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Optimisation of Concentration of Cucumber Juice Using Progressive Freeze Process as a Non-Thermal Process

Nur Nabila Hanani Mohd Rosdi, Norshafika Yahya, Zurina Mohamad, Yanti Maslina Mohd Jusoh, Norzita Ngadi, Zaki Yamani Zakaria, Mazura Jusoh*
School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, UTM, 81310 Skudai, Johor, Malaysia
mazura@cheme.utm.my

Concentration process of cucumber juice is an essential step in cucumber extracts and juice production in the industry in order to minimise the volume and weight for storage and handling purposes. Progressive freeze concentration (PFC) is a non-thermal concentration process that can be used in which water content in the juice will be frozen out in the form of an ice block layer by layer. The ice crystallisation process forms ice crystal lattice that rejects all impurities and in turn will leave behind highly concentrated cucumber juice. This research aimed to optimise the operating parameters involved in concentration of cucumber juice via PFC. The operating parameters involved were operation time, initial concentration, coolant temperature and speed of stirrer. Optimization of the PFC process was carried out with the effective partition constant, K as the indicator of the performance by using Response Surface Methodology (RSM) in STATISTICA software. Highest total phenolic content (TPC) increment achieved was 38.83 % with operating condition at -12 °C of coolant temperature, 413 rpm of stirrer speed, 37.8 min of operation time, and 11 mg/mL of initial concentration and lowest effective partition constant, K value obtained was 0.261 with operating condition at -13.8 °C of coolant temperature, 435 rpm of stirrer speed, 30 min of operation time, and 10.5 mg/mL of initial concentration. The results were supported with good value of R-squared obtained which was 0.85899 for K-value and 0.79365 for TPC increment. The linear effect of operation time was found to be the most significant factor to the response in this study. This work has clearly shown that PFC has potential to be used in concentration of cucumber juice as a non-thermal operation.

1. Introduction

The demand for concentrated cucumber juice and extract is increasing especially in Malaysia due to Its high phenolic content, contributing to its high anti-oxidant properties (Chandra et al., 2014). Phenolic content also has protective function against heart disease and cancer (Abbas et al., 2017). Its potential in cosmetic, pharmaceutical, food and beverage industries urged researchers to put efforts in developing new technology to produce high quality cucumber concentrate.

Currently available concentration methods have some drawbacks which affect the process efficiency and cucumber juice concentrate quality. Evaporation is the process of concentrating fruit juice, evaporated at lower boiling point under vacuum condition because fruit juices are known as heat sensitive material. The colour, aroma, nutritional value and taste of the concentrated juice are usually deteriorated by the heat applied in the process (Ashurst, 2016), provided by the condensation of vapour (Prakash et al., 2019). The bonds that holds the water molecules are broken by the energy applied at boiling point of water (Fellows, 2017). Evaporation requires high energy consumption which could lead to high operation cost due the usage of large amount of heat (Prakash et al., 2019). As the process involves high temperature, it is not suitable for thermally degradable compounds and low vapour pressure components, especially food and beverages that has aromatic components.

Reverse osmosis (RO) is a membrane separation technology and it is driven by a concept of movement of water against concentration gradient where the solvents move from a lower to higher concentration gradient of solutes through membrane (Rastogi., 2016). RO occurs if the pressure applied is higher than the osmotic

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pressure in the solution. Most of the energy required in the process is mechanical energy and it does not involve phase changes (Shibuya et al., 2015). RO has more advantages compared to evaporation which increases the retention of aroma of the product, requires less energy consumption, causes less thermal damage to the product and is low in capital and investment cost, but the major disadvantages of RO is in reaching the ability to concentrate the fruit juice up to standard products produced by evaporation due to the high osmotic pressure limitation (Rastogi, 2016) and the membrane tends to be clogged with the soluble and insoluble materials in the food solution. Once this happens, the membrane needs to be replaced which will result in increased maintenance cost (Miyawaki et al., 2016).
A new alternative method which is freeze concentration (FC) has become more favorable in the industries. FC is also known as a non-thermal process which freezes out the water content in the solution into ice crystals (Samsuri et al., 2015). It was found to be the best method in concentrating sensitive materials due to the low temperature condition in the process that will reduce the losses due to volatility and chemical reaction. According to Miyawaki et al. (2016), FC process occurs when ice crystal is formed and grows from an aqueous solution and expel the impurities to form pure ice crystal. There are two techniques of FC which are suspension freeze concentration (SFC) and progressive freeze concentration (PFC). The difference between SFC and PFC are in the form of the development of ice crystal where SFC starts the ice growth from seed ice usually produced by a scraped surface heat exchanger (SSHE) which finally will produce small ice crystals as a suspension in the mother liquor. PFC on the other hand produces a single large ice block that is formed layer by layer on a cooled surface, so that separation between ice crystal and concentrated solution will be easier. Despite these attractive attributes, the process has low productivity and produces low quality concentrated product, urging more extensive further research. In this work, a new apparatus has been designed, namely Multiple Probe Cryo-Concentrator (MPCC). The research objective was to determine the optimum value of the four factors involved in studying the efficiency of this new apparatus which included coolant temperature, stirrer speed, operation time and initial concentration of cucumber juice. Besides, it is also to reveal the factor that is most significant and influential towards both responses which are effective partition constant (K-value) and TPC increment.

2. Materials and method

2.1 Materials

In this work, cucumber juice was used as raw material. Fresh cucumbers were purchased from Maslee Express, a local supermarket in Johor, Malaysia. Ethylene glycol as a coolant liquid was used in the water bath after being mixed with distilled water (50/50 volume to volume ratio) to maintain the temperature of cucumber juice. Folin-Ciocalteu reagent and anhydrous sodium carbonate powder were used in UV-vis spectrophotometer to analyse the phenolic content.

2.2 Experimental procedure

The newly designed MPCC as shown in Figure 1, consisted of a coolant gas system which was responsible for cooling through suitable refrigerant probes with attached motorised stirrer at the bottom of solution tank. The probe set was immersed in a solution tank and it can rotate the probes that have five fingers at 180°.

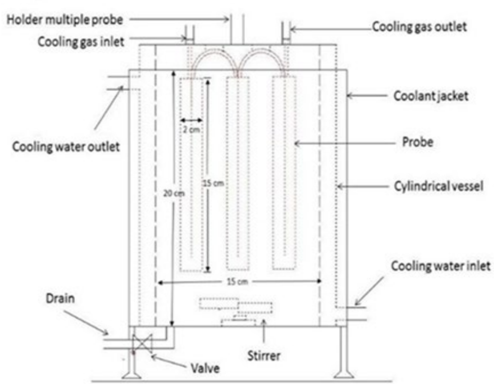

Figure1: Schematic diagram of multiple probe cryo-concentration system

The stirrer speed used was in the range of 250-400 rpm in order to maximise the ice formation on the outer surface of the probe and form a well-mixed solution. In the first step, cool cucumber juice was placed in the solution tank and the temperature needs to be kept constant, close to the freezing temperature at 2 °C (to avoid ice contamination) which was provided by the coolant liquid used in the outer tank jacket. Next, the refrigerant was started up by setting up the desired value of temperature and condition in order to supply cooling to the MPCC system and until the temperature was reached, the probes were immersed in the solution and it started to rotate at 180°. When cooling was adequate, the ice crystals started to develop on the outer surface of the probes and a concentrated cucumber juice was left behind in the tank. A thermocouple was used to measure the temperature of the solution and the data obtained was displayed online throughout the experiment for easy monitoring. The experiment was stopped after applying the designated cooling rate, stirrer speed, certain time duration and initial concentration. The concentrated cucumber juice was collected and the layer of ice crystal was thawed. The concentrated cucumber juice was then analysed for total phenolic content and concentration by using UV-Vis spectrophotometer at absorbance 730 nm.

2.3 Experimental design and statistical analysis

Based on the preliminary result, the range of values for the four variables including coolant temperature (X_1), stirrer speed (X_2), operation time (X_3) and initial concentration (X_4) were designed. The variables and their coded and uncoded values are presented in Table 1.

Table 1: Experimental range and coded value of variables

Variables	Symbol	- α	-1	0	+1	- α
Coolant temperature (°C)	X_1	-14	-12	-10	-8	-6
Stirrer speed (rpm)	X_2	250	300	350	400	450
Operation time (min)	X_3	20	25	30	35	40
Initial concentration (mg/mL)	X_4	4	6	7	8	10

3. Results and discussion

3.1 Optimization variables and model verification

The newly designed apparatus which carried out the PFC process was targeted to improve the concentration performance as well as provide better productivity of the product. Response surface methodology (central composite design) in STATISTICA software was used to predict the optimum values that give the highest process efficiency for each operating parameter. The method of least squares was used to estimate the regression coefficient values and a mathematical model was generated for each response (K-value and TPC increment) by using the coefficients obtained in the regression model. The respective mathematical models are as shown in Eq(1) and Eq(2) below:

$$Y_1 = 1.797582 + 0.05957\ X_1 – 0.001076X_2 – 0.034648\ X_3 + 0.002544\ X_4 +0.004169\ X_1^2 – 2.54E07\ X_2^2 + 0.000068\ X_3^2 + 0.000343\ X_42 + 0.000088\ X_1X_2 - 0.000166\ X_1X_3 + 000385X_1X_4 + 0.000044\ X_2X_3 - 0.000059\ X_2X_4 + 0.001225\ X_3X_4 \quad (1)$$

$$Y_2 =-9.38797 - 1.76125X_1 – 0.010684\ X_2 – 0.020021\ X_3 + 0.38699\ X_4 -0.11439\ X_1^2 + 0.00001\ X_2^2 + 0.00681\ X_3^2 + 0.02525\ X_4^2 + 0.00115\ X_1X_2 - 0.03278\ X_1X_3 - 0.05562\ X_1X_4 - 0.00125\ X_2X_3 - 0.00489\ X_2X_4 + 0.00292\ X_3X_4 \quad (2)$$

where Y_1 is the predicted value of the effective partition constant (K) and Y_2 for TPC increment. X_1, X_2, X_3 and X_4 represent coolant temperature, stirrer speed, operation time and initial concentration. R-squared obtained for K-value, Eq(1), was 0.85899 and TPC increment, Eq(2), was 0.79365; both showing good accuracy of the regression models.

It is necessary to identify the operating parameters that affect the PFC process significantly after the regression model adequacy has been evaluated. It can be measured based on F-values or p-values obtained from the regression analysis of the response. The model term is more significant if larger magnitude of the F-values and smaller p-value were obtained (Montgomery, 2001). The factors are considered important and significant if the p-value obtained is less than 0.05 which provides 95 % confidence for all results. On the contrary, if the values are greater than 0.1, the factors are considered not significant (Figueroa et al., 2012). From Table 2, it can be concluded that linear terms of stirrer speed, operation time and initial concentration and the quadratic term of coolant temperature are significant model terms.

3.2 Three-dimensional (3D) response surface plot analysis

The effects of four process variables that are responsible for the performance efficiency in the PFC system could also be demonstrated by using three-dimensional (3D) surface plot diagram. The response, which in this case are K-value and TPC increment were obtained against two variables, while the other two variables were held constant at its middle range to visualise the 3D response surface. Figure 2a and 2b show some samples of the plot. Figure 2a shows interaction between coolant temperature (-6 to -14 °C) against stirrer speed (250 to 450 rpm) and their effects towards K-value and TPC increment, and they were conveyed according to the generated regression model. Another two factors which are operation time and initial concentration involved in the PFC system were kept constant at its middle range at 30 min and 7 mg/mL. The response surface plot shows a strong interaction between stirrer speed and coolant temperature. From Figure 2a, it can be seen that lower K-value was observed with increasing stirrer speed at coolant temperature in the range between -10 to -14 °C.

Table 2: Regression analysis for K-value and TPC increment

Factor	K-value				TPC increment			
	Coefficient estimation	Standard error	F-value	p-value	Coefficient estimation	Standard error	F-value	p-value
X_1 (L)	0.059568	0.045657	0.78089	0.218633	-9.38797	26.34959	6.05045	0.007284
X_1^2 (Q)	0.004169	0.001541	7.31812	0.020466	-1.76125	1.56299	4.70035	0.283791
X_2 (L)	-0.001076	0.002097	34.86196	0.006178	-0.11439	0.05276	14.27480	0.005296
X_2^2 (Q)	0.000000	0.000002	0.01062	0.919761	0.10684	0.07178	0.00402	0.164752
X_3 (L)	-0.034648	0.019549	5.86221	0.010399	0.00001	0.00008	2.67897	0.950566
X_3^2 (Q)	0.000068	0.000247	0.07679	0.786834	-0.20021	0.66924	0.65084	0.770396
X_4 (L)	0.002544	0.059561	7.76050	0.009666	0.00681	0.00844	1.86567	0.436907
X_4^2 (Q)	0.000343	0.002740	0.01563	0.902750	0.38699	2.03899	0.07249	0.852926
X_1X_2	0.000088	0.000064	1.85987	0.199896	0.02525	0.09380	0.27366	0.792724
X_1X_3	-0.000166	0.000644	0.06616	0.801754	0.00115	0.00220	2.21163	0.611261
X_1X_4	0.000385	0.002146	0.03225	0.860754	-0.03278	0.02204	0.57312	0.165067
X_2X_3	0.000044	0.000027	2.85252	0.119342	-0.05562	0.07348	2.02191	0.464930
X_2X_4	-0.000059	0.000090	0.47495	0.504996	-0.00125	0.00088	2.77011	0.182773
X_3X_4	0.001225	0.000900	2.03594	0.181382	-0.00489	0.00294	0.00985	0.124235

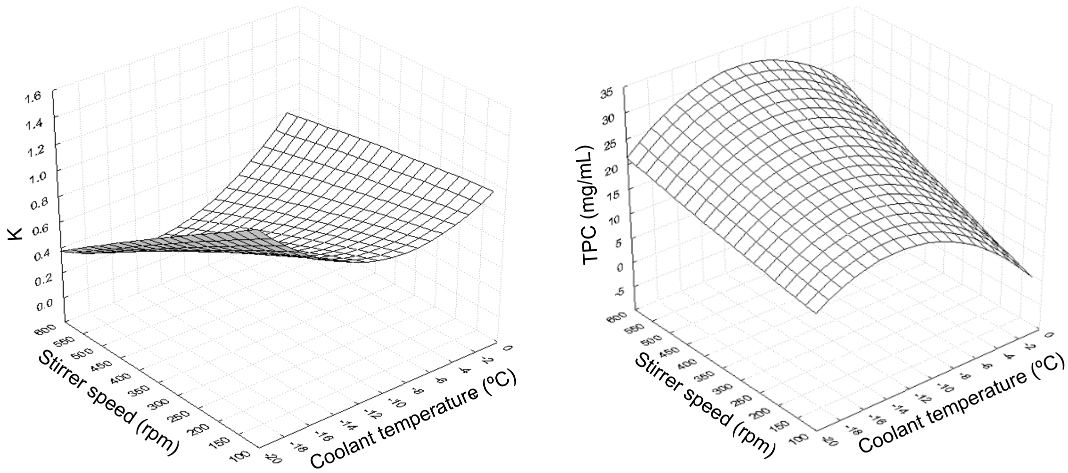

Figure 2: (a) 3D surface plot for K and (b) 3D surface plot for TPC increment

The K-value increased when the coolant temperature applied was higher than the optimum region. The K-value began to increase sharply at coolant temperature lower than -14 °C for all stirrer speed values. The trend of the plotted graph has a wide range for operation time but provide a narrow range for coolant temperature which explains that operation time variable is not to specify the optimum range of the PFC process compared to the coolant temperature. Coolant temperature factor has more significant effect towards K-value and initial concentration has lower significant effect and it is just to complete the interaction of both factors. The optimum range for K-value was found to be lower than 0.5 with coolant temperature in the range of -8 to -12 °C at operation time higher than 40 min. Stirrer speed and operation time which were the other two factors studied were kept constant at 350 rpm and 30 min. It can be observed that K-value has its lowest point at lower than 0.5 with decreasing initial concentration of cucumber juice solution in the range of -8 to -12 °C for coolant temperature. This condition is supported by the theory stated by Zhang and Liu (2018) where the rate of ice formation is controlled by coolant temperature. The solute becomes easily trapped if coolant temperature is too low and as a result, K-value is increased.

For the effects of stirrer speed and operation time on the effective partition constant, K at fixed coolant temperature of -10 °C and initial concentration of 7 mg/mL it was revealed that the optimum condition which gives a low K-value lies at stirrer speed higher than 450 rpm and operation time not more than 40 min. The response for stirrer speed against initial concentration with the other two factors maintained at -10 °C and 30 min showed that low value of K was achieved with stirrer speed more than 350 rpm and low initial concentration of cucumber juice solution. However, interaction between operation time and initial concentration towards K-value with the other two variables kept constant at -10 °C for coolant temperature and 350 rpm for stirrer speed revealed that operation time of higher than 30 min and low initial concentration were determined as the optimal condition to achieve low K-value which indicates high efficiency performance of the PFC system. This condition can be explained in relation to initial concentration and operation time giving the effect towards the system performance which required a longer process time to form ice on the probe's cold surface due to the freezing point depression of the solution and the phenomenon of supercooling (Miyawaki et al., 2016).

Total phenolic content (TPC) increment is the second response investigated through the 3D response surface of the fitted model illustrated in Figure 2b to evaluate the interaction between the level of each factor and the response. The interactions were considered significant if the shape of the 3D surface plot obtained is elliptical and negligible if the contour plot is circular in shape (Anupam et al., 2011).

From Figure 2b, it can be observed that the coolant temperature gives more influence to the process response than stirrer speed because the shape of coolant temperature plot is narrower than the shape of stirrer speed plot. Higher value of stirrer speed gave larger value of the increment of TPC. The optimum condition for the interaction falls between the range of -8 to -10 °C for coolant temperature and stirrer speed of more than 400 rpm. If the coolant temperature applied is too low, it could lead to high solute inclusion into the ice formed due to fast ice growth rate. The effects of coolant temperature and operation time on the TPC showed that the TPC increment increased when operation time was increased, and the best range for coolant temperature was approximately -14 to -12 °C. Operation time higher than 40 min is good for moderate coolant temperature for high TPC increment. High rate of crystal formation is induced when both coolant temperature and operation applied are too low due to large temperature difference between the coolant and solution. This situation can be supported with the low TPC increment obtained when the operation time applied is less than 15 min with coolant temperature lower than -16 °C. The interaction between coolant temperature and initial concentration on the increment of TPC was also observed with the other two factors at 350 rpm and 30 min. Adequate growth of ice crystals was achieved at the optimum condition at low initial solution concentration below than 5 mg/mL and coolant temperature range of -8 to -12 °C. Optimum increment of TPC can be achieved because the phenomenon of constitutional supercooling did not occur in this condition, and dendritic ice crystal structure can be prevented.

The mutual interactive behavior of stirrer speed and operation time can also be observed where the highest increment of TPC was achieved at stirrer speed larger than 400 rpm and operation time longer than 35 min. As the stirrer speed and the operation time increase, the TPC increment in the concentrate is increased. This is due to the facts that the solutes are kept away from the ice-liquid interface which gives enhancement of the heat transfers of the ice crystal. Low contaminant of solute is achieved in the ice layer formed. Other than that, the ice thickness formed is increased when longer operation time is applied. Solid form of high ice purity can be obtained when high stirrer speed is applied. It could wash away the solutes at the dendritic ice structure. From the analysis of the interaction between initial concentration and stirrer speed on the TPC increment it can be evaluated that initial concentration did not give a significant effect towards the response. This can be supported with the high p-value which is 0.43907. However, higher stirrer speed applied could result in higher TPC increment. This is because, high shear force from the high liquid flowrate could carry the solute away in the solution without being trapped in the ice layer formed. Also, the shear force could easily wash away the solutes trapped in the dendritic ice structure (Yahya et al., 2017). The interactive effect of operation time and initial concentration on the increment of TPC at a fixed coolant temperature of -10 °C and stirrer speed of 350 rpm, it has been shown that the optimum condition for highest TPC increment can be achieved at initial concentration lower than 4 mg/mL and operation time higher than 35 min.

3.3 Optimum condition verification

The optimum conditions for the highest TPC generated by the software were -12 °C for coolant temperature, 413 rpm for stirrer speed, 37.8 min for operation time, and 11 mg/mL for initial concentration. As for the lowest K value, the optimum conditions generated were -13.8 °C for coolant temperature, 435 rpm for stirrer speed, 30 min for operation time, and 10.5 mg/mL for initial concentration. Based on experimental result conducted using the optimum values predicted, the value obtained for K-value was 0.261, which when compared to the predicted value of 0.224, is relatively very close to each other. On the other hand, the highest TPC increment observed was 38.83 % compared with predicted value obtained at 41.27 %. The percentage error for the TPC increment is only 5.91 %. The model generated is considered satisfactory to accept the optimum condition analysis for this experiment and can be implemented for future studies.

4. Conclusion

The optimization process in this study was carried out by using STATISTICA software, based on central composite design (CCD) in Response Surface Methodology (RSM). The study involved in analyzing the interaction between four independent variables; coolant temperature, stirrer speed, operation time and initial concentration with two responses which are effective partition constant, K and TPC increment. The regression model analysis had been done and model adequacy check had been analyzed. It was found that the R-squared value obtained for both responses, effective partition constant, K and TPC increment were 0.85899 and 0.79365. Both values were considered reasonable and satisfactory in evaluating the model validity. The best TPC increment achieved is 38.83 % and the lowest K-value obtained is 0.261 which indicates the highest efficiency performance achieved. The outcome from this study will be useful to govern the design and commercialization of future PFC process for other heat sensitive material.

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