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Ultrasound assisted extraction and characterization of pectin from tomato waste

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ABSTRACT

Pectin was extracted from tomato waste using two different extraction methods to assess its potential utilization as an alternative source of commercial pectin production. Tomato waste was treated with ammonium oxalate/oxalic acid by conventional extraction (CE), under reflux and ultrasound assisted extraction (UAE) at 37 kHz and temperatures of 60 °C and 80 °C. The pectin obtained from these methods was analysed and compared in terms of yield, chemical properties and structure. Among examined methods, CE at 60 °C resulted with the highest yield, but UAE during 15 min of sonication produced the pectin of better quality (anhydrouronic acid, methoxy and calcium pectate contents and degree of esterification). NMR and FTIR spectroscopy of isolated pectins revealed predominantly esterified structure, irrespective of extraction conditions. The comparison of the pectin yields obtained after extraction at 80 °C, indicate that similar values were found at times of 24 h and 15 min for CE and UAE, respectively. According to obtained results it can be concluded that main advantage of UAE is considerable shortening of extraction procedure with strong emphasis on environmental friendly processing approach. Therefore, these results suggested that UAE could be used as an efficient technique for the extraction of pectin from tomato waste and by-products.

1. Introduction

Tomato (*Lycopersicon esculentum* Mill.) is widely consumed vegetable crop, with a world production of 161,793,834 tonnes in 2012 (FAOSTAT, 2012). Millions of tons of tomatoes are processed yearly to produce products such as tomato juice, paste, purée, ketchup, sauce and salsa, resulting in generation of large quantities of wastes (Schieber, Stintzing, & Carle, 2001). Tomato waste, obtained after pressing of tomato is composed of 33% seed, 27% skin, and 40% pulp, while dried tomato pomace contains 44% seed and 56% pulp and skin (Kaur, Wani, Oberoi, & Sogi, 2008). Owed to rapidly expanding global demand on manufacturing processes and final products exerting minimal or no environmental risk, fruit and vegetable processing wastes have been the subject of significant research during the last years (Balasundram, Sundram, & Samman, 2006). Tomato processing waste is often utilized as animal feed or fertiliser, but in the recent years the scientific reports (Botinestean, Gruia, & Jianu, 2015; Westphal, Bauerfeind, Rohrer, & Volker Bohm, 2014) showed that tomato by-product fractions could be used as a low-cost source of various functional ingredients, such as vitamins, carotenoids, essential oils and pectin.

The commercially available pectin is almost exclusively derived from citrus peel or apple pomace, by-products from juice manufacturing. The novel plant sources of pectin extraction such as mango peel (Berardini, Knödler, Schieber, & Carle, 2005), cocoa husks (Mollea, Chiampo, & Conti, 2008), passion fruit peel (Kulkarni & Vijayanand, 2010), banana peel (Gopi, Kanimozhi, Bhuvaneshwari, Indira, & Kavitha, 2014) and pomegranate peel (Ganesh Moorthy, Prakash Maran, Muneeswari Surya, Naganyashree, & Shivamathi, 2015) have been reported. To the best of our knowledge, research on the extraction of pectin from tomato by-products is limited (Nincevic Grassino et al., 2016).

Pectins represent a family of the plants cell wall polysaccharides, mostly constituted by D-galacturonic acid and followed by D-galactose and L-arabinose (Caffall & Mohnen, 2009). Almost

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80% of carboxyl groups of galacturonic acid are esterified with methanol.

The galacturonic acid content of food grade pectins shall be not less than 65%, according to EU regulation No. 231/2012, 2012. In contrast to food use, there are no regulations for feed use (EU regulation 68/2013/EU, 2013).

The pectin extraction presents multiple stage physico-chemical process influenced by various conditions, such as temperature, pH, time, solvents, material/solvent ratio and number of extractions. A large number of solvents have been used for pectin isolation from plant tissue, i.e., water, buffer solutions, chelating agents, sulfuric, hydrochloric and nitric acids or organic acids and their salts (Aina et al., 2012; Azad, Ali, Akter, Rahman, & Ahmed, 2014; Khule, Mahale, Shelar, Rokade, & Chaudhari, 2012; Kulkarni & Vijayanand, 2010; Kumar & Chauhan, 2010; Min et al., 2011; Mollea et al., 2008; Ziari, Ashtiani, & Mohtashamy, 2010).

Furthermore, the numerous extraction methods have been developed to improve better extraction efficiency and quality of pectin, such as solvent extraction by stirring and heating, heat refluxing extraction, microwave extraction, enzymatic extraction, ultrasound-assisted extraction, ultrasound-assisted treatment combined with subcritical water (Chen, Fu, & Luo, 2015; Prakash Maran & Priya, 2015a; Thirugnanasambandham, Sivakumar, & Prakash Maran, 2014).

Ultrasound processing is widely used in food industry due to its capability to induce chemical and physical changes of food components (Barba, Grimi, & Vorobiev, 2015; Herceg et al., 2009; Pingret, Fabiano-Tixier, Bourvellec, Renard, & Chemat, 2012. Increased emulsifying capacity, release and diffusion of cell material, enhanced foaming are some of the improvements on foods using sonication (Šic Žlabur et al., 2015).

Prakash Maran and co-authors (Ganesh Moorthy et al., 2015; Prakash Maran & Priya, 2014; Prakash Maran & Priya, 2015a, 2015b) reported that ultrasound assisted extraction (UAE) provided economical and efficient separation of pigments, polyphenols and pectin. That is why we attempted to use this powerful technique for pectin isolation from tomato waste as well. Therefore, the main contribution of this work is utilization of UAE in order to enhance extraction efficiency, reducing time and processing temperature. The effect of extraction processing parameters, i.e., time and temperature on yield and chemical composition of pectins was evaluated as well. Furthermore, although pectin occurs commonly in most of the plant tissues, the number of sources that may be used for the commercial manufacture of pectin is limited. Therefore, this work presents possibility of utilizing tomato waste from food canning industry, among not yet fully explored sources for pectin production.

2. Materials and methods

2.1. Materials

The dried tomato by-product from canning factory was obtained after processing of fresh tomato purchased from the farm markets in the Agro Nocerina area of Campania (Italy). The materials were milled using an electric grinder and packed in polyethylene bags for analysis. Subsequently, the particle size of milled tomato waste was analysed using a Laser particle sizer (Mastersizer 2000, Malvern Instruments, Worcerstershire, UK). The particle size distribution was as follow d (0.1) = 28 μm, d (0.5) = 193 μm and d (0.9) = 416 μm.

The commercially available pectin from apple was provided by Sigma Aldrich. All the chemicals and reagents were of analytical grade.

2.2. Pectin extraction

Pectin was isolated from raw, dried and milled tomato waste according to the method described by Johnson, Dorot, Liu, Chefetz, and Xing (2007) for removal of pectin aqueous material from the plant cuticle in ammonium oxalate/oxalic acid as extracting solvent. Here, the extraction was slightly modified, using two different methods, i.e., conventional extraction (CE), under reflux and ultrasound-assisted extraction (UAE). The extraction under reflux in a condensation system, was performed at 60 and 80 °C during 24 h in the first step and then subsequently with a fresh volume of extracting solvent during 12 h in the second step. UAE was carried out also at temperatures of 60 and 80 °C and frequency of 37 kHz (ultrasonic bath, Elmasonic, Germany). Sonication time was 15, 30, 45, 60 and 90 min. At the end of extraction, the mixture was filtered through filter paper and then the filtrates were passed through Whatman No. 3 filter paper under vacuum. Pectins were precipitated by adding 3 volumes of 96% ethanol. The precipitated residues were filtered under vacuum through Whatman No. 3 filter paper and then were washed with ethanol (70% and 96%) and acetone. Then, the pectin was finally dried at 40 °C in a vacuum oven. Flow diagram of pectin extraction process is presented in Fig. 1.

Pectin yield (%) was expressed as the ratio of dried pectin mass (W_p) obtained after extraction to the initial mass of dried tomato waste (W_t) used for extraction:

$$\text{Yield}(\%) = \frac{W_p}{W_t} \cdot 100 \quad (1)$$

2.3. Determination of ash and total sugar content

Ash and total sugar contents were determined according to the procedure described by Zouambia, Ettoumi, Krea, and Moulai-Mostefa (2014).

2.4. Titrimetric determination of pectin content

Determination of methoxyl (MeO) and anhydrouronic acid (AUA) contents and degree of esterification (DE) in extracted pectins was performed according to the method described by Nazaruddin, Noor Baiti, Foo, Tan, and Ayob (2013). Briefly, in 0.5 g of pectin 5 mL of ethanol (96%), 1 g of sodium chloride and 100 mL of deionized water were added. The mixture was stirred until pectin was fully dissolved and titrated with 0.1 M NaOH with phenol red as indicator. Then, 25 mL of 0.25 M NaOH was added with mixing to de-esterify pectin. After 30 min 25 mL of 0.25 M HCl was added to neutralize NaOH and solution was titrated again with 0.1 M NaOH until the color changes.

2.5. Determination of calcium pectate

The calcium pectate content in the dried pectin extracts was determined according to the gravimetric method described by Ranganna (1995).

2.6. Determination of pectin color

The color of the pectins was measured using calibrated CM-3500d spectrophotometer (Konica Minolta Sensing, Inc. Osaka, Japan) attached with Spectra Magic NX software and expressed as L (lightness: 0 = black, 100 = white), a ($-a$ = greenness, $+a$ = redness), and b ($-b$ = blueness, $+b$ = yellowness) values.