From industrial chestnut shell waste to high-performance magnetic carbonaceous adsorbents for use in biogas improvement

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Introduction

Industrial activity, overpopulation, etc., contribute to the consumption of resources, the waste generation and the pollution. Following criteria of circular economy and sustainability, it is necessary to develop waste management strategies where these low or zero cost materials can be used to obtain bio-fuels or bio-materials, avoiding the ~~use~~ massive use of natural resources and, thus, contributing to the preservation of the environment.

Magnetic activated carbons combine adsorption and magnetic properties, optimum properties that make very versatile materials in various applications (Safarik *et al*. 2012). These materials can replace conventional activated carbons that are not applicable in certain media. If these magnetic adsorbents are obtained from bio-waste, then they also contribute to waste management through their recovery to obtain materials with lower production costs.

In this work, the effect of chemical activation variables (activating agent amount, activation temperature, washing step), the nature of the precursor (waste or bio-char) and the activation methodology (one or two stages) are investigated on the final properties of magnetic activated carbons obtained from chestnut shell waste and its bio-char. The magnetic adsorbents were tested in high-pressure gas adsorption studies to see their potential as CO_2 adsorbents for biogas upgrading and/or gas purification/separation.

Methodology

To obtain magnetic carbonaceous adsorbents, industrial chestnut shell waste and its biochar (obtained by conventional pyrolysis at 500 ºC, 150 ml/min of nitrogen flow and 60 min at the pyrolysis temperature) were used as precursors of these materials. The industrial biowaste selected for this research showed properly characteristics verified in previous works (~~S.~~ Rodríguez-Sánchez *et al*., 2019, 2021, 2022). Industrial food waste was collected and prepared, up to a suitable size (<3 mm), by crushing and sieving.

The magnetic adsorbents materials were obtained in two different ways: I) following a two-stage thermochemical procedure (pyrolysis and chemical activation of the pyrolysis bio-char) and II) using a one-stage thermochemical procedure (the bio-waste was chemically activated without prior pyrolysis). The precursor (bio-waste or bio-char) was physically mixed with different amounts of anhydrous $FeCl_3$ (activating agent); the mixture obtained was subjected to the thermochemical activation process in a conventional tubular furnace, Carbolite CTF 12/65//550, under different experimental conditions. The obtained materials were washed with 1 M HCl solution and water or using only deionized water. Subsequently, the magnetic adsorbents were dried in an oven and stored in appropriate and identified containers.

Then, the materials were characterized by chemical-morphological-textural analysis. The ultimate analysis was performed on a LECO CHN-2000 and a LECO S-144 DR. X-ray diffraction (Bruker D8 Advance diffractometer), Infrared spectroscopy (Nicolet IR 8700 spectrophotometer), Raman spectroscopy (JYV-Jobin Yvon spectrometer model LabRam HR UV 800) were also used. By Scanning Electron Microscopy (ZEISS Model DMS-942) was studied the morphology of the samples. Texture analyses were performed by gas adsorption (Micromeritics ASAP 2420-system and Quantachrome instrument model NOVA 4000). The study of the high-pressure gas adsorption capacity (CO_2, H_2 and CH_4 up to 3, 4 and 8 MPa, respectively) of the magnetic adsorbents was carried out on a Rubotherm-VTI high-pressure balance (Ferrera-Lorenzo *et al.*, 2014).

Results

The chestnut shell waste showed a high carbon and low ash contents (≈50%, <1%, respectively) (Rodríguez-Sánchez *et al*., 2019). The bio-char resulted in a material with higher carbon and ash content (≈84%, ≈2%, respectively). Under the same experimental conditions of chemical activation, the use of bio-char to obtain magnetic adsorbents produced materials with a higher carbon content than those obtained from waste. **Fig. 1** shows a diagram of the magnetic activated carbons preparation from chestnut shell waste or bio-char.

Fig. 1. Preparation of magnetic activated carbons from industrial chestnut shell waste or its bio-char.

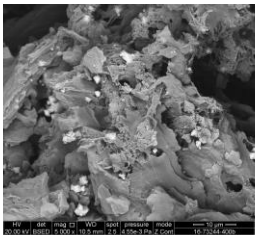

Fig. 2. SEM image (5000x) of magnetic adsorbent.

Fig. 2 shows a SEM image at 5000x of a magnetic activated carbon obtained from the waste at 400 °C; in this figure some crystalline formations, magnetite can be observed. The magnetic adsorbents display different iron species developed after ~~in~~ the chemical activation process and XRD, FTIR, Raman analyses, etc. confirmed their presence. Magnetic activated carbons with a BET surface area up to 830 m^2/g were obtained. The activation temperature, the activating agent amount, the washing step, the precursor nature or the chemical activation methodology influenced ~~in~~ the chemical-textural-magnetic properties developed in the magnetic adsorbents.

Conclusions

Chestnut shell waste and its bio-char were a material suitable to obtain magnetic activated carbons. Under similar experimental activation conditions, magnetic adsorbents derived from bio-char had less iron content. XRD, FTIR, Raman, SEM-EDX confirmed the formation of different iron compounds. High activation temperatures favored the formation of metallic iron. The adsorbents derived from waste presented better textural development, being generally all microporous materials. The magnetic adsorbents showed good, moderate and negligible affinity for the adsorption of CO_2, CH_4 and H_2 at high-pressures. From these results, they could be used to improve biogas, separating CO_2 and to obtain bio-methane, or also pure hydrogen.

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