CHAPTER - 1
INTRODUCTION

1.1 Background

India has emerged as the leading producer of fruits including citrus fruits in the world. India alone contributed 24% of the total world production of citrus fruits in the world. The citrus fruit production in India was about 11.14 Million Tonnes in 2013-14 (Indian Horticulture database-2014). Citrus fruits, which include oranges, kinnow, tangerines, lime, lemons, malta, and grapefruit constitute about 18% of total world fruit production. Annual kinnow production in India is about 1.34 Million Tonnes (http://www.business-standard.com/article). Kinnow is being grown widely in the northern part of India, especially in Punjab, Haryana, Rajasthan, Himachal Pradesh. Besides India, kinnow is extensively grown in different parts of Pakistan.

The kinnow (*Citrus reticulata Blanco*) is a mandarin, and it is a hybrid of two citrus cultivars 'King' (*Citrus nobilis*) × 'Willow Leaf' (*Citrus deliciosa*). The fruit is of medium size, moderately to slightly oblate; both base and apex flattened or slightly depressed. The flesh of the fruit is orange, seedy, and has a rich, distinctive flavour (Puri *et al.* 2011).

Mandarins are characterised by easily peeled rind and open core and deeper orange colour than found in most other types of citrus. The schematic cross section of kinnow (Figure 1.1) shows a thin outer cuticle covering a flavedo layer characterised by deep orange colour and containing numerous oil glands filled with aromatic essential oil. Beneath the flavedo, there is the albedo layer composed of light coloured spongy tissue. The albedo layer is high in pectic materials and certain bitter principles like naringin etc.

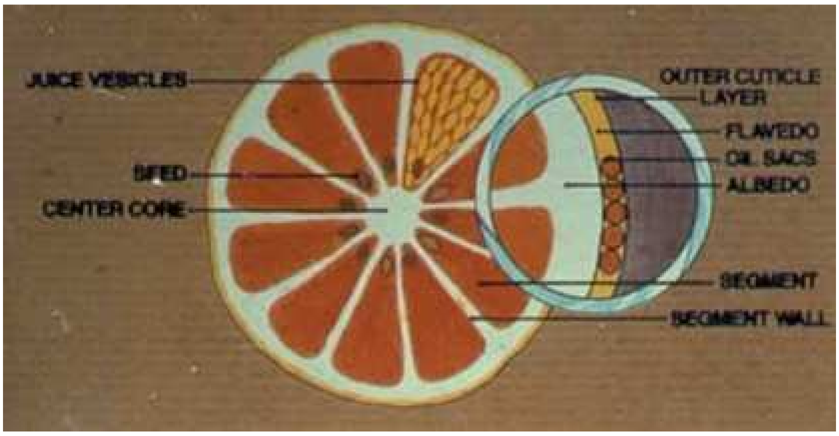

Figure 1.1: Cross section of kinnow

Processing and utilisation of kinnow into various products eventually lead to the generation of waste in the form of peel, pulp and seeds. Kinnow peel and pulp are the byproducts of the kinnow juice processing industry and account for about 55–60% of the fresh fruit weight (Kalra *et al*. 1989). With increasing demand and consumption of kinnow fruit, a large quantity of waste is also increasing. About 10 to 20% kinnow fruits that are dropped in the pre-harvest stage are the waste; and become a problem to farmer as these create a nuisance by rotting and insect rearing ground and thus results in environmental pollution (Bhatlu *et al.* 2016). The photographs of kinnow peels are shown in Figure 1.2.

The peels and the other parts of the fruit are also used as animal feed, but peels of some of the fruits are not consumed by animals. Peels in a small amount are also used as fuel along with dung cake in developing countries like India. The peel from preharvest dropped fruits as well as from seasonally harvested fruits can be utilised for the production of some economically valuable products such as naringin and pectin.

(a) Fresh peels

(b) Dropped peels

(c) Dry peels

Figure 1.2: Kinnow peels

Potential non-juice products of kinnow fruit from kinnow processing waste are same as that of other citrus processing waste. From other citrus fruits, in general, these are candied peel, condiments, peel seasoning, marmalade, baked products, peel fiber, pellets, animal feed, fuel grade alcohol, folded oil, d-limonene, dried pulp, molasses, purees and bases, seed oil, seed meal, limonoids, limonoid glucosides, naringin, peel oil, juice recovery (pulp wash), and pectin (Braddock 1999, Kimball 1991).

On an average, kinnow peel contains 22.45% total solids, 12.50^{o}B TSS, 0.38% acidity, 41.57 mg/100g ascorbic acid, 6.23% total sugars, 5.99% reducing sugars, 0.67% ash, 13.65 mg/100g carotenoids, 7.43 mg/100g β-carotene, 1.85% pectin, 0.77% fat, 0.420 mg/g naringin and 4.69 µg/g limonin (Aggarwal and Sandhu 2003, Premi *et al.* 1994). However, author and other members of the group have observed that naringin content in kinnow peels is 6-8 g/kg of wet peels when extracted with boiling water. The naringin content in dropped fruit peels and immature fruit peels is on the higher side.

The present study aim at the recovery of naringin and pectin from kinnow peels using adsorption-desorption process.

Naringin is a flavonoid found in citrus fruits, have a bitter flavour, and can be detected even at a dilution of 1 part in 10,000 parts water. Its structure is given in Figure 1.3. Its molecular weights, boiling point, melting point and vapour pressure are 580.54, 928.1^{o}C, 166^{o}C, 0 mmHg at 25°C respectively (http://www.lookchem.com/Naringin). It is a valuable compound finds application in pharmaceutics and food industry.

Naringin is used in the manufacture of powder for drinks (citrus soft drinks and tonic), confectionary (bitter chocolate, ice creams, and ices), marmalade and jams, a preservative against bacteria, fungi, and yeast. In pharmaceutics, naringin exhibits antioxidant activity, blood lipid lowering, anticancer activity. It reduces total cholesterol levels, enhances lipid metabolism, protect from carcinogenic matter and protects against toxins in chemotherapy drugs and the environment (Jiang *et al*. 2006)

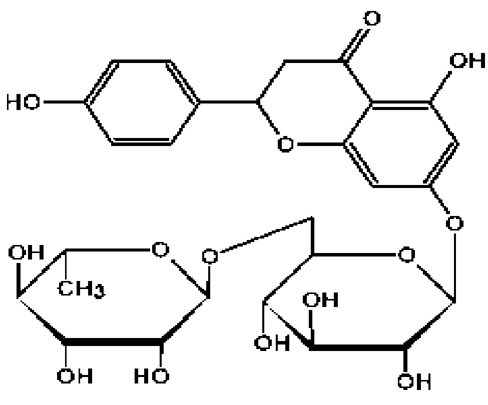

Figure 1.3: Structure of naringin

A pectin is a diverse group of acidic polysaccharides, found in the primary cell wall and the intercellular regions of plants, usually called as “nature’s glue”. Most pectins are composed of D-galacturonic acid unit (a linear galacturonglycan of α-(1-4)-linked D-galactopyranosyl-uronic acid units), which is present in α-(1-4)-linked linear chain in which varying proportions of acid groups are esterified with methanol (May 1990; Seymour and Knox, 2002)

Commercially available pectins contain over 75% of galacturonic acid and methyl esterification in the range of 30 to 80%. The representative structure of pectin is given in Figure 1.4.

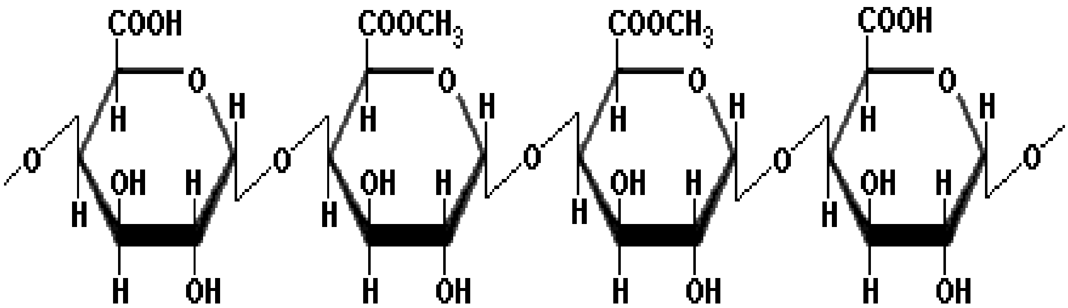

Figure 1.4: Structure of pectin

Pectin finds application in a wide range of cosmetics, food and pharmaceutical products. It is used in the manufacturing of many fruit products like jams, jellies, marmalades, preservatives, glazes, milk gels, desserts, etc. It has an important role in shaping of such products. It also finds use as a thickening agent in sauces, ketchup, flavoured syrups and as a texturing agent in fruit flavoured milk desserts (May 1990, Thakur *et al.* 1997).

Pectins have good emulsification and absorbent properties. It finds use as an antioxidant, anticancer agent, and in the treatment of diabetes mellitus. It also helps to reduce heart diseases and gallstones and decreases cholesterol level in blood. Pectin is an ingredient in many medicinal formulations used in the treatment of wounds, heart burn, constipation and diarrhoea. Pectins act as de toxicant, as regulator and protectant of the gastrointestinal tract, as immune system stimulant and as an anti-ulcer and antinephritic agent. These are also used in tablet formulations as a binding agent; hence pectin is widely used in the fields of pharmacy and cosmetics (McCleary and Prosky, 2001).

In view of commercial applications and uses an efficient method for recovery of naringin and pectin from kinnow peels is required. This technology can be helpful in reducing the waste as well as adding value to waste of citrus fruit and benefit growers and the country as well.

1.2 Aim of study

Value addition to kinnow processing residue, by developing an appropriate technology for recovery of naringin and pectin from it.

1.3 Scope of the work

(1) It was found that from the literature kinnow peels contain appreciable amounts of naringin and pectin.

(2) Kinnow is a seasonal fruit, and fresh fruit would be available during the certain period of the year only (mid-November to mid-March). About 10 to 20% kinnow fruits are dropped in the preharvest stage during early October to mid-November. These fruits are highly bitter and useless and are thrown by farmer on road side. These fruits termed as dropped fruits.

To be able to use the peels later, it is essential that these should be preserved and stored. For that purpose, the peels were dried in a circulatory tray dryer at 60^{o}C and stored for off seasonal experimental purposes.

The experimental studies have been performed with fresh peels, dropped peels and dry peels.

(3) To recover naringin from citrus fruits several techniques have been reported in the literature. In the present study adsorption followed by desorption technique has been used to recover naringin from kinnow peels because it is cheaper than solvent extraction (high solvent cost), supercritical CO_2 extraction (high cost).

(4) Since naringin is soluble in water, by boiling peels with water naringin can be extracted in water. This extract was cooled and termed as kinnow peel boiled water (KPBW). In all experimental studies kinnow peel boiled water was used.

(5) In adsorption, three different types of studies were carried out

(i) Equilibrium studies

(ii) Kinetic studies

(iii) Fixed bed column studies

In desorption also the above three studies were carried out.

Naringin was obtained by Calvarano *et al.* (1996) from bergamot peels with XAD-16 resin by adsorption followed by desorption with ethanol. The X-5 resin was selected from five kinds of macroporous resins for naringin recovery by Jiang *et al.* (2006) because it had higher adsorption and easier desorption of naringin with eluant acetone.

The properties of polystyrene divinylbenzene polymeric resin suitable for naringin adsorption as mentioned by Manlan *et al.* (1990) are high cross-linking >16%, density about 1.2 g/ml for proper submergence of resin beads, large specific surface area > 500 m^2/g of dry adsorbent and low mean pore diameter about 50-60 ^{o}A.

The pore size distributions of indigenous Indion PA-500 and PA-800 adsorbents (resins) were reported excellent by the manufacturer for the removal of the large organic molecules from polar solvents (Product information brochure). Naringin is a large molecule having molecular weight 580 that can be adsorbed from polar solvent like

Kinnow peel boiled water. The properties of the resins suited for our purpose and therefore selected for studies after confirmation with preliminary experiments that the resins adsorb naringin from kinnow peel boiled water (KPBW), and naringin is desorbed from these both with ethanol. These are food grade, polystyrene divinyl benzene, non-ionic, cross-linked resin.

(6) The resins were treated with citric acid. From the literature, it was found that to prevent the protein precipitation in column, the resin should be acidified (Shaw, 1990).

(7) It is also obvious that any process involving the use of polymeric adsorbent resin would be economical only when the adsorbent resin is regenerated and reused. Therefore, the studies were also carried out with regenerated resins with fresh peels.

(8) In all eight systems were encountered; two resins PA 500 and PA 800 with three types of peels (fresh, dropped, and dry) (six systems) and the regenerated resins PA 500 and PA 800 with fresh peels only (two systems).

(9) The outgoing solution from the column studies has been used to recover the pectin.

Focus: The present study is focused on the recovery of naringin followed by pectin.

1.4.Objectives

The main aim of the present study was to recover the naringin followed by pectin from kinnow peels. Naringin was recovered from kinnow peel boiled water (KPBW) by using adsorption-desorption technique and pectin was recovered by acid extraction from KPBW remaining after naringin extraction.

In development of two-step process for recovery of valuable products, naringin and pectin from Kinnow peel, the following were the objectives.

1. To carryout adsorption (equilibrium, kinetics and fixed bed column) studies for naringin from kinnow peel boiled water.

2. To carryout desorption (equilibrium, kinetics and fixed bed column) studies for naringin from resin saturated with it obtained from adsorption column study with kinnow peel boiled water.
3. To carryout adsorption-desorption studies with regenerated resin
4. To propose appropriate governing equation for adsorption/desorption equilibrium and batch kinetics.
5. To recover pectin from kinnow peel boiled water obtained after adsorption column study and to characterize obtained pectin.

1.5 Systems:

To distinguish between different systems, the following classifications were done

System 1	: Fresh peels with resin PA-500
System 2	: Fresh peels with resin PA-800
System 3	: Dropped peels with resin PA-500
System 4	: Dropped peels with resin PA-800
System 5	: Dry peels with resin PA-500
System 6	: Dry peels with resin PA-800
System 7	: Fresh peels with regenerated resin PA-500
System 8	: Fresh peels with regenerated resin PA-800

As mentioned earlier, the focus of the present study was on the extraction of naringin followed by pectin from kinnow peels.

The organization of thesis is described in the preface.