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# Heat Transfer Model: Preservation of Antioxidant via Progressive Freeze Concentration

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Antioxidants have been a vital component of several pharmaceutical and food industries due to their numerous benefits such as reducing the risk of diseases. Cucumbers are known to contain considerable amounts of antioxidants and a significant amount of water, which increase the probability of microorganism growth. Therefore, it is essential to find out the best approach to reduce the water content and preserve the antioxidants in cucumbers. Progressive Freeze Concentration (PFC) is a concentration enhancement process, whereby impurities are removed in a single ice block. This research is intended to determine the effect of coolant temperatures (-2°C to -10°C) on the preservation of antioxidants in cucumbers using the PFC process. The antioxidant content in concentrated cucumber juice was assessed by the 2,2-Diphenyl-1-picrylhydrazyl (DPPH) assay. It was determined that the lower the coolant temperature used in the PFC process, the lower the amount of antioxidant content. The optimum coolant temperature was discovered at a temperature of -2°C, where the antioxidant activity percentage (AA%) was at 93.17 %. A heat transfer model to predict the mass of antioxidants procured was alsoconstructed from the study. Data comparison between experimental values and the model resulted in the Average Absolute Relative Deviation (AARD) value of 0.74% which is considered highly consistent. Therefore, the model constructed to predict the AA% of the concentrated cucumber juice with different coolant temperatures was successful.

## 1. Introduction

Antioxidants are molecules that fight free radicals in the human body which are produced through the oxidation reaction. Antioxidants are essential to the human body as excessive production of free radicals can lead to over-concentration and cause oxidative stress, which harms the body (Lobo et al., 2010). Cucumbers are vegetables that have considerable amounts of antioxidants. Multiple research and analysis have been conducted in the chemical industries to find ways to fully utilize the content of antioxidants in cucumbers that are highly beneficial to the human body.

Progressive Freeze Concentration (PFC) is a process that concentrates a solute in an aqueous solution through partial freezing of the solution which separates the solid and liquid phases, resulting in a concentrated solution (Munson-Mcgee, 2014). The progressive formation of ice crystal layers forms a single ice block on a cooled surface, which ensures an easier separation between the ice crystal and concentrated solution (Rosdi et al., 2021).

The 2,2-Diphenyl-1-picrylhydrazyl (DPPH) method was developed by Blois (1958) and was further modified by Brand-Williams et al., (1995). The DPPH is a stable, long-lived free radical, and possesses a deep purple colour property and strong absorption of around 517 nm (Akar et al., 2017). As the purple colour of the DPPH radical

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solution reacts with antioxidants, a reduced form of the DPPH solution which is pale yellow in colour allows the spectrophotometric determination of the antioxidant activity of the tested medium (Gupta, 2015).
Although the determination of the antioxidant in a food sample has been well developed and widely implemented, there is still a lack of studies on how heat transfer affected the amount of antioxidant recovery in the PFC process. Therefore, the objective of this research was to determine the effect of coolant temperature on the preservation of antioxidants in cucumbers via the PFC process. Additionally, this research was also conducted to analyse the heat transfer involved in the PFC process.

## 2. Materials and methodology

### 2.1 Preparation of cucumber juice

50 g of fresh Japanese cucumbers were sliced and blended with 500 ml of water using an electric blender (LB20ES, Waring, USA). The blended cucumber juice was then sieved to extract the cucumber juice.

### 2.2 Preparation of DPPH solution

Preparation of 0.1 mM of DPPH solution was done by dissolving 3.94 mg of DPPH into 100 ml of methanol in a volumetric flask (Samsuri et al., 2020). The solution was then stored in a volumetric flask and wrapped with aluminium foil to prevent any contact and reaction with light. The solution was also stored in a darkroom and was only taken out before the spectrophotometry test.

### 2.3 Progressive freeze concentration method

The experimental instrument consists of a refrigerated bath, cylindrical crystallizer, stirrer, retort stamp, and clamp. The coolant used for the PFC process was a mixture of 50% ethylene glycol and 50% distilled water. The coolant was then set to the desired temperature. The cylindrical crystallizer was clamped to a retortstand and 500 ml of cucumber juice was poured into the cylindrical crystallizer. The speed of the stirrer was adjusted to its desired speed (175 rpm) and the timer was started simultaneously for 15 minutes.
After a fixed time of 15 minutes, the stirrer was stopped and taken off the refrigerated bath. The concentrated cucumber juice was collected and stored in a beaker and was measured for its volume. 10 ml of the concentrated solution was measured and transferred into a test tube for DPPH assay. The experiment was repeated with different coolant temperatures (-2°C, -4°C, -6°C, -8°C, and -10°C). Figure 1 shows the setup of the PFC process of cucumber juice.

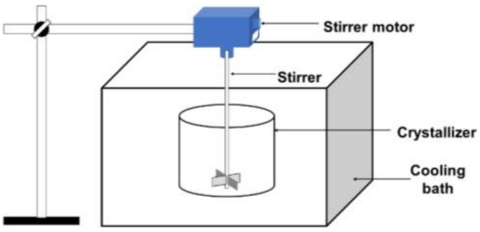



*Figure 1: PFC equipment setup*

### 2.4 Analysis

### 2.4.1 Antioxidant value

As the concentrated cucumber juice undergoes the DPPH assay, its absorption reading was conducted using the UV-Vis spectrophotometer at 517 nm (Pyrzynska & Pękal, 2013). 2.5 ml of concentrated cucumber juice was mixed with 1 ml of DPPH solution and its absorbance reading was measured and recorded. The radical scavenging activity for antioxidant value (AA%) can be calculated using Eq (1), where $A_{sample}$ is the absorbance reading of the solution, and $A_{control}$ is the absorbance reading of the DPPH solution with nothing added (blank).

$$\text{Scav. activity (AA\%)} = \left(1 - \frac{A_{sample}}{A_{control}}\right) \times 100\% \quad (1)$$

### 2.4.2 Heat transfer analysis

To develop the model in predicting the AA%, a few assumptions based on previous studies were made to simplify the development of the model (Samsuri et al., 2018).

1) All the heat transferred to or from the ice is utilized for the melting or freezing of the ice.
2) Ice crystal on the surface of the crystallizer offers resistance, but no thermal capacity.
3) The thickness of ice formed around the surface of the crystallizer is uniformly thick.
4) Physical properties of cucumber juice and ice, such as density, specific heat capacity, and viscosity do notchange during the PFC process.
5) The temperature gradient across the heat transfer surface is assumed to be linear.
6) Thermal property variation of the heat transfer surface material due to temperature change is negligible.
7) Loss of heat to the surrounding is negligible.
8) The temperature of the concentrated cucumber solution, $T_s$, during the PFC process is at 0 °C.

## 3. Results and discussion

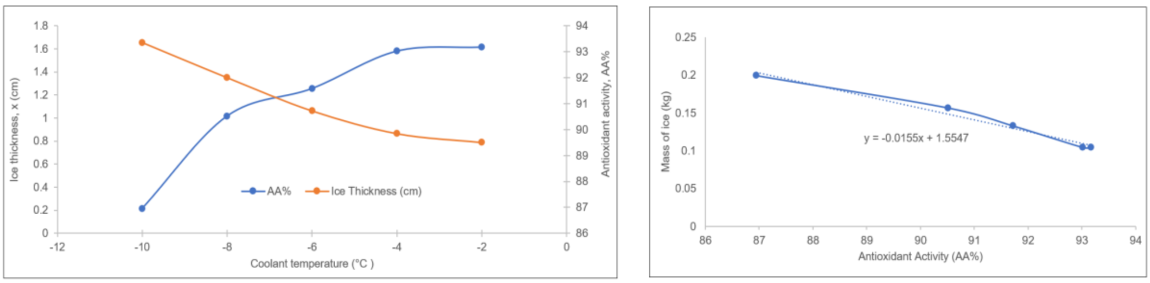
### 3.1 Relationship between coolant temperature and antioxidant activity of cucumber juice

In order to discover the relationship between coolant temperature and antioxidant activity, the other parameters such as operating time, stirrer speed, and initial concentration of cucumber juice were kept constant. The volumes of concentrated juice and ice produced were tabulated in Table 1. The collected concentrated cucumber juice was taken for a spectrophotometer test using the UV-Vis equipment to measure its concentration. From the data recorded in Table 1, the volume of ice increased with the decrease in temperature, which is in line with previous research findings (Miyawaki & Inakuma, 2021). However, the amount of ice formation also affected the antioxidant activity inside the cucumber juice. Therefore, the higher efficiency of ice formation does not lead to better extraction of antioxidants in the cucumber juice as the tendency for the solute (antioxidants) to be trapped in the ice formation increases (Mohd Rosdi et al., 2020).

*Table 1: Volume of concentrated juice and ice at different coolant temperatures*

| Temperature (°C) | -2 | -4 | -6 | -8 | -10 |
|---|---|---|---|---|---|
| Volume of conc. juice (ml) | 390 | 380 | 355 | 320 | 285 |
| Volume of ice (ml) | 110 | 110 | 140 | 165 | 210 |

From Figure 2(a), it is observed that the lower the coolant temperature used in the PFC process, the lower the antioxidant activity (AA%) found in the cucumber juice. The optimum temperature at which the highest amount of AA% was found in the cucumber juice is at -2°C with 93% of AA% detected, showing that at this temperature, most of the antioxidant is successfully preserved. Meanwhile, the least amount of AA% was found at a coolant temperature of -10°C. The decrease in coolant temperature led to an increase in ice thickness but a lower AA%. This would further support the discussion whereby the efficiency of the PFC process in terms of the separation of solute and impurities via ice formation does not necessarily lead to a high AA%. Although the PFC process was successful in terms of ice formation with the decrease in coolant temperature, however, a coolant temperature that is too low will reduce the antioxidant activity of the cucumber juice. Therefore, it is crucial to determine the optimum coolant temperature at which the maximum amount of antioxidant activity is detected while collecting the maximum amount of ice formed. Figure 2(b) correlates the relationship between the mass of cucumber juice obtained post-PFC process and their respective AA%. The graph highlights that the AA% decreased as the mass of cucumber juice collected decreased. This would further support the conclusion that the antioxidants were trapped in the formation of ice as the temperature of the coolant decreased.




(a) (b)

*Figure 2: Relationship between coolant temperature, antioxidant activity % and (a) ice thickness, and (b) ice mass*

### 3.2 Heat transfer analysis and model development

Figure 3 illustrates the proposed heat transfer activities for the PFC process. T represents the temperature for each layer of the interface, whereas $T_s$ is the temperature of the cucumber juice, $T_m$ is the temperature of the ice-liquid interface, $T_i$ is the temperature at the ice-vessel wall interface, $T_w$ is the temperature at the vessel wall-coolant interface and $T_c$ is the temperature of the coolant. Furthermore, q represents the heat transfer entering and leaving the cucumber juice. Lastly, dm/dt is the mass rate of formation of ice.

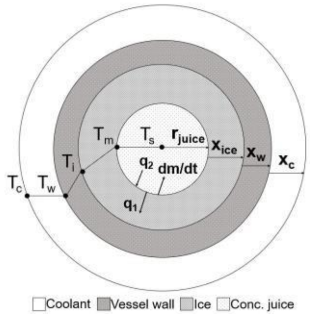



*Figure 3: Schematic diagram of heat transfer activities of PFC equipment*

### 3.2.1 Model formulation

The model for predicting the AA% in the cucumber is based on previous studies (Samsuri et al., 2018), with several modifications. The model was based on the basic understanding whereby the heat that is released by the ice, vessel wall, and coolant, $q_1$, is equal to the heat released by the cucumber juice, $q_2$, and the product of mass of rate of formation of ice, dm/dt, and its latent heat of fusion, $\Delta H$. The equation is expressed in Eq (2).

$$q_1 = q_2 + \left(\frac{dm}{dt}\right) \Delta H \quad (2)$$

Since $q_1 = U_o \Delta T$, and $q_2 = \Delta T/R$, Eq (2) can be further expanded into Eq (3),

$$U_o \Delta T = \frac{\Delta T}{R} + \left(\frac{dm}{dt}\right) \Delta H \quad (3)$$

where $U_o$ represents the overall heat transfer coefficient (W. $m^{-2}$. °$C^{-1}$), $\Delta T$ is the temperature difference (°C), and R is the resistance ($m^2$. °C. $W^{-1}$). Thus, Eq (3) can be expressed as Eq (4),

$$\left(\frac{T_m - T_c}{\left(\frac{r}{k.A}\right)_{ice} + \left(\frac{r}{k.A}\right)_{wall} + \left(\frac{r}{h.A}\right)_{coolant}}\right) = \left(\frac{T_s - T_m}{\left(\frac{1}{h.A}\right)_{juice}}\right) + \left(\frac{dm}{dt}\right) \Delta H \quad (4)$$

where, $x_{ice}$ is the thickness of the ice crystal (m), and $x_w$ is the thickness of the vessel wall (m). $A_{coolant}$ represents the surface area of the coolant ($m^2$), $A_{juice}$ is the surface area of the cucumber juice ($m^2$), $k_{ice}$ is the thermal conductivity of ice (W. $m^{-1}$. °$C^{-1}$), and $k_{wall}$ is the thermal conductivity of the vessel wall (stainless steel) (W. $m^{-1}$. °$C^{-1}$). $h_{coolant}$ and $h_{juice}$ are the convective heat transfer coefficient (W. $m^{-2}$. °$C^{-1}$) for the coolant and cucumber juice, respectively. This study follows the assumption from a previous study (Samsuri et al., 2018), where $T_w$ matches the average temperature between $T_c$ and $T_s$ since the two temperatures gave the most significant effect to $T_w$ as compared to the other temperatures. $T_m$ is also assumed be the water melting temperature (0°C). In addition, the composition of the ice crystal is assumed as pure water. Thus, Eq (4) is converted to,

$$M_{ice} = \left(\left(\frac{- T_c}{\left(\frac{r}{k.A}\right)_{ice} + \left(\frac{r}{k.A}\right)_{wall} + \left(\frac{r}{h.A}\right)_{coolant}}\right) - T_s \, (h.A)_{juice}\right) t \quad (5)$$

Using a simple mass balance, the masses of the concentrated cucumber juice and ice can be obtained. $M_T$ refers to the total mass of solution, which consists of the mass of ice ($M_{ice}$) and concentrated cucumber juice ($M_{conc.juice}$). Eq (6) shows the simplified equation after considering all the elements discussed. The experimental values are listed in Table 3 and constant values involved are listed in Table 4, respectively.

$$AA(\%)=\left(\frac{0.1742T_c}{\left(\frac{x}{2.2\,(A)}\right)_{ice}+447.11}\right)-64.52\left(M_T - M_{conc.\,juice}-1.555\right) \quad (6)$$

*Table 3: Data collected from PFC experiment*

| Temperature (°C) | $x_{ice}$ (m) | $A_{ice}$ ($m^2$) | $A_{conc.\,juice}$ ($m^2$) | $M_T$ (kg) | $M_{conc.\,juice}$ (kg) |
|---|---|---|---|---|---|
| -2 | 0.0079 | 0.0031 | 0.0112 | 0.4750 | 0.3705 |
| -4 | 0.0087 | 0.0034 | 0.0109 | 0.4655 | 0.3610 |
| -6 | 0.0106 | 0.0042 | 0.0102 | 0.4703 | 0.3373 |
| -8 | 0.0135 | 0.0052 | 0.0092 | 0.4608 | 0.3040 |
| -10 | 0.0165 | 0.0062 | 0.0082 | 0.4703 | 0.2708 |

*Table 4: Constant values*

| Parameter | Value | Unit |
|---|---|---|
| $k_{ice}$ | 2.2 | W/m. °C |
| $k_{wall}$ | 15 | W/m. °C |
| $h_{coolant}$ | 676.42 | W/ $m^2$. °C |
| $h_{conc.\,juice}$ | 2,273.45 | W/ $m^2$. °C |
| $A_{coolant}$ | 0.0473 | $m^2$ |
| $A_{wall}$ | 0.0071 | $m^2$ |
| $x_{wall}$ | 0.015 | m |
| ΔH | 334,000 | J/kg |
| t | 900 | s |

### 3.2.2 Error analysis

Table 5 displays the comparison between the AA% of the concentrated juice obtained from the experiment trials and the model in Eq ( 6). Both data from the experiment and model show a decrease in AA% with the decrease in coolant temperature. Thus, it can be concluded that the model can be used to forecast the AA% of a concentrated cucumber juice from a PFC process.

*Table 5: Comparison of AA (%) from model and experiment*

| Temperature (°C) | $AA_{model}$ (%) | $AA_{exp}$ (%) | $\left\lvert\frac{AA_{exp}-AA_{model}}{AA_{exp}}\right\rvert$ |
|---|---|---|---|
| -2 | 93.30 | 93.17 | 0.001 |
| -4 | 93.03 | 93.02 | 0.0001 |
| -6 | 92.93 | 91.72 | 0.009 |
| -8 | 89.13 | 90.52 | 0.015 |
| -10 | 86.11 | 86.95 | 0.010 |
| Total | | | Σ = 0.037<br>AARD = 0.74% |

The Average Absolute Relative Deviation (AARD) is used to determine the deviation between the data obtained from the model and the experimental values. Eq (7) expresses the equation for AARD.

$$AARD\ (\%)=\frac{1}{N}\sum_{i}^{N}\frac{\left|AA_{exp}-AA_{model}\right|}{AA_{exp}}\times 100\% \quad (7)$$

where N is the number of collected data. According to the data, the proposed model seems to have a good correlation with AARD value of 0.74%. The small value of AARD reflects a consistency between experimental data and predictable data. The AARD value less than 10% in margin of error is considered rational and acceptable (Khair et al., 2017). On a laboratory scale, AARD values below 5% are highly consistent (Lucas et al., 2004). Therefore, the model developed can be used to predict the AA% of the concentrated cucumber juice with varying coolant temperatures.

## 4. Conclusions

The extraction of antioxidants from cucumbers can be crucial as a means for preservation and prolonging their lifespan. The PFC process preserves the antioxidants with the removal of water which is one of the conditions for microorganisms to thrive. The coolant temperature has a significant effect on the antioxidant activity of cucumber in a PFC process. The lower the coolant temperature, the lower the antioxidant activity contained in the concentrated cucumber juice. It can be concluded that the optimum temperature at which contains the highest antioxidant activity percentage (93.17%) is obtained at -2°C. The model for predicting the AA% obtained was also successfully developed and can be used to predict the preservation of antioxidant of cucumber juice as the AARD value calculated was 0.74%. AARD values that are less than 5% on laboratory scale are considered highly efficient. This model shows the high accuracy in predicting the antioxidant recovery when varies temperature of coolant has been applied and it can be good guidance in determining the antioxidant activity particularly in the food industry.

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