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ORIGINAL ARTICLE

Assessment of factors influencing the concentration of betacyanin from *Opuntia ficus-indica* using forward osmosis

Concentration of betacyanin using forward osmosis

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Abstract Betacyanin is the red-violet pigment possesses potent antiradical and antioxidant properties. Globally, natural colorants have gained much interest than synthetic colours due to their adverse ill effects. The study aimed to assess membrane technology for the concentration of betacyanin pigment from cactus pear employing forward osmosis. The effect of process parameters such as feed and osmotic agent solution (OAS) flowrate and temperature on betacyanin concentration was investigated using factorial design. Maximum concentration of betacyanin was obtained with 150 mL/min feed flowrate, 50 °C feed temperature, 150 mL/min OAS flowrate and 50 °C OAS temperature. Further, sodium chloride was the best OAS that concentrated betacyanin from 898 to 1325 mg/L with a transmembrane flux of 1.13 L/m^2 h. Physico-chemical characteristics imply high retention of antioxidant activity and other nutrients during concentration process. The results revealed the suitability of forward osmosis for the concentration of betacyanin from *Opuntia ficus-indica* using cellulose acetate membrane.

Keywords *Opuntia ficus-indica* · Betacyanin · Concentration · Factorial design of experiments · Forward osmosis

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Introduction

Betacyanin is one of the principle compounds for red colour stimulating the appetite and attractive in nature formed as a condensed product of cyclodopa with betalamic acid (Strack et al. 2003). Moreover, betacyanins are reported to exhibit antioxidant activity (Tesoriere et al. 2009), induces anti-proliferation in human chronic myeloid leukemia cell line (Sreekanth et al. 2007), anti-inflammatory effect (Gentile et al. 2004), inhibits mast cell degranulation (Chauhan et al. 2015), and reduces hepatic cholesterol levels in rats (Wroblewska et al. 2011). Betacyanin is better known as a natural food colorant, ideal for low acid dairy food products (Herbach et al. 2006). Natural red betanin pigment from beetroot is a Food and Drug Administration, US and European Union approved food additive (E162) and used in confectionaries, drinks and dairy products (Neelwarne 2012). However, commercially available red beet betalain powder perceived to have substandard colour, deep earthy flavour (Geosmin and Pyrazines) and low yield (Nunes et al. 2015). These complications have gained interest towards betalains from cactus pear due to its varied colour spectrum, absences of earthy flavour, minimal water and soil requirement and potential antioxidant pigments.

Fruit juices are concentrated using downstream processing to attain improved shelf life and nutritive value. Conventional methods employed for concentration of fruit juice especially thermal methods affects the product standard and supremacy. Though, chromatography technique is effective, it is expensive and results in low recovery (Nakkeeran et al. 2011). Hence, there exist a strong entail to develop an economically feasible, energy efficient and easily scalable method with minimal deterioration of natural pigment. Membrane filtration process such as ultrafiltration, reverse

osmosis and integrated membrane process were used for concentration of bioactive compounds. However, these membrane processes require high pressure and endure high concentration polarization and membrane fouling (Nayak and Rastogi 2010). Athermal osmotic membrane process, forward osmosis (FO) is an innovation in the field of membrane separation that operates at ambient pressure and capable of concentrating liquid foods to a greater extent without fouling the membrane and deteriorating the bioactive compound (Raghavarao et al. 2005).

FO is an osmotic pressure driven membrane process capable of concentrating thermolabile bioactive compounds through a non-porous semipermeable membrane without deteriorating bioactive compounds. Advent of new generation membranes led to commercial exploitation of forward osmosis (Babu et al. 2006). The significance of forward osmosis over other membrane technology is higher flux and concentration rate with minimal fouling and energy requirement (Nayak and Rastogi 2010). These distinguished advantages have resulted, its usage in food processing for concentration and purification of liquid foods and natural pigments as well as in pharmaceuticals to enrich active compounds as typical osmotic drug-delivery system (Babu et al. 2006). However, literatures reported that process parameters play an important role in concentration and transmembrane flux during processing. In light of the above, attempts were made on the assessment and optimization of process parameters to attain maximum concentration, transmembrane flux and concentrate recovery of betacyanin by considering the effect and response table, interaction graphs, analysis of variance and response optimizer technique to concentrate betacyanin from *Opuntia ficus-indica* employing forward osmosis.

Materials and methods

Materials

Opuntia ficus-indica was collected from Vedaranyam, Tamilnadu, India and stored in sealed polyethylene bags at − 20 °C until processing. Cellulose acetate membrane was procured from M/s. Tech Inc, India. Sodium chloride (NaCl), calcium chloride ($CaCl_2$), potassium chloride (KCl), magnesium sulfate ($MgSO_4$), and ammonium bicarbonate (NH_4HCO_3) were procured from M/s. Himedia, India. All other chemicals used were of analytical grade.

Methods

Extraction of Betacyanin

Opuntia ficus-indica was washed, peeled and mashed using food processor for 30 s. The seeds were removed by

Table 1 2^k full factorial design for betacyanin concentration employing forward osmosis experimental responses and predicted values

Run No.	Coded parameters				Responses[a]									Statistical values[a]					
	A	B	C	D	Transmembrane flux (L/m^2 h)			Concentration factor			Recovery (%)			Transmembrane flux (L/m^2 h)		Concentration factor		Recovery (%)	
					S-1	S-2	Avg	S-1	S-2	Avg	S-1	S-2	Avg	P	R	P	R	P	R
1	− 1	− 1	− 1	− 1	0.56	0.56	0.56	1.01	1.01	1.01	95	95	95	0.51	0.05	1.01	0.00	89	6
2	1	− 1	− 1	− 1	0.69	0.69	0.69	1.01	1.01	1.01	81	81	81	0.78	− 0.08	1.02	0.00	87	− 6
3	− 1	1	− 1	− 1	0.58	0.58	0.58	1.00	1.00	1.00	83	83	83	0.65	− 0.07	1.00	0.00	83	0
4	1	1	− 1	− 1	0.99	0.99	0.99	1.00	1.00	1.00	72	72	72	0.92	0.07	1.00	0.00	72	0
5	− 1	− 1	1	− 1	0.76	0.76	0.76	1.03	1.03	1.03	80	80	80	0.78	− 0.02	1.01	0.02	86	− 6
6	1	− 1	1	− 1	1.08	1.08	1.08	1.00	1.00	1.00	96	96	96	1.05	0.04	1.02	− 0.02	90	6
7	− 1	1	1	− 1	0.76	0.76	0.76	1.09	1.09	1.09	85	85	85	0.80	− 0.04	1.11	− 0.02	86	− 1
8	1	1	1	− 1	0.97	0.97	0.97	1.13	1.13	1.13	81	81	81	1.07	− 0.10	1.11	0.02	81	0
9	− 1	− 1	− 1	1	0.56	0.56	0.56	1.03	1.03	1.03	86	86	86	0.51	0.05	1.05	− 0.03	89	− 3
10	1	− 1	− 1	1	0.76	0.76	0.76	1.20	1.20	1.20	94	94	94	0.78	− 0.01	1.17	0.03	91	3
11	− 1	1	− 1	1	0.66	0.66	0.66	1.23	1.23	1.23	98	98	98	0.65	0.01	1.20	0.03	102	− 4
12	1	1	− 1	1	0.90	0.90	0.90	1.29	1.29	1.29	98	98	98	0.92	− 0.01	1.32	− 0.03	95	3
13	− 1	− 1	1	1	0.69	0.69	0.69	1.12	1.12	1.12	87	87	87	0.78	− 0.08	1.10	0.02	80	7
14	1	− 1	1	1	1.11	1.11	1.11	1.19	1.19	1.19	81	81	81	1.05	0.06	1.21	− 0.03	88	− 7
15	− 1	1	1	1	0.90	0.90	0.90	1.33	1.33	1.33	99	99	99	0.80	0.10	1.36	− 0.02	99	0
16	1	1	1	1	1.11	1.11	1.11	1.50	1.50	1.50	99	99	99	1.07	0.04	1.47	0.03	98	1

[a]Values adjusted to significant numbers, A-OAS temperature (°C), B-OAS flowrate (mL/min), C-BFS temperature (°C), D-BFS flowrate (mL/min). S-1 Experiment set 1; S-2 Experiment set 2; Avg average of S-1 and S-2; P predicted value; R residual value

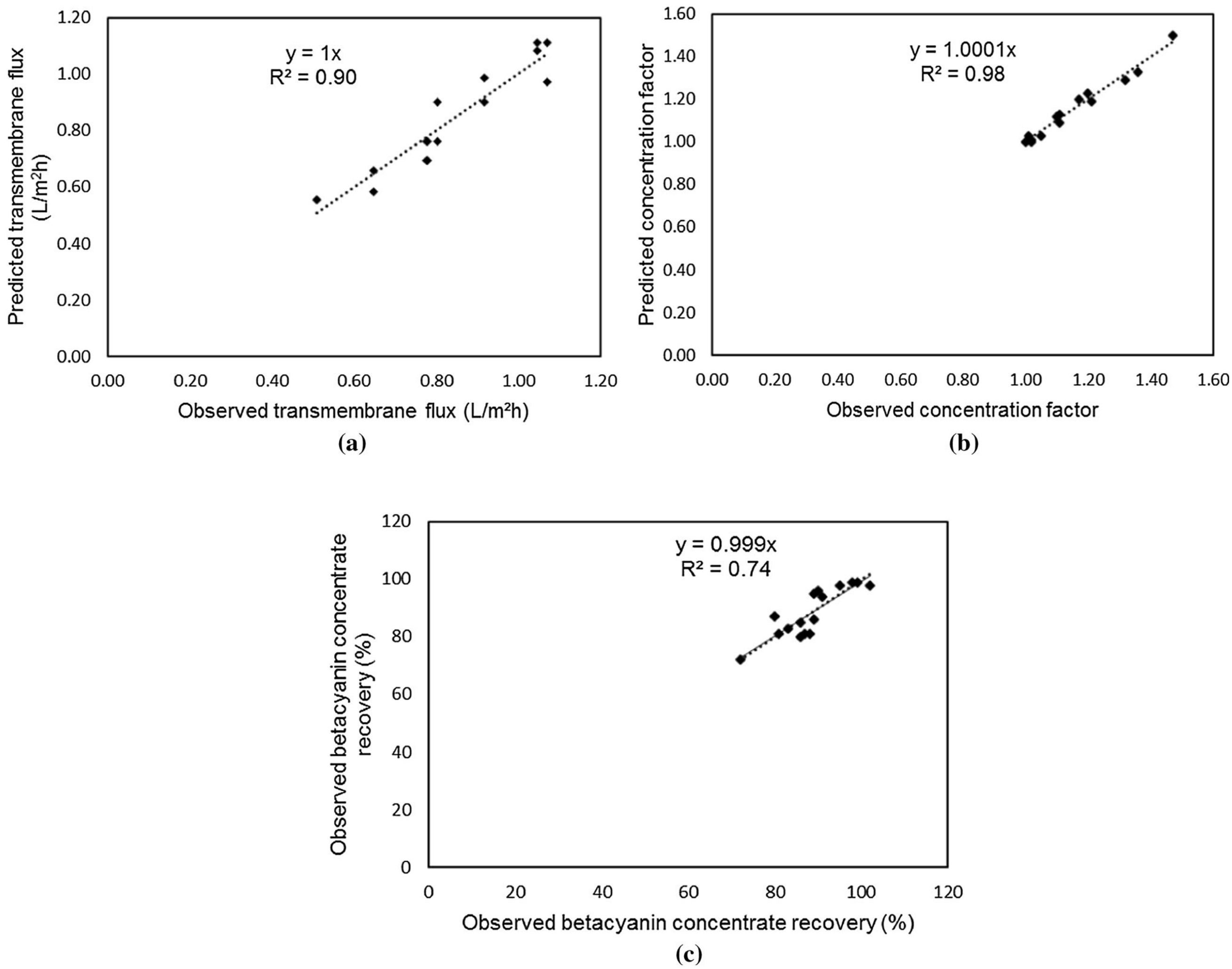


Fig. 1 The relationship between predicted and observed response values of **a** transmembrane flux, **b** concentration factor, **c** concentrate recovery for concentrating betacyanin using forward osmosis

filtration through muslin cloth and stored at 4 °C. The pulp was centrifugated at 1500×*g* for 10 min and supernatant containing betacyanin was used for further processing.

Experimental set up

Concentration experiments were run on a flat membrane module with a membrane area of 36 cm^2. Cellulose acetate membrane was placed over a nylon mesh supported between the silicon gasket and acrylic plate and frame. Betacyanin feed solution (BFS) and the osmotic agent solution (OAS) was subjected to recirculation mode using peristaltic pump in co-current flow. The BFS fed on the active side of the membrane whereas OAS fed on the support layer side of the membrane. The ratio of BFS to OAS was maintained at 1:5 for all the experiments. All the experiments were carried out for a period of 4 h and transmembrane flux was calculated every hour by increase in the volume of OAS. The process parameters such as OAS temperature (A), OAS flowrate (B), BFS temperature (C) and BFS flowrate (D) were optimized using statistical tool MINITAB 16.

Optimization using factorial method

In this study, four independent process parameters were optimized using 2^k full factorial experimental design by MINITAB 16. Each independent process parameters was set at high (+ 1) and low (1) value. The actual and coded values of independent parameters (A, B, C and D) used for the experimental design are A and C, + 1 = 50 °C, − 1 = 20 °C; B and D, + 1 = 150 mL/min, − 1 = 50 mL/min. Design of experiments was generated using factorial design. The experiments were performed in duplicates (2^4 = 16, duplicates 32 runs) and response parameters (transmembrane flux, concentration factor and concentrate

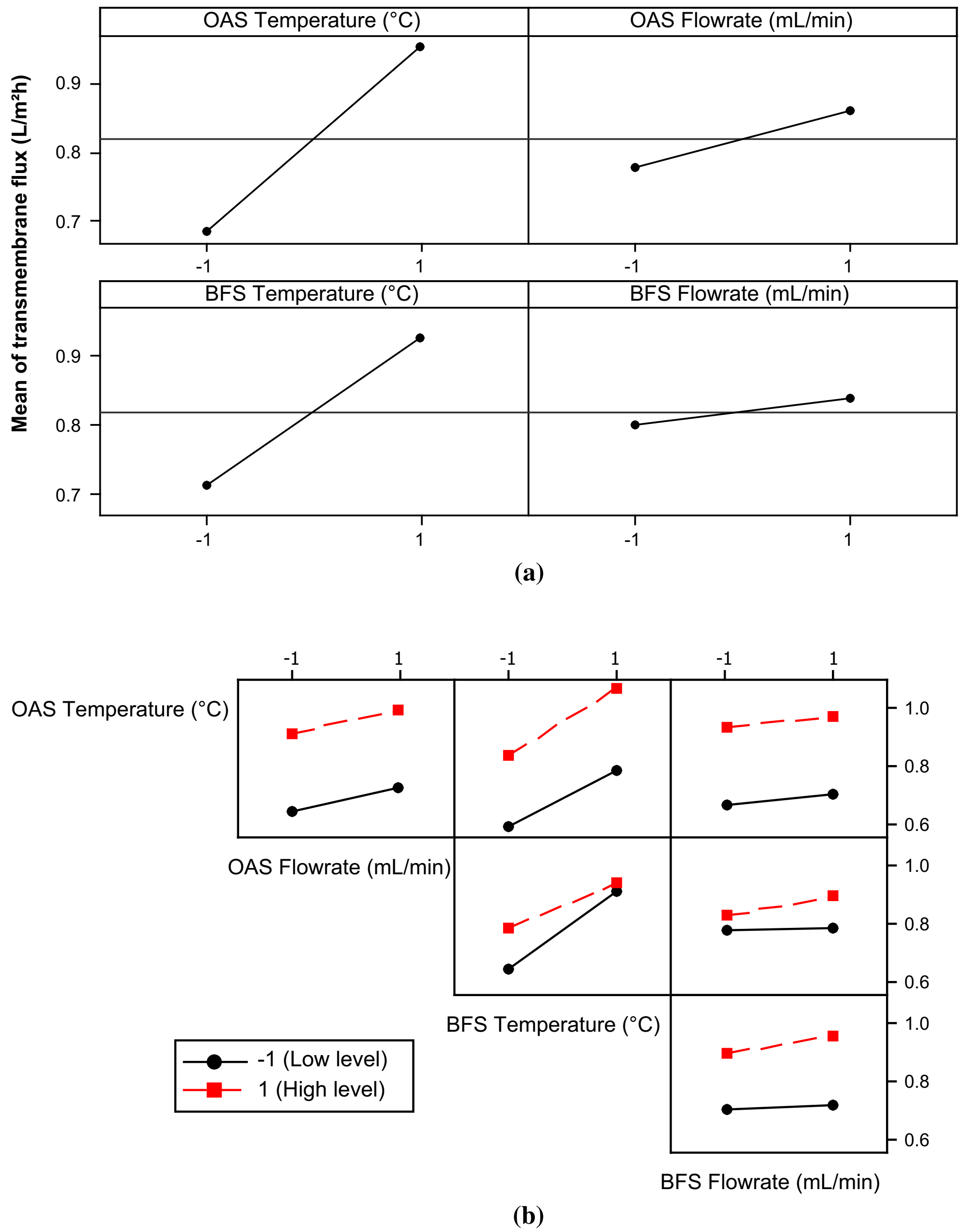


Fig. 2 Transmembrane flux main (**a**) and interaction effect plot (**b**), betacyanin concentration factor main (**c**) and interaction effect plot (**d**) and betacyanin concentrate recovery main (**e**) and interaction effect plot (**f**)

recovery) were recorded. 5.2 M NaCl was used as a standard OAS compound during optimization.

Determination of transmembrane flux, recovery and concentration factor

The transmembrane flux (Zhao et al. 2011), recovery (Nakkeeran et al. 2011) and concentration factor (Zhao et al. 2011) was determined by using the following formulae.

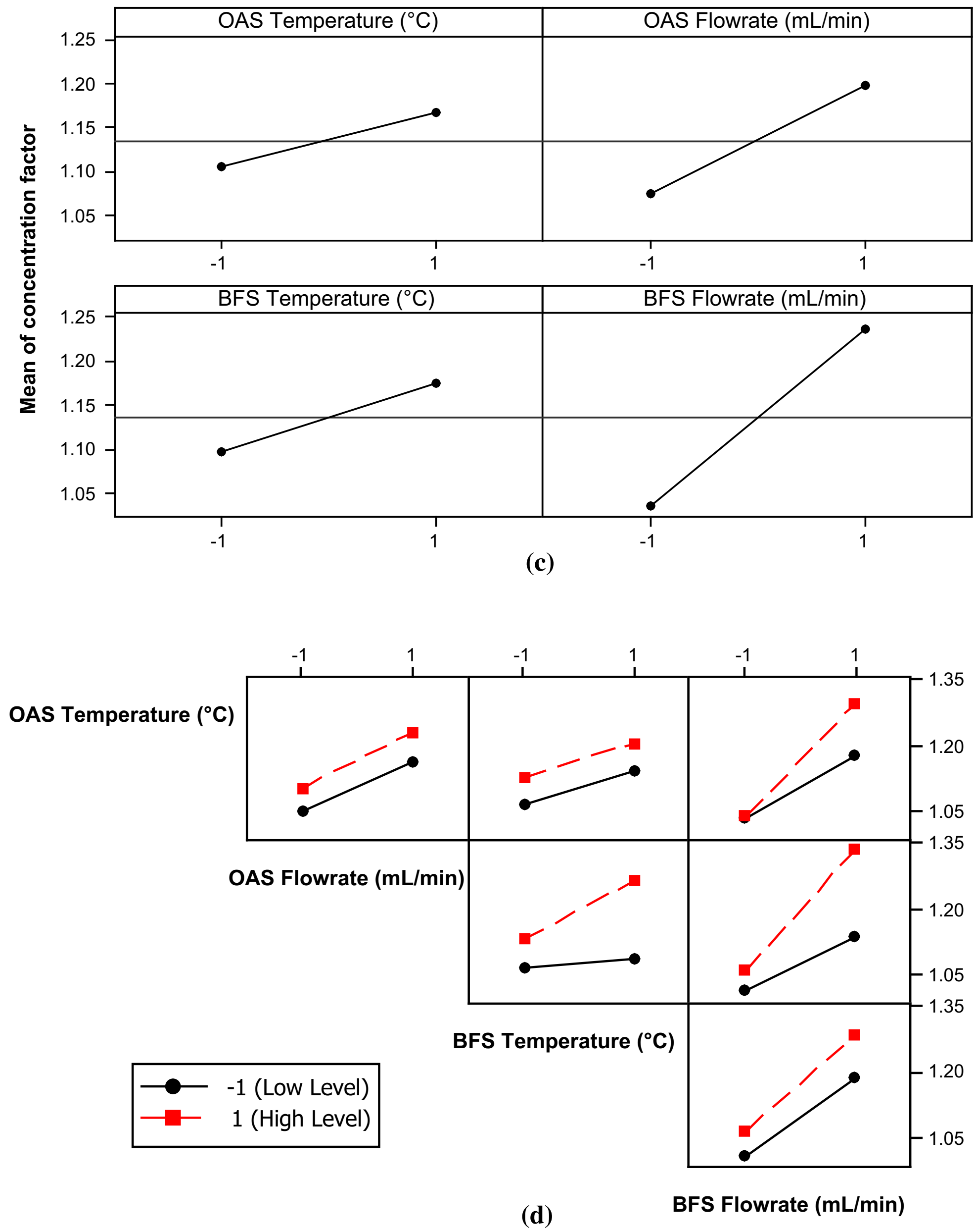
$$Transmembrane\ flux\ (L/m^2h) = \frac{\Delta V}{A \times t}$$

$$Recovery\ (\%) = \frac{V_f \times C_f}{V_i \times C_i} \times 100$$

$$Concentration\ factor = \frac{C_f}{C_i}$$

where ΔV is the increase in OAS volume after 4 h, A is the active membrane area and t is the time taken for concentrating BFS, V_i, V_f, C_i and C_f are initial and final volume and concentration of BFS, respectively.

Fig. 2 continued



Determination of Betacyanin content

Betacyanin concentration (BC) was determined using molar extinction coefficient of betacyanin. BC was expressed as mg/L and calculated by using the following equation (Singh and Hathan 2017).

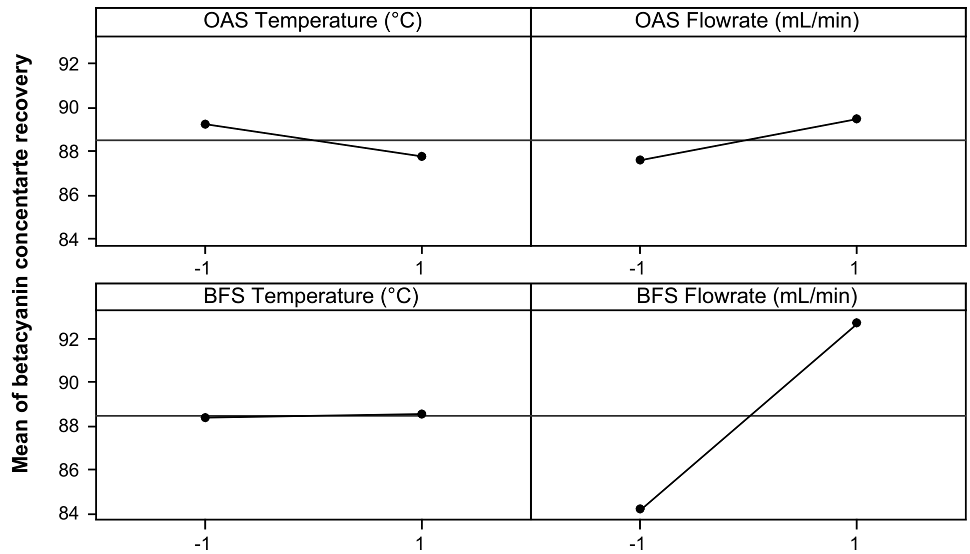
$$BC(mg/L) = \frac{A \times DF \times MW}{\varepsilon \times L} \times 1000$$

where A is absorbance at 536 nm, DF is dilution factor, L is path length of the 1 cm cuvette, MW is molecular weight of betacyanin (550 g mol^{-1}), and ε is molar extinction coefficient of betacyanin (60,000 L mol^{-1} cm^{-1}).

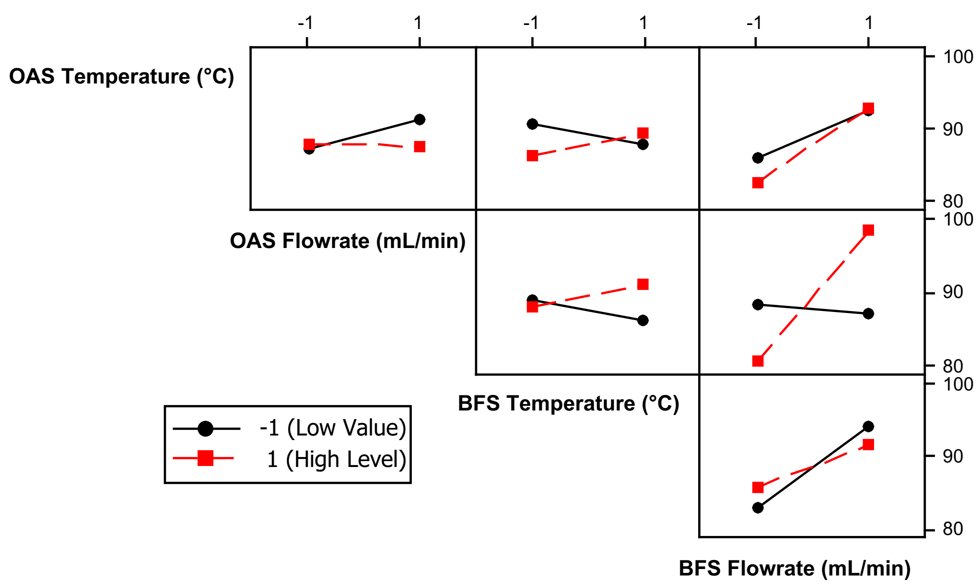
Analyses

Total Soluble Solids (TSS) and pH of the samples were determined using hand held refractometer and pH meter, respectively. Samples were analysed for protein, total carbohydrates, total phenolic content, flavonoid content and antioxidant activity using bradford method (Spector 1978), phenol–sulfuric acid method (Rao and Pattabiraman 1989), folin–ciocalteau colorimetric method (Ainsworth and Gillespie 2007), aluminium chloride colorimetric method (Pękal and Pyrzynska 2014) and 1,1-diphenyl-2-picrylhydrazyl (DPPH) assay (Garcia et al. 2012), respectively.

Fig. 2 continued



(e)



(f)

Results and discussion

Statistical interpretation

The 2^4 full factorial design, experimental responses and predicted values for betacyanin concentration using forward osmosis are shown in Table 1. Using analysis of variance (ANOVA), a model was chosen and fitted to each response. The model equations in terms of coded notations are presented below.

The model regression equation for transmembrane flux (R_{TF}) is

$$R_{TF}\ (L/m^2h) = 0.81901 + 0.13411A + 0.04123B + 0.10634C - 0.02908BC$$

The model regression equation for betacyanin concentration factor (R_{CF}) is

$$R_{CF} = 1.13508 + 0.03046A + 0.06159B + 0.03905C + 0.10042D + 0.02852AD + 0.02829BC + 0.04056BD + 0.01030CD$$

The model regression equation for betacyanin concentrate recovery (R_R) is

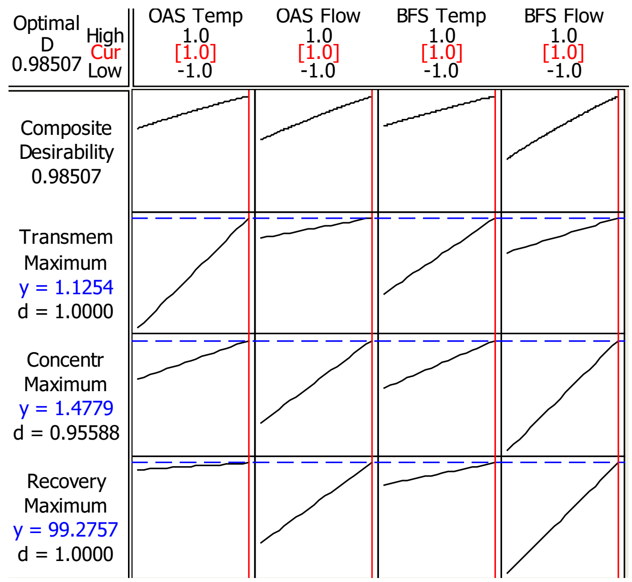


Fig. 3 Optimization plot for concentration of betacyanin using forward osmosis

$$R_R(\%) = 88.489 - 0.751A + 0.949B + 0.093C + 4.262D - 2.193AB + 1.489AC + 0.912AD + 1.5531BC + 4.830BD - 1.429CD$$

Using the model equations, predicted values were generated and presented in Table 1. The relationship between predicted and observed response values for concentration of betacyanin employing forward osmosis is shown in Fig. 1. The model is considered as a good fit if R^2 is at least 0.80 (Büyükakinci and Topkaya 2009). This relationship determines the capability of the model equation represented in the system. In this study, R^2 was determined as 0.90, 0.98 and 0.74 for transmembrane flux, concentration factor and concentrate recovery, respectively after processing. From this relationship, the model significantly fitted.

Significance analysis

The result of ANOVA was carried out for one-way and two-way interactions, since higher order interactions did not reveal any significance for engineering experiments (Antony 2014). The average of duplicates was considered for the analysis. Factorial fit and significance of the process is determined using sum of squares, degree of freedom (DF), effects, coefficients, F-value and p value in the ANOVA analysis. Most of the results showed p value less than 0.05 and found significant. The influence of 2-way interaction on the transmembrane flux was found insignificant in concentrating betacyanin using forward osmosis. The lack of fits in ANOVA results is to identify the variation of data around the fitted model. The statistical influence on the estimated effects of main parameters and its interaction on the response is analysed for 95% confidence level.

Influence of independent parameters on the process

Influence of four independent parameters was investigated using main and interaction effect plots. From main effect plots, temperature of BFS has the most effect on both betacyanin concentrate recovery and transmembrane flux whereas BFS flowrate has the most effect on concentration factor. The main and interaction effects of each parameters on transmembrane flux, betacyanin concentration factor and concentrate recovery are shown in Fig. 2. The main effect plots represent the deviations of the average between the levels and shows the parameters that are significant at 95% confidence level. When the effect of a factor is positive, response increases as the factor changes from low level to high levels. Similarly, the effect of a factor is negative, response decreases as the factor changes from low level to high level. From Fig. 2a, c, e, it is deduced that higher the vertical line, higher the change of responses from low level to high level. The length of the vertical line directly correlated with the significance of the factor. Increase in OAS and BFS temperature and flowrate increased the concentration, recovery and productivity of betacyanin during forward osmosis. The interaction is effective when the change in response from low level to high levels is not parallel with the response of the other factor (Bingol et al. 2010). The interactive effect of process parameters on transmembrane flux is depicted in Fig. 2b, betacyanin concentration factor is showed in Fig. 2d and betacyanin concentrate recovery is depicted in Fig. 2f.

Optimization of process parameters for the concentration of betacyanin

The optimized process parameters were identified using response optimizer in to improve the concentration of betacyanin from *Opuntia ficus-indica* employing forward osmosis. The optimized plot with maximum desirability of 0.98 was obtained and illustrated in Fig. 3. From this plot, it was determined that at higher temperature and flowrate of OAS and BFS maximum concentration of betacyanin was obtained.

Selection of osmotic agent solution

Selection of good OAS with relatively high solubility, greater driving force, non-toxic in nature, economically feasible for recovery and low internal concentration polarization are the major challenges faced by FO process. Under optimum process conditions, various OAS were

Table 2 Assessment and physico-chemical characterisation of various OAS on betacyanin concentration using forward osmosis

Assessment parameters	Crude	NaCl	KCl	$CaCl_2$	$MgSO_4$	NH_4HCO_3
OAS concentration	–	5.2	5.2	5.2	5.2	5.2
Driving force (kPa)	–	23,969	26,761	36,684	26,767	26,764
Betacyanin concentration factor	–	1.5	1.4	1.5	1.1	1.1
Transmembrane flux (L/m^2 h)	–	1.13	1.12	1.14	0.69	0.49
Betacyanin concentrate recovery (%)	–	99	98	99	89	94
pH	3.6	3.5	3.2	3.6	3.4	4.0
TSS (°Brix)	1	6	8	5	3	3
Carbohydrate (g/L)	1389	2099	2002	1488	642	1277
Protein (µg/mL)	175	250	190	155	139	69
Phenol (µg/mL)	426	726	800	400	489	300
Flavonoids (µg/mL)	49	70	83	54	58	41
Betacyanin concentration (g/L)	0.90	1.32	1.30	1.33	1.00	0.99
Antioxidant activity (%)	84	89	76	85	85	78

OAS osmotic agent solution; *TSS* total soluble solids

attempted to obtain maximum concentration of betacyanin using FO and the results are given in Table 2. Among the OAS tested, calcium chloride exhibited maximum concentration of betacyanin. However, sodium chloride (1.32 g/L) exhibited slightly lower concentration of betacyanin compared to calcium chloride (1.33 g/L) but it is economically suitable in terms cost and recovery of betacyanin concentrate. Thus, sodium chloride was construed as the optimum OAS.

The physico-chemical properties of crude betacyanin and concentrated betacyanin using forward osmosis are presented in Table 2. Based on physico-chemical analysis and response of various OAS used for concentration of betacyanin, sodium chloride exhibited its suitability as better OAS for the concentration of betacyanin with 89% of antioxidant activity employing forward osmosis membrane process.

Conclusion

Forward osmosis membrane technology was found effective in concentrating betacyanin from *Opuntia ficus-indica*. Two-level full factorial design was able to reduce the number of runs than the traditional optimization experiments with one factor at a time. Statistical tool was able to generate model mathematic equation that gives improved and closer confirmation with the responses. The effect of process parameters like OAS flowrate and temperature, feed flowrate and temperature on transmembrane flux and betacyanin concentration employing FO was studied. Higher flowrate and temperature of the feed and OAS exhibited to enhance the transmembrane flux and betacyanin concentration. In this study, sodium chloride was found suitable OAS for concentrating betacyanin employing forward osmosis for 4 h of processing. Therefore, forward osmosis technology could be used for the concentration of natural pigment with minimum degradation and energy requirements.

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