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Combustion of a Pb(II)-loaded olive tree pruning used as biosorbent

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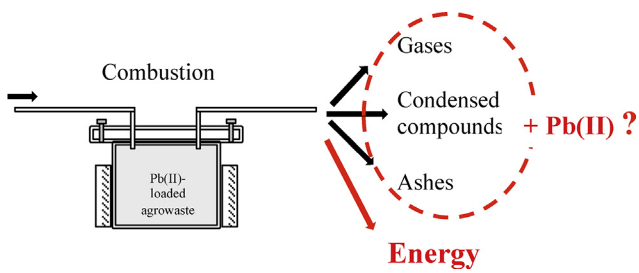
HIGHLIGHTS

- The fate of Pb during combustion at two scales of investigation was studied.
- Results from combustion in a flow reactor and in the thermobalance were consistent.
- The Pb contained in the solid remained in the ashes.
- The Pb does not interfere in the use of OTP as fuel.
- The combustion of Pb(II)-loaded OTP does not cause environmental hazards.

GRAPHICAL ABSTRACT



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ABSTRACT

The olive tree pruning is a specific agroindustrial waste that can be successfully used as adsorbent, to remove Pb(II) from contaminated wastewater. Its final incineration has been studied in a thermobalance and in a laboratory flow reactor. The study aims at evaluating the fate of Pb during combustion, at two different scales of investigation. The flow reactor can treat samples approximately 10^2 larger than the conventional TGA. A detailed characterization of the raw and Pb(II)-loaded waste, before and after combustion is presented, including analysis of gas and solids products. The Pb(II)-loaded olive tree pruning has been prepared by a previous biosorption step in a lead solution, reaching a concentration of lead of 2.3 wt%. Several characterizations of the ashes and the mass balances proved that after the combustion, all the lead presents in the waste remained in ashes. Combustion in a flow reactor produced results consistent with those obtained in the thermobalance. It is thus confirmed that the combustion of Pb(II)-loaded olive tree pruning is a viable option to use it after the biosorption process. The Pb contained in the solid remained in the ashes, preventing possible environmental hazards.

1. Introduction

Discharge of industrial effluents with high amount of heavy metals is a severe environmental hazard, as they are extremely toxic. Its removal from wastewater is important for protecting the environment and the human health [1]. Biosorption is a feasible and economical alternative, which allows keeping the levels of these pollutants in the permissible range [2]. It has significant advantages in comparison with conventional methods, especially from economical and environmental viewpoints [3–6].

Biosorption can be achieved using agroindustrial wastes as active material, contributing to bound a persistent problem caused by agricultural industry, like the accumulation of high volumes of organic wastes. Several countries support the re-using of most generated waste by industry. Sawdust is a widely studied biosorbent in China [7,8]. In the Mediterranean area, the olive industry is constantly searching more effective waste uses, including olive stone [9] and olive tree pruning (OTP) [10].

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This study is focused on the use of OTP, an abundant residue in Mediterranean area without any significant industrial application so far. However, biosorption generates yields a metal-loaded waste and the higher biosorption capacity of OTP involves a higher degree of contamination of the exhausted material. Thus, its disposal could become an issue.

The reutilization of the contaminated residue is crucial for a cost-effective process. Several Authors investigated the viability of a desorption to optimize the yield of the whole biosorption process and to maximize the lifetime of the biosorbent [9,11,12]. Nonetheless, although the biosorbent is used over many cycles, it finally remains as exhausted residue, heavily contaminated by metals that cannot be easily removed. Its combustion could be an interesting alternative. All the agroindustrial wastes are considered an autonomous fuel resource, which reduces the dependence on energy supplies, benefits the economical sustainability and creates employment in of rural areas, contrasting its depopulation. In 1996, Narodoslawsky and Obernberger [13] proposed the energetic utilization of biomass as an environmentally safe way of providing energy, especially for process heat and district- heating purposes.

Combustion, pyrolysis and gasification processes of such wastes provide great benefits over landfilling. Indeed, these processes considerably reduce the volume of waste and produce net energy that can be utilized [14]. Once these concept are applied to a biosorbent, the critical issue is the fate of the heavy metals in it, conferring to the waste an hazardous (toxic) nature.

The aim of this work is to investigate the suitability of Pb(II)-loaded OTP for energy production by combustion. Here, the Pb(II)-loaded OTP combustion in a thermobalance, in a static, atmospheric oven and in a flow reactor, spanning several scales has been carried out. By accurate analytic determinations on the feedstock and the products, including wastes, the study investigates the fate of Pb, to determine any hazard in the Pb(II)-loaded OTP combustion.

2. Materials and methods

The reference biomass is the olive tree pruning (OTP). It is a waste from olive pruning, routinely practiced for maintenance and reshaping of olive trees. The OTP used for this study was obtained from olive plantation located in Vilches, province of Jaen (Spain). The solid was milled with an analytical mill (IKA MF-10) and <1.00 mm fraction was chosen for the study.

The Pb(II)-loaded OTP was obtained after a batchwise biosorption process at the laboratory scale according to experimental procedure followed by Ronda et al. [15]. Raw OTP was soaked for 2 h in a solution with an initial concentration of Pb(II) of 200 mg/L. Then the OTP was separated and dried in an oven at 40 °C during 24 h. The content of Pb(II) was determined by an Atomic Absorption Spectrometry Instrument (AAnalyst 200, Perkin-Elmer).

2.1. Characterization of raw and Pb(II)-loaded OTP

Several properties were determined for Pb(II)-loaded OTP and they were compared with those of raw OTP. The latter were already measured in a previous work [16].

The elemental analysis of the raw OTP on dry basis was given by a CHNS Instrument (Fison EA 1108). The sample was burned in excess of oxygen and the mass of the combustion products (NO_2, CO_2, SO_2 and H_2O) used to calculate the percentage of N, C, S and H contained in the sample. The oxygen content was obtained by difference. The proximate analysis was carried out using the ASTM E871-82, E872-82 and D1102-84 standards, to determine the content of moisture, volatile matter and ashes respectively [17–19]. The fixed carbon was obtained by difference until 100 %. The High Heating Value (HHV) was determined experimentally by a bomb calorimeter (Phywe LEC-02 model) following the procedure described in the standard UNE-EN 14918:2011. Besides, it was calculated by three empirical equations:

- Dulong equation [20]:

$$\text{HHV} \quad (\text{MJ/kg}) = 0.341 \cdot C + 1.44 \cdot (H - O/800) + 0.0929 \cdot S \tag{1}$$

- Milne equation [20]:

$$\text{HHV} \quad (\text{MJ/kg}) = 0.314 \cdot C + 1.322 \cdot H - 0.12 \cdot O - 0.12 \cdot N + 0.0686 \cdot S - 0.0153 \cdot Z \tag{2}$$

- Syed equation [21]:

$$\text{HHV} \quad (\text{MJ/kg}) = 0.3491 \cdot C + 1.1783 \cdot H - 0.1043 \cdot O \tag{3}$$

where C, H, O, S, and Z are the content of the carbon, hydrogen, oxygen, sulfur, and ashes in the waste, as wt%. A sample of the Pb(II)-loaded OTP was analyzed by ICP-MS (Perkin Elmer OES OPTIMA 7300 DV) to determine the initial concentration of inorganic compounds in the solid. Surface morphological images were obtained from scanning electron microscope (SEM), where samples need to be gold coated. FTIR spectroscopy (Spectrometer Perkin-Elmer, Spectrum 65) was used to identify the chemical functional groups present on raw OTP and Pb(II)-loaded OTP. IR absorbance data were obtained in the range of 400–4000 cm^{-1}. The Differential Scanning Calorimetry (DSC) was performed by a DSC Q10 (TA Instruments). The DSC cell was calibrated with indium (K_{cell} = 1.0178). Tests were carried out at a heating rate of 5 °C min^{-1}, from room temperature to 500 °C. DSC tests were performed (in duplicate) on raw and Pb(II)-loaded OTP samples to define the combustion temperature.

2.2. Combustion in the thermobalance

A Perkin Elmer thermobalance model STA 6000 was used for TG measurements. Dynamic experiments were carried out under a heating rate of 5 °C min^{-1}, from 30 °C up to 800 °C. Combustion was performed with an oxidizing atmosphere (air). The flow rate was 20 mL min^{-1} and the approximate weight of samples was 40 mg. Volatile products from the thermobalace were analyzed by FTIR. The thermobalance was coupled to the FTIR by a short heated transfer line. Spectra at resolution of 1 cm^{-1} in a wavelength range from 600 to 4000 cm^{-1} were collected. They allowed to identify and track the gaseous species generated during the thermal degradation.

2.3. Combustion in the flow reactor

Combustion of raw OTP and Pb(II)-loaded OTP was carried out in a stainless steel autoclave which allows a continuous flow of air above the heated sample. A sketch of the set-up, including sampling of the emissions is shown in Fig. 1.

The average sample size was 3 g, two orders of magnitude larger than in TGA. The sample was placed in a crucible. The air flow rate was always set to 10 mL min^{-1}. Two thermocouples were placed in the reactor, one in the center (TC) and one in the periphery (TP) of the OTP sample. The thermal control was provided by an electronic power controller (Omron G3PX). The combustion tests mimicked the TGA measurements, up to a lower temperature. The heating rate was set at 5 °C min^{-1} and the temperature spanned from 30 °C up to 500 °C. Gas products flow through a first filter (Filter 1) to collect the solids entrained, then a condenser where higher boiling species were collected at room temperature. Before the gas analysis two additional filters (Filter 2 and Filter 3) were placed to clean