Phenolic Pigment Extraction from Orange Peels: Kinetic Modeling

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Abstract Fruit and vegetable wastes cause loss of many beneficial substances such as dietary fiber, antioxidants, pectin, fatty acids and vitamins which are important for nutrition. The citrus wastes are very important antioxidant sources because of their flavonoids and phenolic acid contents. Pigments exist intensely in shells that are not consumed as food. In this study, the kinetic model of phenolic pigment production by Soxhlet extraction from waste orange peel supplied from fruit juice production factory was determined and the kinetic constants, which will be reference for large-scale systems, were determined. In the pigment extraction from dried pulpless orange peel with ethanol at 79^{o}C with particles smaller than 0.5 mm and at 40:1 liquid/solid ratio (L/kg), the highest phenolic pigment yield was found as 57.3 % (0.57 g phenolic pigment/g dry peel). Work in this context is expected to shed light on industrial applications and contribute to the development of food industry.

Keywords: Waste orange peel, Phenolic pigment, Soxhlet extraction, Kinetic modeling

1. Introduction

The knowledge and expectations of people about food are increasing in direct proportion to the awareness and development of the community. The awareness of the society not only increases the expectation and the importance given to the individual nutrition but also increases the importance of collecting it in the source of waste and transforming it into new products with added value by providing waste control and development of clean environment consciousness [1]. Fruit and vegetable wastes contain many substances such as dietary fiber, antioxidants, pectin, fatty acids, pigments that are very important for nutrition. Antioxidants from fruit, vegetables and beverages help preventing cancer and cardiovascular diseases, and also decrease the incidence of other diseases and this play an important role for human health. Recent studies have shown that citrus fruits affect the blood circulation and also strengthen the immune system. In the light of these important effects, there has been a noticeable increase in the production and consumption of citrus fruits, and accordingly the amount of pulp released has increased. Orange peel is about half of the total fruit weight and is very rich in pigments [Oroian, M. and I. Escriche, 2015].

The color of the orange peel generally comes from phenolic compounds and carotenoids [Oreopoulou, V., Tzia, C., 2006]. As the phenolic compounds in the peel increase, redness in the peel decreases and jaundice increases. The ionic radiation and storage increase the total phenolic content and thus the color of the shell turns yellow [Moussaid, M., *et al.*, 2004]. Phenolic compounds are a large class of plant secondary metabolites and consist of very simple structures. The main examples are phenolic acids, flavonoids and polyphenols. Phenolic compounds are polymeric structures composed of these classes. Phenolic compounds are of great importance for the quality of plants in the feeding chain. They are responsible for the colors of fruit that pass from yellow to red, fruit juices and wines. They serve as substrates for enzymatic processes and are also responsible for the aromas in the nutrients. Phenolic compounds play a major role in the importance of fruits and vegetables for human nutrition and in being characterized as healthy. During food storage and processing, plant phenolics are transformed into many different compounds.[Cheynier, V., 2012].

Various extraction techniques are applied to obtain bioactive compounds. Parameters such as solvent selection, solvent to solid ratio, time, heat, agitation etc. play important roles in classical extraction techniques [Edge, R., D.J. McGarvey, and T.G. Truscott (1997) and Rock, C.L., 1997]. Solvent extraction constitutes a part of most laboratory processes and analytical processes. The trickle extraction designed by Franz Von Soxhlet in 1879 is still widely used today. Soxhlet extraction with the developing technology is made more suitable for automation, consuming less solvent and shorter extraction time [Sparr Eskilsson, C. and E. Björklund, (2000) and Wan, H.B. and M.K. Wong, 1996].

In this study, kinetic model of phenolic pigment elution by Soxhlet extraction and extraction for different L/S (liquid/solid) ratios in L/kg, which is thought to be used as a dye additive substance from waste orange peels in food sector, has been done.

2. Materials and methods

2.1. Plant material and preparation for extraction

In this study, the fresh orange peels considered as waste remains after use have been used. At the beginning of the work orange peels were firstly collected from the municipal fruit juice extraction plant. Then they were left in the open air to dry in shade. They are named as dried posed orange peel (DPOP). Dried shells were reduced in size, diameter of particle (dp), <0.50 mm with the help of grinder and stored in a dark airless environment until use.

2.2. Experimental method

Extraction experiments were carried out with a quadruple Soxhlet extractor and a refrigerated water circulator re-cooler connected to the extractor to provide condensation of the solvent and also to obtain the phenolic pigment. Ethanol was used as solvent. This process lasted about 6 hours. To obtain orange colored extract in powder form, Heidolph brand Hei-VAP Precision model rotary evaporator was used and the semi-fluidized sample left to dry in the dark.

In the experiments to select the optimum L/S ratio, at 79^{o}C, 200 ml ethanol was mixed with 5,10,15 and 20 g of DPOP; so, different L/S ratios changing between 40:1 and 10:1 L ethanol/kg DPOP were obtained and the effect of L/S ratio on the extraction kinetic and yield was examined.

2.3. Analytical methods

At the end of each siphon (approximately per hour), the phenolic pigment content of the sample was

found at 325 nm, using the pure solvent as the reference, by using a Thermo Scientific Genesis 10 UV brand and model spectrophotometer. For the spectrophotometric determination of the phenolic pigments, the calibration curve obtained by using the powder product was used.

2.4. Mathematical description of the experimental system

The amount of phenolic pigment extracted per unit mass of dry orange peel at any time is stated by q_{phe} and defined as Equation 2.1.

$$q_{phe} = C_{phe}\frac{V}{M} \quad (Eq. 2.1.)$$

$q_{phe;}$ The amount of phenolic pigment extracted per unit mass of dry orange peel at any time (g phenolic pigment/ g dried peel)

$q_{e,phe;}$ The amount of phenolic pigment extracted per unit mass of dry orange peel at the end of the extraction, at steady state, at equilibrium (g phenolic pigment/ g dried peel)

C_{phe}; Concentration of the phenolic pigment passing through the solvent at any time (g phenolic pigment/ L solvent)

$C_{e,phe}$; Concentration of the phenolic pigment passing through the solvent at steady state, at equilibrium (g phenolic pigment/ L solvent)

$C_{t,phe}$; Concentration of the phenolic pigment passing through the solvent at theoretical equilibrium (g phenolic pigment/ L solvent)

V; Solvent volume used in extraction (L).

M; Mass of dried orange peel (g).

t; Time (min)

k_{phe}; the second order kinetic constant (L/g min)

$h_{e,phe}$; the experimental initial extraction rate (g/L min)

$h_{t,phe}$; the theoretical initial extraction rate (g/L min)

w_{phe}; the extraction efficiency of phenolic pigment (%)

The extraction efficiency of phenolic pigment (w_{phe}) expressed in g of phenolic pigment extracted per 100 g of raw material was calculated as seen in Equation 2.2.

$$w_{phe}(\%) = \frac{C_{e,phe}V}{M}\ 100\% \quad (Eq. 2.2.)$$

The second-order kinetic model given in Equation 2.3. is used to explain the mechanism of pigment extraction from the orange peel [M. Wenyan, L.Y., D. Xiojing, L. Rui, H. Ruilin and P. Yuanjian (2009), Rakotondramasy-Rabesiaka, L., Havet, J. L., Porte, C., Fauduet, H. (2009), Qu, W., Pan, Z., Ma, H. (2010), By Devesh K. Saxena, a.S.K.S., b and S. S. Sambic (2011),].

$$\frac{dC_{phe}}{dt} = k_{phe}(C_{phe} - C_{t,phe})^2 \quad (Eq. 2.3.)$$

By arranging and linearizing this equation the initial extraction rate is defined as seen in Equation 2.4.

$$h_{t,phe} = k_{phe} C_{t,phe}^2 \quad (Eq. 2.4.)$$

3. Results & Discussion

3.1. Liquid/Solid ratio effect

The change of the phenolic pigment concentration passing through the solvent with time depending on the L/S ratio is shown in Figure 3.1. As the L/S ratio

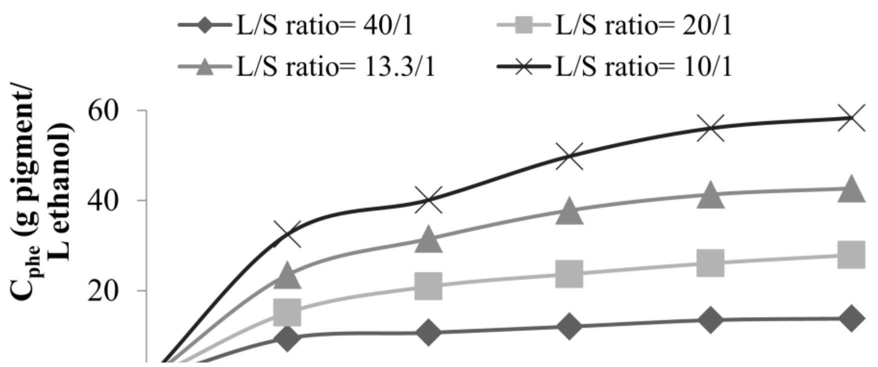

Figure 3.1. Effect of L/S ratio on concentration of the phenolic pigment passing through the solvent from DPOP (dp <0.5mm; Temperature = 79°C; Solvent = 97% Ethanol)

Table 3.1. Concentration of the phenolic pigment passing through the solvent at steady state, at equilibrium ($C_{e,phe}$),the amount of phenolic pigment extracted per unit mass of dry orange peel at the end of the extraction, at steady state, at equilibrium ($q_{e,phe}$) and the extraction efficiency of phenolic pigment (w_{phe}) obtained from the extraction from DPOP at different L/S ratio

L/S Ratio (L/kg)	$C_{e,phe}$ (g/L)	$q_{e,phe}$ (g/g)	w_{phe} (%)
10/1	58.3	0.537	53.7
13.3/1	42.7	0.539	53.9
20/1	27.9	0.544	54.4
40/1	13.8	0.553	55.3

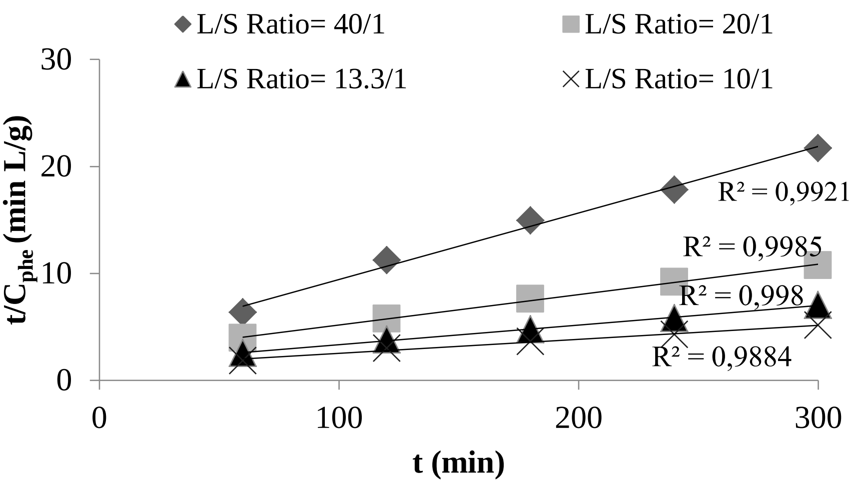

Figure 3.2. Second order kinetic lines obtained from the extraction of phenolic pigment from DPOP at different L/S ratios

Table 3.2. The second order kinetic constants (k_{phe}), the theoretical and experimental initial extraction rates ($h_{t,phe}$, $h_{e,phe}$) and the concentration of the phenolic pigment passing through the solvent at experimental equilibrium ($C_{e,phe}$) and at theoretical equilibrium ($C_{t,phe}$)

L/S Ratio (L/kg)	$k_{phe} \times 10^3$ (L/g min)	$h_{t,phe}$ (g/L min)	$h_{e,phe}$ (g/L min)	$C_{t,phe}$ (g/L)	$C_{e,phe}$ (g/L)	R^2
10/1	0.159	0.912	0.541	75.8	58.3	0.988
13.3/1	0.222	0.663	0.391	54.7	42.7	0.997
20/1	0.344	0.426	0.252	35.2	27.9	0.998
40/1	1.202	0.311	0.157	16.1	13.8	0.992

The change of the phenolic pigment concentration passing through the solvent with time depending on the L/S ratio is shown in Figure 3.1. As the L/S ratio

decreased (amount of solid increases), it appears that the phenolic pigment concentration passing through

the solvent increased, but because the interactions between the solid and the solvent were not sufficient the steady state could be reached later. In the case of large L/S ratios, less phenolic pigment was dissolved in the solvent due to the little amount of solid and the stability was reached in a shorter time due to the good interaction of the solid and the liquid. At the end of the first hour, at 40:1 L/S ratio, 68.5% of the extraction was completed on the other hand at 10:1 L/S ratio only the 55.2% of the extraction was completed.

The % phenolic pigment yields (w_{phe}), $C_{e,phe}$ and $q_{e,phe}$ values obtained at different L/S ratios, are presented in Table 3.1. It is observed that by increasing the L/S ratio the amount of phenolic pigment passing through the solvent decreases significantly due to the decrease of the dry orange peel mass. However, the phenolic pigment amount extracted per unit dry peel mass at steady state and the % phenolic pigment yield increased slightly.

3.2. Extraction kinetic of phenolic pigment

The second order kinetic model of extraction given in Equation 2.1. was applied to the experimental data and the validity of the model was investigated. At all L/S ratios worked, t/C_{phe} versus t graph was sketched (Figure 3.2.) and from the slopes of the lines the $C_{t,phe}$ values, and also the second order kinetic constant, $k_{phe,}$ values were found from the y-axis cut-off points of the graphs and are given in Table 3.2. together with the values of R^2. The initial extraction rate values calculated from Equation 3.4. at different L/S ratios are also presented in the table along with the experimental velocity values.

As can be seen from the Table 3.2., the values of the initial extraction rate and phenolic pigment concentration

in the solvent at steady state vary in inverse proportion to the L/S ratio. Yet, the second-order extraction rate constant is directly proportional to the L/S ratio. When L/S ratio is equal to 10:1, the lowest extraction rate constant (k_{phe}) was reached, while reaching the highest initial extraction rate (h_{phe}) and the phenolic pigment concentration that would pass to the solvent in the theoretical equilibrium. This is because the highest amount of solid sample in the same amount solvent at L/S ratio is equal to 10:1. Achieving high extraction rate constants with increasing L/S ratio appears as a consequence of increased liquid(solvent)/solid ratio and is in agreement with experimental results.

4. Conclusion

In this study it has been aimed to obtain phenolic pigment, a kind of natural flavonoid, which is thought to be used in food sector by Soxhlet extraction from waste orange peel and also to obtain the kinetic constants of this process. Moreover, it has been shown that waste orange peels can be used for extraction of phenolic pigments with high efficiency at a very low cost in this study. Studying with the pulpless, dried, smaller than 0.5 mm orange peels and extraction at 40:1 L/S ratio is the optimum condition for the phenolic pigment extraction from orange peels.

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