Magnetic activated carbons from biomass wastes from the food industry. Strategies in the bioenergy field

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Introduction

Waste generation and environmental pollution are current problems that concern society. Overpopulation, human activities, and consumerism contribute to the generation of waste and environmental pollution throughout the world. One of the main challenges for society is the development of waste management strategies and research into new low-cost and environmentally friendly materials that contribute to environmental conservation.

Magnetic carbon nanomaterials are becoming very important in applications such as energy and hydrogen storage, carbon capture, adsorption, catalysis, cancer detection, etc (Safarik et al. 2012). Within this group are magnetic activated carbons, materials that combine their adsorption properties with magnetic properties. These magnetic adsorbents can be obtained from a lot of precursors based on bio-waste; in this way is possible to contribute to waste management through its recovery in obtaining materials with high added value and with lower production costs.

The objective of this work is to develop magnetic activated carbons from industrial food wastes or industrial food wastes pyrolyzed (MACs or MACPs, respectively) by chemical activation. The influence of activating agent ($FeCl_3$)/precursor weight ratio or activation temperature on the final properties of magnetic adsorbents will be studied. The high-pressure gas adsorption capacity of these materials will be studied as an alternative for high-pressure CO_2 adsorption (pre-combustion processes) and for gas purification/separation.

Methodology

In this work, industrial biomass wastes from the food industry (Chestnut Shells (CH)) were used as precursors of magnetic activated carbons. This biowaste, supplied by an industry located in El Bierzo-León (Spain), were collected, grounded and crushed to particle size of < 3 mm.

The biowaste was chemically activated, with and without a previous pyrolysis step, in a conventional tube furnace, Carbolite CTF 12/65//550 (heating rate 5 ºC/min, N_2 flow 150 ml/min, activation temperature 600-800 ºC and time of 60 min at the activation temperature). Before the chemical activation, the food biowaste (CH) or food pyrolyzed biowaste (CHP) was mixed with different ratios (0.25:1, 0.5:1, 1:1) of the activating agent (anhydrous $FeCl_3$). This methodology is eco-friendlier, cost-effective and faster compared to impregnation commonly used and described in the literature. Once the chemical activation was completed, the adsorbent materials obtained were subjected to different washing processes (deionized water or dilute solution of hydrochloric acid followed by washing with water). After the washing process, the samples were dried in an oven (105ºC) and later in a vacuum oven (60ºC).

All the materials (CH, CHP and magnetic activated carbons) were characterized with different techniques of chemical, morphological, structural and textural analysis, with automatic equipment and standardized analysis. Magnetic properties of the adsorbent materials were performed on a Microsense EV9 vibrating sample magnetometer (VSM) at room temperature.

High-pressure gas adsorption isotherms (CO_2, H_2 and CH_4 up to 3, 4 and 8 MPa, respectively) were obtained on a Rubotherm-VTI Magnetic Suspension Balance at room temperature and under static conditions. This unique experiment device described extensively in Ferrera-Lorenzo et al. (2014).

Results

The chemical characteristics of the food industrial biowaste (CH) make it suitable for use as magnetic activated carbons precursor. In general, the use of biochar (CHP) as precursor of magnetic adsorbents favored a higher carbon content in the magnetic adsorbent materials (up to 72% in MPAC obtained at 800 °C and 1:1 activating agent: precursor mass ratio). Iron content decreases in acid washed materials.

MACs and MPACs developed different species of iron (magnetite, maghemite, metallic iron, etc.) being the materials obtained at temperatures above 700-800 ºC those that present a greater number of iron species. The presence of the magnetic species was confirmed by various analytical techniques: Mossbauer, XRD, FTIR, Raman, SEM-EDX.

Activation temperature played an important role in the morphology development of the magnetic activated carbons. The iron amount detected in the MPACs is lower than in the case of MACs. Despite this, the existence of iron species is obvious in MACPs, where crystals formed of size around 5 µm can be observed, **Figure 1.**

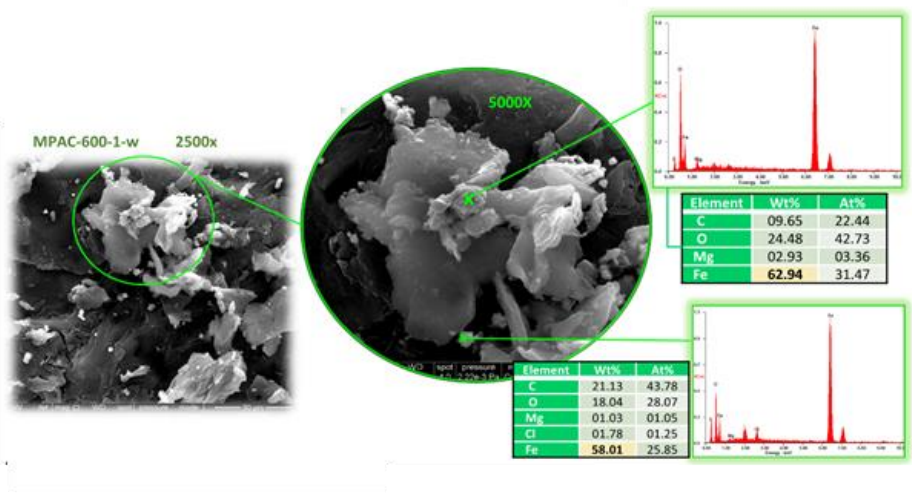

Figure 1. SEM-EDX of MPAC obtained a 600°C and with 1:1 activating agent: precursor mass ratio

Magnetic adsorbents showed a good selectivity for CO_2, moderate for CH_4 and do not showed selectivity towards H_2. There is a clear difference in gas adsorption capacity at high pressure, with MACs presenting the best results. A CO_2 adsorption capacity of up to ≈ 6.58 mmol/g or 28.93% at 3 MPa was achieved. In view of the results, MACs and MACPACs can be used for the separation of gases, turning them into interesting alternatives for the biogas upgrading or for obtaining pure hydrogen.

Conclusions

The use of pyrolyzed biomass as a magnetic activated carbon precursor seems to affect the magnetic parameters, where the coercivity values are notably higher while the magnetization values, MS and MR, are reduced due to the lower amount of iron. The narrow microporosity in the MACPs favored the CO_2 adsorption at low pressures (0.1 MPa); however, MACPs lose efficiency at high pressures (3 MPa) where MACs are more effective because they have larger micropores and some mesoporosity. The material washed with acid presented the best CO_2 adsorption capacity.

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