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Study of "*napier grass*" delignification for production of cellulosic derivatives

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ABSTRACT

Recently, much research on the evaluation of new cellulose sources has been developed. In this context, a promising source is "*napier grass*", which contains 30.40% lignin, 36.34% cellulose, and 34.12% hemicellulose. In this work, conditions for the delignification of "*napier grass*" in the laboratory were studied by using calcium oxide (CaO) and hydrogen peroxide (H_2O_2). The best pulping conditions were 9.00% CaO for a period of 2.73 h, which resulted in 74.99% delignification and 66.58% cellulose. The best conditions for the bleaching process were pH 12 and hydrogen peroxide at concentration of 4.2% for 6 h, at a temperature of 40 °C, which gave 90.98% delignification and 99.21% cellulose. The analyses were performed by using weight percent.

1. Introduction

Lignin, the phenylpropane polymer (C9 units) present in all plants, is one of the major components of lignocellulosic biomass such as sugar cane, corn, rice straws, bamboo, and "*napier grass*". However, the presence of lignin in biomass is a major problem in the cellulose polymer industry, which requires pure cellulose for the production of paper, cellulose-derived polymers, and fuels (López et al., 2011; Zhang et al., 2010).

In this context, many studies on biomass delignification have been carried out, and pulping methods have been the best solution to date, including Kraft pulping, soda pulping, organosolv-CO_2 pulping with basic hydrogen peroxide, and ozone pulping, among other basic processes. These studies are important when it comes to evaluating possible sources of potential new lignocellulosic matrices for attainment of cellulose derivatives from plant residues. (Gonzáles, Cantón, Rodrígues, & Labidi, 2008; Huang, Shi, & Langrish, 2008; López et al., 2010, 2011; Pereira et al., 2007; Xu, Li, & Zhang, 2007).

During the pulping process, the lignin polymer is more readily attacked than cellulose. As a consequence, delignification and purification of the latter compound occur mainly *via* oxidation and chlorination. Oxidation reaction can be achieved without addition of chemicals or oxygen, which makes this procedure a potential solution for the pre-treatment of large quantities of straw. Hemicelluloses are also attacked, thereby culminating in the pure cellulose that is used in the production of bioethanol, polymer derivatives, and composites. Particle size is very important in this context, since it reduces the attack and allows for utilization of reduced pressure. (Ziaie-Shirkolaee, Mohammadi-Rovshandeh, Rezayati Charani, & Khaheheian, 2008).

In this sense, the "*napier grass*" (*Pennisetum purpureum*) species belonging to the family Gramineae, subfamily Panicoideae tribe Paniceae, genus *Pennisetum* L. Rich, and species *P. purpureum* Schumacher is an interesting source of cellulose that is widespread in Brazil (Brunken, 1977).

In this context, this paper describes the effect of the pulping conditions (time and calcium oxide concentration) on the ash content of "*napier grass*" pulps as well as the optimization of the conditions for cellulose bleaching (hydrogen peroxide at different pH). The resulting pulp was analyzed, and the cellulose and lignin percentages were determined, in order to check the possibility of using this plant source for the attainment of cellulose derivatives.

2. Materials and methods

2.1. Materials

The "*napier grass*" obtained from Usina Coraci Destilaria de Álcool Ltda. was employed as lignocellulosic residue. Calcium oxide, hydrogen peroxide 30%, sodium hydroxide, potassium

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Table 1
Optimization of the pulping reaction conditions.

Percentage of CaO)	Reaction time (h)	Percentage of delignification (A)	Percentage of holocellulose (B)	Percentage of cellulose (C)
0	0	33.34 ± 0.05	65.00 ± 0.03	33.00 ± 1.02
3	1	59.66 ± 0.17	86.05 ± 0.11	53.05 ± 1.13
3	2	68.33 ± 0.78	88.97 ± 0.15	60.67 ± 0.55
3	3	73.69 ± 2.03	90.8 ± 0.08	67.55 ± 0.88
7.5	1	65.30 ± 0.98	88.33 ± 0.12	58.69 ± 0.97
7.5	2	9.78 ± 0.10	90.22 ± 0.13	75.45 ± 0.77
7.5	3	70.67 ± 1.15	92.13 ± 0.16	68.05 ± 0.68
12	1	74.66 ± 0.18	91.25 ± 0.05	58.43 ± 1.14
12	2	80.65 ± 0.77	93.00 ± 0.09	54.34 ± 1.28
12	3	84.16 ± 1.70	93.89 ± 0.04	51.28 ± 2.13

Table 2
Optimization of the conditions of the pulp bleaching process.

% H_2O_2	Time (h)	Percentage of delignification (A)	Percentage of holocellulose (B)	Percentage of cellulose (C)
0	0	62.87 ± 0.097	83.50 ± 0.71	90.01 ± 0.87
1	1	84.13 ± 0.64	94.67 ± 0.94	90.18 ± 1.62
3	1	85.21 ± 0.64	94.84 ± 0.23	99.37 ± 0.53
6	1	77.97 ± 0.43	93.50 ± 0.71	92.33 ± 0.04
1	3	77.66 ± 0.74	89.75 ± 0.35	96.40 ± 0.04
3	3	79.23 ± 0.62	94.5 ± 0.71	97.75 ± 0.25
6	3	83.93 ± 0.64	95.00 ± 0	96.80 ± 0.80
1	6	89.99 ± 0.76	96.67 ± 0.47	97.65 ± 0.30
3	6	88.91 ± 0.33	96.50 ± 0.24	97.87 ± 0.035
6	6	91.83 ± 0.45	97.83 ± 0.71	96.60 ± 0.20

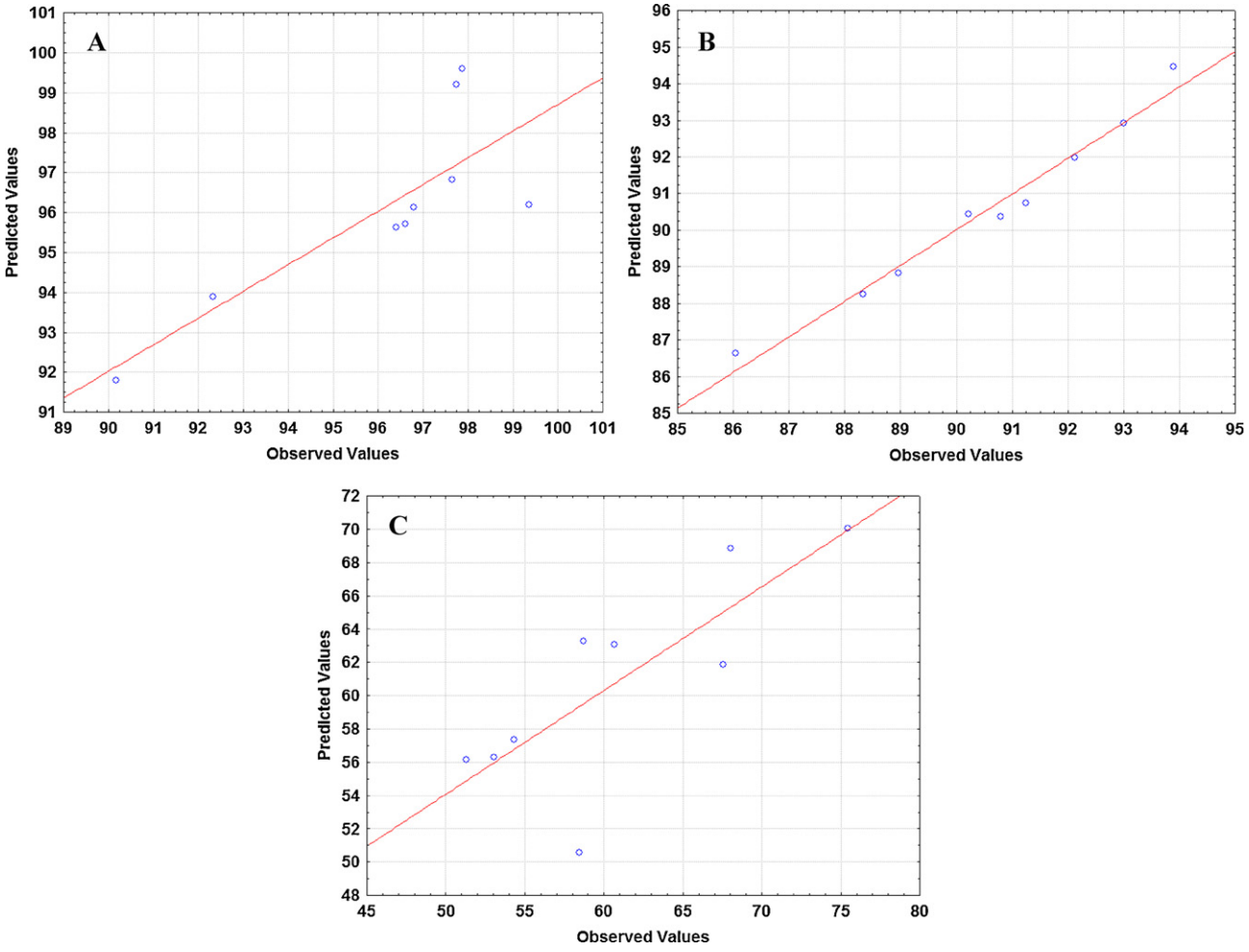

Fig. 1. A comparative plot between the experimental yield and the predicted yield as a function of the pulping reaction time (h) and CaO concentration (w). (A) Degree of delignification, (B) holocellulose percentage and (C) cellulose percentage.

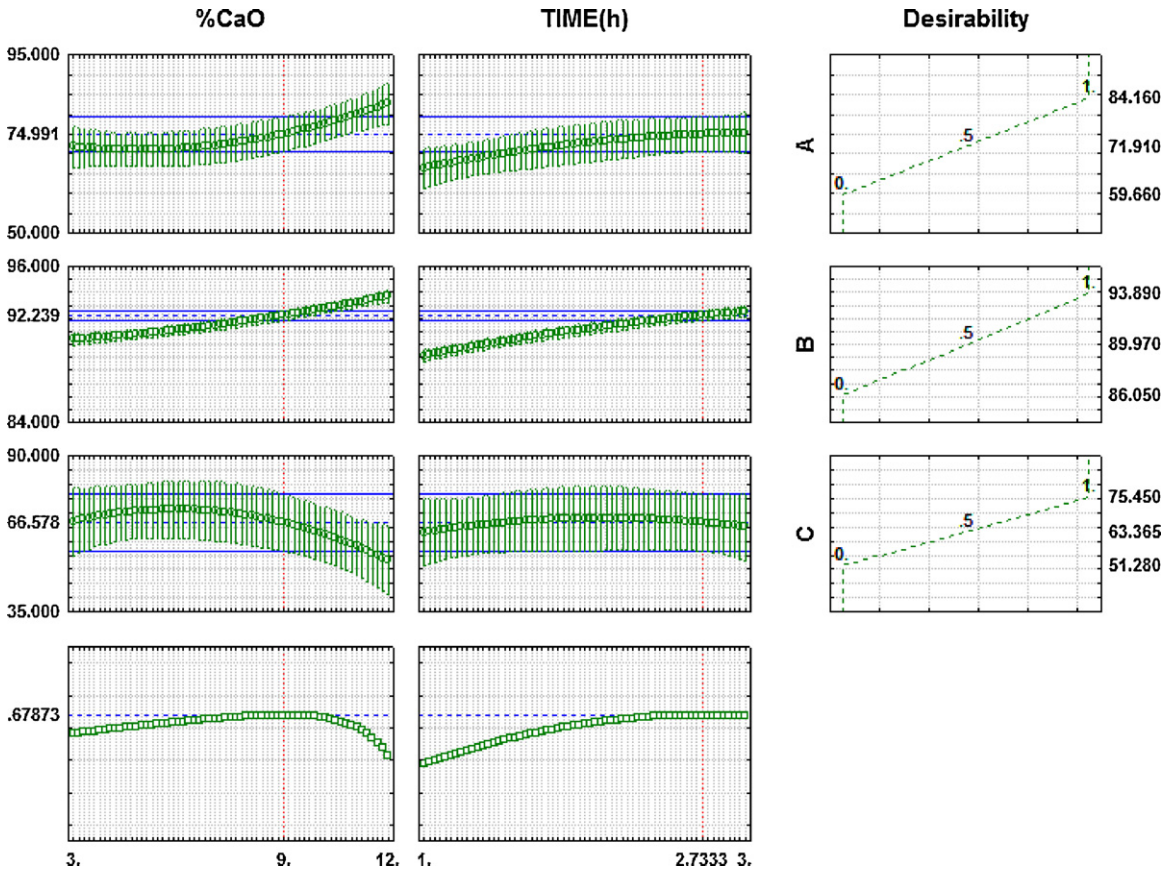

Fig. 2. Global analysis of the cellulose purification process using "*napier grass*", taking the independent and dependent variables into account.

hydroxide, and sulfuric acid 95.0–98.0% were purchased from Mallinckrodt (Baker, Xalostoc, Mexico).

2.2. Methods

For analysis of the source material, "*napier grass*" was dried at 70 °C ± 3 for 72 h, ground in a cutting mill by means of a one-millimeter screen, and analyzed before the pulping process. The α-cellulose (TAPPI 203 os-61, 1979), hollocellulose (Wise & Murphy, 1946), and lignin (TAPPI test method T222 os-76, 1979) contents of the starting material were determined. The results were used for establishment of the best conditions for cellulose pulping and bleaching.

The pulping process was carried out by using the dry plant material (300 g) crushed in a knife grinder and cooked in a batch reactor (5 L). The "*napier grass*" was placed in the reactor together with different concentrations of solid calcium oxide (3.00, 7.50, and 12.0%) and pulped for different time periods (1, 2, and 3 h) (Table 1). These mass concentrations and reaction times were employed for statistical analysis using a design with three levels and two independent variables. Three responses were obtained. Following pulping, the cooked material was washed until pH 7 for removal of the residual cooking liquor and dried at 70 °C ± 3 for 72 h. Pulping conditions: pressure = 2 atm, temperature = 125 °C ± 4, and pulp consistency = 30% (w/v). The volume of the solution used in each pulping with CaO was 3 L.

To perform the bleaching process, the pulping material was placed in a reactor (1 L) and subjected to bleaching with hydrogen peroxide at different concentrations (1, 3.5, and 6%), for different time periods (1, 3.5, and 6 h). The reaction temperature was 40 °C, the pH was 12, and the pulp consistency was 30% (Table 2). Following bleaching, the material was washed until pH 7, for removal of residual products, and dried at 70 °C ± 3 for 72 h. The same statistical design described above was utilized during evaluation of the best bleaching conditions, and the same responses were analyzed, namely degree of delignification and cellulose and holocellulose percentages. The model tested for the pulp and bleaching process was 3^2. The effects of reaction time as well as calcium oxide and hydrogen peroxide concentration on pulping and bleaching, respectively, were determined on the basis of the degree of delignification and holocellulose and cellulose percentages. In both cases, the best condition was considered to be the one that afforded the best delignification and the least pulp degradation (higher cellulose percentage), as revealed by Analysis of Variance (ANOVA). This analysis allowed for evaluation of whether the effect and the interaction among the investigated factors were significant with respect to the experimental error. The significance of the main factors and their interactions were assessed by the *F*-test method with a confidence level of 95% (Calado & Montogomery, 2003; Neto, Scarminio, & Bruns, 2007). Response surface methodology, a mathematical–statistical tool, was employed for modeling of the degree of delignification and holocellulose and cellulose percentages.

The material that had not been submitted to the pulping process and the pulp sample were gravimetrically analyzed for holocellulose, α-cellulose, and lignin yields. Scanning electron microscopy (SEM) of the materials was also accomplished.

3. Results and discussion

The first step involved in cellulose purification consisted in reducing material size in a cutting mill. Particle size was reduced

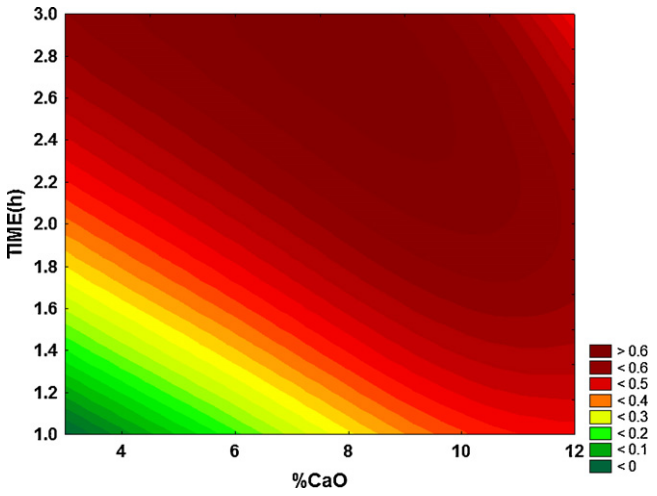

Fig. 3. Contours surface graph and contour surface for the optimization of CaO concentration and reaction time regarding the overall pulping process.

in order to facilitate reaction between calcium oxide and the lignocellulosic material. Particle size reduction is very important for conduction of the work; delignification is facilitated, and there is no need to apply high pressure in industrial processes.

CaO was selected for accomplishment of the pulping process because it provides diminished emission of contaminants (mainly odors), compared with the Kraft process, in which there is emission of sulfur compounds (Jiménez, Rodríguez, Serrano, & Moral, 2008).

The CaO concentration (w) employed in the "*napier grass*" pulping process was varied, in order to determine which pulping conditions would lead to the lowest residual lignin (A), holocellulose (B), and α-cellulose (C) possible. Table 1 summarizes the data from the pulping optimization. Each result is expressed as the arithmetic means of two replicate experiments. Characterization was conducted by gravimetric analysis, and the results from the pulping process were used for statistical analysis.

A preliminary analysis identified that a rise in time is more significant than the excessive increase in CaO concentration, enhancing fiber degradation.

Fig. 1 depicts the experimental values *versus* the predicted values using the model equations developed in this work. Analysis of the results evidences the normality of the residues, since all points are close to the expected values.

Eq. (1A) is related to analysis of the degree of delignification, Eq. (1B) corresponds to analysis of holocellulose percentage, and Eq. (1C) concerns analysis of the cellulose percentage. These equations were employed for prediction of the yield of cellulose purification as a function of time and CaO concentration. Effects with a statistical significance lower than 95%, as verified by the *F*-test, are not reported. Analysis of the graphs reveals good fit of the model, thus demonstrating its reliability. All the results were obtained by gravimetric analysis.

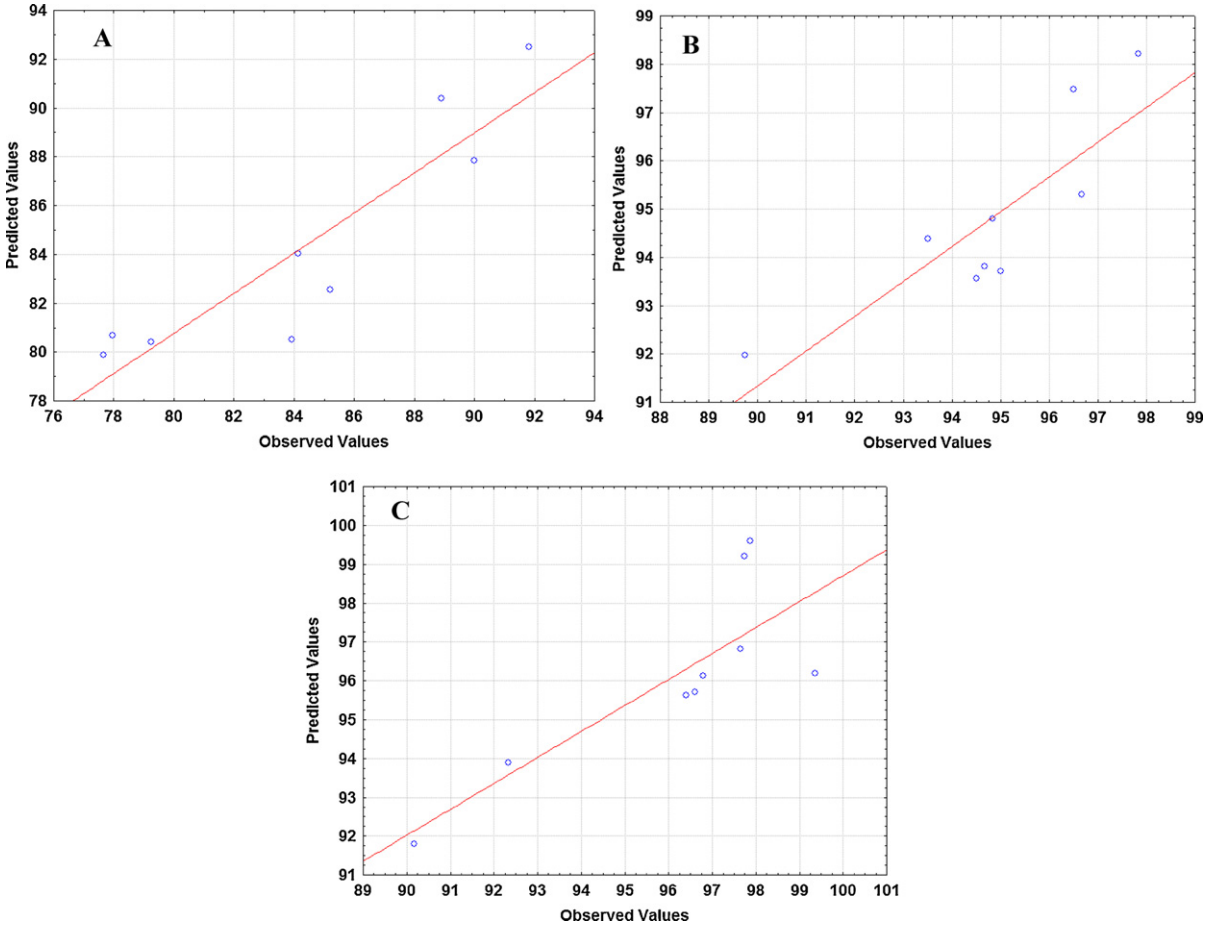

Fig. 4. A comparative plot between the experimental yield and predicted yield as a function of time (h) and H_2O_2 concentration (w). (A) Degree of delignification, (B) holocellulose percentage, and (C) cellulose percentage.

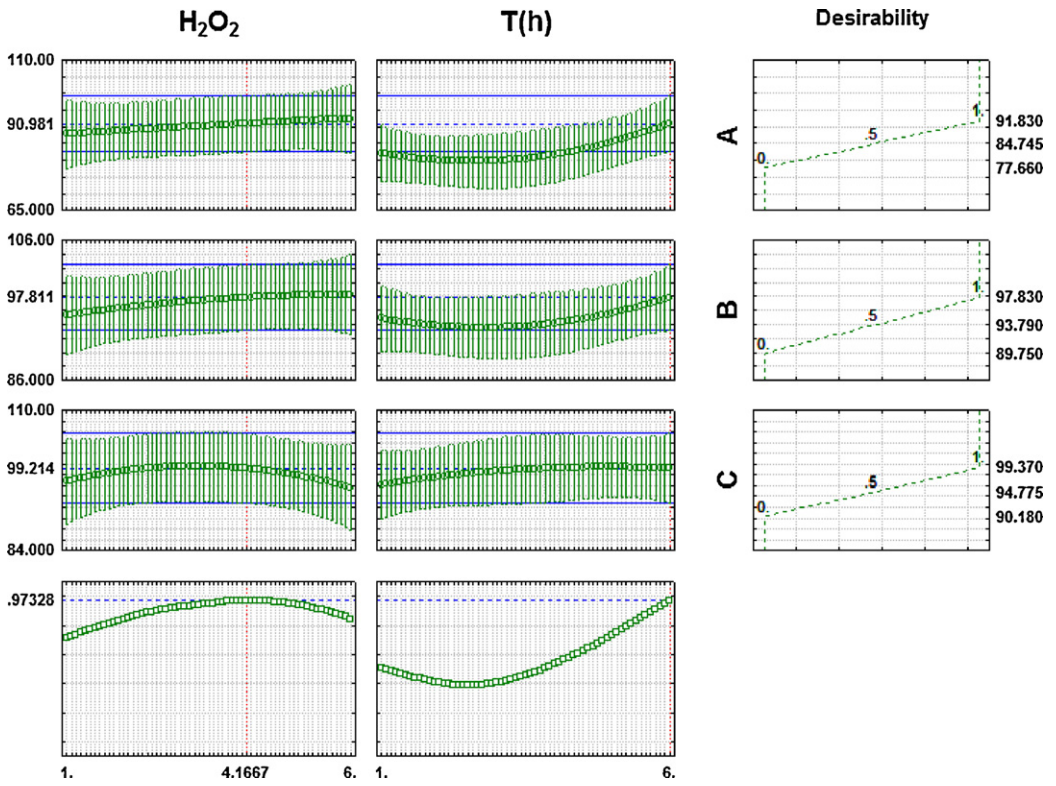

Fig. 5. Global analysis of the purification process of cellulose from "*napier grass*" taking the independent and dependent variables into account.

By using the statistical procedure described previously, the following Eq. (1A)–(1C) were obtained with r^2 at a confidence limit of 95%.

$$A = 51.677 - 1.538 \times [\mathrm{CaO}] + 14.144 \times T + 0.229 \times [\mathrm{CaO}] \times [\mathrm{CaO}] - 0.252 \times [\mathrm{CaO}] \times T - 1.860 \times T \times T \quad (r^2 = 0.968) \tag{1A}$$

$$B = 81.448 - 0.370 \times [\mathrm{CaO}] + 4.031 \times T + 0.021 \times [\mathrm{CaO}] \times [\mathrm{CaO}] - 0.117 \times [\mathrm{CaO}] \times T - 0.322 \times T \times T \quad (r^2 = 0.968) \tag{1B}$$

$$C = 7.965 + 9.059 \times [\mathrm{CaO}] + 27.719 \times T - 0.486 \times [\mathrm{CaO}] \times [\mathrm{CaO}] - 1.203 \times [\mathrm{CaO}] \times T - 3.978 \times T \times T \quad (r^2 = 0.851) \tag{1C}$$

Fig. 2 shows that high CaO concentrations favor delignification, but also enhance cellulose degradation. Thus, it is preferable to work with lower CaO concentrations (9.75%). As for duration of the pulping process, it can be noted that there is no significant increase in the degree of delignification after 2.5 h, so the use of longer reaction times is not justified. Moreover, prolonging the pulping procedure culminates in increased cellulose degradation, which is not desirable.

A rise in the cellulose content due to hemicellulose degradation was detected during pulping. This is because hemicellulose contains a smaller glycosidic chain and is therefore more easily cleaved into the monomers by action of CaO.

Examination of the results furnishes the response surface that describes the overall process (Fig. 3). The optimal pulping conditions were determined as being 9.75% CaO and reaction time = 2.5 h, which gave a degree of delignification of 76.24 ± 0.097% and a cellulose percentage of 59.97 ± 0.87%.

The best pH value to be utilized during the bleaching process in the presence of hydrogen peroxide was also established. The pH values of 10, 11, and 12 were tested, and the best results were obtained at pH 12. The hydrogen peroxide concentration and the reaction time were also optimized, as shown in Table 2. The parameters pH (12), pulp consistency (15), and reaction temperature (40 °C) were kept constant during the optimization study. The temperature of 40 °C was selected for the studies, since it was found that lower temperatures did not favor residual lignin elimination, whereas higher temperatures promoted hydrogen peroxide degradation, thereby

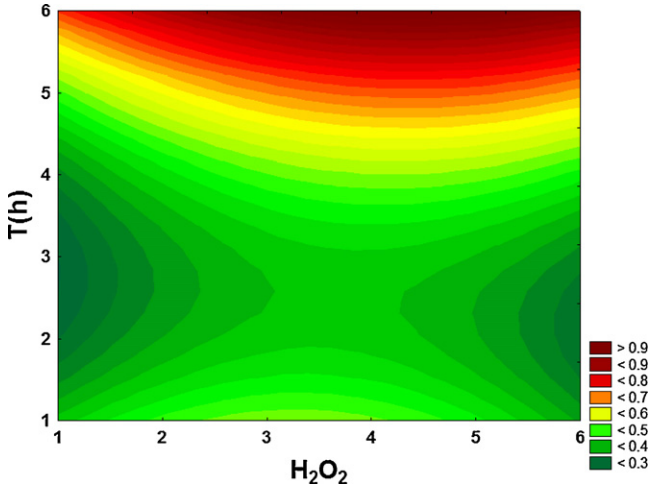

Fig. 6. Contours surface graph and contour surface by study of concentration and time for the optimization of the H_2O_2 concentration and reaction time regarding the overall pulping process.

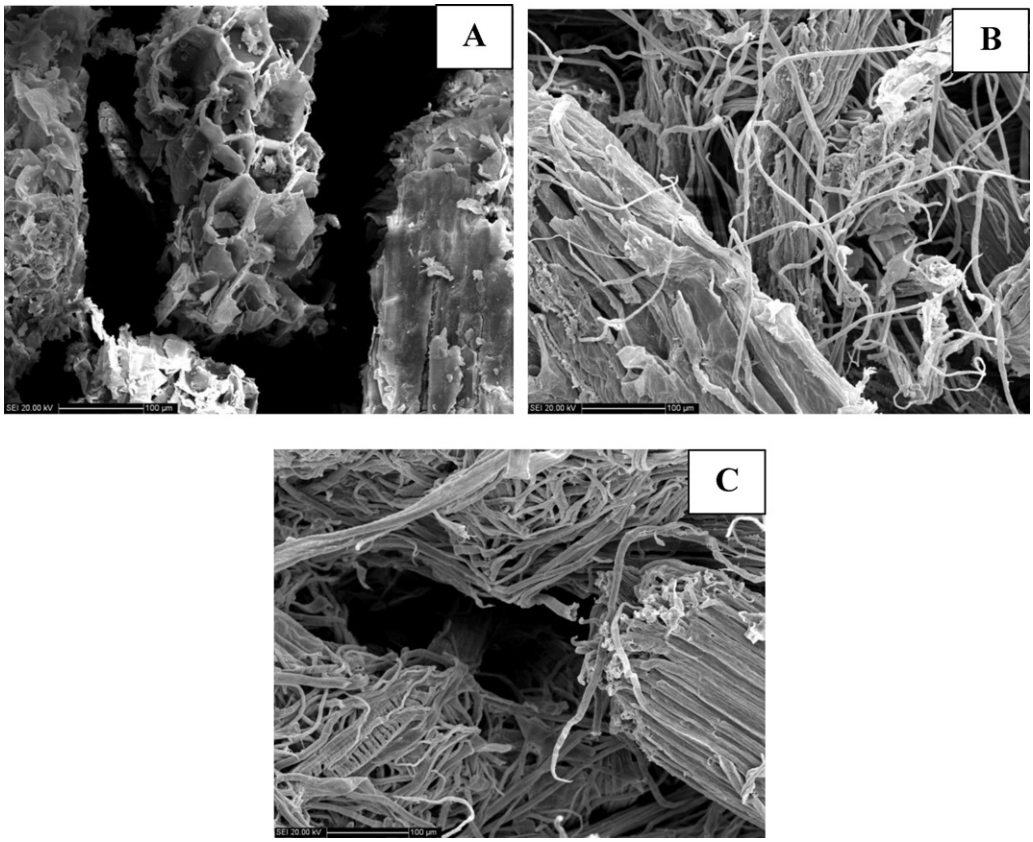

Fig. 7. Scanning electron microscopy image for the obtained materials: (A) starting material, (B) material after pulping, and (C) material after pulping + bleaching.

reducing the peroxide concentration available during the bleaching process.

Fig. 4 corresponds to the plot of experimental values *versus* the values predicted using the model equations developed herein.

Eq. (2A) is related to analysis of the delignification degree, Eq. (2B) corresponds to analysis of the holocellulose percentage, and Eq. (2C) refers to analysis of the cellulose percentage. These equations were utilized for prediction of the yield of cellulose purification as a function of time and hydrogen peroxide concentration. Effects with a statistical significance lower than 95%, as verified by the *F*-test, are not reported. Analysis of the graphs demonstrates considerable fit of the model, thus attesting to the reliability of the method. The times employed for the bleaching process were sufficient for achievement of effective delignification. r^2 values are described next to each equation obtained by statistical analysis.

$$A = 89.908 - 0.768 \times [H_2O_2] - 6.353 \times T - 0.032 \times [H_2O_2] \times [H_2O_2] + 0.320 \times [H_2O_2] \times T + 0.971 \times T \times T \quad (r^2 = 0.8217) \tag{2A}$$

$$B = 95.286 + 0.818 \times [H_2O_2] - 2.689 \times T - 0.114 \times [H_2O_2] \times [H_2O_2] + 0.093 \times [H_2O_2] \times T + 0.414 \times T \times T \quad (r^2 = 0.7212) \tag{2B}$$

$$C = 85.780 + 4.285 \times [H_2O_2] + 2.605 \times T - 0.534 \times [H_2O_2] \times [H_2O_2] - 0.128 \times [H_2O_2] \times T - 0.211 \times T \times T \quad (r^2 = 0.6684) \tag{2C}$$

Taking the results from the bleaching process optimization together, it can be concluded that the best conditions were 4.2% hydrogen peroxide and 6 h of reaction. This condition yielded a degree of delignification of 90.98% and a cellulose percentage of 97.33%. Analysis of these data shows that the use of higher peroxide concentrations is not justified, since the degree of delignification and the percentage of cellulose remain almost constant for hydrogen peroxide concentrations above the optimum concentration. As for the reaction time, prolonging the bleaching process does not significantly increase cellulose concentration (Fig. 5). These results are confirmed by analysis of the response surface graph obtained for the overall bleaching procedure (Fig. 6).

Considering all the results reported above, it is clear that pulp degradation during bleaching was low. Hence, the employed methodology is feasible, and "*napier grass*" is a potential source of cellulose.

In addition to the gravimetric analysis, the efficiency of the delignification and bleaching process was verified by scanning electron microscopy (SEM). Analysis of the microscopy images of the material subjected to drying only (Fig. 7A), the materials obtained after the pulping process (Fig. 7B), and the materials attained after the bleaching procedure (Fig. 7C) confirms that the purification process was efficient, since the fibers in the final material (pulped + bleached) were completely separated.

4. Conclusions

The abundant "*napier grass*" proved to be a promising source for the attainment of new products such as composites, biofuels, and cellulose derivatives like cellulose acetate. A degree of delignification of 90.98% and a final cellulose percentage above 97.33% were

achieved in the conditions optimized for the pulping and bleaching processes, with low degradation. Microscopy analysis confirmed that the final pulp had pure and preserved fibers, thus attesting to the efficiency of the employed procedures.

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