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Preparation of a porous biochar from the acid activation of pork bones

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ABSTRACT

A porous biochar was manufactured through the valorization of waste pork bones, following a three-step process including pre-charring under mild conditions, acid treatment and thermal activation. The influence of the acid (H_2SO_4 and H_3PO_4) and the impregnation ratio on the physicochemical properties of the material was investigated. Acid treatment at 0.2 $mmol_{acid}/g_{precursor}$ increased BET area by about 80%, compared to untreated bone char. When using H_2SO_4, higher impregnation ratios significantly enhanced microporosity (up to 263%). This increased microporosity should be associated to a specific reaction mechanism of H_2SO_4 with a source of carbon. On the contrary, the higher activity of H_3PO_4 led to a dramatic removal of porosity for large impregnation ratios (about 20 mmol/g). The acid activation mechanism involves the formation of cation-deficient HAp, which is thereafter decomposed upon thermal treatment. The maximum uptake of methylene blue was achieved at low impregnation ratios (0.2 and 1.0 mmol/g), and could be related to surface area corresponding to large micropores and small mesopores.

1. Introduction

The use of meat and bone meal (MBM) to feed cattle was forbidden in EU (Commission Decision 94/381/EC), as a result of bovine spongiform encephalopathy crisis. Consequently, there is a high amount of animal food wastes that must be safely disposed or transformed. One of the most reliable methods for the valorization of animal bones is pyrolysis. The solid fraction obtained (bone char) contains about 70–76 wt% calcium hydroxyapatite (HAp), $Ca_{10}(PO_4)_6(OH)_2$, 10 wt% carbon, 8 wt% $CaCO_3$ and other minor constituents (Cheung et al., 2001).

Nowadays, there is a growing research interest for the use of materials based on bone char. The organic content of bones represents a source of carbon, whereas HAp acts as a natural template for the formation of a hierarchical porous structure (Wei et al., 2011), thus resulting in biochars of adequate textural properties for different applications. Bone char is a suitable material for the removal of pollutants, partly owing to the low water solubility and high ion exchange capacity of its major constituent, HAp (Arvanitoyannis and Ladas, 2008).

Bone char-derived materials have been successfully used in catalysis (Obadiah et al., 2012), electrochemistry (Goodman et al., 2013) and as highly specific materials for the removal of both gaseous (Cascarosa et al., 2012; Medellin-Castillo et al., 2014; Rezaee et al., 2009) and liquid pollutants (Cheung et al., 2001; Iriarte-Velasco et al., 2015b; Šljivić-Ivanović et al., 2015).

The applicability of bone char is strongly dependent on its porous structure. The development of porosity of a given precursor requires either chemical (Goodman et al., 2013) or physical activation (Jimenez-Cordero et al., 2013). Chemical activation has been reported as more advantageous than

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physical activation, since it results in higher yield and surface area and better development of porous structures in the resultant product (Lillo-Ródenas et al., 2003; Phan et al., 2006). Moreover, the temperatures used in chemical activation are lower than those required for physical activation. Its main drawback is the need to wash to remove the residual inorganic material.

The most commonly used agents for chemical activation include inorganic salts such as $ZnCl_2$ and K_2CO_3, alkali hydroxides such as KOH and NaOH, and inorganic acids such as H_2SO_4, H_3PO_4, HNO_3 and HCl. Several attempts have been done to prepare porous materials from animal bones by chemical activation. Dimovic et al. (2009) studied the physicochemical properties of bovine bones chemically activated with H_2O_2. Wei et al. (2011) prepared a hierarchical porous material derived from pig bone char activated by KOH. Gumus et al. (2012) and Yusufu et al. (2012) investigated the acid activation of cow bones, using HCl and HNO_3, and H_3PO_4, respectively. In a previous work we studied the physicochemical properties of biochars derived from pork bones prepared by alkaline treatment with NaOH, KOH and K_2CO_3 (Iriarte-Velasco et al., 2015a).

Acid activation is a promising treatment, since it has been successfully used to generate porosity in other waste materials, such as agroalimentary wastes (Moreno-Castilla et al., 2001; Njoku and Hameed, 2011; Reffas et al., 2010). Nevertheless, the literature concerning the preparation of porous materials by the acid activation of animal bones is scarce, and there are important gaps in the fundamentals of the process, regarding the reaction mechanism occurring during the activation process, and its effect on the properties of the material.

In this study, pork bones were selected because, to our knowledge, there is no comprehensive report on the acid activation of pork bones in the open literature. Pork is the most consumed meat in Spain, with around 2.3 Mt in 2014 (Ministry of Agriculture, Food and Environment, 2015). Spain is the second pig meat producer in EU (3.5 Mt produced in 2014). Therefore, pork bone could represent a locally available and abundant food waste for the production of porous materials.

This paper approaches the preparation of porous materials from the acid activation of waste pork bones. The influence of both the type of acid (H_2SO_4 and H_3PO_4) and the impregnation ratio on the physicochemical properties of the final material was investigated. Furthermore, the pyrolysis products of acid impregnated samples were analysed, in order to gain knowledge on the activation mechanism. These results are of great interest to optimize the preparation method, in order to achieve a material with the desired textural properties. Finally, the performance of the materials in the removal of methylene blue (representative for the aqueous removal of organics) was studied.

2. Experimental

2.1. Production of bone char

Samples of bone char (BC) were prepared from pork chop bones collected from a local butcher shop. The preparation protocol was as follows: first, bones were cleaned from meat and cut into pieces of 2–5 cm. In order to remove meat and fat, prior to chemical activation bones were precarbonized at 450 °C in nitrogen atmosphere. From now on, precarbonized sample will be referred as precursor. Precarbonization was performed using a heating rate of 10 °C/min until the desired temperature was reached; temperature was then held constant for 1 h. Nitrogen flow was set at 120 cm^3/min, which corresponds to a residence time of 8 min in furnace. Precarbonized samples were left to cool down in nitrogen atmosphere.

The precursor was sieved and particles in the 0.25–0.35 mm size range were selected. It was then divided into four parts. Two were impregnated with either H_3PO_4 (P) or H_2SO_4 (S) and pyrolyzed. The third part was pyrolyzed without chemical treatment (O), and the last part was not further modified to be used as a reference. For the impregnation step about 2 g of precursor were contacted with 40 cm^3 of a solution containing the activating agent. Solutions were stirred at room temperature (20 ± 2 °C) for 24 h. Samples were then filtered, transferred to a convection oven and dried at 80 °C for 24 h. The pyrolysis step was conducted at 800 °C under operating conditions similar to those used during the precarbonization stage. Samples of bone char were washed with distilled water until neutral pH of solution was reached.

The effect of the impregnation ratio was studied at three levels: 20, 1.0 and 0.2 $mmol_{agent}/g_{precursor}$. The adsorbents prepared at the maximum impregnation ratio were coded indicating the activation agent used: BCO, BCS, BCP. The materials prepared at lower impregnation ratios (1.0 and 0.2 mmol/g) were coded as BCr1.0 and BCr0.2, respectively.

2.2. Physical and chemical characterization

The textural properties of the materials were measured by nitrogen adsorption–desorption at 77 K using a porosimeter (ASAP 2010, Micromeritics). Prior to the measurements samples were dried and outgassed at 200 °C under a nitrogen flow for 15 h. Brunauer, Emmett & Teller (BET), *t*-plot, density functional theory (DFT) and Barrett, Joyner & Halenda (BJH) methods were used.

The point of zero charge (pH_{PZC}) was determined following the method proposed by Babic et al. (1999). About 20 cm^3 of a 0.01 N KCl–0.004 N KOH solution were contacted with 0.1 g of bone char. This solution was titrated with a 0.1 N HCl solution. The titrating solution was added slowly (0.1 cm^3 every 10 min) and data of both the volume of the titrating solution added and the solution pH were recorded. On the other hand, the KCl–KOH solution was also titrated without bone char under the same operating conditions. The pH_{PZC} is the pH at which the titration curve with bone char intersects the titration curve without bone char.

In order to investigate the reactions that take place during the activation process, thermogravimetric (TG) analysis was coupled to mass spectrometry (MS). TG analyses were performed with a Setsys evolution (Setaram) thermal analyser. About 70 mg of sample (impregnated precursor) were put into the alumina crucible and heated under helium atmosphere from room temperature to 1000 °C at a heating rate of 10 °C/min. The thermal analyser exhaust gases were monitored on-line by a mass spectrometer (MKS, Cirrus 3000). The following compounds were collected continuously: H_2O ($m/z = 18$) and CO_2 ($m/z = 44$).

The chemical composition and surface properties of the materials were analysed by a scanning electron microscope (JEOL JSM-7000F) equipped with energy dispersive X-ray detector (EDX). Fourier-transformed infrared (FTIR) spectra were collected with a Nicolet Protégé 460 device in the transmittance mode, in the 400–4000 cm^{-1} with a resolution of 2 cm^{-1}.