Pyrolysis kinetics of the lead-impregnated olive stone by non-isothermal thermogravimetry

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ABSTRACT

The thermal behavior of the lead-impregnated olive-stone during pyrolysis was investigated via thermogravimetric analysis at different heating rates under an inert atmosphere of nitrogen to study the effect of the metal during the thermal process. Thermogravimetric curves showed a little increase of the degradation temperature of hemicellulose and cellulose because of the presence of the metal when the material impregnated with lead was tested. Therefore, calculated kinetic parameters varied slightly after impregnation with lead. Apparent activation energies were 119.72, 238.65 and 68.76 kJ/mol for hemicellulose, cellulose and lignin fractions in raw olive stone and 119.40, 257.00 and 68.46 kJ/mol for the same fractions in the lead-impregnated olive stone.

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1. Introduction

With the increasing industrialization and economic development, the environmental and health issues resulting from heavy metal contaminated wastewater have attracted great attention. In order to treat wastewater a lot of techniques have been developed. Among these, biosorption is a promising and low-cost method, which is a remediation process for pollutant removal and/or recovery from wastewater by inactive biomass (Fomina and Gadd, 2014). However, the large scale application of biosorption generates a metal-loaded waste and its disposal could become an issue. The reutilization of the contaminated residue is crucial for a cost-effective process (Al Chami et al., 2014). Several authors investigated the viability of desorption to optimize the yield of the whole biosorption process and to maximize the lifetime of the biosorbent (Bağda et al., 2017; Kardam et al., 2014; Ronda et al., 2015b; Sun et al., 2017). Nonetheless, although the biosorbent was used over many cycles, it finally remained as exhausted residue, heavily contaminated by metals that cannot be easily removed. Its combustion, gasification or pyrolysis could be interesting alternatives. Authors have proved that the agroindustrial wastes can be considered an autonomous fuel resource and the thermal processes considerably reduce the volume of waste and produce net energy that can be utilized (Moltoí et al., 2013). Therefore, to apply these concepts to the exhausted biosorbent, the critical issue is the fate of the heavy metal in it and its effect on thermal decomposition of the material (Martín-Lara et al., 2018; Ronda et al., 2016).

Olive stone is a typical example of an agroindustrial byproduct that is available in abundant quantities, especially in the Mediterranean area. It is a waste generated mainly for two industries: from olive oil industry and from table olives production for human consumption (Sánchez and San Miguel, 2016). In Spain approximately 7,000,000 t of olive are produced annually (data from campaign 2016–2017), and considering that the stone represents over 15%–20% of the fruit mass, depends of the hydric conditions during its cultivation and of the average weight of the olive, the overall production of olive stones can be calculated around 1,050,000–1,400,000 t per year.

The composition of olive stone is similar to other lignocellulosic resources: it contains, on a dry basis, approximately 15% of soluble compounds, 25% of lignin and 55% of holocelluloses and around 5% of ashes (Martín-Lara et al., 2016a). At present, research activities have showed that olive stone is an effective biosorbent for the removal heavy metals ions from aqueous solutions (Blázquez et al., 2011; Calero et al., 2009; Martín-Lara et al., 2010, 2013, 2016a; Moubarik and Grimi, 2015; Ronda et al., 2014, 2015a; Trujillo et al., 2016) and that it has good prop-

erties as fuel (Costa et al., 2015; Martín-Lara et al., 2013; Pohlmann et al., 2017). In this point, the study of environmental implications of the use of heavy metal contaminated biomass would address several societal problems (the need to reduce the environmental impact of traditional energy from fossil fuels and the disposal of the generated contaminated waste from wastewater treatment). Hence, it could be presented as a green energy source, which is not fully marketed nowadays. Thus, there are some studies about the pyrolysis kinetic of olive stone and similar waste (Fernández et al. (2016) studied six regional lignocellulosic wastes: sawdust, marcs, stalks, peach plum and olive pits), other studies cover the catalytic effect of some metals during the pyrolysis of biomass (Ge et al. (2017) studied the effect of the chromium on the pyrolysis behavior of brown coal), even, the environmental effect of the combustion or pyrolysis of metal-loaded biomass (Ronda et al., 2016; Martín-Lara et al., 2018). Moreover, the pyrolysis is a very complex phenomenon, not well understood and involves heat transfer to and through the particle, chemical reactions within the particle, and escape of volatiles through the particle (Kaushal and Abedi, 2010). In this point, the behavior of the metal during the pyrolysis is very important to future applications of this waste, and there are not studies on the influence of lead onto the decomposition kinetics of the olive stone.

The thermal decomposition and kinetics of pyrolysis of both raw and metal-loaded materials is an important starting point to valorize the generate residue after the biosorption process and to extend the applications of these materials. Pyrolysis is an attractive alternative to use of biomass generating appreciable economic value products (Ronda et al., 2017). Thermogravimetric analysis (TGA) is a widely used analytical technique to observe the thermal decomposition and kinetics of pyrolysis of materials.

The main objectives of this work are to conduct a study on the kinetics of pyrolysis of raw olive stone and lead-impregnated sample after a biosorption process for lead removal from industrial wastewater.

2. Material and methods

2.1. Preparation of materials

The native olive stone (raw OS in figures and tables) was provided by the "Cooperativa Nuestra Señora del Castillo", an olive oil extraction plant placed in Vilches, province of Jaen (Spain). The olive stone was milled using an analytical mill (IKA MF-10) and fractions below 1 mm were selected for impregnation and pyrolysis tests. The solid was completely characterized and studied in previous works (Blázquez et al., 2011, 2014a; Calero et al., 2009). Elemental analysis results showed that OS had an elemental composition consisting mainly of carbon and oxygen. The fraction with a particle size <1 mm, had a specific surface area of $0.16 \, m^2/g$, a total pore volumes of $1.840 \, cm^3/g$ and an average pore width of 453 Å. It showed a high total titratable concentration (0.0694 mmol/kg) and a pH_{PZC} of 5.17, which give to the OS a slightly acidic character.

The lead-impregnated olive stone (lead-impregnated OS in figures and tables) was obtained after a previous contact step with a Pb(II) solution in a fixed bed column. A covering glass column (length of 23 cm, internal diameter of 1.5 cm) was packed with a 15 g of raw material. The metal solution (of 100 mg/L of lead and prepared by dissolving the necessary amount of nitrate salt ($Pb(NO_3)_2 \cdot 3H_2O$) provided by Panreac (Barcelona, Spain) in distilled water) was driven at a constant flow rate (6 cm^3/min) using a peristaltic pump in up-flow mode during 600 min. Table 1 presents the operational data of the laboratory scale fixed-bed column for the impregnation of biomass. Column effluent samples were collected at frequent time intervals and they were analysed to determine the effluent metal concentration. Samples were analysed in an Atomic

Table 1 – Operational data of the laboratory scale fixed-bed column for lead impregnation of olive stone.	
Biosorbent mass	15 g
Bed length (Z)	13.4 cm
Column internal diameter (D)	1.5 cm
Cross sectional area of the column (S)	1.77 cm^2
Bed length/internal diameter	8.93
Bed volume (V$_b$)	23.68 cm^3
Biosorbent particles density (ρ_p)	1.426 g/cm^3
Bed porosity (ε)	0.556
Packing density or bulk density (ρ_b)	0.633 g/cm^3
Volumetric flow rate (Q)	6 cm^3/min
Initial solute concentration (C$_i$)	100 mg/L
Biosorbent particle diameter (d$_p$)	<1 mm
Superficial velocity ($v_{superficial}$)	3.40 cm/min
Interstitial velocity ($v_{interstitial}$)	6.11 cm/min
Residential time (τ)	2.19 min
Mode of operation	Up-flow
Operational time (t$_i$)	600 min

Absorption Spectrometer (Perkin-Elmer, model AAnalyst 200). The experimental procedure is commented in detail in the Supplementary section.

2.2. Experimental procedure

Runs for pyrolysis were carried out on a Perkin Elmer thermobalance model STA 6000. Dynamic experiments were performed in duplicate and the average profile was considered for the modelling, under heating rates of 5, 10 and 20 °C/min, from 200 °C (573 K) up to 800 °C (1073 K). This range allowed to examine the decomposition of main compounds of the material and excluded the effect of moisture content. The flow rate of the carrier gas (high-purity N$_2$) was 20 cm^3/min to guarantee an inert atmosphere and the sample was a weight of approximately 40 mg (the full capacity of the crucible).

Also, new pyrolysis experiments were performed using bigger scale equipment (Nabertherm furnace, model R50/250/12) at same experimental conditions. About 10 g of sample was weighed and submitted to pyrolysis under a nitrogen flow of 5000 cm^3/min and a heating rate of 10 °C/min. The objective of these tests was to analyze composition of the residual char after pyrolysis. Once pyrolysis test was finished, the char was cooled to room temperature. Then, a digestion technique for char was carried out and lead content of resultant digest was determined by Inductively Couple Plasma Optical Emission Spectrometry (ICP-OES) following procedure describe in ISO 16968:2015 standard.

3. Mathematical background

3.1. Pb(II)-impregnation step

The mathematical background for the modeling of breakthrough curves had been explained in detail previously (Ronda et al., 2015b; Martín-Lara et al., 2016b). A summary of all used equation and parameters for the modelling are specified in Table 2.

Modelling of impregnation step was performed by the breakthrough curve concept (normalized Pb(II) concentration at the exit of the column versus the time). The main parameters obtained from this curve were: