

CELLULOSE POWDER FROM OLIVE INDUSTRY SOLID WASTE

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In the present work, a method for extracting cellulose from olive industry solid waste has been developed. The method involves subjecting solid olive waste to kraft pulping, followed by multistep bleaching processes. The totally free chlorine chemical bleaching sequence APEP was the most effective and gave an average cellulose yield of about 35%. The extracted cellulose was extensively characterized using FTIR, EMS, HPLC, and viscometry. Our key finding in this study is that the extracted cellulose was found to have physio-chemical properties that are similar to those of conventional microcrystalline cellulose (MCC). This is important, as our results show how lignocellulosic agricultural wastes can be utilized to produce high value cellulose powder.

Keywords: Olive waste; cellulose; Pulp; Pulping; Bleaching; Hydrogen peroxide; Microcrystalline cellulose; Lignin

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INTRODUCTION

The olive oil industry represents one of the most economically important agro-food sectors in the Mediterranean and Middle Eastern regions. For example, according to the Palestinian Ministry of Agriculture, West Bank and Jordan produce approximately 135 thousand metric tons of olives every year. The size and magnitude of the olive production worldwide means that huge amounts of unexploited agronomic wastes are generated (Azbar *et al.* 2004), thus posing acute environmental problems in the region.

In general, olive mill waste consists of about 44% of olive industry solid wastes (OISW) and 56% of olive industry liquid waste (OILW) (Ayrilmis and Buyuksari 2010a). These wastes are acidic, have extremely high biological oxygen demand (BOD) and chemical oxygen demand (COD) values, and also contain toxic levels of polyphenols (Azbar *et al.* 2004). The waste materials pose a challenge in waste management to the olive mills and a concern to environmentalists, for it presents a serious disposal problem (Azbar *et al.* 2004). In certain countries, the OISW is usually burned or left to rot, thus releasing CO₂ into the atmosphere, while OILW tends to be disposed of via the sewage system, which has implications for water quality.

The challenge in this work is to utilize and convert these waste materials into useful and low-cost marketable products. Previous studies have shown that the olive mill solid waste might be mixed with polypropylene to be used as a filler in the manufacture of wood-plastic composites (Ayrilmis and Buyuksari 2010b) or mixed with pure wood

fiber for the manufacture of fiberboard (Ayrilmis and Buyuksari 2010a). Also, it may be utilized as a soil amendment (Abu-Zreig and Al-Widyan 2002; Alburquerque *et al.* 2007; Sellami *et al.* 2008; Sampedro *et al.* 2009; Shabtay *et al.* 2009; Giannoutsou *et al.* 2004; Aviani *et al.* 2010), a wetting agent (Kalmis *et al.* 2008), an energy source (Zabaniotou *et al.* 2008; Abu-Ashour *et al.*, 2010; Cuevas *et al.* 2010), a biosorbent for heavy metals (Martinez-Garcia *et al.* 2006), or treatment to reduce phytotoxicity (Sampedro *et al.* 1994). There remains a challenge, however, to find an environmentally friendly and economical means of treating both solid and liquid wastes (Aranguiz *et al.* 1994; Bas Jimenez *et al.* 2000).

There are four main components of OISW, in keeping its origin as woody biomass (Browning 1967): extractives, lignin (polyphenols), cellulose, and hemicelluloses (Krässig, 1993). The main component of OISW is cellulose (40 to 45%), making it potentially attractive and a low cost feed material for microcrystalline cellulose.

Microcrystalline cellulose (MCC) is a well-known material with a wide range of applications in pharmaceuticals as a tableting aid, in foods as a stabilizer or fat replacement, in paints, and in personal products (Battista and Smith 1962; Klemm *et al.* 2005). It contributes unique functional properties (viscosity, texture modifier, ice crystal suppressant, water absorbent, emulsifier, emulsion stabilizers, thickener and viscosity regulators in pastes, creams, and lotions, *etc.*) to these products (Laka *et al.* 1998; Laka and Chernyavskaya 2007a).

Microcrystalline cellulose is a highly crystalline particulate consisting primarily of crystallite aggregates. The cellulose within MCC is said to have a level off degree of polymerization (LODP) cellulose, a term first used by O. A. Battista (Battista 1950). MCC is usually made by partial hydrolysis of high quality wood pulps (dissolving grade pulps) that have been extensively processed to remove non-cellulose components, especially hemicellulose or from cotton cellulose by hydrolytic degradation, typically with a strong mineral acid such as hydrogen chloride or sulfuric acid. Acid penetrates the amorphous region and cleaves the β -1,4-linkage between cellulose repeating units to produce water soluble glucose and oligosaccharides, which are removed by washing with water. The remaining part of unhydrolyzed cellulose is recovered as MCC. MCC could also be produced by other methods such as by hydrolysis in an autoclave of ground lignocellulosic materials by heating at 205 to 250 °C for 15 min, followed by bleaching with hydrogen peroxide and then hydrolyzing produced cellulose with mineral acids (Battista and Smith, 1962; Shangraw *et al.*, 1987; Gohel and Jogani, 1999). Treatment of cellulose with enzyme endoglucanase also produces MCC.

In view of the expense of producing MCC, which requires a high alpha dissolving grade pulp and a high concentration of strong acids for hydrolysis, it is desirable to have an alternative source of microcrystalline cellulose, preferably without any requirement for acid hydrolysis.

In the present work, an optimal method for extracting cellulose from OISW was developed. The properties of the obtained cellulose powder were thoroughly investigated.

EXPERIMENTAL

Materials

All reagents were purchased from the Aldrich Chemical Company and used as received unless otherwise specified. Kraft pulping was performed using a high Parr Reactor model: Buchiglasuste, BMD 300. Fresh OISW was obtained from an olive factory near city of Tulkarm in the West Bank and stored in a freezer at about $-5\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$.

Methods

IR analysis was performed using a Nicolet 6700 FT-IR by Thermo Scientific. Scanning Electron Microscopy (S-3400 N Hitachi, Tokyo Japan) was used to study the morphology of the extracted cellulose. HPLC analysis was performed on an L-2400-2-Lachrom Flite HPLC System connected to a refractive index (RI) detector and equipped with an Amino column with dimensions of $150 \times 4.6\text{ mm}$. The mobile solvent used in the analysis was composed of acetonitrile and a buffer solution of NaH_2PO_4 (1.15 g) in water (1 L) at ratio of 80:20.

Removal of Extractable Materials from OISW

Residual materials were removed using the soxhlet extraction method. OISW (200.0 g, OD weight 80%) was added to a round bottom flask (1.0 L) of soxhlet extractor and subjected to extraction with ethyl acetate (500 mL). The extraction was continued for about 4 hr. Then ethyl acetate solvent was removed under reduced pressure using a rotary evaporator to afford 10.0 g (5.6% based on OD weight of OISW) of pale yellow residual liquid.

Pulping of Olive Industry Solid Waste

Pulping by organic acid

The process was conducted in a round-bottom flask (1.0 L) fitted with a magnetic stir bar and a condenser. OISW was suspended in a solution of acetic acid containing various concentrations of sulfuric acid as a catalyst at a consistency of 10%. The flask contents were heated at $80\text{ }^{\circ}\text{C}$ for about 2.0 hr. Then the reaction mixture was allowed to cool to room temperature. The product (mostly cellulose) was collected by suction filtration and washed thoroughly with water to a neutral pH. The procedure was performed on several samples to study the effect of H_2SO_4 concentration and reaction time on Kappa no. and yield. Percent yield was calculated by dividing the dry weight of the produced pulp by the dry weight of the starting OISW. Moisture contents were determined according to the standard method ASTM D-13148. Ash contents were determined using the standard method ASTM D-1107-8. The standard methods ASTM D-111-84 and ASTM D-1107-87 were used to determine water and ether extracts, respectively. Pulp viscosity and degree of polymerization were determined according to standard process ISO 5351-1, which involves the dissolution of the pulp in an aqueous solution of copper ethylene diamine using a Cannon-Fenske viscometer. Kappa number was determined using the TAPPI standard method T236 cm-85. Results are summarized in Table 1.

Table 1. Results of Organic Acid Pulping

Sample Number	Pulping Time (hr)	Acid Content		Yield (%)	Kappa Number	Viscosity (c.p.)
		H ₂ SO ₄ (%)	HOAc (%)			
1	2	----	100	43.7	46.3	----
2	2	0.5	99.5	27.4	28.3	1.68
3	2	1.0	99	26.5	25.7	1.54
4	1	2.0	98	23.6	20.3	1.41
5	2	2.0	98	22.4	16.8	1.34
6	3	2.0	98	21.0	13.3	1.21

Kraft pulping

Kraft pulping was conducted in a high Parr Reactor of one liter capacity. In all experiments, the liquor to OISW ratio, cooking temperature, temperature rising time, holding time, and operational pressure were 4:1, 160 °C, 30 min, 90 min, and 50 psi, respectively. Active alkali charge is defined as [NaOH+Na₂S], and sulfidity is defined as [Na₂S/(NaOH+Na₂S)], where the concentrations are expressed as g/L Na₂O. Active alkali and sulfidity levels ranging from 14% to 20% and from 10% to 25% (based on the oven dried pulp), respectively, were investigated. At the end of pulping, the produced pulp (cellulose left over after the pulping process) was collected by suction filtration, washed several times with tap water, air dried at room temperature, and stored in plastic bags for further use. Various pulp properties were determined according to standard methods mentioned earlier. Results obtained from pulping experiments are summarized in Table 2.

Table 2. Pulping Conditions and Pulp Characteristics

Run	Pulping conditions		Pulp (%)	Yield	Kappa Number	Viscosity (c.p.)
	Sulfidity (%)	Active alkali				
7	12.5	8	48.5		38.2	2.42
8	"	16	45.3		37.1	2.31
9	"	24	41.0		35.6	2.28
10	"	32	38.0		32.4	2.13
11	15	8	46.0		37.6	2.39
12	"	16	44.6		36.1	2.24
13	"	24	40.6		33.2	2.11
14	"	32	36.8		29.8	1.96

The obtained cellulose was analyzed by IR, HPLC, and scanning electron microscope (SEM). (Refer to the results and discussion section for the IR data and SEM images.)

Bleaching of Pulp Extracted from OISW

Bleaching of the obtained pulp was performed using one the following five bleaching sequences: DEH, DEHE, CEDH, DEHEH, and APEP, for which the individual stages were carried out as follows:

D-stage: Conducted in plastic container at 10% consistency, for 1.0 hr at 70 °C, and 1.0% ClO₂ (based on pulp weight), with an end pH of approximately 2.5.

E-stage: Conducted in a plastic bag at 10% consistency for 90 min at 60 °C and with 5% NaOH (5% based on pulp weight). After the completion of the treatment, the produced pulp was filtered and washed several times with water until neutral filtrate was obtained.

H-stage: Conducted in a plastic bag at 10% consistency for 60 min at 60 °C and at a pH of 10. Hypochlorite charge of 2.5% based on pulp weight. NaClO was obtained from a stock solution that contained 5% of NaClO.

A-stage: Performed in a beaker at 5% consistency for 30 min at room temperature, pulp is suspended in a 2% solution of sulfuric acid, then washed with water until almost neutralization.

P-stage: Conducted in a plastic bag at 10% consistency, for 60min, at 60 °C and a pH of 9 to 11 and with 2% H₂O₂, 0.5% MgSO₄·7H₂O, and 3.0% NaOH (based on pulp weight). The mixture was filtered, washed with water until neutralization, and air-dried (Browning 1967; Shangraw *et al.* 1987; Gohel and Jogani 1999).

Sugar Analysis

Cellulose purity of the bleached samples was determined based on monomer content measured after an acid hydrolysis, which was performed as a two-step process. In the first, 300 mg of bleached sample was suspended in 3 mL 72% (v/v) H₂SO₄ at 303.15 K for 60 min. Then the reaction mixture was diluted to 4% H₂SO₄ using de-ionized water and autoclaved at 394.15 K for 1 h. The produced clear solution was filtered on a Gosh filter No. 4. The sugars in the filtrate were determined by normal phase HPLC (Merck Hitachi), equipped with refractive index detector by using an Aminex HPX-87H column (Bio-Rad Labs, Hercules, CA) at 318.15 K, mobile phase H₂SO₄ 5 mol/l and a flow rate of 0.6 mL/min (Browning, 1967). The analyses were carried out in triplicate.

RESULTS AND DISCUSSION

Pulping Processes

OISW was subjected to pulping using two methods, kraft pulping and acid pulping (Atchison 1996). The results of acid pulping are summarized in Table 1. The results represent the effect of cooking time and sulfuric acid concentration on pulp yield, kappa number, and viscosity of produced pulp. As shown in Table1, pulp yield and kappa number as well as the viscosity decreased with increasing cooking time and sulfuric acid concentration. Maximum yield of 27.4% was obtained with 0.5% H₂SO₄ and a cooking time of 1 hr. The pulp yield decreased from 23.6% to 21.0 % and the kappa number from 20.3 to 13.3 with an increase of cooking time from 1 hr to 3 hr. Increasing the

concentration of H₂SO₄ (V/V) from 0.5% to 2.0% improved kappa number from 28.3 to 16.8, however the yield decreased from 27.4% to 22.4%. Under the same condition of pulping at 0% H₂SO₄, pulping resulted in a higher kappa number and yield. In the absence of sulfuric acid (sample run 1), pulp with pieces of OISW that are not completely delignified were observed in the produced pulp. For this reason, the viscosity of the obtained pulp from this run was not determined. The obtained results clearly show that H₂SO₄ plays an important role in delignification of OISW. Also, the low viscosity in acid pulping (<1.8 c.p.) could be attributed to the rapid hydrolysis of carbohydrates under acidic conditions (Krässig 1993). Therefore acid pulping is not convenient in this case, since it produced pulp with low intrinsic viscosity at low yield.

Kraft pulping was carried out at *ca.* 160 °C. Pulping below this temperature produces pulp with a high concentration of particles that are not totally delignified, so temperature below 160 °C is insufficient for the delignification of OISW. When the temperature was raised to 160 °C, OISW was completely disintegrated into micro fibers. Results of kraft pulping are summarized in Table 2. As shown in Table 2, higher pulp yield with acceptable viscosity was obtained with the kraft method.

Bleaching Processes

Pulp samples of 7 and 14 (Table 2) obtained using the kraft method was subjected to various bleaching sequences in an attempt to achieve high purity cellulose. The bleaching sequences and results are summarized in Tables 3 and 4.

Table 3. Bleaching Results for Sample 14

Bleaching Sequence	Intrinsic Viscosity (c.p.)	Kappa Number	Lignin Contents	Ash Contents (%)
DEH	2.12	5.6	0.84	0.91
DEHE	1.97	5.1	0.77	0.86
DEHEH	1.93	2.1	0.32	0.47
DEHP	1.80	1.33	0.20	0.27
APEP	1.76	1.52	0.23	0.29

Table 4. Bleaching Results for Sample 14

Bleaching Sequence	Intrinsic Viscosity (c.p.)	Kappa Number	Lignin Contents	Ash Contents (%)
DEH	1.82	5.3	0.80	0.87
DEHE	1.76	4.88	0.73	0.82
DEHEH	1.73	1.55	0.23	0.49
DEHP	1.67	1.30	0.20	0.23
APEP	1.66	1.41	0.21	0.32

The bleaching sequences investigated include various numbers of stages that include bleaching reagents chlorine dioxide (ClO₂), extraction with sodium hydroxide (NaOH), hypchloride (NaOCl), and hydrogen peroxide (H₂O₂) (Andrews and Singh 1979; Moore 1995). The bleaching performance was evaluated by measuring the amount

of residual lignin (kappa number), pulp viscosity (η) which is indicative of the damage of the cellulosic chain, and ash contents. Tables 3 and 4 show the effect of increasing the number of stages and type of bleaching agents on yield and kappa number of OISW pulp. It is clearly seen that the pulp yield and kappa number decreased with increasing number of stages in the sequences that do not include P stage. Cellulose samples with lowest lignin and ash content was obtained using the sequences DEHP and APEP.

Pulp Analysis

Sugar contents

Cellulose and hemicellulose content of the bleached samples were determined based on monomer content measured after an acid hydrolysis. Sample 14 pulp, produced using bleaching sequence APEP, was subjected to hydrolysis using 70% sulfuric acid, as shown in the experimental part. The results are shown in the HPLC chromatogram (Fig. 1). The results reveal that the hydrolysis product was comprised of almost pure glucose monomer units. Traces of other sugars (D-xylose, D-mannose) are also shown in the chromatogram. These sugars could be attributed to the presence of traces of hemicelluloses in the sample. These results indicate that extracted cellulose could be a valuable source of sugar which then could be fermented into ethanol. This analysis was performed to determine the degree of purity of extracted cellulose, and the results indicate that the purity of the extracted cellulose was over 95%.

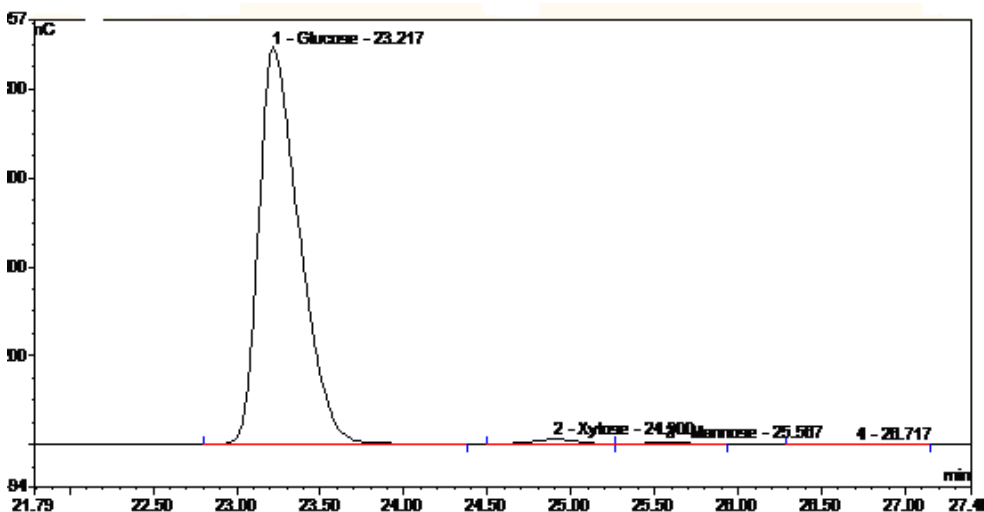


Fig. 1. HPLC of the hydrolysis of cellulose extracted from OISW

Infrared spectroscopy

The IR spectrum of sample 14 is shown in Fig. 2, which also includes the IR spectrum of cellulose powder obtained from Aldrich Chemical Company. As shown from Fig. 2, the two IR spectra are almost in complete match. This could be an indication that the material extracted from OISW is actually high purity cellulose powder cellulose. The band at 3350 cm^{-1} could be attributed to hydrogen bonded hydroxyl group (OH) stretching vibration. The bands at 2920 and 2845 cm^{-1} correspond to the CH stretching vibration in CH and CH_2 in anhydroglucose units of cellulose. The 1430 cm^{-1}

band could be attributed to CH_2 asymmetric bending. The band at 1380 cm^{-1} corresponds to the C-O stretching of ether and alcohol groups. The band at 1160 cm^{-1} corresponds to C-O-C stretching of β -glycosidic linkage. The IR spectrum shows no peaks in the area of 1700 cm^{-1} that would be characteristics of carbonyl group in hemicelluloses. From this we could conclude the absence of hemicelluloses in the extracted cellulose powder. Also the absence of 3070 and 1600 cm^{-1} band is an indication of the absence of lignin.

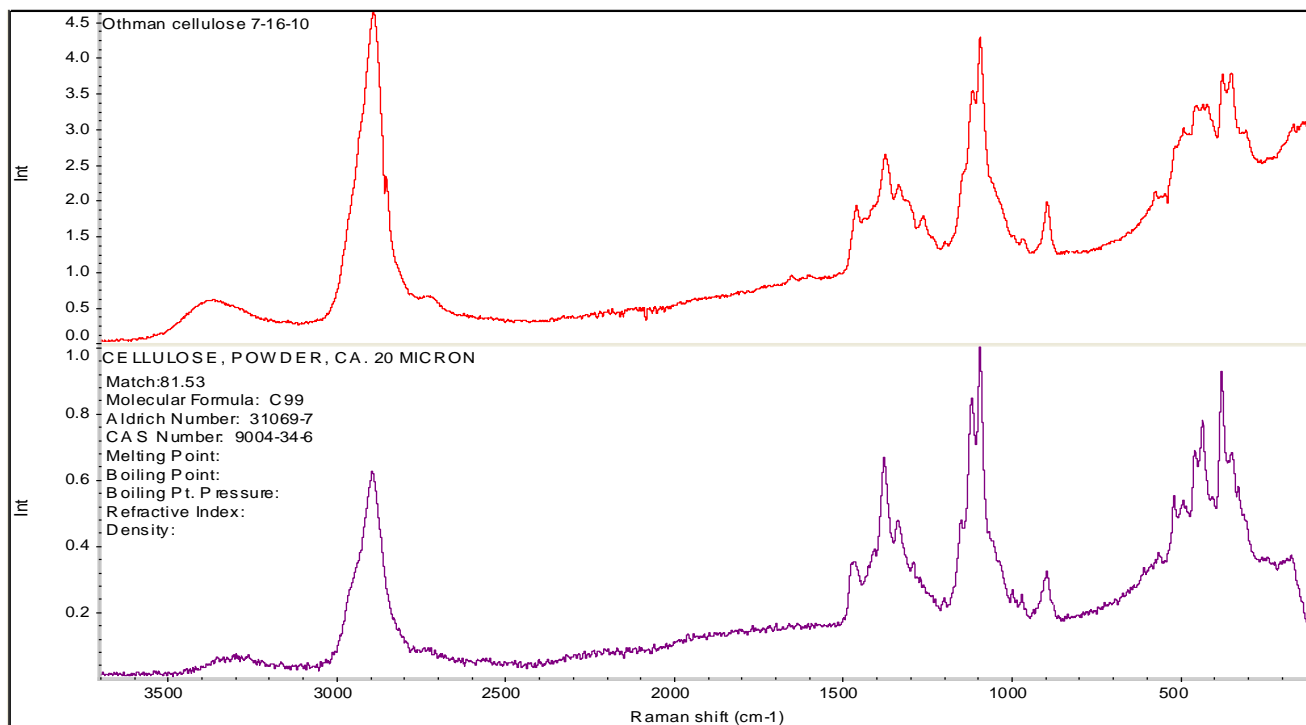


Fig. 2. IR spectra of OISW cellulose and cellulose powder

Scanning Electron Microscopy (SEM)

Cellulose powder extracted from OISW also was investigated by scanning electron microscopy (SEM). Figure 3 shows the SEM images of cellulose powder at three different magnifications; a) 50x, b) 200x, and c) 1000x. These images clearly show that MCC particles have a regular flat shape with semi porous surface. From Figure 3c, the diameter of cellulose powder was found to be *ca.* $6.5\ \mu\text{m}$.

Table 5 shows a comparison of different parameters of cellulose powder obtained from olive waste and a commercial MCC. The parameter values for both samples are comparable. The purity of cellulose powder obtained from olive waste is somewhat lower. This could be attributed to the process of MCC commercial production that involves acid treatment of bleached pulp. More work is underway to determine the degree of crystallinity and the exact nature of the cellulose powder extracted from OISW.

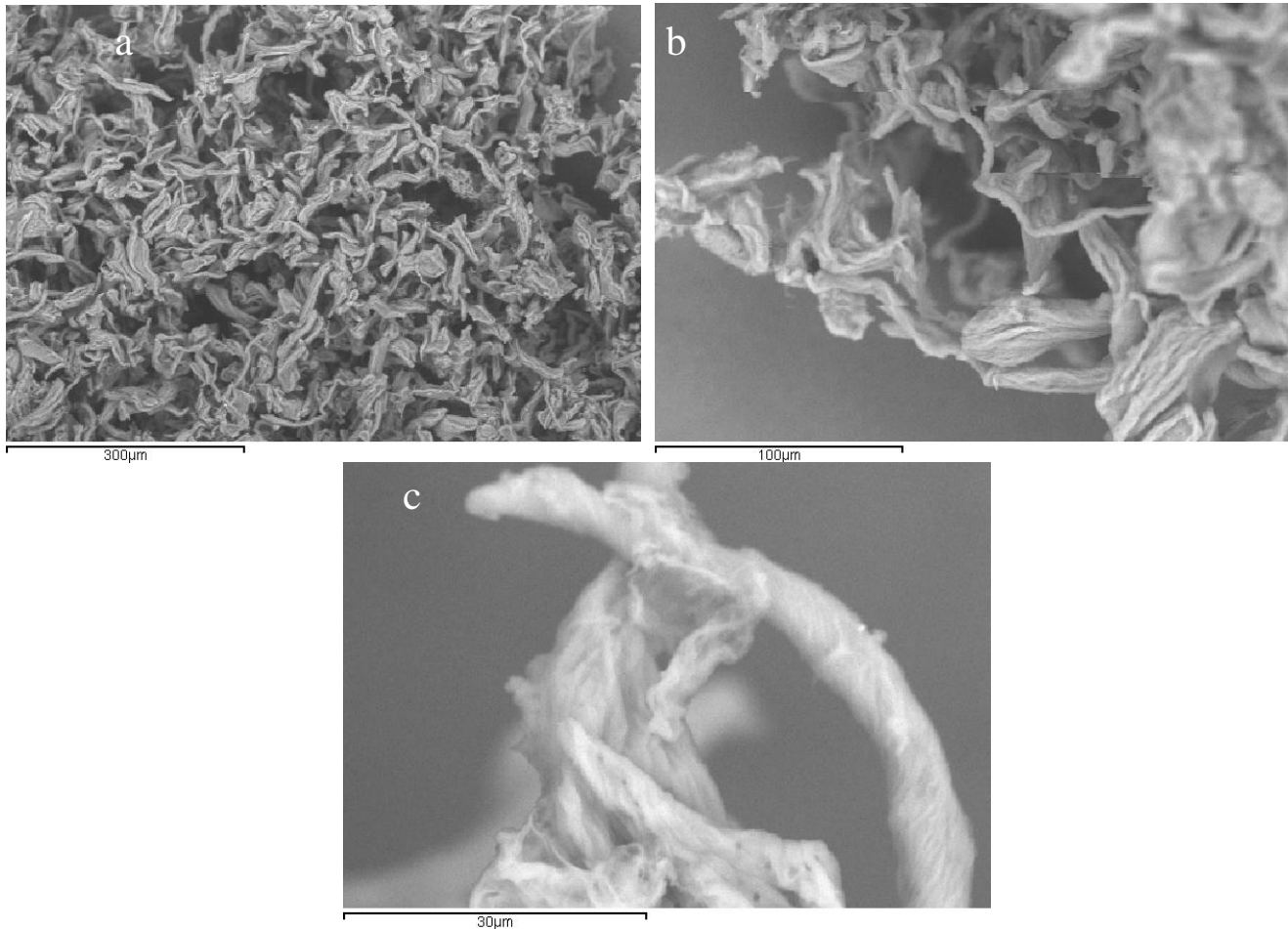


Fig. 3. SEM images of cellulose powder obtained from OISW at three different magnifications; a) 50x, b) 200x, and c) 1000x

Table 5. Comparison between Characteristic Properties of Commercial MCC and Cellulose Powder Obtained from Olive Waste (Laka and Chernyavskaya 2007b)

Pulp Parameters	Commercial MCC*	MCC from OISW
Viscosity (c.p.)	2.38	1.66-2.12
Degree of polymerization	465.6	308-405
pH	6.2	6.4-6.7
Ash (%)	0.1	0.23-0.91
ether extracts (%)	2.5	3.1
Water extracts (%)	0.4	0.68
Density (g/cc)	0.26	0.270-0.285
Moisture contents	4.5	6.1

* (Atchison, 1996)

CONCLUSIONS

1. Solid waste material from the olive industry could be a valuable source of commercially important material microcrystalline cellulose.
2. Cellulose powder was extracted from OISW by conventional kraft pulping, which was then subjected to various bleaching sequences.
3. The best result was obtained with totally free bleaching sequence APEP.
4. The characteristics of the extracted cellulose powder were comparable to those of commercial MCC.
5. Hydrolysis results of cellulose powder extracted from OISW with sulfuric acid have shown that OISW could become a valuable source of bi-ethanol.

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