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Characterization of chemically modified biosorbents from olive tree pruning for the biosorption of lead

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ABSTRACT

This work includes a complete physic-chemical characterization of biosorbents developed by, chemical treatment of olive tree pruning waste. The biosorbents were characterized in terms of their, surface properties, such as surface area and pore size but also in terms of their chemical composition. It is observed that treatments affect mainly the external surface. The SEM micrographs indicated, changes in biomass physical structure. The infrared spectra indicate changes in functional groups, present in the biomass before and after the treatment tests. Results of potentiometric titrations, showed that acid treated OTP contains more acidic groups than untreated OTP, indicating that the, biosorbent surface becomes more negative due to dissociation of weakly acidic oxygen-containing, groups. Finally, lead biosorption experiments showed that these biosorbent materials could be good, candidates to be used for heavy metals removal.

1. Introduction

Spain is the world-leading of olive oil production. Only in Andalusia an average annual amount of 900,000 tons are produced which generates a very abundant olive pruning. If it is assumed that one hectare of olive tree pruning generates 3 tons of olive oil, an average of more than 2 million tons of olive tree pruning per year in Andalusia are produced (Agencia Andaluza de la Energía, 2011). Biomass obtained by pruning of olive trees is an abundant and renewable agricultural residue in the Mediterranean countries for which no industrial applications were yet consistently envisaged (Cara et al., 2012). The removal of pruning of olive tree is necessary to keep fields clean and to prevent propagation of vegetable illness. Usually they are eliminated by either burning or grinding and scattering on fields, which causing economic cost and environmental concerns. Considering the large amount of this yearly generated residue, its need of disposal, low cost, its cellulose content and lignin content, and potential energy capacity, this renewable material has been recently proposed as a source for cellulose pulp output, biomass energy, bioethanol production or wastewater treatment (Ballesteros et al., 2011; García et al., 2012; Requejo et al., 2012; Spinelli and Picchi, 2010).

On the other hand, heavy metals are toxic and problematic contaminants in aquatic environments. Many industries, such as coating, automotive, aeronautical and steel industries generate large quantities of wastewater that contain various heavy metals. Many physical–chemical methods like coagulation, flocculation, ion exchange, membrane separation, oxidation, etc. are available for the treatment of these metals. However, these processes have considerable disadvantages including incomplete metal removal, requirements for expensive equipment and monitoring system, high reagent and energy requirements or generation of toxic sludge or other waste products that require disposal (Demiral et al., 2008). Till date, research in the area of biosorption suggests it to be an ideal alternative for decontamination of effluents containing heavy metals. Despite activated carbon being the most commonly used adsorbent, a number of low-cost adsorbents have been investigated for their metals removal capacity. Among several alternative adsorbents, raw biomass materials is of interest as a large amount is produced annually and there is a trend toward increasing quantities (Blázquez et al., 2011; Hubbe et al., 2011; Sciban et al., 2011; Uzunosmanoglu et al., 2011).

In this work, untreated olive tree pruning and olive tree pruning treated with various chemicals agents (nitric acid HNO_3, sulphuric acid H_2SO_4 and sodium hydroxide NaOH) were characterized with a view to identifying their potential for biosorption of heavy metals as effective substitutes for conventional methods.

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2. Materials and methods

2.1. Untreated biomass

Olive tree prunings (OTP) were obtained from olive plantation located in Vilches, province of Jaen (Spain). The solid was milled with an analytical mill (IKA MF-10) and <1.00 mm fraction was chosen for the characterization and biosorption tests.

2.2. Treatments of biomass

Chemically treated olive tree pruning (OTP) was obtained by reacting OTP with three chemical solutions: nitric acid (HNO_3), sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH). The solutions for treatment were prepared at a concentration of 1 M. The concentration of treatment was selected at 1 M because an experimental design study was conducted in previous studies and it determined that optimal concentration for treated of OTP was 1 M. Treatments were conducted with a biosorbent concentration of 10 g/L and in a flask at constant temperature (50 °C) under stirring during 24 h to establish complete contact. After chemical treatment, solid samples were separated by centrifugation and the biomass was repeatedly washed with distilled water until the pH of rising water remained constant. The treated OTP was then dried in an oven at 40 °C for 24 h and after stored for later use.

2.3. Morphological, physical and chemical characterization of OTP

2.3.1. Particle size distribution

A sieve study of biosorbents was performed, with the objective to determine the size distribution of these solids after to be milled and after to be treated chemically. First, solids were milled and subsequent separation by size, using standard sieve series A.S.T.M. (American Society for Testing Materials). This study was performed using a screening CISA, model RP-15. A sample of 10 g of biosorbent (previously sieved to a size less than 1.00 mm) was taken. After sieving, the amount of biosorbent retained on each sieve was weighed, and the percentage for each fraction was determined.

2.3.2. BET surface area and porosity

Surface area was determined by mercury intrusion porosimetry (MIP) generated using a mercury porosimeter (Quantachrome, model Poremaster 60). The total volume of pores and the average pore diameter were also determined.

The porous structure is analyzed by adsorption–desorption N_2 isotherms at 77 K, CO_2 adsorption isotherms at 273 K, and mercury porosimetry tests.

2.3.3. SEM

The surface morphological image was obtained from scanning electron microscope (SEM). This analysis was performed to untreated and treated OTP and was applied to compare the surface of untreated and treated OTP. Samples were previously assembled on aluminum holder of 12.5 mm of diameter, using silver glue. These were covered with a thin layer of gold to improve their conductivity. Finally, prepared samples were introduced into the microscope chamber with a high vacuum.

2.3.4. Loss of biomass

Furthermore, during the chemical treatment of OTP produced a biomass loss. The percentage of loss can be important, and it has to account. This loss is due, the attack of chemical agents, the solubility of the components in the chemical solutions, or mass loss in washing and filtration process, among other.

The percentage of loss is determined by difference between the initial sample weight (before treatment) and the final sample weight (after completed treatment process) (Eq. (1)).

$$\%\,\text{loss} = \frac{\text{initial weight} - \text{final weight}}{\text{initial weight}} \quad (1)$$

2.3.5. Elemental analysis

Elemental analysis was performed with an EA 1108 CHNS elemental analyzer (Fison's Instruments). The oxygen content was obtained indirectly by difference. Samples were burned in an excess of oxygen and the mass of the combustion products (NO_2, CO_2, SO_2 and H_2O) were used to calculate the percentage of N, C, S and H contained in each sample. The oxygen content was obtained indirectly by difference to 100%.

2.3.6. Proximate analysis

A proximate analysis, as defined by ASTM, is the determination by prescribed methods of moisture, volatile matter, fixed carbon and ash.

The moisture content was performed only for untreated OTP, because this was eliminated during the dried of treated OTP. This was determined by the difference in weight between the wet sample and after drying in an oven (at 60 °C) until constant weight (Pepper et al., 1952). The content of volatile matter was performed according to UNE 32-019-84. The sample was introduced into the oven at 900 °C during 7 min, and volatile matter was determined by difference of weight. The ash content was quantified after combustion for 3 h at 600 °C of 2 g of sample, according to TAPPI T 211 (TAPPI, 2012). The content of fixed carbon was determined by difference of the other components.

2.3.7. Determination of content in hemicelluloses 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 (TAPPI, 2012; Wise et al., 1946).

2.3.8. TOC

The total organic carbon was determined using Dr Lange Method LCK 383 for the range 5–50 mg/L. The liquid samples were prepared by adding 1 g of the biomass to 100 mL of distilled water and extracting samples at 120 min of contact time. The organic content is obtained indirectly as difference between the inorganic carbon and total carbon present in samples.

2.3.9. Potentiometric titrations

Titrations test were performed in a jacketed glass reactor at a constant temperature of 25 °C maintained in a thermostated water bath. Biosorbent suspensions (2 g in 50 mL of deionized water) were fluxed by N_2 to remove CO_2, and titrated by standard solutions of 0.1 N NaOH (basic branch) and 0.1 N HCl (acid branch). After each addition of titrant (NaOH or HCl), the pH of suspension was allowed to reach equilibrium under magnetic stirring and then measured by a pH meter.

2.3.10. FTIR analysis

Untreated and treated OTP were analyzed with a FTIR Spectrometer (Perkin–Elmer, Spectrum 65) in the range of 4000–400 cm^{-1} to identify the chemical groups present in it and to complete the study of the functional groups. No additional preparation of the samples was necessary for this equipment in order to obtain a good quality spectrum.