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Pectin Extraction from Citrus Waste: Structural Quality and Yield with Mineral and Organic Acids

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Abstract

Pectin is a renewable polysaccharide valued for its gelling, stabilising, and encapsulating properties, with broad applications in food, pharmaceutical, and industrial sectors. However, extraction conditions critically affect its yield, structural integrity, and functional performance. Despite citrus peel being a major source of pectin, large amounts remain underutilised as waste. This study systematically investigates how different acid types influence the extraction efficiency and structural quality of pectin derived from citrus peel. Dried citrus peel powder was extracted using four acids—sulphuric, hydrochloric, acetic, and citric—under controlled conditions at 80 °C. Extractions were performed at a fixed time of 90 min for all acids, with additional time trials for sulphuric acid. Extracted pectins were evaluated for gravimetric yield, colour, solubility, degree of esterification (DE) by titration and FTIR, and structural features using FTIR and ^{1}H NMR spectroscopy. Results showed that sulphuric and hydrochloric acids yielded the highest pectin recoveries (30–35% and 20–25%, respectively) but caused significant degradation, evident from dark colour, broad FTIR peaks, low DE (<10%), and poor solubility. In contrast, acetic and citric acid extractions resulted in moderate yields (8–15%) but preserved the pectin backbone and maintained higher DE (>30%) compared to the mineral acid-extracted samples and the commercial low methoxyl (LM) standard, as confirmed by clear FTIR and NMR profiles. These findings demonstrate the trade-off between extraction yield and structural integrity, underscoring the potential of mild organic acids to produce high-quality pectin suitable for value-added applications. Optimising acid type and extraction conditions can support sustainable waste valorisation and expand the industrial use of citrus-derived pectin.

Keywords: citrus peel; pectin; waste valorisation; organic acids; mineral acids

Academic Editor: Tullio Scopigno

Received: 8 July 2025
Revised: 2 August 2025
Accepted: 7 August 2025
Published: 10 August 2025

Citation: Mansor, M.H.; Williamson, L.; Ludwikowski, D.; Howard, F.; Muthana, M. Pectin Extraction from Citrus Waste: Structural Quality and Yield with Mineral and Organic Acids. *Physchem* **2025**, *5*, 32. https://doi.org/10.3390/physchem5030032

1. Introduction

Pectin is a natural structural heteropolysaccharide predominantly located in the primary cell walls of fruits and vegetables, with citrus peels and apple pomace being particularly abundant sources [1–3]. Its backbone mainly comprises homogalacturonan—a linear chain of α-1,4-linked D-galacturonic acid units—along with more complex domains such as rhamnogalacturonan I and II, xylogalacturonan, and various substituted residues including arabinose, galactose, rhamnose, and O-acetyl or O-methyl moieties. These structural features critically

govern the physicochemical and functional properties of pectin, underpinning its broad industrial utility.

Owing to its biocompatibility, thermal stability, pH tolerance, and hygroscopic nature, pectin is widely applied as a renewable functional material in the food, pharmaceutical, and biomedical fields [4–6]. In the food industry, it serves as a gelling agent for jams and jellies, an emulsifier in confectionery, and a stabiliser in various processed products. In pharmaceutical and biomedical contexts, pectin's natural gel-forming ability and biocompatibility enable its use in controlled-release drug delivery systems, wound dressings, and tissue engineering scaffolds. The degree of esterification (DE)—which reflects the proportion of methyl-esterified galacturonic acid residues—plays a vital role in determining pectin's gelling behaviour and suitability for specific applications. High-methoxyl (HM) pectin (DE > 50%) gels in high-sugar, low-pH environments, making it ideal for traditional food gels and emerging nanomedicine systems [7–9]. In contrast, low-methoxyl (LM) pectin (DE < 50%) forms gels through calcium-mediated cross-linking, which is preferable for low-sugar food formulations and biomedical applications such as encapsulation of bioactives and environmental remediation [10–12].

With global population growth and an increasing focus on sustainable food production and pharmaceutical innovation, pectin's versatile functionality and renewable sourcing offer important opportunities for waste valorisation and circular bioeconomy strategies [13]. Despite annual citrus production exceeding 144 million tonnes globally, a significant portion of citrus peel—containing up to 50% pectin by dry weight—is still discarded as processing waste [14,15]. This underutilised biomass contributes to approximately 10 million tonnes of by-product each year, with notable implications for carbon footprint and waste management. Efficient recovery of high-quality pectin from citrus waste streams is therefore both an economic and environmental priority.

Various extraction methods have been developed to isolate pectin, including enzyme-assisted, microwave- and ultrasound-assisted, and subcritical water techniques. While these methods can offer improved yields and shorter extraction times, they also have practical limitations such as high cost, energy demands, and potential thermal degradation of the pectin structure [16–19]. Conventional acid hydrolysis remains the predominant industrial approach due to its relative simplicity, cost-effectiveness, and scalability. However, the choice of acid—whether strong mineral or mild organic—strongly influences pectin's yield, molecular weight, DE, colour, and overall functional integrity. Mineral acids such as hydrochloric and sulphuric acid typically enhance extraction yield through aggressive hydrolysis of cell wall components but often lead to excessive depolymerisation, resulting in lower DE and diminished gelling capacity [20]. Conversely, organic acids like acetic or citric acid offer gentler extraction conditions that better preserve pectin's structural integrity but may result in lower recovery rates [21,22].

Despite the wide use of acid hydrolysis, existing studies report conflicting outcomes regarding the optimal extraction conditions, with differences in acid type, concentration, extraction time, and temperature often yielding inconsistent results [23,24]. A systematic, controlled comparison of mineral versus organic acids under standardised conditions remains limited, hindering clear recommendations for optimising both yield and product quality.

Therefore, this study systematically compared the extraction of pectin from dried citrus peel using sulphuric, hydrochloric, acetic, and citric acids under identical hydrolysis conditions. The extracted pectins were characterised in terms of yield, colour, solubility, degree of esterification (via titration and FTIR), and structural integrity using ^{1}H NMR spectroscopy. By directly contrasting strong mineral and mild organic acids, this work clarifies the trade-off between extraction efficiency and structural quality, addressing

inconsistencies in previous research. These findings will help guide the selection of optimal acid extraction conditions for producing high-quality pectin from citrus waste for food, pharmaceutical, and sustainable biomaterial applications.

2. Materials and Methods

2.1. Materials

Waste Valencia oranges (*Citrus sinensis*) peels were collected from local juice bars in Sheffield, UK. Peels were thoroughly washed with distilled water to remove surface dirt, residual sugars, and contaminants. Cleaned peels were air-dried at room temperature for 24 h and then oven-dried at 50 °C for 48 h until constant weight was achieved. The dried material was ground into a fine powder using a laboratory blender, passed through a sieve with 1 mm mesh, and stored in airtight containers prior to extraction. A commercial low-methoxyl (LM) pectin (degree of esterification < 50%) was purchased from Thermo Fisher Scientific (Altrincham, UK) and used as a reference standard for comparison. All chemicals used were of analytical grade and used as received without further purification. Sulphuric acid (H_2SO_4, 95–98%), hydrochloric acid (HCl, 37%), glacial acetic acid (CH_3COOH), and citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) were purchased from Thermo Fisher Scientific. Absolute ethanol (99.5%) and 70% ethanol were used for pectin precipitation and washing steps. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used for titrimetric analysis of the degree of esterification (DE). Deuterium oxide (D_2O) or DMSO-d_6 for ^1H NMR spectroscopy were obtained from VWR (Leighton Buzzard, UK). All solutions were prepared using distilled water. The instruments employed included a thermostatically controlled water bath (Grant Instruments, Hertfordshire, UK), a laboratory centrifuge (Eppendorf, Hamburg, Germany), a hot-air drying oven (Memmert, Büchenbach, Germany), a Fourier-transform infrared (FTIR) spectrometer with attenuated total reflectance (ATR) accessory (Thermo Nicolet, MA, USA), and a 400 MHz NMR spectrometer (Bruker, MA, USA) for structural characterisation.

2.2. Methods

2.2.1. Extraction of Pectin

Adapted from the method developed by Fakayode and Abobi [25] and preliminary optimisation trials, dried citrus peel powder (10 g) was added to 500 mL of acid solution (solid-to-liquid ratio of 1:50 (w/v)) for each extraction condition. Four acid types were tested: sulphuric acid (0.1 N, pH~1.5), hydrochloric acid (0.1 N, pH~1.5), acetic acid (0.1 N, pH~2.0), and citric acid (0.1 N, pH~2.0). For each acid, extraction was performed in a thermostatically controlled water bath at 80 °C with continuous stirring for 90 min. Additionally, a time series (60, 90, and 120 min) was conducted to assess the effect of extraction duration on pectin yield. After extraction, the mixtures were cooled to room temperature and filtered through muslin cloth to obtain clear filtrates.

2.2.2. Pectin Precipitation and Drying

The filtrates were combined with absolute ethanol in a 1:2 (v/v) ratio in room temperature (RT) to precipitate pectin. Precipitated pectin was recovered by centrifugation at 4000 rpm for 20 min. The pectin was washed twice with 70% ethanol to remove residual acids and impurities and then dried at 50–60 °C in a drying oven until constant weight. Dried pectin was ground into fine powder and stored in airtight containers.

2.2.3. Yield Determination

For yield comparison between acid types, the pectin yield was calculated gravimetrically as follows:

$$Yield\ (\%) = \left(\frac{Weight\ of\ dry\ pectin}{Weight\ of\ dry\ peel}\right) \times 100$$

2.2.4. Colour and Solubility Assessment

The colour of dried pectin samples was visually assessed against a white background and photographed for recording. Quantitative colour analysis using a colorimeter could not be conducted due to equipment unavailability. Visual assessment of pectin colour was qualitatively recorded. Turbidity was assessed as a measure of solubility of pectin products in aqueous solution. Solubility was evaluated by dispersing ~0.025 g of each pectin sample in 10 mL of distilled water at room temperature and at 60 °C. Visual observation and absorbance at 600 nm (A_{600}) were recorded using a UV–Vis spectrophotometer (Shimadzu, Kyoto, Japan) to assess turbidity. Water activity (A_w) measurements using a hygrometer were not performed due to lack of access to appropriate instrumentation during the study period.

2.2.5. Degree of Esterification (DE)

The DE was determined by titration. Approximately 0.025 g of pectin was dissolved in 100 mL of 50% ethanol and titrated with 0.1 N NaOH using phenolphthalein as an indicator. After the initial titration, an excess of NaOH was added for saponification and the mixture was left for 30 min, followed by back-titration with 0.1 N HCl. DE was calculated as

$$DE(\%) = \left(\frac{V_1}{(V_1 + V_2)}\right) \times 100$$

where V_1 is the volume for neutralising free carboxyl groups and V_2 is the volume for saponification.

2.2.6. FTIR Analysis

To determine the degree of esterification, FTIR spectra were recorded in the range of 4000–500 cm^{-1} using an ATR-FTIR spectrometer (PerkinElmer, Connecticut, United States of America). Key peaks corresponding to ester carbonyl (~1740 cm^{-1}), carboxylate (~1630 cm^{-1}), and polysaccharide backbone (1000–1200 cm^{-1}) were identified and compared.

2.2.7. ^{1}H NMR Analysis

To identify the molecular structure of extracted pectin under different acid conditions, approximately 2 mg of each dried pectin sample was dissolved in deuterated solvent (D_2O or DMSO-d_6), sonicated, filtered, and analysed using a 400 MHz NMR spectrometer. Chemical shifts were referenced to the solvent peak, and signals were assigned to methyl ester (~3.7–3.8 ppm), acetyl (~2.0–2.3 ppm), and sugar ring protons (~3.0–5.5 ppm).

2.2.8. Statistical Analysis

All experiments were performed in triplicate. Data are presented as mean ± standard deviation (SD). Statistical differences between groups were analysed using one-way ANOVA followed by Tukey's post hoc test (GraphPad Prism, version 10.5). A value of $p < 0.05$ was considered statistically significant.

3. Results

This study compared the yield and structural characteristics of pectin extracted from citrus peel using four acids—sulphuric, hydrochloric, acetic, and citric—under controlled hydrolysis conditions. The results highlight how acid strength and extraction time affect extraction yield, colour, solubility, degree of esterification (DE), and structural integrity, as determined by gravimetric yield, visual assessment, solubility tests, FTIR, and ^{1}H NMR spectroscopy.

3.1. Pectin Yield Analysis

Pectin yield was influenced by both acid type and extraction duration (Figure 1). Figure 1A shows the average yield at 90 min of extraction at 80 °C for all four acids. Extractions using sulphuric acid produced the highest yields, averaging around 28–30%, followed by hydrochloric acid with yields between 18 and 22%. Citric acid and acetic acid resulted in significantly lower yields, averaging about 6–9% and 2–4%, respectively. Statistical analysis confirmed significant differences between the mineral and organic acid groups ($p < 0.05$ to ** $p < 0.001$).

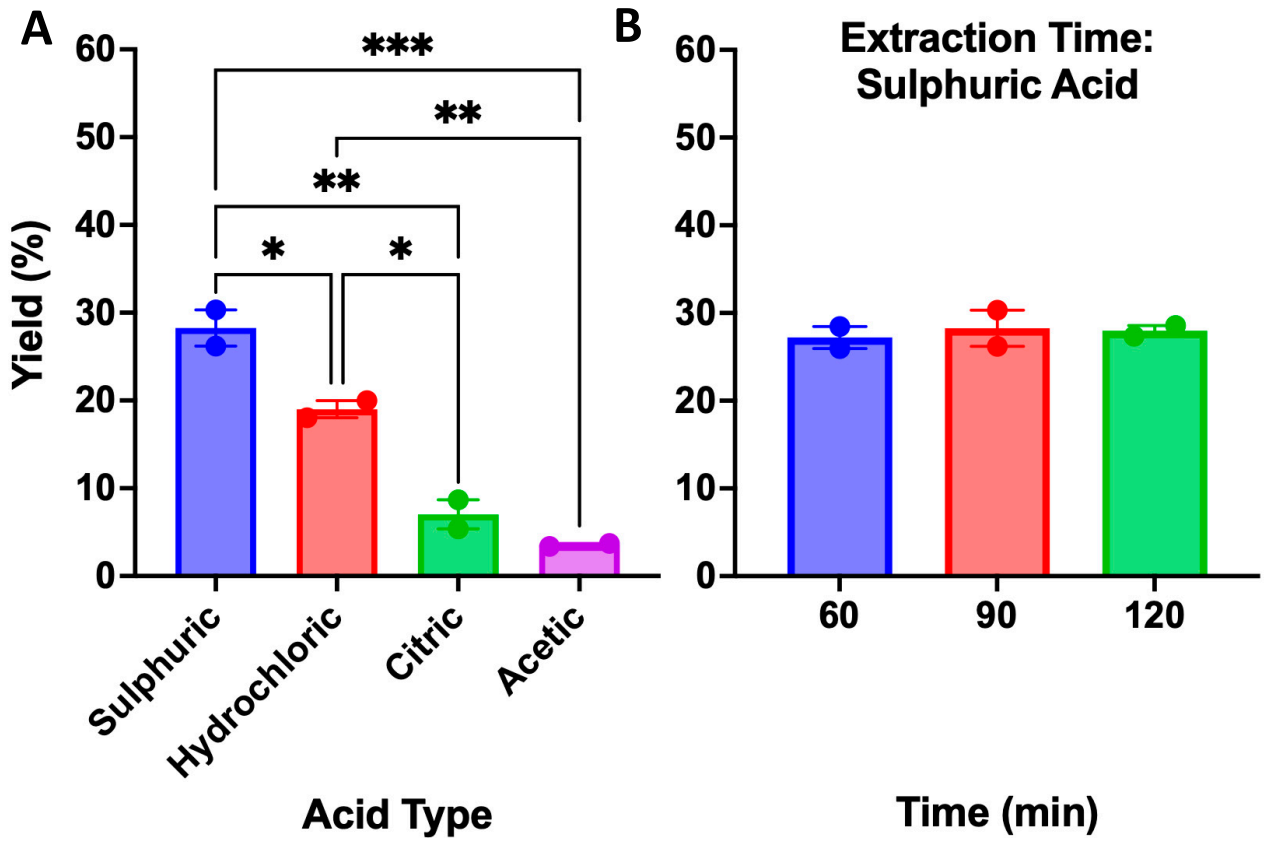

Figure 1. (**A**) Pectin yield (%) extracted from citrus peel using sulphuric, hydrochloric, citric, and acetic acids at 90 min, 80 °C. (**B**) Pectin yield (%) for sulphuric acid at different extraction times (60, 90, 120 min), presented as a representative example. Bars represent mean ± SD ($n = 3$). Significant differences between acid types are indicated (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$). Time-course data for all acids are provided in Table 1.

Table 1. Pectin yield (%) at different extraction times (60, 90, 120 min) using various acids at 80 °C. Data are presented as mean ± SD (n = 3).

Acid Type	60 Min	90 Min	120 Min
Sulphuric Acid	27.2 ± 1.8	28.3 ± 2.9	28.0 ± 0.8
Hydrochloric Acid	17.0 ± 1.1	19.0 ± 1.4	18.8 ± 1.0
Citric Acid	5.2 ± 0.6	7.0 ± 2.3	8.0 ± 1.5
Acetic Acid	2.1 ± 0.4	3.5 ± 0.2	3.9 ± 0.5

Figure 1B shows the effect of extraction time on pectin yield using sulphuric acid. Yields increased from approximately 27.2% at 60 min to 28.3% at 90 min, with no substantial gain observed at 120 min (28.0%), suggesting a yield plateau beyond 90 min. Table 1 expands this time-course comparison across all four acids. Hydrochloric acid followed a similar trend, peaking at 90 min (19.0%) and slightly declining thereafter (18.8%). In contrast, organic acids such as citric and acetic acid showed gradual increases over time. Citric acid yield rose from 5.2% at 60 min to 8.0% at 120 min, while acetic acid improved modestly from 2.1% to 3.9% over the same period. These results indicate that while mineral acids are more efficient for rapid pectin extraction, prolonged extraction may slightly benefit weaker organic acids.

3.2. Colour of Extracted Pectin

The colour of the dried pectin powders varied noticeably depending on the acid used (Figure 2). The commercial pectin (far left) appeared pale cream. Pectin extracted using sulphuric acid was medium brown, while hydrochloric acid-extracted pectin was the darkest, appearing dark brown to nearly black. Citric and acetic acid-extracted pectins (fourth and fifth, left to right) were lighter in colour, ranging from amber to deep orange.

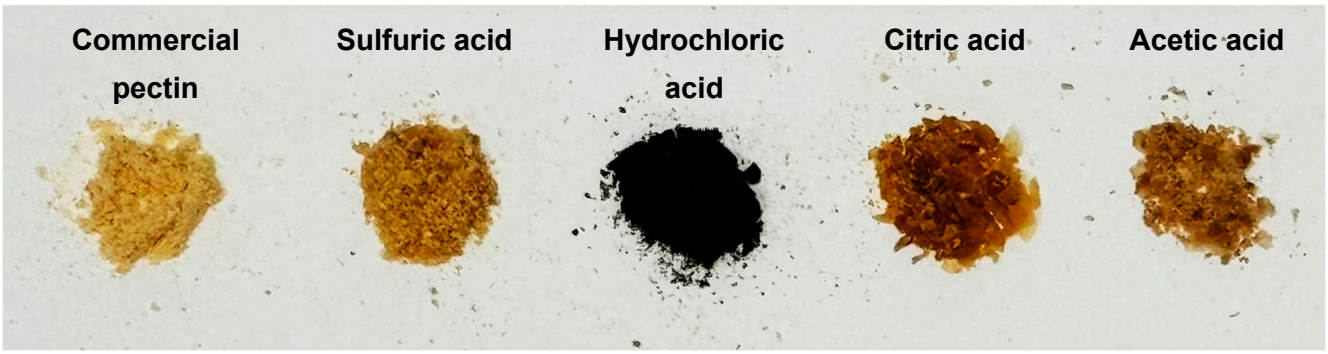

Figure 2. Visual appearance of dried pectin powders extracted from citrus peel using different acids, compared to commercial pectin (far left). Left to right: commercial pectin, sulphuric, hydrochloric, citric, and acetic acid extracts. Samples were photographed on a white background for comparison.

3.3. Solubility and Degree of Esterification

The degree of esterification (DE) of extracted pectins varied substantially depending on the acid used. The highest DE was observed in pectin extracted with hydrochloric acid (36.4%), followed by sulphuric acid (30.5%) and acetic acid (26.4%) (Figure 3A). In contrast, commercial pectin had a lower DE of 8.4%, and citric acid-extracted pectin showed the lowest DE at 3.3%. These findings indicate that both mineral acids and some organic acids can retain esterified groups under certain extraction conditions, although the extent of esterification appears to depend on both acid type and interaction with the citrus matrix.

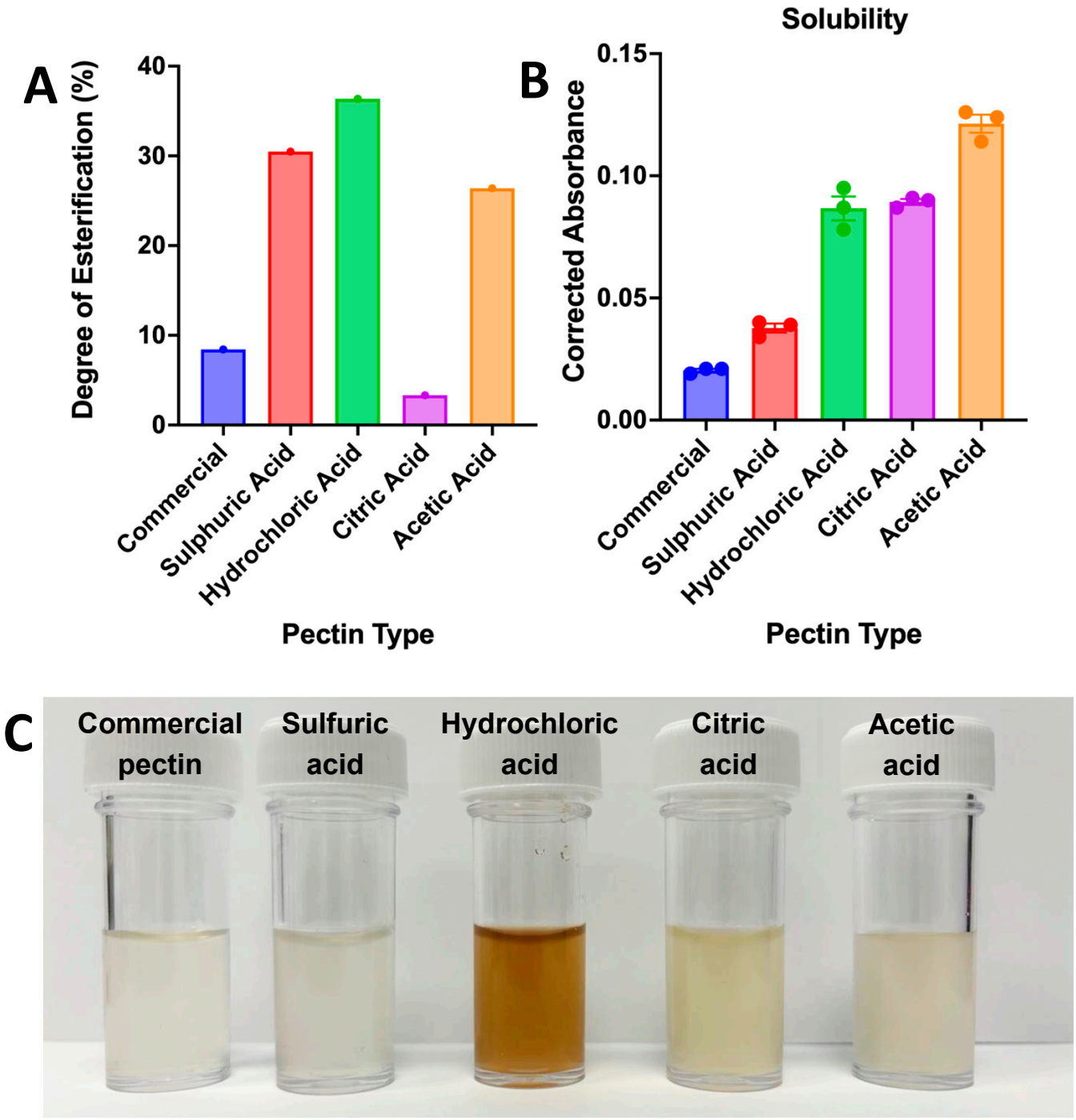

Figure 3. (**A**) Degree of esterification (DE%) of pectin extracted from citrus peel using sulphuric, hydrochloric, citric, and acetic acids, compared to commercial pectin. (**B**) Solubility of extracted pectin samples indicated by absorbance at 600 nm. (**C**) Visual appearance of 0.25% (*w*/*v*) aqueous pectin solutions from each acid type and the commercial standard, labelled accordingly: Commercial, Sulphuric, Hydrochloric, Citric, and Acetic acid. Bars represent mean ± SD (n = 3).

The solubility of the extracted pectins, measured by absorbance at 600 nm, varied depending on the acid used (Figure 3B). The highest solubility was observed in acetic acid-extracted pectin ($A_{600} \approx 0.118$), followed closely by citric acid (≈ 0.112) and hydrochloric acid (≈ 0.085). Sulphuric acid showed lower solubility (≈ 0.042), while the commercial pectin had the lowest value (≈ 0.025). These differences were visually apparent in 0.25% pectin solutions (Figure 3C), with organic acid extracts appearing more transparent

and homogeneous, and mineral acid and commercial samples showing greater turbidity and residue.

3.4. FTIR Analysis of Extracted Pectin

FTIR spectra for the extracted pectin samples and the commercial standard are shown in Figure 4. All samples displayed characteristic polysaccharide absorption regions. The commercial pectin and citric and acetic acid-extracted samples exhibited strong, well-defined ester carbonyl peaks near ~1740 cm^{-1} and clear polysaccharide backbone bands in the 1000–1200 cm^{-1} region. In contrast, pectin extracted with sulphuric and hydrochloric acids showed broader, less distinct ester carbonyl peaks and more pronounced carboxylate bands around ~1630 cm^{-1}, indicating lower esterification and partial chain degradation. The overall backbone signals for the mineral acid-extracted samples were less resolved than those of the commercial and organic acid-extracted samples.

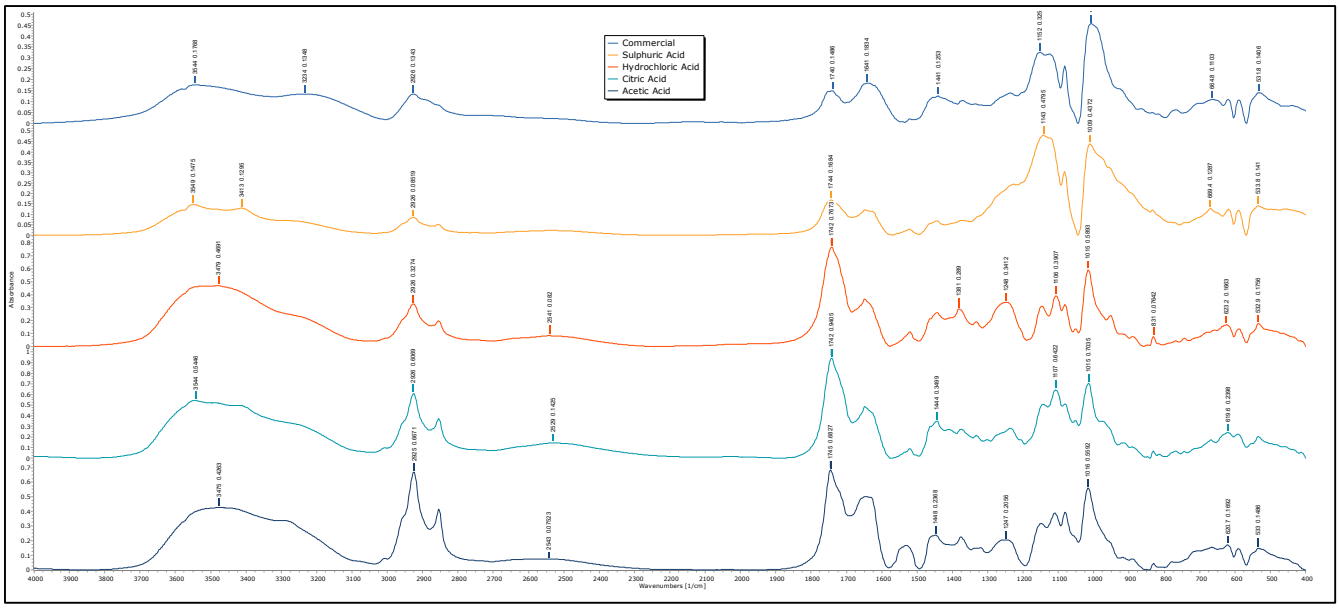

Figure 4. FTIR spectra (baseline-corrected and peak-normalised) of pectin extracted from citrus peel using sulphuric acid, hydrochloric acid, citric acid, and acetic acid, compared to a commercial pectin standard. Key functional group peaks include ester carbonyl (~1740 cm^{-1}), carboxylate (~1630 cm^{-1}), and polysaccharide backbone (~1000–1200 cm^{-1}).

3.5. ^{1}H NMR Analysis of Extracted Pectin

^{1}H NMR spectra for the extracted pectin samples and the commercial standard are shown in Figure 5. All samples exhibited signals corresponding to sugar ring protons between ~3.0 and 5.5 ppm. The commercial pectin and the citric and acetic acid-extracted samples showed well-resolved methoxy signals near ~3.7–3.8 ppm and anomeric proton peaks around 5.0–5.3 ppm, indicating an intact polysaccharide backbone and retained ester groups. In contrast, pectin extracted with sulphuric and hydrochloric acids showed broader, less distinct methoxy signals, and lower signal intensity in the anomeric region, suggesting partial chain degradation and lower esterification. Small peaks in the acetyl region (~2.0–2.3 ppm) were present in the commercial and organic acid-extracted samples but were less prominent in the mineral acid extracts.

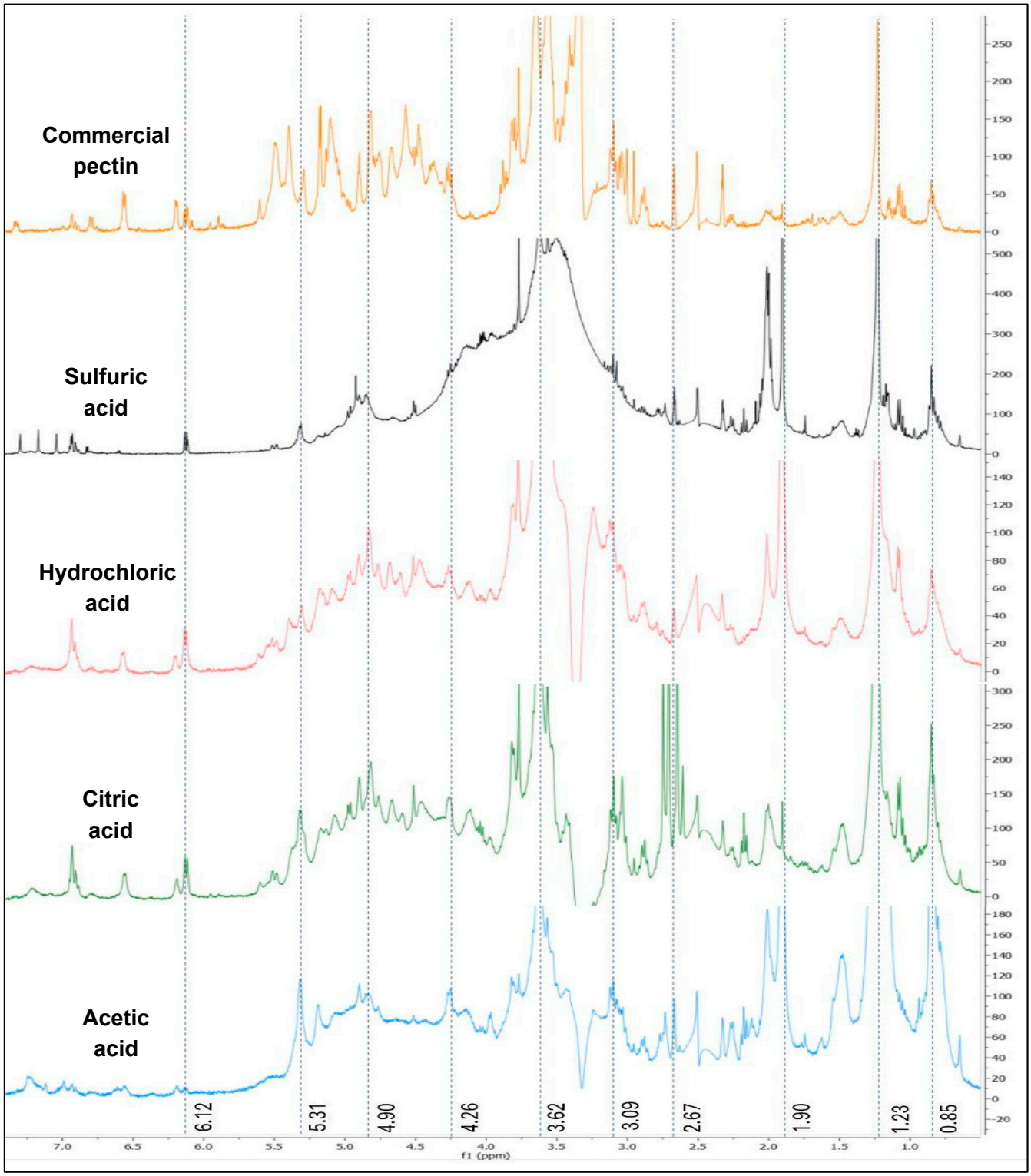

Figure 5. ^{1}H NMR spectra of commercial pectin and pectin extracted from citrus peel using sulphuric, hydrochloric, citric, and acetic acids. Key regions include methoxy protons (~3.7–3.8 ppm), acetyl groups (~2.0–2.3 ppm), sugar ring protons (~3.0–5.5 ppm), and anomeric protons (~5.0–5.3 ppm). Spectra were recorded at 400 MHz in DMSO-d_6.

4. Discussion

This study investigated the effects of four different acids—sulphuric acid, hydrochloric acid, acetic acid, and citric acid—on the yield and structural properties of pectin extracted from

citrus peel. By evaluating gravimetric yield, colour, solubility, FTIR, and ^{1}H NMR spectra, the relationship between extraction conditions and pectin quality was systematically assessed.

Extraction yields were highest for sulphuric acid (~28–30%) and hydrochloric acid (~20–22%), consistent with the stronger hydrolysis power of mineral acids that more aggressively disrupt plant cell walls [26]. However, these harsh conditions also produced pectin with darker colour and lower solubility. The dark colour seen with sulphuric and hydrochloric acid-extracted pectins likely results from sugar caramelisation, Maillard reaction products, and retained coloured impurities formed under stronger acidic conditions [27]. Additionally, the colour and solubility may also be influenced by lower anhydrouronic acid content, which is often used as a measure of pectin purity [20]. While not directly measured in this study, reduced galacturonic acid content or higher levels of neutral sugars and proteins could have contributed to the darker and more turbid appearance of these samples. Solubility measurements confirmed that these samples dispersed poorly in water, with visible undissolved residues.

The effect of extraction time further highlighted key differences in acid performance. For both sulphuric and hydrochloric acids, pectin yield increased initially but plateaued or slightly decreased after 90 min, indicating a saturation point under constant thermal conditions. This may be due to degradation of released pectin or re-condensation of soluble fragments into insoluble compounds [28]. In contrast, organic acids such as citric and acetic acid showed a steady increase in yield across the 60–120 min range. These acids are milder in action, and their extended exposure time appears necessary to fully access pectin from within the cell wall matrix. However, despite the longer extraction times, their yields remained lower than those of mineral acids, aligning with reports that organic acids typically have lower extraction efficiency but can preserve the pectin structure better [19,29,30].

FTIR analysis showed that sulphuric and hydrochloric acid-extracted pectins exhibited broader, less distinct ester carbonyl (~1740 cm^{-1}) peaks and stronger carboxylate (~1630 cm^{-1}) signals, indicating a lower degree of esterification (DE) and partial backbone hydrolysis. The commercial standard also displayed similar FTIR features, consistent with its low methoxylated nature. In contrast, pectin extracted with acetic and citric acids retained clearer ester carbonyl bands and more defined polysaccharide backbone peaks, indicating higher DE and better structural integrity [31,32].

^{1}H NMR spectra supported these trends: citric and acetic acid-extracted samples showed stronger methyl ester proton peaks (~3.7–3.8 ppm) and well-resolved sugar ring signals (~3.0–5.5 ppm), while sulphuric and hydrochloric acid-extracted pectins and the commercial LM standard showed weaker ester signals and broader anomeric regions, reflecting lower DE and more extensive depolymerisation [33,34].

Overall, these results highlight the trade-off between extraction yield and structural quality. While strong mineral acids maximise pectin yield, they can drive the DE below levels that maintain functional gelling or stabilising performance [35]. The commercial pectin used in this study, with DE < 10%, represents a typical low methoxyl (LM) standard designed for calcium-mediated gelation. The fact that mineral acid-extracted pectin also displayed similarly low DE suggests that overly harsh hydrolysis may limit its practical application where higher ester content is required. In contrast, milder organic acids like acetic and citric produced moderate yields but preserved esterification and the polysaccharide backbone better, offering functional properties suitable for conventional gelling and encapsulation applications. Extraction yield can be determined by different protic acids. For example, Ma et al. found greatest extraction yields of mango peel pectin using diprotic and triprotic malic and citric acids, respectively, compared to monoprotic lactic acid [36]. Further, strong acids marked by high K_a were reported to yield higher amounts

of extracted pectin than weak acids. Jong et al. found that mineral acids produced a yield of 10% at 0.1 M compared to 7% from durian rind pectin. Strong acids are reported to solubilise protopectin into small monomeric counterparts at faster rate constants than weak acids to a point where no further monosaccharides can be precipitated with ethanol [20]. This may suggest that large K_a or polyprotic acids may speed up extraction of pectins.

Different sources of citrus pectin, including lime and lemon, can provide high yields under varied pH ranges due to different matrix protein composition and thus differential Schiff base formation rates [26,37].

We hypothesised that longer extraction times produce higher yields, particularly for weak organic acids, owing to time- and or concentration-dependent hydrolysis [38,39]. In addition to facilitating thermal decomposition, we hypothesise that higher incubation temperatures enhance acid diffusion into the solid peel matrix and enhance solubility, particularly of water-insoluble proto-pectin, enhancing extracted pectin yield [37]. While colour and water activity measurements were not conducted in this study, future work will include instrumental analyses to strengthen physicochemical characterisation and storage stability assessments.

These findings provide practical guidance for optimising extraction conditions: balancing acid strength and extraction time can help maximise recovery while preserving functional quality. For food, pharmaceutical, or biomaterial applications requiring higher gelling ability, organic acids may be preferable despite lower yields, especially when integrated with sustainable citrus waste valorisation strategies.

5. Conclusions

This study systematically compared the extraction of pectin from citrus peel using sulphuric, hydrochloric, acetic, and citric acids, examining the influence of acid type and extraction duration on yield and structural quality. Strong mineral acids such as sulphuric and hydrochloric produced the highest pectin yields but led to significant degradation of the polysaccharide backbone, as shown by darker colour, reduced solubility, low degree of esterification, and evidence of structural breakdown in FTIR and NMR analyses. In contrast, extractions with acetic and citric acids yielded pectin with higher degree of esterification and better-preserved backbone integrity than the mineral acid-extracted samples and the commercial low-methoxyl standard, resulting in superior solubility, though with lower overall yield.

These findings underscore the importance of balancing extraction efficiency with structural integrity, depending on the intended application. For functional uses such as gelling, encapsulation, or controlled release, milder organic acids may be preferable to produce high-quality pectin. By comparison, mineral acid extractions may be more suitable for bulk uses where maximum yield is prioritised over detailed structural preservation. This work provides valuable insights to guide the optimisation of pectin extraction conditions for sustainable recovery and high-value use of citrus processing waste.

Author Contributions: Conceptualisation, M.H.M. and M.M.; methodology, M.H.M., L.W., D.L. and F.H.; software, M.H.M. validation, M.M.; formal analysis, M.H.M.; investigation, M.H.M. and M.M.; resources, M.H.M. and F.H.; data curation, M.H.M.; writing—original draft preparation, M.H.M., L.W. and D.L.; writing—review and editing, M.H.M., L.W., D.L., F.H. and M.M.; visualisation, M.H.M. and M.M.; supervision, M.M.; project administration, M.M.; funding acquisition, M.M. All authors have read and agreed to the published version of the manuscript.

Funding: We thank UK Research and Innovation for funding of M.H.M. and M.M. through Engineering and Physical Sciences Research Council (ESPRC) funding (ESPRC grant reference: EP/Z53304X/1).

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

ANOVA	Analysis of variance
A_{600}	Absorbance at 600 nm
A_w	Water activity
DE	Degree of esterification
FTIR	Fourier-transform infrared spectroscopy
HM	High-methoxyl
LM	Low-methoxyl
NMR	Nuclear magnetic resonance spectroscopy
RT	Room temperature
SD	Standard deviation

References

1. Dumont, M.; Lehner, A.; Bouton, S.; Kiefer-Meyer, M.C.; Voxeur, A.; Pelloux, J.; Lerouge, P.; Mollet, J.-C. The cell wall pectic polymer rhamnogalacturonan-II is required for proper pollen tube elongation: Implications of a putative sialyltransferase-like protein. *Ann. Bot.* **2014**, *114*, 1177–1188. [CrossRef] [PubMed]
2. Opanasopit, P.; Apirakaramwong, A.; Ngawhirunpat, T.; Rojanarata, T.; Ruktanonchai, U. Development and characterization of pectinate micro/nanoparticles for gene delivery. *Aaps Pharmscitech* **2008**, *9*, 67–74. [CrossRef] [PubMed]
3. Thibault, J.F.; Ralet, M.C. Pectins, their origin, structure and functions. In *Advanced Dietary Fibre Technology*; Wiley: Sussex, UK, 2000; pp. 367–378.
4. Kaushik, P.; Priyadarshini, E.; Rawat, K.; Rajamani, P.; Bohidar, H. pH responsive doxorubucin loaded zein nanoparticle crosslinked pectin hydrogel as effective site-specific anticancer substrates. *Int. J. Biol. Macromol.* **2020**, *152*, 1027–1037. [CrossRef]
5. Ridley, B.L.; O'Neill, M.A.; Mohnen, D. Pectins: Structure, biosynthesis, and oligogalacturonide-related signaling. *Phytochemistry* **2001**, *57*, 929–967. [CrossRef]
6. Valdés, A.; Burgos, N.; Jiménez, A.; Garrigós, M.C. Natural pectin polysaccharides as edible coatings. *Coatings* **2015**, *5*, 865–886. [CrossRef]
7. Thibault, J.-F.; Ralet, M.-C. Physico-chemical properties of pectins in the cell walls and after extraction. In *Advances in Pectin and Pectinase Research*; Springer: Berlin/Heidelberg, Germany, 2003; pp. 91–105.
8. Bisht, B.; Lohani, U.; Kumar, V.; Gururani, P.; Sinhmar, R. Edible hydrocolloids as sustainable substitute for non-biodegradable materials. *Crit. Rev. Food Sci. Nutr.* **2022**, *62*, 693–725. [CrossRef]
9. Ansari, Z.; Goomer, S. Natural gums and carbohydrate-based polymers: Potential encapsulants. *Indo Glob. J. Pharm. Sci.* **2022**, *12*, 01–20. [CrossRef]
10. Ventura, I.; Jammal, J.; Bianco-Peled, H. Insights into the nanostructure of low-methoxyl pectin–calcium gels. *Carbohydr. Polym.* **2013**, *97*, 650–658. [CrossRef]
11. El-Maraghy, C.M.; Saleh, S.S.; Ibrahim, M.S.; El-Naem, O.A. Green wastewater treatment of repurposed COVID-19 therapy (levofloxacin) using synthesized magnetite pectin nanoparticles, comparison with mesoporous silica nanoparticles. *BMC Chem.* **2023**, *17*, 134. [CrossRef]
12. Lopez-Maldonado, E.A.; Abdellaoui, Y.; Elella, M.H.A.; Abdallah, H.M.; Pandey, M.; Anthony, E.T.; Ghimici, L.; Álvarez-Torrellas, S.; Pinos-Vélez, V.; Oladoja, N.A. Innovative biopolyelectrolytes-based technologies for wastewater treatment. *Int. J. Biol. Macromol.* **2024**, *273*, 132895. [CrossRef]
13. Mishra, R.; Soni, K.; Mehta, T. Mucoadhesive vaginal film of fluconazole using cross-linked chitosan and pectin: In vitro and in vivo study. *J. Therm. Anal. Calorim.* **2017**, *130*, 1683–1695. [CrossRef]
14. Pratiksha; Adhikary, M. Industrial Production of Citrus By-products and Its Processing Techniques. In *Citrus Fruits and Juice: Processing and Quality Profiling*; Springer: Berlin/Heidelberg, Germany, 2024; pp. 391–417.
15. Dubey, P.; Tripathi, G.; Mir, S.S.; Yousuf, O. Current scenario and global perspectives of citrus fruit waste as a valuable resource for the development of food packaging film. *Trends Food Sci. Technol.* **2023**, *141*, 104190. [CrossRef]
16. de Oliveira, C.F.; Giordani, D.; Lutckemier, R.; Gurak, P.D.; Cladera-Olivera, F.; Marczak, L.D.F. Extraction of pectin from passion fruit peel assisted by ultrasound. *LWT–Food Sci. Technol.* **2016**, *71*, 110–115. [CrossRef]

17. Gurev, A.; Cesko, T.; Dragancea, V.; Ghendov-Mosanu, A.; Pintea, A.; Sturza, R. Ultrasound-and microwave-assisted extraction of pectin from apple pomace and its effect on the quality of fruit bars. *Foods* **2023**, *12*, 2773. [CrossRef]
18. Canteri-Schemin, M.H.; Fertonani, H.C.R.; Waszczynskyj, N.; Wosiacki, G. Extraction of pectin from apple pomace. *Braz. Arch. Biol. Technol.* **2005**, *48*, 259–266. [CrossRef]
19. Marić, M.; Grassino, A.N.; Zhu, Z.; Barba, F.J.; Brnčić, M.; Brnčić, S.R. An overview of the traditional and innovative approaches for pectin extraction from plant food wastes and by-products: Ultrasound-, microwaves-, and enzyme-assisted extraction. *Trends Food Sci. Technol.* **2018**, *76*, 28–37. [CrossRef]
20. Jong, S.H.; Abdullah, N.; Muhammad, N. Effect of acid type and concentration on the yield, purity, and esterification degree of pectin extracted from durian rinds. *Results Eng.* **2023**, *17*, 100974. [CrossRef]
21. Haque, S.M.; Kabir, A.; Ratemi, E.; Elzagheid, M.; Appu, S.P.; Ghani, S.S.; Sarief, A. Greener pectin extraction techniques: Applications and challenges. *Separations* **2025**, *12*, 65. [CrossRef]
22. Li, H.; Li, Z.; Wang, P.; Liu, Z.; An, L.; Zhang, X.; Xie, Z.; Wang, Y.; Li, X.; Gao, W. Evaluation of citrus pectin extraction methods: Synergistic enhancement of pectin's antioxidant capacity and gel properties through combined use of organic acids, ultrasonication, and microwaves. *Int. J. Biol. Macromol.* **2024**, *266*, 131164. [CrossRef]
23. Chandel, V.; Biswas, D.; Roy, S.; Vaidya, D.; Verma, A.; Gupta, A. Current advancements in pectin: Extraction, properties and multifunctional applications. *Foods* **2022**, *11*, 2683. [CrossRef]
24. Roy, S.; Priyadarshi, R.; Łopusiewicz, Ł.; Biswas, D.; Chandel, V.; Rhim, J.-W. Recent progress in pectin extraction, characterization, and pectin-based films for active food packaging applications: A review. *Int. J. Biol. Macromol.* **2023**, *239*, 124248. [CrossRef] [PubMed]
25. Fakayode, O.A.; Abobi, K.E. Optimization of oil and pectin extraction from orange (*Citrus sinensis*) peels: A response surface approach. *J. Anal. Sci. Technol.* **2018**, *9*, 20. [CrossRef]
26. Akhter, M.J.; Sarkar, S.; Sharmin, T.; Mondal, S.C. Extraction of pectin from powdered citrus peels using various acids: An analysis contrasting orange with lime. *Appl. Food Res.* **2024**, *4*, 100614. [CrossRef]
27. Gama, B.; Silva, C.D.F.; Da Silva, L.O.; Abud, A.d.S. Extraction and characterization of pectin from citric waste. *Chem. Eng. Trans.* **2015**, *44*, 259–264.
28. Mohnen, D. Pectin structure and biosynthesis. *Curr. Opin. Plant Biol.* **2008**, *11*, 266–277. [CrossRef]
29. Pattarapisitporn, A.; Noma, S. Alternative Solvents for Pectin Extraction: Effects of Extraction Agents on Pectin Structural Characteristics and Functional Properties. *Foods* **2025**, *14*, 2644. [CrossRef]
30. Picot-Allain, M.C.N.; Ramasawmy, B.; Emmambux, M.N. Extraction, characterisation, and application of pectin from tropical and sub-tropical fruits: A review. *Food Rev. Int.* **2022**, *38*, 282–312. [CrossRef]
31. El-Naggar, M.E.; Othman, S.I.; Allam, A.A.; Morsy, O.M. Synthesis, drying process and medical application of polysaccharide-based aerogels. *Int. J. Biol. Macromol.* **2020**, *145*, 1115–1128. [CrossRef]
32. Bichara, L.C.; Alvarez, P.E.; Bimbi, M.V.F.; Vaca, H.; Gervasi, C.; Brandán, S.A. Structural and spectroscopic study of a pectin isolated from citrus peel by using FTIR and FT-Raman spectra and DFT calculations. *Infrared Phys. Technol.* **2016**, *76*, 315–327. [CrossRef]
33. Marcon, M.; Carneiro, P.; Wosiacki, G.; Beleski-Carneiro, E.; Petkowicz, C. Pectins from apple pomace–characterization by ^{13}C and ^{1}H NMR spectroscopy. *Ann. Magn. Reson.* **2005**, *4*, 56–63.
34. Müller-Maatsch, J.; Caligiani, A.; Tedeschi, T.; Elst, K.; Sforza, S. Simple and validated quantitative 1H NMR method for the determination of methylation, acetylation, and feruloylation degree of pectin. *J. Agric. Food Chem.* **2014**, *62*, 9081–9087. [CrossRef] [PubMed]
35. Thakur, B.R.; Singh, R.K.; Handa, A.K.; Rao, M. Chemistry and uses of pectin—A review. *Crit. Rev. Food Sci. Nutr.* **1997**, *37*, 47–73. [CrossRef] [PubMed]
36. Ma, S.; Yu, S.J.; Zheng, X.L.; Wang, X.X.; Bao, Q.D.; Guo, X.M. Extraction, characterization and spontaneous emulsifying properties of pectin from sugar beet pulp. *Carbohydr. Polym.* **2013**, *98*, 750–753. [CrossRef]
37. Saberian, H.; Hamidi-Esfahani, Z.; Ahmadi Gavlighi, H.; Barzegar, M. Optimization of pectin extraction from orange juice waste assisted by ohmic heating. *Chem. Eng. Process. Process Intensif.* **2017**, *117*, 154–161. [CrossRef]
38. Colodel, C.; Petkowicz, C.L.d.O. Acid extraction and physicochemical characterization of pectin from cubiu (*Solanum sessiliflorum* D.) fruit peel. *Food Hydrocoll.* **2019**, *86*, 193–200. [CrossRef]
39. Li, J.; Zhang, L.; Li, J.-F.; Li, D.-Q. Comparative Studies of Combined Influence of Variables on the Esterification Degree of Pectin Extracted by Sulfuric Acid and Citric Acid. *Adv. Polym. Technol.* **2019**, *2019*, 6313241. [CrossRef]