Application of Cationic Hemicelluloses Produced from Corn Husk as Polyelectrolytes in Sewage Treatment

Alan Soares Landim, Guimes Rodrigues Filho, Raquel Maria Ferreira Sousa, Elaine Angélica Mundim Ribeiro, Fúlvio Rafael Bento de Souza, Júlia Graciele Vieira
Instituto de Química, UFU

Rosana Maria Nascimento de Assunção
Faculdade de Ciências Integradas do Pontal, UFU

Daniel Alves Cerqueira
Instituto de Ciências Exatas, Naturais e Educação, UFTM

Abstract: Hemicelluloses were extracted from corn husk and converted into cationic hemicelluloses using 2,3-epoxypropyltrimethylammonium chloride. The degree of substitution was determined as 0.43 from results of elemental analysis. The cationic derivative was also characterized by Fourier transform infrared spectroscopy and Carbon-13 magnetic nuclear ressonance. The produced polymer was employed as coagulant aid in a sewage treatment station (STS) of the municipal department of water and sewer (Departamento Municipal de Água e Esgoto - DMAE) in Uberlândia-Minas Gerais, Brazil, using Jar test experiments. Its performance was compared to ACRIPOL C10®, a commercial cationic polyacrylamide regularly used as a coagulant at the STS. The best result of the jar-test essays was obtained when using cationic hemicelluloses (10 mg L⁻¹) as coagulant aid and ferric chloride as coagulante (200 mg L⁻¹). The resultsof color and turbidity reduction, 37 and 39%, respectively, were better than when using only ferric chloride. These results were also higher than those of commercial polyacrylamide, on the order of 32.4 and 38.7%, respectively. The results showed that the cationic hemicelluloses presented similar or even superior performance when compared to ACRIPOL C10®, demonstrating that the polyelectrolytes produced from recycled corn husks can replace commercial polymers in sewage treatment stations.

Keywords: *Cationic hemicelluloses, corn husk, flotation, sewage treatment.*

Introduction

Due to population increase and industrialization of urban centers there is a growing demand for better effluent treatment processes in order to avoid, or at least reduce, the contamination of water bodies[1,2]. Among the alternatives for sewage treatment, the use of anaerobic reactors followed by post-treatment is widespread[3]. Chemical coagulation and coagulation followed by physical-chemical post-treatment with emphasis on dissolved air flotation (DAF) results in high efficiency on the removal of organic matter, solids in suspension and total phosphate concentration, often present in anaerobic reactor effluents.

Polyelectrolytes are among the chemicals used in the coagulation process[1,2]. Its utilization depends on what kind of effluent is being treated, for instance, a polyelectrolyte used on the treatment of domestic sewage might not work properly on treating industrial effluents, since the physicochemical characteristics of the domestic or industrial wastewater, such as pH, color, turbidity (properties that are routinely used in the sewage treatment stations as indicators of the presence of some substances, usually colloidal, which might be removed by polymers) and predominant type of discarded substances, affect the polyelectrolyte action. Lignocellulosic biomass can be used to produce water soluble polyelectrolytes that might present good performance on treating effluents, with the advantage of being biodegradable and aggregating value to agroindustrial waste.

Hemicelluloses are amorphous natural polymers with variable composition, for which the degree of polymerization can range from 80 to 200 (molecular weight ranging from 25 to 35 kg mol⁻¹). Xylans are the principal component of the hemicelluloses and are composed by chains of β-D-xylose branched with oligosaccharides and different carbohydrates such as L-arabinose and uronic acids[4-7].

The amorphous character and low molecular weight of hemicellulose allow a better accessibility of the polymeric chain and, consequently, lead to better reactivity when compared to other lignocellulosic compounds, such as cellulose. Also, cationic hemicellulose derivatives usually present high solubility in water, which is an important aspect of polyelectrolytes used for effluent treatment[8-10]. Considering the abundance of hemicelluloses in lignocellulosic biomass, the production and application of their derivatives are very important.

Cationic hemicellulose can be prepared by various methods[8-12]. In this paper, hemicelluloses obtained from corn husk were converted into cationic hemicelluloses by quaternization with 2,3-epoxypropyltrimethylamonium chloride (ETA), and then used for sewage treatment at the

municipal department of water and sewer (Departamento Municipal de Água e Esgoto - DMAE) in Uberlândia-Minas Gerais, Brazil. The derivative was characterized by FT-IR and Carbon-13 RMN . Also, its performance in sewage treatment was evaluated by jar-test essays in comparison to a commercial cationic polyacrylamide, ACRIPOL C10®.

Materials and Methods

Materials

Potassium hydroxide, sodium hydroxide, ethanol (98%), glacial acetic acid, hydrochloric acid, ferric chloride and dimethyl sulfoxide were purchased from Vetec. 2,3-epoxypropyltrimethylammonium chloride (ETA) and sodium chlorite were purchased from Sigma-Aldrich. ACRIPOL C10®, produced by Produquímica, a polyacrylamide used as a standard for comparison with cationic hemicelluloses was kindly offered by the sewage treatment station.

Isolation of hemicelluloses from corn husk

In order to isolate hemicelluloses, corn husk was washed with distilled water, dried at 50 °C for 24 h and stored at room temperature. Holocelullose was isolated from the lignocellulosic waste before isolating the hemicelluloses according to the procedure described by Vieira et al.[13], as follows:

5.0 g of corn husk was mixed with 100 mL of distilled water at 75 °C. Then, 2.0 mL of acetic acid and 3.0 g of sodium chlorite were added and the system, which was kept under stirring. After every hour, the same amount of reagent was added to the system, totalizing a digestion period of 4 h. Then, the mixture was cooled to 10 °C and filtered in a fritted funnel. The fibrous residue, holocellulose, was washed with distilled water at 5 °C, presenting a whitish color at the end of the washing step. Holocellulose was dried in an oven at 105 °C for 6 h.

In order to isolate hemicelluloses, holocellulose (3.0 g) was mixed with 100 mL KOH (5%, w/w) under nitrogen atmosphere. The flask was sealed and magnetically stirred for 2 h. The mixture was filtered in a fritted funnel and the residue was washed with 50 mL KOH (5%, w/w) and with 100 mL distilled water. A solution containing ethanol and acetic acid (1/1, v/v) was added to the filtrate in order to precipitate hemicelluloses. The precipitate was filtered in a fritted funnel and dried in an oven at 50 °C for 2 h.

Preparation and characterization of cationic hemicelluloses

The cationic hemicelluloses were produced according to the procedure described by Ren et al. (2008)[9], as follows:

Hemicelluloses (0.5 g) and distilled water (5 mL) were stirred for 30 min at 60 °C; NaOH (0.7 g) was added to the system, which was stirred for 20 min; ETA (3.46 g) was added to the system, which was stirred for 30 min; NaOH (1.1 g) was added to the system, which was stirred for 5 h at 60 °C. The mixture was cooled in ice bath and neutralized with HCl solution. The cationic hemicelluloses were precipitated with ethanol 98% and collected in a fritted funnel.

Fourier transform infrared (FTIR) and Carbon-13 Nuclear Magnetic Ressonance (^{13}C NMR)

FTIR spectra were recorded in a Shimadzu IRPrestige-21 equipment (Kyoto, Japan). The samples were pressed into KBr pellets and the spectra were obtained using twenty scans at 4 cm⁻¹ resolution, from 4400 to 400 cm⁻¹.

^{13}C solid state NMR spectra were measured in a Bruker DRX400/Avance, using cross polarization/magic angle spinning (CP/MAS) with high-power dipolar decoupling. The experiments were carried out at 300 K using 4 mm probes, 5000 scans and relaxation time of 4 s.

Degree of substitution

Elemental analysis was carried out in a Perkin Elmer equipment, model 2400 CHN Elemental Analyzer. The DS was then calculated using Equation 1, according to Schwikal et al. (2006)[14], in which %C and %N refers to the percentage carbon and nitrogen in each material, respectively.

$$DS = \frac{60 \times \%N}{14 \times \%C - 72 \times \%N} \qquad (1)$$

Jar-test experiment

The tests with the polymers were carried out in a STS of DMAE in Uberlândia-MG (STS Uberabinha) from January to June 2010, as follows:

For each test, the effluent (50 L) was collected after passing by the upflow anaerobic sludge blanket reactor (UASB). The samples presented a dark aspect, which is characteristic of effluents containing oxidized organic matter, as usual in anaerobic sewage treatment.

The initial effluent was characterized according to its apparent color, turbidity and pH. Apparent color was measured in a DR 2800 (HACH®) spectrophotometer (U95 %: ± 5 Uc; K: 1.96 - uncertainty related to the color essay). Turbidity was measured in a HI98703 (HANNA®) turbidimeter (U95%: ± 0.1NTU; K: 1.96). pH was measured in a DM-2 (DIGIMED®) pHmeter (U95%: ± 0.2; K: 1.96).

Coagulation tests were carried out in a FlocControl II (Policontrol) jar-test® according to guidelines of the international standard ISO/IEC 17025:2005, as follows:

Beakers of 2 L were filled with effluent and the samples were stirred at 100 rpm for 1 minute. Ferric chloride (100, 150 and 200 mg L⁻¹) was added to each sample, and the cationic polymer was added to the beakers (5, 10, 15 and 20 mg L⁻¹). The mixing rate was reduced to 70 rpm for 2 minutes and 20 rpm for 8 minutes, after which mixing was interrupted and the effluent rested for 10 minutes. Turbidity, pH and color of the supernatant were measured. Commercial polymer ACRIPOL C10®, which is used in the routine procedures of DMAE, was used as standard polymer for comparison.

Results and Discussion

Cationic hemicelluloses

The hemicellulosic derivative presents a net positive charge due to the presence of the trimethylamonium group, which come from 2,3-epoxypropyltrimethylamonium

chloride (ETA). A scheme for the production of the cationic hemicelluloses is shown in Figure 1.

Carbon, hydrogen and nitrogen contents obtained by elemental analysis for the cationic hemicelluloses sample were 59.43%C, 2.73 %H and 3.95%N, respectively.

The DS of the cationic hemicelluloses calculated using Equation 1 is 0.43. This value is close to the result by Ren et al.[8] who used hemicelluloses from sugarcane bagasse.

The structure of the product was confirmed by comparing the infrared spectra of hemicelluloses (Figures 2a and 3a) and modified hemicelluloses (Figures 2b and 3b).

The characteristics of the spectra presented in Figure 2 are typical of lignocellulosic materials, more specifically, polysaccharides such as cellulose and hemicelluloses. The main bands observed at 3416, 2928, 1636, 1044 and 900 cm^{-1} are attributed to the stretching of O-H bonds, the symmetrical stretching of C-H bonds, the scissoring of H-O-H bonds due to the presence of absorbed water, and the stretching of C-O bonds in ether groups and in β-1,4 glycosidic bonds, respectively. Bands in the region
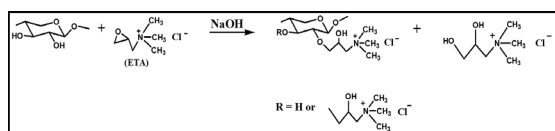
from 1480 to 1070 cm^{-1} are attributed to the deformation of C-H bonds (1480 to 1315 cm^{-1}) and the stretching of C-O-C (1160 cm^{-1}) in sugar unities[10-12].

The main chemical modification of the corn husk hemicelluloses after the chemical reaction can be inferred from the region between 1800 and 800 cm^{-1}, shown in Figure 3. The main differences in the FTIR spectrum are the higher relative intensity of bands in 1478 cm^{-1} and 982 cm^{-1}, attributed to the asymmetric stretching of the C-H bond in CH_3 bonded to nitrogen and asymmetric stretching of the N-C_4 bonds, both related to the presence of CH_3 and R_4N^+ groups of the tetramethylammonium salt [10].

^{13}C NMR (CP/MAS) spectrum of natural hemicelluloses and cationic hemicelulose is shown in Figure 4. The chemical shifts between 63.1 mg L^{-1} and

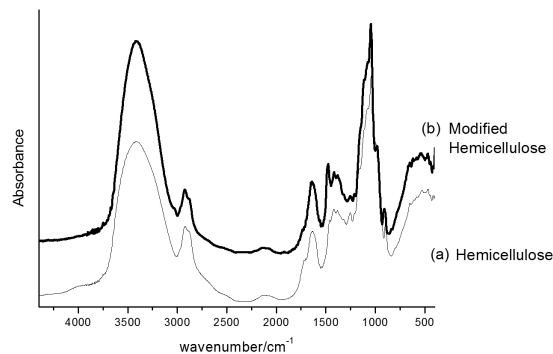**Figure 1.** Scheme of the production of cationic hemicelluloses.

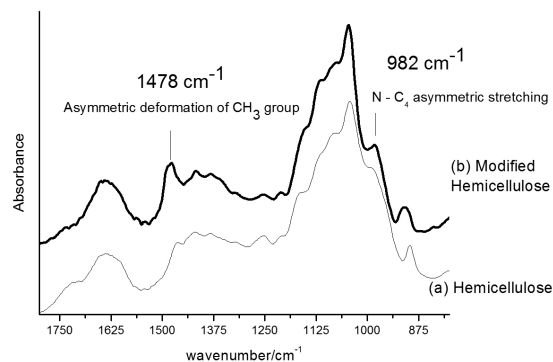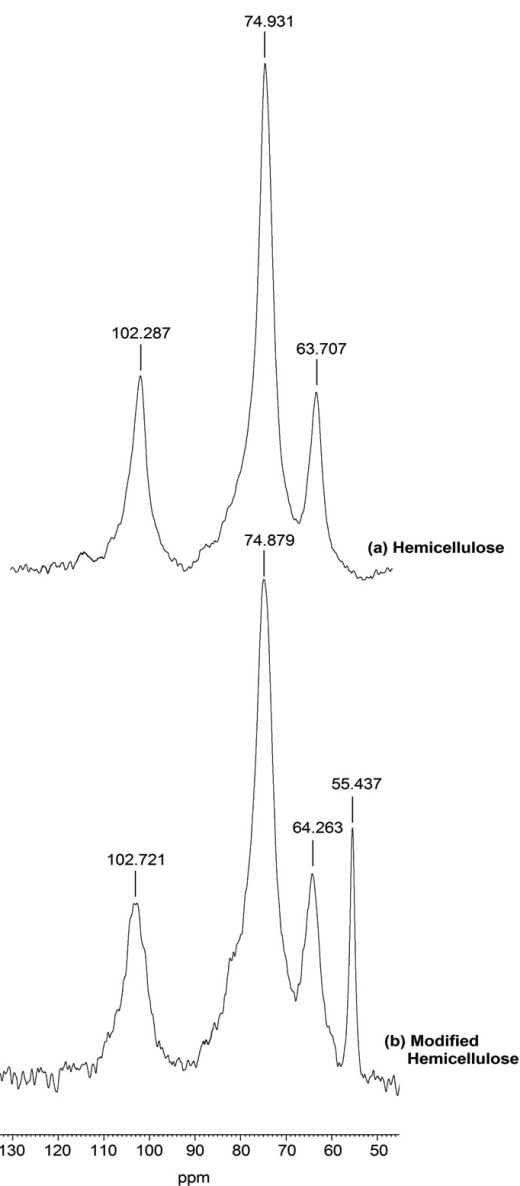**Figure 2.** Infrared spectra of corn husk hemicellulose (a) and modified hemicellulose (b).

Figure 3. Infrared spectra from 1800 to 800 cm^{-1} of corn husk hemicellulose (a) and modified hemicellulose (b).

Figure 4. ^{13}C solid state NMR (CP/MAS) spectrum of natural hemicelluloses (a) and cationic hemicelulose (b).

101.8 mg L⁻¹ are related to carbons C-1, C-4, C-3, C-2 and C-5 of the β-D-xylans of hemicelluloses[8].

The spectrum of the the ¹³C solid state NMR (CP/MAS) of natural hemicelluloses and cationic hemicelulose are similar but it is observed a chemical shift in 55.4 mg L⁻¹, which is related to the carbon of quaternary groups (($CH_3)_3N^+$) added to the hemicellulosic chains, evidencing the chemical reaction[8,11,12].

In addition to the FTIR and ¹³C NMR spectrum analysis, the increase in water solubility of the hemicellulosic derivative also indicates the incorporation of ammonium groups.

Jar tests

Cationic polyelectrolytes may be used as primary coagulants, but their main utilization is as a coagulant aid. Thus, cationic hemicelluloses were tested as auxiliary coagulants in the treatment of sewage effluents, according to the routine procedure adopted by the STS. In this procedure, ferric chloride (100 to 200 mg L⁻¹) was used as primary coagulant, while cationic hemicelluloses were used as coagulant aid. That aimed at improving the removal of suspended solids and also increasing the size of formed flocs, thus easing the separation process. Results are shown in Table 1.

According to the data shown in Table 1, the reduction in turbidity and color was more effective when using the produced cationic hemicellulose as coagulation aid. The best result was observed when using 10 mg L⁻¹ of cationic hemicellulose and 200 mg L⁻¹ of ferric chloride in effluent 3, for which the reduction in color and turbidity were respectively 37% and 39% higher than the blank, i.e., the tests using only ferric chloride. Results of cationic hemicellulose were also better than the commercial polyacrylamide when considering the reduction in color

and turbidity, 32.4% and 38.7%, respectively, for the same effluent.

It was also observed that there was a higher reduction of color and turbidity in all tests with effluent 2 and 3, either by increasing the dose of primary coagulant or by increasing the dose of polymer. However, the best results were obtained when combining the use of the primary coagulant (ferric chloride) and the coagulant aid (polymer).

It is possible to observe the reduction in turbidity and color, i.e., the increase in the removal of suspended solids, when cationic hemicelluloses dose is increased, which can be observed by analyzing the performance of this polyelectrolyte for sewage 3. For the same dose of ferric chloride (150 mg L⁻¹) there is a higher turbidity reduction (23%) when using 10 mg L⁻¹ of cationic hemicellulose than when using 5 mg L⁻¹ (17%). These results agree with the results in which the turbidity and color reduction can be achieved by increasing the polyelectrolyte dose. That can be advantageous since it is possible to reduce the amount of primary coagulant by increasing the cationic hemicelluloses dose, which are easily handled and biodegradable.

It was observed for effluent 2 that when the dose of coagulant rises from 100 mg L⁻¹ to 150 mg L⁻¹ the highest reduction in color and turbidity was obtained using the produced cationic hemicelluloses (5 mg L⁻¹) as coagulation aid, indicating a better interaction between the cationic hemicelluloses and ferric chloride in doses higher than 100 mg L⁻¹.

In some tests in which ferric chloride was used without a coagulant aid, reduction of turbidity and color were observed. These cases, usually occur when the produced flocs are not well formed, big and fragile, and in consequence, these flocs could break under stirring.

Table 1. Experimental results of cationic hemicellulose compared to cationic polyacrylamide.

Dose (mg L⁻¹)		Raw Sewage Characteristics								
		Raw Sewage 1 Turbidity: 205.0 NTU Color: 2177.0 uC pH: 7.2			Raw Sewage 2 Turbidity: 97.8 NTU Color: 1255.0 uC pH :7.0			Raw Sewage 3 Turbidity: 191.0 NTU Color: 2619.0 uC pH: 7.1		
Polymers	FeCl₃, 6H₂O	Turbidity (NTU)	Color (uC)	pH_final	Turbidity (NTU)	Color (uC)	pH_final	Turbidity (NTU)	Color (uC)	pH_final
-	100	29.4(±0.1)	405.0(±5)	6.5(±0.2)	58.5(±0.1)	937.0(±5)	6.7(±0.2)	-	-	-
-	150	-	-	-	10.3(±0.1)	121,0(±5)	6,2(±0.2)	36.0(±0.1)	464.3(±5)	6.5(±0.2)
-	200	-	-	-	-	-	-	18.8(±0.1)	311.0(±5)	6.3(±0.2)
Polyacrylamide	-	-	-	-	-	-	-	-	-	-
5	100	25.2(±0.1)	506.0(±5)	6.5(±0.2)	51.0(±0.1)	897.0(±5)	6.7(±0.2)	-	-	-
5	150	-	-	-	10.1(±0.1)	128.0(±5)	6.1(±0.2)	35.1(±0.1)	517.0(±5)	6.4(±0.2)
10	150	-	-	-	-	-	-	25.5(±0.1)	332.0(±5)	6.5(±0.2)
10	200	-	-	-	-	-	-	18.6(±0.1)	290.5(±5)	6.3(±0.2)
Cationic Hemicelluloses	-	-	-	-	-	-	-	-	-	-
5	100	25.3(±0.1)	426.0(±5)	6.5(±0.2)	51.9(±0.1)	894.0(±5)	6.6(±0.2)	-	-	-
5	150	-	-	-	8.76(±0.1)	116.0(±5)	6.1(±0.2)	33.5(±0.1)	494.0(±5)	6.4(±0.2)
10	150	-	-	-	-	-	-	25.1(±0.1)	344.0(±5)	6.5(±0.1)
10	200	-	-	-	-	-	-	11.4(±0.0)	196.5(±5)	6.3(±0.0)

These problems were eliminated by increasing the polymer dose in order to increase the floc resistance. For example, in effluent 3, when increasing the dose of cationic hemicelluloses and polyacrylamide from 5 mg L^{-1} to 10 mg L^{-1}, turbidity and color presented a higher reduction than tests in which only ferric chloride had been used.

The results presented in Table 1 can be resumed as follows: the performance of the cationic hemicelluloses as coagulation aid is similar or superior in most of essays to polyacrylamide, used in the routine of the STS. That can be advantageous since it is possible to reduce the amount of primary coagulant by increasing the cationic hemicelluloses dose, which are easily handled and biodegradable. Moreover, it was observed an increase in floc size and sedimentation speed in all essays in which the polymers were added.

These results demonstrate that the main observed effect is due to the cationic nature of the polymers since both materials presented similar results. Thus, their main mechanism of action might be similar, i.e., the coagulant aid acts in synergy with the primary coagulant leading to the neutralization of negative charges on suspended particles in the colloidal system, resulting in coagulation.

Conclusion

After comparing the performances of two cationic polymer, ACRIPOL C10® and cationic hemicelluloses produced from corn husk, the most effective reduction of turbidity and color was observed when using 10 mg L^{-1} of the cationic hemicelluloses and 200 mg L^{-1} of primary coagulant, for which the color and turbidity were reduced by 37% and 39%, respectively. These results were better than those obtained using only ferric chloride. Results of color and turbidity reduction using cationic hemicellulose as coagulation auxiliary were also better than those using commercial polyacrylamide, 32% and 38%, respectively, when using the same dosage, what indicates that the cationic hemicelluloses from recycled corn husk could replace cationic polyacrylamide, commonly used in sewage treatment stations as coagulation and flotation aid. However, it is still necessary to perform tests in pilot scale.

Acknowledgments

References

1. Di Bernardo, L. & Dantas, A. D. B. - "Métodos e técnicas de tratamento de água", RiMa, 2. ed., v.1, São Carlos (2005).

2. Bolto, B. & Gregory, J. – Water Res., **41**, p.2301 (2007). PMid:17462699. http://dx.doi.org/10.1016/j.watres.2007.03.012

3. Satyawali, Y. & Balakrishnan, M. - J. Environ. Manage., **86**, p.481 (2008). PMid:17293023. http://dx.doi.org/10.1016/j.jenvman.2006.12.024

4. Ren, J. L.; Sun, R. C.; Liu, C. F.; Chao, Z. Y. & Luo, W. - Polym. Degrad. Stab., **91**, p.2579 (2006). http://dx.doi.org/10.1016/j.polymdegradstab.2006.05.008

5. Silva, S. S.; Carvalho, R. R.; Fonseca, J. L. C. & Garcia, R. B. - Polímeros, **2**, p.25 (1998). http://dx.doi.org/10.1590/S0104-14281998000200005

6. Fengel, D. & Wegener, G. - "Wood: Chemistry, Ultrastructure, Reactions." Walter De Gruyter Inc, Germany (1984).

7. Gáspár, M.; Kálmán, G. & Réczey, K., Process Biochem., **42**, p.1135 (2007). http://dx.doi.org/10.1016/j.procbio.2007.04.003

8. Ren, J. L.; Liu, C. F.; Sun, R. C.; She, D. & Liu. J. C. - E-Polymers, **61**, p.01 (2007).

9. Ren, J. L.; Peng, F.; Sun, R. C.; Liu, C. F.; Cao, Z. N.; Luo, W. & Tang, J. N. - J. Appl. Polym. Sci., **109**, p.2711 (2008). http://dx.doi.org/10.1002/app.28256

10. Ren, J. L.; Peng, F.; Sun, R. C. & Kennedy, J. F. - Carbohydr. Polym., **75**, p.338 (2009). http://dx.doi.org/10.1016/j.carbpol.2008.08.011

11. Liu, Z.; Ni, Y.; Fatehi, P. & Saeed, A. - Biomass Bioenergy, **35**, p.1789 (2011). http://dx.doi.org/10.1016/j.biombioe.2011.01.008

12. Bigand, B.; Pinel, C.; Perez, D. S.; Rataboul, F.; Huber, P. & Petit-Conil, M., Carbohydr. Polym., **85**, p.138 (2011). http://dx.doi.org/10.1016/j.carbpol.2011.02.005

13. Vieira, R. G. P.; Rodrigues Filho, G.; Assunção, R. M. N.; Meireles, C. S.; Vieira, J. G. & Oliveira, G. S. - Carbohydr. Polym., **67**, p.182 (2007).

14. Schwikal, K.; Heinze, T.; Ebringerova, A. & Petzold, K. - Macromol. Symp., **232**, p.49 (2006). http://dx.doi.org/10.1002/masy.200551406