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 2^2 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 m^2/g, and micro- and mesopores with volumes between 0.058 and 0.453 cm^3/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.

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 (Suhas 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 μm) 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),

$$CR = \frac{W_{pi} - W_{pf}}{W_c} \times 100 \tag{1}$$

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

determined by the BET method. Total pore volume was calculated from the nitrogen adsorption isotherm at a relative pressure of 0.99. The t and α_s methods were used to estimate the micropore volume (V_{micro}) and the mesopore surface area (S_{mesop}). The mesopore volume (V_{mesop}) was obtained by difference. BJH and DFT methods were employed for evaluation of the pore sizes distribution.

Elemental composition of lignin (carbon, nitrogen, hydrogen, and sulfur) was determined by combustion of 1 mg sample at 1000 °C. Measurements were carried out in an EA1108 Carlo Erba Elemental Analyser. The oxygen content was estimated by difference [100 − (% C + % H + % N + % S)].

2.5.2. Hydrolysate characterization

Hydrolysate samples were analyzed by high-performance liquid chromatography (HPLC). Glucose, xylose, and arabinose concentrations were determined with a refractive index (RI) detector and a Bio-Rad (Hercules, CA, USA) HPX-87H (300 × 7.8 mm) column at 45 °C, using 0.005 M sulfuric acid as the eluent, flow rate of 0.6 ml/min and sample volume of 20 μl.

Total phenolic compounds concentration was estimated by ultraviolet spectroscopy at 280 nm (Rocha, 2000). The pH of a hydrolysate sample was raised to 12.0 with 6.0 M NaOH and the resulting solution was diluted with distilled water in order to obtain an absorbance reading not exceeding 0.5. For color determination, the pH of the samples was adjusted to 5.5 before they were diluted in distilled water (1:50 ml) and analyzed at 440 nm.

Metallic ions (Ni, Ca, Mg, Zn, Fe, Cr, Al, and Si) concentrations were determined by flame atomic absorption spectrometry, in a equipment PerkinElmer model Analyst 800 (Izario Filho et al., 2001). For analysis, samples of 1 ml were transferred to a glass vessel containing 5 ml ultra pure water (Millipore 18.2 mΩ cm), which was placed onto a heating plate. Two or 3 ml of a mixture containing HNO_3 and HCl (1:1 v/v) were added to decompose the sugars into CO_2 and H_2O. The digestion period lasted 3 or 4 h, when the color of the reaction medium changed. After this time, the sample was cooled and diluted with ultra pure water to a concentration required for analysis.

2.6. Experimental design

Experiments were carried out according to a statistical experimental design, and Statistica v.5.0 (Statsoft, USA) was the software used for regression and graphical analyses of the obtained data. Two variables (acid/lignin ratio and carbonization temperature) were tested on two levels in a 2^2 full-factorial design with two replicates in the center point. The range and levels of the investigated variables are given in Table 1. Two assays in the center point were carried out to estimate the random error needed for the analysis of variance, as well as to examine the presence of curvature in the response surface. The removal of sugars, total phenolic compounds, color and metallic ions were considered as the dependent variables or responses of the experimental design. The design allowed the

estimation of the significance of the parameters and their interaction using Student's t-test.

3. Results and discussion

3.1. BSG lignin

A wide diversity of materials can be used as precursors for producing activated carbon. Among them, lignin is considered a good precursor because of its relatively high carbon content (Sun et al., 2006). Elemental composition of BSG lignin, on a dry ash-free basis, is shown in Table 2. The BSG lignin has a high carbon content (>60% w/w), and is thus suitable for activated carbon preparation. Other lignin sources with similar carbon contents have also been used for activated carbon production (Table 2).

3.2. Carbon yield

Product yield is an important measure of the feasibility of preparing activated carbon from a given precursor. According to Guo and Rockstraw (2006), significant product yield differences can be observed depending on the origins of the Kraft lignin, since the molecular structure of lignin varies with plant species and with the conditions encountered since harvest. Besides the origin of the lignin, temperature and acid/lignin ratio used during the carbonization stage are also factors that affect the carbon yield. In the present study, the temperature increase (300–600 °C) caused a strong decrease in carbon yield from 61.6% and 70.2% to 3.8% and 8.3% depending to the acid/lignin ratio (Table 3). Similar values were reported by Fierro et al. (2006) who observed during the carbonization of Kraft lignin impregnated with phosphoric acid that the carbon yield decreased from 49% at 400 °C, to 8% at 650 °C. Based on thermogravimetric experiments, they explained the corresponding weight loss mechanism as follows: the first sharp weight loss corresponds to the loss of most of the volatile matter; while the second one would correspond: (i) to the volatilization of the P_2O_5 coming from the H_3PO_4 in excess, and (ii) to the resultant carbon combustion once the formerly protecting P_2O_5 is lost.

Besides product yield, chemical recovery is also regarded as indicator of the efficiency of the chemical activation process, since

Table 3
Carbon yield and chemical recovery during the activated carbon production from brewer's spent grain lignin, according to the 2^2 full-factorial design.

Carbon Sample[a]	Carbon yield (%)	Chemical recovery (%)
1	61.6	70.6
2	70.2	68.1
3	3.8	24.6
4	8.3	47.1
5	34.9	66.8
6	37.4	66.3

[a] 1, 2, 3, 4, 5, and 6 correspond to the samples obtained according to the 2^2 full-factorial design.

Table 2
Elemental analysis of brewer's spent grain lignin and other lignin sources used for activated carbon production.

Elemental composition (% dry weight ash-free basis)					References
Nitrogen	Carbon	Hydrogen	Sulfur	Oxygen	
2.18	64.55	8.58	2.01	22.68	Present work
0.05	59.46	5.07	2.15	33.27	(Fierro et al., 2006; Montané et al., 2005)
0.1	59.8	8.3	nr	nr	(Hayashi et al., 2002)
0.1	59.4	5.2	–	35.3	(Sun et al., 2006)
0.1	59.8	5.3	–	34.8	(Hayashi et al., 2000)

nr = not reported.

removing the chemicals left in the carbonized sample by washing will yield porosity in the final carbon structure (Ahmadpour and Do, 1997). Chemical recovery from BSG carbon samples was generally higher the lower the temperature and acid/lignin ratio used in the carbonization process (Table 3).

3.3. Characteristics of the BSG activated carbons

Fig. 1 shows the N_2 adsorption/desorption isotherms of the produced carbon materials (samples 1–6), a commercial activated carbon sample (CC), and the lignin (L) used as carbons precursor. Analysis of the isotherms for the six BSG carbons suggests that samples 2 and 3 had the lowest porosity while sample 1 presented the highest porosity among the produced carbons. Carbons 4, 5 and 6 presented intermediary characteristics, and the highest N_2 adsorption occurred for the commercial activated carbon, suggesting a highly developed microporosity in this sample.

None of the analyzed carbons (produced and commercially obtained) showed a type I isotherm, i.e., with tendency to form a plateau at low relative pressures (Fig. 1), as it is expected for essentially microporous materials. On the contrary, N_2 adsorption continued after saturation of the micropores, indicating the presence of other kinds of surface structures (probably mesopores) with a significant area. Lignin is expected to have a small surface area, since the amounts of N_2 adsorbed are very low. Moreover, the lignin isotherm is very similar to that obtained for sample 3, suggesting a low activation degree for this carbon sample as mentioned previously.
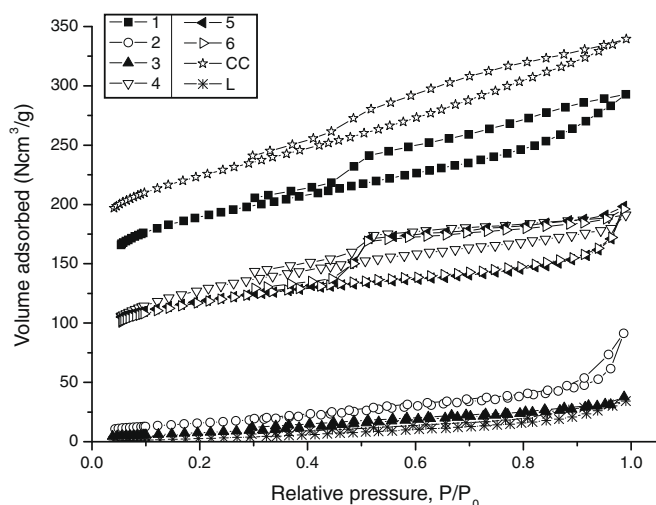

Fig. 1. N_2 adsorption/desorption isotherms at 77 K for the produced BSG carbon materials (samples 1–6), a commercial activated carbon (CC), and the lignin (L) used as precursor.

The results for the BET surface area (Table 4) are in agreement with the observations made from Fig. 1, with sample 1 giving the highest and samples 2 and 3 the lowest values. In fact, very low values for the BET surface area were obtained for samples 2 and 3 and micropores were not detected in these samples. Lignin did not present the micropores observed with samples 2 and 3, and showed a very low BET surface area (15 m^2/g). Commercial activated carbon presented the highest BET area when compared to all the other analyzed samples. When compared to the sample 1, which gave the most similar results, the micropore volume of commercial activated carbon was only 1.1-fold higher, but the surface area of the remaining pores (S_{mesop}) was about 1.4-fold higher.

Sample 1 gave also the highest mesopores volume among the produced carbons, whereas sample 3 presented the lowest value (Table 4). The commercial activated carbon presented a mesopore volume higher than that of sample 1, which is in agreement with its highest BET area. The lignin sample did not contain micropores, and its mesopore volume was only few lower than that of sample 3, which also suggests that sample 3 was few activated.
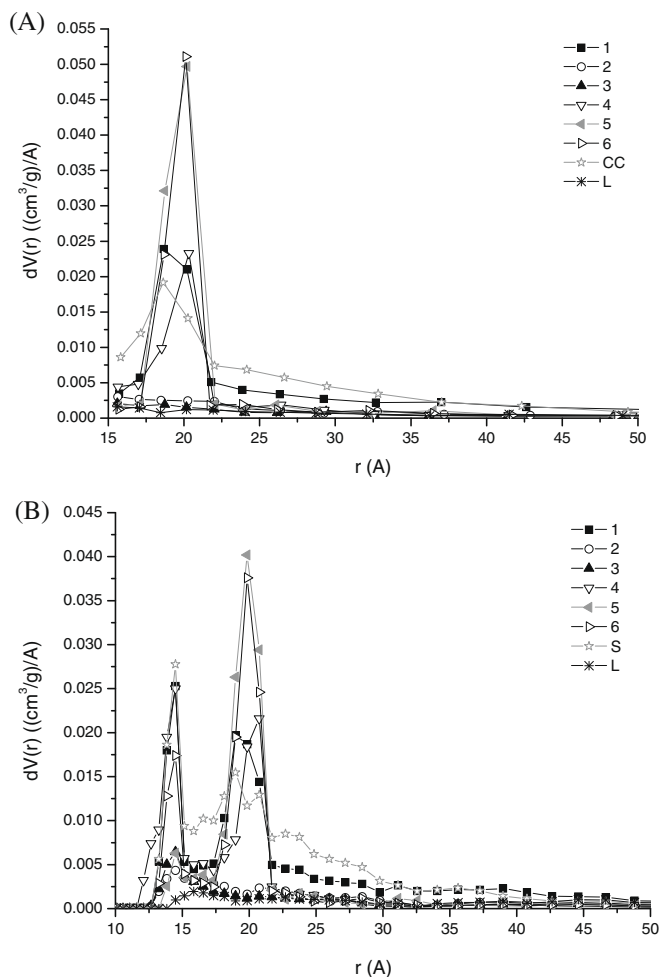
Another important aspect of activated carbons is their mesopore sizes distributions. Fig. 2 shows the results obtained by two different methods: BJH (Fig. 2A) and DFT (Fig. 2B). Analysis of the mesopore size distribution by both methods gave similar results, with samples 2 and 3 not presenting a well defined profile, while carbons 5 and 6 showed a well defined mesoporosity at around 2 nm. All the BSG carbons contained small (<2 nm) mesopores, but only few were present in samples 2 and 3. Carbon 4 presented a profile similar to those of samples 5 and 6, but showed a significantly higher relative fraction of mesopores less than 1.6 nm in size (from 1.2 to 1.6 nm). The pore size distribution of sample 1 was comparable to that of sample 4 for radii lower than 2.2 nm, but sample 1 presented a significant fraction of mesopores with larger sizes. Similarly, the commercial activated carbon also showed a broad distribution of mesopore sizes. Finally, lignin did not show a well defined profile (as it was also observed for sample 3) and its total volume was very low.

In conclusion, when comparing the characteristics of the different produced BSG carbons, it appears that the use of extreme conditions with opposite signals (for example, high temperatures and low acid/lignin ratios) is not appropriate to obtain carbon materials with a well developed porosity.

3.4. Adsorption capacity of the BSG activated carbons

The activated carbons were used for detoxification of BSG hemicellulosic hydrolysate since it contains a mixture of different compounds and thus allows simultaneous evaluation of the capacity of each activated carbon to adsorb different compounds. In addition, BSG hemicellulosic hydrolysate can be used as fermentation medium for the production of value-added compounds, and its

Table 4
Porosity analysis of the produced BSG carbons (samples 1–6), a commercial activated carbon (CC), and the lignin (L) used as precursor.

Sample	S_{BET} (m^2/g)	V_P (cm^3/g)	Method t			Method α_S		
			S_{mesop} (m^2/g)	V_{microp} (cm^3/g)	V_{mesop} (cm^3/g)	S_{mesop} (m^2/g)	V_{microp} (cm^3/g)	V_{mesop} (cm^3/g)
1	692	0.453	194	0.211	0.242	190	0.213	0.240
2	59	0.141	59	0	0.141	66	0	0.141
3	33	0.058	33	0	0.058	36	0	0.058
4	459	0.296	110	0.165	0.131	79	0.189	0.107
5	427	0.307	77	0.157	0.150	79	0.165	0.142
6	429	0.303	83	0.155	0.148	83	0.155	0.148
CC	812	0.525	265	0.232	0.293	269	0.229	0.296
L	15	0.053	15	0	0.053	26	0	0.053

S_{BET}: BET surface area; V_P: total volume of pores; V_{microp}: micropores volume; V_{mesop}: mesopores volume; S_{mesop}: mesopores area.

Fig. 2. Pores size distribution for the produced BSG carbon materials (samples 1–6), a commercial activated carbon (CC), and the lignin (L) used as precursor. Results obtained by using the BJH (A) and DFT (B) methods.

for most of the cases (except for Fe and color removal). According to Suhas et al. (2007) lignin exhibits some adsorption capacity, which can be improved by means of an activation procedure. In agreement with this, Table 5 shows that all the activated carbons presented adsorption capacities higher than those of lignin, for practically all the evaluated compounds.

Removal of sugars (glucose, xylose, and arabinose), Mg and Zn ions was low ($\leqslant$7.0%, 7.8%, and 15.0%, respectively) for all the activated carbons as well as for the lignin, revealing that the activation procedure used was not suitable to produce carbons for use in the removal of these compounds. Nevertheless, the achieved values were similar to those obtained by using the commercial activated carbon (Table 5). Unlike sugars, and Mg and Zn ions, removal of total phenolic compounds and Ni, Ca, Fe, Cr, Al, and Si ions was greatly favored when lignin was activated to carbon. Total phenolic compounds removal, for example, could be increased up to 4.5-fold depending on the conditions used in the activation process. Ni was completely removed from the hydrolysate by carbon produced under the conditions of assay 4 (highest carbonization temperature and acid/lignin ratio), while lignin was able to remove only 6.2% of this element.

Although the carbons' capacity in adsorbing the different species varied according to the conditions of preparation, it is interesting to observe in Table 5 that, in many cases the produced materials presented adsorption capacities comparable to or higher than those of the commercial sample. Removal of Ni, Mg, Cr, and Si, for example, was higher for all the produced carbons than for the commercial product, while the commercial activated carbon was only more efficient for Fe, color and phenolic compounds removal. The dark color of the hydrolysate is closely related to the presence of phenolic compounds, and therefore, when such compounds are removed, the color intensity of the hydrolyzate also decreases (Fengel and Wegener, 1989; Mussatto and Roberto, 2004).

3.5. Statistical analysis for the compounds removal using the produced carbons

The nature of precursor, the impregnation ratio between H_3PO_4 and precursor, and the activation temperature are considered important factors affecting the properties of final activated carbon products (Guo and Rockstraw, 2006, 2007). For this reason, a statistical analysis was performed to evaluate the influence of acid/lignin ratio and carbonization temperature used for BSG lignin activation, on the capacity of the produced carbons for adsorbing sugars, phenolic compounds and metallic ions. According to this analysis, the adsorption of glucose, xylose, arabinose, Zn, and Al ions (species removed in low quantities, <30.5%) did not present any correlation with the conditions by which the carbons were produced, i.e., there was not a statistically significant difference among the carbons for removal of these compounds. In contrast,

fermentability is improved when it is submitted to a detoxification step before fermentation (Mussatto et al., 2005). In fact, detoxification with activated carbon has been previously reported to decrease the toxicity of hemicellulosic hydrolysates obtained from different lignocellulosic materials (Alves et al., 1998; Mussatto and Roberto, 2004; Mussatto et al., 2005; Parajó et al., 1996).

Table 5 shows the compound removal efficiencies by detoxification of BSG hemicellulosic hydrolysate with BSG carbons and lignin. As can be noted, BSG lignin adsorbed compounds from the hydrolysate, but its adsorption capacity was low (less than 10%)

Table 5
Removal of sugars, metallic ions, phenols and color during the detoxification of brewer's spent grain (BSG) hemicellulosic hydrolysate with BSG lignin or with the activated carbons produced by its chemical activation.

Adsorbent used for hydrolysate detoxification[a]	Compounds removal (%)												
	Glucose	Xylose	Arabinose	Ni	Ca	Mg	Zn	Fe	Cr	Al	Si	Total phenolics	Color
Carbon 1	0.0	2.6	2.1	65.1	0.2	1.3	4.5	53.9	54.7	10.6	31.6	23.0	60.4
Carbon 2	2.4	6.4	6.4	65.9	21.1	7.8	1.1	39.6	35.6	7.6	38.1	16.2	61.4
Carbon 3	4.9	6.9	7.0	3.1	27.9	4.7	0.1	61.5	17.3	16.3	33.5	12.2	61.5
Carbon 4	0.0	6.6	6.4	100.0	29.5	1.9	15.0	70.7	39.8	30.5	16.3	33.8	64.4
Carbon 5	0.0	3.5	3.4	61.2	15.9	4.3	7.5	66.9	21.3	12.1	38.8	25.0	62.9
Carbon 6	0.0	3.5	3.4	65.1	23.3	3.0	9.3	67.7	20.5	21.2	38.0	25.7	63.1
Commercial carbon	2.4	4.7	4.6	0.0	26.5	0.3	3.6	77.6	10.9	19.5	1.1	50.7	70.3
BSG lignin	2.4	3.6	4.0	6.2	9.1	0.4	0.4	23.0	8.6	8.4	6.3	7.4	26.2

[a] Carbons 1, 2, 3, 4, 5, and 6, corresponding to the samples obtained according to the 2^2 full-factorial design evaluated in this study.

total phenolic compounds, color, Ni, Ca, Mg, Fe, Cr, and Si removals varied significantly depending on the activated carbon used for detoxification, and a Pareto chart was used for statistical analysis of these experimental data (Fig. 3).

Fig. 3 represents the estimated effects of the variables (acid/lignin ratio (factor 1) and carbonization temperature (factor 2)) used for activated carbon production, on the removal of total phenolic compounds, color and metallic ions from BSG hemicellulosic
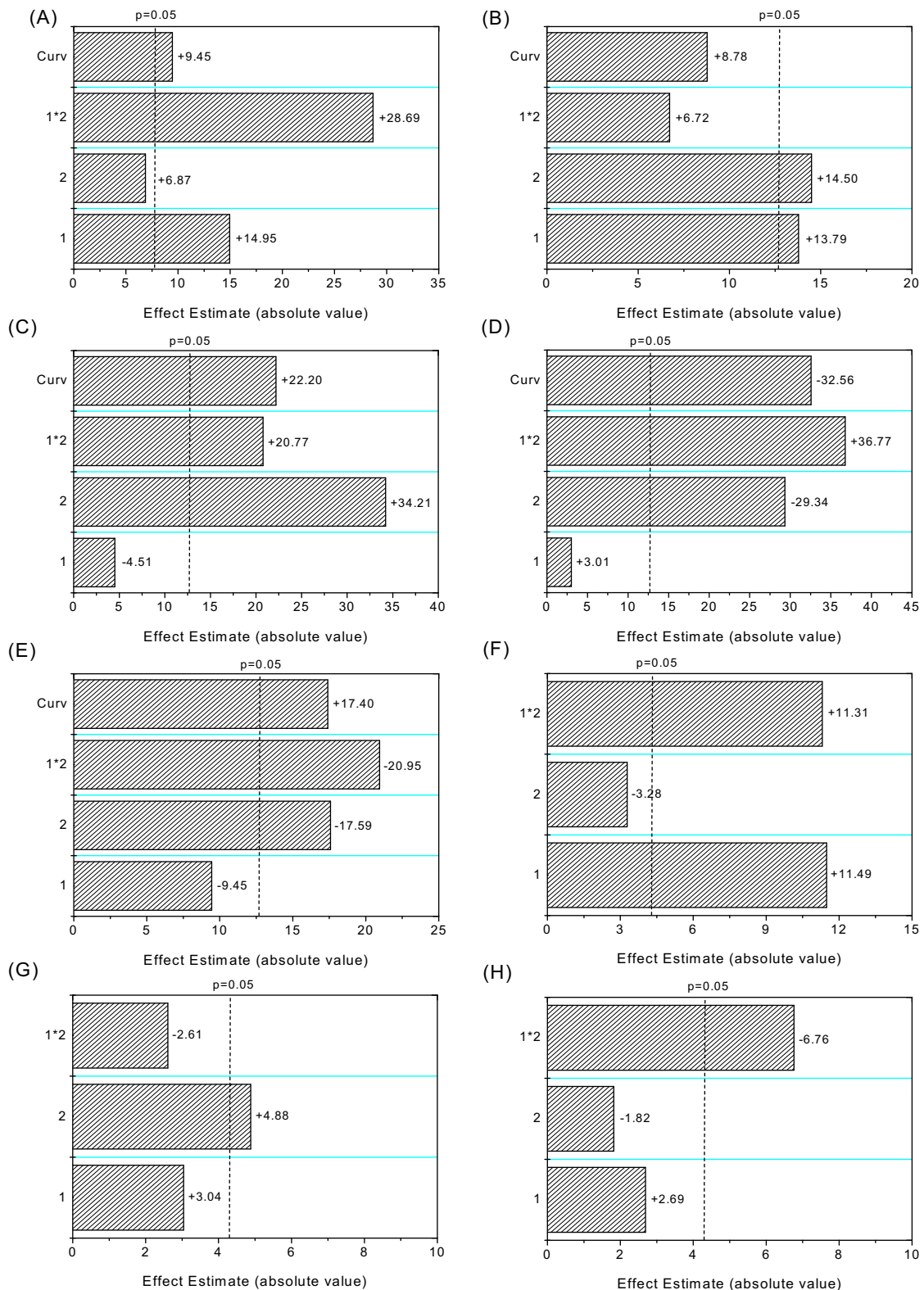
Fig. 3. Pareto chart for the effects of acid/lignin ratio (factor 1) and carbonization temperature (factor 2) used during the activated carbon production from BSG lignin, on their capacity for removal of phenols (A), color (B), and metallic ions Fe (C), Cr (D), Si (E), Ni (F), Ca (G), and Mg (H) from BSG hemicellulosic hydrolysate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

hydrolysate. The length of each bar is proportional to the standardized effect. Bars extending beyond the vertical line correspond to effects statistically significant at 95% confidence level. In some cases, the curvature was maintained in the analysis because it was statistically significant for the response (Fig. 3A, C, D, and E) or if its presence improved the analysis of the data (Fig. 3B). This means that in these cases, a second order polynomial equation would be better to explain the variations in the responses as a function of the acid/lignin ratio and carbonization temperature variations. In the other cases (Fig. 3F, G, and H) a linear equation could explain the responses variations according to the variables variations.

Analysis of the Pareto charts revealed that the acid/lignin ratio only had a significant main effect for removal of phenolic compounds, color, and Ni (Fig. 3A, B, and F, respectively). In all these cases, the variable had a positive effect, meaning that the removal of these compounds was higher as higher the acid/lignin ratio used for the carbons production. For the other analyzed metallic ions, acid/lignin ratio did not present a significant main effect, suggesting that the use of 1, 2 or 3 g H_3PO_4/g lignin did not influence the capacity of the produced carbons to adsorb Fe, Cr, Si, Ca and Mg. However, even though no significant main effect was observed, the acid/lignin ratio presented a statistically significant effect (at least 95% confidence level) when in interaction with the temperature, for removal of all the other analyzed metallic ions (except Ca). This fact reveals that this variable has influence on the metallic ions adsorption capacity of the produced carbons, although such effect is not individually significant.

Carbonization temperature had a significant main effect for the removal of color, Fe, Cr, Si, and Ca ions (Fig. 3B, C, D, E, and G, respectively), and this effect was more significant than that of the acid/lignin ratio. Nevertheless, the effect had a negative signal for Cr and Si, indicating that the removal of these metallic ions was higher when the activated carbons were produced under the lowest temperature (300 °C); whereas for Fe, Ca, and color, the temperature had a positive effect, suggesting that such removals were higher when using the activated carbons produced under the highest temperature (600 °C). This difference can be related to the presence of surface oxygen groups in the carbons, since the presence of such groups may affect the compounds access to the carbon pores (Faria et al., 2004; Gonzalez-Serrano et al., 2004).

In general, most of the compounds were adsorbed in larger amounts in the BSG carbon produced under the highest acid/lignin ratio (3 g/g) and carbonization temperature (600 °C). Gonzalez-Serrano et al. (2004) also reported that the relative adsorption capacity of different carbons normally increases with the activation temperature and impregnation ratio. This observation suggests that carbons with intermediary porosity characteristics and

large numbers of mesopores with sizes between 1.2 and 1.6 nm are more suitable to adsorb the compounds evaluated here.

3.6. Chemical composition of detoxified BSG hydrolysate and perspectives for the activated carbons use

Table 6 shows the chemical composition of detoxified and undetoxified BSG hydrolysates. Removal of sugars by the produced and the commercial activated carbon was not significant. This is advantageous if it is desired to use the hydrolysate in fermentative processes, for example. Unlike sugars, all other compounds identified in the BSG hydrolysate (phenolic compounds and metallic ions) are considered toxic to microorganisms, and fermentation of undetoxified hydrolysates is characterized by slow kinetics with limited yield and productivity (Cruz et al., 2000). Among such compounds, phenolic compounds are considered the most toxic in lignocellulosic hydrolysates (Mussatto and Roberto, 2004). In the present study, removal of phenolic compounds of up to 33.8% was achieved depending on the carbon used. Although this removal efficiency is lower than that obtained with commercial carbon, it is still in the range desired for applications. For example, a similar removal of phenols (27%) from rice straw hemicellulosic hydrolysate improved the fermentation of xylose-to-xylitol by *Candida guilliermondii* by 22% (Mussatto and Roberto, 2001).

The capacity of BSG carbons to remove phenolic compounds is also of interest for wastewater treatment. Phenols are widely used and, phenolic pollutants are found in wastewaters from industries that perform high temperature coal conversion, petroleum refining, polymer synthesis and transformation, synthesis of dyes, pesticides, explosives, and insecticides (Fierro et al., 2008; Gonzalez-Serrano et al., 2004). The presence of even low concentrations of aromatic compounds like phenols affects the use and/or reuse of water. In addition, such compounds are recognized as toxic carcinogens (Sun et al., 2006).

Heavy metal ions like Ni, Cr, and Fe present also high toxicity, which may inhibit enzymes in the microorganism's metabolic pathways. According to Watson et al. (1984), microbial activity of *Pachysolen tannophilus* was slightly reduced when Ni, Cr, and Fe ions were present in the fermentation media in quantities around 5, 100, and 150 mg/l, respectively, but a 60% activity reduction was observed by Ni ions at a concentration of 100 mg/l. All the BSG activated carbons were able to reduce the concentrations of these metallic ions to values below the limits considered toxic for microorganisms (Table 6), thus improving the hemicellulosic hydrolysate fermentability.

Removal of heavy-metal contaminants such as the highly toxic chromium from such sources as wastewater is also important, and the BSG carbons were able to remove up to 54.7% of this element present in BSG hemicellulosic hydrolysate.

Table 6
Concentration of sugars, phenols and metallic ions in brewer's spent grain (BSG) hemicellulosic hydrolysate before and after detoxification with BSG lignin or with the activated carbons produced by its chemical activation.

Hydrolysate sample[a]	Concentration (g/l)				Concentration (mg/l)							
	Glucose	Xylose	Arabinose	Total phenolics	Ni	Ca	Mg	Zn	Fe	Cr	Al	Si
Treated with AC 1	4.1	70.3	32.0	11.4	4.5	1145.5	820.0	85.6	75.9	29.6	297.6	259.5
Treated with AC 2	4.0	67.6	30.6	12.4	4.4	905.5	766.6	88.6	99.5	42.1	307.6	234.8
Treated with AC 3	3.9	67.2	30.4	13.0	12.5	826.9	792.5	89.5	63.3	54.1	278.5	252.2
Treated with AC 4	4.1	67.4	30.6	9.8	0.0	809.4	815.0	76.2	48.2	39.4	231.3	317.6
Treated with AC 5	4.1	69.7	31.6	11.1	5.0	964.8	795.7	82.9	54.5	51.5	292.5	232.3
Treated with AC 6	4.1	69.7	31.6	11.0	4.5	880.6	806.2	81.3	53.1	52.0	262.3	235.3
Treated with commercial AC	4.0	68.8	31.2	7.3	12.9	843.6	828.7	86.4	36.9	58.3	267.9	375.3
Treated with BSG lignin	4.0	69.6	31.4	13.7	12.1	1137.2	827.6	89.2	126.7	59.8	305.1	355.6
Original produced	4.1	72.2	32.7	14.8	12.9	1147.6	831.2	89.6	164.6	65.4	332.9	379.4

[a] AC = activated carbon; 1, 2, 3, 4, 5, and 6 corresponding to the samples obtained according to the 2^2 full-factorial design.

4. Conclusions

Activated carbons absorbing phenolic compounds and metallic ions (mainly Ni, Fe, Cr, and Si), similarly or even better than commercial products were produced by chemical activation of BSG lignin. Activation by impregnation with 3 g H_3PO_4/g lignin at 600 °C resulted in the best product.

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