACs indicating the generation of porosity although some of these pores could be occupied or blocked by the iron compounds formed.

In the MAC obtained at 400 °C, MAC-400, **Figure 5 c)**, showed some iron oxide crystals deposited on the surface of the samples with a well-defined shape and they could be attributed to magnetite crystals as confirmed Mössbauer, Raman, XRD analysis. Iron atomic percentage increased and the carbon percentage decreased respect to the material carried out at 220 °C and these results were reflected in the EDX analysis of the crystals formation which were analyzed, **Figure 5c)**.

The images corresponding to the sample MAC-800, **Figure 5d)** showed that these crystals formed at lower temperatures (400-600 °C) had changed and a conglomerate of iron compounds was formed similar to the aggregated iron oxide particles observed and distributed on the surface of MACs reported by different authors^{12, 17}. As can be seen in the areas analyzed, **Figure 5d)**, a high percentage of atomic iron is detected, up to 28.82% (up to 62.56 wt% Fe), being upper than the atomic iron percentage values presented by MACs obtained at a lower activation temperature.

This high iron percentage in MAC-800 is also reflected in chemical composition, so that this material presented a higher iron content (23.46%) than the MACs obtained at a lower temperature (up to 16.69%). Mössbauer analysis also indicated that this material had the highest number of iron compounds, including iron carbide and metallic iron that do not appear in any of the other materials.

a)

Chestnut Shells

b)

MAC-220

c)

MAC-400

Figure 5. SEM photographs of a) CH; b) MAC-220; c) MAC-400; d) MAC-800

Textural properties. The textural parameters data (S_{BET} , V_{TOT} and the pore size distribution –PSD–) are shown in [Table 3](#).

The helium density is defined as the relationship between the sample mass and the volume of the carbonaceous solid skeleton (and any pore) not accessible to helium. Using He picnometry, the gas is able to enter the smallest pores of a solid without being adsorbed. Thus, the helium density approximates the true density unless the material contains impenetrable and close pores that are inaccessible by helium. Taking into account that MACs are fundamentally microporous materials, as will be seen later with the adsorption of N_2 and CO_2 , the determination of the true density with mercury would not be appropriate since mercury cannot penetrate all the small pores (i.e. micropores and small-sized mesopores). Consequently, the density obtained with mercury would

not equal to the true density of MACs while helium pycnometry seems to be the best available way to approach true density.

Helium density increases from 1.43 g cm^{-3} for chestnut shell residue to $1.48\text{-}2.40 \text{ g cm}^{-3}$ for MACs. Excluding an adsorption occurrence, the high values of He densities may be due to two effects. The first effect could be associated to the release of volatile matter during the activation process that generates closed porosity in the material. The higher the activation temperature the greater the porosity developed. However, in the case of MACs obtained at different temperatures, a second effect should also be considered. The Fe species present in the MACs would also contribute to give high values of the He density. In our results, the He density increases from 1.48 up to 2.40 g cm^{-3} for MAC-220 and MAC-800, respectively, in the same way that iron content increases ($1.06 \text{ \%Fe}$ for MAC-220 vs $23.46 \text{ \%Fe}$ for MAC-800). A high Fe quantity in MACs agrees with a high He density of these type of carbonaceous materials. Furthermore, a comparison of traditional ACs and MACs brings that the helium density of MACs are always slightly higher than those of activated carbons obtained from the same lignocellulosic industrial biomass waste obtained by KOH chemical activation. The characterization of ACs obtained from the same biomass waste is described in B. Ruiz et al²⁸.

N_2 adsorption isotherms at -196°C are presented in **Figure 6**. MACs obtained at temperatures equal or higher at 400°C present a significant amount of adsorbed N_2 at low pressures, which increases as the activation temperature increases. The isotherms of these materials present a hybrid form between types I-IV according to the IUPAC classification, with a cycle of incipient hysteresis which is perfectly developed in the material activated at 800°C (type H4) indicating the presence of mesoporous in this material. Activated carbons developed in our research group using the same biowaste

but with KOH activation and preceded by a pyrolysis step, the isotherms are type I and have a higher nitrogen adsorption (more than double)²⁸.

The magnetite hardly presents adsorption of N₂ at -196 °C and in the isotherm a cycle of hysteresis type H3 can be appreciated as it is described in Thommes et al. work⁵¹.

The raw material and the MAC obtained at 220 °C are very similar with a negligible nitrogen adsorption and low BET surface area ($\leq 3 \text{ m}^2\text{g}^{-1}$) and porosity, **Figure 6**, **Figure 7**, **Table 3**. The SEM images of these materials confirm the absence of significant porosity in these samples (**Figure 5a**, **5b**))

In this work the material obtained at 220 °C did not present textural development in contrast with Oliveira et al.¹⁰ research, where samples obtained using ferric chloride as activating agent at 280 °C in ACs preparation from coffee husks were suitable as adsorbents for cationic dyes and phenol.

The highest BET surface area reached at 800 °C was $568 \text{ m}^2\text{g}^{-1}$, **Table 3**, better than those found in other research works^{32, 35} but lower than the values ($1100\text{-}1790 \text{ m}^2\text{g}^{-1}$) of the activated carbons developed in our research group using the same biowaste although with KOH activation and preceded by a pyrolysis step²⁸. This result may be due, on the one hand, to the formation of iron compounds nanoparticles in surface and inside the porous structure of the MAC obtained blocking porosity which could cause a reduction in the amount of nitrogen adsorption, BET surface area and porosity as reflected in the work of Do et al.³⁶. Another one of the causes is that these MACs obtained presented high ashes content (up to 34.50%) that does not contribute to the total porosity of the magnetic adsorbent materials. The total pore volume obtained at p/p^0 of 0.99 follows a trend similar to the BET surface area increasing from $0.017 \text{ cm}^3\text{g}^{-1}$ for the MAC obtained at 220 °C to $0.294 \text{ cm}^3\text{g}^{-1}$ for the MAC at the highest temperature, **Table 3**.

The PSD showed the existence of microporosity in the MACs obtained from 400 °C (micropore volume up to 0.133 cm³g⁻¹ for MAC-800 and in general with a greater presence of ultramicropores (pore width <0.7 nm) up to 0.081 cm³g⁻¹ for MAC obtained at 600 °C; on the other hand, there is a small contribution of mesopores that generally increases with the activation temperature until reaching the value of 0.033 cm³g⁻¹ in the MAC obtained at 800 °C (Figure 7 and Table 3).

Figure 6. N₂ isotherms at -196 °C for the raw material (CH), the MACs and the magnetite

Figure 7. Incremental pore volume versus pore width based on the N₂ isotherms of the biomass waste, MACs and the magnetite.

Table 3. Textural parameters of the materials.

Sample Ref.	ρ_{He} $g \cdot cm^{-3}$	N ₂ adsorption at -196°C					CO ₂ adsorption at 0°C				
		S_{BET} $m^2 \cdot g^{-1}$	V_{TOT} $cm^3 \cdot g^{-1}$ $p/p^0=0.99$	*V _{umi} $cm^3 \cdot g^{-1}$ <0.7nm	*V _{mmi} $cm^3 \cdot g^{-1}$ 0.7-2nm	*V _{me} $cm^3 \cdot g^{-1}$ 2-50nm	W_0 $cm^3 \cdot g^{-1}$	S_{DR} $m^2 \cdot g^{-1}$	E_0 $KJ \cdot mol^{-1}$	L_0 nm	S_{ni} $m^2 \cdot g^{-1}$
CH	1.43	1	0.007	0.000	0.000	0.003	0.048	125	23.36	0.90	106
MAC-220	1.48	3	0.017	0.000	0.000	0.007	0.078	203	26.50	0.72	217
MAC-400	1.69	285	0.145	0.068	0.023	0.011	0.183	479	28.91	0.62	594
MAC-500	1.71	451	0.209	0.033	0.079	0.012	0.213	558	28.20	0.64	663
MAC-600	1.90	380	0.179	0.081	0.039	0.008	0.219	572	28.49	0.63	692
MAC-700	2.10	518	0.241	0.071	0.061	0.014	0.238	623	27.17	0.68	694
MAC-800	2.40	568	0.294	0.076	0.057	0.033	0.198	519	27.22	0.68	580
Magnetite	4.63	8	0.034	0.000	0.000	0.009	0.002	6	27.92	0.65	7

*V_{umi}: Vultramicropores (volume corresponding to pore width <0.7 nm).

*V_{mmi}: Volume medium-micropores (volume corresponding to pore width 0.7-2nm).

*V_{me}: Volume mesopores (volume corresponding to pore width 2-50 nm.)

CO₂ adsorption isotherms at 0 °C are used in ACs works^{5, 28} to study the narrow microporosity (pore width smaller than 0.7 nm) and to calculate the micropore volume (W_0), energy characteristic (E_0) and micropore size (L_0) applying the Dubinin-Raduskevich equation. However it is an unusual technique in the characterization of MACs as N₂ adsorption is commonly employed to study textural properties. This analysis was carried out to study the activation temperature influence in the ultramicroporosity development of MACs and complement studies of textural characterisation by N₂ adsorption. In **Figure 8**, the CO₂ isotherms at 0 °C of the materials obtained in this work are presented and **Table 3** shows the values of the textural parameters obtained from these isotherms. The raw material and the MAC obtained at the lowest activation temperature (220 °C) have a very similar behaviour although the activated one presented a little more adsorption (**Figure 8**). Likewise, the values for the sample activated at 220 °C increased slightly with respect to the original biomass: W_0 up to 0.078 cm³g⁻¹, S_{DR} up to 203 m²g⁻¹ and S_{mi} up to 217 m²g⁻¹. The micropore size of the biomass waste was 0.90 nm. During the activation process was generated ultramicropore volume and the MAC obtained at 200 °C presented a pore size of 0.72 nm (**Table 3**). In general, with activation temperature ≥ 400 °C, MACs obtained presented a higher CO₂ adsorption, **Figure 8**.

The micropore volume (W_0) increases with temperature up to maximum value of 0.238 cm³g⁻¹ for the MAC obtained at 700 °C, but when the activation temperature is 800 °C this value decreases to 0.198 cm³g⁻¹ which may be due to the collapse of adjacent pore walls. In fact, this may explain why the pore size is wider at higher activation temperatures (0.062 nm for MAC-400 v.s. 0.68 nm for MAC-700 and MAC-800) and very similar to the results obtained at the same temperature range in Ruiz et al study²⁸

where the same biowaste was pyrolyzed and activated with KOH. The S_{DR} (up to 623 $m^2 g^{-1}$) and S_{mi} (up to 694 $m^2 g^{-1}$) at 700 °C are also the highest values obtained in the present work, as it happens at 750 °C in Ruiz et al study²⁸.

Finally, as can be seen in the [Table 3](#) and [Figure 8](#), the magnetite presented a negligible adsorption of CO_2 .

Figure 8. CO_2 isotherms for the raw material (CH), the MACs and the magnetite.

Magnetic properties. [Figure 9](#) shows the field dependence of the magnetization $M(H)$ at RT where hysteretic magnetic properties such as remanent magnetization, M_R , and coercivity, H_c , are depicted in the inset. It is worth noting that the lowest activation temperature (220 °C) only modifies the diamagnetic nature of the raw material (CH) to a paramagnetic substance, characterized both by a linear response of $M(H)$ but with negative or positive slope, respectively. Above this temperature, the rest of samples

seem to be ferromagnetic, the larger M_R and H_c the higher activation temperature, **Table 4**. In addition, the value of saturation magnetization, M_S , can be estimated from the high magnetic field region of the $M(H)$ curves using the following approach-to-saturation law⁵²:

$$M = M_S \cdot \left(1 - \frac{a}{H} - \frac{b}{H^2}\right) + \chi \cdot H \quad (1)$$

showed similar trend that previous magnetic parameters. Besides that, taking into account the iron content of every sample (**Table 1**) and different relative contributions of each phases identified by Mössbauer spectroscopy (**Table 2**), we can explain the saturation magnetization values. Thus, the increase in the ratio between magnetite and paramagnetic phases along the increase in the iron amount are both mainly responsible for the rising in M_S observed for the samples MAC-400, MAC-500 and MAC-600. Furthermore, the formation of metallic iron at the highest activation temperatures leads to an extra increase of M_S due to its higher saturation magnetization value (217 emu/g) compared to that of magnetite (92 emu/g)⁵³. Moreover, coexistence of different ferromagnetic phases and size-dependence effects could be the cause of the increase of in coercivity reported.

Table 4. Magnetic parameters (M_R , remanent magnetization; H_C , coercivity; saturation magnetization, M_S ; a and b parameters in eq. (1), magnetic susceptibility, χ) obtained from the hysteresis loops.

Sample	M_R [emu/g]	H_C [emu/g]	M_S [emu/g]	a [10 ² Oe]	b [Oe ²]	χ [10 ⁻⁶ emu/g·Oe]
CH	-	-	-	-	-	-0.28
MAC-220	-	-	-	-	-	1.61
MAC-400	0.15	45	2.9	0.862	$1.19 \cdot 10^6$	5.50
MAC-500	0.40	33	9.0	0.365	$8.23 \cdot 10^5$	4.60
MAC-600	0.72	65	10.0	-1.920	$1.56 \cdot 10^6$	11.04
MAC-700	1.59	97	17.8	-1.230	$1.63 \cdot 10^6$	6.19
MAC-800	3.88	140	30.8	-1.920	$1.56 \cdot 10^6$	11.04

Figure 9. Field-dependence of magnetization $M(H)$ at room temperature. The inset depicts the central area of the loops.

▪ CONCLUSIONS

- The proposed methodology for obtaining MACs through a single-stage thermochemical process, bringing the waste (chestnut shell) into contact with the activating agent by a direct mixing, has been confirmed with good results.
- The activation temperature has an important influence on the MACs chemical composition. As the temperature increases, so does the percentage of carbon and iron, but the percentage corresponding to oxygen and hydrogen decreases. No activation at temperatures of the order of 220 °C.

- The analysis techniques used: DRX, FTIR, RAMAN and Mössbauer confirmed the presence of magnetite and the appearance of magnetic species such as Fe oxides, carbides and even metallic Fe depending on the temperature at which the thermochemical process is carried out. The results showed the absence of these magnetic species at low activation temperature (220 °C).
- The MACs morphology is also affected by the activation temperature with the appearance of magnetic crystalline species from 400 °C and their evolution towards conglomerates at 800 °C. None of this is appreciated in the MACs obtained at 220 °C.
- In the textural properties of materials, the activation temperature at 800 °C favoured greater BET areas (up to 568 m²g⁻¹), the presence of microporosity (up to 0.133 cm³g⁻¹) and some mesoporosity (up to 0.033 cm³g⁻¹) while at 220 °C there was nothing of textural development (S_{BET}: 3 m²g⁻¹).
- The Mössbauer spectrum recorded from the MAC obtained at the highest temperature (800 °C), was the most complex of all the materials and presented a greater number of iron compounds: non-stoichiometric magnetite, maghemite, a small paramagnetic Fe³⁺ contribution, a component assignable to a nanophasic iron oxide, metallic iron and the iron carbide, Fe³C, cementite. The Mössbauer spectrum corresponding to the material obtained at the lowest temperature (200 °C), was characterized by a very low absorption resulting from its very small iron concentration.
- Magnetic properties of the MACs are improved as the activation temperature increase because of nucleation, growth, structure transformation and interactions between the different iron base phases determine on the analysis techniques used.
- In view of the above, the MACs obtained seem to be suitable materials for environmental applications in both liquid and gaseous phase contaminant removal. On

the other hand, the presence of iron compounds with catalytic properties will be able to regenerate the exhausted MACs by means of advanced oxidation processes.

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■ SYNOPSIS

In a sustainable and circular economy scenario, a single-step thermochemical process was optimized to prepare MACs from biowastes. The activation temperature employed was a key factor related to MACs composition and properties.