Desalination and Water Treatment
www.deswater.com

27 (2011) 66–71
March

1944-3994/1944-3986 © 2011 Desalination Publications. All rights reserved
doi: 10/5004/dwt.2011.2053

Obtaining polymeric composite membranes from lignocellulosic components of sugarcane bagasse for use in wastewater treatment

Simone Coelho Nakanishi[a], Adilson Roberto Gonçalves[a,*], George Rocha[a],
Maria de Lourdes Ballinas[b], Guillermo Gonzalez[c]

[a]*GCBM, Biotechnology Department, School of Engineering of Lorena, São Paulo University, Cx. Postal 116, 12600-000 Lorena, SP, Brazil*
Tel. +55 12 31595033; email: adilson@debiq.eel.usp.br
[b]*Facultad de Ciencias Quimicas, Universidad Autónoma de Chihuahua, Circuito Universitario S/N, Chihuahua, Chihuahua, Mexico*
[c]*Centro de Investigación en Materiales Avanzados, Miguel de Cervantes 120 Compl. Ind. Chih. 31109, Chihuahua, Chihuahua, Mexico*

Received 31 May 2010; Accepted 26 October 2010

ABSTRACT

Currently, several research groups and industries are studying applications for the residues from agrobusiness, other than burning them. Thinking about a better use for the sugarcane bagasse, this study aims to obtain membranes of cellulose acetate composite with oxidized lignin, both isolated from sugarcane bagasse. Thus, we obtain a product with higher commercial value, from a natural fiber, which has applications in water and effluent treatment, and further contributes to the maintenance of the environment. Macromolecular components of bagasse were separated by steam explosion pre-treatment and a basic treatment with NaOH. The pulp obtained was bleached and acetylated, and subsequently membranes of this cellulose acetate were synthesized, incorporating oxidized lignin to these membranes in order to increase the metal retention capacity of them. The acetylated material was analyzed by IR, confirming acetylation. Degree of substitution was determined by volumetry, resulting in a diacetate to the MA I condition and a triacetate to MA II condition. It was observed that for the material with a lower degree of acetylation, it has better incorporation of oxidized lignins. SEM, showed membranes with dense structure. Tests were conducted to evaluate metal retention, and the average capacity of removal was 16% Cu^{+2} in steady-state experiments.

Keywords: Cellulose-lignin membranes; Heavy-metal separation; Sugarcane bagasse utilization

1. Introduction

Brazil is the world leader in sugarcane production, processing around 572 million tons in the 2008/2009 season [1]. However, for each ton of sugarcane harvested, about 140 kg of bagasse are generated.

We know that today, the bagasse produced in the plants is harnessed as an energy source within the plant itself, making them self-sufficient in steam and electricity through the combustion of bagasse. However, there is a surplus, which estimates can reach 50% when using high-pressure boilers [2].

The main application studied today for the cellulose from sugarcane bagasse is in the production of the second generation ethanol. However, there are other possible applications, such as the production of cellulose derivatives, which have chemical and physical properties very peculiar enabling a range of applications.

This way, this study aims to obtain membranes of cellulose acetate composite with oxidized lignin, both isolated from sugarcane bagasse. Membranes are selective barriers that separate two phases and that restrict, in whole or in part, the transport of one or more chemical

---

*Corresponding author.

Presented at the VII Ibero-American Conference on Membrane Science and Technology (CITEM 2010), April 11–14, 2010, Sintra, Portugal

species in phases [3]. The lignin from sugarcane bagasse has a high chelating capacity that can be increased by oxidation. The chelating capacity is the ability in coordinating sites present in the molecule of a substance and cause the formation of ring compounds for complexing a metal ion [4]. Thinking of exploring this ability of lignin is that we want to incorporate oxidized lignins in the membranes for use in water and effluent treatment seeking removal of heavy metals.

Heavy metals represent the major industrial waste contamination of soils, plants and animals with severe toxic effects to humans and the environment. Thus, the study of alternatives in the treatment of effluents that meet economic and socio-economic industries expectations as well as the preservation of the environment is very important now a days.

2. Methodology

The bagasse used in this study was kindly supplied by Usina Vale do Rosário (Orlândia-SP).

2.1. Pulp obtaintion

1. Steam Explosion pre-treatment: performed on an industrial scale, under the conditions: 200°C (15 to 16 kgf/cm^2 pressure) for 7 min;
2. Alkaline Delignification: performed in a pilot scale in stirred reactor with a working volume of 70 l, at the following conditions: NaOH 1% (w/v), solid-liquid ratio (1:10), reaction temperature of 100°C for 1 h [5]. As initial material 7 kg of exploded bagasse was used. After cooling, the material was separated from black liquor by filtration and washed with water until neutral pH. The lignin-rich liquor was stored for the reactions of chemical modifications of this material;
3. Alkaline Extraction: performed in bench using 20g of the delignificated bagasse, under the following conditions: NaOH 5% (w/v), at 65°C for 1h with mechanical agitation. After extraction, the material was filtered and washed with distilled water until neutral pH;
4. Bleaching with H_2O_2: accomplished in bench, in polypropylene bags, containing H_2O_2 (6% m/m), 0.5% MgSO4 (w/w of dry pulp) and distilled water to achieve the consistency of 3%; a temperature of 70°C for 60 min [6].

At each stage, the material obtained was characterized by the mass percentage composition of major components, according to Rocha [7].

2.2. Obtaining and modification of lignin

Lignin was obtained by precipitation with sulfuric acid of the black liquor resulting from the dezincification step of bagasse. The modification of its structure, to increase their chelator capacity, was obtained by oxidation processes, both chemical and enzymatic.

1. Chemical oxidation: To 100 ml water were added 10 mg of lignin and 1 ml HCl 2N as a catalyst. The mixture was placed in a 250 ml flask connected to a condenser which generates reflux and heated to boiling, at which time 50 ml hydrogen peroxide 35% solution was added in the form of drops. The reaction was interrupted after 2 h. Oxidized lignin was filtered and washed with 2 l distilled water to remove acids and residual peroxide. Oxidized lignin was dried in an oven at 65°C.
2. Enzymatic oxidation was performed using two enzymes: a commercial laccase and a tyrosinase extracted from potatoes. The enzymatic oxidation were made in phosphate buffer 50 mmol/l (pH 7.6) and 1,4-dioxane, 3:1 (v/v), totalizing 30 ml, with 300 mg of lignin, 200 IU of enzyme, 0.1% glycerol and 30 ml/min O_2. The experiments are performed at room temperature for 5 h. At the end of the reaction, the mixture remaining in the flask is precipitated with HCl 0.1 mol/l, filtered and washed with distilled water and dried in an oven at 65°C.

2.3. Acetylation of pulp

Acetylation was conducted in glass ampoules with acetic acid, anhydrous acetic acid and H_2SO_4 in a reaction carried out with temperature control according to Muñiz [10]. After acetylation, the degree of acetylation of cellulose was determined by volumetry, according Thiebaud, et al. [8].

2.4. Synthesis of membranes

The membranes were synthesized by the method of evaporation-precipitation under controlled temperature and humidity, as Ballinas [9] and subsequently were analyzed by SEM and DMA.

2.5. Metal retention

Tests for metal removal from water were carried out in steady mode according to Muñiz [10]. Copper was analyzed by atomic absorption spectrometry.

3. Results and discussion

The bagasse “in nature” and the material obtained after each stage of its fractionation was chemically characterized on the content of cellulose, hemicellulose, lignin and ash. The results are shown in Table 1. After steam explosion, the content of hemicellulose greatly reduced as expected but after the alkaline delignification there was not the expected decrease in lignin content.

Other studies have reported obtaining a pulp with less than 8% of lignin after steam explosion and alkaline delignification [5,11]. Probably a redeposition of lignin in the pulp occurred, which was removed in the subsequent step of extraction.

Analyzing the chemical composition along with the yield of each step is possible to calculate the mass loss of each component in each stages of the treatment. The yield and the losses of each component by step are shown in Table 2. This way is easier to see that in the alkaline delignification, in which the loss of lignin should be greater, it did not happen. But, with the alkaline extraction done later, it was possible to remove 73% of the lignin and after bleaching, we obtained a material with 85.5% of cellulose and only 6.5% of residual lignin.

The original lignin precipitated from black liquor of delignification step of and lignin after changed, both chemically and enzymatically were analyzed by FTIR. The comparison of these lignins spectrums is shown in the Fig. 1.

The increase of the intensity in the region of 1700/cm corresponding to carbonyl shows the effective oxidation of the samples. However, peaks in the region of 1510/cm

Table 1
Mass percentage composition of major components

%	“in nature”	Steam explosion	Delignification	Extraction	Bleaching
Cellulose	43.27 ± 1.29	52.46 ± 0.23	66.11 ± 0.63	84.62 ± 0.21	85.54 ± 0.37
Hemicellulose	30.53 ± 0.08	10.05 ± 0.12	5.87 ± 0.04	3.59 ± 0.08	3.66 ± 0.02
Lignin	27.82 ± 0.49	35.24 ± 0.25	25.34 ± 0.19	9.10 ± 0.29	6.51 ± 0.03
Ash	1.35 ± 0.38	3.10 ± 0.11	3.88 ± 0.10	2.46 ± 0.56	3.54 ± 0.43
Total	102.97 ± 2.24	100.85 ± 0.71	101.20 ± 0.96	99.77 ± 1.14	99.25 ± 0.85

Table 2
Yield and loss of components

Step	Yield (%)	Loose of Components (%)			
		Cellulose	Hemicellulose	Lignin	Ash
Steam explosion	63	23.6	79.3	20.2	0.0
Alkaline delignification	60	24.4	65.0	56.9	24.9
Alkaline extraction	75	4.0	54.1	73.1	54.2
Bleaching with H_2O_2	95	4.0	3.1	32.0	0.0

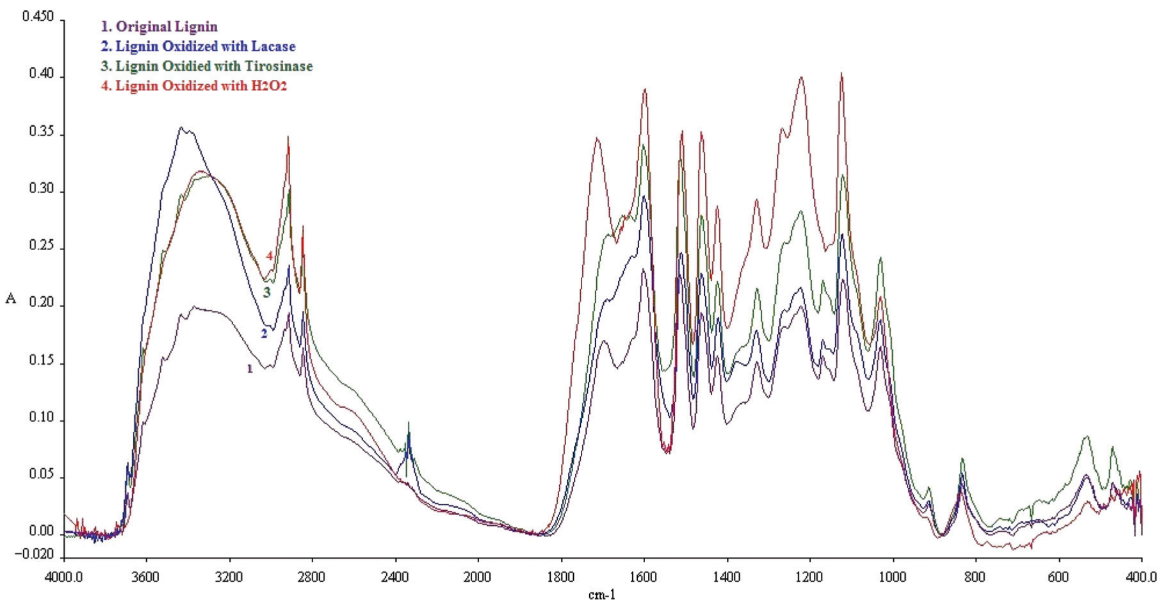


Fig. 1. Lignins FTIR spectrum.

corresponding to aromatic rings, indicates that the oxidation occurred but not so intense to open the aromatic rings.

After acetylation, two acetylated material with different degrees of incorporation of the functional group was obtained. One with 36% of acetyl incorporation and the other with 43%, corresponding to a diacetate (named MA I) and a triacetate (named MA II) respectively.

The evidence of the acetylation is shown by FTIR in Fig. 2, for both materials, by the presence of three major bands of ester linkages: 1750/cm (C=O ester), 1370/cm (symmetric deformation (–O (C=O)(CH$_3$)) and 1200–1250/cm (–CO-vibrations of the acetyl group) [12].

After acetylation, the OH groups of the cellulose chain are replaced by acetyl groups, which bind to the piranosidic ring structures forming ester structures. The replacement of OH groups was evidenced by the reduction of the bands around 3300/cm corresponding to OH stretching of cellulose.

The membranes were synthesized under controlled temperature and humidity, pre-set at 35°C and 70% relative humidity, with the acetylated cellulose from sugarcane bagasse and composite with the lignins, original and oxidized, also extracted from the sugarcane bagasse.

It was observed that the material with lower degree of acetylation (MA I) had better incorporation of oxidized lignins due to the affinity they have for less polar materials. So, MA I (diacetate) yielded membranes with better mechanical properties than the membranes synthesized with MA II (triacetate). The membranes produced with MA II showed no resistance, breaking up at the touch of hands, precluding the determination of its Young's modulus.

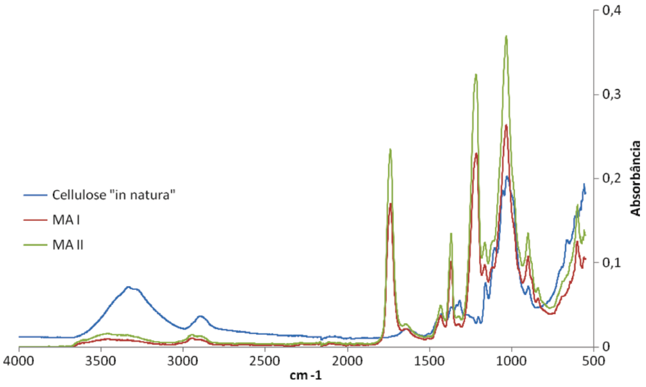


Fig. 2. Comparative IR of cellulose and acetilated cellulose.

Problems with the fragility of membranes prepared from cellulose triacetate obtained from cellulose of sugarcane bagasse have already been reported by other authors [13,14].

Table 3 shows the maximum stress (the maximum force which supports the material before rupture) and Young's modulus for each of the membranes synthesized with MA I in addition to the data for a membrane from a commercial triacetate, synthesized at the same conditions the ones prepared with the material from sugarcane bagasse.

The Young's modulus measures the resistance of the material to elastic deformation. It is a measure of its stiffness. The lower the value of the module, the more elastic is the material behavior when subjected to mechanical stress. All membranes synthesized showed values of Young's modulus greater than the membrane synthesized from commercial triacetate, indicating that they are more rigid and probably not so resistant to the high pressures flow usually applied in separation processes using membranes from cellulose acetate. However, the membranes synthesized with cellulose acetate from sugarcane bagasse resisted a high value of maximum stress, even highest than the one achieved for the membrane of commercial triacetate of cellulose. Highlight the composite membrane with original lignin, which showed a value of Young's Modulus and Maximum Stress very close to the membrane of commercial triacetate.

After structural characterization, the membranes were tested for their chelating capacity. Tests were performed at steady state in which the membranes were placed in a solution of known concentration of copper (50 ppm) with constant stirring for two hours and determined the percentage removal of copper by atomic absorption analysis of copper concentration in the initial and final solution.

Table 4 shows the results in % removal and chelating capacity in mg Cu^{2+} retained/g lignin present in the membrane fraction used.

Table 3
Mechanical properties of the synthesized membranes

	Membranes	Young's modulus (GPa)	Maximum stress (MPa)
35°C/70% hum.	Commercial cellulose triacetate	0.74	46.3
	MA I Pure	2.00	47.8
	MA I + Original lignin	1.00	49.1
	MA I + lignin Oxidized with H_2O_2	2.00	53.6
	MA I + lignin Oxidized with Lacase	2.00	57.3
	MA I + lignin Oxidized with Tirosinase	1.00	39.1

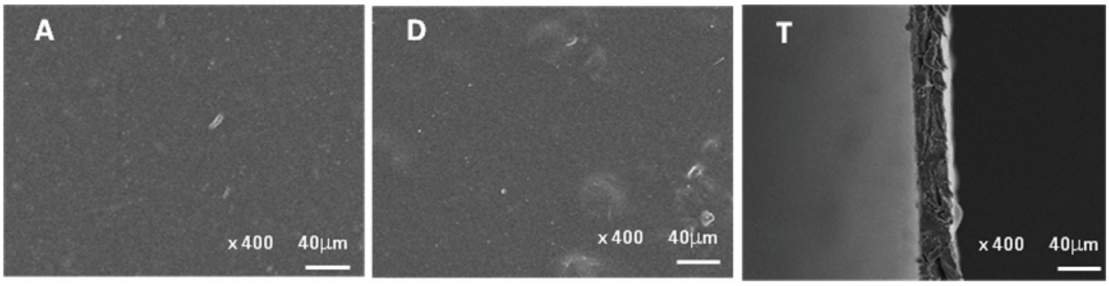
Table 4
Removal capacity of membranes

	Membranes	% Removal	Chelating capacity [mg Cu^{2+} retained/g lignin]
35°C/70% hum.	MA I Pure	16.5	59.4
	MA I + Original lignin	15.0	49.5
	MA I + lignin Oxidized with H_2O_2	18.3	60.7
	MA I + lignin Oxidized with Lacase	16.2	47.4
	MA I + lignin Oxidized with Tirosinase	13.9	44.1

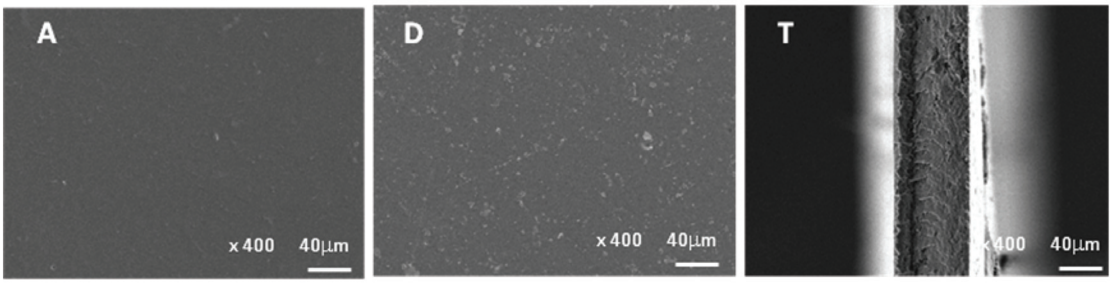
The membranes were able to adsorb on average 16% of copper in solution, which represents a chelating capacity around 52 mg Cu^{2+} retained/g lignin. It is worth remembering that the membrane prepared with pure MA I contains a significant amount of lignin (6.5%) which is present as residual lignin in the cellulose pulp. This residual lignin has also been taken into account for calculation of chelating capacity for all other membranes. The composite membrane with original lignin, which showed the most promising mechanical characteristics, also showed good removal capacity.

It's not possible to say which of the membranes has better chelating ability because the test was performed without replicates. However, these membranes have a good average capacity of retention, in the same order obtained for the retention of oxidized lignins from basic treatment of sugarcane bagasse when tested in separation columns.

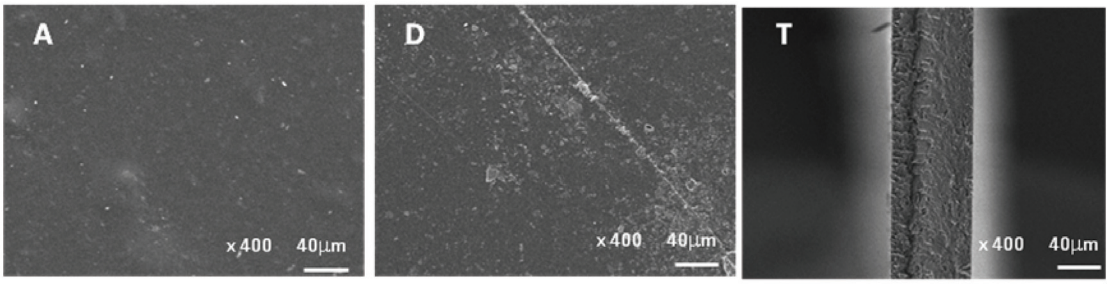
All membranes synthesized were also analyzed by SEM, at magnifications of 400× and 3000×, showing membranes with dense structure and good dispersion of incorporated lignin. Fig. 3 shows the SEM of each side



1. **MA I** Pure (35°C/ 70% humid.)



2. **MA I** + Original lignin (35°C/ 70% humid.)



3. **MA I** + lignin oxidized with H_2O_2 (35°C/ 70% humid.)

Fig. 3. Micrographs of membranes with different compositions (A – Active side; D – Dense side; T – Cross section).

and the cross section, at magnification of 400×, of the membranes that showed better results for mechanical properties and chelating capacity.

4. Conclusions

The treatments applied to the bagasse enable to obtain a pulp of good quality, with only 6.5% of residual lignin. It was found by IR analysis an effective acetylation of fibers, resulting in a diacetate to the MA I condition and a triacetate to MA II condition. It was observed that for the material with a lower degree of acetylation, it has better incorporation of oxidized lignins due to affinity they have to less polar materials. Therefore, MA I yielded membranes with better mechanical properties than the membranes synthesized with MA II. With cellulose from sugarcane bagasse was possible to synthesize cellulose acetate, and from this, dense composite membranes with lignin, also extracted from the sugarcane bagasse, with average capacity of 16% removal of copper ions when tested in steady state.

References

[1] Information on: http://www.agricultura.gov.br

[2] Information on: http://www.ipt.br/institucional/imprensa/midia/?ID=5864

[3] A.C. Habert, C.P. Borges and R. Nobrega, Processos de Separação por Membranas, Ed. COPPE/UFRJ, Rio de Janeiro-RJ, Brazil, (1997).

[4] G.M.M. Calabria and A.R. Gonçalves, Oxidação enzimática da lignina utilizando a enzima polifenoloxidase extraída de batata, In: IV Seminário Brasileiro de Tecnologia Enzimática, Rio de Janeiro, RJ (2004), Abstracts p. 222.

[5] F.T. Silva, Obtenção de insumos químicos a partir do aproveitamento integral do bagaço de cana, PhD Thesis, Instituto de Química-UNICAMP, Campinas, SP, Brazil (1995).

[6] M.L. Bianchi, "Branqueamento de polpas kraft com H_2O_2 ereação de oxidação de compostos modelos de ligninas catalisadas por polioxometalatos" PhD Thesis, Instituto de Química-UNICAMP, Campinas, SP, Brazil (1999).

[7] G.J.M. Rocha, Deslignificação de bagaço de cana de açúcar assistida por oxigênio, PhD Thesis, University of São Paulo, São Carlos, SP, Brazil (2000).

[8] S. Thiebaud, M.E. Borredon, G. Baziard and F. Senocq: Bioresource Technol., 59 (1997) 103–107.

[9] L. Ballinas, L.P. Terrazas, R. Gómez, M. Mendoza, L. Manjarrez and G. González, Polym. advan. Technol., 17 (2006) 991–999.

[10] G. Muñiz, L.A. Manjarrez, J. Prado, A. Ramírez, V. Muñoz, L. Ballinas and G. Sánchez. In: Natural Arsenic in Ground waters of Latin America. Arsenic in the Environment, Chapter 71, Vol. 1. CRC Press (2008).

[11] L.R.M. Oliveira, Estudo de alternativas viáveis de pré-tratamento e hidrólise do bagaço e palha de cana-de-açúcar para obtenção de etanol a partir de celulose, PhD Report nr 1, FAPESP fellowship, contract 2006/07183-0 (2008).

[12] J.E. Mark, Polymer Data Handbook, Oxford University Press Inc., (1999).

[13] G. Rodrigues Filho, S.F. Cruz, D. Pasquini, D.A. Cerqueira, V.S. Prado and R.M.N. Assunção, J. Membr. Sci., 177 (2000) 225–231.

[14] C.S. Meireles, Síntese e caracterização de membranas de acetato de celulose, obtido do bagaço de cana-de-açúcar, e blendas de acetato de celulose com poliestireno de copos plásticos descartados, MSc Dissertation, Instituto de Química, Universidade Federal de Uberlândia, MG (2007).