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Physicochemical Properties of Gel Beads Synthesized from Agricultural By-Products Pectin

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Pectin from agricultural by-products created gel beads with and without activated carbon through freeze-drying and atmospheric drying. In this study, recovered pectin had an extra high molecular weight of 399,498 – 1881,678 kDa and a low methoxyl content of 3.3 %. Pectin: chitosan: activated carbon ratio = 2:2:1 was chosen to reach hard gel beads and original gel shape after drying. FTIR spectra between PCZn-AD and PCZn-FD, PCAZn-AD, and PCAZn-FD had no difference, proving that the drying method did not affect the surface functional groups of the obtained material. Scanning Electron Microscopy images showed that PCZn-AD and PCZn-FD particles were spherical with rough, scaly surfaces; about PCZn-AD, the surface was wrinkled and grouped while the PCZn-FD surface was rough, with many thin layers and more voids. Pectin is a macromolecular material with a specific surface area of 0.02 - 1.32 m^2/g. The swelling degree of the freeze-drying gel beads was higher than the atmospheric drying gel beads. The stability of the gel beads was clearly demonstrated at pH < 7.

1. Introduction

Pectin has the capability to generate three-dimensional networks of hydrophilic macromolecular chains, rendering it highly suitable for the preparation of hydrogels. In comparison to other natural polymers like protein, carbohydrates, chitosan, and collagen, pectin sets itself apart by its remarkable gelling formation properties, which permit the development of sustainable hydrogels under more moderate circumstances. Furthermore, pectin offers the added advantage of controllable gelation and interactions using its modifiability through adjustments in its degree of methoxylation and acetylation (Moia et al., 2019). Its amphiphilic nature facilitates effective interactions with both water and oil, endowing it with versatility in containing hydrophobic bioactive compounds. Large-scale fruit waste created by the fruit processing industries is the main source of pectin extraction. If not used, this trash ends up in landfills, where it releases greenhouse gases and microbial decomposition that deteriorates the ecosystem.

Chitosan (CTS) is regarded as the most adaptable biopolymer within the polymer classes that can be subjected to ionic crosslinking. The biopolymer's natural attributes—such as its availability, renewability, affordability, and environmental friendliness—are the reason for this preference. Furthermore, the chemical structure of CTS allows for (i) favorable water solubility at slightly acidic pH levels; (ii) excellent film-forming capability as a result of the facile formation of intra- and inter-molecular hydrogen bonds; and (iii) convenient chemical changes attributed to the existence of various specific groups (-OH, $-NH_2$, C-O-C) (Sacco et al., 2016). These characteristics make it easier to create simple processes for gel formation and to change the chemical composition of structures based on CTS.

In this study, to get additional knowledge and broaden the use of pomelo–pectin, pomelo–peel–pectin gelled with CTS, Zinc acetate, and activated carbon. For the first time, gel beads from pomelo–peel–pectin gels were dried in two ways: freeze-drying and atmospheric drying to show the appropriate drying method for the gel

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beads. The study also clarifies the influence of activated carbon on the properties of gel beads. From the properties of gel beads, indicate suitable applications for gel beads.

2. Material and methods

2.1 Materials

Pectin was attained from the treatment of pomelo (*Citrus grandis (L.) Osbeck*) peel from Thu Duc market, Ho Chi Minh City. All the reagents, including acid citric, ethanol, sodium hydroxide, sodium chloride, hydrochloric acid, zinc acetate, phenolphtalein, and activated carbon (AC) were purchased from commercial suppliers and used without further purification.

2.2 Preparation methods

2.2.1. Pectin recovery

The pectin extraction process was referenced according to the research of Nguyen et al. (2021). Pomelo peel powder was grounded and dried with a particle size of less than 1 mm. Extract the powder in citric acid solution at 80 °C for 90 min. After extraction, the pH was adjusted to 2 and the residue was filtered using a fabric filter bag. The filtered solution was centrifuged to remove residue. The centrifuged fluid was precipitated with 96 % alcohol at a ratio of 1:4. Solution was filtered to get Pectin and washed with 70 % alcohol, then dried for 4 h at 60 °C. Dried pectin was crushed and stored in a glass jar with desiccant.

2.2.2. Gelation

The process of creating pectin-chitosan gel was carried out at a weight ratio of pectin: chitosan = 1:1; 1:2; 2:1. The recovered pectin was dissolved into CTS solution at 60 ºC and cross-linked with 12 % zinc acetate solution to obtain gel beads. Then filter and rinse the gel with water and alcohol until neutralized. Dry and obtain Pectin-Chitosan gel beads (PCZn).

Pectin–chitosan–activated carbon gel (PCAZn) was created the same as the forward process, AC was added at the same time adding pectin.

2.3 Characterization methods

2.3.1. Analyzation of the properties of pectin

0.5 g of pectin was extracted into a 250 ml Erlenmeyer flask and then 5 ml ethanol, 1 g NaCl, and 100 ml distilled water were added. 6 drops of phenolphthalein and titrate with 0.1 N NaOH were added until the solution turned pink to obtain an indicator point. Equivalent weight was calculated according to the following Eq(1):

$$Eq.W = \frac{m_{mẫu} \times 1000}{V_{NaOH} \times CN_{NaOH}} \quad (1)$$

25 ml of 0.25 N NaOH was added to the neutralization solution above. The mixture was stirred and kept at 25 °C for 30 min and then 25 ml HCl 0.25 N and titrate with NaOH 0.1 N were added to it. Methoxyl Content was defined by the Eq(2):

$$MC = \frac{V_{NaOH} \times CN_{NaOH} \times 3.1}{m_{mẫu}} \quad (2)$$

According to titration results in Equivalent weight and Methoxyl Content definition, Anhydrouronic acid Content (AUAC) can be calculated by the following Eq(3):

$$AUNC\ (\%) = \frac{176 \times 0.1z \times 100}{w \times 1000} + \frac{176 \times 0.1y \times 100}{w \times 1000} \quad (3)$$

Where 176 is the molecular weight of AUA; z (ml) stands for V_{NaOH} from Equivalent weight definition; y (ml) is V_{NaOH} from Methoxyl Content definition; w is sample weight.

The Esterification Degree (DE) of the sample was identified by Methoxyl Content, Anhydrouronic acid Content, and this Eq(4):

$$DE\ (\%) = \frac{176 \times MC \times 100}{31 \times AUAC} \quad (4)$$

The moisture content of pectin was determined by the humidity measuring scale Sartorius MA160 in Ho Chi Minh City of Technology at 105 °C for 150 s.

Average molecular weight was determined by Gel Permeation Chromatography (GPC) in the Vietnam Academy of Science and Technology. This is an important parameter, directly related to impact resistance, heat, oxygen aging, corrosion resistance, tensile, and bending.

The simple sugar content in the polysaccharide chain was determined by hydrolysis of complex polysaccharides, then analyzed by high performance liquid chromatography (HPLC) using Agilent 1200 Series HPLC System: wavelength 245 nm, column temperature 30 °C, flow rate 1 mL/min, mobile phase composition: 82 % ammonium acetate buffer pH 8.5, 18 % ACN, ammonium acetate buffer pH = 8.5.

2.3.2. Gel properties determination methods

Fourier transform infrared spectroscopy (FT-IR) was operated in the 4,000 - 500 cm^{-1} range using Bruker Fulsor 27 (Germany). Each sample received 16 scans with a spectrum resolution of 2 cm^{-1}. It was employed as a diamond-enhanced attenuated total reflectance (ATR) attachment.

The surface morphology of samples was studied with a scanning electron microscope (SEM) (Jeol JSM– IT200) at an accelerated voltage of 10 kV.

The specific surface area and pore characteristics were determined based on the physical adsorption phenomena of an inert gas, nitrogen for instance, through the Brunauer, Emmett, and Teller (BET) adsorption isotherm theory.

The evaluation of thermal stability used a METTLER TOLEDO 3+ Large furnace (Switzerland). The samples were placed in alumina pans and heated at 10 °C /min, from 30 to 800 °C under a nitrogen atmosphere (50 ml/min).

The swelling degree of the gel was determined according to the proportion between the variation of diameter or mass of gel before and after swelling (in water or alcohol) compared to the initial dry seeds. 0.1 g gel was soaked in 10 ml DI water in 1 h. The gel was scaled and calculated according to the Eq(5):

$$Swelling(\%) = \frac{D-D_0}{D_0} \times 100 \text{ or } Swelling(\%) = \frac{W-W_0}{W_0} \times 100 \quad (5)$$

Where D, W are the diameter and mass of the dry grain; D_0, W_0 are the diameter and mass of the expanded grain.

The stability of a material in different environments is one of the factors that determine the environment for using the material. Gel beads are soaked in solutions with pH 2, 4, 7 and 9 (mix the solution with HCl and NaOH). Gel beads were weighted continuously every hour for 5 h.

3. Results and discussion

3.1 Pectin properties

The conductivity of recovered pectin reached 34.568 % at pH = 2, higher than the other study of Phi Nguyen group (12.4 %) with the same solvent extraction (acid citric). This may be due to the soil conditions of each region or the use of ultrasound easily decomposes the material, while acid extraction increases the solubility of pectin by creating hydrogen bonds between pectin and acid (Methacanon et al., 2014). Acid citric also had the highest average value and it is better than the other acids in terms of both economic and environmental considerations (Aguiar et al., 2019).

In this study, recovered pectin had extra high molecular weight (399,498 – 1881,678 kDa) and low methoxyl content (3.255 % < 45 %), greatly influencing the gel-forming ability of pectin. High molecular weight increases pectin viscosity while low epoxy content helps pectin form gel by ionic interactions between free carboxyl groups in galacturonic acid and divalent or polyvalent ions, resulting in cross-linking with divalent cations like Ca^{2+} and Zn^{2+}.

Anhydrouronic acid Content (AUAC), Esterification Degree, and Equivalent weight of recovered pectin as flow were 54.032 %, 34.202 %, and 495.049 g/mol.

The FTIR spectrum of obtained pectin (as shown in Figure 1a) showed similarities with previous reports of pectin. Vibration at 3,436 cm^{-1} characterized the O-H bond. The C-H stretching vibration of the CH_2 group was shown in the region 2,931 cm^{-1}. Moderate vibration in the 1,748 cm^{-1} region and strong vibration in the 1617 cm^{-1} region were recorded corresponding to the C=O stretching vibration of the ester and the stretching vibration of the methyl esterified carboxyl group COO-R. The glycosidic bonds of pectin can be observed in the spectral range 1,106 – 914 cm^{-1}. The vibration at 1,150 cm^{-1} corresponded to the ring vibration combined with the C-OH bending vibration.

Figure 1b shows the monosaccharide components occurring in the recovered pectin. The highest content monosaccharide was glucuronic acid, 16 µg/mg, showing that the extracted pectin had the RGII region with side chains of glucuronic acid, arabinose, and rhamnose with a high branching ratio.

In addition to the neutral sugars that often appear in the structure of pectin, the analysis also detected a small amount of non-pectin sugars such as glucose (3.76 µg/mg), which can be explained by the hydrolyzing the pectin sample, hemicellulosic and polysaccharide residues remained in the hydrolyzed pectin and produced glucose. Although according to theory, galacturonic acid is the main ingredient in pectin, this method only

detected a small amount of galacturonic acid (3.5 µg/mg). This may be due to the stable bond of galacturonic acid leading to slower hydrolysis than other sugars (Pasarin et al., 2023).

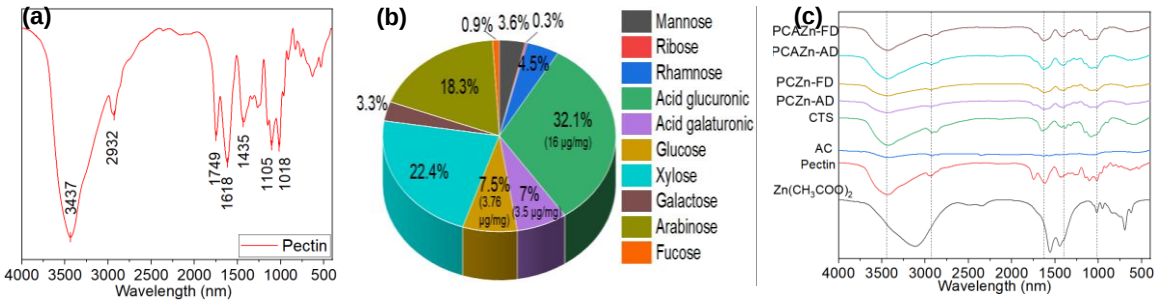

Figure 1: (a) FT-IR spectrum of Pectin, (b) Monosaccharide composition of pectin, (c) FTIR spectrum of materials

3.2 Gel beads characterization

Compared to high methoxyl pectin, low methoxyl and amidated pectin has a different gelation mechanism due to the absence of hydrogen bonding. Instead, intermolecular bonding takes place through the creation of dimers, facilitated by bivalent cations such as Ca^{2+}, Fe^{2+}, and Zn^{2+}, resulting in cross-linking. This cross-linking is achieved through the utilization of two carboxylic groups, which are referred to smilar to the egg-box model. In the case of low methoxyl pectin, gel formation occurs at a greater pH range from 3 to 7. Additionally, it is worth noting that the inclusion of sugar is not a necessary component for gel creation.

In this study, Zn^{2+} was used because it makes a more stable structural network than Ca^{2+}, the particles are more resistant to premature breakdown under acidic conditions in the stomach and are suitable for the application of drug delivery.

Adding CTS to the pectin mixture increased the viscosity of the initial mixture, possibly due to the formation of a complex between the negatively charged pectin chains and the positively charged CTS molecules. The ability of forming PCZn gel beads according to the pectin: CTS ratio was shown in Table 1. From characters of gel beads with other pectin: CTS ratio = 1:1 was chosen as the most suitable ratio to create gel beads.

Table 1: The ability of forming PCZn gel beads

Pectin: CTS ratio	Properties
1:1	Hard gel beads, after drying, the beads retained their original shape
1:2	Hard gel beads, after drying the beads were fragile
2:1	Gel beads were round, soft, and could not retain their original shape after drying

For PCAZn gel beads, with the ratio pectin: CTS: AC = 2:2:1, the obtained gel beads were hard and the original shape is still preserved. Changing the above ratio to 1:1:2, which means the AC content increased, the gel particle structure is unstable, and after drying, the structure can easily collapse, choose the ratio pectin : CTS: AC = 2:2:1. Gel beads were dried in two ways: atmospheric drying (AD) and freeze-drying (FD) to find out a congruous drying method.

FTIR spectrum of Zinc acetate, pectin, AC, CTS, PCZn-AD, PCZn-FD, PCAZn-AD, and PCAZn-FD were shown in Figure 1c. FTIR spectra between PCZn-AD and PCZn-FD, PCAZn-AD, and PCAZn-FD had no difference, proving that the drying method did not affect the surface functional groups of the obtained material. The peak positions of the gel particles had the same position, only different in intensity, due to the appearance of AC. The peak of the gel particles is in the range of 3,500 – 3,000 cm^{-1}, about 1,600 cm^{-1} represented the vibrations of the hydroxyl group O-H, stretching vibrations of -CH and C=O bonds, which were chemical bonds in pectin and CTS. The obtained results are similar to previous publications (Safitri et al., 2021).

Figure 2 shows the surface structure morphology of gel beads through SEM analysis with magnifications of 50 and 250 times. PCZn-AD and PCZn-FD particles were spherical with rough, scaly surfaces. For PCZn-AD, the surface was wrinkled and grouped while the PCZn-FD surface was rough, with many thin layers and more voids. The water in the gel beads evaporated through the drying process, forming voids of different sizes on the gel bed's surface.

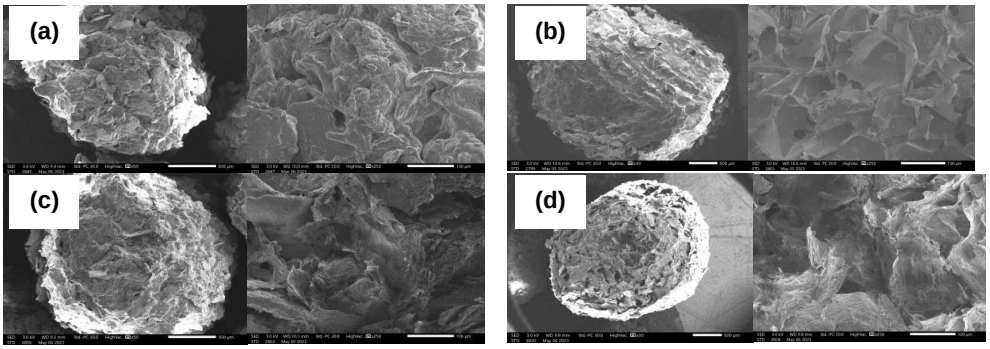

Figure 2: SEM images of (a) PCZn–AD, (b) PCZn-FD, (c) PCAZn–AD, (d) PCAZn–FD

The specific surface area and total pore size of the gel particles are shown in Table 2. The freeze-drying process made the specific surface area and total pore size of the gel particles larger than atmospheric drying. Pectin is a macromolecular material, so during the gel granulation process shrinkage will occur, making the material less porous and the higher the branching ratio of pectin molecules, the lower the gel's durability (Méndez et al., 2023). Differences in specific surface area and pore structure will also affect the solubility, moisture retention, and ability of materials to interact with the environment. Polysaccharide materials with high specific surface area will be ideal for use in making biofilms capable of healing wounds due to good oxygen and nutrient exchange, or in water treatment.

Table 2: Specific surface area and total pore size of gel particles

Sample	Q_m (cm^3/g)	S_{BET} (m^2/g)
PCZn – AD	0.0053	0.0229 + 0.0058
PCZn - FD	0.0363	0.4425 + 0.0044
PCAZn – AD	0.1017	0.4471 + 0.0067
PCAZn – FD	0.3022	1.3155 + 0.0178

The thermal stability of the material was shown through TGA analysis in Figure 3a. The gel particles exhibited three distinct stages of weight loss: water removal, decomposition, further decomposition, and residue oxidation. In the first stage, removing water vapor, PCZn-AD, PCZn-FD, PCAZn-AD, and PCAZn-FD gel particles decreased by 5.75 %, 10.61 %, 7.16 %, and 7.42 % of their initial weight. In the second stage, up to 400 ^oC, the weight loss was 48.33 %, 50.80 %, 34.56 %, and 42.22 % for PCZn–AD, PCZn-FD, PCAZn-AD, PCAZn-FD. The temperature of making gel beads lose their weight by half was higher than that of pectin and CTS materials (196 and 264 °C), proving that the thermal stability of the material particles was higher than that of the original material. The thermal stability of AC was high, so gel samples containing AC had higher thermal stability than gel samples without AC.

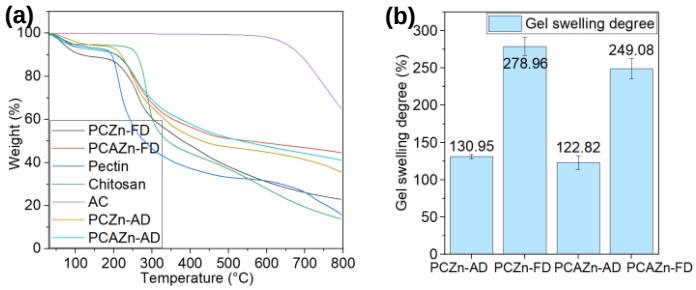

Figure 3: (a) TGA of materials, (b) Gel swelling degree of gel beads

The swelling degree of the gel beads was evaluated and shown in Figure 3b. Due to the hydrophilic nature of pectin, the gel beads had a high degree of swelling. Freeze-dried gel particles have significantly higher water adsorption capacity than atmospheric drying: PCZn-FD, PCZn-AD, PCAZn-FD, and PCAZn-AD gel particles have swelling degrees of 278.96 $\pm$ 12.16, 130.95 $\pm$ 2.77 %, 249.08 $\pm$ 13.67 % and 122.82 $\pm$ 9.18 %. This may be due to the larger pore volume and specific surface area of the freeze-dried gel beads. The high water absorption ability showed that the synthesized material was suitable for hydrogel or water treatment.

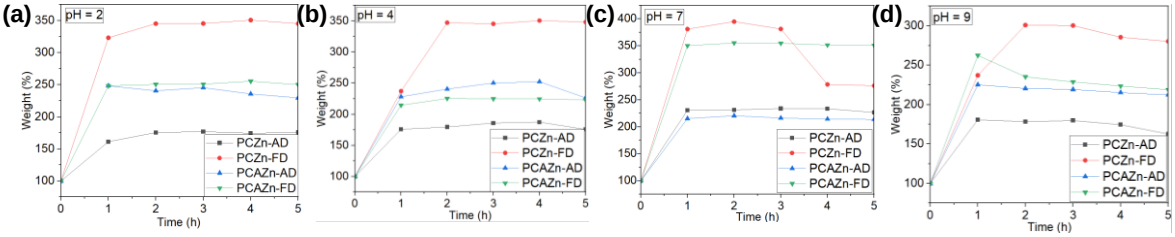

Figure 4: Material stability at (a) pH = 2, (b) pH = 4, (c) pH = 7, (d) pH = 9

The high stability of gel beads is one of the important factors in the application of treating alkaline wastewater (Wang et al., 2019) or as a drug carrier in the stomach with an acidic environment. Investigation of the stability of gel beads at different pH (2, 4, 7, and 9) was shown in Figure 4. In pH 2, 4, and 7 environments, the weight of gel beads decreased significantly after 2 to 6 h. For pH = 9, the weight loss of gel beads after 2 h was significantly higher than in the remaining pH environments. The reason is the exchange between Zn^{2+} in the gel beads and Na^{+} in the test environment: part of the gel was dissolved because Na^{+} moved into the pectin-Zn^{2+} network (Günter and Popeyko, 2016).

4. Conclusion

This study has studied the use of pectin extracted from agricultural by-products to create gel granules through two methods freeze-drying and atmospheric drying. Gel beads had much higher heat stability than the ingredients and gel beads with AC had higher heat stability than gels without AC. Freeze-dried gels had significantly greater swelling than atmosphere-dried gels. Synthetic gel particles were more stable in a pH < 7 environment, suitable for medicinal applications carried into the stomach. The high water absorption ability showed that the synthesized material was suitable for hydrogel or water treatment.

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