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Xylan from corn cobs, a promising polymer for drug delivery: Production and characterization

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ABSTRACT

Although many authors have reported several beneficial effects ascribed to xylan, such as inhibitory action on mutagenicity activity, antiphlogistic effects, and mitogenic and comitogenic activities, few papers have investigated a systematic study on the technological properties of this polymer. The aim of the present work was to evaluate xylan as a promise raw material for the pharmaceutical industry. The water-insoluble xylan samples were extracted from corn cobs following several steps. The obtained powered sample was analyzed by infrared and RMN spectroscopy, and characterized regarding their particle size, bulk and tap densities, compressibility index, compactability, Hausner ratio, and angle of repose. According to the results, infrared and RMN spectroscopy were shown to be able to evaluate the xylan structural conformation and composition, respectively. In addition, rheological data demonstrated that xylan powder obtained from corn cobs may be characterized as a material with low density and very cohesive flow properties.

1. Introduction

Xylan is the second most abundant biopolymer in the plant kingdom (Ebringerova and Hromadkova, 1999; Garcia et al., 2000). It is not only the most common hemicellulose but also the major non-cellulosic cell wall polysaccharide of angiosperms, grasses, and cereals, where it occurs in many different compositions and structures. Its main chain is constituted of D-xylopyranose units in the backbone linked through $1 \rightarrow 4$ glycosidic bonds. The majority of D-xylans have other sugars in side chains, such as 4-*O*-methyl-D-glucuronic acid, *O*-acetyl-L-arabinose, L-arabinose, and D-glucuronic acid. Concerning, specifically, the xylan from corn cobs, it has been demonstrated that such polymer presents a chemical composition of 4-*O*-methyl-D-glucuronic acid, L-arabinose and D-xylose in the proportion of 2:7:19, respectively (Ebringerova and Hromadkova, 1999; Garcia et al., 2000; Karucákova et al., 1994; Silva et al., 1998; Whistler and Smart, 1953).

Corn cobs contain a considerable amount of xylan-type hemicelluloses, which were recognized as a satisfactory source of xylose by early studies (Ai et al., 2005; Collins et al., 2005). The corn cob xylan can be characterized by two different structural types. One is a low-branched arabinoglucuronoxylan, which is mostly water-insoluble (wis-X), and the second is a highly branched water soluble heteroxylan (ws-X) (Hromadkova et al., 1999).

In previous papers, the xylan isolated from corn cobs has been shown to be applicable as an additive in papermaking and textile printing, as well as in the pharmaceutical industry (Hromadkova et al., 1999). In addition, the fermentative process of xylan and other hemicelluloses has been studied as a method for production of biofuels (Pauly and Keegstra, 2010; York and O'Neill, 2008). Several beneficial effects associated to xylans have been reported by many authors. For instance, inhibitory action on mutagenicity activity and heating seems to increase the detoxification ability of dietary fibers, antiphlogistic effects, and both mitogenic and comitogenic activities (Ebringerova and Hromadkova, 1997;

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Ebringerova et al., 1998, 1995, 2002; Kayserilioglu et al., 2003). An important characteristic of wis-X is its ability to remain intact in the physiological stomach environment and small intestine. This property, together with the presence of specific enzymes for colon biodegradability, makes this copolymer a suitable raw material for the medical field, especially as a colon-specific drug carrier (Ebringerova and Heinze, 2000; Rubinstein, 1995; Silva et al., 2007; Sinha and Kumria, 2001).

Because of the distal location of colon at the gastrointestinal tract (GIT), a colon-specific drug delivery system should prevent drug release in the stomach and small intestine, and provide an abrupt onset of drug release upon entry into the colon. For that purpose, a triggering element in the system that can respond to physiological changes in the colon is needed. Overall, the physiological changes along the GIT can be generally characterized as continuum, with decreases in enzymatic activity, motility, and fluid content and an increase in pH. These gradual changes in physiological parameters are not suitable for triggering elements to perform a sudden and dramatic change in the performance of a delivery system in order to obtain colon-specific delivery. However, the presence of specific bacterial populations in the colon is the exception that has been extensively explored as triggering components for initiating colon-specific drug release. This strategy is highly promising because non-starch polysaccharides, like xylan, remain undigested in the stomach and the small intestine and can only be degraded by the vast anaerobic colon microflora, like Bifidobacterium. Because of these characteristics, xylan may be considered as a promising polymer for drug delivery systems (Rubinstein, 1995; Sinha et al., 2004; Yang et al., 2002a,b).

Nevertheless, only a few papers have investigated the properties of this polymer and the influence of such characteristics on the application of xylan in the pharmaceutical field. Such data may be applied either by the pharmaceutical industry in the development of drug delivery systems based on xylan or by scientific research groups on colon-specific carriers. The aim of the present work was to extract the wis-X xylan from corn cobs, a renewable raw material which is widely cultivated around the world. In addition, an analytical method to identify the extracted xylan was proposed by using the infrared spectroscopy, which is a usual and low-cost technique, and RMN spectroscopy. The physical properties of this polymer were also evaluated.

2. Methods

2.1. Materials

Ethanol, polysorbate® 20, polysorbate® 80, and sodium hydroxide were purchased from Vetec Chemical (Brazil); acetic acid, methanol, and isopropanol were purchased from Sigma Chemical Co. (USA). Xylan samples, from corn cobs, were obtained after a single extraction process in our laboratory.

2.2. Xylan extraction

The polymer was extracted from corn cobs following the technique described by Garcia et al. (2000) with some modifications. After grinding, the dried corn cobs were dispersed in water under stirring for 24 h. Then, the sample was treated with 1.3% (v/v) sodium hypochlorite in order to remove impurities. Afterwards, an alkaline extraction was carried out by using 4% (v/v) sodium hydroxide solution. The extract was neutralized with acetic acid, and xylan was separated by settling down after methanol addition. Subsequently, several washing steps were performed by using methanol and isopropanol. Finally, the sample was filtered and dried at 50 °C. The characterization process was made from the same single bulk of polymer.

2.3. Fourier transform infrared FT-IR spectroscopy and NMR spectroscopy

The powered samples were analyzed by infrared spectroscopy measured in KBr translucent pellets using a Thermo Nicolet Nexus 470 FT-IR spectrophotometer. ^{13}C-Solid-State NMR experiment was carried out in 4 mm double bearing rotor made from ZrO_2 on Bruker DSX 200 MHz spectrometer with resonance frequency at 75.468 MHz. The pulse length was 3.5 μs and the contact time of ^{1}H–^{13}C CP was 2–5 ms.

2.4. Morphology and particle size analysis

Morphology analysis of xylan dry powder was conducted by microscopy on a scanning electron microscope (XL 30 ESEM, Philips, The Netherlands). The frequency of the size distribution and mean particle diameter of xylan were analyzed using a laser light scattering particle size analyzer (Cilas, 920L – France). The mean diameter was calculated by "The Particle Expert" software built on the Cilas equipment, and consisted of the "De Brouckere" mean diameter. The technique is based on the principle of Fraunhofer diffraction to determine the particle size. Xylan powder samples were pretreated using a liquid dispersing agent (sodium hexametaphosphate) to avoid the flocculation process and, then, dispersed in distilled water (Silva et al., 2007).

2.5. Flow properties

2.5.1. Powder densities

Samples of 2 g of xylan, from the same bulk, were placed into a 25 mL glass graduated cylinder and their volumes were measured. Then, the graduated cylinder was fixed to a mountain plate autotap apparatus (Varian Inc., USA) and run for 1250 taps. The volume (V) and number of taps were recorded after 10, 500 and 1250 taps. The bulk density (ρbul) was calculated as the ratio of the net weight (m) and the initial volume powder (V_0). The tap density (ρtap) was calculated as the ratio of the net weight (m) and the final volume powder (V_{1250}), as illustrated in Eqs. (1) and (2) below (Foster and Leatherman, 1995).

$$\rho\text{bul} = \frac{m}{V_0} \tag{1}$$

$$\rho\text{tap} = \frac{m}{V_{1250}} \tag{2}$$

2.5.2. Compressibility index and Hausner ratio

The compressibility index and Hausner ratio were calculated using Eqs. (3) and (4), respectively.

$$\frac{\rho\text{tap} - \rho\text{bul}}{\rho\text{tap}} \times 100 \tag{3}$$

$$\frac{\rho\text{tap}}{\rho\text{bulk}} \tag{4}$$

2.5.3. Angle of repose

The samples of xylan, from the same bulk, were sifted through a glass funnel with 8 mm in diameter. A constant distance of 7 cm was maintained between the funnel and the base for all analyses. The powder was allowed to flow through the funnel onto the base, forming a cone-shaped powder heap. A graduated ruler was used to measure the height of the powder cone and the diameter of the circle. The angle of repose was measured using the height