Production and Characterisation of Pectin from Cocoa Bean Shells

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ABSTRACT

Cocoa bean shells constitute the major waste generated from the industrial processing of cocoa beans. The shells contain about 9% of pectin and extracting it would be of economic and ecological importance. However, limited knowledge on the characteristics of the pectin from cocoa bean shells and the extraction conditions, which would yield pectin of good quality and sufficient quantity, restrict the possible use of the shells as a source of commercial pectin. The objective of this study was to extract and characterise pectin from cocoa bean shells, with focus on finding the optimum extraction conditions. The conventional hot dilute acid extraction method was used. 12 M hydrochloric acid was used to acidify water to pH 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0. Extractions were carried out at temperatures of 60, 70, and 80 °C, for different times of 0.5, 1, and 2 h. The effects of each of the conditions on yield and other properties of pectin were evaluated. Depending on the conditions under which cocoa bean shells were treated, both high methoxyl and low methoxyl pectins were extracted. At the optimum conditions of pH 3.5, extraction time of 2 h and 80 °C extraction temperature, high methoxyl pectin was obtained. The yield was 4.7%, the degree of esterification was 68.9% and the anhydrouronic acid content was 71.2%. While the methoxyl content was 8.6%, the equivalent mass was found to be 805.8 g/eq. Moisture and ash contents were 6.7 and 10.3%, respectively, and the pH of the pectin hydrocolloid was 3.7. Fourier Transform Infrared (FT-IR) spectra confirmed the presence of functional groups found in the pectin structure. The intrinsic viscosity varied between 0.075–0.088 m3/kg and the molecular mass ranged from 23,470-42,384 g/mol. The results revealed that the shells are a viable source for commercial pectin, while necessary investigations focusing on the gelling, thickening, emulsifying, texturing, and stabilising potentials of the pectin from cocoa bean shells would inform of the areas of application.

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INTRODUCTION

Cocoa, a tropical cash crop of huge economic significance in the world, is the backbone of the economies of some countries in West Africa including Cote d’Ivoire and Ghana, where it is largely cultivated. Cote d’Ivoire is the leading producer of the world, with an average annual production of 40%, followed by Ghana with 20% (Afoakwa et al., 2011; Kongor et al., 2016). The third largest producer is Indonesia, with 10% (Tothmihaly & Ingram, 2017).

The beans are mostly exported to industrialised countries, where they are used in the confectionary and chocolate industries (Bastide, 2007). Some of the importers of the cocoa beans include the Netherlands (25%), United States (13%), Germany (11%), Belgium (9.8%), Malaysia (6.4%) among many others (Simoes, 2017). By-products from the processing of the beans include cocoa mass (cocoa liquor), raw cocoa powder, cocoa cake, and cocoa butter. The by-products are also known as intermediary products and are either exported or used domestically, in the chocolate industry of the country where the beans are processed (Afoakwa et al., 2011; Bastide, 2007).

A whole cocoa bean consists of the cotyledon (nib) enclosed in the shell. The shell is crispy brown (Ogunsipe et al., 2017) and provides adequate protection to the nib from mould and insect infestations. They are not desired in any of the cocoa bean products and constitute the highest amount of waste generated from cocoa processing. As waste, most of the cocoa processing companies in Ghana burn the shells as fuel for their boilers (Okiyama et al., 2017), while some power plants use the shells as a biomass fuel to produce electricity (Roos, 2010). The shells are also used as organic mulch (fertilizer) for soil conditioning (Afoakwa et al., 2011), and has been experimented for the preparation of animal feed for weaner rabbits, by treating with hot water and adding to the diet (Adeyina et al., 2010). Goats (Aregheore, 2002), chicken and sheep (Ogunsipe et al., 2017) have also been fed with the shells. In addition to these, the shells are used as an initiator to prepare binderless activated carbon monoliths, which possess high micropore volume and good mechanical performance (Plaza-Recobert et al., 2017), and as an alkalizing agent in cocoa powder and butter (Osundahunsi et al., 2007). The shells are also used as source of fibre and antioxidant, and to produce biodegradable European paper packaging (Nieburg, 2013). If any of the above potential avenues of use are unavailable, the shells are disposed of at landfills (Awarikabey et al., 2014).

However, research shows that the shells contain about 9% pectin (Okiyama et al., 2017; Mollea et al., 2008), as well as tannins, steroids, terpenoids, glycosides, flavonoids, and purine alkanoids. The shells also contain theobromine (Adamafio, 2013), mycotoxins, fibres, fat, and phenolic compounds such as catechins, epicatechins and procyanidins (Okiyama et al., 2017). These reported nutritional values of cocoa bean shells have led many researchers to propose its use as a source of food additives (Okiyama et al., 2017).

The objective of this study was to extract and characterise pectin from cocoa bean shells, at different conditions of pH, time, and temperature, and find the optimum extraction conditions.

MATERIALS AND METHODS

Raw Material

The raw material for this research work was cocoa bean shells, obtained from the Cocoa Processing Company Ltd. (CPC), located in the Heavy Industrial Area of Tema in the Greater Accra Region of Ghana.

To avoid any contamination that could influence the pectin extraction in any way, the cocoa bean shells were sorted by hand of impurities such as...
traces of nibs, unbroken beans, twines, sticks, dead germ, stones, and any other noticed foreign material. Fines were removed by sieving, using a laboratory sieve of 1 mm size on a shaker. Further cleaning of the shells of any fines attached to them was done by washing with water. The wet shells were air-dried.

To characterise the cocoa bean shells, its moisture content, particle size distribution, and ash content were determined. The moisture content was determined by oven drying of 5 g cocoa bean shells at 110 °C for 1 h. The moisture content was calculated for wet basis. The particle size distribution was determined by sieving of 100 g dried cocoa bean shells through sieves of 4, 2, and 1 mm, and 500, and 125 μm sieves arranged in series and vibrated on a shaker. The cocoa bean shells retained on each sieve was weighed.

The ash content was determined according to the method described by Sluiter et al. (2008). Dry cocoa bean shells were ashed in porcelain crucibles in a Nabertherm muffle furnace at 600 °C for 4 h and the cooled crucibles then weighed, the ash content calculated.

Experimental Design

The variables studied for the pectin production were extraction pH, extraction time, and extraction temperature. To determine the optimum conditions, a total of 13 extraction experiments were conducted by varying one of the conditions at a time, and keeping the other two constant. First the optimum extraction pH, then the optimum extraction time and finally the optimum temperature were determined as shown in Table 1–3. Finally, pectin was extracted under the determined optimum conditions.

### Table 1: Determination of optimum pH

| SN | pH  | Time, h | Temperature, °C |
|----|-----|---------|-----------------|
| 1  | 1   | 2       | 80              |
| 2  | 1.5 | 2       | 80              |
| 3  | 2   | 2       | 80              |
| 4  | 2.5 | 2       | 80              |
| 5  | 3   | 2       | 80              |
| 6  | 3.5 | 2       | 80              |
| 7  | 4   | 2       | 80              |

### Table 2: Determination of optimum extraction time

| SN | Time, h | Temperature, °C | pH              |
|----|---------|-----------------|-----------------|
| 1  | 0.5     | 80              | Optimum value   |
| 2  | 1       | 80              | Optimum value   |
| 3  | 2       | 80              | Optimum value   |

### Table 3: Determination of optimum extraction temperature

| SN | Temperature, °C | Time, h        | pH              |
|----|-----------------|----------------|-----------------|
| 1  | 60              | Optimum value  | Optimum value   |
| 2  | 70              | Optimum value  | Optimum value   |
| 3  | 80              | Optimum value  | Optimum value   |

Extraction of Pectin

The hot dilute acid extraction method was used to extract pectin from cocoa bean shells, with a constant solid-liquid ratio of 1:16 for all the runs (Mohamed, 2016; Zhang et al., 2013). The production process of pectin is shown in Figure 1.
For each experimental run, 750 g of cocoa bean shells powder of particle size under 2 mm was weighed to 0.01 g accuracy into a 15 L aluminium cooking pot containing dilute acid of appropriate extraction pH. 12 M hydrochloric acid was added to set the pH of the mixtures to 1, 1.5, 2, 2.5, 3, 3.5 and 4. The slurries were heated under continuous stirring to temperatures of 60, 70 or 80 °C. Extraction of pectin was carried out for durations of 0.5, 1, or 2 h. After extraction, the slurries were allowed to cool to room temperature (Miceli-Garcia, 2014).

**Pectin Recovery and Purification**

Alcohol precipitation was used to recover and purify the extracted pectin from each crude extract. The slurry from the extraction process was decanted, and then, filtered through a Büchner funnel with a Whatman No. 4 filter paper, connected to a vacuum filtration system.
Pectin recovery was achieved by mixing an equal volume of 96% ethanol to the filtrate (Pasandide et al., 2018) and stirred with an electric stirrer for 10 min at room temperature. The precipitate and ethanol were separated by centrifugation at 4000 rpm for 10 min. The precipitate was washed in 1.5 L of 70% ethanol and stirred at room temperature for 10 min at 250 rpm. Ethanol was recovered by centrifuging the mixture (Miceli-Garcia, 2014). The washed pectin was freeze dried for 72 h (Sharma et al., 2014).

**Characterisation of Pectin**

The extracted pectins were analysed both qualitatively and quantitatively. In all the extractions, yield, equivalent mass (EM), methoxyl content (MeO), anhydrouronic acid content (AUA), and degree of esterification (DE) were determined. In addition to these, pectin extracted under the optimum extraction conditions was also studied for the moisture content, ash content, colour, pH, solubility in cold and hot water, viscosity, and viscosity-average molecular mass. Fourier Transform Infrared (FT-IR) was conducted to determine the functional groups present in the extracted pectin.

**Colour**

The colour of pectin powder was determined using a Chroma Meter CR-410 to measure the CIELab (International Commission on Illumination) coordinates $L^*$, $a^*$ and $b^*$, ($L^* =$ Lightness, $a^* =$ redness and $b^* =$ yellowness) of the extracted pectin. The measured values were used to calculate the hue angle. To measure the coordinates, the glass Petri dish of the instrument was filled with pectin powder sample and covered. The chroma meter was then placed over the covered dish to measure the $L^*$, $a^*$ and $b^*$ values of the pectin (Wang et al., 2015).

The hue angle ($\theta_{ab}$) was calculated by the following equation:

$$\theta_{ab} = \tan^{-1}(b^*/a^*)$$

**Equivalent Mass**

To determine the equivalent mass, 0.5 g of pectin was measured on an analytical balance and moistened with 5 ml of 96% ethanol in a conical flask. 1 g of NaCl was added to the mixture in order to sharpen the end point of the titration. Six drops of phenol red indicator and 100 ml of distilled water were added to the mixture. The mixture was well stirred with a magnetic stirrer. The solution was slowly titrated with 0.1 N NaOH solution until a pink colour, which persisted for at least 30 s was observed at the endpoint. The pH of the solution was measured with a pH meter (Ismail et al., 2012). Five parallel determinations were done. The equivalent mass was calculated as:

$$\text{Mass of pectin sample} \times 1000 = \frac{\text{Mass of pectin sample (g)}}{\text{Volume of NaOH (ml)} \times \text{Normality of NaOH}}$$

(Devi et al., 2014)

**Methoxyl Content (MeO)**

The methoxyl content was determined by saponification of the pectin followed by titration of the liberated acid (Grassino et al., 2016). 25 ml of 0.25 N NaOH solution was measured and added to the neutralised solution obtained from the determination of equivalent mass containing 0.5 g pectin ($m_{\text{pectin}}$), to de-esterify it. The mixture was stirred thoroughly with a magnetic stirrer and...
allowed to stand for 30 min at room temperature. 25 ml of 0.25 N HCl solution was measured with a burette and added to neutralise the NaOH. The solution was then titrated with 0.1 N NaOH solution until a faint pink colour was observed. The methoxyl content (MeO) was calculated as:

$$\text{MeO} = \frac{\text{Volume of NaOH (ml) } \times \text{Normality of NaOH}}{m_{\text{pectin}}}$$

(Devi et al., 2014)

**Anhydrouronic Acid (AUA) Content**

Pectin content is the percentage of uronic acid in the extracted pectin (Miceli-Garcia, 2014). AUA% of pectin is determined as:

$$\text{AUA} = \frac{176 \times 0.1 \times z \times 100}{m_{\text{pectin}} \times 1000} + \frac{176 \times 0.1 \times y \times 100}{m_{\text{pectin}} \times 1000}$$

(Devi et al., 2014)

where 176 is the molecular mass of AUA; $m_{\text{pectin}}$ is the mass of measured pectin sample, g; $y$ is the volume of 0.1 N NaOH from methoxyl content determination, ml; $z$ is the volume of 0.1 N NaOH from equivalent mass determination, ml.

**Degree of Esterification (DE)**

The degree of esterification of pectin was calculated as:

$$\text{DE} = \frac{176 \times \text{MeO}}{31 \times \text{AUA}} \times 100, \%$$

(Ismail et al., 2012)

**Viscosity**

The viscosity of the hydrocolloid solutions of pectin were determined at 30, 60, and 90 °C. Pectin hydrocolloid solutions were prepared at concentrations (C) of 0.5, 1, 1.5, and 2 g/l, using distilled water. The viscosity of the colloidal solutions at the three temperatures was determined using a Cannon–Fenske viscometer by measuring the efflux times (t). The kinematic, specific, relative, and intrinsic viscosities were then calculated.

**Kinematic viscosity ($\eta$)** in Stokes was determined by multiplying the efflux time (t) in seconds with the viscometer constant (k):

$$\eta = t \times k$$

**Relative viscosity ($\eta_r$)** is the dimensionless ratio of the viscosity of the polymer solution of known concentration to the viscosity of the pure solvent at the same temperature. In addition to using the ratio of the viscosities, the efflux times (t) of the solution and the pure solvent ($t_o$) can also be used to calculate its value:

$$\eta_r = \frac{t}{t_o}$$

**Specific viscosity ($\eta_sp$)** is the viscosity due to the presence of a polymer in the solution. It can be calculated as the relative viscosity of the polymer solution of known concentration minus 1, where $\eta_o$ is the viscosity of the solvent water:

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} \text{ or } \frac{t - t_o}{t_o} \text{ or } \eta_r - 1$$

**Intrinsic viscosity ($\eta_i$)** of a polymer solution is the measure of the capacity of the polymer to enhance the viscosity of its solution. It is useful in the determination of the molecular mass of polymers and it is measured in m³/kg:

$$\eta_i = \left[ \frac{2(\eta_{sp} - \ln \eta_r)^{0.5}}{C} \right]$$

(Wang et al., 2015)

**Pectin Viscosity-average Molecular Mass**

The viscosity-average molecular mass was estimated from the intrinsic viscosity by applying the Mark-Houwink-Sakurada equation:

$$\eta_i = kM_v^a$$

(Wang et al., 2015) where $\eta_i$ is the intrinsic viscosity, m³/kg; $M_v$ is the viscosity-average molecular mass, g/mol; k and a are constants, that depend on solution temperature as follows:

$$k = 2.26 \times 10^{-5} \text{ l/g at 30 °C}; \quad 2.08 \times 10^{-5} \text{ l/g at 60 °C} ; \text{ and } 1.94 \times 10^{-5} \text{ l/g at 90 °C}$$

$$a = 0.8215 \text{ at 30 °C}; \quad 0.8066 \text{ at 60 °C}; \text{ and } 0.7881 \text{ at 90 °C}$$

(Masuelli, 2014)

**Pectin FT-IR Analysis**

Fourier Transform Infrared (FT-IR) spectroscopy was used to determine the functional groups in the extracted material. FT-IR spectra were recorded on potassium bromide (KBr) disks, over the wavenumber range of 4000–400 cm⁻¹, using a Perkin Elmer Spectrum Version 10.03.09, at the resolutions of 4 cm⁻¹. 24 scans were run.
RESULTS AND DISCUSSIONS

Characterisation of Cocoa Bean Shells

Particle Size Distribution

Table 4 shows the particle size distribution of cocoa bean shells. 79.8% of cocoa bean shells were larger than 4 mm and none was smaller than 0.5 mm.

Table 4: Particle size distribution of cocoa bean shells

| Sieve size, mm | Shells retained, % |
|---------------|-------------------|
| 4             | 79.8              |
| 2             | 18.3              |
| 1             | 1.5               |
| 0.5           | 0.4               |
| 0.125         | 0                 |

Moisture and Ash Contents

The average moisture content of the shells was 13.0 ± 0.1% and the average ash content was 8.4 ± 0.1%. The moisture content of the shells depends on the temperature and duration of bean roasting, therefore there are various values between 5–15% reported by other researchers (Bentil, 2012; Hartati, 2010). Ogunsipe et al. (2017) reported an ash content of 5.2% in cocoa bean shells from Nigeria, Hartati (2010) obtained an ash content of 9% in shells from Indonesia, and Bentil (2012) got 6–10.8% of the shells from Ghana.

Determination of Optimum Extraction Conditions

The optimum conditions were found on the basis of the effect of the extraction conditions on the yield, anhydrouronic acid content (AUA), degree of esterification (DE), equivalent mass (EM), and methoxyl content (MeO).

Optimum pH

pH is one of the most crucial extraction parameters that affects both the yield and the molecular characteristics of extracted pectin (Wonago, 2016), such as the degree of esterification, ratio of galacturonic acid to rhamnose, average molecular mass, gel strength, and setting time (Liu et al., 2010). The extraction time and temperature were kept constant at 2 h and 80 °C, respectively. Table 5 shows the amount of pectin obtained, the yield, and the characteristics of pectin as a function of pH. To select the optimum pH, the decisive parameter was the degree of esterification. On that basis, the optimum pH was chosen to be 3.5. At that pH, the pectin yield was higher than the yield at pH 4.

Optimum Extraction Time

The optimum extraction time was determined as indicated based on Table 6, having the optimum extraction pH to be 3.5 at 80° extraction temperature. On the basis of anhydrouronic acid content, the optimum extraction time was chosen to be 2 h.

Optimum Extraction Temperature

To find the optimum extraction temperature, pectin was extracted at 60, 70, and 80 °C, at constant pH of 3.5 and extraction time of 2 h. The properties exhibited by the pectins at the various temperatures are presented in Table 7. Yield was the decisive parameter and, on that basis, the optimum extraction temperature was chosen to be 80 °C.

Based on below results the optimum conditions for pectin extraction were found to be extraction pH of 3.5, extraction time 2 h, and extraction temperature of 80 °C. The properties of the pectin extracted under these conditions are shown in Table 8. To improve purity, ash content and pH of the hydrocolloid solution of the pectin, extractions under the selected conditions were repeated, and the pectin precipitated in an extract-ethanol ratio of 1:2 and the precipitate washed three times with 96% ethanol. 0.25 N HCl was used to adjust the pH of the extract (Mohamed, 2016).
### Table 5: Properties of pectin extracted in the determination of the optimum extraction pH

| Extraction pH | Amount of pectin obtained, g | Yield, % | pH of pectin solution | Equivalent mass, g | Methoxyl content, % | Anhydrous uronic acid content, % | Degree of esterification, % |
|---------------|-------------------------------|----------|-----------------------|-------------------|--------------------|-------------------------------|-----------------------------|
| 1             | 50.15                         | 6.7      | 3.0                   | 525 ± 12          | 5.5 ± 0.3          | 64.8 ± 1.7                    | 47.9 ± 1.2                  |
| 1.5           | 40.14                         | 5.4      | 3.8                   | 1047 ± 21         | 2.2 ± 0.2          | 29.4 ± 1.0                    | 42.4 ± 1.8                  |
| 2             | 60.59                         | 8.1      | 3.8                   | 1581 ± 68         | 1.0 ± 0.1          | 16.6 ± 0.8                    | 32.5 ± 2.6                  |
| 2.5           | 47.92                         | 6.4      | 3.9                   | 1519 ± 214        | 1.0 ± 0.2          | 17.3 ± 2.1                    | 31.6 ± 4.2                  |
| 3             | 43.68                         | 5.8      | 5.9                   | 6283 ± 1164       | 2.0 ± 0.3          | 14.3 ± 1.9                    | 80.1 ± 4.9                  |
| 3.5           | 44.65                         | 6.0      | 6.3                   | 6280 ± 666        | 5.1 ± 0.5          | 31.9 ± 2.5                    | 90.8 ± 1.5                  |
| 4             | 18.78                         | 2.5      | 6.2                   | 8973 ± 1562       | 3.6 ± 0.6          | 22.4 ± 3.2                    | 90.8 ± 2.1                  |

Extraction time = 2 h, extraction temperature = 80 °C

### Table 6: Properties of pectin in the determination of the optimum extraction time

| Extraction time, h | Amount of pectin extracted, g | Yield, % | pH of pectin solution | Equivalent mass, g | Methoxyl content, % | Anhydrous uronic acid content, % | Degree of esterification, % |
|-------------------|-------------------------------|----------|-----------------------|-------------------|--------------------|-------------------------------|-----------------------------|
| 0.5               | 29.20                         | 3.9      | 6.1                   | 5982 ± 342        | 1.6 ± 0.3          | 12.1 ± 1.8                    | 75.3 ± 3.5                  |
| 1                 | 28.41                         | 3.8      | 6.3                   | 5462 ± 222        | 1.3 ± 0.3          | 10.6 ± 1.7                    | 69.3 ± 5.9                  |
| 2                 | 44.65                         | 6.0      | 6.3                   | 6281 ± 687        | 5.1 ± 0.6          | 31.7 ± 3.5                    | 90.8 ± 1.8                  |

Extraction pH = 3.5, extraction temperature = 80 °C

### Table 7: Properties of pectin in the determination of the optimum extraction temperature

| Extraction temperature, °C | Amount of pectin extracted, g | Yield, % | pH of pectin solution | Equivalent mass, g | Methoxyl content, % | Anhydrous uronic acid content, % | Degree of esterification, % |
|----------------------------|-------------------------------|----------|-----------------------|-------------------|--------------------|-------------------------------|-----------------------------|
| 60                         | 41.06                         | 5.3      | 6.2                   | 5444 ± 224        | 1.7 ± 0.3          | 12.9 ± 1.4                    | 75.0 ± 3.3                  |
| 70                         | 42.38                         | 5.7      | 6.3                   | 5326 ± 273        | 3.4 ± 0.6          | 22.7 ± 3.3                    | 85.5 ± 2.2                  |
| 80                         | 44.65                         | 6.0      | 6.3                   | 6281 ± 688        | 5.1 ± 0.6          | 31.7 ± 3.5                    | 90.8 ± 1.8                  |

Extraction pH = 3.5, extraction time = 2 h
The moisture and ash content, solubility and colour of the final product are also presented in Table 8.

**Table 8: Properties of pectin extracted under the selected optimum extraction conditions**

| Property                                | Pectin extracted at optimum conditions | Pectin extracted at optimum conditions after purification | Industrial requirement |
|-----------------------------------------|---------------------------------------|----------------------------------------------------------|-------------------------|
| Yield, %                                | 5.7 ± 0.6                             | 4.7 ± 0.4                                                | —                       |
| Anhydrouronic acid content, %           | 29.7 ± 0.4                            | 71.2 ± 0.8                                               | ≥ 65                    |
| Methoxyl content, %                     | 1.1 ± 0.7                             | 8.6 ± 0.4                                                | 0.2 – 12                |
| Degree of esterification, %             | 70.0 ± 0.3                            | 68.9 ± 0.3                                               | 70 – 80                 |
| Equivalent mass, g/eqv.                | 6618 ± 318                            | 806 ± 13                                                 | —                       |
| Moisture content, %                     | 5.4 ± 0.8                             | 6.7 ± 0.05                                               | ≤ 12                    |
| Ash content, %                          | 16.9 ± 0.8                            | 10.3 ± 0.1                                               | 10 – 15                 |
| pH of pectin solution                   | 6.6                                   | 3.7                                                      | 3 – 4                   |
| Colour                                  | Dixon brown                           | Brown, white, light yellow                               |                         |
|                                        | [Lightness L’ = 43.06]                |                                                          |                         |
|                                        | [Redness a’ = 3.61]                   |                                                          |                         |
|                                        | [Yellowness b’ = 7.93]                |                                                          |                         |
|                                        | [Hue angle = 65.5°]                   |                                                          |                         |
| Solubility in hot water                 | Yes                                   | Yes                                                      |                         |
| Solubility in cold water                | No                                    | No                                                       |                         |
| Viscosity average molecular mass, g/mol | 18 343 – 42 331                       | 23 470 – 42 384                                          | 10⁴ – 10⁵               |

**Intrinsic Viscosity and Viscosity-Average Molecular Mass**

The viscosity-average molecular mass was estimated with the help of the intrinsic viscosity values of the pectin hydrocolloid solutions. The intrinsic viscosity varied between 0.075 – 0.088 m³/kg and the viscosity-average molecular mass ranged from 23,470–42,384 g/mol. The viscosity-average molecular mass was within the typical values of 10⁴–10⁵ g/mol of pectins of other sources. The intrinsic viscosity and viscosity-average molecular mass of pectin extracted from sunflower by Iglesias and Lozano (2004) varied from 0.19–0.27 m³/kg and 35,300–52,600 g/mol, respectively. The relatively low molecular mass of pectin from cocoa bean shells, compared to the high 109,500 g/mol of pectin extracted from grapefruit peel via the ultrasound-assisted heating method by Wang et al. (2015), could have been the consequence of the extraction method and the conditions under which the pectin was extracted, as these can cause wide variations in the structure and properties of pectin.

**Structural Analysis**

The Fourier Transform Infrared (FT–IR) spectrum of pectin extracted under the optimum extraction conditions are shown in Figure 2. The spectrum shows the functional groups present and give structural information.
Figure 2: FT-IR spectrum of pectin extracted from cocoa bean shells under the optimal extraction conditions

The 3301.69 cm\(^{-1}\) peak, which is in the broad and strong area of absorption between 3200 - 3500 cm\(^{-1}\) corresponds to O–H stretching due to the vibrational modes of inter- and intra-molecular hydrogen bonds of the galacturonic acid polymer backbone (Kpodo et al., 2017; Chen et al., 2014). The peak at 2922.45 cm\(^{-1}\) is attributed to C–H modes which include CH, CH\(_2\), and CH\(_3\) stretching vibrations (Pasandide et al., 2018). C–H stretching and bending vibrations in pectin are generally observed in the 2500-3600 cm\(^{-1}\) range. (Chen et al., 2014). Methyl esterified and –COOH groups result from C=O stretching vibration and their absorption bands are observed between 1700 - 1800 cm\(^{-1}\) (Kpodo et al., 2017). The peak at 1231.38 cm\(^{-1}\) corresponded to –CH\(_3\)CO stretching (Kpodo et al., 2017). The intense absorption at 1016.30 cm\(^{-1}\) is characteristic of glycosidic linkage between sugar units. Pectin consists of D-galacturonic acids connected by these glycosidic linkages to form a backbone. Absorption bands between 1100-1200 cm\(^{-1}\) related to ether (R–O–R) and cyclic C–C bonds in the ring structure of pectin molecules (Ismail et al., 2012). The identification of major chemical groups of polysaccharides is in the region of 800 and 1200 cm\(^{-1}\), and the spectra are referred to as the “fingerprint” region for carbohydrates. These are difficult to interpret (Pasandide et al., 2018; Chen et al., 2014). The FT-IR analysis therefore suggests that the extracted material is rich in polygalacturonic acid.

CONCLUSION

Extracting and characterising pectin from cocoa bean shells was successful at different extraction conditions of pH, extraction time, and extraction temperature. Analysis of the results obtained confirmed that good quality of high methoxyl pectin could be produced from cocoa bean shells using the hot dilute acid method under optimised conditions of pH 3.5 for a period of 2 h and at a temperature of 80 °C. The characteristics of the pectin extracted under the optimum conditions
showed that cocoa bean shells are a viable source for commercial pectin.

**DECLARATIONS OF COMPETING INTERESTS**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this manuscript.

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