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DEVELOPMENT OF PROCESS TECHNOLOGY FOR RECOVERY OF NARINGIN FROM KINNOW (*CITRUS RETICULATA BLANCO*) PEELS USING INDIGENOUS RESIN

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ABSTRACT

Kinnow peel is a waste of the citrus fruit processing industry and its disposal is becoming a major problem due to cause's environmental pollution. The peel consists of 0.6-1.0 g of naringin per kg of peels on a wet basis, which is used in food and pharmaceutical industries. For the recovery of naringin, kinnow peels were boiled in water to extract naringin in water. This extract was passed through macroporous polymeric adsorbent resin Indion PA 800, naringin was adsorbed on it. The adsorbed naringin was desorbed with ethanol. Ethanol-naringin solution was distilled to the concentrated solution. This was filtered through Whatman filter paper No.42. The filtered solution was passed through membrane syringe followed by evaporation to obtain naringin. The naringin finally obtained had 91-94% purity.

Keywords: Naringin, Indion PA 800, Ethanol, Adsorption, Desorption

I. INTRODUCTION

Kinnow (*Citrus Reticulata Blanco*), a hybrid between "King and Willow leaf" belongs to the citrus family of fruits and is an important fruit of India. Kinnow fruit is grown widely in the northern part of India, especially in Punjab, Haryana, Rajasthan, Himachal Pradesh. Its annual production in India is about 0.5 million tons (MT) [1]. Processing and utilization of kinnow fruit into various value added products eventually leads to the generation of waste in the form of peel, pulp, and seeds and in the process of juice extraction from kinnow 30-40% peel is obtained [2]. Kinnow waste is conventionally used as animal feed. The peel has potential use in the extraction and recovery of naringin and pectin; if a suitable technology is developed. This will not only reduce the waste but also add value to citrus fruit and benefits growers and the country as well. To the best of our knowledge recovery of naringin had been successfully investigated the first time in the present work.

Naringin belongs to a group of chemicals called flavonoids, It is a bitter compound and found in grapefruit, as well as many citrus fruit peels. Naringin is used in food industries as well as in medical applications. It is used in the manufacture of powder drinks (citrus soft drinks and tonic), confectionary (bitter chocolate, ice creams, and ices), marmalade and jams, a preservative against bacteria, fungi, and yeast. It is also used in antioxidative

stabilizer of many diseases like diabetes, herpes, overweight, heart failure, hypercholesterolemia, alcoholism, chronic venous insufficiency, bruising etc [3, 4].

So, In view of its useful pharmaceutical and commercial application, an effective method for recovery of naringin from kinnow peels is required. Several techniques have been used to recover naringin from citrus fruits. Shesadri [5] mentioned a method for solvent extraction of naringin from Kamala orange peels with the help of ether and alcohol. Davis [6] describes a method rapid Soxhlet extraction to recover naringin from grapefruit rind. Yu [7] extracted limonoids and naringin from grapefruit (*Citrus paradisi Macf*.) seeds by a supercritical carbon dioxide (SC-CO_2) extraction technique. Crandall and Kesterson [8], Tripodo [9] extracted the naringin with water from grapefruit albedo, bergamot peel respectively. Kong [10] extracted the naringin using ultrasonic extraction.

The different adsorbents reported to adsorb naringin from citrus juice are Polyamides, Polyvinylpyrrolidone, Nylon polymers, β- cyclodextrin polymers, α- cyclodextrin polymers, Cellulose acetate, Cellulose acetate derivatives like Cellulose acetate butyrate, cellulose triacetate, cellulose ester in gel form, Polystyrene divinyl benzene resins, A mixture of acryl divinyl benzene resins and polystyrene divinyl benzene adsorbent resins [11]. However nonionic polystyrene divinyl benzene cross-linked polymeric adsorbents are being commercially exploited for debittering of citrus juices as mentioned by Shaw [12]. Singh [13] has used INDION NPA-1 for debittering of kinnow juice by adsorptive removal of naringin

Calvarano [14] obtained naringin from bergamot peels with XAD-16 resin by adsorption followed by desorption with ethanol. Jiang [15] selected X-5 resin from five kinds of macroporous resins for naringin recovery, because it had higher adsorption and easier desorption of naringin with eluant acetone. So keeping in the view, after exploratory trails Indion PA-800, a macro porous polymeric adsorbent resin, an indigenous one was chosen for studies, which have the properties to adsorb naringin and the same can easily be desorbed from it. It was cheaper than XAD-16 resin.

II. MATERIALS AND METHODS

Resin PA-800 was obtained from INDION Exchange India Ltd. Naringin was purchased from Sigma Aldrich chemicals. Diethylene glycol, citric acid, hydrogen chloride and ethanol were purchased from Merck specialties Pvt. limited. Sodium hydroxide and potassium metabisulfite were purchased from Qlualigens fine chemicals limited. All the chemicals used were of analytical reagent grade. Distilled water was used for preparing all the solutions. Kinnow peels used in the experiment were collected from the market in Varanasi, India from juice vendors in the month of January of the years 2013, 2014, and 2015.

2.1 Naringin extraction in boiled water from kinnow peel

The peels were combined with four times their weight of water and boiled for 60 min and peel solution is filtered through muslin cloth, and the extract set aside. The residue was mixed with another four parts by weight of water and boiled for another 60 minutes, then filtered through muslin cloth. Repeat the same step for one more time. The three extracts of peel samples were brought to room temperature and combined. After that potassium metabisulfite (KMS) was added to prevent microorganism growth in the peel boiled water, here in after called kinnow peel boiled water (KPBW). The naringin extraction process has been shown in Fig. 1.

2.2 Analytical Procedures

Naringin content in the solutions was analyzed by the Davis test [16]. In this method, the color was developed using 10 ml of 90% diethylene glycol was transferred to a test tube and 0.1 ml of the sample was added to it and after that 0.1 ml of 4N NaOH solution was added, the solution was mixed and allowed to stand for 10 min. The absorbance of the sample was measured on the spectrophotometer at 420 nm, comparing it with distilled water blank. The naringin content was found by comparing the absorbance with the standard calibrated graph of absorbance vs naringin concentration values.

2.3 Experimental Procedures

Before adsorption experiments, the resin was conditioned to remove little organic or inorganic impurities as usual procedure [17]. The conditioned resin was stored in distilled water. The conditioned resin was treated with citric acid of concentration 4g/l to prevent the protein adsorption in a column. For adsorption of naringin on the resin, a glass column with ID 20mm was used; the swollen resin about 150 gm was transferred to the column and the peel boiled water was allowed to pass through the bed of resin at a constant flow rate 2ml/min. The setup used in this study shown in Fig. 2. The kinnow peel boiled water was passed through column till saturation of resin with naringin.

The naringin desorption was carried out in the same setup (figure 3), as used in adsorption column studies; the column was filled with same resin saturated with naringin, obtained from adsorption column study and ethanol was allowed to pass through the column. The ethanol-naringin solution coming out of column was collected for recovery of naringin till the concentration of naringin does not changes; about 1.5 liters of ethanol was passed through the column.

2.4 Distillation of Desorbed Alcohol Solution

The desorbed alcohol solution which was about 1.5 liters was distilled by using simple distillation till volume reduced to 200 ml. After that, the concentrated naringin liquid was filtered using filter paper. The filtrate solution was passed through membrane syringe filter of size 0.45 µm and filtrate were evaporated by heating till disappearance of liquid and thereafter put in an oven at 60^{o}C to recover naringin solid.

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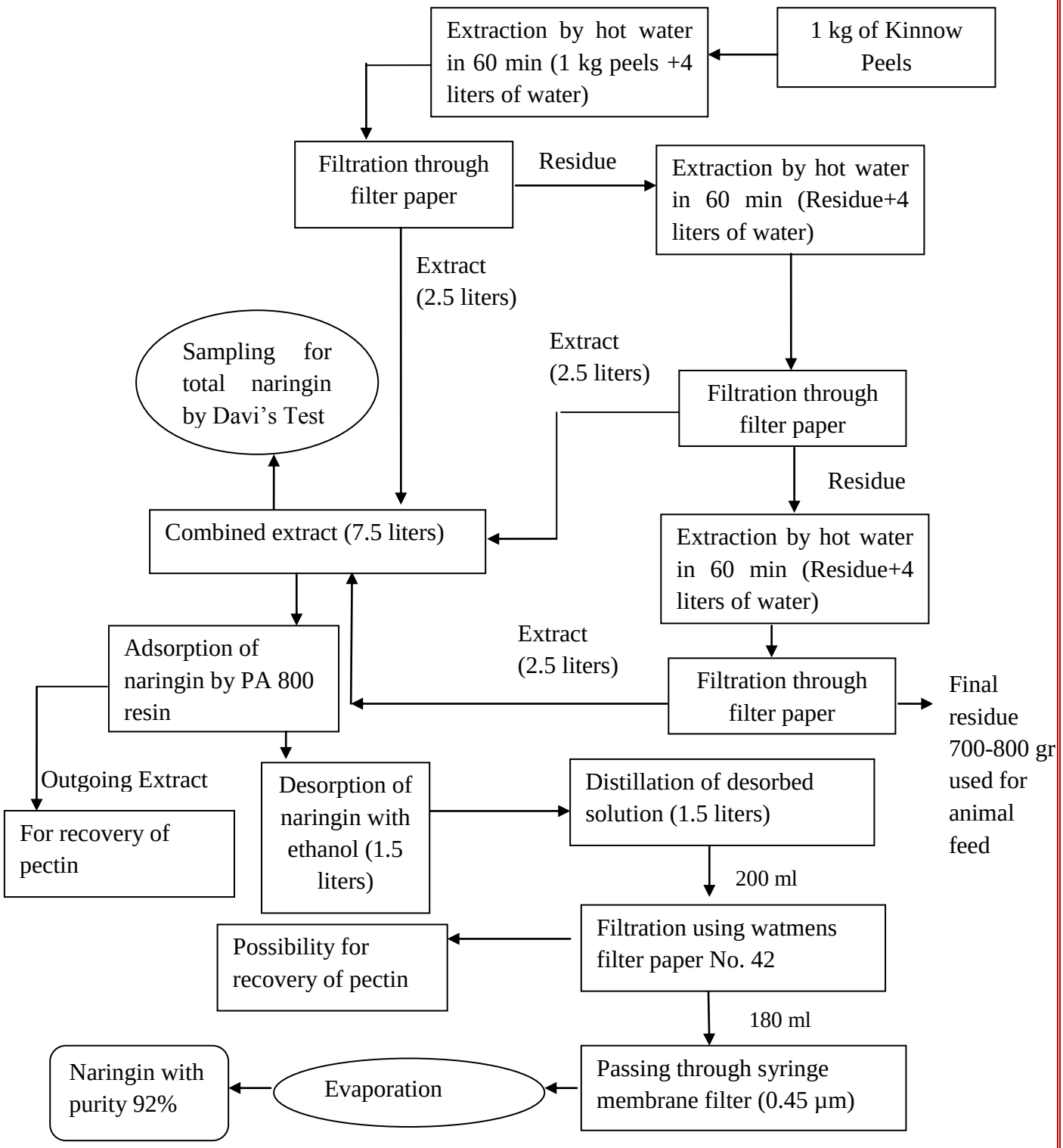

Fig. 1: Naringin Extraction Process flow sheet

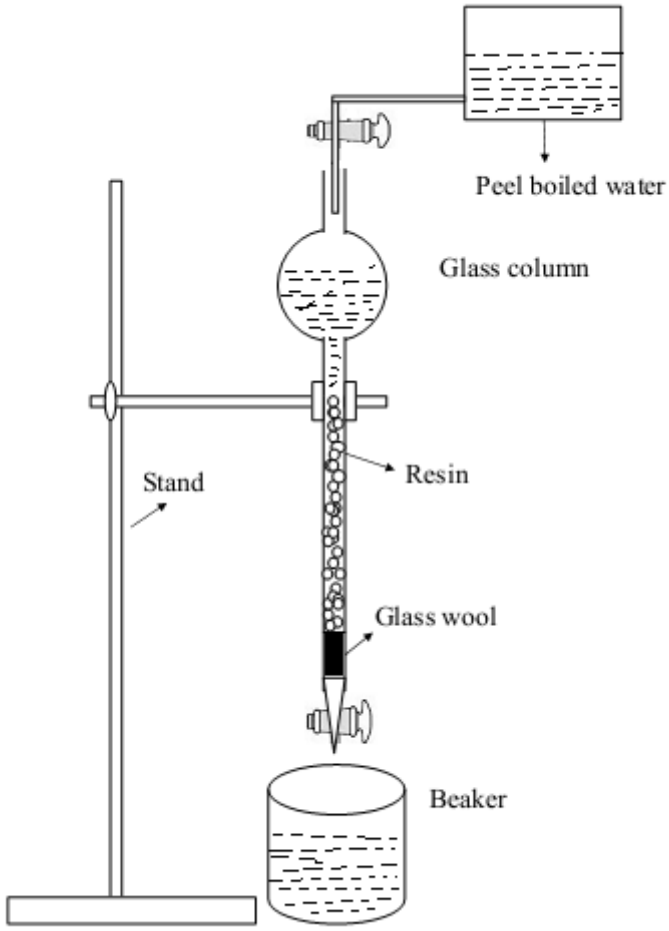

Fig. 2: Set-up for Column Studies

III. RESULTS AND DISCUSSIONS

The naringin content of peels from the three years sample (2013, 2014, and 2015) extracts was determined and were found to be 0.790 kg/m3, 0.740 kg/m3 , and 0.750 kg/m3. Recovery of naringin was calculated by using the formula given below.

$$\text{Recovery of crude naringin} = \frac{\text{wt. of crude naringin} \times \text{purity}}{\text{liters of KPBW passed} \times \text{conc. of naringin in KPBW}}$$

Recovery of naringin was to be 49.4, 48.2, and 48.1% in the years 2013, 2014, 2015 respectively. The recovery and purity are tabulated in Table 1.

TABLE 1: Recovery and purity of naringin obtained from KPBW

S.No	Year	Naringin concentration in KPBW kg/m^3	Raw naringin obtained (g)	Purity (%)	%Recovery
1	2013	0.790	2.2	91.0	49.4
2	2014	0.740	2.0	94.0	48.2
3	2015	0.750	2.1	93.0	48.1

The recovery of naringin was to be 49-48% compared to Kong [10] obtained 82% with ultrasonic extraction, Suetsugu [18] obtained 50 to 60% with SC-CO_2 extraction, Giannuzzo [19] obtained 14.2 % with SC-CO_2 extraction, Sudto [20] obtained 2-3% with water extraction followed by crystallization, Calvarano [14] obtained 73-93% with adsorption followed by desorption. The purity of naringin was to be 91-94%, however, Sudto [20]obtained 98% purity with extraction followed by crystallization, Tang [21] obtained 78% purity from pomelo peels.

Ultrasonic extraction, SC-CO_2 extraction may not be feasible at industrial scale due to high initial investments and operating costs. In water extraction followed by crystallization, the recovery is very less and hence may not be feasible because of the high cost. The present adsorption on Indigenous Resin is cheaper relative to XAD-16 and process may be carried out at small scale level. The naringin obtained in this process having sufficient purity and can be used as feedstock in the preparation of sweetener (when naringin is treated with potassium hydroxide, it becomes a dihydrochalcone that is roughly 300-1800 times sweeter than sugar at threshold concentrations).

IV. CONCLUSION

A new process technology for recovery of naringin from kinnow peels was developed. This method was proven to be of high purity, low cost, simple process, and easy. This process technology reduces the waste and adds value to citrus fruit. Naringin purity is varied from 91-94%. Recovery of naringin was found 49.4, 48.2, and 48.1% in the years 2013, 2014, 2015 respectively.

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