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Comparison of osmotic membrane distillation and forward osmosis membrane processes for concentration of anthocyanin

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ABSTRACT

The present work deals with comparison of osmotic membrane distillation and forward osmosis membrane processes for concentration of anthocyanin extract as well as to study the effect of various process parameters such as osmotic agent concentration, flow rates of feed and osmotic agent on transmembrane flux. Mechanism of mass transfer in case of osmotic membrane distillation and forward osmosis has been explained. Mass and heat transfer coefficients for feed side, osmotic agent side, membrane mass transfer coefficient and overall transfer coefficient have been determined. In case of forward osmosis, the anthocyanin extract was concentrated from 49.63 mg/l to 2.69 g/l in 18 hours; however, it was coupled with migration of sodium chloride (0.21 moles/m^2s). However, in case of osmotic membrane distillation process, the concentration of anthocyanin was achieved up to 72 mg/l for the same time without any transfer of osmotic agent. The transmembrane flux in case of osmotic membrane distillation was low as compared to forward osmosis. These techniques may prove to be potential techniques for concentration of natural colorant. The concentration of kokum extract using forward osmosis membrane process has advantages over the thermal concentration in terms of higher stability, lower browning index and less conversion of hydroxycitric acid to its lactone form.

Keywords: Osmotic membrane distillation; Forward osmosis; Heat and mass transfer; Anthocyanin

1. Introduction

New athermal membrane processes such as forward (direct) osmosis (FO) or osmotic membrane distillation (OMD) employ semi-permeable dense hydrophilic or hydrophobic membranes, respectively, which separate feed and osmotic agent solutions. The difference in osmotic pressures between feed and osmotic agent solution acts as a driving force in case of FO, whereas in case of OMD, it is difference in vapor pressure. FO as well as OMD are non-pressure driven membrane processes capable of concentrating liquid foods at ambient conditions without product deterioration [1–3]. It offers several advantages compared to that of conventional processes such as solvent extraction, conventional membrane processes and evaporation. These include low energy consumption, higher retention of thermoliable components and achievement of higher concentration without product deterioration [4–10]. In case of FO, the flux is higher as compared to OMD. Transfer of small amount of osmotic agent to product side limits the application of FO in food processing. However, many researchers have used sodium chloride as an osmotic agent for the concentration of vegetable juices [11]. In view of reducing salt uptake, mixed solute consisting of sodium chloride and sucrose as an osmotic agent was

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used for the concentration of pineapple juice [1]. Selection of these techniques depends upon the choice of the product to be concentrated and tolerance limit of the osmotic agent in the final product.

The colorants extracted from the natural sources contain a good amount of water. Concentration of these colorants using traditional processes involving thermal evaporation results in degradation of colorant. It is necessary to concentrate these colorants using techniques involving no or less heat treatment to improve shelf life, stability, and to reduce storage/transportation costs [12,13]. In this situation, the use of membrane techniques could be used as a perfect alternative. Membrane processes such as microfiltration, ultrafiltration and reverse osmosis are being employed for clarification and concentration of natural color extracts [14]. The existing membrane techniques such as reverse osmosis can be used up to an extent, beyond which higher pressure is required for the concentration of product, which may result in membrane damage. Other limitations of the membrane processes are limit to attain maximum concentration, concentration polarization and membrane fouling. FO and OMD may prove to be the potential techniques for the concentration of natural colorant.

Anthocyanin pigments comprise diverse groups of intensely colored pigments. These are responsible for appealing spectacular orange, red, purple and blue colors of many fruits, vegetables, flowers, leaves, roots and other plant organs. The solubility of anthocyanin pigments in water makes them the best candidate for incorporation into aqueous food systems [15,16]. Conventional concentration methods are energy intensive and degradation of anthocyanin pigment takes place, which in turn reduce the recovery of the anthocyanin pigment as well as product deterioration [15–17].

Nayak et al. [17] have recently reviewed the bioactive constituents of *Garcinia indica* and indicated that it is a rich source of anthocyanins. The chemical and spectral investigations have revealed that the rinds of the it contains two water soluble anthocyanin pigments, which were identified as cyanidin-3-glucoside and cyanidin-3-sambubioside [18,19]. Concentration of natural color extracts by conventional method such as evaporation results in loss of hue and chroma resulting in low quality product, besides being energy intensive.

The objectives of the present work are (i) to compare FO and OMD processes for the concentration of anthocyanin pigment from *Garcinia indica*; (ii) to study the effect of various process parameters such as osmotic agent concentration and flow rate on transmembrane flux during both the membrane process; and (iii) to identify and evaluate the different transport resistances. Attempts were made to compare physicochemical characteristics of product before and after the FO and OMD membrane processes.

2. Materials and methods

2.1 Kokum extraction

The fresh Kokum (*Garcinia indica Choisy*) fruits were handpicked from the orchards near Mangalore, India. The fruits were cut into four equal pieces (rinds) parallel to the major axis and seeds were removed. The fruit rinds were washed, sliced and grinded. The pulp, thus obtained, was mixed with 1:2 ratio of acidified water (0.1% hydrochloric acid). The mixture was subjected to hydraulic press (M/s. B. Sen & Berry, New Delhi, India). The extract was filtered using muslin cloth and stored in cold room at 4–5°C for further studies. The concentration of anthocyanin and total solids in the extract was found to be 49.63 mg/l and 2 °Brix, respectively.

In order to compare the membrane process (FO process) with thermal concentration, the crude extract was concentrated using flash evaporator (Rotovap Model 410, M/s Bucchi, Switzerland). The temperature and vacuum were maintained at 60°C and 675 mm of Hg, respectively.

2.2 Chemicals

Sodium chloride, sodium acetate and potassium chloride were procured from Ranbaxy Ltd., India. All the chemicals were of analytical grade.

2.3 Osmotic agent solution

Osmotic agent solutions for osmotic membrane distillation and forward osmosis experiments were prepared by dissolving sodium chloride in distilled water in various proportions (1, 2, 3, 4, 5 and 6 M). These solutions were kept overnight at room temperature before use to ensure complete dissolution of sodium chloride. Osmotic pressure and vapor pressure of the sodium chloride solution were calculated as per the procedure reported elsewhere [20].

2.4 Experimental set up

Experiments were performed using a flat membrane module having a membrane area of 0.0114 m^2, shown in Fig. 1. The module consists of forward osmosis membrane or osmotic membrane distillation, which was placed over a polyester mesh (0.25 mm), supported in between Viton gasket (3.0 mm) and two frames made of stainless steel (SS 316). Feed solution (Kokum extract) and osmotic agent solution were circulated on either side of the membrane in co-current mode using peristaltic pumps (Model 72-315-230, Barnant Company, IL, USA). The ratio of feed solution to osmotic agent solution was maintained at 1:10 for all the experiments conducted. The transmembrane flux was calculated by measuring the increase in volume of osmotic agent every hour. All the experiments were

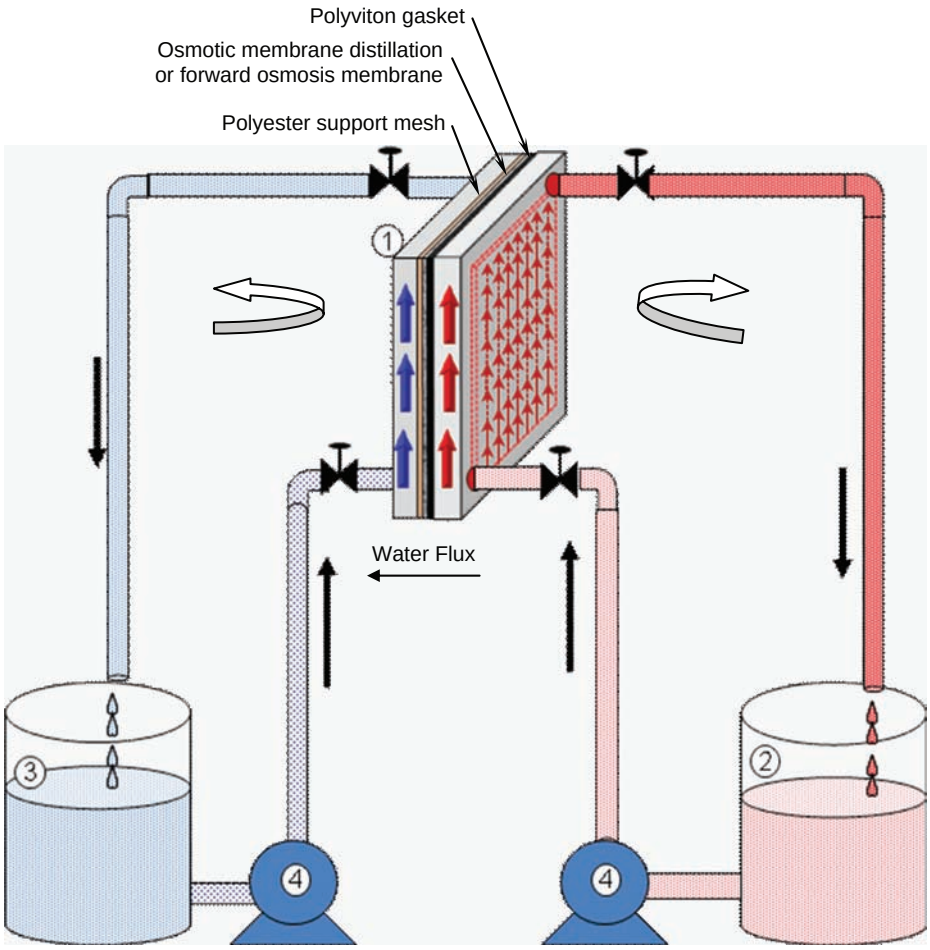

Fig. 1. Flat membrane module for forward osmosis/ osmotic membrane distillation process. (1) forward osmosis/ osmotic membrane distillation flat membrane module (2) feed reservoir (3) osmotic agent reservoir (4) peristaltic pump.

performed for a period of five hours and the average values of the flux were reported. All the experiments were carried out at the temperature of 25 ± 2°C.

2.5 Membranes

Membranes for osmotic membrane distillation and forward osmosis were procured from Acurel, Germany and Osmotek, Inc., Corvallis, OR, USA, respectively. The forward osmosis membranes were asymmetric, which consisted of very thin semi-permeable non-porous active skin layer of cellulose triacetate and embedded in a nylon mesh as porous support layer for an increased strength. The membrane was highly hydrophilic in nature. The thickness of the membrane as determined by scanning electron microscope was found to vary between 50 and 100 μm.

Osmotic membrane distillation membrane was of hydrophobic micro-porous membrane and the main characteristics of the membrane are thickness, 175 μm and pore diameter, 0.2 μm (as specified by the supplier). Properties of membranes such as porosity (ε, 0.75), tortuosity (τ, 2), thermal conductivity of gas (k^T_{gas}, 0.025 W/m. K) and thermal conductivity ($k^T_{polymer}$, 0.2 W/m. K) of material were taken from the literature [8].

2.6 Anthocyanin concentration measurements

The monomeric anthocyanin content in whole extract was determined calculated using pH differential method [21]. The anthocyanin content was calculated using the following equation.

$$\text{Anthocyanin content (mg/L)} = \frac{A \times M \times DF \times 10^3}{\varepsilon \times l} \qquad (1)$$

Where, A = Total absorbance = $[(A_{\lambda max} - A_{700})_{\text{at pH 1.0}} - (A_{\lambda max} - A_{700})_{\text{at pH 4.5}}]$, M is the molecular weight of anthocyanin (449 g mol^{-1}), DF is the dilution factor, ε is the extinction coefficient (29,600 L cm^{-1} mol^{-1}) and l is the path length (1.0 cm). A double beam spectrophotometer (Shimadzu,

Japan, Model UV-160A) was used for the spectral analysis. The concentrated anthocyanin samples were diluted with distilled water before analysis. All the experiments were carried out in triplicate and average values were reported.

2.7 Color analysis

The color characteristics L*, a*, b* of concentrated anthocyanin obtained in different membrane processes were measured using a Hunter colorimeter (Hunterlab, D25 A-9, NJ, USA). The samples were placed in a 1 cm path length optical glass cell and CIE L*, a*, b* values were noted in the total transmission mode, using illuminant C and 2° observer angle. Hue angle ($\tan^{-1}(b^*/a^*)$) and chroma $(a^{*2} + b^{*2})^{1/2}$ are also determined [22].

2.8 Soluble solid contents

Total soluble solids was measured using Erma's Handheld refractometer at 25 ± 2°C. Results were reported in degree Brix (°B).

2.9 Estimation of sodium chloride

The concentration of sodium chloride was determined from samples taken during the course of the experiment and measured using handheld conductivity meter (Eutech, Model: CON110, Singapore). Calibration curve was made using the conductivity of solution of sodium chloride in water against the mass fractions of NaCl [23,24]. The rate of salt transfer through the membrane was reported in terms of moles/m²s.

2.10 Determination of mass and heat transfer coefficients during osmotic membrane distillation

Transmembrane flux in osmotic membrane distillation (J_{omd}) based on the mass transfer coefficients for feed side (k_f), osmotic agent side (k_{OA}), membrane mass transfer coefficient (k_{mp}) and overall mass transfer coefficient (K_{omd}) is given as [25,26]

$$J_{omd} = k_f(a_f - a_{fm}) = k_{OA}(a_{OAm} - a_{OA}) = k_{mp}(p_{fm} - p_{OAm}) = K(a_f p^*_{fm} - a_{OA} p^*_{OAm}) \quad (2)$$

where, a_f and a_{OA} are the bulk water activity coefficients for feed and osmotic agents side, respectively. The variables with subscript 'm' refer quantities at the boundary. p_{fm} and p_{OAm}, are the partial vapor pressures near the membrane surface on feed and osmotic agent side, respectively. The variables with superscript '*' refer vapor pressures on the either of the boundary layer near membrane surfaces at the existing temperatures.

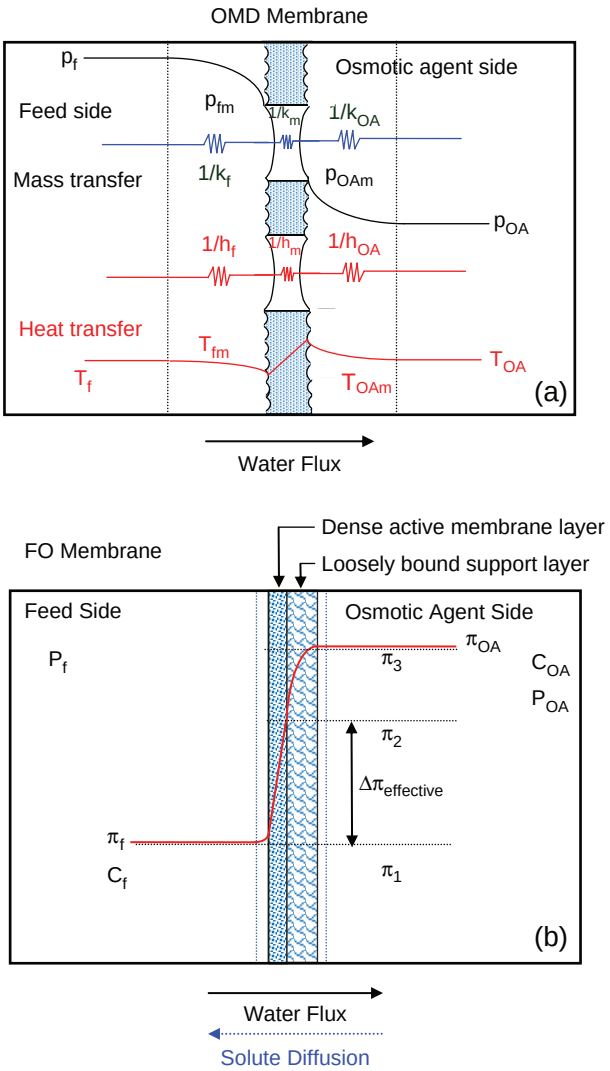

Fig. 2. (a) Vapor pressure and temperature profiles during osmotic membrane distillation process (where $p_{w1} = a_1 p^*_{w,T1}$; $p_{w2} = a_2 p^*_{w,T2}$; $p_{wm1} = a_{m1} p^*_{w,Tm1}$; $p_{wm2} = a_{m2} p^*_{w,Tm2}$). k_f, k_{OA} and k_m and h_1, h_2 and h_m are the feed side, osmotic agent side and membrane mass and heat transfer coefficients, respectively. (b) Mechanism of forward osmosis (π_1, π_2 : Osmotic pressure of feed and osmotic agent solution, respectively; P_1,P_2:Feed side and osmotic agent side hydraulic pressure, respectively)

The overall mass transfer coefficient during osmotic membrane distillation process (which accounts for both concentration and tempserature polarization effects as shown in Fig. 2a) can be obtained by substituting the values of a_f and a_{OA} from second and third expression, respectively to the last expression in Eq. (2)

$$K_{omd} = \frac{1}{\frac{p^*_{fm}}{k_f} + \frac{1}{k_{mp}} + \frac{p^*_{OAm}}{k_{OA}}} \quad (3)$$

Similarly, heat flux in osmotic membrane distillation (Q_{omd}) based on the heat transfer coefficients for feed side (h_f), osmotic agent side (h_{OA}), membrane heat transfer coefficient (h_{mp}) and overall heat transfer coefficient (U) is given as [26,27].

The heat flux in the boundary layers can be defined in terms of respective individual heat transfer coefficients by the following equations.

$$\begin{aligned} Q &= h_f\left(T_f - T_{fm}\right) = h_{OA}\left(T_{OAm} - T_{OA}\right) \\ &= \left(J_{omd}\,\rho\,\Delta H_v\right) - h_{mp}\left(T_{OAm} - T_{fm}\right) \\ &= \frac{1}{U}\left(\frac{J_{omd}\,\rho\Delta H_v}{h_{mp}} - (T_{OA} - T_f)\right) \end{aligned} \quad (4)$$

where T_f and T_{OA} are the bulk temperatures of feed and osmotic agent, respectively, T_{fm} and T_{OAm} are the corresponding temperatures near the membrane surface; ΔH_v is the water latent heat of vaporization [27]. The last term of Eq. 4 was obtained by substituting the values of T_{fm} and T_{OAm} from second and third terms to fourth term.

The overall heat transfer coefficient U is given by

$$U = \frac{1}{\frac{1}{h_f} + \frac{1}{h_{mp}} + \frac{1}{h_{OA}}} \quad (5)$$

Membrane mass and heat transfer coefficient (K_{mp}, h_{mp}) were calculated as per the following equations reported elsewhere [27,28].

$$k_{mp} = \frac{1.8\times10^{-5}}{RT\delta}\left(\frac{3\tau}{\varepsilon d_P\left(\frac{8RT}{\pi M_w}\right)^{0.5}} + \frac{p_{air}.\tau}{\varepsilon.\,(4.46\times10^{-6}T^{2.334})}\right)^{-1} \quad (6)$$

$$h_{mp} = \frac{k^T}{\delta} = \frac{\varepsilon k^T_{gas} + (1\times\varepsilon)k^T_{polymer}}{\delta} \quad (7)$$

where, p_{air} is the air partial pressure, R the gas constant, T the absolute temperature, M_w is the water molar mass, ε the membrane porosity, δ the membrane thickness, τ the membrane tortuosity, d_p the membrane pore diameter, k^T is a combination of thermal conductivity of the gases (a mixture of air and water vapor) and of the membrane polymer [28]. Membrane mass transfer coefficient was determined to be 2.50×10^{-10} $ms^{-1}Pa^{-1}$ and heat transfer coefficient was determined to be 392.86 $W\,m^{-2}\,K^{-1}$.

The boundary layer mass and heat transfer coefficients can be estimated from the following empirical correlations, respectively [25].

$$N_{Sh} = 0.66.N_{\mathrm{Re}}{}^{0.50}N_{Sc}{}^{0.33} \quad (8)$$

$$N_{Nu} = 0.66 \quad N_{\mathrm{Re}}{}^{0.50} \quad N_{\mathrm{Pr}}{}^{0.33} \quad (9)$$

where, $N_{Sh} = \frac{kL}{D_w}$, $N_{\mathrm{Re}} = \frac{uL\rho}{\mu}$, $N_{Sc} = \frac{\mu}{\rho D_w}$, $N_{Nu} = \frac{hL}{k^T}$ and $N_{\mathrm{Pr}} = \frac{\mu C_P}{k^T}$, N_{Sh}, $N_{Re,}$ N_{Sc}, N_{Nu}, $N_{Pr,}$ the Sherwood, Reynolds, Schmidt, Nusselt and Prandtl numbers, k is the mass transfer coefficient, L the characteristic length, D_w the water diffusion coefficient, ρ the solution density, μ the solution dynamic viscosity, k the feed or osmotic agent side liquid mass transfer coefficient, c of feed or osmotic agent solution, C_p the specific heat of feed or osmotic agent solution, h the boundary layer heat transfer coefficient of feed or osmotic agent side and u the velocity of the fluid, flowing over the membrane surface.

2.11 Determination of membrane resistivity during forward osmosis

Forward osmosis membrane process employs a semi-permeable dense hydrophilic membrane, which separates the feed as well as the osmotic agent solutions (Fig. 1). Osmotic pressure difference between the feed as well as osmotic agent solutions acts as a driving force for transport of water. The asymmetric membrane used in forward osmosis consisted of two layers, one is the loosely bound support layer and other is the dense active membrane layer. The membrane was placed between the feed and the osmotic agent solutions such that the feed was towards active layer and osmotic agent was towards the support layer [29].

The resistivity of the membrane (support and active layer) during forward osmosis process was calculated as per the following equation for dilutive internal concentration polarization [29–32]:

$$K_r = \left(\frac{1}{J_w}\right)\ln\left(\frac{B + A\pi_{OA}}{B + J_w + A\pi_{Feed}}\right) \quad (10)$$

where J_w is the transmembrane flux during forward osmosis, K_r is the resistivity of membrane (support and active layer) (s/m), π_{OA} and π_{Feed} are the osmotic pressure of osmotic agent and feed, respectively. The constant 'A' (0.027 m/atm-day) and 'B' (0.011 m/day) refer to the water and solute permeability coefficients of the active layer of the membrane, respectively [29,31].

2.12 Non-enzymatic browning and degradation constant

Non-enzymatic browning of crude, thermally concentrated and forward osmosis concentrate was estimated using spectrophotometer (Shimadzu 160A, Japan) at 420 nm. The estimation was carried out at same concentration as that of fresh sample i.e. 2°Brix. The degradation constant (K_D) for the anthocyanin content in

Table 1
Estimated mass transfer coefficient and heat transfer coefficients for osmotic membrane distillation process.

Process conditions	Osmotic membrane distillation							
	Mass transfer				Heat transfer Wm^2/Ks			
	k_f ($\times 10^{-6}$) m/s	k_m ($\times 10^{-10}$) m/sPa	k_{oa} ($\times 10^{-4}$) m/s	K_{omd} ($\times$ X 10^{-10}) m/sPa	h_f	h_m	h_{oa}	U
OA concentration (m)								
1	6.42	2.50	0.80	2.15	889.34	392.86	11014.54	265.91
2	6.42	2.50	1.01	2.16	889.34	392.86	11038.00	265.92
3	6.42	2.50	1.16	2.16	889.34	392.86	10805.12	265.79
4	6.42	2.50	1.27	2.16	889.34	392.86	10590.32	265.65
5	6.42	2.50	1.37	2.16	889.34	392.86	10394.10	265.53
6	6.42	2.50	1.46	2.17	889.34	392.86	10212.61	265.41
OA flow rate (ml/min)								
50	6.42	2.50	0.92	2.16	889.34	392.86	6459.02	261.46
75	6.42	2.50	1.13	2.16	889.34	392.86	7910.65	263.41
100	6.42	2.50	1.30	2.16	889.34	392.86	9134.44	264.59
125	6.42	2.50	1.46	2.17	889.34	392.86	10212.61	265.41
Feed flow rate (ml/min)								
50	4.06	2.50	1.46	2.01	562.47	392.86	10212.61	226.18
75	4.98	2.50	1.46	2.09	688.88	392.86	10212.61	244.20
100	5.75	2.50	1.46	2.13	795.45	392.86	10212.61	256.38
125	6.42	2.50	1.46	2.17	889.34	392.86	10212.61	265.41

the extract was determined considering first-order degradation kinetics as per the following equation [33].

$$\ln\left(\frac{C_o}{C_t}\right) = K_D t \tag{11}$$

where, C_o is the initial anthocyanin content, C_t is the anthocyanin content at a specified time t. The degradation studies were carried out for 15 days at room temperature and anthocyanin content was measured each day.

3. Results and discussion

Osmotic membrane distillation and forward osmosis experiments were carried out using anthocyanin extract as a feed material and sodium chloride as an osmotic agent. Experiments were performed at different concentrations to evaluate the effect of osmotic agent concentration on transmembrane flux. The effect of feed or osmotic agent flow rate on transmembrane flux was evaluated by varying the feed or osmotic agent solution flow rate from 50 to 125 ml/min for the osmotic solution consisting of 26% sodium chloride. Finally, the concentrated anthocyanin extracts by osmotic membrane distillation and forward osmosis were compared.

3.1 Transport phenomenon in osmotic membrane distillation and forward osmosis

Mechanism for osmotic membrane distillation is illustrated in Fig. 2a. The vapor pressure difference across the membrane is the driving force for the mass transfer of water across the membrane. It employs a porous hydrophobic membrane, which separates the feed (anthocyanin extract) and osmotic agent (sodium chloride) solution. The water evaporates from surface of the membrane in contact with the feed solution, which is at a higher vapor pressure (p_{fm}). The water vapor passes through the pores of the membrane and condenses on the surface of the membrane in contact with osmotic agent, which is at a lower vapor pressure (p_{OAm}). This migration of water in the form of vapor results in the concentration of the feed and dilution of the osmotic agent solution [26]. Water activity, temperature profiles, and mass as well as heat transfer resistances in osmotic membrane distillation are presented in Fig. 2a. Evaporation of water vapor from feed results in cooling near the membrane surface (T_f to T_{fm}). While, condensation of

water vapor in the osmotic agent near membrane surface results in heating (T_{OAm} to T_{OA}). Simultaneous mass and heat transfer during the water transport in osmotic membrane process leads to the difference in concentration and temperature near the membrane surface compared to the bulk stream. Hence, there is a decrease in the water vapor pressure in the feed side as well as increase in vapor pressure in the osmotic agent side. The overall mass and heat transfer coefficients are the summation of respective resistances offered by the feed side, membrane and osmotic agent side resistances.

Mechanism of forward osmosis membrane process is illustrated in Fig. 2b. It employs a semi-permeable dense hydrophilic membrane, which separates the feed as well as the osmotic agent solutions. The difference in osmotic pressure across the membrane is the driving force for transport of water. The transfer of water takes places till the osmotic pressures on both the sides of the membrane become equal. Forward osmosis membrane consists of loosely bound support layer (osmotic agent side) and dense active membrane layer (feed side, as indicated in Fig. 2b). The water from the feed is diffused into the active layer, which, in turn, is diffused to the support layer and then to the bulk through the boundary layer. Since, the solute used for osmotic agent is generally of low molecular weight, it is also diffused into the support layer to the interior surface of the active layer before flux can occur. As water flux crosses the active layer into the support layer, the solute is diluted due to convection. The solute diffuses back to the interior surface. A steady-state is reached quickly, but the concentration at the interior surface of the active layer is far lower than in the bulk solution [29,30]. The combined effect of diffusion of water through the active layer and osmotic agent into support layer will result in setting up of an internal concentration polarization (Fig. 2b). The extent of external concentration polarization towards support layer (feed) as well as active layer (osmotic agent) will be much less as compared to internal polarization and hence can be neglected.

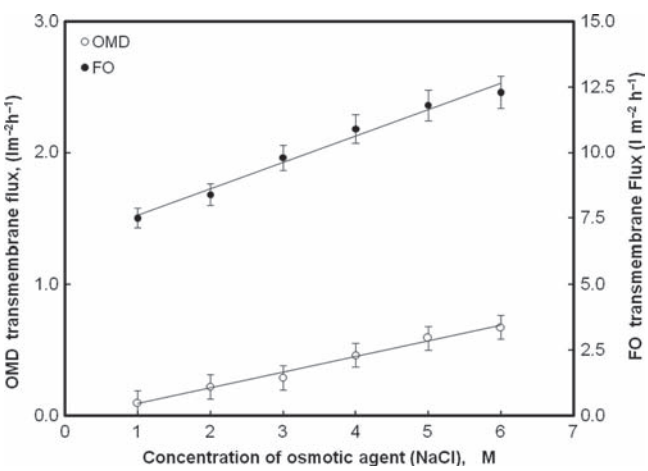

Fig .3. Effect on the osmotic agent concentration on transmembrane flux for FO and OMD.

The membrane resistivity (K_r) of the membrane was calculated using Eq. 10, which remained constant (12.07 d/m) irrespective of concentration of osmotic agent. The hydrodynamic properties such as density, viscosity and diffusivity are dependent on the concentration. The density of the osmotic solutions varies slightly with concentration whereas the diffusivity practically remains constant.

3.2 Effect of concentration of osmotic agent solution on the transmembrane flux

The effect of osmotic agent (sodium chloride) concentration on transmembrane flux during concentration of anthocyanin extract was estimated for both the membrane processes and is presented in Fig. 3. The feed side and osmotic agent side flow rates during the experiments were maintained at 125 ml/min. In case of osmotic membrane distillation and forward osmosis, the transmembrane flux was increased from 0.14 to 0.68 l/m^{2}h and 7.5 to 12.3 l/m^{2}h, respectively, with an increase in sodium chloride solution concentration from 1.0 to 6.0 M. The increase in transmembrane flux with an increase in the concentration of osmotic agent in case of osmotic membrane distillation and forward osmosis can be attributed to the increase in vapor and osmotic pressure difference across the membrane (or driving force), respectively. Forward osmosis membrane process was found to have higher transmembrane flux compared to that of osmotic membrane distillation [2].

The boundary layer mass and heat transfer coefficients for osmotic membrane distillation were calculated as per Eqs. 8 and 9 and shown in Table 1. The mass transfer coefficient at the osmotic agent side of the membrane is increased from 0.80×10^{-4} to 1.46×10^{-4} m/s with an increase in the osmotic agent concentration (1.0 to 6.0 M), whereas the heat transfer decreased from 1.10×10^4 to 1.02×10^4 W/m^{2}K. This increase in mass transfer coefficients are attributed to increase in vapor pressure difference across the membrane with an increase in osmotic agent concentration. The membrane mass and heat transfer coefficients are much higher and dominant as compared to the respective coefficients at boundary layers. Due to this fact, the variation in the overall heat and mass transfer is not significant.

The transmembrane flux during forward osmosis was found to increase from 7.5 to 12.3 l/m^{2}h with an increase in osmotic agent concentration from 1 to 6 M. The rate of migration of sodium chloride (0.21 moles/m^2 s) in the feed side was found to be maximal when the osmotic

Table 2
Physicochemical characteristics of kokum extsract concentrate by forward osmosis and osmotic membrane distillation membrane process

Characteristic	Fresh extract	FO extract concentrate	OMD extract concentrate
Brix	2.0 ± 0.2	52.0 ± 0.5	5.0 ± 0.5
Anthocyanin Concentration (mg/L)	49.63 ± 2.0	2692 ± 10.0	72 ± 2.0
pH	3.5 ± 0.1	2.8 ± 0.1	3.0 ± 0.1
Color Values			
L*	0.62 ± 0.01	5.33 ± 0.10	4.93 ± 0.10
a*	0.27 ± 0.05	2.54 ± 0.20	1.84 ± 0.20
b*	0.40 ± 0.02	0.14 ± 0.02	0.24 ± 0.02
Hue angle $\tan^{-1}$ (b*/a*)	55.98 ± 0.10	3.15 ± 0.05	7.43 ± 0.05
Chroma $(a^{*2}+b^{*2})^{1/2}$	0.48 ± 0.05	2.54 ± 0.05	1.85 ± 0.05
Density (kg/m^3)	1025 ± 10	1100 ± 10	1030 ± 10
Viscosity (mPas)	1.11 ± 0.05	1.78 ± 0.05	1.13 ± 0.05
Rate of salt transfer (moles/m^2 s)	Nil	0.21 ± 0.01	Nil

agent concentration was 6 M (Fig. 4). In case of osmotic membrane distillation, the theoretical flux was calculated by accounting all the feed side, membrane and osmotic agent side resistances for water transport. The experimental fluxes were found to be in good agreement with that of theoretical fluxes (data not shown).

3.3 Effect of feed and osmotic agent flow rate on the transmembrane flux

The effect of feed flow rate on transmembrane flux in case of osmotic membrane distillation and forward osmosis for concentration of anthocyanin is shown in Fig. 5a and b. With an increase in feed flow rate from 50 ml/min to 125 ml/min in case of osmotic membrane distillation and forward osmosis, the transmembrane flux was found

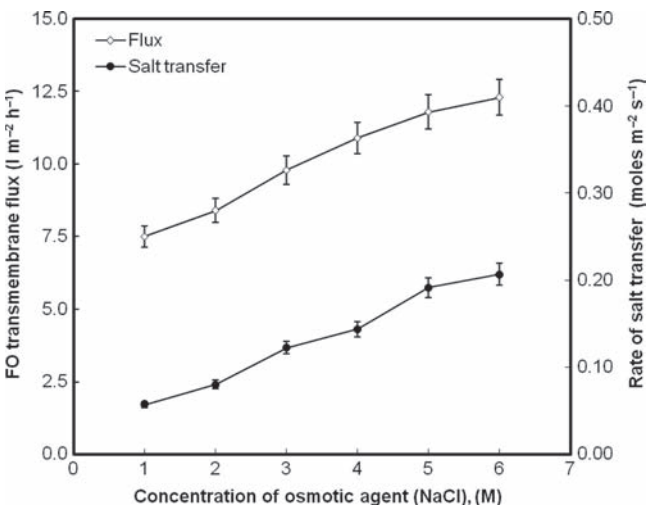

Fig. 4. Effect of osmotic agent concentration on transmembrnae flux with salt transfer in forward osmosis membrane.

to increase from 0.32 to 0.65 l/m^{2}h and from 10 to 12.7 l/m^{2}h, respectively. During the experiments, the flow rate and concentration of osmotic agent was maintained at 125 ml/min and 6.0 M, respectively. The concentration of osmotic agent and physical properties (like density and viscosity) were kept constant throughout the experiment. The change in flux was not found to be significant ($p < 0.05$) at for the increase in feed flow rate up to 75 ml/min, however, it was found to be significant beyond that value for both the membrane process (Fig. 5a).

The effect of osmotic agent flow rate on transmembrane flux is as presented in Fig. 5b. The transmembrane flux was found to increase from 0.37 to 0.89 l/m^{2}h and 11.4 to 12.5 l/m^{2}h with an increase in osmotic agent flow rate 50 ml/min to 125 ml/min for osmotic membrane distillation and forward osmosis, respectively. The osmotic agent concentration and feed flow rate during the experiments were maintained at 6.0 M and 125 ml/min, respectively. The increase in flux with an increase in velocity may be attributed to the reduction of concentration polarization effect due to the reduction in hydrodynamic boundary layer thickness [1,26].

In case of osmotic membrane distillation, the overall mass transfer coefficient (K_{omd}) and heat transfer coefficients (U) were found to increase with an increase in feed or osmotic agent flow rate (Table 1). The increase in transfer coefficients may be attributed to reduction in hydrodynamic boundary layer thickness thereby increasing the driving force across the membrane [11,30].

3.4 Performance of osmotic membrane distillation and forward osmosis in large scale

Anthocyanin extract was concentrated using the conditions (125 ml/min feed as well as the osmotic agent flow rate and 6.0 M sodium chloride as osmotic

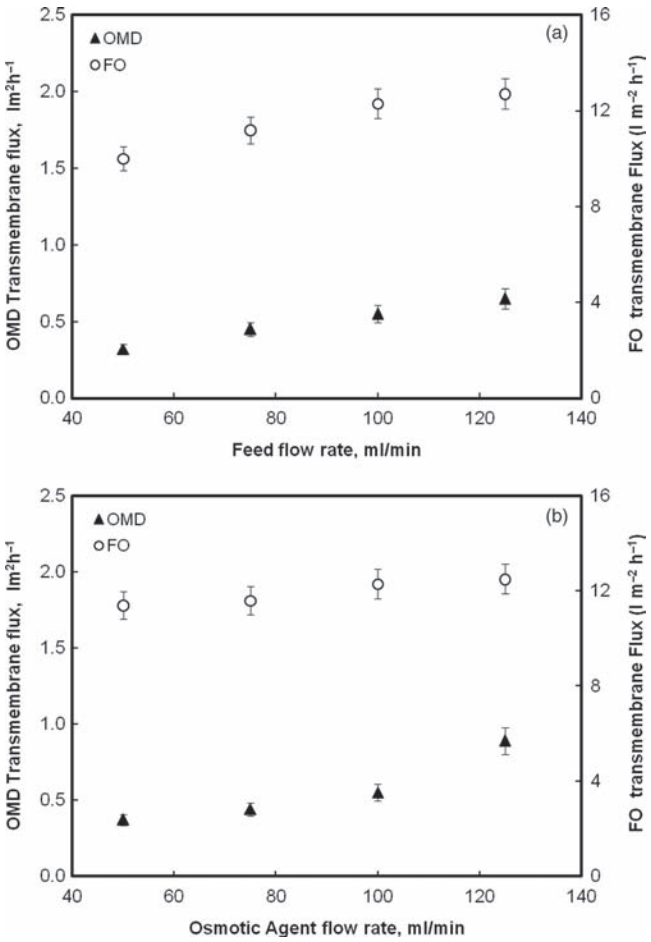

Fig. 5. Effect of (a) feed flow rate, (b) osmotic agent flow rate on transmembrane flux of forward osmosis and osmotic membrane distillation membrane process.

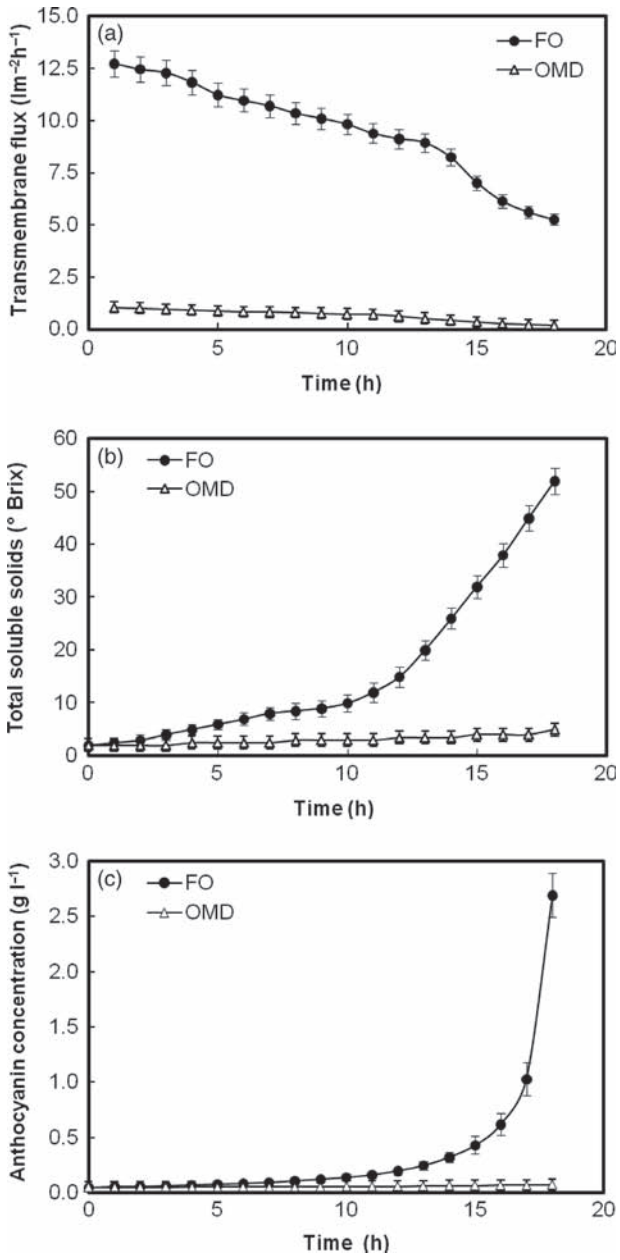

Fig. 6. Variation in (a) Flux (b) Total soluble solids (c) Anthocyanin concentration during concentration of anthocyanin from kokum extract by direct osmosis membrane process and osmotic membrane distillation.

agent) in a large scale experiment for both the membrane processes. Around 2000 ml of the crude anthocyanin extract (anthocyanin concentration 49.63 mg/l, 2°Brix) was concentrated up to 18 hours. The transmembrane flux and concentration were measured at every hour interval during the concentration. The final anthocyanin concentrations achieved were 72 mg/l (5°Brix) and 2.69 g/l (52°Brix) in case of osmotic membrane distillation and forward osmosis, respectively (Fig. 6a and b). Similarly, red radish colorant was concentrated up to 17 °Brix from an initial concentrate of 1.3 °Brix using forward osmosis membrane process by Rodriguez Saona et al [6]. Sugar solutions was also concentrated to a concentration factor of 5.7 by Garcia-castello et al.[35]. The transmembrane flux was found to decrease with time due to increased feed concentration, which in turn was responsible for the reduced driving force across the membrane.Further, increase in transmembrane flux can be obtained by application of acoustic field [34]. The physico-chemical properties of fresh anthocyanin extract as well as concentrated using osmotic membrane distillation and forward osmosis are shown in Table 2. This indicates that rate of sodium chloride transfer in case of forward osmosis was 0.21 moles/m^2 s, whereas no transfer of sodium chloride was observed in case of osmotic membrane distillation (Table 2).

The reconstitution of the extract was carried out by addition of distilled water to the concentrated extract produced by osmotic membrane distillation or forward

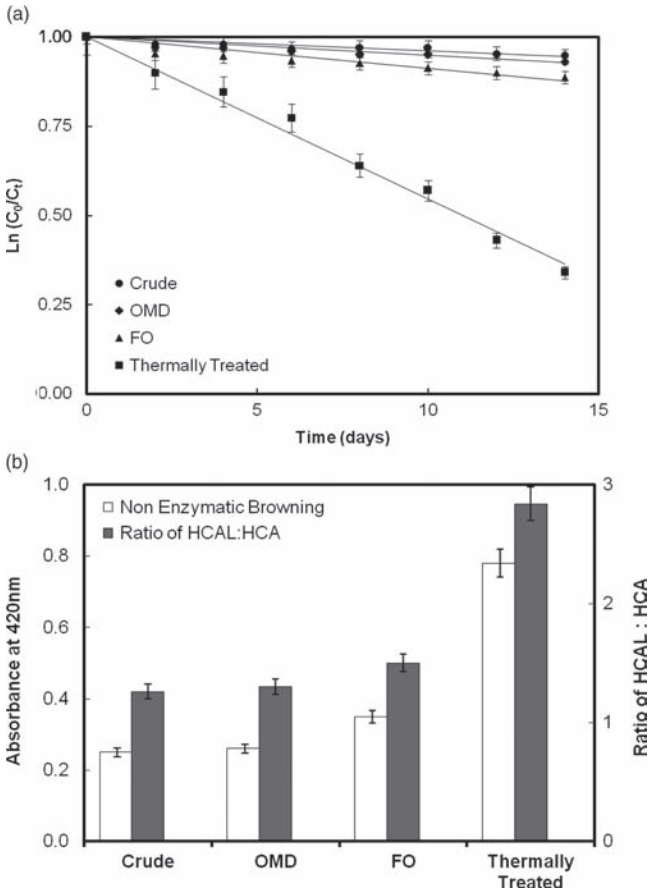

Fig. 7. (a) Effect of stability of anthocyanin pigments of kokum, (b) Non-enzymatic browning and degradation constant for anthocyanin pigments of kokum.

osmosis till the extract concentration was similar to that of the initial concentration. The reconstitute extract properties were found to be as that of the fresh extract.

3.5 Comparison of concentrate produced by membrane process with thermally concentrated sample

The degradation of anthocyanin was found to follow first order kinetics. The degradation constant for concentrate produced by forward osmosis (8.0×10^{-3} day^{-1}) was almost eight times higher than the thermally concentrated sample (63.0×10^{-3} day^{-1}, Fig 7a). Non-enzymatic browning index for thermally concentrated sample was found to be 0.78, whereas it was 0.35 for the concentrate produced by forward osmosis and for fresh kokum extract, it was 0.25 (Fig 7b). The non-enzymatic browning index of thermally concentrated sample was higher due to excessive exposure of sugar present in kokum extract to process temperature during thermal treatment. Moreover, after thermal concentration of kokum extract ratio of HCA lactone to HCA (2.84:1, Fig 7b) was found be high as compared to concentrate produced using forward osmosis (1.50:1, Fig 7b). These results clearly indicate that the concentration of kokum extract using forward osmosis has advantages over the thermally concentration in terms of higher stability, lower browning index and less conversion of HCA.

4. Conclusion

The effect of various process parameters such as osmotic agent concentration, flow rate of feed and osmotic agent on transmembrane flux during the concentration of anthocyanin extract by osmotic membrane distillation and forward osmosis process were studied. In case of forward osmosis and osmotic membrane distillation process, the anthocyanin was concentrated from 49.63 mg/l to 2.69 g/l and 72 mg/l, respectively. Forward osmosis resulted in higher transmembrane flux; however, it was coupled with 0.21 moles/m^2 s rate of sodium chloride migration. However, no transfer of sodium chloride was observed in case of osmotic membrane distillation. It may be concluded that even though forward osmosis yields high concentration of the product for a given time as compare to osmotic membrane distillation, but it results in migration of osmotic agent in the feed side. Whereas in case of osmotic membrane distillation, transmembrane flux is low, but no transfer of osmotic agent takes place. Hence, the selection of these two techniques may be done based on the advantages and disadvantages of both the processes, allowable limit of the osmotic agent as well as characteristic of the product. The concentrate obtained using forward osmosis membrane process has advantages over the thermally concentration in terms of higher stability, lower browning index and less conversion of hydroxycitric acid to lactone form.

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Nomenclature

a_f	bulk water activity at feed side
a_{OA}	bulk water activity at osmotic agent side
a_{fm} ,a_{OAm}	bulk water activity near membrane surface
C_o	initial anthocyanin concentration (mg/L)
Cp	specific heat of feed or osmotic agent (J/mole K)
C_t	anthocyanin concentration at specified time (mg/L)

d_p	membrane pore diameter (m)
h_f	heat transfer coefficient for feed side (Wm^2/K)
h_{OA}	heat transfer coefficient for osmotic agent side (Wm^2/K)
h_{mp}	heat transfer coefficient for membrane (392.86 Wm^2/K)
ΔHv	change in latent heat of vaporization for water (J/mole)
J_{FO}	transmembrane flux during forward osmosis (L/m^2h)
J_{omd}	transmembrane flux during osmotic membrane distillation (L/m^2h)
k_f	mass transfer coefficient at feed side (m/s)
k_{mp}	membrane mass transfer coefficient ($2.5X10^{-10}$ m/sPa)
k_{OA}	mass transfer coefficient at osmotic agent side (m/s)
K_D	degradation constant (per day)
K_{omd}	overall mass transfer coefficient (m/sPa)
K_r	resistivity of membrane support layer (d/m)
K^T_{gas}	thermal conductivity of gas (W/mK)
$K^T_{polymer}$	thermal conductivity of membrane material (W/mK)
N_{Nu}	Nusselt Number
N_{Pr}	Prandtl Number
N_{Re}	Reynolds Number
N_{Sc}	Schmidt Number
N_{Sh}	Sherwood Number
p_{fm} p_{OAm}	partial vapor pressure near membrane surface (Pa)
Q_{omd}	heat flux in osmotic membrane distillation (W/m^2)
R	the gas constant (8314 J/mole K)
$T_{f,}$ T_{OA}	bulk temperature of feed and osmotic agent (K)
T_{fm}, T_{OAm}	corresponding temperature near the membrane surface (K)
u	velocity of the fluid (m/s)
U	overall heat transfer coefficient (Wm^2/K)

Greeks

δ	membrane thickness (m)
ε	porosity
μ	dynamic viscosity (Pa s)
π_{OA}	osmotic pressure at osmotic agent (Pa)
π_f	osmotic pressure at feed solution (Pa)
ρ	density (kg/m^3)
τ	tortuosity factor

Subscripts

f	feed
m	membrane
OA	osmotic a gent

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