



# Volatile and semivolatile emissions from the pyrolysis of almond shell loaded with heavy metals



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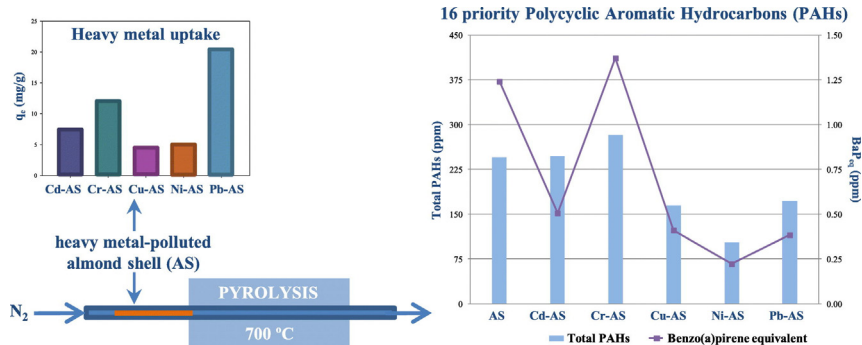
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## HIGHLIGHTS

- Metals did not change the main degradation pathways of thermogravimetric curves.
- Nickel-loaded sample presented the highest H<sub>2</sub> and CO yields in the pyrolysis gases.
- Nickel is the most effective in the higher aromatic tar reduction.
- Higher carcinogenic potency values were found in native and chromium-loaded samples.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Heavy metal-loaded almond shell was subjected to pyrolysis to understand the effect of the presence of different heavy metals on its thermal degradation. Pyrolysis behavior of native and metal-loaded samples was studied by thermogravimetric analysis. Similar shapes of thermogravimetric curves indicate that the presence of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni) and lead (Pb) did not change the main degradation pathways of almond shell. However, the temperature at which the decomposition in each stage takes place at a higher rate and char yield was considerably modified by the presence of Cr and Ni. Then, pyrolysis tests of the almond shell samples were performed in a moving tubular reactor at 700 °C. Gases and volatile organic compounds were collected using Tedlar bags and semivolatile organic compounds were collected using a resin as adsorbent. Significant changes were obtained in the composition of the gaseous fraction as a result of the metal impregnation. The main changes in the composition of the gas were observed for Ni-loaded sample, which presented the highest H<sub>2</sub> and CO yields. Also, the yields of most of the light hydrocarbons decrease in the presence of metal, while the rest remain quite similar. The total PAH yields reached 103 µg/g for nickel-loaded sample (Ni-AS), 164 µg/g for copper-loaded sample (Cu-AS), 172 µg/g for lead-loaded sample (Pb-AS), 245 µg/g for native sample (AS), 248 µg/g for cadmium-loaded sample (Cd-AS) and 283 µg/g for chromium-loaded sample (Cr-AS). Nickel is the most effective in the higher aromatic tar reduction, followed by Cu and Pb, whereas the presence of Cd does not affect the total emissions of PAHs. Finally, the carcinogenic potency of the samples was calculated. Native sample and the sample loaded with Cr presented slightly higher values associated to the presence of small amounts of benzo(a)pyrene.

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## 1. Introduction

Since the beginning of the industrial revolution, with increasing industrialization and economic development, pollution of the water

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with toxic heavy metals has intensified strongly (Lievens et al., 2008b). Consequently, heavy metal-contaminated wastewaters have attracted great consideration and, in order to remove heavy metals from wastewater, a lot of techniques have been developed. Sometimes, the treatment of heavy metal-contaminated wastewaters can be more problematical than any other manufacturing process (Vilchez-Vargas, 2005). Among the physical and chemical treatment processes, biosorption has been proposed as one of the most promising technologies because it can be highly effective, cheap and easy to adapt (Zhao et al., 2011). Biosorption is based on metal-sequestering properties of non-viable biomass to remove heavy metals when they are present in water at low concentrations. Availability is a most important factor to be taken into account to select a biosorbent for clean-up purposes. In this regard, abundant lignocellulosic materials have been principally proposed as potential biosorbents for heavy metals (Vieira and Volesky, 2000).

One essential item related to the application of biosorption at industrial scale is the management of the heavy metal-loaded biomass. Some authors have suggested direct combustion of contaminated biomass in order to decrease the waste amount and to recover the heavy metals (Keller et al., 2005). However, during direct combustion of contaminated biomass, high temperatures are reached, which can produce the volatilization of heavy metals and, also, many other toxic pollutants can be produced as dioxins and furans. Therefore, other mild thermal processes, like pyrolysis, have been explored to reduce the amount of heavy metal-loaded biomass and to obtain less polluting fractions that can be used as fuel products (Al Chami et al., 2014; Collard et al., 2012; Jiu et al., 2015; Lievens et al., 2008b).

World production of almonds was 2.9 million tonnes in 2013, with the United States as the largest producer with 1.8 million tonnes. The Spanish production, in second place, accounts only for 149,000 tonnes, with a total harvested area of 534,100 Ha in 2013 (FAO Data, n.d.). The almond industry generates large quantities of waste products that need to be recycled or processed. In general, almond shell is a material used as fuel in boilers and sometimes in domestic heating systems and barbecues. To that respect, there are few studies that have evaluated the use of almond shells as heavy metal biosorbent. Calero et al. (2013) presented the ability of almond shell to remove Cu(II) ions from aqueous solution in a packed bed column. The effect of various parameters, flow rate, initial Cu concentration and mass of biosorbent was analyzed. Khan et al. (2015) reported the removal of Ni(II) and Cu(II) ions from aqueous solution using almond shells. Batch experiments were carried out to determine the effect of various factors such as initial pH, temperature, particle size and contact time on the adsorption process. These authors showed that the adsorption of Ni(II) and Cu(II) by almond shell was good. Pehlivan and Altun (2008) investigated the potential of removing Cr(VI) ion from aqueous solutions through biosorption using almond shell. These authors found relatively good results. Also, Pehlivan et al. (2009) showed that almond shells are suitable sorbents for the removal of Pb(II) ions from aqueous solutions. Finally, the effect of Pb(II) on biosorption of Cu(II) by almond shell in a binary metal mixture was studied and compared with the single metal ion situation in a batch stirred system and in a continuous system. Results showed good Cu and Pb biosorption ability of almond shell. Others studies, however, have investigated the use of almond shell as biomass fuel in pyrolysis processes (Caballero et al., 1997; González et al., 2005; Grioui et al., 2014).

Regarding the use of pyrolysis as a potential thermal treatment for metal-loaded samples, some authors (Collard et al., 2012; Jiu et al., 2015; Lievens et al., 2008a) have analyzed the gases and the bio-oil obtained during pyrolysis of different metal-loaded biomass types. However, only a couple of studies have been found that focus on the thermal degradation, and more specifically on the pyrolysis emissions, of metal-loaded almond shell samples (impregnated with  $\text{CoCl}_2$  in these studies) (Font et al., 1990; Conesa et al., 1997).

In this work, heavy metal-loaded almond shell samples were pyrolyzed at 700 °C in order to study the influence of the different heavy

metals on the pyrolysis behavior of almond shell. Special attention has been brought to the characterization of the emissions and its toxicity, covering the analyses of the main gases ( $\text{H}_2$ , CO,  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ), light hydrocarbons (from methane to xylenes), semivolatiles and polycyclic aromatic hydrocarbons (PAHs).

## 2. Material and methods

### 2.1. Samples preparation and characterization

Almond shell (AS) was supplied by a factory of Granada (Spain), Carsan Biocombustibles S.L. Prior to use, almond shell was ground to a particle size <1 mm.

The impregnation was carried out by biosorption as follows: 40 g of almond shells were well mixed with individual heavy metals solutions prepared with distilled water (if another type of water is used, the metals could speciate with other compounds present in the water, affecting their availability and therefore the ability of the almond shell to adsorb them) of a concentration of 200 mg/L and a volume of 4 L in different batch reactors. The mixtures were maintained at a constant temperature of 25 °C until equilibrium was reached (approximately 2 h, when the metal concentration in the solution kept constant with time). The metallic salts used for impregnation were nitrate salts of different heavy metals (Cd(II), Cr(III), Cu(II), Ni(II) and Pb(II)) purchased to Panreac Química, S.L.U., Castellar del Vallès, Spain. Then, the solid samples were filtered, washed with deionized water to remove any of the metal ions not bound to the material and finally, the metal-loaded samples were dried in an oven at 40 °C for 24 h.

The concentration of the heavy metal solutions (200 mg/L) was selected because it is high enough to guarantee a good amount of metal biosorbed in the almond shell and consequently, greater possible effects on the pyrolytic degradation of the samples. In addition, it is low enough for biosorption applications and can be representative of the real concentration found in some industrial wastewaters.

The amount of metal biosorbed or metal uptake (mg/g) was calculated according to the mass balance of the biosorption system after determining residual or final metal concentration in solution by an atomic absorption spectrometry instrument (model AAnalyst 200, Perkin-Elmer, Inc., Massachusetts, USA). It is assumed that the decrease in the metal concentration in the solutions corresponds to the amount of metal adsorbed by the almond samples. Other sources of metal loss are negligible: the adsorption of heavy metal ions on the glass surface of the reactor is unimportant and aerosols at 25 °C will be not produced. To confirm this, blank experiments were performed with metal solutions and no adsorbent material under the same experimental conditions and no metal was lost during these tests. In addition, some authors (Eichholz et al., 1965) have investigated the adsorption of ions in dilute aqueous solutions on glass and plastic surfaces, concluding that the total adsorption losses are small, except for yttrium and the rare earths.

Moreover, another blank experiment was carried out in which distilled water and native almond shell were in contact during 2 h at the same experimental conditions, and initial and residual metal concentrations in the solution were determined by atomic absorption spectrometry. In this way, the results of the metal impregnation experiments were corrected for any background metal concentration found on the almond shell samples.

The moisture, volatile matter and ash content were determined following ISO 18134-1, 2015, ISO 18123, 2015 and ISO 18122, 2015 applicable standards, respectively. Fixed carbon content was determined by subtracting the percentages of moisture, volatile matter and ash from the original mass of the sample. The higher heating value (HHV) was determined by a calorimeter (model LEC 02, Phywe Systeme GmbH & Co, Göttingen, Germany) according to the procedure described in the standard EN 14918, 2011.

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