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Clean Extraction of Pectin from Dragon Fruit Peels, Pomelo Peels, Okra, and Pineapple Peels Using Deep Eutectic Solvents and Ionic Liquids

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Abstract

Pectin is the main constituent of fruit peels that contributes to the fruit's solid and firm shape. Having wide applications in the food, pharmaceutical, and cosmetics industries, its extraction from bioresources would mark a sustainable advancement in biotechnology. The biomaterials for pectin extraction targeted in the study were dragon fruit peels (*Hylocereus costaricensis*), Pomelo peels (*Citrus grandis*), okra (*Abelmoschus esculentus*), and pineapple peels (*Ananas comosus*). Aqueous extractions of pectin from fruit peels were performed in a sono-reactor using deep eutectic solvents (DESs). Ionic liquids such as (Choline acetate ≥ 95%) [Ch][Ac] and (1-ethyl-3-methylimidazolium acetate ≥ 97%) [EMIM][Ac] were also employed as extraction solvents. Morphological screening with the electron microscope (SEM) and FTIR showed that the extracted pectin had a similar surface as commercial pectin. The extracted pectin can completely dissolve in water to form a homogenous suspension. The pectin yield from dragon fruit peels was 60±2.00 wt% with a degree of esterification at about 66-72%. This study introduces a clean extraction that can potentially substitute solvents in the pectin industry.

1. Introduction

Pectin is structurally the most complex polysaccharide abundant in plant cell walls (Mohnen, 2008). It is a natural polymer composed mainly of D-galacturonic acid molecules linked by α-(1,4)-glycosidic bonds with specific esterification levels (Liew *et al.*, 2018a). Thus, pectin is a family of polysaccharides rich in galacturonic acid (Mohnen, 2008). Pectin can be classified into two main types, i.e. high methoxyl (HM) and low methoxyl (LM). It has a degree of esterification (DE), ranges between 55-80% and forms gel at low pH in the presence of sugar (Barrera *et al.*, 2002) and a DE value > 50% (Liew *et al.*, 2018). Pectin is mainly employed in the food and pharmaceutical industries as a source of safe fibre in food additives, stabilizers, and gelling agents. It can also be added to strengthen orthopaedic casts and construction-grade cement.

A wide variety of edible fruits is produced and grown in Malaysia's tropical climate. Fruit consumption produces a lot of waste products, causing disposal problems. About 30-40% of certain fruit weight is the peel with good pectin supply (Liew *et al.*, 2018). For instance, pomelo (*Citrus grandis*), pineapple (*Ananas comosus*), jackfruit (*Artocarpus heterophyllus*), cempedak (*Artocarpus integer*), and dragon fruit (*Hylocereus costaricensis*) consumption leads to the production of fruit peels as waste, which are good sources of pectin. Commercial pectin extracted using acidic extraction agents (strong mineral acids) produces reasonable amounts of pectin and is a time-saving approach. However, the highly acidic process accelerates the corrosion and formation of rust in apparatus, entering the water hence causing health and environmental hazards. Although strong acids have various uses in food manufacture, their usage for extraction often generates negative attitudes among consumers due to the related dangers and safety issues. To address these issues, researchers have investigated alternate methods for extracting pectin. Recent studies emphasize the limitations of conventional techniques that employ abrasive mineral acids and underscore the necessity for more environmentally friendly approaches (Dao *et al.*, 2023). Pectin extraction technique has shown promise in utilizing organic acids and sustainable solvents such deep eutectic solvents (DES) and ionic liquids (ILs). (Turan *et al.*, 2024). These environmentally friendly solvents not only resolve safety issues but also provide improved efficiency in extracting pectin from different corps sources, such as dragon fruit peels, pomelo peels, okra, and pineapple peels. The transition towards more ecologically sustainable and secure techniques for pectin extraction is clearly apparent.

Table 1: Summary of several recent studies carried out for pectin extraction approaches, highlighting the solvents, methods, and yields obtained

Fruit	Extraction Method	Conditions	Yield	Reference
Calamansi lime	Water-based extraction	Distilled water, pH 1-5, 80°C for 10 minutes centrifugation	45.7%	(Zainudin *et al.*, 2021)
Grapefruit	Thermal treatment extraction	90°C for 5 minutes, oven drying under vacuum at 50°C overnight	56.84%	(La Cava *et al.*, 2018)
Pomelo peel	Deep eutectic solvent (DES) extraction	Lactic acid–glucose–water DES (6:1:6), pH 1.80, 88°C for 141 minutes	39.72%	(Liew *et al.*, 2018b)
Apple pomace	Enzymatic extraction	Enzyme Celluclast, doses 20-60 µL/g, 40-60°C, 12-24 hours	97.46%	(Dranca & Oroian, 2019)
Pomelo peel	Sonication and water bath extraction	Sonication at 60°C for 120 minutes, water bath at 75°C for 120 minutes	96.37%	(Elgharbawy *et al.*, 2019)
Lemon peel powder	Ohmic Heating-Assisted extraction	pH 2, 90°C, 30 minutes, solid: liquid ratio of 1:40 g/mL	16.91%	(Tunç & Odabaş, 2021)

As an example, Liew *et al.* (2018) demonstrated this change by isolating pectin from *Citrus grandis* by the utilization of both citric acid and deep eutectic solvents (DESs). The extraction process, carried out at a temperature of 88 °C for a duration of 141 minutes, resulted in a pectin yield of 39.72% with a DE% value of 57.56%.

Considering the reported promising yields, the properties of the extracted pectin would be worth investigating into to ascertain their applications. Hence, we aim to identify properties of extracted pectin from pomelo peel, pineapple peel, dragon fruit peel, and okra using different extraction solvents: ionic liquid (IL), deep eutectic solvent (DES), HCl, water assisted-ultrasonication and heating. The use of various extraction solvents and conditions can identify the potential solvents and optimize the extraction process condition while reducing energy input and devising a cleaner extraction without the involvement of a large quantity of chemicals.

2. Materials and methods

The biomaterials used in this study were dragon fruit peels (*Hylocereus costaricensis*), Pomelo peels (*Citrus grandis*), okra (*Abelmoschus esculentus*), and pineapple peels *(Ananas comosus*). They were obtained from a local market in Selangor, Malaysia. All collected feedstocks were of the same ripeness and same batch (to avoid inconsistency due to variations). After washing them with water, all the fruit peels were cut except for the okra. The samples were dried at 50 °C until a constant weight was achieved. The dried peel was ground into powder (<500 µm) and stored in an airtight container in a dry atmosphere. All solvents and chemicals used in this study were of analytical grade. Ionic liquids (Choline acetate ≥ 95%) [Ch][Ac], and (1-ethyl-3-methylimidazolium acetate ≥ 97%) [EMIM][Ac], used in this study were purchased from Merck, Malaysia. Commercial pectin was purchased from a local baking supplier in Kuala Lumpur, Malaysia.

2.1 Deep Eutectic Solvent (DES) preparation

Choline chloride and glycerol with a molar ratio 1:2 was employed to prepare the DES. The optimal preparation ratio of the DES is selected according to previous literature (Hayyan *et al.*, 2013); (Tommasi *et al.*, 2017). Choline chloride (ChCl) and glycerol (gly) were mixed at the specific molar ratio, heated at 80°C and stirred (350 rpm) using a hot stirrer plate for 2 hours until the sample was homogenised, and a clear solution was obtained. The water content of the DES varied between 0.43–1.23% (Karl-Fischer titration).

2.2 Pectin extraction

The experiment was conducted at a constant condition in the pectin extraction, and the solvents were screened to determine their capacity in the extraction process. The solvent with the highest extractive capability was used for characterization. A 3 g sample of dried powder was mixed with each ILs, HCl, and DES (ChCl:gly) at a ratio of 1:3 (water). The mixture was incubated at 60°C for 120 minutes using a sonication bath. The sonoreactor aided in the extraction of the pectin. On the other hand, heat extraction of pectin using a water bath was conducted using the same

conditions and ratio but at a temperature of 75°C, Applying the stated techniques (Dranca & Oroian, 2018).

2.3 Pectin yield determination

After the sonication cycles were complete, the tubes containing the mixture were centrifugated for 5 minutes in 1900 ×g (8 x 50 mL Fixed Angle Rotor). A 1.5 volume of absolute ethanol was added to the obtained filtrate for coagulation and left to set overnight. Fabric filters were used to strain the formed pectin, and it was subsequently washed with distilled water followed by 96% ethanol. The obtained precipitate was freeze-dried in a freeze dryer for 48 hours. The pectin yield was calculated using Equation (1) (Raji *et al.*, 2017):

$$Yield\ of\ Pectin\ (\%) = \frac{w}{w_0} \times 100 \qquad (1)$$

where dried pectin weight is expressed as w in grams, and the initial powder's weight is w_0 in grams.

2.4 Characterisation of pectin

2.4.1 Degree of esterification (DE)

The degree of esterification DE is determined by measuring the presence of esterified carboxyl groups in the galacturonic acid groups. Liew *et al.* (2018) described the titration method to measure the pectin DE. Ethanol was added to 0.2 g of the obtained pectin and incubated in a 45°C water bath, with intermittent shaking until complete dissolution was observed. The phenolphthalein was added to the mixture and titrated against 0.1 N NaOH to initiate the titration. The final volume was measured once the titration reached the endpoint. Next, the solution was completely neutralized by adding 10 mL of 0.1 N NaOH. Pectin was de-esterified by shaking the sample and allowing it to sit for two hours at room temperature. NaOH was neutralized with 10 mL 0.1 N HCl until its pink tint disappeared. Phenolphthalein was added, and the second reading was recorded with 0.1 N NaOH when a pink hue first appeared. The percentage of DE was calculated using the following formula:

$$DE\ (\%) = \frac{Final\ titration\ volume\ (ml)}{Initial\ titration\ volume\ (ml) + Final\ titration\ volume\ (ml)} \times 100 \qquad (2)$$

2.4.2 Fourier Transform Infrared (FTIR) spectroscopy chemical structure

Chemical structures of extracted pectin were analysed using Fourier Transform Infrared (FTIR) Spectroscopy. FTIR absorbed electromagnetic radiation that interacted with a substance and transmitted, reflected, scattered, or had photoluminescence (PL), which provided significant information on the substance's molecular structure and energy level. In this study, the infrared spectra of the functional groups of extracted pectin were measured with a Thermo Scientific FTIR spectrometer. The absorbance of the different extracted pectin was acquired over the wavenumber range of 4000 to 1000 cm^{-1}.

2.4.3 Raman Spectroscopy

To compare their chemical structures, Raman spectroscopy was performed on extracted and commercialised pectin. inVia™ Qontor® confocal Raman microscope at 20× magnification was used with an extended Raman range of 734 – 1787 cm^{-1} and an exposure time of 10 seconds. Laser power was adjusted at 1% and 785 nm edge.

2.4.4 Differential Scanning Calorimetry (DSC) thermal analysis

Differential Scanning Calorimetry (DSC) was used to measure the samples' melting and crystallisation points. Thermal characteristics of extracted pectin were performed on a Mettler Toledo Flash DSC equipped with a Freon intercooler maintained at -105°C and nitrogen gas purge of 20 mL/min. All extracted pectin was scanned between 25°C to 500°C.

2.4.5 Analysis of pectin samples using Scanning Electron Microscope (SEM)

The extracted pectin and the commercial sample were analysed using scanning electron microscopy (SEM) to determine their surface morphological properties, such as porous pattern and surface structure. The dried pectin samples were observed under a scanning electronic microscope (SEM) by Hitachi SU1510 SEM at the magnifications of X500, X1000 and X5000 at BSE mode.

3. Results and discussion

3.1 Screening of the co-solvents for pectin extraction

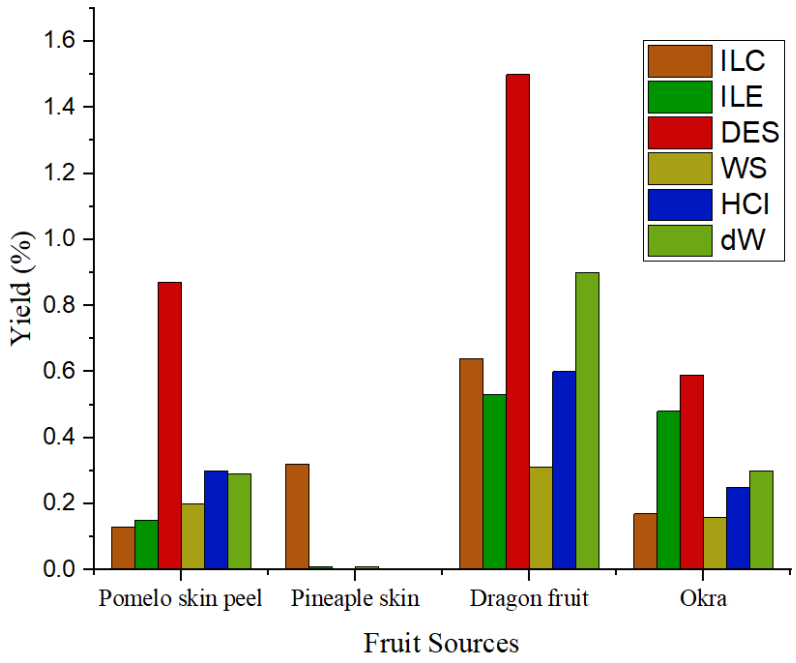
Heat-assisted extraction with water resulted in a higher pectin yield than the DES used for the dragon fruit sample. Water-assisted extraction reduces the viscosity and consequently improves the extraction of pectin (Kalhor & Ghandi, 2019). Likewise, ultrasonication-assisted extraction with water also produced pectin with a higher yield than DES. The results obtained proved that water can be useful as an alternative extraction solvent because the hydrodynamic property of the pectin molecular chains is significantly improved by the addition of water and enhancing the mass transfer as a result of the dilution of the pectin aggregates (Migliori *et al.*, 2011). Meanwhile, the extraction using both ionic liquids recorded the highest pectin yield, 29.33% and 35.33%, respectively. This concords with the findings that ionic liquids are better extraction solvents for higher extraction yield (Guolin *et al.*, 2012). As explained by (Xiao *et al.*, 2018), the good extraction ability of ionic liquids is due to their chemical compositions, which consist of organic cations and inorganic or organic anions, thus making them able to extract compounds better (Montalbán *et al.*, 2018) at low vapour pressure. Likewise, DES acts in a similar way to the ILs.

3.2 Degree of esterification of extracted pectin

To classify the type of pectin and their potential industrial application, the degrees of esterification were evaluated for pectin extracted from pomelo peel, pineapple peel, dragon fruit peel and okra and the results were summarized in Figure 1(b).

The current study found that pectin extracted from dragon fruit recorded a high degree of esterification, i.e., above 50%, but not for other fruit peels; it is worth noting that only significant pectin DE% values were consistent using different extraction techniques for dragon fruit peel. Another interesting finding is

a)



b)

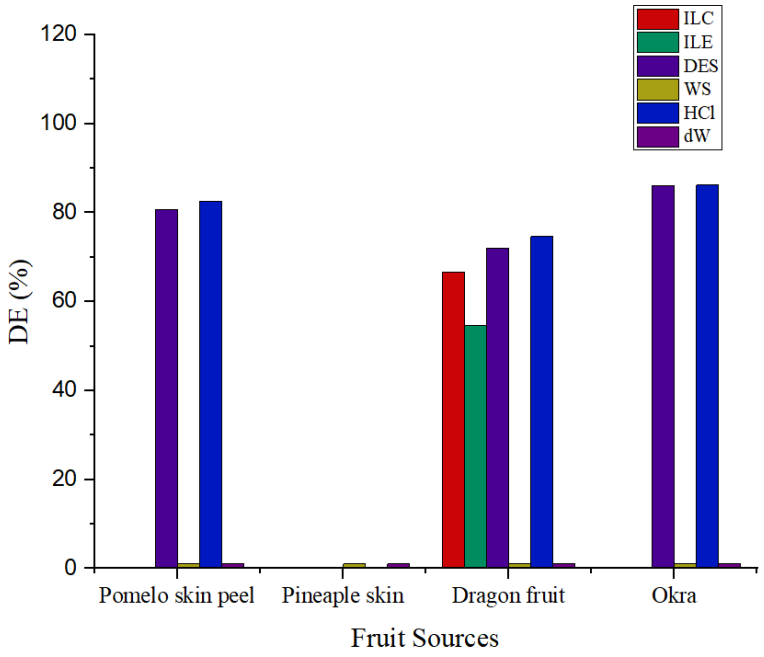


Figure 1: (a) Bar-graph of Pectin yield from various fruit sources using different co-solvents (b) Degree of esterification (DE%) of extracted pectin derived for diverse biomaterials
*the value is too small and almost neglectable. HCl- hydrochloric acid, WS- water-ultrasonication-assisted extraction and WH-water-heated assisted extraction

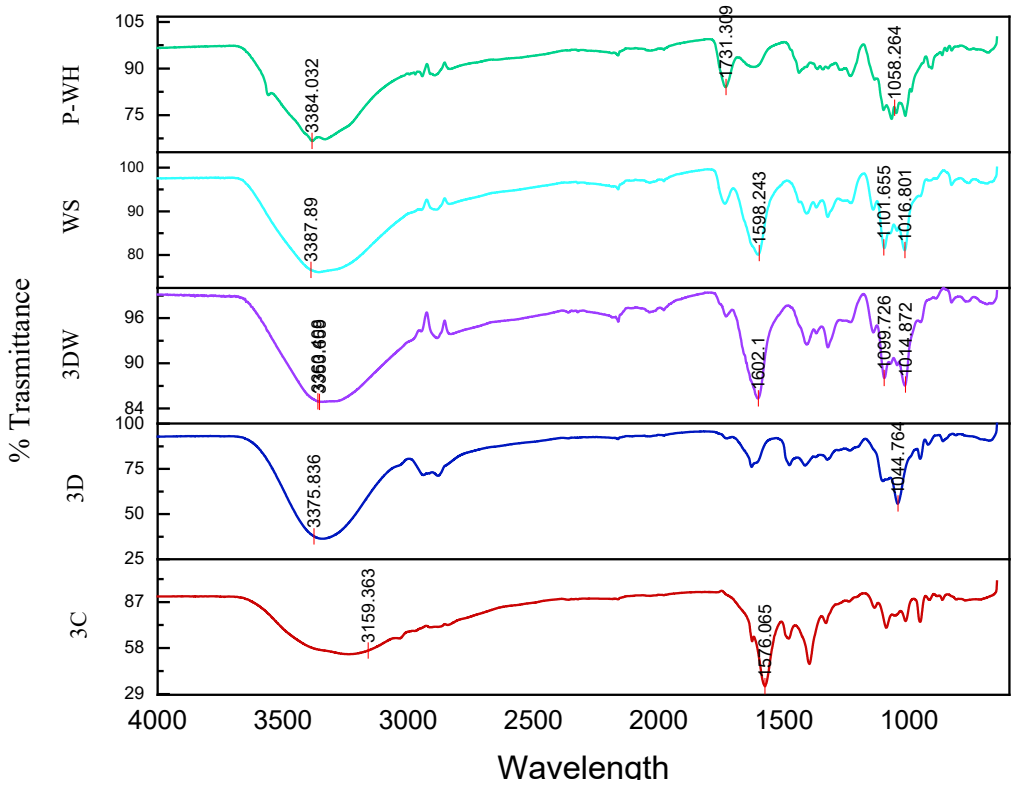


Figure 2: Stacked result of FTIR Spectra of extracted pectin using different treatment methods.
Note*: 3C- Commercial pectin, 3D-Ionic Liquid [EMIM][Ac] assisted extraction, 3DW- DES (ChCl: gly 1:2) assisted extraction, 31- WS: Water-ultrasonication assisted extraction, P- WH: Water-heat assisted extraction at the following wavenumbers: 3500 cm-1 to 1000 cm-.

on a similar pectin yield was obtained from the pomelo peel, and the dragon fruit peel registered a comparable yield of DE above 70%. The overall average value of pectin esterification was 66.32% for all samples (Figure 1b). The highest DE was attained when the fruit peels were treated with hot water. Both ILs showed a lower degree of esterification than water heat-assisted extraction, although they produced the highest pectin yield. Meanwhile, DES showed a promising result for the esterified carboxyl group, indicating that it can be an alternative solvent to hot water for pectin extraction. According to Zanella and Taranto (2015), a good grade pectin, as specified by the Food and Agriculture Organization (FAO), has a Galacturonic acid level greater than 65%. The dragon fruit peel is a potential source of HM pectin and is feasible to extract by applying different extraction techniques and solvents.

Table 2. FTIR Spectra of the stacked extracted pectin using different treatment methods at the following wavenumbers: 3500 cm^{-1} to 1000 cm^{-1}

Wavelength number /cm^{-1}	Peak Vibration
3238.39 - 3383.03	-OH stretching
1603.68 -1627.02	Carbonyl group of carboxylate ion (COO–)
1575.54	Diketones
1481.12	O=C–O stretching
1324.56 -1398.39	–OH bending
1098.99 - 1102.59	C–O–C stretching
1021.69 - 1070.53	Alkyl amine
1015.74 - 1018.09	–CH–O–CH stretching

3.3 Observation of pectin sample's chemical structure

From the FTIR spectrum analysis depicted in Figure 2, the chemical structure of pectin extracted using ionic liquid-assisted extraction and water heat-assisted extraction showed similar results as compared to commercial pectin in which the absorption bands for both solvents indicated carboxylic acid at 3341.41 cm^{-1} and 3356.35 cm^{-1} respectively. Both extraction techniques produced several peaks (Table 2) indicating the presence of aliphatic hydrocarbons and primary aliphatic alcohol at absorption bands of 1603.68 cm^{-1} and 1099.39 cm^{-1} for ionic liquid extraction and 1604.01 cm^{-1} and 1098.99 cm^{-1} for water heat-assisted extraction.

The extracted pectin contained mainly carboxylic acid and secondary alcohol at absorption bands of 3356.35 cm^{-1} and 1099.39 cm-1 compared to commercial pectin at 3383.03 cm^{-1} and 1102.59 cm^{-1} respectively. The FTIR spectra within 3500 cm^{-1} to 3000 cm^{-1} indicating O-H stretching vibration due to free and bound hydroxyl group of carboxylic acid (van Tran *et al.*, 2019). Meanwhile, Bichara *et al.*, (2016) reported that the absorption band of commercial pectin in between 2000 cm^{-1} to 1000^{-1} was due to the deformation vibration of -OH group as well as due to C-O stretching which explained the result obtained. Furthermore, Rahmati *et al.*, (2019) revealed that FTIR spectra ranging from 800 cm^{-1} to 1300 cm^{-1} were attributed to the pectin fingerprint indicating the presence of pure pectin.

Meanwhile, it was observed that pectin extracted using DES-assisted extraction exhibited carboxylic acid at 3238.39 cm^{-1} absorption spectra whereas the existence of anhydride group was at 1045.74 cm^{-1} for water ultrasonication-assisted

extraction. This suggests that ionic liquid is more suitable to be used in extracting pectin compound whereby it provides similar characteristics and structure as the commercial pectin. The finding is substantiated by a study on ionic liquid being an excellent solvent in extracting and separating organic materials (Guolin *et al.*, 2012).

Table 2 shows the tabulated form of the vibrational peaks of the FTIR spectra of commercial pectin and the other extracted pectin using the different types of solvents. The strongest vibrational band observed in the FTIR spectra is at 3383.03 cm^{-1} which is attributed to the -OH stretching functional group of the pectin. The presence of this -OH stretching region in the pectin is due to the presence of hydrogen bonds in the galacturonic acid polymer. This vibrational band was seen to be shifted to 3238.39, 3342.36, 3341.41, and 3356.35 cm-1 for the Commercial pectin, [EMIM][Ac], (ChCl: gly 1:2), and Water-ultrasonication, respectively. On the other hand, the vibrational band at 1102.59 cm^{-1} was assigned to C–O–C stretching of the Water-heat assisted extraction of the pectin. This vibration peak has been shifted to wavenumbers of 1098.99 and 1099.39 cm^{-1} for ChCl: gly and Water-ultrasonication, respectively. The band observed at 1070.53 and 1021.69 cm^{-1} were related to the Alkyl amine functional groups and this vibration peak is found to be shifted to 1045.74 cm^{-1} in the [EMIM][Ac]. The peak at 1015.74 cm^{-1} was ascribed to the –CH–O–CH stretching, and this peak shifted to 1017.38 and 1018.09 cm^{-1} for ChCl: gly and Water-ultrasonication, respectively. Furthermore, in the commercial pectin showed peaks at 1627.02, 1575.54, 1481.12 and 1398.39 cm^{-1} which were not consequently present in the Water-heat assisted extraction (WH) and belonged to the functional groups of carbonyl group of carboxylate ion (COO–), Diketones, O=C–O stretching, and –OH bending, respectively. The difference of vibration peaks in the pectin structure demonstrates the presence of complex pectin structures and the various depth of extraction ability using different solvent systems.

The results based on the FTIR spectra analysis were further supported by an analysis conducted using RAMAN in which chemical structures of extracted pectin using ionic liquid-assisted extraction and commercial pectin have a close resemblance. Both extracted and commercialized pectin produced several peaks at the wavelength ranging from 100 cm^{-1} to 650 cm^{-1}. The results obtained from the RAMAN spectra are shown in Figure S1.

The interpretation of Raman spectra can be categorized into two sections based on their wavenumbers where the region less than 1600 cm^{-1} are sensitive to the structures of cellulose backbone and the region above 2700 cm^{-1} are sensitive the structure relating to hydrogen bonds (Szymańska-Chargot *et al.*, 2011). Since, most of the spectral range of the peaks varies between 100 cm^{-1} to 1650 cm^{-1}. Hence, the pectin extracted are more influenced by the structures of cellulose backbone. The Raman images reveal that most of the changes in the pectin is related to the cell corner zones, implying the release of pectin in the junction corner during fruit harvesting contribute to the mechanical resistance of tissue. (Szymańska-Chargot *et al.*, 2016). The different proportion of the vibration peaks indicates the different capacity of the solvents in penetrating the different functional groups and composition present inside the pectin apart from the commercial pectin. The wavelength peak close at 700 cm^{-1} indicates the presence of highly mixed complex molecule of C-C bonds.

3.4 Thermal properties of pectin samples

Thermal properties of pectin were analysed using Differential Scanning Calorimeter (DSC) in the study. Pectin extracted using water-ultrasonication assisted extraction shows similar result as that of the commercial pectin in which it had only an endothermic peak (decomposition temperature) at 118.73°C which is slightly lower compared to 235.74 °C for the latter; and both are without an exothermic peak (degradation temperature). The decomposition temperature for commercial pectin reported by Ruano *et al.*, (2019) was 234.73°C. The pectin molecules in commercial pectin is tightly bound to water due to the high degree of esterification and galacturonic acid content (Wang & Lü, 2014). Thus, the decomposition temperature of commercial pectin was higher as more heat or energy is required to break the bond.

Extracted pectin has lower decomposition temperature due to having a different chemical structure from commercialized pectin (Cava *et al.*, 2018). This is evident from the FTIR result for the pectin extracted using water-ultrasonication assisted extraction with anhydride group at 1045.74 cm^{-1}. Anhydride is a compound which has two acyl groups bonded to the same oxygen atom forming van der Waals dispersion and dipole-dipole attractions (Buttkus *et al.*, 1965). The bonds are weaker than hydrogen bonds which reduces the decomposition temperature of the pectin structure.

Meanwhile, pectin extracted using ionic liquid-assisted extraction, water-heat assisted extraction and DES-assisted extraction recorded both endothermic and exothermic peaks. The endothermic peaks for the three extraction techniques were observed at 137.13°C, 179.42°C and 302.81°C while exothermic peaks were observed at 243.65°C, 249.33°C and 227.45°C, respectively. The high degradation temperature indicated that the pectin samples had enough energy to form ordered arrangements and undergo crystallization. This further indicates that pectin extracted using DES was more stable compared to pectin by other methods as it requires higher decomposition temperature to break down the bond.

The evaluation of the DSC for the thermal properties is a result of the measure of the glass transition temperature (T^g), which measures the heat capacity when the polymer matrix changes from glass to rubber state due to interactions of the intermolecular, molecular weight, cross-linking density, etc (Perumal *et al.*, 2018). The figure below shows similar patterns of the endothermic peaks visible at time 21 minutes for commercial pectin while the extracted pectin similar peak at 28 minutes, 23 minutes, 24 minutes, and 16 minutes for [EMIM][Ac], (ChCl: gly 1:2), WS and WH, respectively. Commonly, the endothermic peak indicates the capability of the pectin polysaccharide to retain the water content, and this is connected to the hydrophilic properties of the pectin sample. Hence, the lower and higher endothermic peak reflects the low and high content of galacturonic acid and the degree of methylation (D_w) (Wang & Lü, 2014). While the exothermic peak was observed only for the Water-heat assisted extraction at 22 minutes, which is usually related to the degradation property of the pectin sample and consequently, it reflects the sample's chemical profile.

3.5 Morphology of pectin samples

To gain insight into the morphological structure of the extracted pectin, the morphology of pectin extracted from dragon fruit peels was examined and compared with commercial pectin

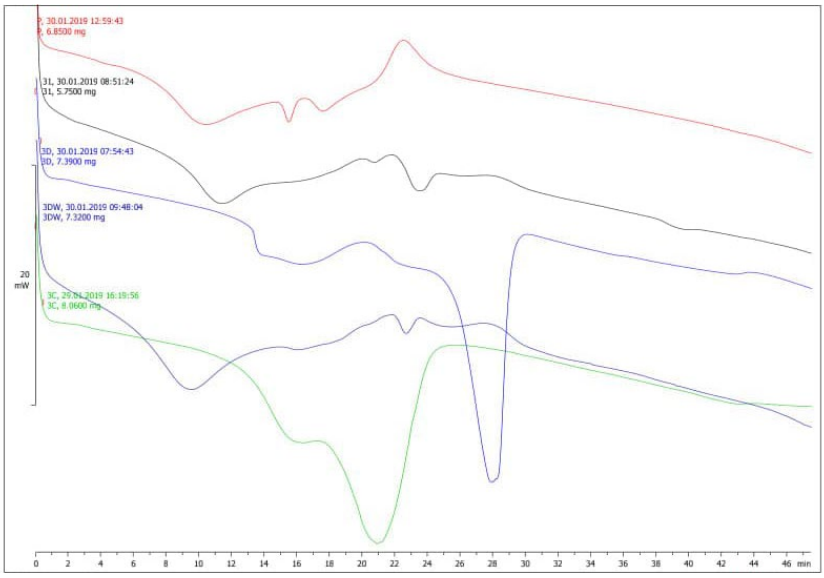


Figure 3. Thermal properties of extracted pectin using different treatment methods shown in a differential scanning calorimeter (DSC).

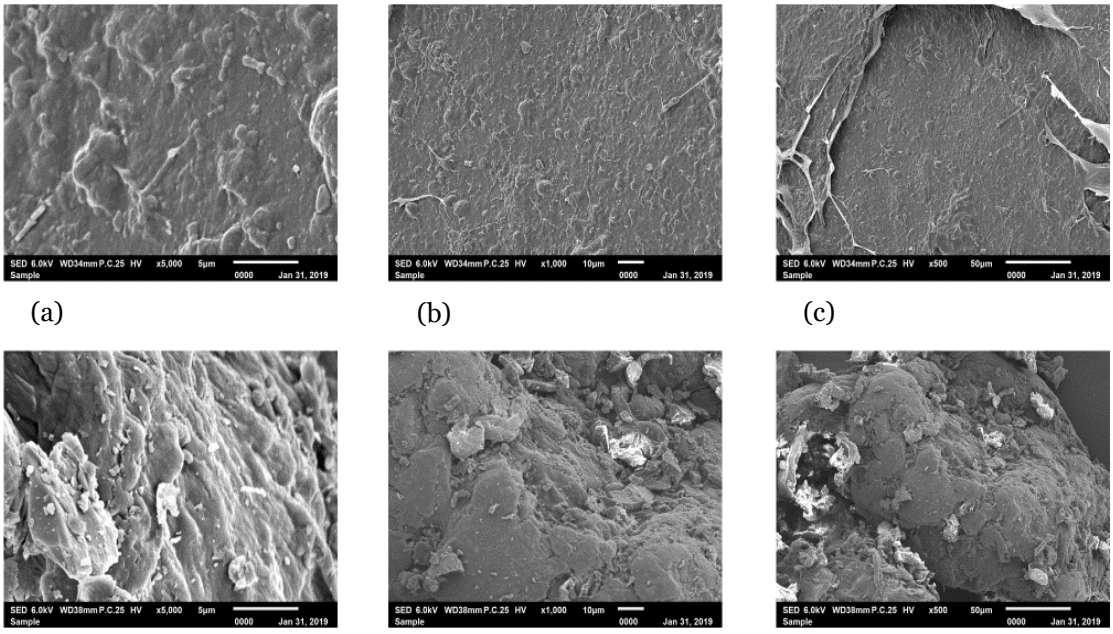


Figure 4: (a) water-heat assisted extraction pectin, mag: X500, (b) water-heat assisted extraction pectin, mag: X1000, (c) water-heat assisted extraction pectin, mag: X5000, (d) commercial pectin, mag: X500, (e) commercial pectin, mag: X1000, (f) commercial pectin, mag: X5000.

(shown in Figure S2(c)). The morphology of the extracted pectin from water heat-assisted extraction and commercial pectin was observed using Scanning Electron Microscopy (SEM) as shown in Figure 4. Figure S2 (a) and (b) are the images of the extracted pectin before and after filtration (for Figure S1, S2, and Table S1, please refer to Supplementary Figures and Tables). The image of the extracted pectin in Figure S2 (b) manifests a jelly-like structure after filtration. This shows the capability of pectin to be used in the designing of food products and their versatile gelling properties. These properties are used in the industry to make jellies, fruit juice, jams, confectionery products etc. Furthermore, the degree of methylation (DM) is the parameter to observe the gelling capabilities using the infrared spectroscopy, which will further allow to understand and apply their use in the food industry. The different gelling properties were related to the different charged carboxyl groups (Gawkowska *et al.*, 2019).

Figure 4 (a) - (c) are the micrographs of extracted pectin from water-heat assisted extraction and Figure 4 (d) - (f) are the micrographs for commercial pectin at magnifications of X500, X1000 and X5000, respectively. Both the extracted and commercial pectin samples showed better images at magnification of X5000. The extracted pectin showed smooth and less aggregate surfaces as compared to the commercial pectin which had more aggregate surfaces. Nevertheless, the extracted pectin contained relatively less porous surfaces compared to the commercial pectin. Moreover, the extracted pectin is not as dense and less compact in structure comparatively. The observation was supported by Rahmati *et al.* (2019) in which pectin extracted from dragon fruit peel exhibited a uniform, compact, and dense structure.

A similar pattern was observed by Benassi *et al.*, (2021) in the orange peel for the surface structure under the SEM giving a similar morphological distinction between the commercial pectin and the extracted pectin. The commercial pectin showed a granular shape while the extracted pectin was seen as flat surface. The stressed surface with deep cavities reflected the use of harsher conditions while the milder conditions are reflected by its smoother surface. On the other hand, the micrograph images from a passion fruit peel revealed similarly that the nano structure of the extracted wet pectin was smooth and compact plus the surface showed little wrinkles (Liew *et al.*, 2014). Thus, the images of the extracted pectin were shown to have structural surface that were smooth with little mound-shaped pellets present.

4. Conclusion

Using ionic liquid for extracting pectin from dragon fruit resulted in much higher yields compared to other solvents. More precisely, the extraction of pectin employing ionic liquid resulted in a yield that was 60±2.00 wt% greater than the extraction obtained from other fruit sources examined in this work. Furthermore, the use of ionic liquid resulted in an esterification degree of approximately 66-72%, demonstrating a desirable combination of a substantial yield and a moderate level of esterification. The results demonstrate that ionic liquid is the optimal solvent for extracting pectin from dragon fruit due to its superior performance in terms of both yield and esterification levels. Furthermore, water is an effective solvent capable of generating a pectin structure that closely resembles commercial pectin, which is composed of carboxylic acid and secondary alcohol. On the other hand, DES showed more stable thermal properties which is an important aspect for extraction solvent. These findings conclude that both ionic liquid and DES can be potential extraction solvents attributing to higher yield, degree of esterification, better chemical structure, and thermal properties compared to commercial solvent.

5. Fund statement

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7. Conflict of interest

The authors declare no conflict of interest.

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Supplementary Figures and Tables

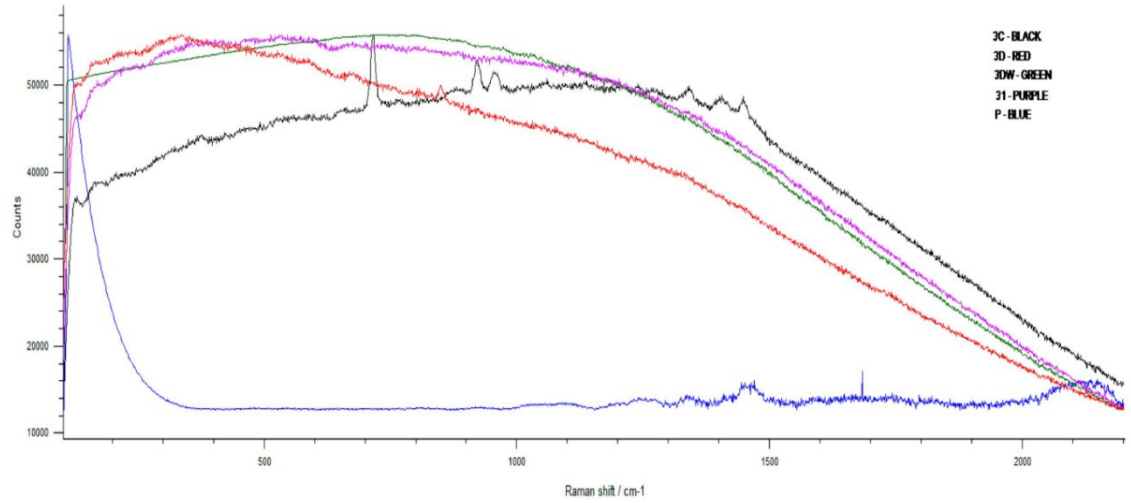

Figure S1. RAMAN Spectra of extracted pectin using different treatment methods: (a) Commercial pectin, (b) Ionic Liquid (1-ethyl-3-methylimidazolium acetate ≥ 97%) [EMIM]OAc assisted extraction, (c) Deep Eutectic Solvent (Choline chloride and glycerol, 1:2) assisted extraction, (d) Water-ultrasonication assisted extraction, (e) Water-heat assisted extraction at the following conditions: 20× magnification, extended Raman range : 734 – 1787 cm^{-1}, exposure time: 10s, laser power: 1% 785 nm edge.

(a) (b) (c)

Figure S2. (a) Water-heat assisted extraction pectin before filtration (b) Commercial Pectin in powdered form. (c) Water-heat assisted extraction pectin after filtration.

Table S1: Thermal properties of the extracted pectin using different treatment methods. Note: Ionic Liquid - [EMIM]OAc assisted extraction, DES - (ChCl: gly 1:2) assisted extraction, WS- water-ultrasonication assisted extraction and WH- water-heated assisted extraction. at the following wavenumbers: 3500 cm^{-1} to 1000 cm^{-1}

Method of Pectin Extraction	Glass Transition Temperature (T^g)(˚C)
Commercial Pectin	179.16˚C – 235.74˚C
[EMIM][Ac]	137.13˚C – 258.31˚C
(ChCl: gly 1:2)	162.37˚C - 302.81˚C
WS	118.73˚C - 251.02˚C
WH	126.34˚C – 249.33˚C