Carbohydrate Polymers 74 (2008) 617–620

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Adsorption of sulphate ions by modification of sugarcane bagasse cellulose

Daniella Regina Mulinari [a,*], Maria Lúcia C.P. da Silva [b]

[a] *Departamento de Materiais e Tecnologia, Faculdade de Engenharia de Guaratinguetá, Av. Dr. Ariberto Pereira da Cunha, 12516-410 Guaratinguetá, São Paulo, Brazil*
[b] *Departamento de Engenharia Química, Escola de Engenharia de Lorena, 12600-000 Lorena, São Paulo, Brazil*

ARTICLE INFO

Article history:
Received 10 September 2007
Received in revised form 3 April 2008
Available online 16 April 2008

Keywords:
Modified sugarcane bagasse
Adsorption
Cellulose/hydrous zirconium oxide

ABSTRACT

This work describes the preparation of sugarcane bagasse cellulose with zirconium oxychloride for adsorption of sulphate ions in aqueous solution. The materials were prepared by using an ammonium solution as precipitating agent. The obtained materials were characterized by thermogravimetry, scanning electron microscopy and surface area measurements. Sulphate ion was adsorbed on the Cell/$ZrO_2 \cdot nH_2O$ by immersing this solid in an aqueous solution of sulphate sodion. The analyses to determine the concentration after the adsorption were made using UV–vis spectrum, in a wavelength of 420 nm. The results were satisfactory showing that the Cell/$ZrO_2 \cdot nH_2O$ materials obtained presented good adsorption capacity. The adsorption capacity was 0.4 mol g^{-1} for both materials.

1. Introduction

Sulphate is a major ion occurring in natural waters and wastewaters. The main natural source of sulphate in surface and ground water is the processes of chemical weathering and dissolution of sulphur-containing minerals. Other natural sources are the oxidation of sulphides and elemental sulphur, and the decomposition of animal and plant residues. Sulphur is a nutrient essential for the synthesis of proteins and it is released upon their degradation (Radojevic & Bashkin, 1999).

Measurement of sulphate is a crucial step in environmental monitoring, regulatory inspection and compliance, especially in the treatment of mining-influenced waters. Determination of sulphate is useful in assessing the redox state of the system because sulphur is a critical element in controlling the fate and solubility of polluting elements in the aquatic environmental (Baird, 1995).

Sulphate ions are measured using many direct and indirect analytical principles including ion chromatography (IC), inductively coupled plasma absorption spectrophotometry (ICP-AES), turbidimetric, colorimetric and gravimetric methods (Morais, Souto, Lopes, & Rangel, 2003; Reisman, Sundaram, Al-Abed, & Allen, 2007). However, the turbidimetric method is very rapid, where an excess of barium chloride is added to the sample. The barium ion reacts with the sulphate to precipitate barium sulphate. The colloidal suspension is measured using a spectrophotometer and the sulphate concentration determination by comparison with standards (Radojevic & Bashkin, 1999).

Agricultural residues have been used for production starting materials. Reusing and recycling these residues can minimize the environmental problems associated with their build-up reducing the use of noble starting materials. This trend has contributed to the reconsideration of the use of traditional biomaterials such as natural fibers to substitute synthetic polymers.

Sugarcane bagasse is a residue produced in large quantities by sugar and alcohol industries. According to Cerqueira, Rodrigues Filho, and Meireles (2007), 1 ton of sugarcane generates 280 kg of bagasse and 3×10^8 tons of sugarcane is processed annually in Brazil. About 80% of this residue is used in distillery plants as a source of energy (Pandey, Soccol, Nigam, & Soccol, 2000). Thus, on account of the importance of bagasse sugarcane as an industrial waste, there is a great interest in developing chemical methods for recycling it. Sugarcane bagasse has around 50% cellulose, 27% polyoses, and 23% lignin. These three biological polymers have many hydroxyl and/or phenolic functions that can be chemically reacted to produce materials with new properties (Pasquini, Belgacem, Gandini, & Curvelo, 2006; Rodrigues Filho et al., 2000; uma, Silva, & Meireles, 2005).

Cellulose, the most abundant of all naturally occurring substances, is the principal structural cell wall component of all major plants and accounts for about a half of the total bagasse. It is nontoxic, renewable, biodegradable and modifiable, and has great potential as an excellent industrial material. Chemical modification of cellulose is one method for the production of value added products. It is based on reactions of the free hydroxyl groups in the anhydroglucose units, resulting in the production of cellulose derivatives (Karnitz et al., 2007; Liu et al., 2007a,b).

Despite many studies of the chemical modification of cellulose published around the world in this area, only a few have been investigated about the modification of sugarcane bagasse (Liu, Sun, Zhang, Ren, & Geng, 2006; Liu et al., 2007a,b).

---

[*] Corresponding author. Tel.: +55 12 31232865; fax: +55 12 31232852.
E-mail address: pos07002@feg.unesp.br (D.R. Mulinari).

0144-8617/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2008.04.014

In the present work, we describe the chemical modification of sugarcane bagasse cellulose and evaluation to adsorb sulphate ions in aqueous solution.

2. Experimental

2.1. Isolation crude cellulose from sugarcane bagasse

To isolate the cellulose, the sugarcane bagasse was pretreated with 10% sulphuric acid solution (reactor of 350 L at 120 °C, 10 min), followed by centrifugation with the purpose of separating the rich pentosanes solution. Extracted lignocellulosic fraction was deslignificated with 1% sodium hydroxide solution (reactor of 350 L at 100 °C, 1 h) being obtained the crude pulp and bleached with sodium chloride. Furthermore the bleached cellulose dried in a store at 50 °C, 12 h (Rocha, 2000).

2.2. Preparation of the hydrous zirconium oxide

Five grams of zirconium oxychloride were dissolved in 100 mL of aqueous hydrochloric acid solution (0.5 mol L^{-1}). The precipitate was obtained adding an ammonium solution (1:3) at pH 10.0, under stirring, which was filtered, rinsed several times with distilled water for the complete removal of chloride ions (negative silver nitrate test). Finally, the product was dried at 50 °C for 24 h.

2.3. Preparation of the cellulose/hydrous zirconium oxide hybrid materials

About 2 g of zirconium oxychloride were dissolved in 100 mL of aqueous hydrochloric acid solution (0.5 mol/L) and 5 g of cellulose were immersed in this solution. The material was precipitate with ammonium solution (1:3) at pH 10.0 and under stirring. The solid after being exhaustively washed with distilled water and the residual solvent was removed under vacuum. The product was dried at 50 °C for 24 h. The resulting material was designated as Cell/$ZrO_2 \cdot nH_2O$ (2 g). The preparation was repeated using the same procedure, but changing the amount of the metal oxide precursor reagent, i.e., 3 g of zirconium oxychloride.

2.4. Adsorption sulphate ions in the cellulose/hydrous zirconium oxide hybrids materials

About 0.2 g of Cell/$ZrO_2 \cdot nH_2O$ material was shapen for 5 min at 298 K in 50 mL of Na_2SO_4 solution whose initial concentrations varied between $0.5.10^{-4}$ and 5.10^{-4} mol L^{-1}. The amount of sulphate in the supernatant solution was determined using turbidimetric method by UV–vis absorption spectra, in the wavelength at 420 nm. The amount of adsorbed sulphate ions was determined by applying the equation Pavan, Francisco, Landers, & Gushikem 2005):

$$N_f = \frac{N_i - N_s}{m} \tag{1}$$

where N_i and N_s are the initial and equilibrium condition mol number of sulphate sodium and m is mass of the solid.

2.5. Characterization of the materials

The materials were characterized by thermogravimetry, scanning electron microscopy and surface area measurements. Thermogravimetry (TG) measurements were obtained in a Shimadzu thermogravimetric instrument model TGA-50. Thermal behavior for each one of the preparations was studied by recording the TG/DTG curves between 40 and 800 °C rates under nitrogen atmosphere using weighted samples between 5 and 10 mg with a heat rate of 20 °C min^{-1} in N_2 atmosphere. Surface area measurements (BET) were obtained in a Quantachrome instrument model NOVA 1000 in nitrogen atmosphere, followed by pre-treatment at 50 °C for 3 h of samples. Micrographs (SEM) were obtained in a scanning electron microscope LEO1450 V using low vacuum, in backscattered electrons for the cellulose and hybrids materials. Samples were dispersed on a brass support and fixed with a double face 3 M tape.

3. Results and discussion

Cell/$ZrO_2 \cdot nH_2O$ hybrids materials were obtained with a satisfactory degree of coated with oxide on the cellulose surface. The amount of $ZrO_2 \cdot nH_2O$ incorporated into the Cell/$ZrO_2 \cdot nH_2O$ hybrids materials were determined calcining 0.3 g of sample at 1173 K in air for 3 h and weighing the residue (Table 1).

The deposited hydrous zirconium oxide is amorphous because the specific surface area, S_{BET}, increased from 0 $m^2 g^{-1}$ (see Table 1) in pure cellulose to 57 $m^2 g^{-1}$ for the material Cell/$ZrO_2 \cdot nH_2O$.

These effects can be confirmed by TG curves. TG curves obtained of materials are presented in Fig. 1. Curve 1A corresponds to bleached cellulose, curve 1B to hydrous zirconium oxide and curves 1C and 1D to the hybrids materials. Bleached cellulose present two decomposition steps: first at 300 °C corresponds to degradation temperature and second one at 380 °C corresponds to decomposition temperature completed. Cell/$ZrO_2 \cdot nH_2O$ (2 g) hybrids materials show two different steps in relation to bleached cellulose: one at 260 °C and the other one at around 338 °C. Cell/$ZrO_2 \cdot nH_2O$ (3 g) is similar to Cell/$ZrO_2 \cdot nH_2O$ (2 g). This progressive decrease in temperature of hybrids materials in relation to bleached cellulose may be attributed to the presence of the dispersed oxide particles on cellulose surface, indicating a strong interaction between hydrous zirconium oxide and cellulose fibers The condition of the preparation of hybrid materials (acid medium at the beginning and basic medium in the end) did not degrade the cellulose fiber, because it is known that the cellulose degradation

Table 1
Quantity of $ZrO_2 \cdot nH_2O$ incorporated on cellulose surface

Samples	$ZrO_2 \cdot nH_2O$ incorporated (wt%)	S_{BET} (m^2/g)
Cellulose	–	0
$ZrO_2 \cdot nH_2O$	–	254
Cell/ $ZrO_2 \cdot nH_2O$ (2 g)	3.66	36
Cell/ $ZrO_2 \cdot nH_2O$ (3 g)	5.45	57

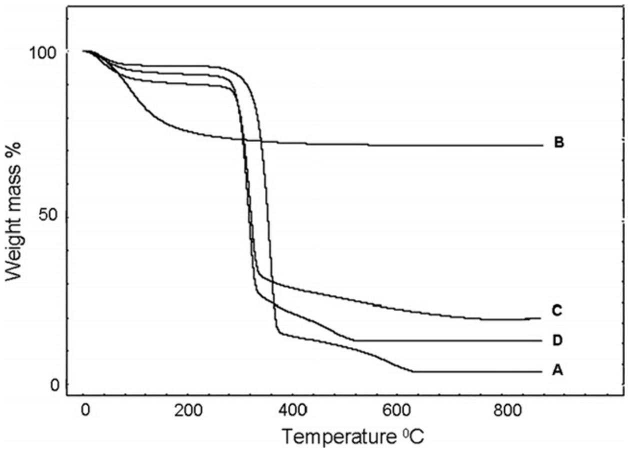

Fig. 1. TG curves: (A) pure cellulose; (B) $ZrO_2 \cdot nH_2O$; (C) Cell/$ZrO_2 \cdot nH_2O$ (2 g); (D) Cell/$ZrO_2 \cdot nH_2O$ (3 g).

occurs at pH 10 (Borgo & Gushikem, 2002). Due to this, during the process, care was taken not to pass this pH. (Mulinari, Da Silva, & Da Silva 2006). Toledo, Gushikem, and Castro (2000) studied the antimony (III) oxide film on a cellulose fiber surface and it was observed similar results.

Table 2 shows the values of percentage mass loss in the respective temperature range and residue occurred in the materials.

TG curve of the pure cellulose presents a higher mass loss in relation to the hybrids materials in temperature range 200–500 °C, due to the presence of metallic oxide in the cellulose surface. Comparing TG curves of the pure cellulose with of hydrous metallic oxide in this temperature range, was observed that the oxide present a lesser mass loss in relation the pure cellulose, therefore the pure cellulose was practically all degraded while that the oxide presented a 71% residue. It was also observed that the amount of residue in the hybrids materials increased, due to the amount of $ZrOCl_2{\cdot}8H_2O$ in the reactional system. The residue of each hybrid material presents the amount of oxide which was not degraded.

By means of the TG curves can be calculated the amount of grafted material in hybrids materials. Table 3 shows the percentages of $ZrO_2{\cdot}nH_2O$ grafted in the cellulose, being that the loss mass corresponds to the interval of 200–300 °C (see Fig. 1), where occurred higher loss mass.

It was also observed that the Cell/$ZrO_2{\cdot}nH_2O$ (3 g) presented a higher grafted that the Cell/$ZrO_2{\cdot}nH_2O$ (2 g) with an increase of approximately 92%.

The results were confirmed by scanning electron microscope (SEM). The bleached cellulose micrograph (Fig. 2A) shows a great amount of fibers presents forms flattened while the hydrous zirconium oxide (Fig. 2B) presents as a porous agglomerates. Fig. 2C and D shows the hydrous zirconium oxide dispersed on the surface of the fibers cellulose. However, it is noticed that the oxide was not deposited of a uniform way on the surface fibers cellulose. As expected, it was observed an increase of oxide in the Cell/$ZrO_2{\cdot}nH_2O$ (3 g) (Fig. 2D).

After the characterization of materials, it was determined the amount of sulphate ions incorporated on the Cell/$ZrO_2{\cdot}nH_2O$ hybrids materials surface.

Figs. 3 and 4 show the adsorption isotherm of sulphate ions on the Cell/$ZrO_2{\cdot}nH_2O$ hybrids materials surface, determined at 298 K. At the limit of saturation of the surface, the maximum adsorption capacity of sulphate ions was 0.4 mol g^{-1} for both materials.

Table 2
Results of the thermogravimetrics curves of the materials, with the losses mass (m), in the respective range of temperature (ΔT) and its respective residues (R)

Material	m (%)	ΔT (°C)	R (%)
Cellulose	4.7	40–200	2.8
	83.9	200–500	
	8.6	500–800	
$ZrO_2{\cdot}nH_2O$	28.3	40–500	71.1
	0.6	500–800	
Cell/$ZrO_2{\cdot}nH_2O$ (2 g)	7.1	40–200	12.3
	77.7	200–500	
	2.9	500–800	
Cell/$ZrO_2{\cdot}nH_2O$ (3 g)	9.7	40–200	19.1
	64.3	200–500	
	6.9	500–800	

Table 3
Percentages of grafted materials in the Cell/$ZrO_2{\cdot}nH_2O$

Material	Initial mass (mg)	Loss mass (mg)	Final mass (mg)	Grafted material (%)
Cell/$ZrO_2{\cdot}nH_2O$ (2 g)	4.2	3.3	0.9	29
Cell/$ZrO_2{\cdot}nH_2O$ (3 g)	5.0	3.2	1.8	55

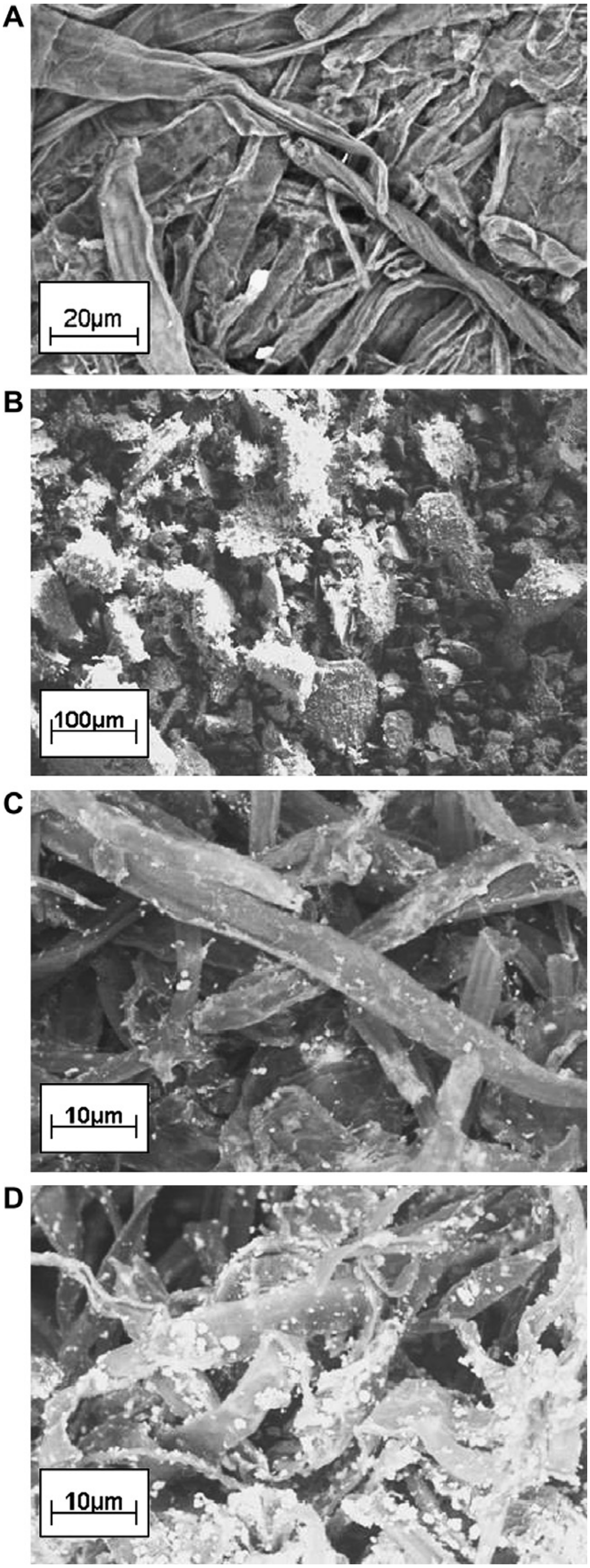

Fig. 2. Micrographs: (A) pure cellulose; (B) $ZrO_2{\cdot}nH_2O$; (C) Cell/$ZrO_2{\cdot}nH_2O$ (2 g); (D) Cell/$ZrO_2{\cdot}nH_2O$ (3 g).

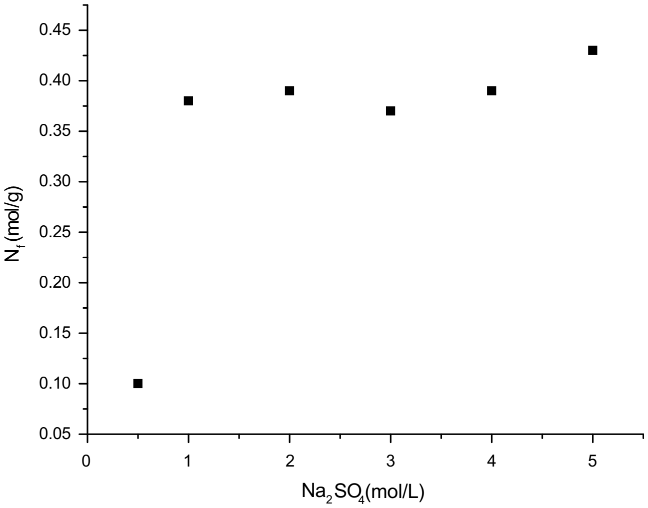

Fig. 3. Adsorption of sulphate ions on the Cell/$ZrO_2{\cdot}nH_2O$ (2 g).

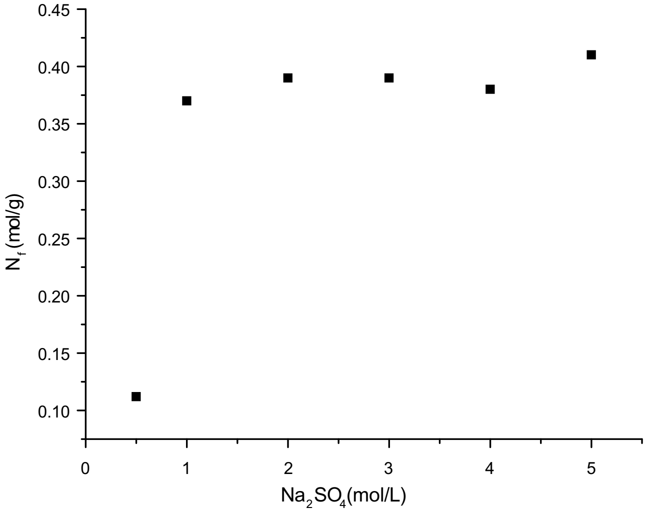

Fig. 4. Adsorption of sulphate ions on the Cell/$ZrO_2{\cdot}nH_2O$ (3 g).

Under such conditions, assuming that all the ZrO_2 particles dispersed on the cellulose surface reacted with sulphate ions, the adsorption process may occur by reaction of sulphate ions and the zirconium reactive center, designated as Zr-OH, can be expressed as follows (Suzuki, Bomani, Matsunaga, & Yokoyama 2000):

Protonation at lower pH

$$\mathrm{Cell/Zr{-}OH_{(sol)}} + \mathrm{H^+} \rightarrow \mathrm{Cell/Zr{-}OH_2^+} \tag{2}$$

Followed by bonding of a sulphate ion

$$\mathrm{Cell/Zr{-}OH_2^+} + \mathrm{SO_4^{-2}} \rightarrow \mathrm{Cell/Zr{-}OH_2^+SO_4^{-2}} \tag{3}$$

Analyzing the results it was observed that both Cell/$ZrO_2{\cdot}nH_2O$ hybrids materials presented good adsorption capacity. As the Cell/$ZrO_2{\cdot}nH_2O$ hybrids materials showed close specific surface area (see Table 1), it was expected the materials to present similar adsorption capacity, since the adsorption capacity is related to specific surface area (Da Silva, Da Silva, & Caetano 2002; Peixoto, Da Silva, & Da Silva 2006).

4. Conclusions

The hybrids materials Cell/$ZrO_2{\cdot}nH_2O$ were obtained with a high degree of dispersion with hydrous zirconium oxide on the cellulose fiber surface. However the metal oxide was heterogeneously dispersed on the cellulose fiber surface. These results were confirmed by characterization techniques. The results obtained for adsorption capacity from solutions of sulphate sodium, that both Cell/$ZrO_2{\cdot}nH_2O$ hybrids materials showed good adsorption capacity.

Acknowledgement

The authors express their acknowledgements to CAPES for the financial support.

References

Baird, C. (1995). *Environmental chemistry*. New York: W.H. Freeman and Company.

Borgo, C. A., & Gushikem, Y. (2002). Zirconium phosphate dispersed on a cellulose fiber surface: preparation, characterization, and selective adsorption of Li^+, Na^+ and K^+ from aqueous solution. *Journal of Colloid and Interface Science, 246*, 343–347.

Cerqueira, D. A., Rodrigues Filho, G., & Meireles, C. S. (2007). Optimization of sugarcane bagasse cellulose acetylation. *Carbohydrate Polymers, 69*, 579–582.

Da Silva, G. L. J. P., Da Silva, M. L. C. P., & Caetano, T. (2002). Preparation and characterization of hydrous zirconium oxide formed by homogeneous precipitation. *Materials Research, 5*, 149–153.

Karnitz, O., Jr., Gurgel, L. V. A., Melo, J. C. P., Botaro, V., Melo, T. M. S., Gil, R. P. F., et al. (2007). Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. *Bioresource Technology, 98*, 1291–1297.

Liu, C. F., Sun, R. C., Zhang, A. P., Ren, J. L., & Geng, Z. C. (2006). Structural and thermal characterization of sugarcane bagasse cellulose succinates prepared in ionic liquid. *Polymer Degradation and Stability, 91*, 3040–3047.

Liu, C. F., Sun, R. C., Zhang, A. P., Ren, J. L., Wang, X. A., Qin, M. H., et al. (2007a). Homogeneous modification of sugarcane bagasse cellulose with succinic anhydride using an ionic liquid as reaction medium. *Carbohydrate Research, 342*, 919–926.

Liu, C. F., Suna, R. C., Qin, M. H., Zhang, A. P., Ren, J. L., Xu, F., et al. (2007b). Chemical modification of ultrasound-pretreated sugarcane bagasse with maleic anhydride. *Industrial Crops and Products, 26*, 212–219.

Morais, I. P. A., Souto, M. R. S., Lopes, T. I. M. S., & Rangel, A. O. S. S. (2003). Use of a single air segment to minimise dispersion and improve mixing in sequential injection: Turbidimetric determination of sulphate in waters. *Water Research, 37*, 4243–4249.

Mulinari, D. R., Da Silva, M. L. P., & Da Silva, G. L. J. P. (2006). Adsorção de íons dicromato nos compósitos cellulose/$ZrO_2{\cdot}nH_2O$ preparados pelos métodos da precipitação convencional e em solução homogênea. *Química Nova, 29*, 496–500.

Pandey, A., Soccol, C. R., Nigam, P., & Soccol, V. T. (2000). Biotechnological potential of agro-industrial residues: I. Sugarcane bagasse.. *Biosource Technology, 74*, 69–80.

Pasquini, D., Belgacem, M. N., Gandini, A., & Curvelo, A. A. S. (2006). Surface esterification of cellulose fibers: Characterization by DRIFT and contact angle measurements. *Journal of Colloid and Interface Science, 295*, 79–83.

Pavan, F. A., Francisco, M. S. P., Landers, R., & Gushikem, Y. (2005). Adsorption of phosphoric acid niobium oxide coated cellulose fiber: Preparation, characterization and ion exchange property. *Journal Brazilian Chemistry Society, 16*, 815–820.

Peixoto, A. L. C., Da Silva, G. L. J. P., & Da Silva, M. L. C. P. (2006). Estudo da temperatura na síntese de óxidos hidratados de nióbio e zircônio e adsorção de íons Ag^+ e Pb^{2+}. *Cerâmica, 52*, 249–254.

Radojevic, M., & Bashkin, V. N. (1999). *Practical environmental analysis*. Cornwall, UK: MPG Books Ltd., Bodmin.

Reisman, D. J., Sundaram, V., Al-Abed, S. R., & Allen, D. (2007). Statistical validation of sulfate quantification methods used for analysis of acid mine drainage. *Talanta, 71*, 303–311.

Rocha, G. J. M. (2000). Deslignificação de Bagaço de Cana de Açúcar Assistida por Oxigênio. *Tese de Doutorado, Universidade Federal de São Carlos*.

Rodrigues Filho, G., Cruz, S. F., Pasquini, D., Cerqueira, D. A., Prado, V. S., & Assunção, R. M. N. (2000). Water flux through cellulose triacetate films produced from heterogeneous acetylation of sugar cane bagasse. *Journal of Membrane Science, 177*, 225–231.

Rodrigues Filho, G., Silva, R. C., & Meireles, C. S. (2005). Water flux trough blends from waste materials: Cellulose acetate (from sugar cane bagasse) with polystyrene (from plastic cups). *Journal of Applied Polymer Science, 96*, 516–522.

Suzuki, T. M., Bomani, J. O., Matsunaga, H., & Yokoyama, T. (2000). Preparation of porous resin loaded with crystalline hydrous zirconium oxide and its application to the removal of arsenic. *Reactive & Functional Polymers, 43*, 165–172.

Toledo, E. A., Gushikem, Y., & Castro, S. C. (2000). Antimony (III) oxide film on a cellulose fiber surface: Preparation and characterization of the composite. *Journal of Colloid and Interface Science, 225*, 455–459.