CELLULOSE CHEMISTRY AND TECHNOLOGY

FRUIT WASTE-SOURCED PECTIN AS NATURAL CO-COAGULANT FOR ORGANIC MATTER AND TURBIDITY TREATMENT IN WASTEWATER

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Received October 2, 2024

Bio-based coagulant agents are increasingly regarded as a viable partial substitute for synthetic coagulant compounds, primarily due to environmental concerns. Pectin, being biodegradable, non-toxic, and applicable for the treatment of various types of wastewaters, has shown potential as an effective chemical in the coagulation-flocculation process. In this study, fruit peels, including grapefruit (GF), orange (OC), dragon fruit (DF), passion fruit (PF), and apple (AP) peels, were collected from local markets and used as raw materials for the extraction of pectin, which was then combined with poly aluminum chlorohydrate (PAC) in the water treatment process. The optimal conditions, namely, the material/solvent ratio, pH, and extraction time, were investigated to evaluate the pectin content extracted from each type of fruit peel. The results showed that the highest pectin content was extracted from passion fruit (12.2%), followed by grapefruit (10.4%), orange (10.2%), dragon fruit (8.6%), and the lowest from apple (6.3%) peels. However, the degree of esterification was observed to have the opposite tendency, which meant apple, dragon fruit and orange peels contained high-methoxyl pectin, compared to grapefruit and passion fruit peels, which had low-methoxyl pectin. In the water treatment experiment, the chemical oxygen demand (COD) gradually improved when poly aluminum chlorohydrate was combined with pectin at a concentration of 15 mg/L. The enhancement in removal efficiency reached 30% for dragon fruit, approximately 50% for grapefruit and orange, 58.2% for passion fruit, and up to 82.3% for apple peels. Regarding turbidity reduction, pectin derived from orange, passion fruit, and apple peels, in similar amounts, achieved removal efficiencies of 58.1%, 67.6%, and 83.8%, respectively. These findings indicated that pectin is a promising natural co-coagulant and deserves further investigation for its application in wastewater treatment.

Keywords: bio-coagulant, fruit peel, pectin, wastewater treatment

INTRODUCTION

In the wastewater treatment process, coagulation and flocculation are critical for removing turbidity, suspended solids, chemical oxygen demand (COD), and contaminants through sedimentation and filtration. Neutralization facilitates the agglomeration of small, suspended particles, which coalesce into larger flocs through surface forces, which eventually settle out. To enhance the size and stability of these flocs, reduce the risk of re-stabilization due to excess coagulants, and improve treatment efficiency at lower costs, chemical coagulants are of help. Commonly used synthetic inorganic and organic coagulant aids include polyacrylamide (PAM), poly aluminium chloride sulfate (PACs), poly ferric chloride (PFC), aluminum chlorohydrate (ACH) and poly aluminium silicate chloride (PASC).[1] The coagulation process relies on two main mechanisms: charge neutralization and adsorption bridging.[2] Thus, any factors that affect these mechanisms will influence the coagulation and flocculation processes.

The dosage of coagulant plays a crucial role in the effectiveness of coagulation, as it impacts both the extent of charge neutralization and the aggregation of particles.[3,4] If the dosage is inadequate or excessive, it can lead to inefficiencies in the coagulation process, reducing its ability to remove contaminants like COD and turbidity. For example, a study comparing different coagulants in brewery wastewater treatment found that varying dosages of polyamine and ACH significantly impacted the removal efficiency of COD and turbidity, demonstrating the importance of optimizing coagulant dosage.[5] Further research has shown that the choice of coagulants and their dosages can also influence the structure and strength of the flocs formed. Factors such as the type of coagulant, the water chemistry, and the method of coagulant addition must all be optimized to enhance the removal of contaminants.[6]

Several derivatives of polyacrylamide (PAM) are challenging to degrade, and their breakdown can release acrylamide monomers, which are known neurotoxins and potential carcinogens. Acrylamide has been shown to pose significant risks to aquatic life and can persist in the environment due to its low biodegradability. The presence of acrylamide monomers in PAM degradation intermediates heightens these hazards. Studies have confirmed that acrylamide induces neurotoxic effects in humans and is a suspected human carcinogen.[7]

In this context, natural and environmentally friendly bio-coagulant agents have indeed gained significant traction as viable alternatives to synthetic coagulants. Natural coagulants, such as those derived from plant materials, offer promising potential for replacing chemical coagulants in water treatment processes. For example, *Moringa oleifera*, known for its effective coagulating properties, has been extensively studied for its ability to significantly reduce turbidity in wastewater, achieving removal rates as high as 92%.[8] Other natural coagulants include starch, dextrin, cellulose, and activated silica, which all have demonstrated varying degrees of effectiveness.[9] Several studies highlight the benefits of bio-coagulants extracted from agricultural waste or plant sources. For instance, research has shown that coagulants derived from acorn leaves and other plant materials are effective in improving water quality, while producing less sludge compared to traditional inorganic options.[10] Additionally, bio-coagulants have been noted for their lower environmental impact due to their organic and biodegradable nature.[11] Overall, the shift towards using natural coagulants aligns with global trends aimed at promoting sustainable and eco-friendly technologies in water treatment. This not only addresses environmental concerns, but also enhances the efficiency and effectiveness of water purification processes.[9] Research indicates that natural coagulants derived from plant materials are gaining popularity as sustainable alternatives to traditional synthetic coagulants like aluminum sulfate and ferric chloride. These bio-coagulants are recognized for their lower toxicity and environmental impact.[12,13] These references collectively underscore the growing recognition of natural coagulants, such as pectin, in the field of water treatment, highlighting their effectiveness, safety, and sustainability. Several studies highlight the effectiveness of pectin as a natural coagulant in water treatment processes. For example, it has been demonstrated that pectin can significantly improve turbidity removal in various water conditions, making it a viable alternative to conventional coagulants.[14] Several studies have shown that pectin is a promising coagulant agent and can be used as a novel, safe, and biodegradable natural coagulant aid with effective water treatment properties, posing no toxicity to humans or the environment.[9]

Pectin is indeed a vital polysaccharide that serves essential structural functions in the cell walls of fruits and vegetables. Its backbone is made up of D-galacturonic acid units, which can exist in both free and esterified forms, containing key functional groups like carboxyl (–COOH) and methoxyl ($-OCH_3$). This structural complexity allows pectin to form gels, primarily through hydrogen bonding between its hydroxyl (–OH) groups and various organic or insoluble compounds. The methoxyl content of pectin is crucial as it affects its gelling properties and functionality. Higher methoxyl content (generally above 50%) characterizes high-methoxyl pectin (HMP), which forms gels in the presence of sugar and acid, making it ideal for traditional jam and jelly applications. Conversely, low-methoxyl pectin (LMP), which contains less than 50% methoxyl groups, can gel in the presence of calcium ions, offering a broader range of applications, including in low-sugar and sugar-free products. The methoxyl content affects not only the gelling behavior, but also the thickening and stabilizing properties of pectin in food systems.

High-methoxyl (>50%) pectins tend to form firmer gels, which is desirable in many food products, while low-methoxyl (<50%) pectins offer versatility in low-sugar applications.[12] Based on these chemical properties, pectin is considered a potential biomaterial for application in water treatment.[15] The chemical structure of pectin is presented in Figure 1.

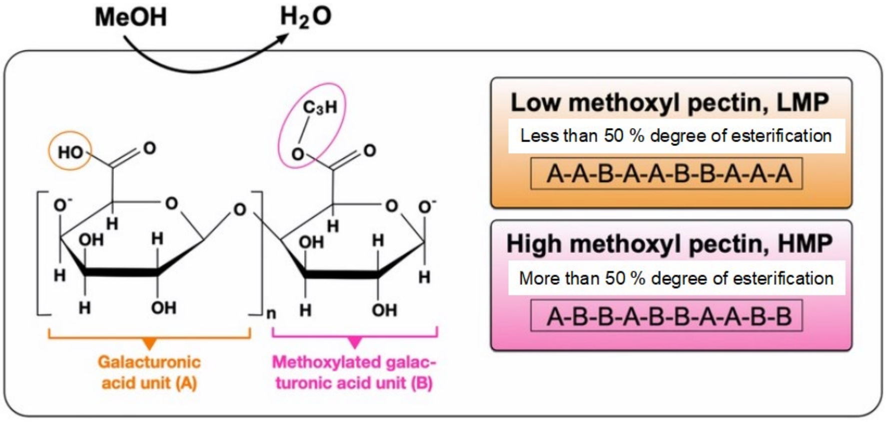


Figure 1: Chemical structure of high-methoxyl and low-methoxyl pectin[16]

Fruit waste, particularly from common varieties like grapefruit, orange, dragon fruit, passion fruit, and apple peels, presents an excellent opportunity for producing biomaterials to be used in wastewater treatment. Fruit peels contain valuable bioactive compounds, such as pectin, polyphenols, and enzymes, which can be effectively extracted and utilized.[17] For instance, passion fruit peels can constitute 50–60% of the total fruit weight, while grapefruit peels represent about 30% of their respective fruit weight.[18-20] Unfortunately, a significant amount of these peels is discarded during processing and consumption, resulting in economic losses and environmental concerns.[21] Utilizing fruit peels not only aids in waste reduction, but also contributes to sustainable practices by repurposing these materials into valuable resources for water treatment applications. This process can alleviate some environmental issues associated with waste disposal, while simultaneously promoting resource efficiency.[22] In addition to pectin, these fruit peels also contain a range of bioactive components, making them a rich source for developing natural coagulants in water treatment.[23] By harnessing these natural materials, wastewater management challenges can be addressed, while promoting sustainability.[24] The implementation of nature-based solutions in water management fosters a circular economy by utilizing green infrastructure, which helps in nutrient recovery and promotes the use of waste-sourced materials.[25] Thus, it is of interest how fruit by-products can be transformed into valuable resources, including natural preservatives, dietary fiber, and essential oils.[26] Therefore, in the present study, waste fruit peels, originating from grapefruit (GF), orange (OC), dragon fruit (DF), passion fruit (PF), and apples (AP), were collected from local markets in Vietnam, with a view of extracting pectin from them. Several parameters relevant to the pectin extraction process were analyzed for each initial material. Then, the prepared pectin was evaluated for its potential to treat chemical oxygen demand (COD) and turbidity in water.

EXPERIMENTAL

Materials

Fruit peels of oranges, pomelos, dragon fruit, passion fruit, dragon fruit and apples were collected from a local market at Linh Chieu Ward, Thu Duc City. The following chemicals were utilized in the study: citric acid solution, ethanol solution (C_2H_5OH), sulfuric acid solution (H_2SO_4), sodium hydroxyl (NaOH) and hydrochloric acid (HCl), purchased from Xilong Chemical Reagent Co., Ltd., China. polyaluminium chloride (PAC – $(Al_2(OH)_nCl_{6-n}xH_2O)_m$) was obtained from India. Standard solutions of potassium dichromate ($K_2Cr_2O_7$), iron(II) (Fe(II)) and ferroin indicator for analytical purposes were purchased from Nacalai, Japan. Wastewater samples were collected from a student dormitory of Vietnam National University, Ho Chi Minh City.

Methods

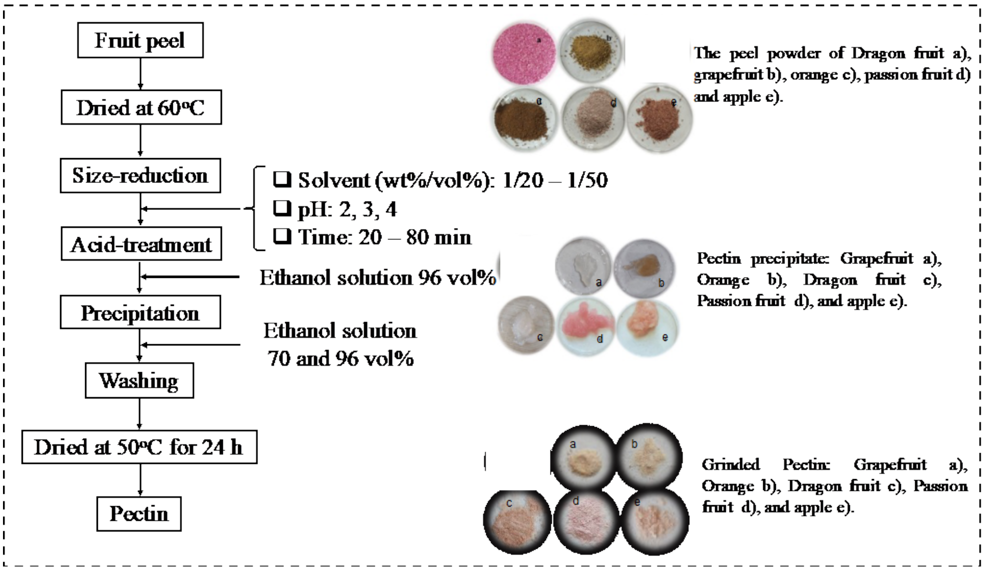
Extraction of pectin from fruit waste

Fruit peels that were free from bruises, damage, and discoloration were collected; the green tips were removed from the dragon fruit peels. The selected peels were then thoroughly washed, cut into small pieces, and rinsed again with distilled water to remove impurities. After that, these materials were ground and sieved using a 245-µm sieve, followed by being dried at 60 ºC for 24 h to reduce the water content and achieve a stable moisture level for the preservation and utilization of the ingredients. Briefly, about 5 g of the peel powder of the initial material was immersed in 0.1 M citric acid solution at the mixing ratio (wt%/vol%) of 1/20 – 1/50 when the pH was varied from 2 to 4 during 20 to 80 min at 80 ºC. After extraction, the mixture was filtered to separate the liquid containing pectin from the solid residues. Pectin was then precipitated from the filtered solution using 96 vol% ethanol solution, which increased the recovery of pectin from the solution. The precipitated pectin is collected and purified through washing and further drying to remove any residual solvent and impurities with 70 and 96 vol% ethanol solution. Finally, the pectin was successfully prepared by dried at 50 ºC for 24 h.

Prior to measurements, the extracted pectin was characterized for its properties, to assess its suitability for the water treatment. The pectin extraction process from fruit peel waste is illustrated in Figure 2. The pectin content is calculated using the formula:

$$\text{Pectin } \% = \frac{m}{m_0} \times 100 \qquad (1)$$

where m and m_0 represent the mass of the dried pectin (g) and the mass of the fruit peel (g).



The peel powder of Dragon fruit a), grapefruit b), orange c), passion fruit d) and apple e).

Pectin precipitate: Grapefruit a), Orange b), Dragon fruit c), Passion fruit d), and apple e).

Grinded Pectin: Grapefruit a), Orange b), Dragon fruit c), Passion fruit d), and apple e).

Figure 2: The process of pectin extraction from waste fruit peels

Characterization of the obtained pectin

The degree of esterification (DE) was established based on findings from a prior study.[27] In summary, approximately 0.1 g of the isolated pectin was dissolved in 2 mL of a 96% ethanol solution, which was subsequently mixed with 20 mL of distilled water. Following this, 5 mL of phenolphthalein solution was added and titrated with 0.1 M NaOH solution until the appearance of a light pink color, at which point the volume was recorded as V1 (mL). Next, 10 mL of 0.5 M NaOH solution was thoroughly mixed into the solution, which was then allowed to stand at room temperature for 20 min. Afterward, 10 mL of 0.5 M HCl solution was added and mixed until the pink color disappeared. Finally, an additional 5 drops of phenolphthalein were added to the mixture, and titration with 0.1 M NaOH solution was conducted once more, with the volume recorded as V2 (mL). The degree of esterification (DE) was calculated as follows:

$$\text{DE } (\%) = V_2 \times 100/\,(V_1 + V_2) \qquad (2)$$

The presence of specific chemical groups in the prepared pectin was analyzed using an FT-IR spectrometer (JASCO FT-IR/4100, Japan) at the wavelength range of 4000–500 cm^{-1} in transmittance mode.

The morphology of dried pectin was investigated by scanning electron microscopy (SEM) (JSM-5300LV, JEOL, Japan). The samples were fractured using liquid nitrogen and subsequently subjected to freeze-drying for 24 h and coated with a thin layer of platinum. After that, the SEM images were taken at the acceleration of 5 kV.

The equilibrium water absorption (EWC) values of the extracted pectin were determined at ambient temperature by submerging the dry samples in distilled water. Following immersion for varying durations ranging up to 24 h to achieve equilibrium sorption, the samples were extracted and promptly dried with tissue paper to eliminate unbound water molecules before being weighed. The value of EWC was calculated for each sample by:

$$\text{EWC } (\%) = (m - m_0) \times 100/\, m_0 \qquad (3)$$

where m_0 is the initial dry weight of the sample, and m is the weight after immersing in distilled water for 24 h.

Wastewater treatment for COD and turbidity removal

To determine the coagulation activity and evaluate the potential of pectin as a potential bio-coagulant, the optimal amount of PAC, the pH, and pectin dosage for water treatment processes were determined based on the Jar test method at 27 ºC. The removal efficiency of COD was measured according to TCVN 6491:1999 (ISO 6060:1989) for Water Quality (Determination of the chemical oxygen demand).[28] Briefly, the concentration of COD (mg/L) was tested by adding 5 mL of 0.025 N $K_2Cr_2O_7$ solution and 2 mL of the sample to a COD analysis tube, followed by heating for 2 h at 150 °C. After cooling to room temperature, the solution was transferred to a 250 mL flask, to which 2 mL of concentrated H_2SO_4 and 2 drops of Ferroin indicator were added.

The solution was then titrated with 0.025 N Fe(II) solution. The 0.1 N Fe(II) solution used for titration was verified daily using a standard 0.1 N $K_2Cr_2O_7$ solution. The COD value was calculated using the following formula:

$$\text{COD (mg/L)} = \frac{(Vo - V) \times N \times 8000}{Vsample} \qquad (4)$$

where N is the equivalent concentration of the Fe(II) solution (N), V_o is the volume of the Fe(II) solution used for titration of the blank sample (mL), and V is the volume of the Fe(II) solution used for titration of the wastewater sample (mL), 8000 is the the molar mass of 1/2 O_2 (mg/L).

The removal efficiency, H of COD was calculated by the equation:

$$H_{COD}\ (\%) = (C_{0,COD} - C_{1,COD}) \times 100/C_0 \qquad (5)$$

where $C_{0,COD}$ and $C_{1,COD}$ are the concentration of COD (mg/L) before and after the coagulation process, repectively.

In the turbidity removal test, a UV-Vis spectometer was employed, to obtain the difference in absorbance at the wavelength of 420 nm for the sample with and without adding various amounts of pectin extracted from fruit peels. After that, the concentration of turbidity in NTU (nephelometric turbidity units) was determined. The removal efficiency, H, of turbidity was calculated by the equation:

$$H_{NTU}\ (\%) = (C_{0,NTU} - C_{1,NUT}) \times 100/C_0 \qquad (6)$$

where $C_{0,NTU}$ and $C_{1,NTU}$ are the concentration of turbidity (NTU) before and after the coagulation process, repectively.

Effect of the amount of PAC

About 500 mL of wastewater adjusted to pH 7 was poured into a beaker and the appropriate amount of PAC was gradually added to the beaker at concentrations ranging from 50 to 300 mg/L. The beakers were then placed on a Jar test apparatus, where rapid mixing was conducted at 150 rpm for 2 min, followed by slow mixing at 50 rpm for 25 min. After sedimentation, the left solution was collected for turbidity measurement and COD analysis using the dichromate method.

Effect of pH

Building on the results of the prior experiment to determine the optimal PAC dosage, the pH was varied between 3 and 11. The remaining parameters were held constant in the Jar test model, with rapid stirring at 150 rpm for 2 min, followed by slower agitation at 50 rpm for 25 min. Once sedimentation was complete, the supernatant was extracted for turbidity assessment and COD analysis.

Effect of pectin dosage

Based on the previous experiment, with pH adjustments and PAC coagulant added as per the conditions outlined above, 500 mL of wastewater sample was rapidly stirred at 150 rpm for 2 min. After that, pectin was added at concentrations ranging from 5 to 20 mg/L, followed by slow stirring at 50 rpm for 25 min. Following sedimentation, the supernatant was retrieved for turbidity and COD measurement.

RESULTS AND DISCUSSION

Extraction of pectin from fruit peel waste

As seen in Figure 2, the color of the pectin extracted from the fruit peels under study can be attributed to the inherent characteristics of the raw materials used. For example, the pectin from DF was grey-pinkish, compared to that of GF, which was greyish, while that of OC was light-orange and that of AP was pinkish.

The yield of pectin extracted from each initial fruit waste varied depending on the preparation conditions. It is also noted that if the extraction process is extended beyond the optimal duration, the pectin's molecular structure can become compromised. This degradation can reduce the quality of the pectin and decrease the efficiency of precipitation processes.[29] In this study, the effects of the mixing ratio between citric acid solution and the ground powder of waste peels, along with those of varying pH from 2 to 4, and extraction time from 20 to 80 min at 80 ºC, are discussed.

Effect of solvent mixing ratio

Increasing ratios of raw material to solvent, specifically 1/20, 1/30, 1/40, and 1/50 (wt%/vol%) were examined to identify the optimal mixing for the extraction of pectin from each type of fruit peel. In this test, the pH was fixed at 3 and the extraction time was 40 min, and the results are shown in Figure 3. As may be seen, varying the raw material to solvent ratios yielded different pectin contents. The highest pectin content was obtained from PF (11.4%) and AP (5.2%) at the same raw material to solvent ratio of 1/20. The maximum pectin content from OC was 8.5% when the mixing ratio of citric acid solution to initial material was 1/30. The highest pectin content from GF as 9.8% was observed at a raw material to solvent ratio of 1/40. Meanwhile, pectin yield from DF was 8.1% attained at the mixing ratio of 1/50 of the raw material to solvent.

The extraction of pectin involves several factors that significantly influence the yield. An adequate solvent volume is typically required to ensure effective dissolution. The ratio of solid to liquid is another critical factor in the extraction process. Higher solid-to-liquid ratios can enhance the pectin yield, because they increase the concentration gradient, improving mass transfer from the plant material to the solvent. Previous studies have shown that increasing the ratio from 1/10 to 1/30 g/mL can significantly boost pectin yields.[30] An optimal amount of solvent is crucial for extracting maximum pectin. Insufficient solvent can lead to lower yields because it fails to adequately penetrate the tough cell walls of the plant material. Conversely, using too much solvent can lead to pectin degradation because of low pH levels and high temperatures, especially if the extraction process is prolonged.[31] Moreover, using a large volume of solvent, without achieving a higher yield results in wastage and complicates subsequent steps, such as requiring more energy and effort to filter the extraction solution with an excessive amount of solvent.

Effect of the extraction solution pH

To determine the optimal pH for the pectin extraction process, the extraction solution pH was adjusted to 2, 3 and 4. The optimal parameters for the raw material/solvent ratio determined in the previous experiment for each type of fruit peel were used with an extraction time of 40 min (Fig. 4). Under the same pH condition of 2, the highest pectin yield was obtained from GF (9.8%), PF (11.6%), and AP (6.3%). In the case of OC and DF, a higher pH of 3 resulted in a better amount of pectin as 9.1% and 8.1%, respectively. In low pH environments, the acidic conditions can lead to the disruption of the hydrogen bonds and other interactions between polysaccharide chains in the cell walls and the middle lamella, facilitating the release of pectin. This is due to the increased solubility of pectin when these bonds are weakened.[32] However, if the pH is too low, hydrolysis can occur, not just affecting high molecular weight substances, but also leading to the degradation of the polygalacturonic acid chains that make up pectin. This degradation results in lower recovery efficiency, because the polysaccharide chains are broken down into smaller fragments that are less effective in forming gels.[33] Research emphasizes the importance of optimizing extraction conditions, such as pH, to maximize yield and maintain the functional integrity of pectin. While lower pH may facilitate extraction, there is a critical threshold beyond which pectin recovery diminishes due to structural breakdown.[29]

Effect of extraction time

Experiments were conducted to investigate the optimal extraction time (20, 40, 60, and 80 min) for obtaining pectin from various fruit peels, while maintaining the previously determined optimal raw material/solvent ratio and pH conditions. The results are summarized in Figure 5. This approach allows the determination of the most effective extraction time for each type of fruit peel.

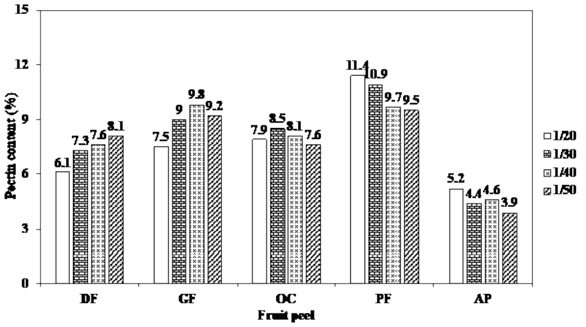


Figure 3: Pectin content (%) extracted from fruit peels at different mixing ratios: 1/20, 1/30, 1/40 and 1/50

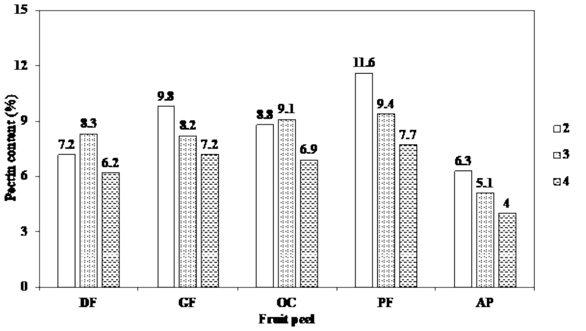


Figure 4: Pectin content (%) from fruit peels at different pH values: 2, 3, and 4

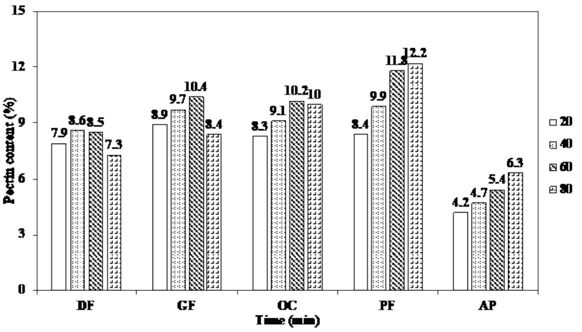


Figure 5: Pectin content (%) when extracted from fruit peels at extraction times of 20 min, 40 min, 60 min, and 80 min

It could be observed that as the extraction time increased from 20 to 80 minutes, the pectin content relatively varied. The optimal extraction time for GF, and OC was found to be 60 min, yielding pectin contents of 10.4% and 10.2%, respectively. The highest pectin yield from DF (9.6%) occurred at an extraction time of 40 min. In contrast, a higher extracting duration was required for PF (12.2%) and AP (6.3%), which was achieved at 80 min.

Each type of fruit peel requires a sufficient amount of time for the solvent to penetrate the material and for pectin to diffuse completely. For example, some studies found that citrus peels exhibit optimal pectin extraction yields at around 60 min, while others suggested varying times for different types of fruits.[34] With shorter thermal treatment times, the cleavage of bonds between the components within the material might not be adequate, resulting in low pectin extraction efficiency because of the weak precipitation of acid galacturonic linkages within the chemical structure of pectin molecules. Conversely, as the thermal treatment time increased, the extraction process became more effective, leading to higher yields.

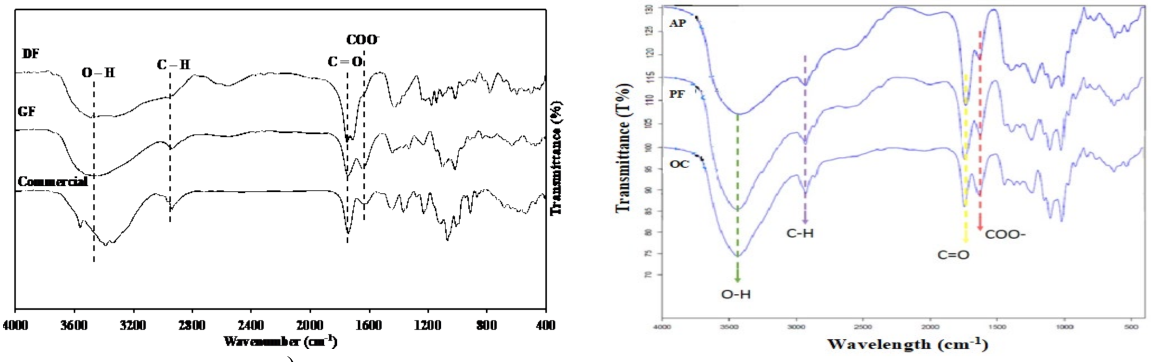
Properties of the prepared pectin

FT-IR spectra

Infrared spectroscopy is instrumental in identifying the characteristic vibrations of bonds or functional groups present within a molecule. Conducting FT-IR spectroscopy on the extracted pectin served the purpose of validating the nature of the pectin produced, compared to that of commercially available pectin. Figure 6 presents the FT-IR analysis results of pectin extracted from various fruit peels, compared to commercial pectin. The absorption bands observed in the range of 3421–3484 cm^{-1} indicated the presence of O–H functional groups. The primary functional groups of pectin were in the region between 2000 and 1000 cm^{-1}. The absorption bands appearing at 1623–1635 cm^{-1} corresponded to the vibrations of free carboxyl groups (COO^{-}). Additionally, the absorption bands at 1736–1749 cm^{-1} were associated with the vibrations of carbonyl ester groups (C=O). The short vibration band in the range of 2928–2948 cm^{-1} signified the C–H bonds present in the pectin structure. These clearly indicated that the pectin extracted from fruit peels in this study showed similarity to commercial pectin, and is in agreement with the results described by A. Kozioł *et al.*[35]

Degree of esterification

Figure 7 illustrates that pectin extracted from different fruit peels exhibited varying degrees of esterification (DE). Based on these results, the higher DE was found in pectin from AP (85.5%), followed by PF (69.4%), and OC (51.8%), which confirmed these fruit peels were high methoxyl pectin (HMP). Meanwhile, pectin extracted from GF (38.6%) and DF (32.8%) peels can be classified as low methoxyl pectin (LMP).



a) b)

Figure 6: FT-IR spectra of commercial pectin, pectin extracted from GF and PF (a), and those of pectin extracted from OC, PF and AP (b)

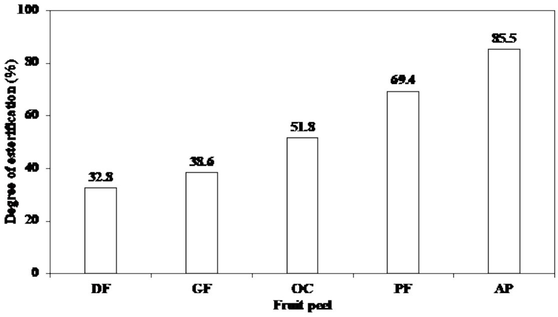


Figure 7: Degree of esterification (%) of pectin extracted from different fruit peels

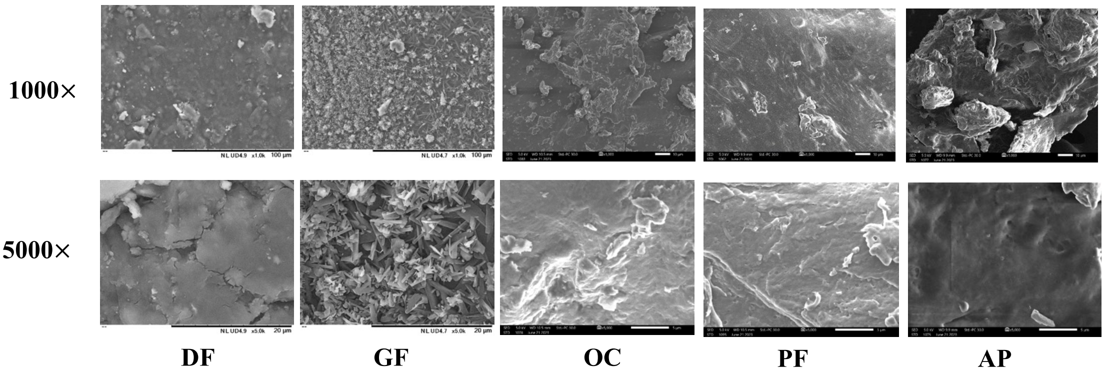


Figure 8: SEM images of pectin extracted from different fruit peels at 1000× and 5000×

The classification of pectin based on its methoxylation is significant, as it influences the gelling properties and the potential applications of pectin in wastewater treatment. Both HMP and LMP could be tailored for specific applications depending on the treatment needs, making pectin a versatile component in water treatment strategies. HMP forms gels primarily through hydrogen bonding, requiring higher concentrations of sugar and lower pH.[36] Therefore, HMP could aid in the aggregation of suspended particles in water due to its gelling properties, which can help in clarifying water by trapping impurities. Moreover, HMP enables the stabilization of emulsions and suspensions, improving the effectiveness of treatments designed to remove contaminants.[37] In contrast, LMP is used as a biopolymer flocculant to form gels in the presence of divalent cations, facilitating the aggregation of particles and aiding in sedimentation.[32,38] This ability of pectin of interacting with diverse contaminants is essential for improving the overall efficacy of wastewater treatment processes.

Morphology

As seen in Figure 8, the surface morphology of pectin extracted from different fruit peels has a heterogeneous formation, exhibiting various morphological structures and pore distributions. At the magnification of 1000×, the pectin extracted from AP showed a relatively rough surface, while the other provided a smoother surface. Observing the pectin extracted from GF at 5000 × magnification revealed more pores, whereas the pectin extracted from other fruit peels has a smoother surface, making it difficult to observe the pores. It has been known that pectin with a rougher surface and more visible pores, as observed in AP and GF, might have a greater surface area for interaction, which could enhance its gelling properties or its ability to bind with other molecules in applications. However, pectin with smoother surfaces and fewer visible pores may be less reactive in interaction. In general, the differences in surface morphology and pore structures in pectin extracted from various fruit peels suggested that not all pectin samples were similar in morphological formation, and these variations could significantly impact their functional performance.

Hydrophilicity

Hydrophilicity is one of the most important parameters of biopolymers intended for water treatment applications. As shown in Figure 9, the pectin extracted from fruit peels possessed a good water absorption capacity, of more than 90%, and reached saturation after a short period of time – of 180 min. In particular, the AP-based pectin gained the highest equilibrium water content (EWC) at 402.1%, followed by those from PF (388.82%), OC (346.8%), GF (309.57%), and DF (255.5%). According to the study by Thakur *et al.*, the higher the DE of pectin, the greater its water absorption capacity and the better its solubility in water.[39]

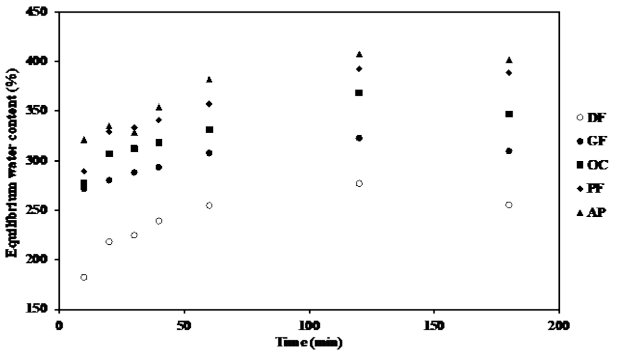


Figure 9: Equilibrium water content (%) of pectin extracted from different fruit peels

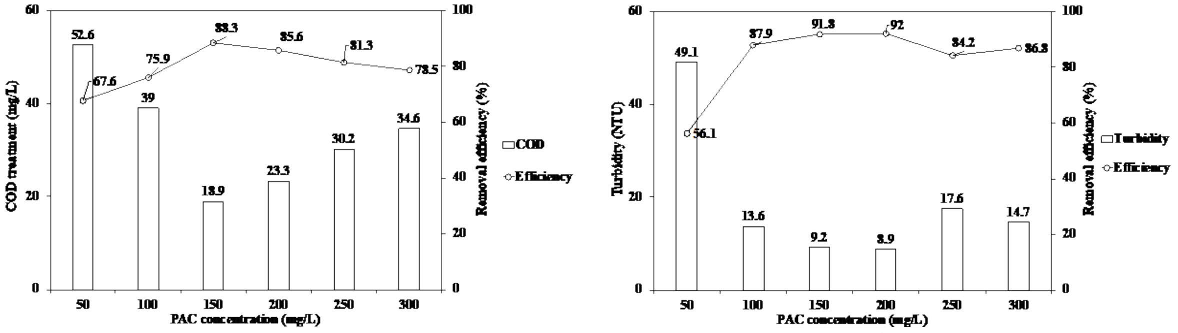
In the case of HMP, the methoxyl groups (–OCH_3) in the pectin molecules have not been replaced by acid groups on the galacturonic acid sugar units, which might create many interaction forces between pectin molecules and form hydrogen bonds with water molecules. This causes pectin to swell and dissolve better in water

Removal of COD and turbidity in water

Effect of PAC dosage

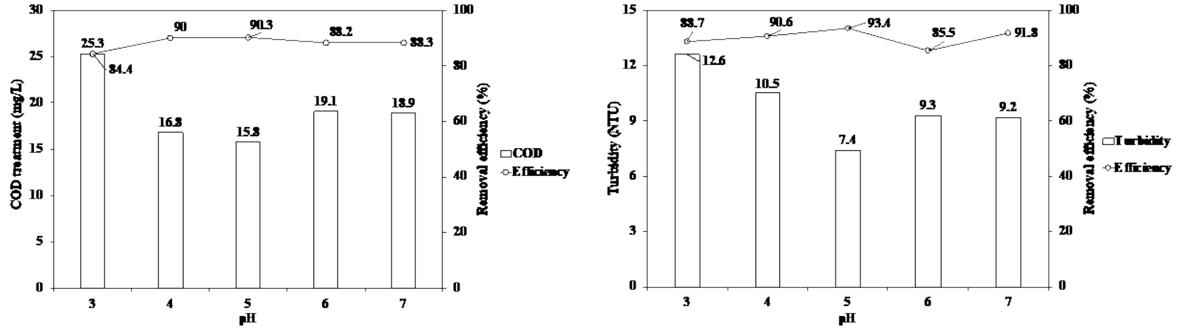
After adjusting the pH of the wastewater to 7 and increasing the PAC dosage to 150 mg/L, the COD removal efficiency reached a maximum of 88.3%, while the turbidity removal efficiency was 91.8%. When the PAC dosage was increased to 200 mg/L, the highest turbidity removal efficiency was not significantly changed as 92.02%. Meanwhile, the COD removal efficiency decreased to 85.6% (Fig. 10). At lower doses, PAC destabilized the colloidal particles by neutralizing their surface charges, allowing them to aggregate and be removed. However, beyond a certain point, excess PAC might reintroduce positive charges, restabilizing the colloids and reducing their ability to coagulate, which diminished COD removal efficiency.[40] Also, higher PAC dosages could result in the formation of excess aluminum hydroxide or other residual PAC compounds in the water. These residuals seemed to contribute to the organic load or interact with the existing organics, preventing effective COD reduction. In addition, an increment in PAC amount caused the competition between PAC particles and the contaminants for available binding sites. Excessive coagulants might also interfere with the adsorption processes necessary for COD removal, reducing the overall efficiency.[41] Based on the results, there was a noticeable difference in the treatment efficiency of COD and turbidity across different dosages of PAC. The dosage of PAC at 200 mg/L yielded the highest turbidity removal efficiency; however, this was not significantly greater than the efficiency observed at

150 mg/L PAC. As this was merely a pre-treatment stage, to reduce costs and minimize the release of coagulant chemicals into the environment, the dosage of 150 mg/L PAC was selected as the optimal condition for subsequent experiments.



a) b)

Figure 10: Effect of PAC dosage on the removal of COD (a) and turbidity (b)



a) b)

Figure 11: Effect of pH solution on the removal of COD (a) and turbidity (b)

Effect of solution pH

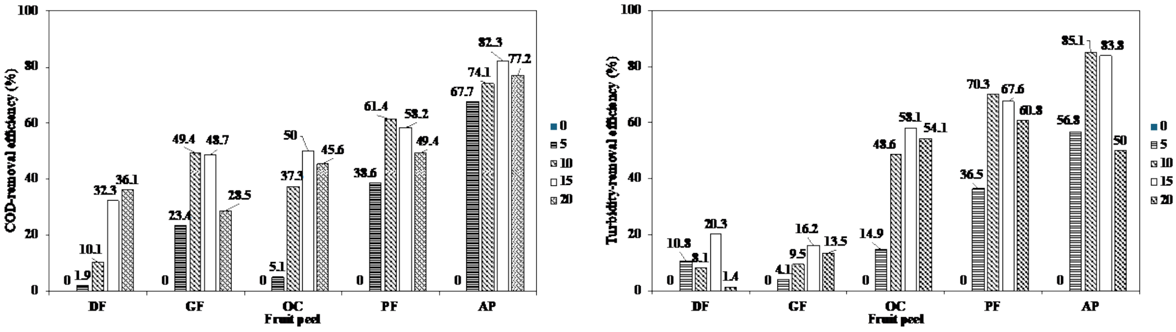
The wastewater sample was tested using an optimal dosage of PAC at 150 mg/L, with the solution pH varying from 3 to 7. The results presented in Figure 11 indicated that, at pH 5, the COD reduced to 15.8 mg/L (90.3%), and the turbidity decreased to 7.4 NTU (93.4%).

However, when the pH was increased to 7, the removal efficiency of COD showed no significant change, remaining at 88.3%. At pH around 5, optimal coagulation occurred due to favorable interactions between the PAC and the contaminants.[1] As the pH increased to 7, while the coagulation process remains effective, it might not significantly enhance the removal of dissolved organic matter, which was primarily responsible for COD. Also, the chemical equilibrium of certain reactions could be shifted, reducing the effectiveness of the coagulant in removing specific types of organic pollutants. The balance between charged particles was able to stabilize at this pH, leading to a plateau in removal efficiency.[42] Additionally, the treatment efficiency for turbidity improved, reaching 91.8% at pH 7. When the pH was increased to 7, the charge of these particles can neutralize from positive charge at pH 5, allowing for better agglomeration and flocculation. This means that particles could stick together more easily, forming larger clumps that can settle be removed from the water more effectively.[43] Many coagulants used in water treatment (like alum or ferric chloride) were more effective at neutralizing the charges on suspended particles at neutral to slightly alkaline pH levels. As pH increased, the solubility of these coagulants decreased, enhancing their ability to remove turbidity.[2,37] Therefore, pH 7 was selected as the optimal condition for the upcoming test.

Effect of the addition of pectin in different amounts

The investigation focused on the effectiveness of combining PAC with pectin extracted from various fruit peels to enhance water treatment processes. It can be seen that different concentrations of pectin indicated improvements in the removal efficiency of COD and turbidity. In Figure 12 (a), the combition between PAC and fruit waste derived pectin was able to enhance the treatment of COD when the added amount of pectin was up to 15 mg/L with the presence of PAC. For example, at the concentration of 5 mg/L, the elimination percentage of COD increased to 1.9% for DF, 5.1% for OC, 23.4% for GF, 38.6% for PF and 67.7% for AP. Notably, these values were gradually improved when a higher amount of the prepared pectin was added at 15 mg/L. Here, the removal efficiency was enhanced to more than 30% for DF, about 50% for GF and OC, 58.2% for PF and 82.3% for AP.

In terms of turbidity reduction (Fig. 12 (b)), when PAC was mixed with 15 mg/L of pectin obtained from OC, PF, and AP, an increase of the removal efficiencies of 58.1, 67.6 and 83.8% was achieved. These findings underscored the potential of using PAC in conjunction with fruit peel derived pectin as an effective strategy for improving water treatment processes through enhanced coagulant performance (Fig. 13).



a) b)

Figure 12: Effect of different dosage of fruit-based pectin on the removal of COD (a) and turbidity (b)

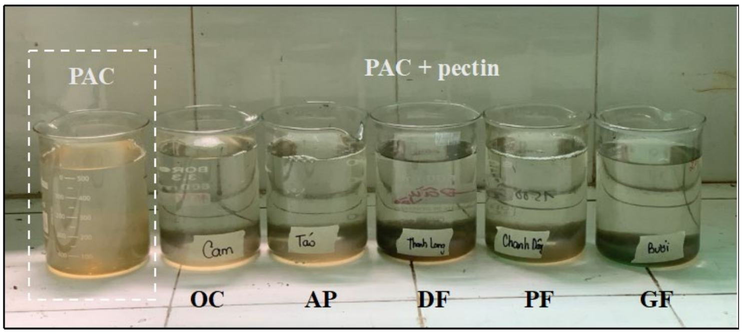


Figure 13: Image of using PAC combined with fruit-peel-based pectin at 15 mg/L

In addition, this study indicated that pectins extracted from fruit peels with higher DE and EWC were more effective than those having lower values in treating COD and turbidity. According to the research findings of Javier Martínez-Sabando *et al.*,[44] it could be explained by the presence of numerous methoxyl groups in the molecular structure of highly esterified pectin, which interacted better with insoluble solids in wastewater through surface adsorption processes due to the formation of temporary bonds or Van der Waals interactions with molecules on the surfaces of organic compounds and insoluble particles. Especially, surface adsorption might increase the size and aggregation capacity of colloidal particles in water, thereby rendering them heavier and facilitating their sedimentation. Furthermore, when pectin dissolved in water, the increased surface area created more adsorption sites, enhancing interactions with organic compounds and insoluble solids in water, thus improving the efficiency of the coagulation process. Moreover, previous experiments and the results from SEM have demonstrated that higher esterification levels of the material correlated with increased EWC. Consequently, pectin extracted from AP exhibited the highest ability in the treatment of COD and turbidity, followed by pectin from PF, OC, and GF. In contrast, pectin extracted from dragon fruit peels, which has the lowest degrees of esterification and EWC showed the least effective results in treating COD and turbidity. Once again, the present study highlighted the imperative to enhance the recycling of waste materials abundant in chemicals and to combine them with diverse compounds to tackle environmental challenges. Such initiatives are essential for advancing sustainable development, reducing emissions, and optimizing the circular economy in the future.

CONCLUSION

Fruit wastes constitute a significant portion of agricultural by-products. Converting these materials into value-added products not only minimizes the environmental impact associated with waste disposal, but also contributes to a circular economy, where materials are reused and recycled. Here, pectin derived from different fruit peels were studied at various conditions and used as a bio-coagulant for the treatment of COD and turbidity in water. The results showed that the yields of pectin depended on specific extracting parameters, and that the degree of esterification and EWC were strongly affected. It also suggested that apple peel-based HMP offered better performance, compared to those of other pectins, when mixing with PAC at a similar concentration in treating COD and turbidity in water. For future studies, the presence of various contaminants, including heavy metal ions and other mineral components, in aqueous environment should be considered.

REFERENCES

[1] M. B. Bahrodin, N. S. Zaidi, N. Hussein, M. Sillanpää, D. D. Prasetyo *et al.*, *Curr. Pollut. Rep.*, **7**, 379 (2021), https://doi.org/10.1007/s40726-021-00191-7

[2] V. Saritha, N. Srinivas and N. V. Srikanth Vuppala, *Appl. Water Sci.*, **7**, 451 (2017), http://doi.org/10.1007/s13201-014-0262-y

[3] J.-Q. Jiang, *Curr. Opin. Chem. Eng.*, **8**, 36 (2015), https://doi.org/10.1016/j.coche.2015.01.008

[4] N. Wei, Z. Zhang, D. Liu, Y. Wu, J. Wang *et al.*, *Chin. J. Chem. Eng.*, **23**, 1041 (2015), https://doi.org/10.1016/j.cjche.2015.02.003

[5] K. P. Shabangu, B. F. Bakare and J. K. Bwapwa, *Water*, **14** (2022), http://doi.org/10.3390/w14162495

[6] S. Sonal and B. K. Mishra, in "Role of Coagulation/Flocculation Technology for the Treatment of Dye Wastewater: Trend and Future Aspects", edited by A. Singh, M. Agrawal and S. B. Agrawal, Springer, Singapore, 2021, pp. 303, https://doi.org/10.1007/978-981-15-8358-2_13

[7] S. J. Joshi and R. M. M. Abed, *Environ. Process.*, **4**, 463 (2017), https://doi.org/10.1007/s40710-017-0224-0

[8] B. S. Nzeyimana and A. D. C. Mary, *Discov. Water.*, **4**, 15 (2024), https://doi.org/10.1007/s43832-024-00069-x

[9] B. Othmani, M. G. Rasteiro and M. Khadhraoui, *Clean Technol. Environ. Policy*, **22**, 1025 (2020), https://doi.org/10.1007/s10098-020-01858-3

[10] A. Benalia, K. Derbal, A. Panico and F. Pirozzi, *Water*, **11** (2019), http://doi.org/10.3390/w11010057

[11] A. Hadadi, A. Imessaoudene, J.-C. Bollinger, A. A. Assadi, A. Amrane *et al.*, *Water*, **14** (2022), http://doi.org/10.3390/w14203324

[12] R. J. Baquerizo-Crespo, Y. Nuñez, J. Albite, J. A. Macías-Alcívar, N. Cedeño-Zambrano *et al.*, in "Biocoagulants as an Alternative for Water Treatment", edited by N. R. Maddela, L. C. García Cruzatty and S. Chakraborty, Springer, Singapore, 2021, pp. 313, http://doi.org/10.1007/978-981-15-8999-7_12

[13] Y. Hadj Mansour, B. Othmani, F. Ben Rebah, W. Mnif, M. Saoudi *et al.*, *Water*, **15** (2023), http://doi.org/10.3390/w15142602

[14] F. Shao, J. Xu, J. Zhang, L. Wei, C. Zhao *et al.*, *Water. Environ. Res.*, **93**, 2261 (2021), https://doi.org/10.1002/wer.1598

[15] H. Salehizadeh, N. Yan and R. Farnood, *Biotechnol. Adv.*, **36**, 92 (2018), https://doi.org/10.1016/j.biotechadv.2017.10.002

[16] F. Blanco-Pérez, H. Steigerwald, S. Schülke, S. Vieths, M. Toda *et al.*, *Curr. Allergy Asthma Rep.*, **21**, 43 (2021), https://doi.org/10.1007/s11882-021-01020-z

[17] M. Güzel and Ö. Akpınar, *Food Bioprod. Process.*, **115**, 126 (2019), https://doi.org/10.1016/j.fbp.2019.03.009

[18] J. A. Rather, N. Akhter, Q. Ayaz, S. A. Mir, A. Singh *et al.*, *Curr. Res. Food Sci.*, **1**, 63 (2023), https://doi.org/10.1007/s43555-023-00007-3

[19] D. L. Gómez-Aguilar, J. P. Rodríguez-Miranda and O. J. Salcedo-Parra, *Molecules*, **27** (2022), http://doi.org/10.3390/molecules27072124

[20] P. Thi Tuyet Mai and N. Thi Sen, *Vietnam J. Sci. Technol. Eng.*, **62**, 32 (2020), http://doi.org/10.31276/VJSTE.62(1).32-37

[21] N. M. 'Aqilah, K. Rovina, W. X. Felicia and J. M. Vonnie, *Molecules*, **28** (2023), http://doi.org/10.3390/molecules28062631

[22] N. P. Nirmal, A. C. Khanashyam, A. S. Mundanat, K. Shah, K. S. Babu *et al.*, *Foods*, **12** (2023), http://doi.org/10.3390/foods12030556

[23] M. C. Otálora, A. Wilches-Torres, C. R. Lara, G. R. Cifuentes and J. A. Gómez Castaño, *Polymers*, **14** (2022), http://doi.org/10.3390/polym14183832

[24] M. Smol, *Energies*, **16** (2023), http://doi.org/10.3390/en16093911

[25] A. Stefanakis in "Nature-Based Solutions for a Circular Water Economy: Examples of New Green Infrastructure", edited by A. Stefanakis, H. V. Oral, C. Calheiros and P. Carvalho, Springer International Publishing, 2024, pp. 35, http://doi.org/10.1007/978-3-031-50725-0_3

[26] M. Râpă, R. N. Darie-Niță and G. Coman, *Waste*, **2**, 258 (2024), http://doi.org/10.3390/waste2030015

[27] S. S. Hosseini, F. Khodaiyan and M. S. Yarmand, *Carbohyd. Polym.*, **140**, 59 (2016), https://doi.org/10.1016/j.carbpol.2015.12.051

[28] The Vietnamese Standard TCVN 6491:1999 (ISO 6060:1989) Water Quality – Determination of Chemical Oxygen Demand (COD), Ministry of Science, Technology, and Environment, Vietnam; 1999. https://thuvienphapluat.vn/TCVN/Tai-nguyen-Moi-truong/TCVN-6491-1999-chat-luong-nuoc-xac-dinh-nhu-cau-oxy-hoa-hoc-902941.aspx, accessed 19/02/2025

[29] V. Chandel, D. Biswas, S. Roy, D. Vaidya, A. Verma *et al.*, *Foods*, **11** (2022), http://doi.org/10.3390/foods11172683

[30] B. L. Chua, S. F. Tang, A. Ali and Y. H. Chow, *SN Appl. Sci.*, **2**, 621 (2020), https://doi.org/10.1007/s42452-020-2415-y

[31] R. Virginia Rodríguez and V. Lucía Isabel Castro in "Pectin - Extraction, Purification, Characterization and Applications", edited by M. Martin, IntechOpen, 2019, Ch. 3, https://doi.org/10.5772/intechopen.85588

[32] R. Surolia and A. Singh in "Pectin—Structure, Specification, Production, Applications and Various Emerging Sources", edited by M. Thakur, Springer, Switzerland, 2024, pp. 267, https://doi.org/10.1007/978-3-031-46046-3_13

[33] M. A. Wan Chik, R. Yusof, M. H. Shafie and R. Mohamed Hanaphi, *J. Food Meas. Charact.*, **18**, 6101 (2024), https://doi.org/10.1007/s11694-024-02632-5

[34] B. Pasandide, F. Khodaiyan, Z. Mousavi and S. S. Hosseini, *Food Sci. Biotechnol.*, **27**, 997 (2018), https://doi.org/10.1007/s10068-018-0365-6

[35] A. Kozioł, K. Środa-Pomianek, A. Górniak, A. Wikiera, K. Cyprych *et al.*, *Coatings*, **12** (2022), http://doi.org/10.3390/coatings12040546

[36] C. L. Loor-Moreira, K. J. Fernández-Andrade, G. S. Cedeño-Solórzano, G. M. Manzaba-Salazar, Y. Gómez-Salcedo *et al.*, in "Generalities of the Coagulation-Flocculation Process: A Perspective on Biocoagulants", edited by N. R. Maddela and L. C. García, Springer International Publishing, 2021, pp. 333, http://doi.org/10.1007/978-3-030-80108-3_16

[37] S. B. Pillai and N. V. Thombre in "Coagulation, Flocculation, and Precipitation in Water and Used Water Purification", edited by J. Lahnsteiner, Springer International Publishing, 2020, pp. 1, https://doi.org/10.1007/978-3-319-66382-1_63-1

[38] J. Duah, F. M. Kpodo, V. Kontogiorgos, F. K. Saalia and J. K. Agbenorhevi, *Food Biophys.*, **19**, 490 (2024), http://doi.org/10.1007/s11483-024-09840-y

[39] B. R. Thakur, R. K. Singh, A. K. Handa and M. A. Rao, *Crit. Rev. Food Sci. Nutr.*, **37**, 47 (1997), https://doi.org/10.1080/10408399709527767

[40] X. Huang, B. Gao, Q. Yue, Y. Wang, Q. Li *et al.*, *J. Chem. Eng.*, **229**, 477 (2013), https://doi.org/10.1016/j.cej.2013.06.029

[41] S. O. Nti, R. Buamah and J. Atebiya, *Water Pract. Technol.*, **16**, 1215 (2021), https://doi.org/10.2166/wpt.2021.069

[42] M. Y. D. Alazaiza, A. Albahnasawi, G. A. M. Ali, M. J. K. Bashir, D. E. Nassani *et al.*, *Water*, **14** (2022), http://doi.org/10.3390/w14020140

[43] F. A. Concha in "Particle Aggregation by Coagulation and Flocculation", edited by A. F. Concha, Springer International Publishing, 2014, pp. 143, https://doi.org/10.1007/978-3-319-02484-4_7

[44] J. Martínez-Sabando, F. Coin, J. H. Melillo, S. Goyanes and S. Cerveny, *Materials*, **16** (2023), http://doi.org/10.3390/ma16062207