Bioresource Technology 196 (2015) 406–412

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Physico-chemical characterization of pine cone shell and its use as biosorbent and fuel

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HIGHLIGHTS

- Pine cone shell (PCS) has been completely characterized.
- Nickel biosorption using pine cone shell was performed in a fixed-bed column.
- Pyrolysis and combustion of raw and metal-loaded-PCS was studied via non-isothermal TGA.
- The presence of nickel in metal-loaded-PCS did not modify the thermochemical process.

ARTICLE INFO

Article history:
Received 26 June 2015
Received in revised form 28 July 2015
Accepted 29 July 2015
Available online 4 August 2015

Keywords:
Biosorption
Fuel
Nickel
Physico-chemical characterization
Pine cone shell

ABSTRACT

Physico-chemical properties of pine cone shell have been determined. Results of characterization study showed that pine cone shell could be used as biosorbent of nickel from aqueous solutions in a fixed-bed column and later as input material in thermochemical processes. To study the behavior of Ni-loaded pine cone shell as fuel, non-isothermal thermogravimetric tests were performed. These tests showed that, in nitrogen atmosphere, the main decomposition occurs from 200 °C to 500 °C and, in oxidant atmosphere, the behavior is of type "combustion + pyrolysis" (at higher temperatures there is a clear decomposition of residue formed during the initial steps). Finally, the effect of the presence of Ni was analyzed. Thermogravimetric curves did not change their profile and the total amount of nickel was detected in char-ash fraction and not in flue gases. These results suggest that nickel does not form volatile compounds at considered operational conditions.

1. Introduction

Nowadays, high amount of waste from agroindustrial activity are eliminated by burning or are scattered on fields, which causing economic cost and environmental concerns. Agroindustrial wastes are a valuable resource for different industrial applications, their recovery and recycling assumes even greater significance. In this point the study of possible use of waste from agroindustrial activities is very important. Due to the lignocellulosic structure of most of them, more feasible alternatives are the use as biosorbent and the use as fuel.

Recently several raw waste products from industrial or agricultural operations have been tested to remove heavy metals from aqueous effluents (Calero et al., 2013; Flores-Garnica et al., 2013; Martín-Lara et al., 2013; Ronda et al., 2013, 2014). In particular, pine cone shell (PCS) may constitute promising low-cost adsorbent among biomaterials, since this waste is produced in great quantities in the Mediterranean area, and is of no market value. Spain is the country with a highest land of stone pine cultivated, with around 460,000 hectares. Andalusia has the 50% of this surface and taking into account an average production of 240 kg of pine cone by 1 hectare of cultivar, the Andalusian pine cone production is nearly 55,200 tons (Senneca, 2007). Pine cone shell remains available as a waste product after picking the pine nuts (a fruit with a high economic value), for which no important industrial use has been developed, it is only used as fuel in domestic oven, and however, the amount destined to this application is low. So, it is normally incinerated or dumped to field without control. Therefore, the study of other alternative uses and their derived environmental concerns are extremely important.

The removal of heavy metals from wastewater is a matter of great interest in the field of water pollution, due to the presence of heavy metal contaminants in wastewater can cause severe water contamination problems in the world over. Heavy metals, such as cadmium, chromium, copper, lead, nickel or zinc are among the most common pollutants found in industrial effluents. Ni(II) is one them frequently encountered in wastewater streams from

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http://dx.doi.org/10.1016/j.biortech.2015.07.109
0960-8524/

several industries such as stainless steel manufacturing plants, paint formulation, porcelain enameling, electroplating, ceramic, mining and metallurgy, and from steam-electric power plants (Flores-Garnica et al., 2013). Ni(II) is a highly toxic, carcinogenic and non-biodegradable heavy metal. It can cause headache, nausea, vomiting, dizziness, chest pain, tightness, cyanosis, skin dermatitis, rapid respiration, pulmonary fibrosis, renal edema, extreme weakness and severe damage to the lungs, kidney, nervous system and mucous membranes (Flores-Garnica et al., 2013). Although there are several conventional alternatives to remove heavy metal ions from industrial effluents, such as chemical precipitation, ion ex-change, reverse osmosis, and electrochemical treatment, they pose several technical and economic constraints. Biosorption of heavy metals is an ecofriendly alternative technique, which uses inactive/dead biological materials as sorbents which are generally available at low cost, non hazardous and abound in nature.

Additionally, the use of an agroindustrial waste as fuel can be a feasible alternative to conventional fossil fuel to decrease the rate of fuel demand. The development of renewable, clean energies such as biomass has become an important working area of many researchers of world over (Aydin and Ilkiliç, 2015). Concretely, the use of the pine cone shell as fuel is in progress and it could represent a good economic added value to this waste (Blázquez et al., 2012). Biomass can be become one of the most worthwhile methods to reduce pollutant emissions from energy-production processes, besides adjustments required to power plants entail low costs (Collazo et al., 2012).

There are some studies related with this waste: Statheropoulos et al. (1997) analyzed the thermal degradation of pine-needles using various analytical methods and analyzed the volatile compound emitted; Lee et al. (2005) obtained the optimum conditions for the analysis of volatile component of pine needles by double shot pyrolysis gas chromatography; Senneca (2007) analyzed the pyrolysis kinetics of pine seed shells from TG and DTG data, considering only one reaction and Font et al. (2009) and Blázquez et al. (2012) studied the thermal degradation of pine cone and pine needle respectively. However a full characterization of this waste has not been found, neither the analysis of its properties to be used as biosorbent or as fuel. The physico-chemical characterization is useful to know its possible applications and for understanding its behavior when it is used in each one of these applications.

In this work a thorough characterization of pine cone shell biomass is carried out with focus in different properties useful to be used as biosorbent or as fuel. The aim of this study is to deepen in the relation between the physico-chemical properties of pine cone shell and its applications, evaluating the possibility of managing this waste as biosorbent of nickel from aqueous solutions and later as input material in thermochemical processes.

2. Methods

2.1. Solid waste

A typical agro-forestry waste (pine cone shell, PCS) coming from Granada City in Spain, was used as material in this study. Concretely, PCS sample was supplied by Carsan Biocombustibles S.L. factory. The solid was ground with an analytical mill (IKA MF-10) and sieved. All fractions collected below mesh size of 2 mm were chosen for experiments.

2.2. Physico-chemical characterization of PCS

2.2.1. Particle size distribution

The particle size distribution is important between other factors from an economic point of view, due to the milling of the solid involves high energy consumption and a suitable particle size of the solid for the application reduces the cost of the process. The study of particle size distribution of PCS was made using standard sieve series A.S.T.M. (American Society for Testing Materials). First, PCS was milled and was subsequently separated. Mesh ASTM/size mm: 10/2.000; 14/1.400; 18/1.000; 25/0.710; 35/ 0.500; 45/0.355; 60/0.250). This study was performed using a screening CISA, model RP-15. A sample of 10 g of PCS (previously sieved to a size less than 1.00 mm) was taken and was later sieved. After that, the amount of PCS retained on each sieve was weighed, and the percentage for each fraction was determined.

2.2.2. Surface area and porosity

The determination of Brunauer–Emmett–Teller (BET) surface area by was performed by mercury intrusion porosimetry (MIP) generated using a mercury porosimeter (Quantachrome, model Poremaster 60).

The pore size distribution was analyzed by nitrogen adsorption–desorption isotherms at 77 K, CO_2 adsorption isotherms at 273 K, and mercury porosimetry tests.

2.2.3. Field emission–scanning electron microscopy (FE–SEM) analysis

Field emission scanning electron micrographs (FE–SEM) was performed by a high-resolution scanning electron microscope (Carl Zeiss Merlin) coupled with EDX and WDX analytical capability of Oxford. To perform this analysis, the sample was dried at 50 °C in a hot air oven and metallized utilizing a Polaron SEM E-5000 coating unit.

2.2.4. Elemental analysis

Elemental analysis of dried PCS sample was accomplished by combustion analysis using an Elemental Fison's Instruments EA 1108 CHNS.

2.2.5. Proximate analysis

The moisture content of PCS was determined by the difference in weight between the wet sample and after drying in an oven (at 105 °C) until constant weight (UNE-EN 14774-2:2010).

Volatile matter content was calculated according to standard UNE-EN 15148:2010. A sample without contact with ambient air is heated to 900 °C for 7 min. The percentage of volatile matter is calculated from the mass loss of the test sample minus the mass loss due to moisture. Ash content is determined by calculation from the mass of residue remaining after the sample was heated in air for at least 60 min at a temperature of 550 °C according to standard UNE-EN 14775:2010. Fixed carbon content was calculated by difference until 100%.

2.2.6. Determination of content in holocelluloses and lignin

For these determinations, first removal of soluble hot water extractives was performed according to the TAPPI T 257. Then, ethanol–benzene extractable was determined according to TAPPI T 204. Finally, lignin and holocellulose were determined according to TAPPI T 222 and Wise method respectively (Wise et al., 1946; TAPPI, 2012).

2.2.7. Fourier transform infrared spectroscopy (FTIR) analysis

PCS was analyzed by Fourier Transform Infrared Spectroscopy (Perkin–Elmer, Spectrum 65) in wavelength range of 4000–400 cm^{-1} to obtain information about the chemical groups present in the sample.

2.2.8. Real and apparent densities

The real density was measured with helium by picnometry in a ACCUPYC II 1340, from Micromeritics at 27 °C with a total of 10 purges and cycles.