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Chemical conversion of paper industry effluents into carboxymethylcellulose

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ABSTRACT

The synthesis of carboxymethylcellulose was investigated using effluents containing short cellulose fibers. Carboxymethylcellulose was synthesized according to the slurry process using different amount of sodium hydroxide and different incubation times at 30 °C after the etherification reaction as variables. Characterization of the product was conducted by Fourier transformed infrared spectroscopy, X-ray diffraction, degree of substitution, average degree of polymerization, water imbibing capacity, color, rheological properties, apparent viscosity and trace elements content. Incubation time slightly increased the yield of the reaction and the degree of substitution during the first 12 h. The reaction yield and degree of substitution both decreased when the initially concentration of NaOH was increased from 7.0 g/mL to 10.5 g/mL. The carboxymethylcellulose obtained was darker and had lower hydration properties than commercial samples. Trace elements content suggests that the product could be only used in paint factories or building materials industries.

Keywords: Short cellulose fibers; Carboxymethylcellulose; Paper; Recycled sludge; Effluents; Solid Waste

1. Introduction

In Argentina, at least 180 million metric tons of municipal solid waste are annually generated and disposed in landfills. The opportunities for landfilling of municipal solid waste are rapidly declining with depleting available cheap land resources (Choy et al., 2004). Typically, pulp and paper derivative products constitute about 45% of the municipal waste. However, in the last decade due to environmental concerns, governmental regulations and economic considerations, there is an increased effort in the paper recycling endeavor.

In the recycled paper industry, different primary sludge grades have been defined according to the strength and length of the fibers. The paper recycling processes involve mechanical and thermal successive treatments in aqueous solution to cleave, cut and modify the original cellulose fiber. The liquid effluents generated during this process contain a significant amount of short cellulose fibers (SCF) not suitable for being incorporated into the network of recycled paper (Ochoa de Alda, 2008).

Recycled paper sludge composition is approximately 25–30% of SCF and 70–75% water. These residues are usually landfilled or incinerated after dewatering, which is costly. The conversion of waste materials into useful products would reduce the environmental impacts of paper manufacturing (Pushpamalar et al., 2006). Recommended waste water

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reduction methods include the recycling of waste water with simultaneous recovery of fibers. The reuse of fibers is not always possible to be carried out in the same company where it is generated; as a consequence, a management alternative is required. The most widely researched non-conventional management alternative has been the reuse of primary sludge as feedstock in the manufacture of hardboard (Eroglu and Saatci, 1993), fiberboard (Geng et al., 2007), building materials such as cement and concrete (Naik et al., 2004), bricks (Andreola et al., 2005), and land application cover material (He et al., 2009a,b). In order to increase the options for the reuse of primary sludge new methods for recycling must be investigated.

Concerning to this point, carboxymethylcellulose (CMC) is the most widely used cellulose ether today, with applications in a large number of industries, thus, there is a high range of required qualities for this polymer. CMC was synthesized from sago waste (Pushpamalar et al., 2006), cellulosic wastes from textile and garment industries (Fakrul Alam and Mondal, 2013), water hyacinth (Barai et al., 1997) and paper sludge (He et al., 2009a,b). The slurry process (Heinze and Koschella, 2005) is used for large scale production of CMC. In this method the CMC synthesis is carried out in two steps. The first step is the basification in which cellulose is suspended in alcohol–water–sodium hydroxide system. The second step is the etherification with monochloroacetic acid. Several factors affect the carboximethylation of cellulose and the resultant properties of the CMC, such as type of solvents (Pushpamalar et al., 2006) sodium hydroxide concentration, temperature, monochloroacetic acid concentration and reaction time (Khullar et al., 2005; He et al., 2009a,b; Wang et al., 2010). At the moment no information is available about the yield of the reaction when the reaction mixture is incubated at 30 °C after the etherification reaction at different sodium hydroxide content. Thus, the purpose of this work is to explore the effect of these variables on the yield of the reaction, degree of polymerization and degree of substitution of CMC obtained using SCF from paper recycled sludge. We also evaluated the quality of the CMC obtained by analyzing the trace element content, rheology, color and water imbibing capacity.

2. Material and methods

2.1. Chemical reagents

All chemicals used were of analytical grade. Deionized water (electrical conductivity around 0.055 μS/cm) was used for atomic absorption assays. Commercial carboxymethylcellulose (Gelfix S.A, Buenos Aires, Argentina) with a degree of polymerization of 1405 and degree of substitution of 0.92 was used as reference (CMC_R).

2.2. Sampling

The samples were obtained from a repulping plant in La Plata city (Buenos Aires, Argentina), which generates a high amount of solid by-product referred to as 'sludge effluent'. The plant has a makepaper line of tissue type with an effluent flow of $51.8 \pm 9.3\ m^3/h$. Four sampler points were selected based on their emission relevance corresponding to the cyclone, papermaker line, recuperation tank and pulp thickener effluents. The samples were collected in plastic containers (10 L) and stored at 4 °C until analysis.

2.3. Sludge effluent flow measurements

The sludge effluent flow was determined according to Bos (1989). The cellulose flow emission was estimated from the sludge effluent flow at the critical points process. The total cellulose content was determined according to the colorimetric method described by Gottipati and Mishra (2011).

2.4. Sludge effluent analysis

The chemical oxygen demand and sedimentable solids at 10 and 60 min were determined according to the ASTM methods (1991).

2.5. SCF recovery

In order to obtain the solid fraction of the crude SCF, 45 mL of the sludge effluent from the cyclone was decanted and centrifuged for 5 min at 3500 × *g* (Rolco CM 2036, CABA, Argentina). The solid obtained was washed three times with distilled water, centrifuged, washed with methanol and dehydrated at 100 °C to constant weight, expressed as grams per liter of effluent. It was assumed that this solid offer a good estimation of total cellulose content. The dried crude SCF has a brownish color and cotton appearance with fine in particle size.

2.6. Carboxymethylation of crude SCF

CMC was synthesized according to the slurry process (Heinze and Koschella, 2005) with some modifications using dry crude SCF as a raw material. Briefly, 50 mL of isopropanol, 2 g of crude dry SCF in 20 mL of sodium hydroxide (7 g/100 mL or 10.5 g/100 mL) were mixed in a 250 mL reaction vessel. After stirring 1 hour at room temperature, 10 g of solid monochloro acetic acid in 8 mL of isopropanol was slowly added and the mixtures were stirred for 3 h at 55 °C. The reaction mixtures were cooled down at 30 °C and incubated up to 21 h. After incubation or not, the reaction mixtures were centrifuged and the solid fractions were neutralized with acetic acid (10 mL/100 mL). The substances obtained were dissolved in aqueous solution of potassium chloride (1.5 g/100 mL), and solutions were centrifuged for elimination of insoluble impurities. Supernatants were precipitated with ethanol, washed with acetone three times and dried at 40 °C. Different samples of the reaction mixtures were assayed each 3 h for yield, degree of substitution and degree of polymerization. The yield (Y) was calculated according to the following equation:

$$Y(\%) = \left(\frac{mCMCt}{mSCF}\right) \times 100 \quad (1)$$

where mCMCt is the mass of CMC obtained at different times and mSCF is the mass of SCF used as raw material (2 g).

2.7. Spectroscopic characterization

Fourier transformed infrared spectroscopy and X-ray diffraction were carried out to verify the success of the synthesis. The measures were carried out in a Nicolet IR200 instrument (ThermoScientific, WI, USA) in the transmission mode between 500 and 4000 cm^{-1}. The powdered dried solids were mixed with potassium bromide (1/100 g/g) and grounded in an agate mortar. Twenty eight scans were collected at room temperature for each spectrum at a resolution of 4 cm^{-1}. Deconvultion

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