**Wood Wastes Valorization Through the Development of Eco-Friendly Cellulose-Based Polyelectrolytes for Potential Industrial Applications.**

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**Highlights**

* Wood wastes valorization, evaluation of influence of lignin content.
* An alternative replacement for traditional, oil-based, synthetic polyelectrolytes
* Environmental friendly cationic bio-polyelectrolytes for industrial applications.

**1. Introduction**

Low biodegradability, being harsh to the environment or to human health, are just some of the drawbacks when traditional synthetic polyelectrolytes (PEL) are used. There is then, a strong need for the replacement of oil-based materials by more eco-friendly, biodegradable, non-toxic, easy available solutions. Bearing in mind wood is the world’s most important source for industrial purposes, not only for furniture or pulp and paper production, but also as a feedstock for the extraction and production of chemicals for various industries [1], the production of cellulose-based added value materials, reusing lignocellulosic wastes, appears as a viable and added value solution to deal with such wastes, and is going to be addressed here, especially production of cellulosic PELs.

Unmodified cellulose presents insolubility in water and in most organic solvents [2]. Consequently, introduction of new functional groups into the cellulose backbone is required to improve the cellulose properties, which will strongly depend on the types of substituent groups and on the degree of substitution (DS), as well as on their distribution in the cellulose backbone. As a result, new applications of cellulose can be achieved with potential replacement of oil-based materials. Regarding PELs production, the path of oxidation/cationization with sodium periodate and Girard’s reagent T (GT) was used to produce highly charged water soluble cellulose based PELs. The aim of this study was to establish a procedure to successfully prepare cellulose-based PELs, with diverse DS, starting from more complex cellulosic raw materials with higher content of lignin and lower cellulose content, thus minimizing pre-extraction procedures. Some studies in the literature refer cationization of cellulose [3][4], but, as far as we know, these reactions have never been performed starting from highly complex cellulosic materials, with a low degree of cellulose purity.

**2. Methods**

*Eucalyptus* wood chips wastes were submitted to soft kraft pulping using 14 % or 19 % active alkali charges to previously hot water extracted and non-extracted wood. The produced pulps were thoroughly washed with water and dried. Resulting materials were characterized and corresponded to different lignin content based on kappa number, being 10.2 or 13.9 (pulps with hot water pre-treatment) and 16.1 or 26.7 (pulps without hot water pre-treatment). Highly oxidized pulps were first produced from those raw materials, by oxidation using NaIO4. After 3 h at 75 °C, the dialdehyde cellulosic product (DAC) was filtered and washed with water. The aldehyde content of DAC was determined based on the oxime reaction [5]. Cationization of non-dried DAC followed through reaction with GT in aqueous media [5]. After 1 h at 70 °C the soluble products from reaction mixture were precipitated with isopropanol and centrifuged and the cationic product was oven-dried. The GT/aldehyde ratio varied from 0.975 to 3.9 to obtain bio-PELs with different cationization degree.

**3. Results and discussion**

Modification of cellulosic-rich materials (obtained from *Eucalyptus* wood wastes with various lignin levels) by introduction of charged quaternary ammonium groups was chosen, as these groups are widely present in successfully applied synthetic PELs. The main objective was to allow the introduction of high content of ionic groups to obtain sufficiently charged cellulose-based materials. The pre-modification to DAC, by selective oxidation with periodate, allowed a high modification degree, since two highly reactive aldehyde groups were introduced per AGU unit. Finally, for the cationization, reaction of DAC with GT was conducted. This treatment allowed to introduce more than one cationic group per AGU unit, yielding highly charged end products which were soluble in in water at room temperature. The charge density and DS of the end product depended on the cationization conditions (temperature, time, pH, molar ratio GT/aldehyde) and also on the properties of the pre-treated cellulosic sample, used as starting material. Typically with the increase of kappa number the DS and charge of PEL decreases when applying the same GT/aldehyde ratio. However, even when using cooked pulp with the highest lignin content (kappa 26.7) and for the lowest GT/aldehyde ratio of 0.975, water soluble PEL with DS of 0.79 and zeta potential of 40±3 mV was produced. When applying the same low GT/aldehyde ratio to the hot water pre-treated/cooked pulp with the lowest kappa of 10.2, the produced PEL exhibited DS of 0.96 and zeta potential of 51±2 mV. Moreover, the obtained PELs, independently of the chemical complexity of raw pulp used in the modification procedure, showed high performance in the treatment of several model coloured effluents and in a real industrial effluent treatment, namely in colour removal.

**4. Conclusions**

Valorization of cellulosic wastes to provide end products with higher added value (PELs) by applying a sequence of two reactions, oxidation followed by cationization, was investigated. Cellulosic raw materials with different lignin content (kappa number 10.2-26.7) were used. The cationic bio-PELs proved to be efficient biopolymeric flocculation aids in the tested model waters and in an industrial effluent. The developed products can be considered as an alternative to traditional synthetic PELs.

**References**

[1] E. Guibal, J. Roussy, React. Funct. Polym. 67 (2007), 33–42.

[2] D. Klemm, B. Heublein, H. P. Fink, A. Bohn, Angewandte Chemie - Int.Ed. 44 (2005), 3358–3393.

[3] J. Sirviö, A. Honka, H. Liimatainen, J. Niinimäki, O. Hormi, Carbohydr. Polym. 86 (2011), 266–270.

[4] H. Liimatainen, J. Sirviö, O. Sundman, M. Visanko, O. Hormi, J. Niinimäki, Bioresour. Tech. 102 (2011), 9626–9632.

[5] K. Grenda, J. Arnold, J. A. F. Gamelas, M. G. Rasteiro, Water Sci. Tech. 76 (2017), 1490–1499.

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