Production of Natural Pectin from Locally Available Fruit Waste and Its Applications as Commercially Value-added Product in Pharmaceuticals, Cosmetics and Food Processing Industries

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ABSTRACT
The raise in production of fruit products, such as marmalade, low-caloric foods, juice, frozen foods, jellies and jams, has led to the generation of large volume of fruit wastes as a by-product. These agro-industrial wastes cause serious environmental pollution, and hence, there is an urgent need for their recycling and appropriate utilization via extraction and production of biologically and chemically functional ingredients (i.e. pectin). This review work demonstrates the importance of pectin molecule, its chemical compositions and general biochemical properties, its gelation techniques or mechanisms and its applications as functional and value-added ingredients in pharmaceuticals, cosmetics and food processing industries. Normally, pectin exists in the cell wall of plant cell or fruit cell possessing biopolymer or polysaccharide structures. This by-product has received increasing recognition in modern processing industries and can also be obtained from fruit wastes preponderantly through extraction process. Several factors, such as Degree of esterification, Molecular size, Temperature, Presence of other solutes (i.e. sugar), Charge density on the molecule, and pH values strongly affect the nature of gel formation entire the pectin molecule. Therefore, suitable and effective extraction mechanisms have to be employed to produce this valuable product (i.e. pectin) from locally available fruit wastes.

Keywords: Fruit waste, Degree of Esterification, Gelling agent, Pectin, Pharmaceuticals, Polysaccharide
1. INTRODUCTION

Industrial fruit processing and consumption of the comestible part of fruits, such as orange, pineapple, banana, mango, papaya, lemon, citrus fruit and others, has turned out generation of large quantities of fruit wastes and landfills into the environment, and it has been considered as one of the major sources of environmental pollution. Poor techniques of fruit wastes and landfills management system will cause emissions of particulate matter, methane gas, carbon dioxide and other volatile organic compounds [1] and moreover, combustion or incineration of the fruit wastes will involve releasing of pollutants and other subsequent secondary wastes, such as furans, hydrogen sulfide, dioxins and other acid gases [2], which has become a serious environmental hazards. Careful attention and serious consideration is required for proper utilization of fruit wastes and hence, there is a need to look for alternative methods of resource recycling and production of value-added products from fruit wastes in order to minimize environmental problems and insure cleaner environment. To do so, using the most beneficial techniques, extraction and recovering of valuable bioactive components in the fruit wastes, for instances, pectin and other phenolic compounds, and revealing their significant contributions in pharmaceuticals, cosmetics and food processing industries [3] provides great opportunity for a considerable economic welfares, while insuring the improvement of environmental quality.

Pectin is one of the most valuable bioactive ingredients that can be extracted and obtained from fruit wastes. It normally exists in fruit cell walls and has significant technological and nutritional attributes, principally due to its capability to form gels with acids and sugars in appropriate conditions [4] and it do possess a number of applications (i.e. as gelling and thickening agent) in juice, jam, marmalade, cosmetics, pastes and pharmaceuticals processing industries.

2. SOURCES OF NATURAL PECTIN

Pectin naturally exists in several fruit cell walls and fruit peels, such as papaya peels, grape peels, banana peels, lemon peels, mango peels, sunflower heads, sugar beets, citrus peel and apple pomace and can be obtained by means of extraction. The chemical compositions, structure and amount of pectin will vary, comparatively from one plant to another plant or from one fruit to another fruit, and entirely in different parts of a single plant from time to time [5]. Most plants often comprise pectin in the intercellular layer, the layer exists between the cell wall of adjoining cells of the corresponding plant cell and the maximum concentration of pectin in the subjected plant cell wall has been observed in the middle lamella, with a decrease in concentration gradually from the initial plant cell wall towards the cell membrane. Furthermore, pectin exists in an adequate quantities comparatively in soft plant tissues under circumstances of sufficient or higher moisture contents and rapid growth rate. It appears to play substantial roles in control of the flow of plant fluids and water molecules via the rapidly growing parts of the plant cells [6]. It also makes significant contributions for the structure and firmness of plant tissue as the principal component of the plant cell wall and as the major portion of middle lamella necessitated in an intercellular adhesion system [6], [7]. The strength of the plant cell walls depends upon the link or interconnectedness force, physical
and mechanical attributes and structural orientation between the cellulose fibers and pectic substances [8].

3. STRUCTURE AND CHEMICAL COMPOSITIONS OF PECTIN

3.1. Structure of Pectin

Pectin structure is principally composed of rhamnogalacturonan, which is a heteropolymer of replicating (1,2,α-L-rhamnosyl and α-D-galactosyluronic acid disaccharide units) and D-galacturonic acid, which is a homo-polymer of (1,4,α-D-galactopyranosyluronic acid units with variable degree of methyl esterified carboxyl groups [9]. The Pectin molecule is formed between the pyranose rings of D-galacturonic acid units by L-1,4-glycosidic linkages. Moreover, clarification of pectin structure is vitally important in order to empathize its function in the growth and development of plant tissues, especially in a period of fruit ripening, as a nutritionary fiber and in food processing. Similar to another most polyose, pectins are structurally of type polymolecular and polydisperse, and hence, they are heterogenous regarding to molecular weight and nature of chemical structure. The pectin compositions will vary depending upon the geographical location of selected plant, source (type of plant), methods and conditions of extraction process, environmental factors, such as temperature, pH value, nature and characteristics of soil in the plant site [10]. The pectic substances existing in the principal cell wall of plant comprises comparatively longer side chemical chains than the pectin of middle lamella, and higher proportion of oligosaccharide chemical chains on their corresponding backbones [11]. Pectin obtained from a sugar beet or an apple cell wall by means of extraction at different temperatures and pH values do have various quantities and compositions, such as neutral and acidic sugars, and another important attribute is that its gel forming properties decreases with increasing extraction temperature; whereas its ash content increases with increasing processing temperature [12], [13].

3.2. Chemical compositions of Pectin

Pectin is basically linear polysaccharide and its chemical compositions changes based on the technique or conditions used during isolation from the selected source, extraction or processing methods, purification and storage of the final product [14]. The chemical composition of pectin mainly involves unbranched and long chain of polygalacturonic acid with partly esterified carboxylic group by methyl alcohol. Based on the percentage content of galacturonic acid that has been esterified with methanol, the pectin obtained by extraction process can be classified into two major categories: a high methoxyl pectin, with degree of methoxylation (DM) greater than 50 percent and a low methoxyl pectin, with degree of methoxylation (DM) less than 50 percent [15].

4. GENERAL PROPERTIES AND INTERACTION OF PECTIN

4.1. General properties of pectin

The quality and physicochemical attributes of pectin principally depends upon the considered conditions of production processing and the selected raw materials [16] and an important physicochemical property of pectin is its water solubility. With this regard, a
univalent cation salts of pectic and pectinic acids are often soluble in water, whereas divalent and trivalent cations salts of pectin molecules are insoluble or weakly soluble in water. When dried powder of pectin molecule is added into water molecule, it exhibit an adequate propensity to combine with water, undergoes hydration and provides clumps rapidly. The formation of clumps in the mixture of dry pectin powder and water can be avoided by using pectin with ameliorated dispersibility via particular treatment techniques during production process or by mixing dry powder of pectin in water using stirrer [17]. The concentrated pectin solution would exhibit attributes of the non-Newtonian fluids, whereas partially diluted or dilute pectin solution exhibit attributes of the Newtonian fluids, for example, a number of factors that promote the increase in the strength of gel formation will decrease the solubility and increase viscosity as well as increase the gelling propensity of the pectin solution [18].

The most crucial application of pectin is based on its power of gel formation, for instances a high-methoxyl pectin forms gels with acid and sugar, however, unlike that of low-methoxyl pectin, it does not comprise an adequate acid groups in order to precipitate with calcium ions (Ca$^{2+}$), even though another ions, like Iron, copper or aluminum ions induce precipitation under a certain circumstances. Furthermore, a hydrophobic interaction and hydrogen bonding are important interaction forces in the collection of pectin molecules together [19]. The formation of a colloidal gel is mainly induced due to the presence of hydrogen bonding between adjacent molecules of the hydroxyl groups and between free carboxyl groups on the corresponding pectin molecules. Most of a non-esterified carboxyl groups exist as partly ionized salts in a neutral or sparingly acid distribution of the pectin molecule. Whenever an acid is added to the mixture of pectin molecule, the carboxyl ions are changed over to predominately unionized carboxylic acid groups. The reduction in the quantities of negative charges lowers the attraction force between pectin and water molecules as well as it depresses the repulsions force between pectin molecules. Furthermore, the degree of esterification (DE) affects the rate at which formation of gel takes place. A higher degree of esterification (DE) induces more immediate setting. The immediate-set pectin, for instances pectin with degree of esterification (DE) greater than 72% forms gel at lower soluble solids and higher levels than slow-set pectin (i.e. pectin with degree of esterification between 58-65%) [20].

4. 2. Interaction of Pectin

The gels formed from pectin molecule can be competently explained as an intermediate phase between a liquid and solid state, comprising of a three-dimensional (3D) interconnected system of pectin making the molecules incapable of movement entire the aqueous phase constituent. In a solution of high methoxyl pectin, formation of gel takes place through a non-covalent bonding between juxtaposed polymer chains with both hydrophobic interactions and hydrogen bonding between adjacent chains leading to establishment of colligation zones [21]. Formation of the bond between a neighboring pectin chains happens mainly at these colligation zones, which varies from 18-250 galacturonic-acid units. Hydrogen bonding exclusively inadequate to commence gelation though its occurrence in a higher methoxyl pectin (i.e. pectin with degree of esterification greater than 70%) is approximately twice that of the hydrophobic effects. Hence, an aquaphobic or hydrophobic interaction between two conterminous methyl ester groups, is very much indispensable for formation of gel. A high-methoxyl pectin also forms gels only in an acidic media and when its sugar content (i.e. sucrose) is at minimum fifty five percent [22]. Furthermore, low pH value inhibits a
dissociation of free carboxylic acid groups, minimizing its electrostatic repulsive force [23], while on the contrary the presence of sugar molecules (i.e. sucrose) stabilizes aquaphobic or hydrophobic interactions among the methyl ester (ME) groups [22], [24]. The size of colligation-zone and the magnitude of standard free energy for formation of gel increases proportionally as the square of degree of esterification (DE) increases [22]. On the other hand, low-methoxyl pectin (i.e. pectin with degree of esterification less than or equal to 50%) is capable to form gels via completely separate mechanism from that of a high-methoxyl pectin. Unlike a high-methoxyl pectin, a low-methoxyl pectin can form gels in presence of bivalent cations like calcium ions (Ca$^{2+}$) and it does not necessitate a high level of sugar content (i.e. sucrose) or low pH value in order to commence gelation process. The presence of bivalent cations (i.e. calcium ions - Ca$^{2+}$) gelation process in low-methoxyl pectin becomes a preponderating mechanism and hence, it initiates formation of connections among the sequences of charged species on juxtaposed chains and the potential of low-methoxyl pectin to form gels with minimum amount of sugar requirement enables manufacturing of dietary products, such as jellies, jams and juices [21].

Low-methoxyl pectins can also be produced from high-methoxyl pectins through several treatment techniques, such as enzyme-catalyzed, base-catalyzed or acid catalyzed de-esterification mechanisms. An acid-catalyzed de-esterification mechanism can be carried out during the initial extraction process of pectin molecule from the selected and suitable raw materials (i.e. fruit wastes) [25] though such treatment techniques decrease the molecular weight (MW) of extracted pectin molecule [26]. Moreover, some of sources of pectin, for instances sunflowers are normally very low in degree of esterification (DE), and hence, cautious extraction processes have to be carried out in order to produce a valuable product relatively with high molecular weight (MW) [27]. The activation energy required for formation of a low-methoxyl pectin gel is very much less than the activation energy required for formation of a high-methoxyl pectin gels, adumbrating that shorter segments of the polymer backbone are necessitated in the process of low-methoxyl pectin gel formation [28]. Water solubility of pectin molecule is inherently associated with its corresponding degree of polymerization, molecular distributions and number of methoxyl groups. Even though the pH value of solution, temperature and pectin processing mechanisms strongly influence the nature and interactions of pectin molecule, normally the solubility of pectin molecules increases with decreasing molecular weight and increases in the esterified carboxyl groups [29], [30].

5. FACTORS INFLUENCE THE NATURE AND INTERACTION OF PECTIN

A number of factors, such as pH value, degree of esterification of pectin, temperature and pectin processing mechanisms strongly influence the nature of pectin molecule and its interactions.

5. 1. Effect of pH value

Appropriate pH value of the media is a critical parameter for successful formation of gel or gelation with pectin molecules, peculiarly a high-methoxyl pectin. A Low pH value has led the increase in percentage of non-ionized carboxyl groups, thereby decreasing the electrostatic force of repulsion among the conterminous chains of pectin molecule. Pectin with lower
degree of esterification and slow-set pectin will undergo formation of gel at lower pH values, whereas pectin with higher degree of esterification and rapid-set pectin undergo gelation process comparatively at higher pH values; however, it has been observed that there is an insignificant difference between their corresponding pH values (i.e. the optimum pH value for a rapid-set pectin is approximately 3.4 and for that of slow-set pectin is about 3.1) [31]. A replacement of other sugars instead of sucrose (i.e. by modification of an aquaphobic or hydrophobic interactions among chains of pectin molecule) enables formation of gels at relatively higher pH value [32]. Due to its dependence on the presence of calcium ions (Ca$^{2+}$) bonding effect in gelation process, a low-methoxyl pectin exhibits attributes of gelation at higher pH value than a high-methoxyl pectin. Generally, formation and preparation of gels takes place intimately at neutral pH values [28], [33], providing a number of advantages in pharmaceuticals, cosmetics and food processing industries.

5. 2. Degree of Esterification

Pectin molecule can be formed primarily in an extremely esterified form, carrying out the de-esterification process after it has been put either in middle lamella or cell wall of the plant cell. Degree of esterification (DE) is highly contingent on the source or types of plant species, maturity and tissue of the plant cells. The percentage content of degree of esterification (DE) of pectin in plant tissue is variable within the range of 60 - 90% and moreover, it has been indicated that the dispersion of free carboxyl groups entire the chains of pectin molecule is fairly regular and the free carboxylic groups are predominantly separated from each [34]. Depending upon the magnitude of degree of esterification, pectin can also be categorized as a high methoxyl pectin (i.e. pectin with degree of esterification greater than 70%) and a low methoxyl pectin (i.e. pectin with degree of esterification less than or equal to 50%). The value of degree of esterification for commercial-grade low methoxyl pectin is found to be in the range of 20 - 40%, whereas for that of commercial-grade high-methoxyl pectin is in the range of 60 - 75%. A high methoxyl pectin needs a minimal quantity of soluble solids and a narrow interval of pH value (i.e. approximately 3.0) for production of good quality gels and the resulting product is also thermally reversible. In addition, a high methoxyl pectin is readily soluble in hot water and it also comprise a dispersion or scattering agents, like a dextroglucose or dextrose in order to preclude chunking. On the other hand, a low methoxyl-pectin is not as sensitive to pH value as a high methoxyl-pectin, and it can undergo a gelation process independently under manipulated conditions of calcium ion (Ca$^{2+}$) quantity or other bivalent cations without the requirement of sugar. The strength of ionic bond in such gelation process is highly contingent upon the degree of esterification (DE) and indeed, the quantity of low methoxyl-pectin needed for production of the gel is proportionally decreases with decreasing degree of esterification [35].

5. 3. Effect of Temperature

The supply of significant amount of heat energy in the preservation and processing of pectin comprising foods often requires appropriate temperature control mechanisms [36]. Temperature highly affects the structural, functional and mechanical attributes of pectin gels, for instances, the raise in cooling rate reduces the elasticity of the gel (i.e. reduces the tendency of pectin gel to return to its original shape after it has been processed) and reduction in temperature of pectin gels from 50 °C to 10 °C enhances the loss modulus (i.e. a measure
of viscous response of the gel and energy dissipated as heat) and the storage modulus (i.e. a measure of viscoelastic response of pectin gel and energy stored) [24]. Furthermore, the pace of structural growth and development of pectin gels also raises when pectin molecule is primarily pre-hydrous, concentration of pectin molecule is high and at lower operating temperature [37]. The increase in temperature of the pectin-water solution often causes an immediate reduction in the ratio of radius of rotation to the mean molecular weight (MW) leading to the raise in tightness or compactness of pectin molecule and the flexibility of chain entire the molecule which successively, induces a reduction in an intrinsic viscosity of the solution [38].

6. APPLICATIONS OF PECTIN IN FOOD AND PHARMACEUTICALS PROCESSING INDUSTRIES

In food processing industries, pectin is an indispensable functional ingredients possessing a number of applications, gelling agent, stabilizer, emulsifier, texturizer and thickener during production of several types of foodstuff, like marmalade, jellies, beverages, salads, milk products, juice, soft drinks, ice-creams, and jams [39-41]. An industrial pectin can be extracted and produced through different extraction mechanisms (i.e. by using a multi-stage physicochemical extraction process) along with addition of alcohol and hot dilute mineral acids in the extraction steps, followed by purification and retrieval of final product via precipitation with alcohols [42].

To regulate the purity and quality of extracted pectin as a suitable food element, parameters of the physicochemical extraction mechanisms will be compared with parameters of Food Chemicals Codex (FCC) standard. The Food Chemicals Codex (FCC) is a collection of internationally accepted standards for deciding the quality and purity of the concerned food components and hence, it is a worthful potential resource for demonstrating an incredibly important and various constituents of foodstuff, like nutrients, preservatives, processing mechanisms, colorants and flavorings [43].

Furthermore, in pharmaceuticals processing industries, a hydrogel pectin has been applied as a gelling agent in the process of tablet preparation [44], [45] and it has been used in manipulated-relinquish preparation of matrix tablet [46], [47]. It has been found that high methoxyl-pectins have a number of advantages and possess sufficient potential values in the process of a manipulated-relinquish matrix tablet preparation, drug production and deliverance systems [48].

The presence of pectin in the diet also provides great opportunity to access its medicinal values, for instances, it inherently helps to regulate the level of cholesterin in the blood circulation system. According to previous study, it has been shown that pectin aids to decrease the amount of cholesterin in the blood [49]. The ingestion of pectin, i.e. at minimum 6 gm per day, is very much indispensable due to its substantial influences in the diminution of blood cholesterin [50] and pectin also contributes significant roles as naturally existing protective material and hence, it removes the envenoming toxic substances, harmful cations and other unnecessary materials from the body. Moreover, it has been indicated to be powerful and influential in getting rid of mercury (Hg) and lead (Pb) from respiratory organs (i.e. any organ involved in the process of respiration) and the digestive tract or alimentary canal [51].
7. CONCLUSIONS

Production and extraction of natural pectin from locally available fruit wastes plays substantial roles as valuable and commercially value-added ingredients in modern processing industries, like pharmaceuticals, cosmetics and food processing industries and it also provides great opportunity for sustainable resource (i.e. fruit waste) recycling and utilization, while insuring the improvement of appropriate mechanisms for prevention of environmental pollution. In food processing industries, pectin has a number of applications as a gelling agent, emulsifier and viscosity modifier, texturizer, stabilizer, and in low-calorie food as a sugar (i.e. sucrose) substituent during production of marmalade, juices, jams, jellies and frozen foods, whereas in pharmaceuticals processing industries, pectin has been utilized potentially during drug preparation and formulation of other pharmaceuticals as well as biologically and chemically active agents. The chemical constituents and attributes of gel formation of pectin molecules have allowed this naturally existing biopolymer or polysaccharide structure in plant cell walls to be utilized properly for the desired purposes. Moreover, gel formation is the most significant attribute of pectin molecule that makes it a substantial constituents of pharmaceuticals and food products. By choosing particular type of pectin molecule from specified source, conditions of gel formation (i.e. suitable pH value, degree of esterification, temperature), attributes and dosage rate of different morphology, it is possible to reveal and exploit the potential applications of this valuable product. Regardless of its accessibility and availability in several and various plant cell walls, recently, there is limitation of sources of commercial-grade pectin molecule in the market across the world. Consequently, there is a need to search and looking for alternative sources of commercial-grade pectin or to some extent modification of the existing sources of pectin and its extraction mechanisms in order to receive the pectin molecule with desired characteristics.

References


