From fly ashes of lignocellulose waste combustion to sustainable activated carbons for VOCs removal

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Introduction

The increase in the world population results in a greater exploitation of natural resources, an increasing energy demand as well as the generation of large amounts of waste of all types and nature (Lisbona *et al*., 2023). The combustion of tree lignocellulosic wastes biomass to produce thermal and electric energy is neutral from the point of view of CO_2 emissions; however, it generates large amounts of solid wastes in form of fly ashes. There are several reasons to reuse fly ash, some of which, among others, are: a) the costs involved in the disposal of this waste are minimized; b) less land is set aside for disposal, allowing for other land uses; c) these wastes can replace scarce or expensive natural resources in some applications (M. Ahmaruzzaman, 2010).

The objective of this work is to obtain efficient carbonaceous adsorbents from the organic fraction of the combustion fly ashes to use in the removal of volatile organic compounds (VOCs). Toluene was selected as a representative compound of VOCs of anthropogenic origin. The fly ashes comes from the combustion of *Eucalypus globulus* bark in the most efficient cellulose biofactory in Europe located in the north of Spain. These are composed of an inorganic fraction (predominant component) and an organic fraction (unburned carbons). In order to separate the two fractions, the methodology developed by Giron et al. (2012) was used.

Methodology

The raw sample (80 kg) was dried and then quartered to obtain fractions of 2kg. One of these fractions was dry sieved and the granulometric fraction >500 μm, the richest in unburned carbons, was used as activated carbon (AC) precursor. The ACs were obtained by chemical activation using KOH and NaOH as activating agents. Prior to the activation process, the biowaste was physically mixed with the activating agent at different weight ratios and the mixture was activated in a horizontal tubular furnace (Carbolite CTF 12/65/550). The experimental conditions were: 5ºC min^{-1} as heating rate, temperature of 750°C and 60 min of residence time at that temperature. Once the process was completed, the materials obtained were washed with 5 M HCl and deionized water (Milli-Q). After that, the ACs were dried in a conventional oven (105 °C) and then in a vacuum oven (60 °C).

Fly ashes and ACs were chemical, morphological and texturally characterized. The ultimate analysis (C, H, N, S, O) was carried out on LECO CHN-2000 and LECO S-144-DR equipment's. The oxygen content was determined by difference. The morphological study was performed by scanning electron microscope (SEM), ZEISS Model DMS-942. The textural properties of the ACs was carried out by N_2 adsorption isotherms at -196°C on a Micromeritics ASAP 2420 apparatus.

Dynamic adsorption tests of gaseous toluene were performed in glass columns using fixed bed of 250 mg of AC. Each material was sieved to obtain particle size of 212-425 μm. The experimental device and scheme for the dynamic toluene adsorption experiments were described in a previous work (Anfruns *et al*., 2011). For comparative purposes, commercial activated carbons were also tested.

Results

The unburned carbons-based ACs have a high carbon content (76-87%) and a low-moderate ash content ranging from 4-16%. Exceptionally, an AC prepared at 950 °C and washed only with water had the highest ash content (24.62%) and the lowest carbon content (66.7%). The water used in the washing stage showed a lower capacity to dissolve the mineral matter compared to the capacity of HCl+water. The commercial ACs showed very

high carbon contents (~90%) and very low ash contents (4-5%). **Fig. 1** shows an SEM image of the morphology of an AC; it is observed that the particle preserves the vegetal structure.

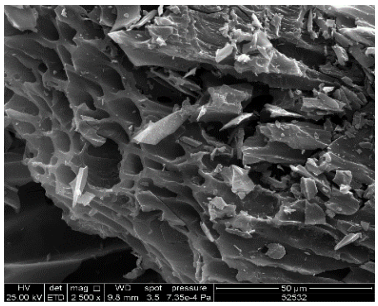

***Fig. 1** SEM image of AC*

The N_2 adsorption-desorption isotherms of ACS obtained with small amounts of KOH or NaOH are of type I of the BDDT classification. However, the ACs obtained with greater amounts of activating reagent, or at a higher activation temperature (950°C), presented type I-IV isotherms, suggesting a broader distribution of micropores, as well as the presence of mesopores, **Fig. 2**. The ACs showed good textural development; these carbonaceous adsorbents are mainly microporous with high BET surface area (900-2000 m^2g^{-1}) and total pore volume (up to 1.05 cm^3g^{-1}).

The capacity of experimental ACs to remove VOCs (toluene), up to 540 mg g^{-1}, was higher toluene uptakes that commercial ACs (up to 400 mg g^{-1}). The results are also better than that the corresponding obtained with sludge-based adsorbents (up to 350 mg g^{-1}). All of the above offers new opportunities for the valorisation of fly ashes in a circular economy scenario in a pulp biofactory.

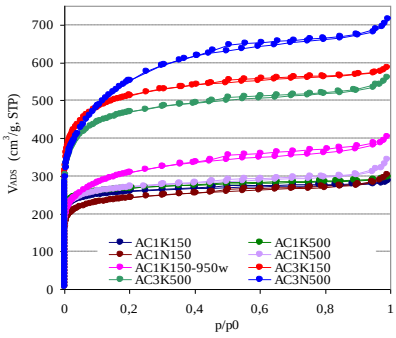

***Fig 2**. N_2 isotherms of the ACs*

Conclusions

The combustion of forest biomass, Eucalyptus globulus, generates high amounts of fly ash with high mineral matter content. With the methodology developed in this research it is possible to obtain a precursor of activated carbons with high concentration in unburned carbons and moderate mineral matter content.

Alkaline chemical activation of unburned carbons of fly ashes resulted in ACs with low ash content (4.06–15.58%) and good textural properties appropriate for VOCs adsorption. The washing stage of the activated materials was key in their properties. The experimental ACs had high BET surface area, up to 2035 m^2 g^{-1}, and high total pore volume, up to 1.055 cm^3 g^{-1}. The developed adsorbents in this research were very effective in the adsorption of toluene. The experimental fly ash-based ACs showed higher toluene adsorption (up to 540 mg g^{-1}) than commercial activated carbons (up to 400 mg g^{-1}). Thus, these sustainable adsorbent materials produced from the valorisation of fly ashes waste can be beneficially used for the removal of volatile organic compounds from waste gaseous effluents. All of the above is part of a circular economy in a pulp biofactory.

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