# Magnetic activated carbons from chestnut lignocellulosic industrial wastes as sustainable adsorbents for gas storage at high pressure.

S. Rodríguez-Sánchez<sup>1</sup>, B. Ruiz<sup>1</sup>, D. Martínez-Blanco<sup>2</sup>, I. Suárez-Ruiz<sup>1</sup>, M.A. Diez<sup>1</sup>, J. A. Blanco<sup>3</sup>, <u>E. Fuente<sup>1</sup></u>

<sup>1</sup>Biocarbon & Sustainability Group. Instituto Nacional del Carbón (INCAR), CSIC, 33011, Oviedo, Spain. <sup>2</sup>Scientific-Technical Services, University of Oviedo, 33006, Oviedo, Spain.

<sup>3</sup> Department of Physics, University of Oviedo, 33007 Oviedo Spain.

**Keywords:** valorisation chestnut industrial wastes, chemical activation, magnetic activated carbon, high pressure gas storage, magnetic properties.

Presenting author email: enriquef@incar.csic.es

## Introduction

Waste generation and pollution are problems that concern society and the scientific world. Several factors such as overpopulation, different modern human activities and consumerism have contributed to the accumulation of a large amount of waste and pollution all over the world. Nowadays, one of the main challenges is the development of waste management strategies and research into new low-cost and eco-friendly materials to contribute to the conservation of the environment.

Activated carbons are considered as important adsorbent materials to remove different pollutants from the air, water or for gas separation and storage. The starting raw materials can be obtained from agricultural or industrial wastes (Ruiz, 2017; Gil, 2014; Ferrera-Lorenzo, 2014). Furthermore, the search for more optimal, sustainable and effective materials has recently resulted in the production of magnetic activated carbons (MACs) (Safarik, 2012). The residues employed as precursors in MACs obtention are of diverse origin and a little studied lignocellulosic waste in this field is chestnut shells (CH) in spite of the fact that chestnut is a fruit that is commonly consumed in many countries, including Europe.

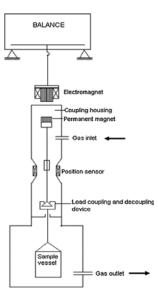
The aim of this work is the valorization of a food industrial waste, CH, through its transformation into high value adsorbent materials, MACs, for the purification/ separation of gas mixtures.

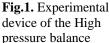
## Methodology

The raw material used in this research was industrial Chestnut Shells (CH) wastes supplied by an industry located in El Bierzo-León, in the north of Spain. This waste, the precursor of MACs, was previously ground and crushed to a small size. The residue was then activated in a conventional tubular furnace, Carbolite CTF 12/65//550, at a heating rate of 5°C/min and under a 150 ml/min N<sub>2</sub> flow employing a maintenance time of 60 min at the final temperature, with (*P*) and without a previous pyrolysis step, using a ferric salt as activating agent. Different experimental conditions were employed: an activation temperature (*A*) between 700-800°C and activating agent:precursor weight ratios (*H*) of 0.25:1, 0:5:1, 1:1. After chemical activation the samples were washed several times with deionized water (Milli-Q) (*w*) or with hydrochloric acid solution (*a*1) followed by rinsing with deionized water. Finally the samples were dried in a stove at 105°C, and then in a vacuum stove at 60°C.

The MACs obtained were characterized by different chemical and textural analysis techniques: CHN, sulphur, oxygen and ash analyses; ICP-MS to determine iron content; X-Ray Diffraction (DRX); Infrared Spectra (FTIR); Raman; Scanning Electron Microscopy (SEM-EDX); helium picnometry and N<sub>2</sub> and CO<sub>2</sub> adsorption isotherm analysis.

Magnetic measurements were performed on a Microsense EV9 vibrating sample magnetometer (VSM) at room temperature. The adsorption capacity of  $CO_2$ ,  $H_2$  and  $CH_4$  at high pressure was measured using a Rubotherm-VTI high pressure balance at ambient temperature and under static conditions, Fig.1.



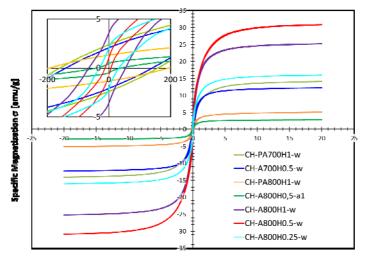


#### Results

The high carbon content (50%) and low ash contents of the raw material (CH) make it suitable for use as a MACs precursor. The data show an increase in carbon content up to72% in the MACs obtained by chemical activation with and without a previous pyrolysis step and washed with water. However, the sample washed with acid presented the highest carbon content up to 90%. The ash contents in these materials increased or decreased

at high temperatures depending on the experimental process carried out. The nitrogen content obtained in this research study is similar to that reported by Ruiz *et al.* (2017) for ACs.

The materials analyzed in the present study also developed important BET surface areas and all of them are fundamentally microporous materials with some mesoporosity.



**Fig.2.** Room temperatura hysteresis loops measured up to 20 kOe (Inset depicts the central area of the loops).

## Conclusions

precursor ratio had an influence on the materials analyzed due to the presence of iron and iron derived species, mainly magnetite, as revealed by DRX, FTIR and Raman spectra which evidence peaks characteristic of these species. Moreover, the morphological shapes observed in SEM images confirm the presence of these iron oxides which differ from the AC images of B. Ruiz et al. (2017) obtained at higher temperatures. The iron oxide phases are responsible for the soft-ferromagnetic behavior shown by every MACs obtained. coercive field and saturation The magnetization values obtained from the hysteresis loops are ascribed to the iron content, the composition and morphology of which are shown in Fig.2.

Likewise, the activating agent:

In this research study, circular economy played an important and interesting role with the valorization of an industrial biomass waste (CH) and the different environmental applications of the materials obtained (CAMs). The CH studied in the present work proved to be an appropriate precursor for obtaining CAMs with a good textural development. Indeed, the high pressure adsorption isotherms recorded in the high pressure balance show these magnetic adsorbent materials to be good candidates for  $CO_2$  capture and gas storage.

## Acknowledgements

The financial support for this work was provided by the National Research program under the Project CTM2014-58435-C2-1-R. The authors thank the industry Palacio de Canedo (El Bierzo-León, Spain) for providing the chestnut-shell industrial waste used in this work.

## References

Ruiz, B.; Ferrera-Lorenzo, N.; Fuente, E., Valorisation of lignocellulosic wastes from the candied chestnut industry. Sustainable activated carbons for environmental applications. *Journal of Environmental Chemical Engineering* **2017**, *5* (2), 1504-1515.

Gil, R. R.; Ruiz, B.; Lozano, M. S.; Fuente, E., Influence of the pyrolysis step and the tanning process on KOH-activated carbons from biocollagenic wastes. Prospects as adsorbent for CO2 capture. *Journal of Analytical and Applied Pyrolysis* **2014**, *110*, 194-204.

Ferrera-Lorenzo, N.; Fuente, E.; Suárez-Ruiz, I.; Ruiz, B., Sustainable activated carbons of macroalgae waste from the Agar–Agar industry. Prospects as adsorbent for gas storage at high pressures. *Chemical Engineering Journal* **2014**, *250*, 128-136.

Safarik, I.; Horska, K.; Pospiskova, K.; Safarikova, M., Magnetically Responsive Activated Carbons for Bio - and Environmental Applications. *International Review of Chemical Engineering (I.RE.CH.E.)* **2012**, *4* (3).