Characterization of Jackfruit (*Artocarpus heterophyllus*) Waste Pectin as Influenced by Various Extraction Conditions

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**Abstract**

Pectin was extracted from jackfruit (*Artocarpus heterophyllus*) waste using three different extraction conditions to assess its potentiality as an alternative source of commercial pectin. Jackfruit waste was treated separately with ammonium oxalate, dilute sulphuric acid and sodium hexametaphosphate. The pectin obtained from these methods was compared in terms of yield, physicochemical properties and chemical structure. Among the three solvents, extraction with sodium hexametaphosphate gave the highest yield, however it contained high ash and showed the lowest solubility. Fourier transform infrared spectroscopy of jackfruit waste pectin irrespective of extraction condition revealed a similar surface structure to commercial pectin.

**Keywords:** Pectin extraction; jackfruit waste; yield; FTIR; physicochemical properties

1. Introduction

Jackfruit (*Artocarpus heterophyllus*) is a fruit crop widely distributed in Bangladesh and very popular with the people. In 2010-2011 Bangladesh produced 0.96 million ton of jackfruit in a total cultivated area of 10652 ha (BBS, 2012). The edible bulbs of ripe jackfruit are consumed fresh or processed into various products like canned products, jam, chips etc. About 60% of the whole fruit is inedible consisting of the outer prickly rind, inner perigones (non-edible perianth) and central core, which are unutilized waste (Subburamu et al., 1992). These fruit wastes are a

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problem to the processing industries and pollution monitoring agencies. Suitable methods can be used to convert these wastes into value-added products. By-product recovery from fruit wastes not only can improve the overall economics of processing units but also reduce the problem of environmental pollution considerably. Pectin is a valuable by-product that can be obtained from these fruit wastes.

Pectin is a complex heteropolysaccharide that contains 1,4-linked α-D-galacturonic acid residues; part of which esterified by methanol (Levigne et al., 2002). It is commonly found in the cell walls and middle lamellae of higher plants. This is a secondary food ingredient widely used as gelling, emulsifying and stabilizing agents in food products (Koubala et al., 2008a). Consumption of these polysaccharide has important positive effects on human health include reducing cancer development (Jackson et al., 2007), lowering blood cholesterol and blood glucose level (Behall and Reiser, 1986; Brown et al., 1999), and stimulating the immune response (Inngjerdingen et al., 2007). FAO (1969) recommended pectin as a safe additive and that can be taken daily without limits.

Developing countries like Bangladesh have to import this secondary ingredient at high prices which enormously affects the cost of products. It is interesting that this biopolymer can be found abundantly in fruit pulp, core and skin which are mostly discarded during processing. It is therefore worthy to identify the potential source of this valuable by-product by determining the pectin content of fruit waste. Pectin content of raw samples can be determined by estimating calcium pectate or by direct precipitation by ethanol or acetone. Pectins are commercially extracted from citrus peels and apple pomace with yields of about 25% (May, 1990) and 15-18% (Walter, 1991), respectively. Other sources of pectin include sunflower head residues and sugar beet (Miyamoto and Chang, 1992), cocoa husk (Mollea et al., 2008), soy hull (Kalapathy and Proctor, 2001), mango and amberalla peels (Koubala, 2012). To date, little or no research has been done on the extraction of pectin from jackfruit. For these reasons, an attempt was made to produce pectin from the jackfruit waste as an alternative source for apple and citrus pectin.

Pectin extraction process principally involved the preparation of alcohol insoluble residue (AIR) to reduce low molecular compound (Happi et al., 2008), aqueous extraction of pectin from AIR, the isolation of the extracted pectin and purification (Joye and Luzio, 2000) and followed by the drying process. The yield and properties of pectin usually depends on the raw materials used to extract pectin and the extraction conditions, such as temperature, extraction time, pH, and type of extraction solvents (Yeoh et al., 2008). Gelling properties of extracted pectin varies with its degree of esterification (DE), and hence, pectin is divided into high methoxyl pectin (DE>50%) and low methoxyl pectin (DE <50%) based on the degree of esterification (Mesbhai et al., 2005). Among the factors that influence the yield and type of pectin, different types of solvents used to extract pectin are crucial. The aims of the present study were to evaluate the potential parts of jackfruit waste containing pectin and determine the impact of different extraction conditions on the yield and physico-chemical and structural characteristics of pectin derived from the jackfruit waste.

2. Materials and methods

2.1 Raw materials

Jackfruit was collected from the germ plasm center, Bangladesh Agricultural University, Mymensingh, Bangladesh. Inedible portion of jackfruit were collected and stored in the deep freezer at -20 °C.

2.2 Estimation of pectin as calcium pectate

Pectin content in different parts of different variety jackfruit fruit were determined as calcium pectate using the gravimetric method described by Rangana (1986). The 50 g blended samples were extracted with 400 ml 0.05 N hydrochloric acid (HCl) for 2 hours at 85 °C. Then volumes were made up to 500 ml with distilled water and filtered through No. 4 What man paper. To the 100 ml aliquots, 250 ml distilled water was added and the acid was neutralized with 1 N sodium hydroxide. Then 10 ml of 1 N sodium hydroxide was added in excess and allowed to stand overnight. 50 ml of 1N acetic acid was added and after 5 minutes 25 ml of 1 N calcium chloride was added with continuous stirring. The solution allowed to stand for 1 hour, and boiled for 1–2 minutes. Then it was filtered through previously prepared (washed with hot water and dried at 102 °C for 2 hours), weighed filter paper and the
residue remained on the filter paper was dried to constant weight and weighed along with the filter paper. The pectin content was calculated and expressed as per cent calcium pectate using the equation below:

\[
\% \text{ calcium pectate} = \frac{\text{Weight of calcium pectate} \times 500 \times 100}{\text{weight of sample} \times \text{ml of aliquot taken for estimation}}
\]  

(1)

2.3 Alcohol insoluble residue (AIR)

Jackfruit waste was washed with water to remove all adhering substances, cut into small pieces and dried in a cabinet dryer at 50 °C. The dried waste was powdered using a mechanical grinder. The ground powder was then suspended in 85% (v/v) ethanol at 70 °C for 20 min in a shaking water-bath. The resulting alcohol-insoluble-residue (AIR) was collected and air-dried at 50°C. The method was modified from Koubala et al. (2008a).

2.4 Pectin extraction

Pectin was extracted from the jackfruit waste using three different extraction solvents (ammonium oxalate, sulfuric acid and sodium hexametaphosphate) and compared to determine the best condition for good quality pectin recovery from jackfruit waste. Five gram of AIR was heated separately with 200 ml of extraction solutions: with the use of ammonium oxalate (0.25%), pH 4.6 ±0.01 adjust with 0.01 N oxalic acid (Ismail et al., 2012) at 85 °C for 1 hour; acidic solution pH 2.5 ±0.02 adjusted with 0.1 N sulfuric acid at 80 °C for 1 hour (Rehman et al., 2004); and 0.6 g of freshly ground sodium hexametaphosphate solution pH adjusted 2.2±0.02 with 3N HCl heated at 80 ±5 °C (Mohamed and Hasan, 1995). The extracts were separated from the AIR residue by filtering through four fold cheese cloth and cool immediately by chilled water, dispersed in an equal volume of 95% ethanol, stir 5 min for proper mixing and allowed to stand for 1 h. In the case of sodium hexametaphosphate, the extract was dispersed in an equal volume of 95% ethanol containing 0.5 M HCl. The precipitate was collected, washed 3-4 times by 70% acidic ethanol (0.5% HCl), 70% ethanol, followed by 95% ethanol. The product was then dried at 40 °C in an air oven to constant weight. The dried pectin was ground to 400 micron mesh and stored at room temperature for further experiment and compared with commercial pectin from Luba chemie Pvt. Ltd.

2.5 Physico-chemical parameters

The moisture and ash content were determined by AOAC (1980) method. Weighed ash was treated with 0.5 M HCl, and the colloidal solution was filtered, ignited and weighed to obtain the acid insoluble ash (Gee et al., 1958)

2.6 Solubility of pectin powder in water and alkali

Pectin samples (0.5%) were moistened with 95% ethanol, dispersed in deionized water, and stirred in a vortex mix to dissolve. To obtain the hot water soluble fraction, the mixture was heated at 90 °C for 15 min (Fishman et al., 1984). Exactly 1 ml of 1 N NaOH was added to 5 ml prepared pectin solution, mixed properly and heated at 90 °C for 15min to observe the changes in alkali solution (Joslyn, 1980).

2.7 Surface structure analysis

Fourier transform infrared spectra (FTIR) of jackfruit waste pectin samples were collected using the Perkin Elmer, GX spectrum model with wavelengths ranging from 400 - 4000 cm⁻¹.

2.8 Viscosity of pectin solution

The viscosity of 3% pectin solution in deionized water (wt/wt) was determined with a controlled stress Rheometer (AR G2, UK) with the cone plate measuring system (cone dia. 60mm truncation 30 micrometer) at a constant share rate (51 s⁻¹) and constant temperature (20 °C).
2.9 Statistical analysis

The experiments were conducted in three replicates. The values were expressed as the mean ± standard deviation. Statistical analysis was performed using the Statistical Package for Social Sciences (SPSS) (version 21) for Windows. The Duncan test was performed to evaluate significant differences between mean values. The confidence limits used in this study were based on 95% ($P<0.05$).

3. Results and discussion

3.1 Estimation of pectin content in jackfruit

Total pectin constituent of jackfruit was estimated as calcium pectate. Table 1 shows the calcium pectate content in the different portion of three jackfruit varieties. The results revealed that the calcium pectate content varied with variety and within the variety it varied with the different parts of the jackfruit. The amount, structure and chemical composition of pectin was highly inconsistent and influenced by many factors. It has been known to vary among different plants, plant varieties, plant tissues, and was also dependent on the stage of plant growth (Nelson et al., 1977). Edible portions (bulb) of the jackfruit contained 1.14-1.60% calcium pectate which is comparatively lower than that of the inedible portion (rind and core). Patil et al. (2011) had also found higher calcium pectate content in the inedible portion of jackfruit than the edible portion. This may be due to pectin found in and between the cell walls as an integral structural component of cells which helps to give them rigidity. Hence the hard parts of fruits contain more pectin than the soft parts.

Table 1. Effect of variety and parts on calcium pectate content of jackfruit.

<table>
<thead>
<tr>
<th>Variety of Jackfruit</th>
<th>% Calcium Pectate (fresh weight basis) in different parts of jackfruit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rind$^1$</td>
</tr>
<tr>
<td>Khaja</td>
<td>1.57±0.10</td>
</tr>
<tr>
<td>Gala</td>
<td>2.28±0.16</td>
</tr>
<tr>
<td>Durasha</td>
<td>1.72±0.14</td>
</tr>
</tbody>
</table>

Average of three replications ± standard deviation.$^1$ outer prickly surface with inner non edible perianth.

3.2 Pectin yield

The yield of pectin extracted from jackfruit waste varied from 8.94 to 15.14% of the weight of jackfruit dry waste, depending on the various extraction conditions used. Pectin yield found in this study was lower than that obtained by Mohamed and Hasan (1995) from jackfruit waste (22.5%). The yield, moisture content, ash content and acid insoluble ash content of pectin extracted from jackfruit waste (Durasha variety) are presented in Table 2. The highest yield of pectin (15.14%) was obtained in the extraction with sodium hexametaphosphate/HCl whereas the lowest pectin (8.94%) yield was obtained with the acid extraction (0.1 N H$_2$SO$_4$). Extraction with ammonium oxalate/oxalic acid gave 12.07±0.8% of pectin. There were significant difference ($P<0.05$) in the yields of pectin for all extraction conditions. Pectin extraction is a multiple stage physical-chemical processes in which the hydrolysis and extraction of pectin macromolecules from plant tissue occur sequentially. Different factors, mainly extraction temperature, pH, time and solubilizing agents affect the extraction of pectin (Yeoh et al., 2008; Kertesz, 1951). Previous studies also revealed higher extraction yield by sodium hexametaphosphate and ammonium oxalate than simple acid hydrolysis (Nazaruddin et al., 2013; Ismail et al., 2012; Koubaia et al., 2008b and Mohamed and Hasan, 1995). In the middle lamella of plant cells, pectins are physically bound in situ via metallic cations, especially divalent cations. Sequestering agents such as sodium hexametaphosphate and ammonium oxalate which readily bind those cations and help to release the pectins from cell walls (Yeoh, 2008).
Table 2. Yield, moisture content, ash content of pectin extracted from jackfruit waste.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield</th>
<th>Moisture content</th>
<th>Ash content</th>
<th>Acid insoluble ash content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium oxalate extracted pectin</td>
<td>12.07±0.80a</td>
<td>9.78±0.95b</td>
<td>4.77±0.71b</td>
<td>0.06±0.03a</td>
</tr>
<tr>
<td>Sulfuric acid extracted pectin</td>
<td>8.94±0.91b</td>
<td>7.72±0.75a</td>
<td>3.71±0.64b</td>
<td>0.08±0.03a</td>
</tr>
<tr>
<td>Sodium hexametaphosphate extracted pectin</td>
<td>15.19±0.35c</td>
<td>14.73±0.61c</td>
<td>8.15±0.30c</td>
<td>0.27±0.15b</td>
</tr>
<tr>
<td>Commercial pectin</td>
<td>ND</td>
<td>10.94±0.89b</td>
<td>1.86±0.51a</td>
<td>0.02±0.10a</td>
</tr>
</tbody>
</table>

Mean value from triplicate mean± standard deviation. Values with different superscript in the same column are significantly different (p< 0.05). ND=Not done

3.3 Physico-chemicals parameters

Moisture contents of all the samples were in the acceptable range (below 12%) except the one extracted with sodium hexametaphosphate (14.73%)(Table 2). Pectins should have low moisture contents for safe storage. Elevated moisture content may accelerate the growth of microorganisms that can affect the pectin quality due to the production of pectinase enzymes (Muhamadzadeh et al., 2010). The results showed that sodium hexametaphosphate extracted pectin contained higher moisture content compared to ammonium oxalate extracted pectin (9.78%), acid extracted pectin (7.72%) and commercial pectin (10.94%). The inorganic impurities in pectin are indicated by the ash content. Pectin extracted by sodium hexametaphosphate had the highest (8.15%) and sulfuric acid extracted pectin had the lowest (3.71%) ash content. Commercial pectin contained significantly lower (P < 0.05) ash than that of extracted pectin from jackfruit waste. Acid insoluble ash of all extracted pectins were found to be between 0.06%-0.27% and did not show significant differences (P<0.05) with commercial pectin except for sodium hexametaphosphate extracted pectin. Ranganna (1986) stipulated that the ash content in pectin could vary from the 0.76 to 10.69%. Since low ash content is more favorable for gel formation, it could be reduced by washing with acidified alcohol. Previous study also reported the high ash content in ammonium oxalate (Ramli and Asmawati, 2011) and sodium hexametaphosphate extracted pectin (Mohamed and Hasan, 1995). This could be due to the ability of chelating agents to solubilize indigenous minerals in the jackfruit waste.

3.4 Solubility of the pectin

Solubility in water, pH and the effect of alkali on different types of extracted pectins from jackfruit and commercial pectin are presented in Table 3. The ammonium oxalate extracted pectin showed the highest solubility whereas the lowest solubility was exhibited by the pectin extracted with sodium hexametaphosphate dispersed both in cold and hot water. However, commercial pectin was completely dissolved in cold water. According to the definition, pectin should be soluble in water. The results showed that a decrease in esterified carboxylic group reduced the solubility of extracted pectin. This insolubility of the extracted pectin is probably due to the presence of electrolytes in de-methylated pectic acid. High ash content and the drying process of extracted pectin may be other reasons for reduced pectin solubility. The results also revealed that the pectin solution was yellow in colour in strong alkali, which turned into a white precipitate while heating at 90 °C for 15 min. Pectin is unstable in alkali solution (Fishman, 1993) which is used as a conformation test of pectin in solution.

Table 3. Solubility of pectin in water and reaction with alkali.

<table>
<thead>
<tr>
<th></th>
<th>Ammonium oxalate extracted pectin</th>
<th>Sulfuric acid extracted pectin</th>
<th>Sodium hexametaphosphate extracted pectin</th>
<th>Commercial pectin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility in cold water</td>
<td>Partly soluble, swell and produce suspension</td>
<td>Partly soluble, swell and produce suspension</td>
<td>Insoluble</td>
<td>Soluble and produce suspension</td>
</tr>
<tr>
<td>Solubility in hot water</td>
<td>Some insoluble portion present and produce suspension</td>
<td>Some insoluble portion present and produce suspension</td>
<td>Partly soluble and produce suspension</td>
<td>Soluble, and produce suspension</td>
</tr>
<tr>
<td>Changes in cold alkali</td>
<td>yellow colour formed</td>
<td>yellow colour formed</td>
<td>yellow colour formed</td>
<td>yellow colour formed</td>
</tr>
<tr>
<td>Changes in hot alkali</td>
<td>Produce white sediment</td>
<td>Produce white sediment</td>
<td>Produce white sediment</td>
<td>Produce white sediment</td>
</tr>
</tbody>
</table>
3.5 Surface structure

Fourier Transform Infrared (FTIR) spectra were analyzed to confirm the identity of extracted pectins and to estimate the degree of esterification (DE). The FTIR spectra showed the functional groups and structural information of different extracted pectins and the pure pectin in the region between 1,000 and 2,000 cm\(^{-1}\) (Kalapathy and Proctor, 2001; Walner et al., 1998). Wavelength range of 950 and 1200 cm\(^{-1}\) are considered as the ‘finger print’ region for carbohydrates as it allows to identify the major chemical groups (ether R-O-R and cyclic C-C bond) in polysaccharides (Cerna et al., 2003). Similar spectra of the jackfruit waste extract and the pectin standard (commercial pectin) in the “fingerprint” region implied that the extracts were effectively pectin. The carbonyl bands at 1630-1650 and 1740-1760 cm\(^{-1}\) indicate the presence of free and esterified carboxyl groups, respectively (Gnanasambandam and Proctor, 2000). The increase in degree of esterification (DE) values will also increase the intensities and band area of the esterified carboxyl groups. Pectin DE can be determined using the peak area in relation to the free carboxyl groups (1650 cm\(^{-1}\)) and esterified groups (1750 cm\(^{-1}\)) (Gnanasambandam and Proctor, 2000). Pectin extracted by ammonium oxalate and sulfuric acid showed higher absorbance of esterified carboxylic groups than that of free carboxylic groups, and hence indicate a higher DE. However, the sodium hexametaphosphate extracted pectin showed higher absorbance of free carboxylic groups than esterified ones. In these spectrum, the band from 1320-1000 cm\(^{-1}\) suggest the presence of small amount of ferulic acid linked to the extracted pectin (Sebastiana et al., 2009). The broad band, from 2,900 to 3,600 cm\(^{-1}\), was due to absorbed moisture in the pectin samples.

Fig. 1. FTIR spectra of jackfruit waste pectin extracted by ammonium oxalate (1), sulfuric acid (2) sodium hexametaphosphate (3) and commercial pectin from Luba chemie pvt.Ltd. (4).

Fig. 2. Viscosity of different pectin at 51 s\(^{-1}\) shear rate: Ammonium oxalate (1), sulfuric acid (2), sodium hexametaphosphate (3) extracted pectin and commercial pectin from Luba chemie pvt.Ltd. (4).
3.6 Viscosity

The viscosity of the different pectins extracted under different extraction condition from jackfruit waste and pure pectin are presented in Fig. 2. In this figure the viscosity of the pectins were plotted at a shear rate of 51 which is close to the shear rate of mastication process (50 s⁻¹) (Sherman, 1976). Ammonium oxalate extracted pectin demonstrated significantly (P <0.05) highest viscosity (0.884 Pa.s) and sodium hexametaphosphate extracted pectin was found to have significantly (P<0.05) the lowest viscosity among all pectin samples. Sulfuric acid extracted pectin also showed higher viscosity (0.347 Pa.s) but was not significantly different from the commercial pectin (0.191 Pa.s). Degree of esterification has a great impact on viscosity. Higher degree of esterification shows higher viscosity (Monsoor and Proctor, 2001). Sodium hexametaphosphate extracted pectin showed lower degree of esterification, a higher ash content, and a very low viscosity.

4. Conclusions

Jackfruit waste can be a good source of highly esterified pectin. Extraction conditions and solvent types had a major impact on the yield and physicochemical properties without any significant effects on the pectin’s structure. However, the extracted pectin was poor in terms of solubility and high ash content compared to the commercial pectin. Further research is underway in order to improve the solubility of extracted pectin and explore the gelling properties of these pectins.

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References


Food Hydrocolloids 19, 731-738.


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