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Utilization of tomato peel waste from canning factory as a potential source for pectin production and application as tin corrosion inhibitor

Antonela Ninčević Grassino*, Jasna Halambek, Senka Djaković, Suzana Rimac Brnčić, Maja Dent, Zorana Grabarić

Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottijeva 6, 10000 Zagreb, Croatia

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Citric acid (PubChem CID: 311)
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Ethanol (PubChem CID: 702)
Oxalic acid (PubChem CID: 971)
Pectin (PubChem CID: 441476)
Potassium bromide (PubChem CID: 253877)
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Sodium chloride (PubChem CID: 5234)
Sodium hydroxide (PubChem CID: 14798)

ABSTRACT

Background: The possibility of utilizing the bioorganic tomato peel as a cheap source for pectin production and its application as a corrosion inhibitor was investigated to implement viable cyclical economy principle in solving the main problem of waste disposal.
Methodology: Pectin, from two batches (A and B) from canning factory, was extracted in two steps with ammonium oxalate/oxalic acid, under reflux. Physico-chemical properties, characterisation of structure (FTIR and NMR spectroscopy) and application as corrosion inhibitor of pure tin for isolated pectin were investigated.
Results: The highest pectin yield of 32.6 and 31.9% in two batches, respectively, but the lowest pectin quality, i.e. methoxy and anhydrouronic acid contents and degree of esterification, were obtained in the second extraction step, which points out that higher pectin yields are not necessarily connected with higher pectin quality. The results of total anhydrouronic acid content for batches A (52.9%) and B (39.6%) show that sample origin have a considerable effect on pectin quality. Degree of esterification around 82% categorizes extracted pectin as high methoxy pectin. Corrosion results point out that pectin is efficient inhibitor (73%) even at very low concentrations, much better then commercially available pectin.
Conclusion: According to chemical profile, rheological properties and structural characterisation of extracted pectins, it can be concluded that tomato peel is a suitable source for pectin isolation. The obtained results show that under-utilised biomass waste from tomato canning industry can be used for development of new generation of corrosion inhibitors and as valuable additive in food industry.

1. Introduction

The industrial processing of tomato (*Lycopersicum esculentum*) results in the accumulation of large amounts of by-products composed of tomato peels, seeds and small amount of pulp. This material is currently disposed as a solid waste or used as animal feed, but the abundance of bioactive compounds in by-products suggests possibility of utilizing them as a cheap source of different bioactive compounds and high value functional ingredients, such as soluble dietary fibers (i.e. pectin). Pectin is not only found in the primary cell walls but also in the middle lamellas between plant cells where it helps to bind the cell together (Mohnen, 2008). For commercial manufacture of pectin a citrus peel and apple pomace are used. The alternative sources for pectin extractions from *Cissampelos pareira* (Singthong, Cui, Ningsanond, & Goff, 2004), cocoa husks (Mollea, Chiampo, & Conti, 2008) and passion fruit peel (Kulkarni & Vijayanand, 2010) are described. To the best of our knowledge, little or no research has been done on the extraction of pectin from tomato waste.

Pectins are mainly used in food processing industry as gelling and thickening agents, as well as stabilizers in jams, jellies, confectionery products and fruit juices. Pectin is also used in medicine,

* Corresponding author.
E-mail address: aninc@pbf.hr (A.N. Grassino).

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pharmaceutical and cosmetic industry as natural prophylactic, as binding agent in tablet formulations and as carrier of a variety of drugs.

The functionalities of pectins depend mainly on the plant source as well as on the extraction conditions used. For extraction of pectin from plant tissues different solvents have been reported, such as sulphuric, hydrochloric, and nitric acid (Aina et al., 2012; Azad, Ali, Akter, Rahman, & Ahmed, 2014; Kulkarni & Vijayanand, 2010; Mollea et al., 2008; Singthong et al., 2004; Ziari, Ashtiani, & Mohtashamy, 2010), or organic acids and their salts (Azad et al., 2014; Min et al., 2011). A large number of extraction methods (Srivastava & Malviya, 2011) have been developed to obtain maximal yield and quality of pectin. The techniques most frequently used are: *i*) solvent extraction by stirring and heating, *ii*) heat refluxing extraction and *iii*) microwave heating extraction.

To determine chemical characteristics of pectin powder, i.e. quality and purity, methoxy content, anhydrouronic acid and degree of esterification are measured by standard titration methods as preferred techniques (Anese, Mirolo, Beraldo, & Lippe, 2013; Kulkarni & Vijayanand, 2010; Mollea et al., 2008). Concentration of galacturonic acid, as an another criteria of pectin quality, is usually determined spectrophotometrically (Mollea et al., 2008; Ranganna, 1995, chap. 2). Frequently used techniques for quantification and characterization of pectin extracts are NMR and FTIR spectroscopy, too (Gopi, Kanimozhi, Bhuvaneshwari, Indira, & Kavitha, 2014; Khule, Mahale, Shelar, Rokade, & Chaudhari, 2012; Min et al., 2011).

A few papers reported the application of pectin extracted from food industrial waste as a corrosion inhibitor. Fiori-Bimbi, Alvarez, Vaca, and Gervasi (2015) used pectin from citrus peel as corrosion inhibitor for mild steel in HCl solutions and Fares, Maayta, and Al-Qudah (2012) used commercially available pectin as corrosion inhibitor for aluminium in hydrochloric acid. Therefore, the isolation of pectin from a cheap and abundant renewable resource, such as tomato waste, and its application as corrosion inhibitor of tin and food additive, is the main contribution of this work, moreover makes the transition towards a circular economy to happen. Thus, the evaluation of this bioorganic material was performed in four steps: *i*) analysis of tomato peel by-products obtained from food canning factory as a potential sources for pectin production, *ii*) comparison of physico-chemical properties of pectin extracted from two types of tomato peels, *iii*) characterisation of pectin structure using FTIR and NMR spectroscopy and *iv*) application as corrosion inhibitor of pure tin.

2. Methods

2.1. Materials

Two batches (A and B) of dried tomato peel were 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.

The commercially available pectin from apple with degree of esterification approx. 80% was provided by Sigma Aldrich. Pure tin (99.9%) for corrosion experiments was supplied from Primet d.o.o.–International metal trader, Slovenia.

All the chemicals and reagents were of analytical grade.

2.2. Chemical composition of dried tomato peel

Moisture (method 920.36), ash (method 942.05), crude fat (method 920.39) and fiber content (method 978.10) were estimated using AOAC methods (AOAC, 1995). For determination of sulphated ash, the method 942.05 was followed by moistening the ash with concentrated sulphuric acid and ignition at 600 °C to constant mass. The available carbohydrates were calculated by differences. Crude protein content was determined by Biuret method (Keppy & Allen, 2009). Titrable acidity and pH were determined according to the procedure described by Jamilah, Shu, Kharidah, Dzulkifly, and Noranizan (2011). The colour was measured using calibrated CM-3500d spectrophotometer (Konica Minolta Sensing, Inc. Osaka, Japan) attached with SpectraMagic NX software and expressed as L (lightness: 0 = black, 100 = white), a ($-a$ = greenness, $+a$ = redness), and b ($-b$ = blueness, $+b$ = yellowness) values.

Heavy metals and trace elements (Pb, Cd, Cu, Zn, Cr, Ni, Mn, Fe, V and As) were determined by atomic absorption spectrometry-inductively coupled plasma optical emission spectroscopy (AAS ICP OES) after microwave digestion with HNO_3 (European standard – EN 14084-1, 2003). Obtained solutions were analysed using Perkin Elmer ICP OES - model Optima 8000, USA.

2.3. Pectin extraction

Pectin was extracted from two dried tomato peel batches (A and B), under reflux in a condensation system at 90 °C, using ammonium oxalate (16 g/L) and oxalic acid (4 g/L) as extracting solvents, in two extraction steps (24 and 12 h, first and second step, respectively).

The flow chart for the extraction of pectin from two dried tomato waste batches is shown in Fig. 1.

Pectin yield was expressed as the ratio of dried pectin mass obtained after extraction to the initial mass of tomato peel.

2.4. Determination of pectin composition with titrimetric method

Methoxy (MeO), anhydrouronic acid (AUA) and degree of esterification (DE) in extracted pectins was measured 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 colour 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, chap. 2).

2.6. Determination of pectin rheological properties

Rheological characterization was performed using a rotational viscosimeter with cylindrical measurement system–Rheometric Viscometer (Model RM 180, Rheometric Scientific, Inc., Piscataway, USA) equipped with the measuring system 33 (measuring tube Ø 15.18 mm and measuring bob Ø 14 mm, volume 17 mL). Flow behaviour was determined at a constant temperature (20 °C) in the shear rate values from 0 to 1290 s^{-1}. Viscosity was studied using 1% (by mass per volume) aqueous solution of pectin with 55% (mass per volume) sucrose content at pH = 3.7. The shear rate versus shear stress was interpreted using the Rheometric computer program. The values for n and k were obtained from plots of log shear stress versus log shear rate, according to the power law equation: