



Production, characterization and application of activated carbon from brewer's spent grain lignin

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ABSTRACT

Different types of activated carbon were prepared by chemical activation of brewer's spent grain (BSG) lignin using H_3PO_4 at various acid/lignin ratios (1, 2, or 3 g/g) and carbonization temperatures (300, 450, or 600 °C), according to a 2² full-factorial design. The resulting materials were characterized with regard to their surface area, pore volume, and pore size distribution, and used for detoxification of BSG hemicellulosic hydrolysate (a mixture of sugars, phenolic compounds, metallic ions, among other compounds). BSG carbons presented BET surface areas between 33 and 692 m²/g, and micro- and mesopores with volumes between 0.058 and 0.453 cm³/g. The carbons showed high capacity for adsorption of metallic ions, mainly nickel, iron, chromium, and silicon. The concentration of phenolic compounds and color were also reduced by these sorbents. These results suggest that activated carbons with characteristics similar to those commercially found and high adsorption capacity can be produced from BSG lignin.

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1. Introduction

Lignocellulosics, including agricultural wastes and agro-industrial by-products, are materials whose major constituents are cellulose, hemicellulose, and lignin. These polymers are associated with each other and constitute the cellular complex of the vegetal biomass (Kuhad and Singh, 1993). Nowadays, there is a great interest in re-using lignocellulosic materials, both from economical and environmental viewpoints. Therefore, many studies have been performed on the production of added-value compounds, mainly from hemicellulose and cellulose fractions. However, lignin is also a macromolecule present in large proportion in the lignocellulosic structure and its utilization would add value to such materials.

Lignin is a three-dimensional polyphenolic macromolecule of very complex structure whose function is to provide rigidity and cohesion to the material cell wall, to confer water impermeability to xylem vessels, and to form a physicochemical barrier against microbial attack (Fengel and Wegener, 1989). Various processes can be used to remove and isolate lignin from lignocellulosic structure, such as alkaline hydrolysis, for example. In this process, the lignin is solubilized in the reaction medium (black liquor) and

can be subsequently separated by precipitation with mineral acids, such as sulfuric or hydrochloric acid (Fengel and Wegener, 1989; Mussatto et al., 2007; Santos and Curvelo, 2001). The isolated lignin can be used as starting material for a series of useful products, such as activated carbon, vanillin, benzene, dispersant, emulsificant and chelant agents, antioxidants, pesticides, fertilizers, phenols, polymers, adhesives, concrete additives, among others (Gargulak and Lebo, 2000).

Activated carbons are adsorbents that are industrially used in multiple processes for product separation and purification, and for the treatment of liquid and gaseous effluents (Montané et al., 2005). Despite its frequent use in the water and waste industries, activated carbon remains an expensive material. In view of the high cost and the tedious procedures for the preparation and regeneration of activated carbons, there is a continuing search for low-cost potential adsorbents. The preparation of activated carbons from lignin is an attractive way of giving added value to this material, which is mainly used as in-house fuel for the recovery of both energy and residual inorganic matter (Fierro et al., 2006, 2008). Over the past few decades, some studies have been carried out on the activation of agricultural lignocellulosic waste materials to carbons, due to their low cost and high availability (Guo and Rockstraw, 2006), but there are no reports on the production of activated carbon from brewer's spent grain (BSG) lignin. Use of BSG lignin as starting material for activated carbon production is

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interesting because BSG (the main brewery by-product) is produced in large amounts all year, and is a lignin-rich material (Mussatto et al., 2006a).

Lignin can be converted in activated carbon by physical or chemical activation, the last one being more amply used than physical activation, because it requires lower activation temperatures and gives higher product yields (Guo and Rockstraw, 2007). Chemical activation consists of the treatment of the lignin with a chemical agent (H_3PO_4 , KOH or NaOH), and heating at 450–900 °C so that carbonization and activation occur simultaneously (Suhás et al., 2007). Among the chemical agents that can be used in this technique, H_3PO_4 is commonly utilized due to economic and environmental reasons, since it requires relatively low activation temperatures (approximately 400–500 °C) and can be recovered at the end of the process (Diao et al., 2002; Guo and Rockstraw, 2007; Hsisiheng et al., 1998).

The purpose of the present work was to prepare activated carbon from BSG lignin, by chemical activation using phosphoric acid as impregnating agent, and to examine the influence of preparation conditions (acid/lignin ratio and carbonization temperature) on the textural characteristics of the materials produced (surface area, volume of pores, and pores size distribution) as well as on its adsorption capacities.

2. Methods

2.1. Raw material pre-treatment and hydrolysate prepare

The BSG used in the experiments was supplied by the Microbrewery of the Engineering College of Lorena, and presented the following chemical composition (% dry weight, w/w): 16.8 cellulose, 28.4 hemicellulose, 27.8 lignin, 4.6 ashes, 15.2 proteins, 5.8 extractives, and 1.4 acetyl groups. As soon as obtained, the material was washed with water (for removal of the residues originating from wort) and dried at 50 ± 5 °C until approximately 10% moisture content.

Dried BSG was pre-treated with dilute sulfuric acid under previously optimized conditions (Mussatto and Roberto, 2005). At the end of reaction, the solid residue was separated by centrifugation, washed with water until neutral pH and dried at 50 ± 5 °C to approximately 50% moisture content. The liquid phase (BSG hemicellulosic hydrolysate) was concentrated under vacuum in a 4-L evaporator to increase the sugars content about fourfold.

2.2. Black liquor and lignin precipitation

The black liquor was obtained by alkaline hydrolysis (Mussatto et al., 2006b) of pre-treated BSG residue generated in the previous step of diluted sulfuric acid hydrolysis. After hydrolysis, the reaction medium was cooled in an ice bath and filtered through 100% polyester cloth to separate the black liquor.

For lignin precipitation, the pH of the black liquor was reduced from 12.56 to 2.15, by addition of concentrated sulfuric acid (98% w/w), as previously established (Mussatto et al., 2007). After acid addition and medium homogenization, the liquor was filtered through 100% polyester cloth to separate the precipitated lignin. The precipitate was washed thoroughly with distilled water until the supernatant was neutralized, filtered through a 100% polyester cloth and dried at 40 °C to constant weight.

2.3. Activated carbon production

Dried lignin (3% moisture) was soaked, sieved with a 170-mesh screen, and the particles that passed through this sieve ($<88 \mu\text{m}$) were used for activated carbon production. The lignin activation

process was performed using different H_3PO_4 /lignin ratios (1, 2 and 3 g/g) and carbonization temperatures (300, 450 and 600 °C), according to the 2^2 full-factorial design given in Table 1. Lignin was initially mixed with H_3PO_4 (85% w/w) and the blend was left for an impregnation time of 1 h at room temperature in air. After this time, the blend was transferred to a muffle furnace, where carbonization was carried out under air atmosphere. The furnace was heated at 17.5 °C/min up to 170 °C, and maintained at this temperature for 1 h for allowing the free evolution of water, obtaining a black sticky solid. The oven was heated to the desired carbonization temperature, and this temperature was maintained for 2 h. After cooling to room temperature, the solid was washed with ultra pure water at 60 °C to remove excess H_3PO_4 . The carbon samples were dried at 105 °C for 2.5 h and ground with mortar and pestle for further test.

The final weight of dry sample, calculated on a chemical free basis, was recorded to determine the carbon yield. Chemical recovery (CR) was estimated according to Eq. (1),

$$CR = \frac{W_{pi} - W_{pf}}{W_c} \times 100 \quad (1)$$

where W_{pi} and W_{pf} are the weight of product before and after washing, and W_c is the weight of chemical agent used.

2.4. Adsorption tests

The activated carbons produced under the different experimental conditions were assayed for detoxification of the hemicellulosic hydrolysate produced during the BSG pre-treatment with dilute sulfuric acid (item 2.1). Hydrolysate treatment consisted in the addition of 2.5 g of activated carbon to each 100 g hydrolysate (pH adjusted to 2.0 by addition of NaOH pellets) and subsequent stirring at 150 rpm, 45 °C for 60 min, as previously described (Mussatto and Roberto, 2004). After each treatment, the precipitate was removed by centrifugation at 1100g for 20 min. The undetoxified and detoxified hydrolysates were analyzed to determine the contents of sugars (xylose, glucose and arabinose), total phenolic compounds, color, and metallic ions (nickel, calcium, magnesium, zinc, iron, chromium, aluminum and silicon), so that the efficiency of compounds adsorption could be determined. A similar detoxification procedure was also performed by using a commercial activated carbon sample (Synth, Labsynth, São Paulo, Brazil), to compare the adsorption efficiency of the produced carbons with that of a commercially available product.

2.5. Analytical methodology

2.5.1. Activated carbons and lignin characterization

The surface characteristics were determined by N_2 adsorption/desorption isotherms at 77 K using an analyzer Quantachrome Instruments Nova 4200e. Prior to the adsorption analyses, the samples were pre-degassed at 250 °C for 3 h under vacuum to remove moisture and other impurities. Nitrogen was used as adsorbate at liquid nitrogen temperature. Specific surface area (S_{BET}) was

Table 1

Values of the independent process variables used for activated carbon production from brewer's spent grain lignin, according to the 2^2 full-factorial design.

Assay	Acid/lignin ratio (g/g)	Carbonization temperature (°C)
1	1	300
2	3	300
3	1	600
4	3	600
5	2	450
6	2	450

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