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Integration of Maceration and Freeze Concentration for Recovery of Vitamin C from Orange Peel Waste

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Abstract. Vitamin C (L-ascorbic acid) is found in orange which provides health benefits to a human body. Orange peel is considered as a waste and dumping the peel can be avoided by extracting it to get valuable compound such as vitamin C. However, none of the vitamin C presents in orange peel has been utilized. Thus, integration of maceration and progressive freeze concentration (PFC) for recovery of vitamin C from orange peel was studied. Maceration is a conventional extraction technique that mostly used for obtaining compound extracts from plant and PFC is currently become attention for concentration process. For this purpose, different operating conditions for maceration and PFC were evaluated with regard to vitamin C recovery. The operating conditions that were analysed are drying temperature (30 to 45 °C), coolant temperature (-10 to -16 °C), cooling time (20 to 35 minutes) and stirring rate (200 to 800 rpm). Titration was done to analyse and correlate the increase of vitamin C in a concentrated solution for different operating conditions. Highest recovery was found at 35 °C of drying temperature, -12 °C of coolant temperature, 20 minutes of cooling time and 400 rpm of stirring rate. The highest value of recovery was found to be 72.06 %. Integrating both maceration and PFC methods add value to the orange peel waste and provide solution for environmental problems.

1. Introduction

Orange (*Citrus Sinensis*) is a type of citrus fruit which widely are known by consumers for its health benefits around the world. It mainly contains a rich source of L-Ascorbic Acid (Vitamin C) [1]. There are number of alternatives proposed by several researchers that have utilized the orange peels in a form of consumables for animals, pectin and biogas. Biogas is considered as highly desirable product [2-4]. However, none of the methods used nowadays have benefited from the rich amount of vitamin C. Vitamin C is a very important water-soluble antioxidant which helps to maintain a human body immunity system. It is known to help prevent cardiovascular diseases, reduce the risk of getting kidney stones and eliminate toxins from the body [1].

The orange peels are a common waste by-product from mass producing orange juice. Large amount of orange waste is constantly being thrown away every year [5]. It was stated that large production of the waste orange peels has been causing major environmental problems [6]. During production of orange juice, large amount of orange waste produced causes ecological and economic problems such as lack of valuable area space to dump the wastes and accumulation of highly organic material [2]. The best way of solving the problem caused by orange wastes is by utilizing them to create useful products. Some common methods for utilizing the waste is by spreading the orange peels on soil, feed to animals or burning [7]. However, the method adding the orange peels on the soil proved to be ineffective as it produces highly polluted wastewater which can negatively affect the soil.



To enhance the recovery of Vitamin C from orange peels, a combination of two methods which are maceration and progressive freeze concentration (PFC) is an attractive option. The maceration method helps draw out the valuable contents from the peel constituents. This method produced extracted peel solution which needed to be concentrated by PFC process. PFC is a type of freeze concentration (FC) which produces ice crystal progressively on a cooled surface layer by layer until a large and single crystal block is formed around the concentrated solution [8]. It is widely used in industry mainly food industry for concentration of liquid type of food [9]. The practice not only applies to high quality of concentration for liquid food such as beer or fruit juice, but also for waste water treatment application [10], low thermal of energy regeneration, and freeze-concentration-crystallization of thermally unstable materials [11]. The benefit of using the FC is that it can preserve and retain thermally sensitive nutrients in the concentrated peel solution [12], facing the obstacles in thermal process such as evaporation. Evaporation is a mature and common process that being used to concentrate a solution. However, due to heat applied, quality of the concentrated solution might be deteriorated. Thus, FC is introduced to replace the evaporation while preserving the original characteristics of the solution.

The aim this study is to extract and recover the vitamin C from orange peels using proposed new integrated process and to investigate the effect of drying temperature for peel extraction and coolant temperature, stirring rate and cooling time for PFC on the retention of vitamin C from orange peel solution. The effect of these operating parameters was evaluated through the percentage of vitamin C recovery.

2. Materials and methods

2.1. Orange peels

The oranges used in this study was obtained from supermarket, AEON Station 18, Perak, Malaysia. Oranges were removed from the peels. Then, the peels were washed with distilled water to remove dirt particles and dried in an oven under 30 °C for at least 12 hours. The dried orange peels were cut into small pieces and then blended for 1 minute using an electronic blender (LB20ES, Waring, USA). Same procedure was repeated for different drying temperature at 35 °C, 40 °C and 45 °C.

2.2. Maceration

30 g of blended dried peels were weighed and macerated with 500 mL of distilled water in 1 L beaker. Aluminium foil was used to cover the beaker. Maceration was done for 4 hours under continuous stirring of 1150 rpm with the help of magnetic stirrer and extraction temperature at 50 °C, as shown in Figure 1.

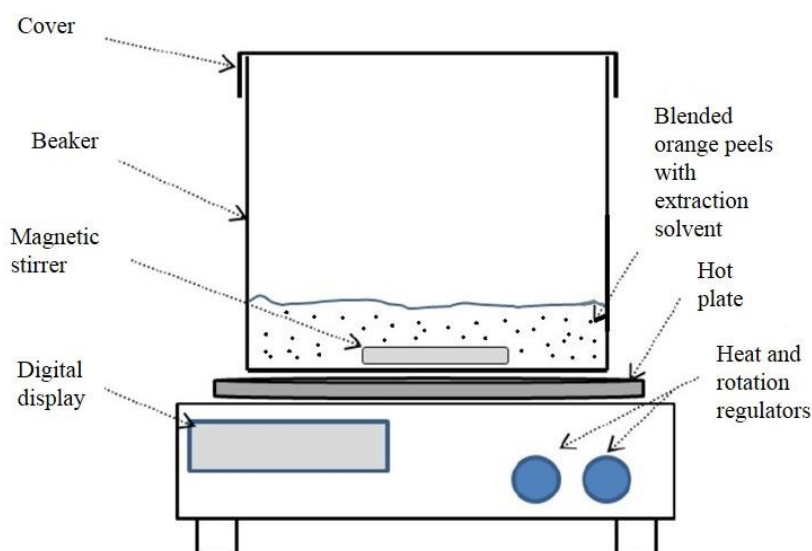


Figure 1. Maceration Set-up

2.3. Progressive freeze concentration

The extracted solution was filtered using a sieve to sieve out the bigger size peels. The filtration was continued with filter paper to remove the excess peels. Refrigerated bath (630D, PROTECH, Malaysia) for PFC was prepared with ethylene glycol and water were mixed as coolant with a volume ratio of 1:1, as depicted in Figure 2. The refrigerated bath was switched on and was set at -10°C . Once the desired temperature has reached, a cylindrical vessel was added to the refrigerated bath and was clamped to a retort stand to prevent any movement in the bath. A stirrer together with a transparent cover were then slowly inserted into the cylindrical vessel. The stirrer was set at 200 rpm and the timer for the cooling time was started. The transparent cover was used to prevent any splashes of solution from the cylindrical vessel. During the process, ice was formed in layer on the inner cooled surface of cylindrical vessel leaving behind a more concentrated peel solution. The process was stopped at the designated time. The concentrated peel solution was drained out from the vessel and the ice was detached from the cooling surface of the vessel. For different operating conditions, the entire procedure had been repeated from the start.

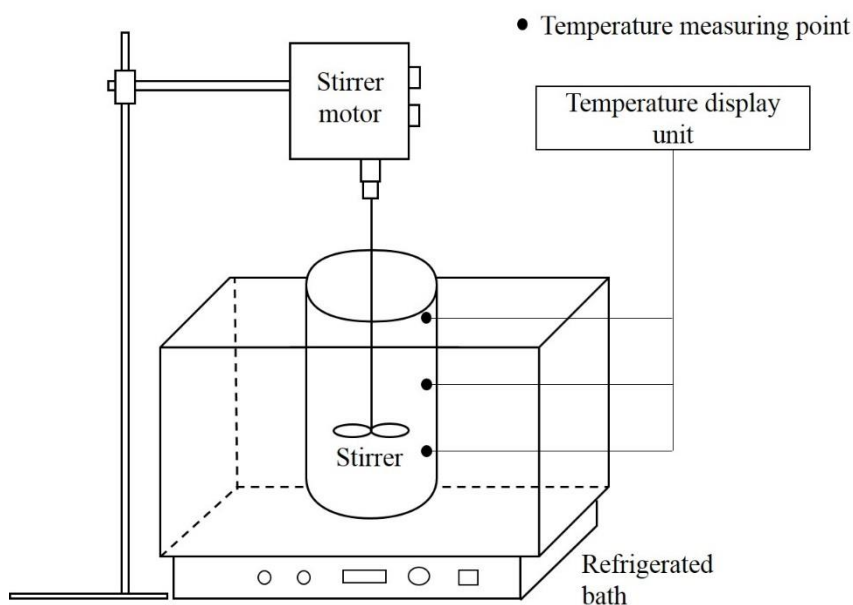


Figure 2: PFC Experimental set-up

2.4. Titration

Titration is laboratory method of find a concentration of a sample. In this titration, iodine was used as a reactant and starch was used as an indicator. The samples that were evaluated are the initial peel solution and final concentrated peel solution. To find the amount of vitamin C in a sample, it is required to note the amount of iodine solution needed to react with known amount of vitamin C. Before titration was done on the samples, a standard vitamin C solution of 1 mg/ml was prepared to standardize the project measurements. 500 mg vitamin C tablet was crushed and added to a distilled water of 500 ml to obtain 1 mg/ml solution of vitamin C. The solution was stirred until the tablet was fully dissolved. 20 ml from the vitamin C solution was measured and added to 250 ml conical flask to begin titration. For starch indicator solution, 2 ml starch was added to the flask that contains 20 mg of vitamin C.

Iodine solution was added to a burette in order to rinse the burette. Then, burette was filled with 50 ml of iodine solution. Then, titration of iodine solution was started on vitamin C and starch mixture. Each drop of iodine oxidized the vitamin C and then reacted with starch. The endpoint of the titration

is identified as the first permanent trace of a dark blue colour due to the starch-iodine complex. The titration process was done 5 times and the average value was taken.

2.5. Vitamin C Recovery, C

PFC system focused for concentration process. Solute recovery or vitamin C recovery is deemed necessary to evaluate the yield of vitamin C in the concentrated solution. The value for vitamin C recovery was calculated using equation (1).

$$C = \frac{C_L m_L}{C_O m_O} \quad (1)$$

Where C_L and C_O are the concentration of peel solution in the concentrated and initial peel solution, respectively while m_L and m_O are the mass of concentrated and initial peel solution, respectively.

3. Results and Discussion

In order to get highest recovery of vitamin C, four operating conditions were investigated such as peel drying temperature, coolant temperature, cooling time and stirring rate. This investigation is helpful in improving the future freezing process as well as for other applications.

3.1. Effect of Peel Drying Temperature on Maceration

Orange peels that were dried at different temperatures had different effects on the maceration process. To select the best drying temperature, the vitamin C content as well as the hardness of the orange peels should also be taken into consideration. It is better to have a hard orange peels as it is very easy to grind them into finer particles, which are more favourable. This is due to having a larger surface area which allows more diffusivity of the constituents. In addition, when the finer particles were soaked in a solution, much easier and faster for solvent to extract the vitamin C from the peel. However, since vitamin C content will be lost if higher temperature has been used, thus 45 °C was chosen as the highest drying temperature for peel.

As depicted in Figure 3, the best temperature for peel drying is 35 °C. It indicates that temperature of 35 °C retained most of the vitamin C which is 72.06 % and did not affect the stability of vitamin C. Therefore, strict temperature control is important in the manufacture of orange peel products to that maintain its vitamin C. 30 °C of drying temperature shows low value of vitamin C contents since the peels were not hardened enough. The blended peels for this drying temperature were not very fine thus affect the diffusivity of the peels towards the solvent. Higher drying temperature such as 40 °C and 45 °C shows that thermal degradation was the main mechanism for reduction of vitamin C content [13].

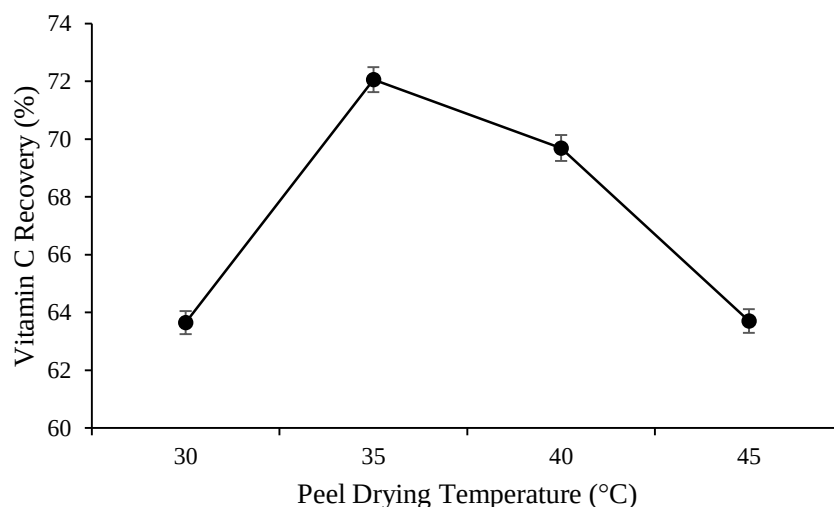


Figure 3. Effect of peel drying temperature on maceration

3.2. Effect of Coolant Temperature on Progressive Freeze Concentration

Figure 4 shows the evolution of vitamin C recovery as a function of coolant temperature. Better outcome was obtained at -10°C where it shows the highest recovery of vitamin C which is 54.7 %. As ice crystal was formed and grown, latent heat was released into the coolant and the peel solution. Low temperature is required to maintain constant peel solution temperature because latent heat generated in the system was greater when larger ice crystal was formed. This low temperature provides an adequate initial supercooling for the ice nucleation formation. In the ice crystal growth phase, inclusion of solutes would not be allowed by the perfect crystal structure of the ice which produces pure ice from PFC process. However, too low temperature such as -14 and -16°C induced fast initial growth. Thus, these temperatures accelerated the formation of ice crystal and yielded larger amount of ice crystal. Also at these temperatures, the freezing entrapped many peel solutes inside the ice crystal. This is because there are many ice nuclei formed due to rapid heat removal. These ice nuclei combined together and this led to a high speed of moving ice front, which results in larger ice crystal. During this time, ice crystal had grown faster which had overtaken the movement of solute particles in the direction of the solution flow. Thus, there is a high solute inclusion in the ice formed [14].

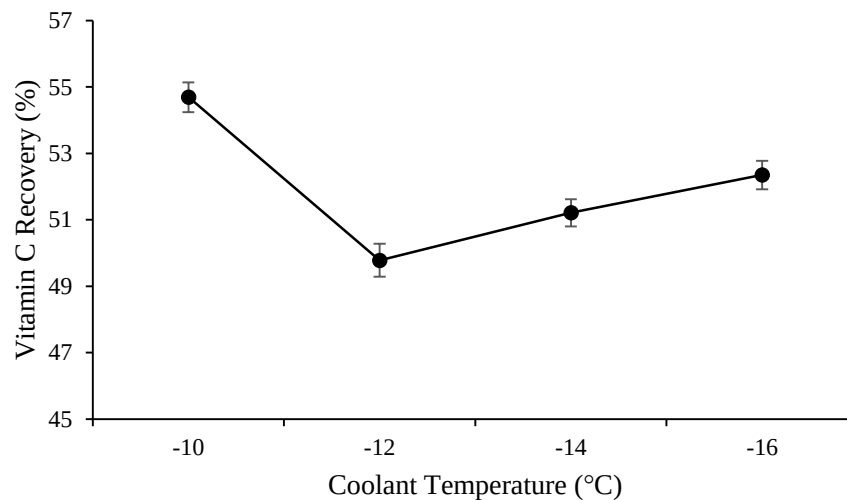


Figure 4. Effect of coolant temperature on PFC

3.3. Effect of Cooling Time on Progressive Freeze Concentration

It can be observed in Figure 5 that the value of vitamin C recovery decreased through the circulation time of 20 to 35 minutes. The circulation time affected the ice thickness where the ice thickness gradually increased with time. Too long of circulation time becomes inefficient because the volume of the vessel is smaller due to the increased ice layer attached to the inner wall of the vessel. An increase in ice layer thickness reduces the rate of ice formation. The peel solutes also became saturated in the concentrated solution and this led to the contamination of solutes in the ice crystal. Furthermore, high accumulation of solutes at the ice-liquid interface lowers the freezing point of the peel solution, thus increases the difficulty for the freezing process to take place. Therefore, PFC process should be stopped once a desired ice crystal thickness has been reached in order to avoid more accumulation of solutes into the ice crystal. However, this finding is advantageous for this system since the process would become costly when the cooling time is too long.

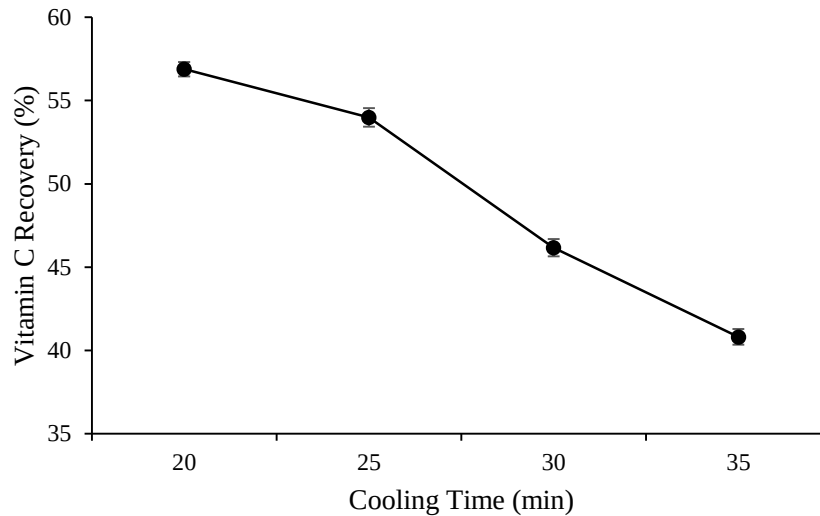


Figure 5. Effect of cooling time on PFC

3.4. Effect of Stirring Rate on Progressive Freeze Concentration

From Figure 6, it can be seen that the best recovery for vitamin C is at 400 rpm of stirring rate which prevented the build-up of peel solute layer at the interface. Stirring in PFC promotes the movement of the solution at the ice liquid interface [15] and prevent the accumulation of peel solutes at the interface. Peel solutes were more easily separated by distributing and mixing the peel solutes well in the solution via stirred freezing. However, the more intense stirring rate will erode not only the interface containing peel solutes, but also the pure ice crystal formed on the inner wall, thus making the solution less concentrated. This suggests that the PFC favoured intermediate stirring for its effectiveness. Solutes with smaller size like blended peels would be tempted to get trapped into the ice phase than the large sized solutes [16].

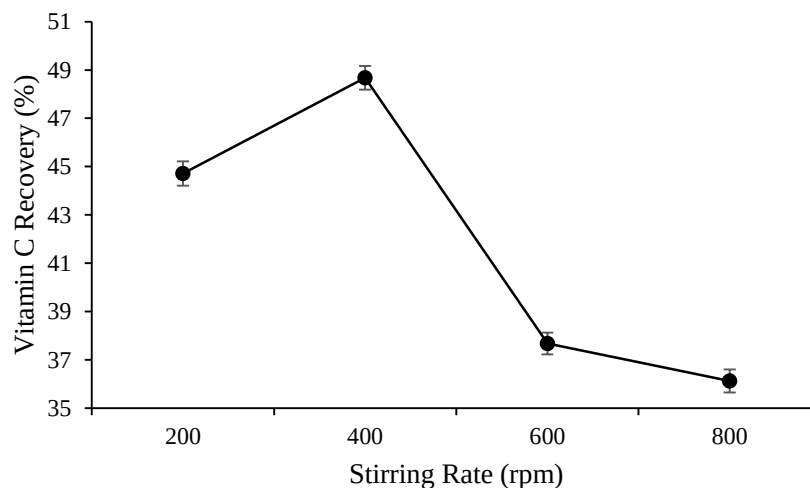


Figure 6. Effect of stirring rate for PFC

Conclusion

Orange peel extracts showed that orange peel is a rich source of vitamin C and has higher concentration in such compound when compared to orange pulp. This point highlights the importance of giving a proper process for the orange waste, which should be considered a valuable processing coproduct rather than a residue. The highest recovery was found to be 72.06 % at 35 °C of drying temperature, -12 °C of coolant temperature, 20 minutes of cooling time and 400 rpm of stirring rate.

Suitable operating conditions enhance stability of extract and diffusivity coefficient, which increase the peel extract recovery. Rate of reaction between solvent and extract has been developed giving higher recovery of peel extract. The used PFC system could be a basis to develop an industrial prototype.

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