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Extrication of Pectin from Waste Peels: A Review.

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ABSTRACT

Pectic substances are a group of closely associated polysaccharides that extensively occur in middle lamella of plant cell wall. They play a major role in pharmaceutical, food, chemical and biomedical industries as a thickener, stabiliser and gelling agent as they are regarded as safe by food and drug administration. Pectin has been recovered and utilised from waste peels of fruits and vegetables in recent years for economic and environmental reasons. This review gives an outline of various sources of pectin, their physico-chemical properties and emerging methods of extraction techniques.

Keywords: Polsaccharides, Pectin, Galacturonic acid, Degree of Esterification, Gelation.

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INTRODUCTION

Pectin is a curdled form of polysaccharide which plays a major role in ripening of fruit, processing of food and act as a potential source for biosorption of heavy metals from waste water [1]. It contributes to about 30% in primary cell wall of plants. It is a part of human's consumption through fruits and vegetables without any addition of nutrition in diet. Peels of fruits like apple, orange, quince, plums and mango waste are some important sources of pectin. Pectins are not only found in vegetables like potatoes or tomatoes but also finds its presence in legumes like peas and grains. However other sources of pectin includes sugar beet pulp, soyhull, pumpkin, peaches etc., Pectin is composed of galacturonic acid, linear chains of linked galacturonic acid called homogalacturonans, substituted galacturonans, rhamno-galacturonans-I which is a combination of galacturonic acid with neutral sugars like galactose, arabinose, xylose and highly branched chains of galacturonic acid called rhamno-galacturonans- II [2-5]. The molecular weight of pectin ranges from 60–130,000 g/mole which depends on the source and their method of extraction. The extraction of pectin is a challenging task as they might be present along with other components in plant tissue or exist as a polymerized derivatives. Various methods like conventional solvent extraction, flash extraction with steam injection, microwave assisted extraction, ultrasound extraction and enzymes extraction are available for extraction of pectin with major factors like pH, temperature, time, solvent to feed ratio influencing the extraction rate. As consumers expect a product with a good shelf life, there is an accelerating demand for ingredients with better and satisfying properties. Thus the structure of pectin has also been modified during their production to improve its function.

Physico-Chemical Properties of Pectin

Elucidation of the fine chemical structure of pectin has been made possible due to the availability of advanced chromatographic and spectroscopic techniques. Pectins belong to the family of complex polysaccharides which contain galacturonic acid [Gal-A] residues. Fig 1 shows the chemical structure of Pectin. If the acid group of the chain is made to react with alcohol, they form esterified pectin as shown in Fig. 2. The ratio of esterified Galacturonic acid to the total Galacturonic acid is called Degree of Esterification[DE]. If the degree of esterification is higher than 50%, they are called high ester pectin and when less than 50%, they are called low ester pectin.They are called pectates when the degree of esterification is less than 5%. Unesterified pectins are the ones which contain free carboxylic acids and form salts with sodium, potassium or calcium. When Galacturonic Acid reacts with ammonia, it forms carboxylic acid amide called amidated pectin. Another widely available form of pectin in plants are Proto pectins and this original water insoluble substance give rise to pectin up on restricted hydrolysis.

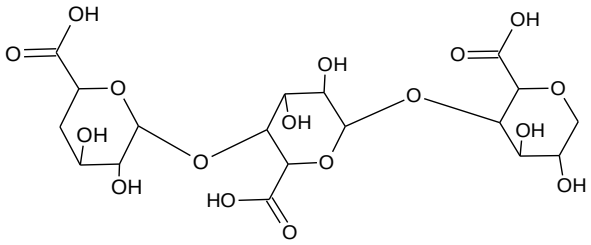

Figure 1: Structure of Pectin

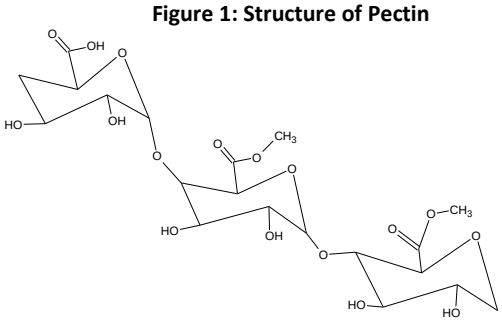

Figure 2: Structure of Esterified Pectin

Estimation of Degree of esterification

The Degree of esterification identified using Fourier transform infrared spectroscopyseems to be promising and it is calculated according to the following equation:

$$DE = 124.7\ R + 2.2013$$
$$R = A1740/\ [A1740 + A1630]$$

A1740 and A1630 are the absorbance intensities for methyl-esterified and nonmethyl-esterified carboxyl groups at 1740 $cm^{-1}$and 1630 cm^{-1}, respectively. These peaks are accounted for vibrations of ester and carboxylic group. The main parameters influencing the degree of esterification are extraction time, temperature and pH. The extraction time and pH did not show a significant effect on the DE of UAE of pectin from grape pomace. Pectin with a relatively high DE [~58%] could be obtained at a low pH and high temperature for short extraction time and also with higher pH and longer extraction time**.** It has been [6] reported that the DE of pectin extracted from banana peels was strongly influenced by temperature and extraction time. On the contrary [7,8] observed that time and pH had a great effect on the DE of pectins obtained from sugar beet pulp and durian rind, respectively.

Estimation of Molecular weight

The molecular weight of pectin is determined by high performance size exclusion chromatography. Average molecular weight of pectin was found to improve for an increase in pH of citric acid used in the case of pectin extracted from grape pomace using ultrasound. On the contrary, a high molecular weight of Pectin with higher contents of neutral sugars arerecovered from citrus peel using citric acid treatment at neutral pH [9].The highest molecular weight was obtained for shorter extraction time at a mild temperature for a increase in pH [10].This result was found to agree well with average molecular weight of pectins extracted from sugar beet pulp using microwave [11] and pectin extracted from banana peels using conventional heating method [12] while contradictory to the pectin extracted from thermally treated olive oil by products [13]**.**

Physical properties

Pectin is an odourless mucilaginous white coloured solid which is soluble in pure water, warmed glycerol, dimethyl sulfoxide and formamide but mostly insoluble in many other organic solvents. The solubility of pectin was found to be dependent on extraction temperature, time and type of solvent used for extraction whereas viscosity of a pectin depends on the molecular weight, DE, concentration, pH, temperature and strength of ions in the solution. Dilute pectin solutions exhibit newtonian behaviour but up on increasing the concentration, it exhibit non-newtonian and pseudoplastic characteristics. Storage of pectin at high heat and humidity lead to softening, smoothing and swelling of surface and finally result in the agglomeration of particles due to the reduction of pores between them [14]. This property inturn depends on the structure, as cation salts of pectins are highly ionised in solution and the presence of this ionic charges along the molecule tend to keep it away from one another by means of coulombic repulsion [15]. As the pH is lowered, ionisation of the carboxylate groups is reduced and as a result the polysaccharide molecules will no longer repel each other and associate to form a gel.It has been suggested [16] that hydrogen bonding and hydrophobic interactions are important forces in the aggregation of pectin molecules. Gel formation is caused by hydrogen bonding between free carboxyl groups of the pectin molecules and also between the hydroxyl groups of neighbouring molecules. If a molecule of pectin is slightly acidified, the carboxyl groups that are not esterified will be present as ionised salts and thereby aquire a negative charge and attract layer of water with the hydroxyl groups. The repulsive forces between these groups, due to their negative charge, can be sufficiently strong to prevent the formation of a pectin network. When acid is added, the carboxyl ions are converted to mostly unionised carboxylic acid groups. This decrease in the number of negative charges not only lowers the attraction between pectin and water molecules, but also lowers the repulsive forces between pectin molecules. When cooled, the unstable dispersing of less hydrated pectin forms a gel, a continuous network of pectin holding the aqueous solution. Thus the rate at which gel formation takes place is also affected by the degree of esterification. HM pectin form gels at an acidic pH in the presence of soluble solids. LM-pectins require the presence of divalent cations [usually calcium] for proper gel formation and are not sensitive to change in pH. Amidation increases or improves the gelling ability of LM-pectin and need less calcium to gel and are less prone to precipitation at high calcium levels. As expected for any polymer, the lower the molecular

weight, the weaker is the gel. Thus, Gel formation results when the polymer chains interact over a portion of their length to form a three-dimensional network. This aggregation of chains occurs through hydrogen bonding, divalent cation cross bridging and/or hydrophobic interactions.

Extraction Techniques

Solid-liquid extraction

The primary step in the preparation of crude extract from plants involves the separation of solute from plant material using a solvent. These are widely used even today because of their availability, applicability and ease of use. The pectin was found to be well extracted in an acidic aqueous medium and the widely used extraction solvents for pectin extraction are water with mineral acids like nitric, hydrochloric or sulphuric acid, phosphoric acid, citric acid [17,18,19]. Pectin was also extracted from banana peels, pomegranate peels, pomace of peento peaches using aqueous acidic solution in a magnetic thermostatic stirrer [20]. Similar results were obtained for the extraction of pectic substances from the rind of yellow passion fruit by making use of ammonium oxalate in addition to the dilute acid solutions[21] Extraction of pectin from apple peel using citric acid resulted in a low grade pectin which is possibly due to enzymatic action on pectin during transportation and the preservation of pectin extract by SO_2.A combination of high temperature, time, and volume of alcohol was found to be desirable for the recovery of pure pectin. But long period of heating in hot water extraction results in rupture of pectin chains and inturn lead to difficulty in separation of target from nontargeted residues. Also, acid treatments may initiate corrosion and pollution whereas the alkaline extraction reduce the chain of galacturonic acid by beta-elimination. Therefore, advanced methods are developed to counteract these effects.

Flash extraction

Flash extraction method involves mixing, heating and maintenance of pectin containing sample in an acidic medium under pressure to a target temperature by steam injection and allowed to flash in a tank to extract pectin. Yield of pectin was found to be lower than that obtained from commercial citrus pectin but comparable with microwave heating under pressure for the acid extraction of pectin from orange albedo by steam injection under pressure [22].

Microwave-assisted extraction

Microwave-assisted extraction [MAE] is an extraction technique that make use of microwave energy to heat the solvent and the sample to enhance the mass transfer rate of the solutes from the plant part to the solvent. MAE is classified in to closed system and open system in which the former refers to system which operates above atmospheric pressure in a sealed-vessel with different mode of microwave radiations and the latter below atmospheric pressure as it is mainly developed to extract thermoliable materials. Recent advancements in microwave extraction such as high pressure microwave-assisted extraction has improved the extraction rate by allowing more penetration of solvent which is accomplished through breakage of cell structure. Appropriate selection of equipment, procedure and parameter is desirable for successful extraction of pectin through microwave technique. Till now, various MAE techniques coupled with other techniques like simple boiling and pre or post treatment with ultrasound has improved the performance in plant extraction [23].It is reported that microwave-assisted extraction from sugar beet pulp and orange peels under different operating conditions could extract pectin in minutes rather than hours as required by conventional heating[24,25]with Sonication time and bath temperature to be the influencing factors of extraction [26].

Ultrasound-assisted extraction

Ultrasound assisted extractionis a less expensive process that uses acoustic energy and solvents to extract specific compounds from various plant matrices in relatively shorter times than with conventional extraction techniques with a higher yield [27,28].The increase in extraction is mainly due to the passage of ultrasound wave to the solvent which results in acoustic cavitations [29]. It also results inincreased penetration of solvent into the tissue and thereby the solute leaches out from the solid phase to the solvent phase [30].High efficiency was observed for the extraction of homogalacturonan from grape pomace by the usage of ultrasound treatment [31]. Similar results were observed for the ultrasound assisted extraction of pectin from

waste pomegranate peels[32] and when ultrasound was used as a pretreatment for the microwave heating, the process was found to yield better results.

Enzyme assisted extraction

Enzymes represent the alternate extraction method for green synthesis of pectin and aims at reducing water pollution and waste as extraction using acids generates large quantity of effluents which require further treatment. Enzymes degrade the pectin by selective depolymerisation or isolate pectin by breakage of cell wall. Pectolytic and cellulolytic enzymes solubilised a high percentage of the pectin material from Bergamot Peel which is a major Byproduct of Essential Oil Extraction [33]. Similarly enzymes like Celluclast, Econase and Viscoferm were also used for isolation of pectin which showed a higher yield and galacturonic acid content. These studies concluded that Enzymes can extract pectins with a higher yield for a smaller molar mass than acid-extracted pectins [34]. Inspite of the fact that extraction of pectin using enzymes require low temperature and reduce corrosion of equipment, their high cost, process difficulties and degradation of pectin in an uncontrolled environment make them less attractive.

Influence of Solvent Ratio, Temperature, Time and pH on Pectin Yield

The extraction efficiency of any process is influenced by important factors like temperature, time, pH and solvent type. The extraction yield was calculated as follows.

Yield of pectin=[Amount of pectin recovered(grams)/Amount of sample taken (grams)]*100

Yield was found to increase with increase in temperature and time by disruption of ester linkages and hydrogen bonds [35-37]. Increase in solvent ratio and pretreatment of sample with tap water was found to improve the yield because of formation of ionic bonds between calcium in tap water and carboxyl groups in Gal-A while pH and pretreatment with protease enzyme was not found to influence due to the narrow range of pH studied and degradation of pectin by the enzyme used in the study [38]. EDTA which was being used to mobilise the pectin as it remained immobilised by its reaction with calcium and magnesium ions in peels is not recommended as it leads to degradation and lower the recovery of pectin. Increase in time period was found to increase the yield in the case of conventional boiling but up on continuous heating it leads to thermal degradation by depolymerisation of galacturonan chain. In case of microwave heating, yield was found to have small increase for increase in time and then decreases as a result of burning of peels. Thus the time period of 15 min is required for microwave heating rather than 3 hours as required by normal boiling for obtaining similar yield. The reason for reduction in time period was due to the improved penetration of solvent in to the tissues as a result of increase in pressure which open up capillary pores by means of breakage of cell structure. Yield of pectin increases with decrease in pH. As the concentration of hydrogen ions increase, the hydrolysis of insoluble protopectin increases and as a result it gets converted to soluble pectin and cellulose. Also, the presence of polyvalent ions like calcium and magnesium increases the insolubility of protopectin but up on acid hydrolysis, conversion to soluble pectin occurs. Good amount of pectin was also found to be recovered in alkaline pH but as it remains unstable it decomposes thereby cannot be precipitated up on addition of alcohol.

Applications of Pectin

Pectin has been successfully utilized for food applications by promoting their gelling ability through acidification or addition of divalent ions like Ba^{2+}> Ca^{2+}> Mg^{2+} [39]. Recently, composite scaffold which showed controlled swelling and degradation has been developed from a mixture of pectin, chitin and nano $CaCO_3$which will be suitable for its application in the fields of tissue engineering and drug delivery [40]. As the presence of antimicrobial agent in packaging system reduce the growth rate of microorganisms, single and composite films of pectin were prepared by making use of natamycin as an active agent which improved the soluble matter in water, water vapor permeability, opacity and decreased the tensile strength[43]. Pectin was also found to stabilize oil-in-water-emulsions by increasing the viscosity of the aqueous phase. The emulsifying behaviour of pectin was found to be dependent on their molecular structure. The Oxidized form of pectin was found to act as a reducing agent for the formation of flower like silver nano particles with nanosilver in the core surrounded by a polymer.

CONCLUSION

Pectins are expected to play a significant role in future. Many studies were performed for the identification of promising technique to extract and recover pectin from waste peels with good qualitative and quantitative characteristics. So further research is needed to develop new methods for the recovery of pectin to overcome the limitations of existing processes. Pectin with advanced functions has to be developed with small modifications so as to fit for its desired use in near future without sacrificing its reputation as natural product.

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