

## A RESEARCH ON KINETIC MODELLING ON EXTRACTION OF TOTAL POLYPHENOL FROM OLD TEA LEAVES

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### ABSTRACT

In this study, kinetic modeling by investigating the effect of material sizes, water/material ratios and temperatures was conducted. Polyphenol concentration increased with reducing size, increasing the water/material ratio and temperature. The results showed that under extraction conditions such as the material size of 0.3 mm, the water/sample ratio of 15/1, the extracting temperature of 60 °C, and extracting time of 40 minutes, the polyphenol content obtained was of 77.33 mgGAE.g<sup>-1</sup> with value of initial extraction rate reached 50.90 mgGAE.g<sup>-1</sup>.min<sup>-1</sup> and the activation energy was determined as 16.162 kJ/mol. Polyphenol extraction dynamic model from the old tea leaves relied on the assumption of the quadratic function has been successfully constructed to predict the extraction process and mechanism. Based on the kinetic equation, extraction parameters, including C<sub>e</sub> extraction ability, extraction velocity, extraction constant k, and activation energy E can be determined, facilitated optimization, designed, simulated and controlled significant industrial projects.

*Keywords:* kinetic extraction, old tea leaves, total polyphenol content.

### 1. INTRODUCTION

The tea tree is scientifically named *Camelia Sinensis O. Ktze*. Tea has been a nutritious drink with high biological value due to cure some cardiovascular diseases, digestive, diuretic, and anti-inflammatory. In tea producing process, young leaves are harvested, while the old leaves are not to use. The old tea leaves have a large amount of polyphenol, especially EGC and EGCG [1]. Therefore, studying the extraction of polyphenol compounds from the old tea leaves has been a new direction for the tea industry of Viet Nam.

The usage of mathematical models to study the extraction process has been studied successfully in a number of subjects. Kinetic model extraction of oil from jatropha seeds supported by DIC technology has been used for calculating the impact on grain structure of DIC technology [2]. With pomegranate marc, Qu et al. have built models to determine the kinetic of extraction capabilities, speed and constant extraction of the antioxidant [3]. Besides, Bucic – Kojic and associates have shown the influence of particle size, the ratio of solvent/material and temperature on polyphenol extraction from grape seed. At the same time, the extraction kinetic

model was also constructed based on the Peleg equation [4]. The Arrhenius model is used to describe the relationship between extraction rate and temperature. However, there is no project built for polyphenol extraction dynamic models from old tea leaves. The objective of this study was to develop efficient extraction methods for producing polyphenol from old tea leaves. The parameters have been established to predict the extraction process and improved the efficiency of extracting compounds.

## **2. MATERIALS AND METHODS**

### **2.1. Materials**

Raw materials used were the old tea leaves collected in Loc Chau Commune (Bao Loc City, Lam Dong Province). Tea leaves were guaranteed fresh, not damaged, crushed or pestilent. The tea was steamed in hot steam at 95-100 °C for 2 minutes and dried at 40-50 °C for 8 hours. Moisture content of raw materials was  $6.5 \pm 0.2$  %. Tea after drying was minced into many different sizes such as 0.3 mm,  $0.3 < L \leq 0.5$  mm,  $0.5 < L \leq 1.0$  mm,  $1.0 < L \leq 2.0$  mm and stored in closed plastic bag, dark color, avoided direct light.

Folin-Ciocalteu reagent, Gallic acid were purchased from Sigma-Aldrich. Sodium carbonate was obtained from Merck.

### **2.2. Research methods**

#### *2.2.1. Effects of polyphenol extraction parameters from old tea leaves*

Three parameters affected the extraction process studied in this research were: material sizes, water/material ratios, and temperatures.

*Effects of material sizes (L):* Each tea sample was accurately weighed (about 1 g) in different sizes (0.3 mm, 0.3 - 0.5 mm, 0.5 - 1.0 mm and 1.0 - 2.0 mm), and then extracted with distilled water (15 g) at a temperature of 50 °C with 0, 20, 40, 60 and 80 minutes.

*Effects of water/material ratios (Z):* 1 g of old tea leaves powder (0.3 mm) was mixed with water samples corresponding to 10, 15, 20, 25, 30 g water to produce water/material ratios of 10/1, 15/1, 20/1, 25/1 and 30/1. The extraction was performed at 50 °C for 0, 20, 40, 60 and 80 minutes for each sample.

*Effects of extraction temperatures (T):* The material size of 0.3 mm and water/material ratio of 15/1 were chosen. The extraction temperatures used were 50, 60, 70 and 80 °C for 0, 20, 40, 60 and 80 minutes.

In the extraction process, the sample solutions were contained in sealed glass and covered with lid to avoid the oxidation. All samples were soaked in the thermostat tank corresponding to each temperature treatment. The mixture after extracting was centrifuged at 3000 g for 10 minutes and the liquid extracts were determined the total polyphenol content.

#### *2.2.2. Modeling of polyphenol extraction*

The polyphenol extraction dynamic model from the old tea leaves was proposed based on the report of Qu, et al. [3]. The general second-order kinetic model can be written as:

$$\frac{dC_t}{dt} = k(C_e - C_t)^2 \quad (1)$$

where:  $k$  is the second-order extraction rate constant (g/mg.min),  $C_e$  is the extraction capacity (the equilibrium concentration in the extract) (mg/g),  $C_t$  is the concentration at a given extraction time (mg/g).

The integrated rate law for a second-order extraction under the boundary conditions  $t = 0$  to  $t$  and  $C_t = 0$  to  $C_t$ , can be written as a linearized Eq. (2):

$$\frac{t}{C_t} = \frac{1}{kC_e^2} + \frac{t}{C_e} \quad (2)$$

Then when  $t$  approaches 0, initial extraction rate  $V_o$  (mg/g.min), can be written as:

$$V_o = k.C_e^2 \quad (3)$$

After rearranging the Eqs. (2) and (3),  $C_t$  can be expressed as:

$$C_t = \frac{t}{(1/V_o) + (t/C_e)} \quad (4)$$

The  $V_o$ ,  $C_e$ , and  $k$  were determined experimentally from the slope and intercept by plotting  $t/C_t$  against  $t$ .

It was assumed that the second-order kinetic model could be applied to measure the influences of variables ( $L$ ,  $Z$  and  $T$ ). Therefore, the  $V_o$ ,  $C_e$ , and  $k$  had relations with those variables and were fitted by functional models. Arrhenius equation was used to describe the relationship between extraction rate constant ( $k$ ) and temperature ( $T_a$ ), which is written as:

$$k = k_o \exp\left(-\frac{1000E}{RT_a}\right) \quad (5)$$

where:  $k_o$  is the temperature-independent factor (g/mg.min),  $E$  is the activation energy of extraction (KJ/mol),  $R$  is the gas constant (8.314 J/mol.K) and  $T_a$  is extraction temperature ( $^{\circ}$ K).

### 2.3. Methods of data analysis and processing

#### 2.3.1. Analytical methods

The total polyphenol content (TPC) was determined based on the colorimetric procedure at 765 nm, using Folin-Ciocateu reagent and the standard gallic acid [3]. The concentration of total polyphenol (mgGAE/g) was calculated using Eqs. (6), where  $V_t$  is the total volume of liquid extract at a given extraction time  $t$  (L),  $W$  is the dry weight of sample (g). The moisture contents of all samples were determined by drying each sample to a constant weight at 105  $^{\circ}$ C [3].

$$TPC = 1000 \times \frac{C_t V_t}{W} \quad (6)$$

#### 2.3.2. Data processing methods

Each experiment was repeated three times, the results presented as mean  $\pm$  standard deviation. Evaluation of significant differences between the samples was done by statistical ANOVA, LSD test ( $p < 0.05$ ) on Statgraphics Centurion XV.

### 3. RESULTS AND DISCUSSION

#### 3.1. Effects of polyphenol extraction parameters from old tea leaves

##### 3.1.1. Effect of material sizes

Total polyphenol content increased rapidly and then reached stability with an increase in extraction time (Fig. 1). At the same time, the smaller the material size was, the higher the total polyphenol content obtained. The material size of 0.3 mm was the highest polyphenol content because smaller particle size means a shorter mass transfer distance and larger resolve surface area, which ultimately reduces the extraction time and increases the extraction efficiency. Similarly, the total polyphenol content significantly increased with a reduction in particle size during the extraction of antioxidants from blank currant juice press residues [5]. At the material size of 0.3 mm, when increasing the extraction time from 0 to 80 minutes, the total polyphenol content increased by 1.43 times. From 0 to 40 minutes, the concentration of total polyphenol increased very rapidly, however, the extraction time increased from 40 to 80 minutes, the total polyphenol content increased negligible. Similar results were also found in research of Nguyen Ngoc Tram [6]. That was because the difference in the extracted concentration between the solvent and the substrate at the initial stage, the diffusion process occurs quickly. In the next stage, the difference in concentration is small and the extracts come out slowly. Therefore, the size of 0.3 mm with the extraction time of 40 minutes was the appropriate choice.

##### 3.1.2. Effect of water/sample ratios

Figure 2 shows the total content of polyphenol under different extraction times and water/sample ratios. The total polyphenol content increases when the water/sample ratios increase, the higher water/sample ratios result in a larger concentration gradient during the diffusion from internal material into the solution, extraction efficiency increased. This figure increases significantly at a water/sample ratio of 15/1, it is smaller than the 20/1; 25/1; 30/1 but not worth considering. Besides, at water/sample ratio of 15/1, it can be seen a slight increase in total content of polyphenol (1.59 %) from 0 to 20 minutes, then increases dramatically from 20 minutes to 40 minutes (37.08 %) and intensifies a little bit after 40 minutes or achieves state of equilibrium. Therefore, extraction time of 40 minutes and water/sample ratio of 15/1 are the most relevant for extraction to save time and cost.

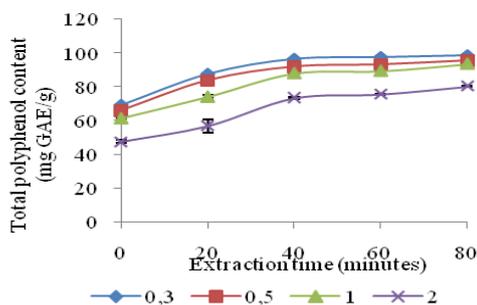


Figure 1. Effect of material sizes on total polyphenol content for different extraction times.

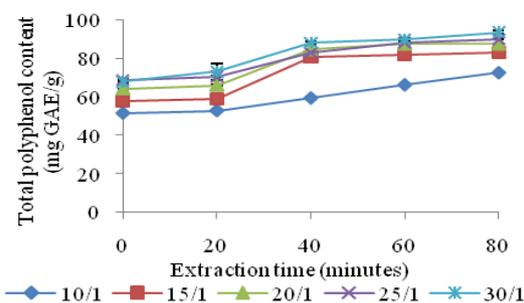


Figure 2. Effect of water/sample ratios on total polyphenol content for different extraction times.

### 3.1.3. Effect of extraction temperatures

The total content of polyphenol increases when temperature and extraction time increase (Fig. 3). Total content of polyphenol at 50 °C; 60 °C; 70 °C; 80 °C correspondently were 73.49, 77.33, 78.07, 80.37 mg GAE/g at the extraction time of 40 minutes. The total polyphenol content were significantly extended with increasing in extraction temperature. This might be due to enhancing solubility and diffusion coefficient of polyphenol at a high temperature. The result showed that the polyphenol concentration increased in 1.05 times when increasing temperature from 50 °C to 60 °C. Then the total concentration of polyphenol increases a little bit from 60 °C to 80 °C and reaches state of equilibrium. By considering the total content of polyphenol and operation cost, the recommended temperature is 60 °C.

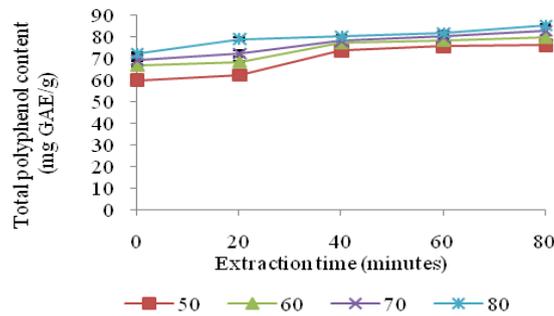


Figure 3. Effect of extraction temperatures on total polyphenol content for different extraction times.

### 3.2. Kinetic model for total polyphenol extraction

Table 1. Parameters of second-order kinetic model for polyphenol extraction from dry old tea leaves with different particle sizes, water/sample ratios, and extraction temperatures.

| Variable types                   |      | Initial extraction rate<br>$V_o$ (mg/g.min) | Extraction rate constant<br>$k$ (g/mg.min) | Equilibrium concentration of total polyphenol<br>$C_e$ (mg/g) | $R^2$  |
|----------------------------------|------|---|--|---|--------|
| Particle size<br>L (mm)          | 0.3  | $83.82 \pm 1.20^a$                          | $0.0084 \pm 0.0001^a$                      | $100.00 \pm 0.000^a$  | 0.9990 |
|                                  | 0.5  | $66.58 \pm 2.08^b$                          | $0.0073 \pm 0.0003^a$                      | $95.85 \pm 0.432^b$   | 0.9987 |
|                                  | 1.0  | $36.09 \pm 2.55^c$                          | $0.0040 \pm 0.0003^b$                      | $94.94 \pm 0.424^b$   | 0.9952 |
|                                  | 2.0  | $20.55 \pm 4.95^d$                          | $0.0031 \pm 0.0008^b$                      | $82.21 \pm 1.140^c$   | 0.9870 |
| Water/sample ratio<br>Z (g/g)    | 10/1 | $16.38 \pm 0.29^a$                          | $0.0031 \pm 0.0000^a$                      | $73.17 \pm 0.2530^a$  | 0.9951 |
|                                  | 15/1 | $23.20 \pm 0.57^b$                          | $0.0031 \pm 0.0001^{ab}$                   | $86.46 \pm 0.7007^b$  | 0.9888 |
|                                  | 20/1 | $30.28 \pm 0.56^{bc}$                       | $0.0037 \pm 0.0001^{ab}$                   | $90.64 \pm 0.3861^c$  | 0.9926 |
|                                  | 25/1 | $32.02 \pm 1.04^c$                          | $0.0038 \pm 0.0002^{ab}$                   | $92.31 \pm 0.4004^d$  | 0.9947 |
|                                  | 30/1 | $35.26 \pm 7.87^c$                          | $0.0039 \pm 0.0009^b$                      | $95.24 \pm 0.7407^e$  | 0.9940 |
| Extraction temperature<br>T (°C) | 50   | $37.22 \pm 1.78^a$                          | $0.0062 \pm 0.0004^a$                      | $77.73 \pm 0.7563^a$  | 0.9968 |
|                                  | 60   | $50.90 \pm 7.02^b$                          | $0.0079 \pm 0.0013^{ab}$                   | $80.66 \pm 1.0624^b$  | 0.9981 |
|                                  | 70   | $62.17 \pm 8.51^{bc}$                       | $0.0091 \pm 0.0013^{bc}$                   | $82.64 \pm 0.0000^c$  | 0.9983 |
|                                  | 80   | $74.71 \pm 2.46^c$                          | $0.0103 \pm 0.0004^c$                      | $84.99 \pm 0.3414^d$  | 0.9984 |

<sup>a,b,c,d,e</sup>Different letters in the same column represent statistically significant differences in statistical ANOVA ( $p < 0,05$ ).

The  $V_o$ ,  $C_e$ , and  $k$  values for different  $L$ ,  $Z$ , and  $T$  were respectively obtained from the slopes and intercepts by plotting  $t/C_t$  against  $t$  listed in Table 1.

These kinetic parameters decreased with the increase of particle sizes as expected based on the experimental results. Because the  $h$ ,  $k$ , and  $C_e$  were dependent on  $L$ , the  $h$ ,  $k$ , and  $C_e$  values for different  $L$  values were fitted by linear and power functions with high coefficients of determination ( $R^2 = 0.950-0.986$ ). The functions are expressed as:

$$C_e = -9.8652L + 102.62 \quad R^2 = 0.9507 \quad (7)$$

$$V_o = 35.862L^{-0.762} \quad R^2 = 0.9886 \quad (8)$$

$$K = 0.0044L^{-0.569} \quad R^2 = 0.9674 \quad (9)$$

$$C_{(t,L)} = \frac{t}{(1/(35.86L^{-0.762})) + (t/(-9.8652L + 102.62))} \quad (10)$$

This equation can be used to predict the polyphenol extraction under different particle sizes at a given time with the extraction temperature of 50 °C and water/sample ratio of 15/1 (w/w).

The extraction at ratio of 30/1 displayed the highest  $C_e$ ,  $V_o$  and  $k$  values compared to those at ratios of 10/1, 15/1, 20/1, 25/1. Qu and et al. also reported similarly result about extraction modeling and activities of antioxidants from pomegranate marc [3]. According to the model assumption, the parameters were expressed by the variable of  $Z$ . Therefore, the relationships between kinetic parameters and  $Z$  were nonlinearly fitted by second-order polynomial functions ( $R^2 = 0.9673 - 0.9908$ ). The functions are written as:

$$C_e(z) = -0.0656Z^2 + 3.6291Z + 44.455 \quad R^2 = 0.9673 \quad (11)$$

$$k_z = -(2.10^{-6})Z^2 + 0.0001Z + 0.0017 \quad R^2 = 0.9800 \quad (12)$$

$$V_o(z) = -0.0429Z^2 + 2.6693Z - 6.6526 \quad R^2 = 0.9908 \quad (13)$$

$$C_{(t,Z)} = \frac{t}{(1/(-0.0429Z^2 + 2.6693Z - 6.6526)) + (t/(-0.0656Z^2 + 3.6291Z + 44.455))} \quad (14)$$

This equation can be used to predict the polyphenol extraction under different water/sample ratios at a given time with the particle size of 0.3 mm and extraction temperature of 50 °C.

Temperature had an accelerative influence on these kinetic parameters. The relationships between kinetic parameters and  $T$  were fitted by linear, second-order polynomial, and exponential functions ( $R^2 = 0.9749-0.9991$ ).

$$C_e = 0.2376T + 66.061 \quad R^2 = 0.9940 \quad (15)$$

$$V_o = -0.0029T^2 + 1.6079T - 35.866 \quad R^2 = 0.9991 \quad (16)$$

$$K = 0.0027\exp(0.0169T) \quad R^2 = 0.9749 \quad (17)$$

$$C_{(t,T)} = \frac{t}{(1/(-0.0029T^2 + 1.6079T - 35.866)) + (t/(0.2376T + 66.061))} \quad (18)$$

This equation can be used to predict the polyphenol extraction under different temperatures at a given time with the particle size of 0.3 mm and water/sample ratio of 15/1, w/w.

When the Arrhenius equation was used to determine the relationship between  $k$  and  $T_a$ , the  $k_o$  and  $E$  were determined from the plot of  $\ln(k)$  against  $1000/T_a$ . The high coefficient of determination ( $R^2$ ) of 0.98 confirmed that Arrhenius equation can be used to describe the relationship between second-order extraction rate constant with temperature. Therefore, the relationship of  $k$  and  $T(^{\circ}\text{C})$  is written as:

$$k = 2.6013 \exp\left(-\frac{16.162}{8.314 \times 10^{-3}(T + 273.15)}\right) \quad (19)$$

Empirical Eqs.(14), (18) and (19) are the kinetic models for predicting total polyphenol extraction from old tea leaves. Even though the statistical models might not completely account for the phenomena governing extraction processes, they still could be used to determine the influences of particle sizes, temperatures and water/sample ratios on the polyphenol extraction capacity by extraction times. The results obtained from these models should provide the guidance for the improvement of extraction process, and reductions in extraction operating costs and times.

#### 4. CONCLUSIONS

Old tea leaves are also a good source of material for polyphenol production. The results showed that content of total polyphenol increased with reduced particle size, increased water/material ratio and extraction temperature. By considering the content of polyphenol and operation cost, the recommended conditions are particle size of 0.3 mm, water/sample ratio of 15/1 (w/w), temperature of 60 °C, and extraction time of 40 min. The kinetic models were successfully developed for describing the extraction processes under different extraction parameters, including particle size, water/sample ratio, and extraction temperature. The activation energy of polyphenol extraction was determined as 16.162 kJ/mol based on the Arrhenius model.

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## TÓM TẮT

### NGHIÊN CỨU ĐỘNG HỌC QUÁ TRÌNH TRÍCH LI POLYPHENOL TỔNG TỪ LÁ CHÈ GIÀ

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Trong nghiên cứu này, mô hình động học thông qua việc khảo sát ảnh hưởng của kích thước nguyên liệu, tỉ lệ dung môi : nguyên liệu và nhiệt độ đã được khảo sát. Hàm lượng polyphenol tăng lên khi giảm kích thước và tăng tỉ lệ dung môi/nguyên liệu và nhiệt độ. Kết quả nghiên cứu chỉ ra rằng tại các điều kiện trích li như kích thước nguyên liệu 0.3 mm, tỉ lệ dung môi/nguyên liệu là 15:1, nhiệt độ trích li 60 °C, thời gian trích li 40 phút thì hàm lượng polyphenol thu được là 77,33 mg GAE/g chất khô nguyên liệu) với tốc độ trích li ban đầu 50,90 (mg GAE/g.phút) và năng lượng hoạt hóa là 16,162 kJ/mol. Mô hình động học trích li polyphenol từ lá chè già dựa trên giả thiết của hàm số bậc hai đã được xây dựng thành công để dự đoán được cơ chế trích li. Dựa vào phương trình động học có thể xác định được các thông số như: khả năng trích li  $C_e$ , vận tốc trích li  $V_0$ , hằng số trích li  $k$ , năng lượng hoạt hóa  $E$ , tạo điều kiện thuận lợi cho việc tối ưu hóa, thiết kế, mô phỏng và kiểm soát đáng kể các chi phí ở quy mô công nghiệp.

*Từ khóa:* động học trích li, hàm lượng polyphenol tổng, lá chè già.