Activation process of spherical and fibrous carbon precursors for Gas phase adsorption of volatile organic compounds

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Objetives and novelty:

Activated carbons (ACs) are amongst the most promising materials in environmental applications. Hence, new applications are emerging constantly, which imply that the world consumption of these materials is steadily increasing. Among the different methods employed in the preparation of new carbon materials, the interest on the hydrothermal treatment for the preparation of spherical materials can be remarked due to the advantages that the spherical carbons have in comparison with granular activated carbons or powdered activated carbons. The lignocellulosic and carbohydrate materials are interesting precursors for the preparation of spherical carbons by hydrothermal treatment due to their low cost and for environmental concerns.

Additionally, although several authors have reported that hydrothermal treatment is a method to get a wide range of spherical carbon materials with controlled and functionalized structures (or nanostructures) from cheap and abundant precursors, few studies have analyzed the porosity development of the spherical carbons once the spheres have been prepared, and in each paper only one activation method is studied.

In this sense, this PhD Thesis has focused on the study of the preparation of spherical carbons and spherical activated carbons (SAC) by hydrothermal treatment of two natural bio-fibre precursors (banana pseudostem and coconut fibre matting) using three carbohydrates with different structure, a monosaccharide (glucose), a disaccharide (saccharose) and a polysaccharide (cellulose). Afterwards, the activation of these materials by several techniques, keeping the spherical morphology, has been deeply investigated. Regarding the hydrothermal preparation of spherical carbons, the effect of different variables (treatment time, treatment temperature, type of precursor and concentration of carbohydrate) on the spherical carbons formation and their properties have been analyzed.

For the development of the adsorption capacity of these spherical carbons, different activation methods have been analyzed (chemical activation with H_3PO_4, NaOH or KOH or physical activation with CO_2). The effect of some variables such as the precursor, the activation method, the activating agent/precursor ratio (in chemical activation) or the activation time (in physical activation) on the textural properties of the prepared spherical activated carbons has been deeply studied. Also, for comparison purposes a commercial spherical carbon (GE) and a commercial spherical activated carbon (BAC) have been selected as precursors to prepare spherical activated carbons through physical activation with CO_2 and/or steam.

All the prepared samples have been characterized by SEM, thermogravimetry, N_2 adsorption at -196 ºC and CO_2 adsorption at 0 ºC. The pore size distributions were obtained applying the nonlocal density functional theory (NLDFT) to the N_2 adsorption data at -196 ºC. The characterization of the surface oxygen chemistry of all the samples has been performed by temperature-programmed desorption (TPD). The prepared materials have been employed in the adsorption of volatile organic compounds (VOCs): a non-polar volatile organic compound (toluene) at low concentration, a polar volatile organic compound (ethanol) at low relative pressures (lower than 0.01) and relative pressure near unity, and in gasoline vapors in conditions similar to those in vehicle tanks.

Results:

Spherical activated carbons have been prepared from spherical carbons that had been previously obtained by hydrothermal treatment of glucose and saccharose and, also, from a commercial spherical carbon (GE) and a commercial spherical activated carbon (BAC). H_3PO_4 , KOH, NaOH, CO_2 and steam activation have successfully developed the textural properties in these materials, maintaining the spherical morphology and reaching surface areas higher than 3100 m^2/g, micropore volumes up to 1.21 cm^3/g, narrow micropore volumes up to 0.76 cm^3/g or mesopore volumes up to 0.57 cm^3/g. Besides their textural properties, the prepared SACs must be remarked in terms of variability of their surface oxygen chemistry content, strongly dependent on the preparation method selected, which makes these materials very interesting for the adsorption of polar or non-polar VOCs adsorption at different concentration ranges. The SACs prepared have high microporosity and low surface oxygen groups content, which make them interesting for their application for nonpolar VOCs adsorption at low concentrations. In this sense, SACs with high adsorption capacity have been prepared, leading to gravimetric adsorption capacities as high as 70 g toluene/100 g, higher than those achieved with the commercial WVA1100 AC. Also, considering the high gravimetric adsorption capacities and the high bed densities for these materials, especially in the case of the SACs prepared from commercial precursor, the volumetric adsorption capacities achieved are quite high, up to 236 g of toluene/L AC, for the SACs obtained from GE, much higher than that obtained with the commercial WVA1100 AC (see Fig. 1). Thus, besides the textural properties, high bed densities are required for getting high volumetric adsorption capacities.

The adsorption results at low ethanol relative pressures on five spherical activated carbons (from BAC), which have similar textural properties but different surface oxygen chemistry, show that surface chemistry has an important influence on the ethanol adsorption capacity. This influence is not due to the total oxygen content of the samples, but especially to the kind/nature of these oxygen functional groups.

Thus, the presence of carboxyl and anhydride groups, generated by HNO_3 oxidation, favours ethanol adsorption at low concentration, whereas the presence of phenols and carbonyls, generated by air oxidation, is negative. On the contrary, the analysis performed at high ethanol concentration

shows that the adsorption capacities depend only on the porosity, and not on the surface chemistry of the ACs, which is confirmed by the 14 samples selected and studied. In particular, the total micropore volume governs ethanol adsorption in these conditions, as it can be seen in Fig. 2.

The activated carbons prepared from lignocellulosic precursors through H_3PO_4 activation have developed high apparent surface areas, up to 2500 m^2 g^{-1}, high micropore volumes (above 1.00 cm^3 g^{-1}) and high mesopore volumes (1.41 cm^3 g^{-1}). Most of the activated carbons obtained in this study perform very well for adsorbing gasoline vapours, being their performance linearly related to their micro+mesoporosity development. Some of the samples prepared are comparable, or even better, to a commercial activated carbon currently used in gasoline automobiles for evaporative emissions control. To confirm the importance of the mesopores, the sample microporosity has been minimised filling it with n-nonane. Fig. 3 confirms the dependence of the gasoline vapours adsorption with the mesopore volume of the samples (after microporosity has been filled). Additionally, our comparative study shows that the ACs prepared perform very well, even better than WVA1100, a well known commercial activated carbon used to control automobile hydrocarbons emissions.
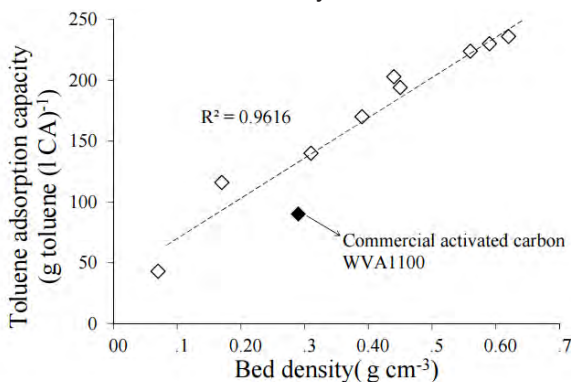

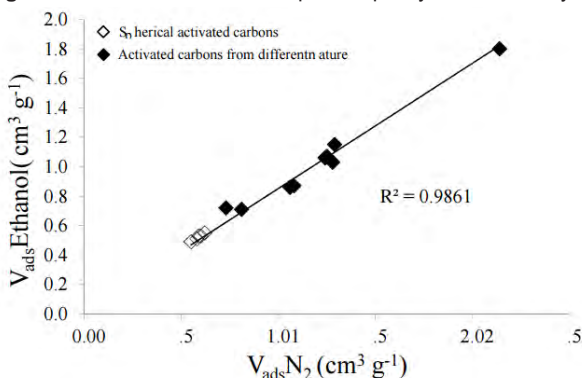**Fig 1.** Gravimetric toluene adsorption capacity vs bed density.

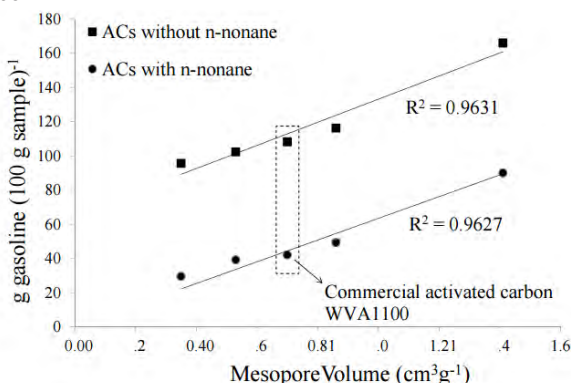**Fig 2.** Volumes of N_2 vs ethanol adsorbed (asliquids) at P/Po = 0.95

Fig 3. Evaporative gasoline test. Relationship between gasoline uptake and mesopore volume.

Conclusions:

In this PhD Thesis many activated carbons and spherical activated carbons have been prepared with a wide range of surface areas, micropore volumes and mesopore volumes, and they have been applied to the adsorption of polar and non- polar volatile organic compound at low and high relative pressures. At low relative pressures it has been confirmed that spherical activated carbons with low oxygen groups contents and high narrow micropore volumes lead to high toluene adsorption capacity.

Besides the high micropore volumes in the spherical activated carbons, the high bed densities of these materials have allowed to achieve high volumetric adsorption capacities. The adsorption of ethanol at low relative pressures is favored by oxygen groups, especially by the presence of carboxyl and anhydride groups generated by HNO_3 oxidation, whereas at relative pressures near unity porosity controls ethanol adsorption capacity. Finally, gasoline vapor adsorption has been proved to be controlled by the mesoporosity of the activated carbons. The ACs prepared in this Thesis present higher gasoline adsorption capacity than a commercial activated carbon especially designed and used for this application.

Related Publications

[1] Romero-Anaya AJ, Lillo-Ródenas MA, Linares-Solano. Spherical activated carbons for low concentration toluene adsorption. Carbon 2010; 48:2625-2633.

[2] Romero-Anaya AJ, Molina A, Garcia P, Ruiz-Colorado AA, Linares-Solano A, Salinas-Martínez de Lecea C. Phosphoric acid activation of recalcitrant biomass originated in ethanol production from banana plants. Biomass and Bioenergy 2011; 35:1196-1204.

[3] Romero-Anaya AJ, Lillo-Ródenas MA, Salinas-Martínez de Lecea C, Linares-Solano A. Hydrothermal and conventional H_3PO_4 activation of two natural bio-fibers. Carbon 2012;50(9):3158-69.

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Full Thesis can be downloaded from:

http://hdl.handle.net/10045/30715