Kinetics of thermal decomposition of some biomasses in an inert environment. An investigation of the effect of lead loaded by biosorption

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ABSTRACT

The thermal behavior of some types of raw and lead-polluted biomasses typical in south Spain was studied by non-isothermal thermogravimetry. Experiments were carried out in nitrogen atmosphere at three heating rates (5, 10 and 20 °C/min). The results of thermogravimetric tests carried out proved that the presence of lead did not change the main degradation pathways of selected biomass (almond shell (AS) and olive pomace (OP)). However, from a point of view of mass loss, lead-polluted samples showed higher decomposition temperatures and decomposition at higher rate. The determination of activation energies was performed by isoconversional methods of Flynn–Wall–Ozawa (FWO), Kissinger–Akahira–Sunose (KAS) and Friedman (FR). In general, lead-polluted samples showed lower activation energies than raw ones. Then, Coast-Redfern method was applied to determine kinetic function. The kinetic function that seems to determine the mechanism of thermal degradation of main components of all samples was nth order reaction. Finally, a model based on three parallel reactions (for three pseudocomponents) that fit to nth order reactions was evaluated. This model was appropriate to predict the pyrolysis behavior of the raw and lead-polluted samples in all pyrolysis conditions studied.

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1. Introduction

Heavy metals in the environment are a major problem worldwide as a result of global industrialization. The most widespread heavy metal ions are cadmium, lead, zinc, nickel, copper, mercury and chromium (Abdolali et al., 2017). They are considered very toxic pollutants as they induce multiple organ damage, even at lower levels of exposure. Even, these metallic elements are considered as human carcinogens (Tchounwou et al., 2012). Particularly, lead produces different diseases and according to the World Health Organization Standards, the maximum quantity of lead present in drinking water must be 0.01 mg/L. However, it has been discovered that the concentration in some industrial wastewaters is much higher (Siahkamari et al., 2017).

Many different technologies had been investigated for heavy metals removal such as precipitation, photocatalysis, biological treatments, ion exchange, ultrafiltration and osmosis. However, these techniques present a high number of drawbacks such as high operational cost, low efficiency at low metal concentrations and generation of by-products such as sludge (Kumar et al., 2017; Ali, 2016). Biosorption is reported to be as one of the simplest, economical, efficient and eco-friendly technique. There are a number of different commercial adsorbents available such as activated carbon but it is less cost-effective compared to other alternative adsorbents (Bediako et al., 2016). In recent years, the study of contaminants removal by low-cost adsorbents has been intensified. Materials locally available such as chitosan, zeolites, agricultural and forestry wastes or industrial by-products can be used in treatment of wastewaters. Some of these materials can be used as adsorbents with little or no processing. Even the conversion of some of these materials into activated carbon would improve economic value by helping industries reduce the cost of waste disposal and providing a potential alternative to commercial activated carbon (Babel and Kurniawan, 2003; De Gisi et al., 2016; Mondal and Garg, 2017; Wang et al., 2017). In this sense, many different biomass wastes have been reported to work as good biosorbents. For example, Wang et al., (2017) reported values of maximum adsorption capacity for Pb(II) of 130.2 mg/g when a lignin-based biosorbent was developed. Also, lentil husk was found to be a promising low cost adsorbent for removal of lead presenting a lead uptake capacity of 81.43 mg/g (Basu et al., 2015). Blázquez et al.,

(2013) reported a comparative table of metal removal capacities of different biomass wastes and commercial activation carbon observing similar or higher metal biosorption capacities in some cases. Wang et al., (2016) also published a lead biosorption capacity of 185.2 mg/g for camphor leaf waste. The main problem of using biomass as a biosorbent is the metal enriched residue generated after the process (Li et al., 2017; Lievens et al., 2008a; Lievens et al., 2008b). Different methods for reducing the volume of the waste and for recovering the valuable pollutants had been studied, such as thermal, microbial, physical or chemical methods. The proposed solutions in other papers include landfill, anaerobic digestion, incineration and pyrolysis. Generally, if cheap biomass is used as biosorbent, destructive methods as pyrolysis would be economically feasible (Martín-Lara et al., 2016). When the biosorbent was submitted to thermal treatment, the heavy metals would be transferred to the gas phase, to the solid phase (ash/char), and/or to the liquid phase (bio-oils), and then new fractions contaminated with the metal are produced. In addition, metal can modify behavior during thermal decomposition. In this sense, the role of metal during thermal treatment is a very important issue. Authors as Lievens et al. (2008a) or Martín-Lara et al., (2016) found that heavy metals concentrate in the ash/char fraction which is interesting for recycling making the rest of fractions suitable for both fuel and chemical stock applications. Among all thermal techniques, pyrolysis is a promising thermochemical method (Chami et al., 2014). Pyrolysis is a thermochemical conversion in absence of oxygen that turns the biomass (feedstock) into three fractions: chars (solid fraction), tars or oils (liquid fraction) and gases. These products of the process can be transformed into chemical compounds, biofuels or energy (heat or electricity) (Collard et al., 2012). The main advantage of pyrolysis is that depending on process conditions, the desired product can be maximized. There are three types of pyrolysis according to experimental conditions: flash pyrolysis, fast pyrolysis and conventional/slow pyrolysis. Flash pyrolysis is an extremely rapid thermal decomposition pyrolysis, with high heating rate and temperature. The main products are gases. Fast pyrolysis uses an approximate reaction temperature of 500 °C and a very short residence time (∼1 s). These conditions generally produce a higher yield of liquid product. Finally, conventional/slow pyrolysis reaction temperature is approximately 100 °C lower than that for fast pyrolysis and residence times are longer. As a consequence, the quantity of liquid, solid char and gas products obtained are very similar. Slow pyrolysis can also use low temperatures and very long residence times, achieving a high yield in char (Zhang et al., 2010). There are other process parameters that affect the yield of the different pyrolysis products apart from residence time and reactor temperature such as the heating rate, physic-chemical pre-treatment, particle size, geometrical configuration of the reactor and solid heat carrier (Lievens et al., 2008a).

The effect of heavy metals in thermal decomposition of biomass has been studied in some previous investigations (Chami et al., 2014; Collard et al., 2012; Jiu et al., 2015; Lievens et al., 2008a, 2008b; Martín-Lara et al., 2016; Paduraru et al., 2015; Shen et al., 2014). Thermogravimetric analysis is the most common method to study thermal pyrolytic decomposition of metal enriched biomass. However, although, lead effect in biomass thermal decomposition has been investigated in literature (Jiu et al., 2015; Mayer et al., 2012; Martín-Lara et al., 2016), no studies have been published about thermal decomposition of lead-polluted almond shell or lead-polluted olive pomace for looking into the potential valorization of these metal-polluted biomasses.

The objective of this work is to study the effect of lead in the pyrolytic thermal decomposition of two biomass wastes that are inexpensive and abundant in Spain: olive pomace and almond shell. Additionally, these biomass wastes have been proved as biosorbents for heavy metal removal.

2. Materials and methods

2.1. Samples preparation

Almond shell (AS) was supplied by Carsan Biocombustibles, S.L. (a young and dynamic company dedicated to the manufacture and distribution of stoves and boilers of biomass) of Granada (Spain).

Olive pomace (OP) was supplied by the industrial plant "Daniel Espuny S.A.U" located in Linares-Baeza, province of Jaen (Spain) dedicated to the production of olive–pomace oil.

Previously, all samples were cut into smaller particles and sieved into fractions below 1 mm to be used in the biosorption tests and thermogravimetric analysis following EN 14780:2012 standard.

For the preparation of lead-polluted samples, biosorption experiments in a fixed-bed column were conducted. Firstly, a covering glass column (length of 23 cm, internal diameter of 1.5 cm) was packed with a 15 g of raw biomass (in wet basis). Then, the metal solution (100 mg/L of lead) was driven at a constant flow rate (6 mL/min) using a peristaltic pump in up-flow mode. Lead solution (initial concentration of 100 mg/L) was prepared by dissolving the necessary amount of nitrate salt ($Pb(NO_3)_2$) in distilled water.

Column effluent samples were collected at frequent time intervals (0, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220 and 240 min) and analyzed for effluent metal concentration. The Pb (II) in the residual solution was analyzed in an Atomic Absorption Spectrometer (Perkin-Elmer, model AAnalyst 200). Operational data of the laboratory scale fixed-bed column and equations for calculating amount of lead retained in solid (mg/g) were reported in a previous work (Martín-Lara et al., 2012).

2.2. Characterization of the samples

Proximate analysis was performed according to ISO 18134-2:2015 (moisture content), ISO 18122:2015 (ash content), ISO 18123:2015 (volatile matter) and fixed carbon by difference. Ultimate analysis was carried out using an elemental analyzer Fison's Instruments EA 1108 CHNS. Determination of calorific value was performed using a calorimetric pump, model Phywe LEC-02 calibrated through certified benzoic acid combustion, according to UNE-EN 14918:2011. Perkin-Elmer FT-IR spectrometer, Spectrum-65 model, was used for determining the infrared spectra of absorption of biomass in the range of 4000–400 cm^{-1} and scanning electron microscope Quanta 650 FEG for SEM micrographs.

Finally, lead biosorption capacity was evaluated using Langmuir and Freunlich isotherms. Lead solutions with different initial metal concentrations (10–400 mg/L) were put in contact with solid adsorbent suspensions (10 g/L) under magnetic stirring at constant pH of 5. After equilibrium conditions were reached (120 min), a solid–liquid separation was performed by centrifugation (7000 rpm for 10 min) and lead residual concentrations in liquid phase were analyzed. This set of experiments was conducted by duplicate, with the average reported in the results. This study was conducted to identify whether the sorption equilibria fitted the Langmuir and Freundlich models and to determine the maximum uptake capacity of the biomass. The biosorption capacity at equilibrium time (q_e) was determined according to the following equation:

$$q_e = \frac{(C_i - C_f)V}{m} \tag{1}$$

where C_i and C_e are the initial and equilibrium lead concentrations (mg/L) in solution, respectively, V is the solution volume (L) and m is the mass (g) of the biosorbent.