



# Activated carbons from biocollagenic wastes of the leather industry for mercury capture in oxy-combustion



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## HIGHLIGHTS

- Activated carbons obtained from leather industry waste may retain mercury.
- Different mercury behavior was observed in oxygen and oxy-combustion atmospheres.
- Mercury retention capacity of activated carbons decreased in presence of acid gases.
- High percentage of mercury oxidation was produced in an oxy-combustion atmosphere.

## ARTICLE INFO

### Article history:

Received 30 April 2014

Received in revised form 20 October 2014

Accepted 5 November 2014

Available online 17 November 2014

### Keywords:

Mercury

Activated carbons

Biocollagenic wastes

Leather industry

Oxy-combustion

## ABSTRACT

This study evaluates the capacity of a series of activated carbons obtained from leather industry waste to retain mercury. The behavior of these materials was compared in two simulated flue gas compositions at laboratory scale. The atmospheres were (i) a typical coal oxy-fuel combustion atmosphere and (ii) an  $O_2 + N_2$  atmosphere. The activated carbons displayed different behaviors depending on their characteristics and the gas composition. The best results were obtained for the activated carbon with the highest surface area and greatest amount of micropores, sulfur and acidity character, these results being comparable to those of an activated carbon impregnated with sulfur specifically designed for capturing elemental mercury. The highest level of mercury retention was achieved in a  $O_2 + N_2$  atmosphere. However, independently of the ability of these materials to capture mercury, their most interesting characteristic was their ability to oxidize mercury in an oxy-combustion atmosphere, since this would facilitate the retention of mercury in flue gas desulfurization units with the consequence that the risk of damage to the  $CO_2$  compression and purification units would be reduced or even removed.

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## 1. Introduction

Mercury and its compounds are highly toxic species which have a considerable impact on human health. Human activity has increased the mobilization of mercury species in the environment, raising the amounts in the atmosphere, soils, fresh waters, and oceans. Given the seriousness of these problems and the growing awareness about them, there is now global agreement on the need to reduce the emissions and release of mercury to the atmosphere. The Board of Directors of the United Nations Program for Environment (UNEP) in its Decision GC 25/5, created an Intergovernmental Negotiating Committee (INC) to develop a legally binding international agreement for mercury. Governments agreed to the text of a global legally binding instrument on mercury that was adopted in

October 2013 [1]. The Treaty covers all aspects of the mercury life cycle, including anthropogenic mercury emissions to the air.

Anthropogenic sources of mercury emissions account for about 30% of the total amount of mercury entering the atmosphere each year [2]. The main industrial sources are coal combustion, metal production, the chlor-alkali industry, waste incineration, artisanal and small-scale gold mining and cement production [3]. In Europe 53.2% of the total amount of mercury emissions to the air recorded in 2010 came from coal combustion [4]. It must be remembered that mercury species are emitted to the air from industrial sources in three primary forms. One is gaseous elemental mercury ( $Hg^0$ ), and all the other compounds in gas phase are grouped into what is called gaseous oxidized mercury ( $Hg^{2+}$ ). The third group is mercury bound to particulates ( $Hg^p$ ). In addition to the environmental problems caused by mercury species, mention should be made of the technological problems that  $Hg^0$  may cause in oxy-combustion processes. Oxy-combustion is the combustion of fossil fuels in a highly oxygen-concentrated environment rather than air, as a

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result of which nitrogen is eliminated from the combustion process. The result is a flue gas composed primarily of water and CO<sub>2</sub>. The high concentration of CO<sub>2</sub> and absence of nitrogen in the flue gas simplify the separation of the CO<sub>2</sub> for storage or beneficial use. However, CO<sub>2</sub> compression and purification units can be damaged by Hg<sup>0</sup> due to the fact that this amalgamates with the aluminium of the heat exchangers [5,6].

Until now, the main solution for reducing mercury emissions has been to clean the gases produced from industrial sources by means of solid sorbents. In this way, mercury species are confined in a product that can be controlled. Various solid sorbents have been evaluated and used for the removal of inorganic mercury species in gas phase (Hg<sup>0</sup> and Hg<sup>2+</sup>). They include non-carbon materials such as zeolites and calcium- and iron-based sorbents [7–9]. However, the most studied and commercialized sorbents for mercury capture have been activated carbons. Some activated carbons may be effective in capturing Hg<sup>2+</sup> but in order to retain Hg<sup>0</sup> chemical impregnated sorbents are generally necessary [10–12]. A number of works in the literature describe the preparation and utilization of activated carbons for mercury removal, and some reviews have summarized this information [13–16]. In the search for high-quality sorbents different variables are taken into account, among which economic and environmental limitations need to be considered. This is the reason why some researchers have focused on the use of industrial or agricultural wastes as sorbents for mercury or as precursors for obtaining mercury sorbents [17–20]. The advantage of using this kind of material is not only the reduction in cost but also the environmental benefit gained from the revalorization of an industrial waste. In the search for a precursor for the preparation of activated carbons, solid wastes generated from the vegetable tanning of bovine skin in the leather industry (shavings, trimmings and buffing dust), were considered in this study. The leather waste mixtures (BCT) have low ash, high carbon and nitrogen contents and insignificant amounts of metal species, making this material a highly suitable bioprecursor of activated carbons. Moreover, the use of BCT to obtain activated carbons provides a way to recover vegetable-tanned leather waste instead of disposal or incineration. A previous study using activated carbons derived from biocollagenic wastes from a vegetable tanning process demonstrated its high capacity for toluene adsorption compared to several commercial activated carbons [21].

The present research study aims to revalorise these types of biomaterials to obtain high added value activated carbons which can be used as adsorbent materials for different toxic elements, including mercury. Activated carbons with different physical and chemical characteristics were prepared to establish the main parameters that affect mercury retention. The behavior of these activated carbons for capturing mercury species was evaluated both in air and oxy-combustion atmospheres.

## 2. Experimental part

### 2.1. Materials

A leather waste blend was obtained by mixing and homogenising three types of solid bovine skin wastes; shavings, trimmings and buffing dust, from vegetable tanning. The blend was prepared by mixing each waste in the proportion in which it was generated in the leather industry; 84%, 15% and 1%, for shavings, trimmings and buffing dust, respectively. The total sample of the solid leather wastes (100 kg) was sampled for a period of one month being ground to <1 mm. A representative sample of 2 kg, obtained from the total sample, referred to as Biomaterial: Collagen & Tannins (BCT) was used as bioprecursor of the activated carbons.

Two methods were used to obtain the three activated carbons for mercury retention. The first method consisted in a two-stage process: (i) carbonization of the raw material (BCT) to obtain a carbonized material or char (BCTP) and (ii) chemical activation with KOH at a weight ratio of 1:1. This procedure gave the activated carbon labelled BCTP1. The second method consisted in the chemical activation of BCT with KOH at a weight ratio of 0.33:1 without the pyrolysis step. This activated carbon was labelled BCT0.33.

The precursor (BCT or BCTP) and the activating agent (KOH) were mixed in a solid state (physical mixture). After chemical activation the samples were washed to remove the activation products blocking the porosity. The samples were treated with a 5 mol dm<sup>-3</sup> hydrochloric acid solution, rinsed with ultrapure water and dried at 105 °C. A third activated carbon labelled BCTP1\* was obtained from BCTP1 and washed at 100 °C with hot water instead hydrochloric acid.

The mercury retention capacities were compared with that of a commercial activated carbon impregnated with sulfur (Norit RBHG3) specifically prepared for the capture of Hg<sup>0</sup>.

### 2.2. Experimental device for pyrolysis and activation experiments

The experimental arrangement employed for the carbonization and activation of the precursor material has already been described in a previous work [22]. The pyrolysis and activation processes were carried out in an alumina crucible placed inside the tubular furnace under a 150 cm<sup>3</sup> min<sup>-1</sup> flow of N<sub>2</sub> up to 750 °C, at a heating rate of 5 °C min<sup>-1</sup> for 1 h. The optimal conditions for the pyrolysis step were previously established [22]. About 10 g of BCT was used for the pyrolysis experiment and 5–10 g of BCT or BCTP and activating agent were used in the activation experiment.

### 2.3. Characterization of the raw materials and products

The moisture and ash contents of the sample were determined following the UNE 32002 and 32004 norms respectively, and the carbon, hydrogen, nitrogen and sulfur contents by means of automatic equipment. The concentration of chlorine was determined by means of an ion selective electrode.

The pH of the aqueous solutions obtained in every washing of the activated carbons were measured with a TIM870 Radiometer. The final conditions in the washing step were selected by controlling the pH until a constant value was obtained. The final pH value in the aqueous solutions is reflecting the chemical nature (acidity or basicity) in the activated carbons obtained.

The morphology of the samples was examined using a Scanning Electron Microscope equipped with an Energy-Dispersive X-Ray analyzing system (SEM/EDX).

Textural characterization was performed by measuring the N<sub>2</sub> adsorption isotherms at –196 °C. The isotherms were used to calculate the specific surface area  $S_{BET}$  and total pore volume,  $V_{TOT}$ , at a relative pressure of 0.95. The pore size distributions, microporosity and mesoporosity, were obtained by applying the density functional theory (DFT) model to the N<sub>2</sub> adsorption data, assuming slit-shaped pore geometry. Additionally, the narrow microporosity (pore width smaller than 0.7 nm) was estimated from CO<sub>2</sub> adsorption isotherms at 0 °C using 1.023 g cm<sup>-3</sup> as the density of adsorbed CO<sub>2</sub> and 0.36 as the b parameter. The CO<sub>2</sub> isotherms were used to calculate the micropore volume ( $W_0$ ), micropore size ( $L_0$ ), energy characteristic ( $E_0$ ) applying the Dubinin–Raduskevich equation. In addition, the water vapor adsorption isotherms of the samples were determined at 25 °C for water activity (aw) from 0 to 1. The equilibrium moisture content was expressed as grams per g of dry solid. The true density of the materials was obtained by helium pycnometry. Before these experiments were performed the samples were outgassed under vacuum at 120 °C overnight.

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