Bioresource Technology 102 (2011) 10013–10019

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

Cellulose extraction from orange peel using sulfite digestion reagents

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ARTICLE INFO

Article history:
Received 8 June 2011
Received in revised form 8 August 2011
Accepted 10 August 2011
Available online 17 August 2011

Keywords:
Orange peel
Cellulose
Hemicellulose
Sulfite pulping
Response surface methodology

ABSTRACT

Orange peel (OP) was used as raw material for cellulose extraction. Two different pulping reagents were used, sodium sulfite and sodium metabisulfite. The effect of the main process parameters, sulfite agent dosage and reaction duration, on cellulose yield was investigated. A central composite rotatable design involving two variables at five levels and response surface methodology were used for the optimization of cellulose recovery. Other two invariable parameters were reaction temperature and hydromodulus. The optimum yields, referred to the weight of double extracted OP, were 40.4% and 45.2% for sodium sulfite and sodium metabisulfite digestions, respectively. The crude celluloses were bleached with hypochlorite and oxygen. The physicochemical characterization data of these cellulose materials indicate good levels of purity, low crystallinities, good whitenesses, good water retention and moderate molecular weights. According to these specific properties the recovered celluloses could be used as fillers, water absorbents, or as raw materials for cellulose derivatives.

1. Introduction

Orange peel (OP) produced as a primary byproduct by the fruit-processing industry, if disposed on the land, can cause environmental pollution (Ververis et al., 2007; Mamma et al., 2008; Wang et al., 2008; Siles López et al., 2010). For this reason, the correct management of this byproduct constituted a permanent problem for the juice, canning, or chemical industries (Ma et al., 1993; Laufenberg et al., 2003; Siles López et al., 2010). To prevent such serious pollution problems and still with economic benefits, numerous studies regarding the establishment of the chemical composition of OP (Eaks and Sinclair, 1980; Ma et al., 1993; Marin et al., 2007; Wang et al., 2008), and the conversion of the identified components into useful value-added products were performed. Initially, attempts were made to use dried OP as natural feed additive (Bampidis and Robinson, 2006), and even as medicinal supplement (Callaway et al., 2008) for animals. But, owing to both their low nutritional intake, or owing to the diseases caused to the consuming animals (mycotoxicosis, rumen parakeratosis), this end use proved to be a low profitable one, with a limited extension (Bampidis and Robinson, 2006; Ververis et al., 2007). Other several research studies pursued extraction of some natural byproducts as sugars (Eaks and Sinclair, 1980; Grohmann et al., 1995), pectin (Ma et al., 1993), carotenoids and flavonoids (Manthey and Grohmann, 1996; Marin et al., 2007; Wang et al., 2008), oils and perfumes (Braddock et al., 1986), very useful in food industry or in keeping the human health. Much more research studies were devoted to the conversion of OP to other valuable products, such as ethanol (Grohmann et al., 1994; Wilkins et al., 2007), citric acid (Rivas et al., 2008), succinic acid (Li et al., 2010), methane (Martin et al., 2010), enzymes (Mamma et al., 2008; Rangarajan et al., 2010), by hydrolytic and fermentative processes.

Much less numerous studies concerning the recovery of the polysaccharides from OP as polymer materials, but not as raw material for the hydrolysis and fermentation processes, were reported. This, the more so as some of the above mentioned processes can produce such polymer materials as fibrous residues (Aravantinos-Zafiris et al., 1994; Liu et al., 2006; Marin et al., 2007). Furthermore, the up to date review of the literature concerning the extraction of cellulose from citrus peels shows that it was entirely carried out according to the alkaline process (Xuan et al., 2006; Yasar et al., 2007; Li et al., 2008; Ejikeme, 2008). The resulting fibrous materials were used as additives in the papermaking processes (Ververis et al., 2007), as adsorbent substrates for retention of metal ions (Xuan et al., 2006; Li et al., 2008), or as raw material for the preparation of the cellulose derivatives (Yasar et al., 2007). But, no studies have been reported on the extraction of cellulose from OP by sulfite process. The sulfite pulping process is known as being that in which the raw material is cooked in a solution containing sodium salts of sulfurous acid, as sulfites or bisulfites. The sulfite process is an acid one and under these conditions, dissolves lignin, hemicelluloses and other cellulose accompanying substances. The resulting cellulose has special properties such as high alpha-cellulose content, high brightness and whiteness, uniform molecular weight distribution (Biermann, 1996), and is suitable for the production of regenerated cellulose

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doi:10.1016/j.biortech.2011.08.041

and cellulose derivatives, or of other cellulose-based end products (Elg-Christoffersson, 2005).

That is why the purpose of the present paper is to prepare chemical grade cellulose with high chemical accessibility and reactivity, starting from OP and using sulfite cooking reagents.

2. Methods

2.1. Plant materials and chemicals

Navel oranges, purchased from the open market, were peeled (flavedo + albedo). The peels were segmented in the humid state to a particle size of about 2 × 2 cm, air-dried to an approximate 10% moisture content, coarsely milled in a laboratory milling machine, and sieved. Only the peel fraction having a particle size distribution range of 1.0 up to 3.0 mm was used in the present experiments. The dried and ground OP was defatted by extraction with the trichloromethane–hexane azeotrope (72/28, w/w, b.p. 69 °C) in a Soxhlet apparatus for 10 h. This azeotrope was chosen for the extraction of fats, resins, oils, waxes and coloring maters, so-called liposoluble fraction, because some preliminary experiments showed that such a mixture is able to ensure high extraction efficiency. The defatted OP was dried in open air at room temperature (25 °C) and again extracted, this time using the azeotrope water/ethanol/toluene (21/55/24, w/w/w, b.p. 74 °C), for 32 h. This ternary azeotrope proved to be very efficient for the extraction of both the water soluble pectin fraction and flavonoids (especially hesperidin, the most abundant flavonoid in Navel orange peel) by the aqueous ethanol component, and of the other compounds, such as unextracted waxes or dyes, by the aromatic hydrocarbon component. The slightly prolonged duration of extraction (up to 32 h) was required, on the one hand, by the relatively low solubility of hesperidin even in the hot alcohols and on the other hand, by the need to entirely extract hesperidin from the processed OP. If not, the presence of hesperidin in the final bleached cellulose, even as traces, could cause its yellowing as time goes. It is well known that hesperidin easily dissolves into the alkaline media. But, because the sulfite process is an acid one, appears the risk to transfer hesperidin to the end product if it was not completely removed from OP by the extraction with the organic solvents.

The chemicals used in the present research were of reagent grade. Sodium sulfite, sodium metabisulfite, hexane, sodium hypochlorite were bought from Sigma–Aldrich (Steinheim, Germany). Methanol, ethanol, hydrogen peroxide, trichloromethane and toluene, were purchased from Chemical Company SA (Iasi, Romania).

2.2. Analytical methods

2.2.1. Chemical analysis of OP and cellulose materials

Orange peel was analyzed for cellulose, hemicellulose, lignin, ash, crude fats, liposoluble fraction, alcohol soluble fraction, flavonoids and protein. The analyses were carried out in duplicate and the average was reported. All results were calculated on an oven-dry matter basis.

The elemental analysis (C, H and N) was performed with a Perkin-Elmer CHNS-2420 analyzer. Protein content was calculated by multiplying the nitrogen content by the factor 6.25 (Rivas et al., 2008). The crude fat content was determined gravimetrically by extraction with the trichloromethane/hexane azeotrope (72/28, w/w, b.p. 69 °C) for 10 h. The weight of the dry residue remained after the recovery of the solvent was referred to the weight of OP taken for analysis to give the fat content. The amount of soluble pectin was determined by the extraction of defatted OP with the water/ethanol/toluene triple azeotrope (21/55/2, w/w/w, b.p. 74 °C) for 32 h, and was expressed as percent of the weight of OP. Some chemical components were determined on the same defatted OP by using the standard analytical procedures: ASTM D1102-84 for ash content, ASTM D1106-84 for Klason lignin content, ASTM D1104-56 for holocellulose content, ASTM D1103-60 for cellulose content and ASTM D1110-84 for water extractives. Average degree of polymerization (DP_n) of cellulose was determined from the specific viscosity data using Eq. (1) (Klemm et al., 1998).

$$DP_n = \frac{2000\eta_{spec}}{c(1 + 0.29\eta_{spec})} \tag{1}$$

where $\eta_{spec} = (t_1 - t_0)/t_0$, t_1 is the efflux time of cellulose solution, t_0 the efflux time of solvent and c the concentration of cellulose solution (g/L). Viscosity measurements were performed on the cuprammonium cellulose solutions at 25 °C with an Ubbelohde viscometer.

2.2.2. Physical analysis

Water retention value (WRV) of cellulose was measured by immersing the cellulose material in distilled water (0.5% consistency) at 20 °C for 12 h, filtering at a centrifugal force of 1000g for 10 min, weighing the obtained wet mass, drying it at 103 °C for 6 h, weighing again the dried mass, and using Eq. (2):

$$\mathrm{WRV}(\%) = 100(W_1 - W_0)/W_0 \tag{2}$$

where W_0 and W_1 were the weights of dry and wet cellulose, respectively.

Fourier transform infrared spectra (FTIR) were recorded on a Bruker Vertex 70 spectrophotometer, with KBr pellets. The CIE whiteness of the bleached cellulose was estimated using CIE $L^*a^*b^*$ system. The L^*, a^* and b^* color coordinates were determined with a Pocket Spec Color QA spectrophotometer provided with a sensor head of 6 mm. Whiteness was determined on the powdered cellulose placed in a ring and pressed with a plunger by hand. Measurements were made using the CIE D65 illuminant and a 10° standard observer. The color coordinates were used to calculate CIE whiteness according to Eq. (3) (Ganz and Pauli, 1995).

$$W_{CIE} = 2.41 \cdot L^* - 4.45 \cdot b^*[1 - 0.009(L^* - 96)] - 141.4 \tag{3}$$

Loose bulk densities of cellulose powders were determined according to the standard ASTM D7481-09. Cellulose crystallinity was studied by means of X-ray diffractometry technique. Wide angle X-ray diffraction (WAXD) was performed with a Bruker AD8 Advance diffractometer at 40 kV and 40 mA. WAXD patterns were obtained using Cu Kα radiation $\lambda = 1.541$ Å and a diffraction angle 2θ ranging from 4° to 40°. The crystallinity index (CrI) was calculated using Eq. (4) (Cao and Tan, 2005).

$$\mathrm{CrI}(\%) = (I_{002} - I_{am})/I_{002} \times 100 \tag{4}$$

in which I_{002} is the maximum intensity of the crystalline plane (0 0 2) reflection ($2\theta = 22.5°$) and I_{am} the maximum intensity of amorphous phase ($2\theta = 18°$).

2.3. Experimental procedure

2.3.1. Sulfite pulping

The sulfite pulping experiments were carried out in a 0.25 L laboratory rotary glass vessel equipped with an air cooled condenser and a thermometer. The reaction vessel was immersed in a hot oil bath held at 105 °C. All the above and the rotating system were tapped from a rotary evaporator. The inclination of mechanical device was set at 45° and the rotational speed at 40 rpm. OP was charged into the digester together with the cooking liquor including distilled water and sulfite reagent, and was allowed to stand for 30 min to impregnate. Always 20.0 g of oven dry (o.d.) OP and 150 g of cooking solution (liquor to solid OP ratio 7.5:1) were