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ORIGINAL ARTICLE

Physico-chemical properties of ultrafiltered kinnow (mandarin) fruit juice

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Abstract Kinnow fruit juice was clarified with ultrafiltration hollow fiber membrane module with cross flow. The surface modified polysulfone based membrane having MWCO 10, 30 and 44 kDa (three cartridges) were used in these studies. The transmembrane pressure drop, cross flow rate and operating condition effects on the quality of the juice have been analyzed. The quality of clarified kinnow fruit juice were evaluated in terms of pH, viscosity, vitamin C, conductivity, total sugar, titratable acidity, TSS, protein, polyphenol, naringin, pectin, pulp content and organoleptic test. The results showed that the membrane with molecular weight cut off 30 kDa was best membrane among the three membranes. The juice could be stored for at least 60 days without any additive.

Keywords Ultrafiltration · Kinnow fruit juice · Pectin and pulp content

Introduction

Citrus fruits contain high amount of valuable and important nutrients like vitamin C, polyphenol, protein etc., which have positive effect on human health. Therefore, the consumption of citrus fruits and the products originating from these fruits is beneficial. The kinnow, a citrus, is a high yielding mandarin hybrid cultivated extensively in the Punjab, Haryana and Rajsthan in India and also main horticulture crop of Pakistani Punjab. A Kinnow fruit has distinct aroma and flavour content therefore, it is relevant as table fruit and for processing. Kinnow mandarin is a hybrid of (*C. nobilis* × *C. deliciosa*). Annual kinnow fruit production in India is about 1.34 Million Tonnes (http://www.business-standard.com/article.IndianHorticulturalDatabase.2014).

The harvest and post harvest losses in kinnow are in the tune of 25–30% (Singh et al. 2016). To reduce these losses, it is desirable to process the fruits. From citrus fruits the major processed product is juice. Kinnow juice turns bitter like some other citrus juices which have bitterness problems such as grapefruit juice; navel orange juice etc. The fresh kinnow juice extracted is non-bitter and its turn bitter within 3–4 h (Premi et al. 1994). Bitterness in kinnow juice is mainly due to limonin (triterpene derivative) and naringin (a flavonoid). Limonoate A-ring lactone found primarily in the membrane tissues of fruit. When these membranes are ruptured during juice extraction, the limonoate A-ring lactone comes into contact with acid environment of the juice, and slowly converted to the bitter limonin.

Kinnow fruit has limited shelf life due to high water content. Kinnow fruits are prone to microbial spoilage, mainly caused by fungi, bacteria, yeast and mould. It is a seasonal fruit and available only from mid December to mid March. To reduce the wastes in glut period, it become essential to process the kinnow fruit in its peak season of production (Jan to Feb). Bitterness in kinnow fruit juice is a major hurdle in its processing. The fruit can be processed to juice, if the juice can be debittered by suitable technology.

Among the various technologies which have been tried to debitter citrus juices, only adsorption of bitter compounds on polystyrene divinilbenzene based non-ionic

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(neutral) food grade resins commercialized (Shaw et al. 2000). In debittering of citrus juice, the juice is centrifuged to separate pulp and the clear centrifuged juice is passed through the column to get debittered clear juice, which is reblended with the separated pulp to get the debittered juice (Shaw 1990). However, the centrifuged juice also had some pulp (< 1%). It was observed that, the pulp clog the fixed bed resin column so it becomes essential to remove pulp completely. The membranes can be used for the clarification of fruit juices (Ilame and Singh 2015).

In general, pulp and suspended solids in citrus juices consist of pectin, carbohydrates complexes with proteins, oil globules and other particle having size in the range of 0.05 to few hundred µm (Kalvons et al. 1994). The major constituents of kinnow fruit juice are total sugars which include sucrose, glucose, fructose, etc. and acids like citric acids and various pectin derivatives are major components of kinnow fruit juices. The typical pectin content in kinnow mandarin juice is 0.97% when extracted with a screw type juice extractor (Lotha and Khurdiya 1994). Citrus fruit juice has higher molecular weight compound, 'pectin' which has in the range 100–200 kDa and consist of 150–1500 galacturonic acid units (Bennett 1987).

Hollow fiber membranes are used for ultrafiltration of citrus juices prior to debittering. It may be noted that before ultrafiltration (UF), juice is centrifuged and microfiltered (Rouseff 1990). Use of ultrafiltration for clarification of grapefruit juice is reported in a flow sheet of debittering the fruit juice (Wethern 1991). Ultrafiltration membrane retain the large species like micro-organism, vitamins whereas salt and sugar molecule flow through the membrane (Cassano and Basile 2013) thus, the chances of microbial loading in the permeate are very low. Since, membrane treatment is carried out at low temperature, the loss of volatile aroma compounds can be neglected and the thermal treatment is also avoided. The clarified citrus juices, which contain no pulp or suspended solids, is debittered using a neutral polystyrene divinylbenzene cross linked resin as mentioned earlier and the separated pulp in centrifugation is then reblended with the debittered clarified juice.

Nutritional and sensory characteristics are better preserved during the clarification by membrane process relative to the other processes used for clarification of fruit juices. Therefore, they are potentially attractive (Rai et al. 2010). If membranes are to be used for clarification method then it is essential requirement that, the juice quality must be conforming the juice standards and also the process should be efficient. The juice quality is influenced by MWCO/membrane pore size. With the increase of pore size, relatively higher molecular weight compounds flow through the membrane which increase in dark color and higher turbidity in permeate stream. The difference in parameters like turbidity, browning of color, total polyphenols, aroma and flavour compound was observed between apple juice and UF treated apple juice (Padilla and McLellan 1989) and it was dependent on MWCO of membrane used. The permeate flux and product quality are the two important parameters in selection of size of membrane for clarification of fruit juice (Rai et al. 2007).

The aim of the present study is to understand the effect of MWCO, cross flow rate (CFR) and transmembrane pressure drop (TMP) on the quality of kinnow fruit juice when ultrafiltered with polysulfone hollow fiber membrane. For analyzing the above effect hollow fiber ultrafiltration cross flow module was used. Three cartridge of surface modified polysulphonic membranes were used with MWCO 10, 30 and 44 kDa. In present work, the effects of CFR and TMP drop on permeate juice quality were studied. The permeate juice parameters like pH, viscosity, vitamin C, conductivity, total sugar, titratable acidity, TSS, protein, polyphenol, naringin, pectin and pulp content were determined.

Materials and methods

Preparation of kinnow fruit juice for ultrafiltration

Fresh, mature kinnow fruits were purchased from local market, Varanasi, (Uttar Pradesh) India. Kinnow fruits were washed, peeled and then the juice was extracted with screw type juice extractor. The kinnow fruit juice was centrifuged at 1000 rpm for 20 min using a Remi Moto centrifuge, made by M/s. Elektro technik Ltd, Kolkata, India. After that, the centrifuged clear juice was collected. The centrifuged cleared juice was used for primary clarification through hollow fiber polyacrylonitrile (PAN) microfiltration membrane. The cleared portion of centrifuged kinnow fruit juice was microfiltered at TMP 69 kPa with CFR 20 l/h for higher amount of cleared juice. The permeate of the microfiltrated kinnow fruit juice was used as a raw feed for ultrafiltration experiments. Small portion of the microfiltered juice sample was used for the characterization of measurable juice (quality) parameters. The measurable quality parameters used for characterization of juice are pH, viscosity, vitamin C, conductivity, total sugar, titratable acidity, TSS, protein contents, polyphenol, naringin, pectin and pulp content.

Ultrafiltration studies

Membrane and hollow fiber module

Three cartridge of polymeric ultrafiltration hollow fiber membrane made of polysulfone (PSU) as the base polymer with surface modification, with MWCO 10, 30 and 44 kDa were used. The hollow fibers were hydrophilic. The average pore size was 22, 42 and 55 Å for 10, 30 and 44 kDa membrane. The effective area of the membrane was 0.028 m^2. The permeability of the membrane was 5.8×10^{-11}, 5.6×10^{-10} and 7×10^{-10} m/pa s, for 10, 30 and 44 kDa membranes respectively. These membrane and set up were purchased from Technoequips Ltd, IIT Khragpur, West Bengal, India.

UF apparatus

The sketch of set up used for the microfiltration and ultrafiltration is shown in Fig. 1.

Procedure

For each ultrafiltration experiment 700 ml of microfiltered Kinnow juice was used. To find the effect of operating conditions on the characteristics of clarified kinnow juice, three transmembrane pressure drops 35, 52 and 69 kPa and cross flow rates 10, 15, and 20 l/h were applied. With all three membranes, total 9 experiments were performed. The samples of permeate were collected at steady state (usually reach in 50 min). All UF experiments were carried out at 25 ± 2 °C. The valve B and F as shown in figure were used for adjusting and maintaining the TMP drop and CFR independently. A small portion of permeate was used for determination of measurable quality parameters.

Analysis

The viscosity of kinnow fruit juice was measured with a falling ball viscometer made by M/s, Pisco, Kolkata, India, at temperature 26 ± 1 °C. Conductivity and pH values of juice were measured using a multi parameter pocket tester made of Iso-Tech System, Sigra, Varanasi, India. The total phenolic content was determined by the Folin–Ciocalteu's phenol reagent using spectrophotometer made of Elico, model no. SL 210 (Vasco et al. 2008) and it was expressed in mg Gallic acid equivalent per 100 ml of fruit juice (mg GAE/100 ml). Protein concentration was determined with spectrophotometer using Lowry method (Lowry et al. 1951) at 660 nm with bovine serum albumin (BSA) as standard. The total sugar content (%) was determined using Lane and Eynon method (Rangana 1986). Vitamin C content was determined with the help of 2,6-dichlorophenol-indophenol visual titration method (Rangana 1986). Naringin content was measured by Davis test at 420 nm (Kimball 2012). Pectin content was measured at 525 nm with the help of colorimetric method (Rangana 1986) and the results were expressed as anhydrogalacturonic acid (AuA). Titratable acidity is determined with N/10 NaOH using phenolphthalein indicator solution (AOAC 1980). The pulp was determined with the help of lab centrifuge (Kimball 2012). All the chemicals were analytical grade. The clarity of the juice was measured at 660 nm using spectrophotometer made of Elico, model no. SL 210.The color of juice was measured by using ColorFlexEZ (Hunter lab, Ratson, USA) with CIE (Commission Internationale De L'Eclarage) lab color scale. The hunter color values L*, a*, b* were determined. The Chroma and Hue angle were calculated by the formulas, $C^* = (a^{*2} + b^{*2})^{1/2}$ and $H^* = \tan^{-1}(b^*/a^*)$ respectively.

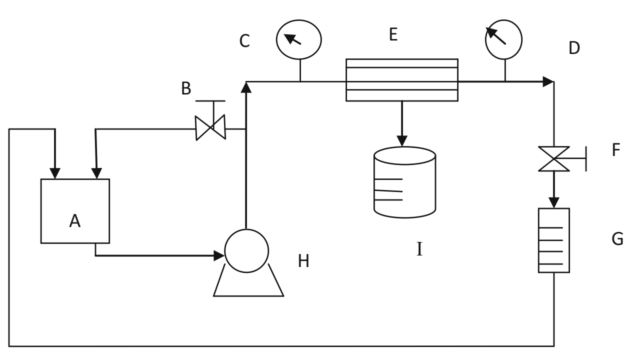

Fig. 1 Schematic diagram of ultrafiltration unit with recycle mode. A Feed tank, B bypass valve, C upstream pressure gauge (0–60 psi), D downstream pressure gauge (0–60 psi), E hollow fiber module, F needle valve, G rotameter (0–50 LPH), H Booster pump, I permeate collector

Organoleptic sensory evaluation of juice

The organoleptic and sensory analysis were done by test panellist on 9 point hedonic scale (Rangana 1986).The sensory analysis was also carried out during storage at different time intervals. The samples were chosen randomly in triplicate, which were stored at 4 °C for 60 days in a refrigerator. The organoleptic test was done for the parameters color, taste, flavour, bitterness score and overall acceptability.

Statistical analysis

The values were determined in 3 replicates. The data were analyzed by ANOVA using IBM SPSS statistical software package version 20, critical difference value was used to find the significant difference at 5% level.

Results and discussion

Physico-chemical properties of clarified kinnow juice by UF

The values of permeate flux through 10, 30 and 44 kDa membrane at the 35 kPa pressure and 10 l/h flow rate were

8.11, 54 and 43 l/m^2 h. The 10 and 44 kDa membrane offers higher resistance against the solvent flux which result into lower flux. For 30 kDa membrane, pore blocking is less than 10 and 44 kDa membranes. The value of flux for 30 kDa membrane was highest as compared to 10 and 44 kDa membranes. Thus, the 30 kDa MWCO hollow fiber membrane was observed to be the best for the UF operation of microfiltered kinnow fruit juice based on flux.

The physico-chemical properties of ultrafiltered kinnow juice which was passed through the 30 kDa membrane with various operating condition viz, TMP drop and CFR at steady state flux are given in Table 1.

The pH of ultrafiltered juice was in the ranged 5.21–5.35. The variation was due to the ambient temperature variation which affects the dissociation of acids. Viscosity of micro-filtered juice was 1.09 mPa s. The viscosity of ultrafiltered juice was found in the range 1.01–1.05 mPa s. The least viscosity was found with TMP 69 kPa, the reason seems that at higher TMP, the pectic substances were retained on the surface of membrane and lower molecular weight compounds flow in permeate side, which tend to decreased the viscosity. For the ultrafiltration of enzymatically treated banana juice with Polysulfone membrane of MWCO 27 kDa similar trends were observed (Sagu et al. 2014). The viscosity of ultrafiltered mosambi juice obtained by passing depectinised mosambi juice through the polyamide membrane was 1.03 mPa s, when the feed was subjected to enzyme plus centrifuged treatment i.e. 1.09 mPa s and initially it was 3.67 mPa s (Rai et al. 2007).

It was noticed that, the content of vitamin C decrease during ultrafiltration of kinnow fruit juice. It was 47.21 mg AA/100 ml in fresh juice which reduced to 31.02 mg AA/100 ml in microfiltration (MF). However, in UF it further reduced and ranged from 13.5 to 26.4 mg AA/100 ml. The juice collected at low TMP and lower CFR have higher amount of vitamin C content. Vitamin C content decreased with increasing transmembrane pressure drop and cross flow rate. The vitamin C was lost probably by oxidation, because the juice was continuously recycled around the UF module. Ascorbic acid is sensitive to light exposure and ascorbate oxidase which promote the transformation of L-ascorbic acid to dehydroascorbic acid (Casaano et al. 2011). Similar results were observed in ultrafiltration of blood orange juice (Galaverna et al. 2008).

Conductivity of fresh juice and MF juice were 3.10 and 4.13 μS/cm, whereas for UF juices, it was 4.41–9.92 μS/cm. The increase in conductivity is attributed to the fact that due to reduced viscosity of permeates the mobility of ions increases.

The total sugar (TS) in fresh juice was 7.75%. For juices obtained in different operations of UF it was in the range 7.64–7.71% whereas, the microfiltered juice having 7.73% total sugar. Only a little change was observed in total sugar. This is due to the fact that sugars are very small molecules relatively to membrane pore size. Acidity of fresh juice was 0.78%, and it ranged from 0.82 to 0.99% acid during ultrafiltration. There was a slight increase in acidity in UF Juice in our case, which may be attributed to the removal of pulp and suspended matter, which contribute to the volume of juice; whereas the total acids (dissolved in juice) remains the same. In mosambi juice and Clementine mandarin juice there was no change in acidity during UF treatment (Rai et al. 2005; Cassano et al. 2009). In both cases, depectinised fruit juice has been used for ultrafiltration. In depectinisation, pulp might have removed hence they observed no changes in acidity.

The total soluble solid in fresh juice is 11.6 °Bx, after microfiltration it was 10.3 °Bx when these microfiltered juice was passed through the UF membrane at TMP 69 kPa and CFR of 10, 15 and 20 l/h, the °Bx of juice were 10.1, 10.1 and 10.0. There was almost no change in °Bx as the Brix meter having count 0.1 °Bx. The TSS content of permeate decreased slightly with UF. Decrease in TSS was probably due to the removal of suspended solid (Scott et al. 1960). The amount of TSS are higher in retentate stream than the permeate stream. The higher TSS in permeate is perhaps attributed to the presence of higher suspended solid. These results are corroborated from the observation of clarified blood orange juice with different UF membranes (Toker et al. 2014). The similar trend was observed with the two other TMP 35 and 52 kPa.

The initial content of protein in fresh juice was 3.74 mg/l and it reduced to 2.18 mg/l in MF. The protein content in UF clarified kinnow juice was about 1.194–1.764 mg/l for 30 kDa membrane. Protein reduction can be attributed to solute-membrane interactions i.e. protein adsorption on the surface or inside pores of the membrane (Cassano et al. 2010). The polyphenol content in feed was about 857.2 mg GAE/100 ml and in MF it was about 843.2 mg GAE/100 ml. In ultrafiltered juice, it ranged from 591.7 to 808.1 mg GAE/100 ml. The polyphenols reduced by ultrafiltration and reduction ranged between 4.2% at TMP 35 kPa and CFR 20 l/h to 29.8% at TMP 52 kPa and CFR 10 l/h. Amongst the three TMP, minimum content of polyphenols was at 52 kPa whereas maximum was at 35 kPa at all the three CFR i.e. 10, 15 and 20 l/h. However, no particular trend could be ascertained for the effect of TMP on polyphenol content in UF juice. At constant TMP, polyphenol content in UF juice increased with increasing of CFR when TMP was 35 and 52 kPa. At higher TMP 69 kPa an opposite trend was observed. Thus, no systematic variation of polyphenols content with CFR was observed. In kinnow juice, some phenols are associated with pulp and other suspended particles which were

Table 1 Physico-chemical characteristics of clarified kinnow fruit juice by UF (30 kDa)

S.no.	Operating conditions		pH	Viscosity	Conductivity	Vitamin C	Total sugar	TSS	Acidity	Polyphenols	Protein
	TMP (kPa)	CFR (l/h)		(mPa s)	(µS/cm)	(mg AA/100 ml)	(%)	(°Bx)	(% acid)	(mg GAE/100 ml)	(mg/l)
1	35	10	5.35 ± 1.73	1.05 ± 0.01	4.41 ± 0.03	26.4 ± 0.04	7.71 ± 0.03	10.2 ± 0.04	0.82 ± 0.02	697.2 ± 0.01	1.194 ± 1.15
2		15	5.35 ± 0.1	1.04 ± 0.02	4.82 ± 0.04	23.9 ± 0.03	7.70 ± 0.02	10.1 ± 0.02	0.88 ± 0.01	774.6 ± 0.03	1.187 ± 4.04
3		20	5.36 ± 0.20	1.04 ± 0.03	4.97 ± 0.03	21.8 ± 0.01	7.68 ± 0.01	10.0 ± 0.01	0.93 ± 0.01	808.1 ± 0.01	1.181 ± 2.08
	R_o^a (%)									11.3	68.6
4		10	5.28 ± 0.15	1.03 ± 0.03	5.12 ± 0.03	18.7 ± 0.04	7.68 ± 0.02	10.0 ± 0.01	0.95 ± 0.01	591.7 ± 0.02	1.996 ± 4.5
5	52	15	5.29 ± 0.1	1.03 ± 0.04	6.19 ± 0.02	16.8 ± 0.02	7.67 ± 0.01	10.0 ± 0.02	0.96 ± 0.02	659.7 ± 0.01	1.884 ± 3.0
6		20	5.29 ± 0.1	1.02 ± 0.03	7.41 ± 0.03	16.2 ± 0.02	7.67 ± 0.02	10.0 ± 0.01	0.98 ± 0.01	672.2 ± 0.02	1.776 ± 4.04
	R_o^a (%)									25.1	49.6
7		10	5.17 ± 0.15	1.04 ± 0.03	8.51 ± 0.02	15.8 ± 0.03	7.65 ± 0.03	10.1 ± 0.02	0.98 ± 0.03	695.8 ± 0.02	1.819 ± 3.60
8	69	15	5.18 ± 0.2	1.01 ± 0.01	9.62 ± 0.03	15.6 ± 0.02	7.64 ± 0.01	10.1 ± 0.01	0.99 ± 0.02	692.4 ± 0.02	1.793 ± 2.51
9		20	5.21 ± 0.3	1.01 ± 0.02	9.92 ± 0.03	13.5 ± 0.02	7.64 ± 0.02	10.0 ± 0.02	0.99 ± 0.03	680.2 ± 0.02	1.764 ± 2.1
	R_o^a (%)									19.4	52
	C.D.(5%)										
			0.058	0.039	0.303	0.612	0.171	NS	0.127	0.094	0.132
MF			6.14 ± 0.03	1.09 ± 0.04	4.13 ± 0.02	31.02 ± 0.04	7.73 ± 0.04	10.3 ± 0.02	0.80 ± 0.04	843.2 ± 0.03	2.18 ± 3.4
Feed			6.71 ± 0.02	3.64 ± 0.02	3.10 ± 0.01	47.21 ± 0.02	7.75 ± 0.02	11.6 ± 0.03	0.78 ± 0.03	857.2 ± 0.02	3.74 ± 7.01

S. no.	Operating Conditions		Naringin	Pectin Content	Pulp	Clarity	Color			Chroma intensity	Hue angle
	TMP (kPa)	CFR (l/h)	(ppm)	(mg/lit)	(%)	660 nm (%)	L*	a*	b*	C*	H*
1		10	280.3 ± 0.03	5.78 ± 0.02	ND	96.8 ± 0.05	59.68	-0.61	1.27	1.408	115.66
2	35	15	278.4 ± 0.02	3.30 ± 0.01	ND	97.9 ± 0.01	60.37	-0.54	1.04	1.171	117.43
3		20	278.2 ± 0.02	2.21 ± 0.03	ND	98.8 ± 0.01	59.6	-0.57	0.96	1.116	120.69
	R_o^a (%)			94.6							
4		10	276.7 ± 0.03	4.86 ± 0.04	ND	98.8 ± 0.02	58.88	-0.61	3.49	3.542	99.91
5	52	15	275.4 ± 0.01	2.03 ± 0.04	ND	98.8 ± 0.01	59.54	-0.65	1.38	1.525	115.22
6		20	275.1 ± 0.02	1.66 ± 0.02	ND	99.4 ± 0.02	59.23	-0.62	1.15	1.306	118.33
	R_o^a (%)			95.9							
7		10	273.8 ± 0.04	4.99 ± 0.04	ND	99.6 ± 0.02	60.34	-0.78	1.82	1.98	113.19
8	69	15	272.4 ± 0.03	1.17 ± 0.03	ND	99.8 ± 0.01	60.71	-0.66	1.56	1.693	112.93
9		20	270.5 ± 0.01	0.4 ± 0.02	ND	99.9 ± 0.02	60.22	-0.77	1.9	2.05	112.06
	R_o^a (%)		NS	96.8	–	0.154					
	C.D (5%)			0.652							
MF			286.3 ± 0.04	61.54 ± 0.02	0.8 ± 0.2	84.7 ± 0.01					

Table 1 continued

S. no.	Operating Conditions		Naringin	Pectin Content	Pulp	Clarity	Color			Chroma intensity	Hue angle
	TMP (kPa)	CFR (l/h)	(ppm)	(mg/lit)	(%)	660 nm (%)	L*	a*	b*	C*	H*
Feed			302.6 ± 0.02	70.5 ± 0.04	9 ± 0.01	68.8 ± 0.2	33.06	8.08	17.44	19.22	425.14

R_o^a observed retention in %. Average over the three cross flow rates, *C.D* critical difference, *NS* non-significant

Mean values ± standard error of the three independent experiments. *ND* not detected

rejected by membrane, hence reductions in polyphenols are observed.

Naringin is responsible for characteristics flavour in kinnow fruit juice. To understand the changes in naringin content due to membrane processing, naringin was determined. The naringin content of kinnow fruit juice was about 302.6 ppm when extracted from peeled fruit with screw type juice extractor. These values of naringin content in fresh juice are in agreement with values reported (Premi et al. 1994, Singh et al. 2009). The naringin content in MF juice was 286.3 ppm and in UF juice was 270.5–280.3 ppm.

Pectin content (mass of pectin per unit volume of juice) in fresh juice was about 70.5 mg/l and in MF it was about 61.54 mg/l. It decreased in ultrafiltration. In ultrafiltered juice, it ranged 0.4–5.78 mg/l. Pectin's are large size molecules (100–200 kDa) which are retained on membrane. Pectin reduction is desirable for juice so that it passes easily through the debittering column. Similar trend was obtained in UF of passion fruit juice (Jiraratananon and Chanachai 1996). Pectin was 0.66% in raw mosambi juice and after UF there was no pectin found when the feed juice was enzymatically treated in an unstirred batch cell (Rai et al. 2005).

The fresh kinnow juice had 9% pulp and in centrifugation it was about 0.8% also present in microfiltration but not measurable. Whereas in UF, no pulp was detected in permeate. This is most desired, since the pulp settle down in voids of absorbent bed in fixed adsorption column and clog the column during debittering.

The L values were found to increase indicating increase of lighter color, which is also evident visually. The color parameters of the UF juice were located in the second quadrant (− a* + b*), corresponding to green and yellowness. The a* values were positive initially showing redness whereas after ultrafiltration, these were shifted to greenness. The red pigmentation was reduced, which may be attributed to the possible reduction of β-carotene (reddish orange) along with pulp. The b* values are positive for fresh as well as UF treated juice indicating yellowness, but the values were reduced in UF juice. The initial value was 17.44; whereas in UF treated juice, values in the ranged 0.96–3.49. The main pigments in citrus juices which are responsible for orange, yellow color are α-carotene, β-carotene, zeta-antheraxanthin and β-cryptoxanthin. The reduction of these pigments (imparting yellow color) by ultrafiltration was the reason of lower values of b* (yellowness) in UF treated juice. The yellow colors have been removed along with pulp and particles. Color of the fresh fruit juice having chroma intensity 19.22 and Hue angle was about 425.14 respectively. The chroma intensity in ultrafiltration was 1.408–2.05 and Hue angle was 112.06–115.66 respectively. It may be noted that, the separated pulp is reblended in clear debitter juice and the juice re-gain the color. Clarity of the UF kinnow juice ranges from 96.8 to 99.9% which is higher when compared to fresh juice 68.8% and microfiltered juice 84.7%. This is due to the suspended colloidal particles and soluble solids of high molecular weight are removed in ultrafiltration.

Statistical analysis was performed on Table 1 for major parameters which were important for filtration. pH, Viscosity, vitamin C, conductivity, titratable acidity, protein content, polyphenol, pectin content and clarity were found to vary significantly with TMP and CFR at critical difference 5% whereas, total sugar, TSS and naringin did not vary significantly. From the values of various quality parameters of ultrafiltered kinnow juice, it was observed that the values conform the standards of citrus juice.

Storage study of ultrafiltered kinnow juice

The ultrafiltered juice was stored at 4 °C for 60 days. The measurable parameters like pH, viscosity, content of vitamin C, total sugar, TSS, protein, polyphenol, naringin and pectin as well as sensory attributes like color, taste, flavour, bitterness score and overall acceptability were evaluated at an interval of 15 days. The pH of the stored juice was 4.18. The pH of the stored kinnow juice with added KMS as a preservative was reported in the range of 3.3–3.5 (Khurdiya and Lotha 1994). The viscosity was 1.01 mPa s during entire period of storage. Vitamin C contents ranged 13.6 mg AA/100 ml during storage of ultrafiltered kinnow juice. However, no consistence pattern in change of vitamin C was observed during the entire storage period. Vitamin C is unstable and decrease on storage has been reported earlier (Shaw and Moshonas 1991).

The content of total sugar was 7.64%. The TSS of the treated ultrafiltered juice (J1) during storage did not change; it remained 10.0 °Bx throughout the storage period. Similar results were obtained in the storage study of ultrafiltered mosambi juice (Rai et al. 2008), storage of debittered kinnow juice (Singh et al. 2009). The content of protein was 1.764 mg/l and polyphenol was 680.2 mg GAE/100 ml remained the same in entire storage period. The naringin content of the treated UF juice did not change during the entire storage period (60 days) which was 270.5 ppm. Similar result also reported in debittered kinnow juice storage (Singh et al. 2009). No change in pectin content was detected in storage period which was 0.4 mg/l. Clarity was 99.9% and unaffected by the storage. All the parameters during storage study did not vary significantly at critical difference level 5%.

Sensory evaluation was carried out for three types of juice samples which are given in Table 2. The juice obtained by UF termed as (J1) and the UF sample with added pulp was termed as (J2) whereas, the fresh kinnow juice termed as (J3). The color value decreased by membrane treatment significantly. The membrane treated UF juice (J1) was not acceptable (poorly rated) by test panellists when compared with fresh juice (J3). The color loss may be attributed to the filtration of color containing compounds or particles by membrane treatment. The substances imparting the color to the juice are flavonoids, carotenoids and the colored pulp particles. Addition of pulp (J2) in the treated juice (J1) increases the rating. Addition of pulp in the treated juice (J1) improves color, taste and flavour. Color, taste, flavour, bitterness score and overall acceptability were varied significantly after addition of pulp in UF treated juice at critical difference 5%. There was no significant difference between the juices (J2) and (J3) fresh juice.

Table 2 Sensory evaluation during the storage of ultrafiltered kinnow juice (30 kDa)

Days	0	15	30	45	60
Sample					
Color					
J1	3.3	3	3.1	3.1	3
J2	8.3	8.1	8.2	8	8.1
J3	8.4	8.2	8.2	8.1	8
C.D (5%)	0.21	0.41	0.03	0.09	0.098
Taste					
J1	5	5.2	5.1	4.9	4.9
J2	8	8.2	8.2	8.1	7.9
J3	8.3	8.2	8.2	8.2	8
C.D (5%)	0.046	0.134	0.004	NS	0.012
Flavour					
J1	4.4	4.3	4.3	4.1	4
J2	6.4	6.2	6.3	6.1	6
J3	8	8.1	8.1	8.2	8
C.D (5%)	0.025	0.090	0.016	0.028	0.279
Bitterness score					
J1	3	3.1	3.1	3.1	3
J2	6	6.2	6.2	6.1	6.2
J3	7.5	7.4	7.4	7.2	7.1
C.D (5%)	0.69	0.112	0.641	0.601	0.086
Overall acceptability					
J1	3.5	3.2	3.2	3.1	3.1
J2	7.5	7.3	7.3	7.2	7.1
J3	8.4	8.2	8.2	8.1	8
C.D (5%)	0.193	0.135	0.024	0.992	0.568

J1 UF juice, *J2* UF juice with added pulp 6%, *J3* Fresh juice, *C.D* critical difference, *NS* non-significant

Two litter (2×10^{-6} m^3) ultrafiltered juice was passed through a fixed bed of INDION PA-500 (Ion Exchange India Ltd) food grade adsorbent resin (in burette) for debittering the juice. The resin macroporous, non-ionic, hydrophobic, cross-linked polymeric adsorbent. It was observed that the column did not clog and juice was debittered; otherwise it clogged with 950 ml of centrifuged juice.

Conclusion

Kinnow fruit juice was clarified by hollow fiber ultrafiltration module. MWCO of 30 kDa polysulfone membrane was the most suitable membrane which was selected by the criteria: permeate flux and juice quality. The UF treated juice can be stored for 60 days without adding any preservative in a refrigerated condition at 4 °C. Thus, the kinnow fruit juice can be clarified by UF membrane and can be debittered without clogging the adsorption column. From the values of various quality parameters of UF treated juice and stored juice, it was observed that the values conform the standards of citrus of juice.

References

AOAC (1980) Official methods of analysis, 13th edn. Association of official analytical chemists, Washington

Bennett R (1987) From presentation to the citrus products technical committee at the USDA fruit and vegetable laboratory. California, 13 March

Cassano A, Basile A (2013) Integrating different membrane operations and combining membranes with conventional separation techniques in industrial processes. In: Basile A (ed) Handbook of membrane reactors: reactor types and industrial applications, 1st edn. Woodhead Publishing, UK, pp 296–343

Cassano A, Tasselli F, Conidi C, Drioli E (2009) Ultrafiltration of Clementine mandarin juice by hollow fiber membrane. Desalination 241(1–3):302–308

Cassano A, Conidi C, Drioli E (2010) Physico-chemical parameters of cactus pear juice by microfiltration and ultrafiltration processes. Desalination 250(3):1101–1104

Casaano A, Conidi C, Drioli E (2011) Clarification and concentration of pomegranate juice using membrane processes. J Food Eng 107(3):366–373

Galaverna G, DiSilvestro G, Cassano A, Sforza S, Dossena A, Drioli E, Marchelli R (2008) a new integrated membrane process for the production of blood orange juice: effect on bioactive compounds and antioxidant activity. Food Chem 106(3):1021–1030

Ilame SA, Singh SV (2015) Application of membrane separation in fruit and vegetable juice processing: a review. Crit Rev Food Sci Nutr 55(4):964–987

Jiraratananon R, Chanachai A (1996) A study of fouling in the ultrafiltration of passion fruit juice. J Memb Sci 111(1):39–48

Kalvons JA, Bennett RD, Vannier SH (1994) Physical/chemical nature of pectin associated with commercial orange juice cloud. J Food Sci 59(2):399–401

Khurdiya D, Lotha R (1994) Kinnow mandarin storage and processing. Ind Food Pack 48:33

Kimball D (2012) Citrus processing: quality control and technology. Springer, Berlin

Lotha R, Khurdiya D (1994) Effect of methods of juice extraction from kinnowmandarine on the composition and quality of juice, pomace and peel. J Food Sci Technol 31(5):380–384

Lowry OH, Rosebrough NJ, Nira J, Farr LA, Randall RJ (1951) Protein measurement with the Folin phenol reagent. J Biol Chem 193(1):265–275

Padilla O, McLellan M (1989) Molecular weight cut-off of ultrafiltration Membranes and the quality and stability of apple juice. J Food Sci 54(5):1250–1254

Premi BR, Lal BB, Joshi VK (1994) Distribution pattern of bittering principles in kinnow fruit. J Food Sci Technol 31(2):140–141

Rai P, Majumdar GC, DasGupta S, De S (2005) Understanding ultrafiltration performance with mosambi juice in an unstirred batch cell. J Food Eng 28(2):166–180

Rai P, Majumdar GC, Gupta SD, De S (2007) Effect of various pretreatment methods on permeate flux and quality during ultrafiltration of mosambi juice. J Food Eng 78(2):561–568

Rai P, Rai C, Majumdar GC, Gupta SD, De S (2008) Storage study of ultrafilteredmosmbi (*Citrus sinensis* (L) Osbeck) juice. J Food Process Preserv 32(8):923–934

Rai C, Rai P, Majumdar GC, De S, DasGupta S (2010) Mechanism of permeate flux decline during microfiltration of watermelon (Citrulluslanatus) juice. Food Bioprocess Technol 3(4):545–553

Rangana S (1986) Handbook of analysis and quality control for fruit and vegetable products. Tata McGraw-Hill education, New York

Rouseff RL (1990) Bitterness in foods and beverages. Elsevier; Distributers for the United States and Canada, Elsevier Science Pub. Co, Amsterdam

Sagu ST, Karmakar S, Nso EJ, Kapseu C, De S (2014) Ultrafiltration of banana (*Musa acuminate*) juice using hollow fibers for enhanced shelf life. Food Bioprocess Technol 7(9):2711–2722

Scott WC, Morgan DA, Veldhuis MK (1960) The determination of soluble solids in citrus juices; the effect of non-sucrose constituents on refractometer values. Food Technology, Inst Food Technologists Suite 300221N Lasalle ST, Chicago, IL 60601-1291

Shaw PE (1990) Citrus juice debittering: current status worldwide. Citrus Ind 71(6):54–55

Shaw PE, Moshonas MG (1991) Ascorbic acid retention in orange juice stored under simulated consumer home conditions. J Food Sci 56(3):867–868

Shaw PE, Baines L, Milnes BA, Agmon G (2000) Commercial debittering processes to upgrade quality of citrus juice products. Functional chemicals in agriculture and foods. In: ACS symposium series

Singh SV, Jain RK, Gupta RK (2009) Change in quality of debittered kinnow juice during storage. J Food Sci Technol 46(6):598–600

Singh SV, Jain RK, Gupta AK (2016) Adsorptive reduction of naringin from kinnow mandarin juice with non-ionic macroporpus adsorbent resin. Indian Chem Eng 58(2):136–156

Toker A, Karhan M, Tetik N, Turhan I, Oziyci HR (2014) Effect of ultrafiltration and concentration processes on the physical and chemical composition of blood orange juice. J Food Process Preserv 38(3):1321–1329

Vasco C, Ruales J, Kaml-Edlin A (2008) Total phenolic compounds and antioxidant capacities of major fruits from Ecuador. Food Chem 111(4):816–823

Wethern M (1991) Citrus debittering with ultrafiltration/adsorbtion combined technology. In: Transactions of the citrus engineering conference (USA)