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Kinetic study of the pyrolysis of pine cone shell through non-isothermal thermogravimetry: Effect of heavy metals incorporated by biosorption

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ABSTRACT

The study concerns the pyrolysis kinetics of exhausted pine cone shell after its use as biosorbent of copper and lead from aqueous solutions in a fixed bed column. First, breakthrough curves of biosorption process were obtained. Main dynamic biosorption parameters were determined and analyzed. Then, non-isothermal thermogravimetric experiments were carried out with raw and metal-loaded biomass in a thermobalance under nitrogen atmosphere at different heating rates. A comparative study was performed. The activation energy dependent on the conversion rate was estimated by Flynn–Wall–Ozawa (a free integral or iso-conventional method) and a mechanistic model (an integral or model-fitting method that considers three independent parallel reactions). The fluctuation of activation energy in Flynn-Wall Ozawa model can be considered the result of thermal degradation reactions of different pseudo-components of the lignocellulosic material (hemicellulose, cellulose and lignin). For raw pine cone shell and metal-loaded-pine cone shell, best fit parameters were determined according to a three independent parallel reactions scheme. The copper and lead present in metal-loaded samples did not modify values of determined parameters which describe the pyrolysis process. Finally, chemical analysis of the chars indicated that about 95% and 99% of copper and lead presented on original waste was recovered in generated chars.

1. Introduction

Solid waste treatment techniques such as thermal treatment with energy recovery could be applied as an alternative for the final disposal of the exhausted biosorbent. This is an essential issue not only from a waste treatment perspective but also from the use of alternative fuel to energy perspective. Nowadays, different countries are addressing the need to achieve energy security for energy generation in the future. In addition, global warming is already limiting the use of fossil fuels. Concretely, the EU aims to get 20% of its energy from renewable sources by 2020. Therefore, renewable energies have been deeply developed in recent years and are currently under investigation. Among these, biomass has a great potential to contribute to get energy from renewable resources. At present, an extensive research is carrying out for converting biomass into both energy and chemicals [1–5].

Some of the challenges for the industrial application of biosorption process are the final disposition of the exhausted biosorbent and pollutant desorption (including recovery of loaded pollutants when they are valuable and simultaneous regeneration of the solid material for recycle). The utility of a particular biosorbent depends on its biosorption capacity (higher biosorption capacity, better biosorbent), but also on its possibility of easy regeneration and recycling, its availability and requirement or not of pre-processing and so on [6]. However, most researchers have evaluated only the biosorption capacity of studied biosorbent, some of them have considered its possibility of regeneration but very few authors have studied the disposition of the exhausted biosorbent required for industrial applications [7]. The methods used for desorption and recovery of loaded pollutants can be destructive or non-destructive, and the selection of the most appropriate method depends on factors such as the intensity of the pollutant binding, the possibility of recovery, and reuse of the pollutant, the loss of sorption capacity of the sorbent material, and the total cost of the operation. Generally, if cheap biomass is used as biosorbent, destructive recovery of valuable pollutants would be economically

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feasible [8]. To the use of the exhausted biosorbent as an energy recovery the role of metal during the thermal treatment is a very important issue. Thus, although several researchers studied pyrolysis of pine cone shell [9–11], there are not studies on the effects of Cu(II) and Pb(II) on the mechanism of thermal decomposition of pine cone shell in an inert environment. The results of this work may be useful for the design and operation of pyrolysis units fed by lignocelullosic wastes even after its use as biosorbent of heavy metals in a fixed bed column.

Pyrolysis technology is receiving great attention from the scientific community, because by the pyrolysis process at fast heating rate, the biomass can be converted into an easily-stored and easily-transportable liquid fuel (bio-oil) of high energy content. Moreover, pyrolysis is an important substage of gasification technology influencing the producer gas for further electricity supply [12,13].

In this paper a preliminary study on the possible use of exhausted biosorbent in pyrolysis reactors is presented, comparing the kinetics of thermal decomposition in an inert atmosphere of native and exhausted pine cone shell. Concretely, pyrolysis of the exhausted biosorbent is investigated in this work through non-isothermal themogravimetric experiments.

2. Materials and methods

2.1. Raw material

The samples used in this study were pine cone shells (PCS) of Mediterranean pine (*Pinus halepensis*) supplied by a factory of Granada (Spain), Carsan Biocombustibles S.L. Previous to the runs; the 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.

2.2. Biosorption experiments

2.2.1. Preparation of Cu(II) and Pb(II) solutions

Metal solutions of Cu^{2+} and Pb^{2+} (initial concentration of 100 mg/L) were prepared by dissolving the necessary amount of nitrate salts (2.28 g of $Cu(NO_3)_2 \cdot 3H_2O$ and 0.96 g of $Pb(NO_3)_2$, respectively) provided by Panreac (Barcelona, Spain) in 6 L of distilled water.

2.2.2. Fixed bed column tests

For continuous biosorption experiments, a covering glass column (length of 23 cm, internal diameter of 1.5 cm) was packed with a 15 g of PCS. The metal solution (100 mg/L of copper or lead) was driven at a constant flow rate (6 cm^3/min) using a peristaltic pump in up-flow mode. Biosorption tests were performed in duplicate at best operational conditions which were found by performing a factorial design changing bed depth, flow rate and inlet metal concentration. Table 1 presents operational data of the laboratory scale fixed-bed column and a schematic illustration about the general experimental setup is presented on Supplementary Material. Column effluent samples were collected at frequent time intervals and analyzed for effluent metal concentration. The Cu(II) and Pb(II) in the residual solution were analyzed in an Atomic Absorption Spectrometer (Perkin-Elmer, model AAnalyst 200).

Table 1
Operational data of the laboratory scale fixed-bed column.

Biosorbent mass, g	15
Bed length (Z), cm	13.4
Column internal diameter (D), cm	1.5
Cross sectional area of the column (S), cm^2	1.77
Bed length/Internal diameter	8.93
Bed volume (V_b), cm^3	23.68
Biosorbent particles density (ρ_p), g/cm^3	1.44
Bed porosity (ε), g/cm^3	0.560
Packing density or bulk density (ρ_b), g/cm^3	0.633
Volumetric flow rate (Q), cm^3/min	6
Initial solute concentration (C_i), mg/L	100
Biosorbent particle diameter (d_p), mm	<1
Superficial velocity ($\upsilon_{superficial}$), cm/min	3.40
Interstitial velocity ($\upsilon_{interstitial}$), cm/min	6.06
Residence time (τ), min	2.2
Mode of operation	Up-flow

2.3. Pyrolysis experiments

2.3.1. Thermogravimetric experiments

Runs for pyrolysis were carried out on a Perkin Elmer thermobalance model STA 6000. Dynamic experiments were carried out in duplicate, under heating rates of 5, 10 and 20 °C/min, from 30 °C (303 K) up to 800 °C (1073 K), including in this way the entire range of decomposition. The flow rate of the carrier gas (N_2; purity $\geq$ 99.5%) was 20 mL/min and the sample had a weight of approximately 40 mg.

2.3.2. Determination of copper and lead on raw PCS, metal-loaded PCS and chars

An energy dispersive X-ray analyzer (PHILIPS Magix Pro (PW-2440)) was used for qualitative detection and distribution of elements present in the solid samples (raw PCS, metal-loaded PCS and chars generated in pyrolysis process).

The determination of amount of copper and lead presented in chars generated in pyrolysis process was performed following European Standard EN 15297 (Solid biofuels. Determination of minor elements).

3. Theoretical background

3.1. Mathematical description of biosorption in a fixed-bed column

The performance of the fixed-bed columns is described using the breakthrough curve concept. The breakthrough curves show the loading behavior of metal to be removed from solution in a fixed bed and are usually expressed in terms of a normalized concentration, defined as the ratio of effluent metal concentration to inlet metal concentration (C/C_i) versus flow time (t_{total}) or volume of effluent (V_{eff}) for a given fixed-bed depth [14].

From a practical perspective, service or breakthrough time (t_b) is set when the effluent concentration reaches its maximum tolerable level of discharge and exhaustion time (t_{ex}) is set when the concentration in the effluent exceeds 90%–95% of the inlet metal concentration.

The volume of the effluent at breakthrough, exhaustion or total flow time, can be calculated through the following equation,

$$V_{eff} = Q \cdot t_i \quad (1)$$

where V_{eff} is the volume of effluent (mL), t_i is the breakthrough, exhausted or total flow time (min) and Q is the volumetric flow rate, (mL/min).

The total mass of metal biosorbed is equal to the area under the breakthough curve (plot of the biosorbed Cu(II) or Pb(II) concentration C_R (mg/L) versus time (min)), for a defined feed concentration and flow rate is calculated from following equation: