(RESEARCH ARTICLE)

Modeling of polyphenols extraction process from green tea and the effect of temperature on the process

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Abstract

Two mathematical models of polyphenols extraction from green tea leaves were tested: Peleg's model and First-order model. Thermodynamical parameters of the process were determined.

For the Peleg's model we got the following analytical equation: $C_t = t/(0.2570207+0.0324377*t)$. C_t is a concentration of polyphenols in extract at the time t. For the First-order model analytical equation describing the extraction process was as follows: $C_t = 23.09278*(1-\exp(-0.1418264*t))$. Goodness of fit of the both models were high but the first-order model prognosed equilibrium concentration of polyphenols in tea infusion with much more precisely than the Peleg's model. Activation energy for the First-order model was equal to 2798 j/mol. Entropy change (ΔS) of this process was equal to 52 (J, (mol, K^{-1})), and enthalpy change (ΔH) was equal to 16304 ($Jmol^{-1}$). The ΔG value gradually decreased as the extraction temperature increased, indicating that increasing the extraction temperature can make the extraction easier. First Order Model of tea polyphenols extraction was shown to be well describing the process. The most useful conditions for polyphenols extraction from green tea leaves were 70 ℃ and 20 min.

Keywords: Tea; Extraction; Kinetic models; Thermodynamic parameters

1. Introduction

Green tea has gained widespread popularity due to its numerous health benefits attributed to the presence of polyphenols, which are known for their antioxidant and anti-inflammatory properties [1, 2, 3, 4] Truong et al., 2022; Bag et al., 2022; Ahammed and Le 2022; Shaukat et al., 2023]. The extraction process of polyphenols from green tea is a complex phenomenon influenced by various factors, including temperature, time, solvent composition, and particle size [5] Bindes et al., 2019]. Gaining a comprehensive understanding and optimizing this procedure is critical in maximizing the efficiency of extraction and obtaining top-notch polyphenol extracts. Multiple techniques and conditions are available to extract polyphenols from plant-based materials [6] Sridhar et al., 2021]. Employing mathematical modeling facilitates effective planning, improvement, and regulation of the investigative process [7] Anis and Ahmed 2022]. Various types of models, such as theoretical, empirical, and semi-empirical models, can simulate the extraction of bioactive substances from plant materials using solid-liquid extraction techniques. Researchers investigated how the solvent, temperature, and extraction time influence the extractability of total polyphenols from milled soybeans variety Ika [8,9] Jokić et al., 2010; Reungoat et al., 2021. The application of mathematical models demonstrated a strong correlation with experimental results, allowing their use in modeling and optimizing the solid-liquid extraction process for obtaining total polyphenols from plant materials.

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In this study, the aim was to evaluate mathematical models and determine the most suitable one that accurately represents experimental observations. The selected model will provide insights into the extraction mechanisms involved in extracting polyphenols from green tea leaves. Another aim was to determine the thermo-dynamic parameters such as Gibbs free energy, enthalpy change and entropy change of the green tea polyphenols extraction process.

We conducted a set of extraction trials under carefully controlled conditions and obtained experimental results. These results were utilized to validate our proposed models and shed light on the crucial factors influencing extraction efficiency. Specifically, we focused on the impact of temperature and extraction time, while keeping other variables constant. With the aid of the developed models, manufacturers have the ability to create effective extraction procedures that achieve a high yield of polyphenols, conserve resources, and uphold product quality.

2. Material and methods

2.1. Reagents and materials

Folin-Ciocalteu reagent and Gallic acid were provided by Merck (Darmstadt, Germany), Sodium carbonate was purchased from Chem Cruz (Chem Cruz Biochemicals, USA). All other reagents were purchased from local market and were of analytical grades.

Plant material: green tea "Georgian Fannings" was purchased from a local market.

2.2. Extraction process

The ratio of green tea and extraction water was fixed at 1:6 (w/). 300 ml of water was added to 50 g of green tea and kept at different temperatures in a glass container and for different durations. In the conditions of the first type of experiments, the extraction temperature (70 ^{0}C) was fixed and the concentration of polyphenols in the extract was measured at different time points. In the second type of experiments, the duration of extraction was fixed (20 min) and the concentration of polyphenols in the solution was measured at different temperatures.

2.3. Kinetic models

Numerous modeling investigations have been carried out to explain the process of extracting various substances from different plant materials: Peleg Model, Power Law, Parabolic Diffusion Model, Elovich Model, Exponential Model, Weibull Model, Patricelli Model, So and Macdonald Model Hadrich et al., 2016; [6, 10] Sridhar et al., 2021). In our research we tested the following kinetic models: The model proposed by Peleg in 1988 [11] (Peleg, 1988) and the First order model [12] (Harouna-Oumarou et al., 2007).

2.4. Determination of TPC

The total phenolic content (TPC) of the extracted green tea samples was determined using a UV 1609 spectrophotometer from A&E Lab Co LTD, UK, following the Folin-Ciocalteu method [13] (Bond et al., 2003). In brief, individual disposable test tubes were filled with 1 mL of the extracted green tea samples and mixed with 5 mL of Folin-Ciocalteu phenol reagent, which was previously diluted with a 1:10 ratio in distilled water. After an 8-minute interval, 4 mL of a Sodium Carbonate solution (7.5% w/v) was added to each test tube. The mixtures were thoroughly stirred and left to stand for 60 minutes at room temperature to facilitate color development. Subsequently, the optical densities of the mixtures were measured at 765 nm using a 10 mm path length cell, with water as the reference. A standard working solution of Gallic acid (10-50 μg mL-1) was used, and a calibration curve plotting absorbance against the concentration of the standard solution was employed to determine the TPC. The results were expressed in milligrams of gallic acid equivalents (GAE).

2.5. Determination of total dry matter

To measure the dry matter, 50 mL of the tea infusion was poured onto a porcelain basin and then subjected to evaporation on a water bath. Subsequently, the moisture was completely removed from the samples through oven drying at 105 °C for a duration of 16 h. The total dry matter was determined by measuring the residue that remained after the drying process using a gravimetric method.

2.6. Statistical Analysis

All physicochemical analyses were done in triplicate and data are expressed as mean ± standard deviation. The data fitting process was carried by online fitting calculator at the https://mycurvefit.com/ by using a nonlinear least squares regression method. The concordance between the experimental data and calculated value were established by the following measures of goodness of fit:

- AIC - Akaike's Information Criterion; this provides an estimate of the quality of the curve-fitting model for comparison against other models.
- AICc -Akaike's Information Criterion corrected for small sample sizes.
- BIC - Bayesian Information Criterion
- F - the F-statistic
- P - the P-value
- DOF – Degree of freedom
- R^2 -1 minus the ratio of sum of the squares of the residuals divided by the sum of the squares of the differences between Y fit and the mean Y value
- aR^2 - the adjusted R^2 value
- SE - the standard error.
- SEE – standard error of estimate

3. Results

3.1. Kinetics of polyphenols extraction process

Contents of polyphenols in tea infusion were measured at different time of extraction at 70 ^{0}C. Results are shown in Table 1. and Fig. 1.

Table 1 Experimental data of kinetics of polyphenols extraction process

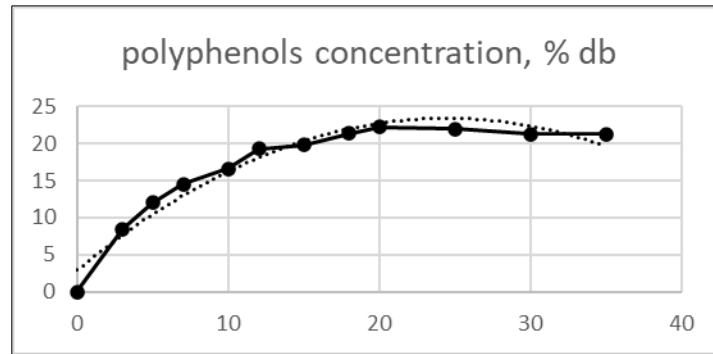| t, extraction time, min.	C_t, Polyphenols concentration, % on extract db
0	0
3	8 ± 0.2
5	12.5 ± 0.2
7	14 ± 0.2
10	16.8 ± 0.3
12	19.5 ± 0.2
15	20 ± 0.2
18	21.6 ± 0.3
20	22.5 ± 0.3
25	22.1 ± 0.3
30	21.5 ± 0.3
35	21.4 ± 0.2

Figure 1 Polyphenols concentration vs time, experimental data

The polyphenols concentration increased with the time up to around 25 min. After this moment the polyphenols concentration started to decrease. Perva-Uzunalić et al. [14] (2006) and [15] Vuong et al. (2011) noted that the degradation of polyphenols initiates at 80 °C, while Kumar et al. [16] (2012) found that a higher concentration of polyphenols was obtained at 80 °C compared to 60 °C. In an extensive review on extraction methods from Camellia sinensis, Banerjee and Chatterjee [17] (2015) reported that most studies in the literature collected data at temperatures around 80 °C. Furthermore, Perva-Uzunalic et al. [14] (2006) suggested either a high temperature (95 °C) with a short extraction time (5–10 min) or a lower temperature (60 or 80 °C) with a longer extraction time (20 min) to prevent catechin degradation.

As a result, our findings regarding the impact of temperature on the extraction of polyphenolic compounds from green tea leaves align with the established data in the existing literature.

Therefore in our kinetic models we used data before 25 min of extraction time and maximum 70^0C temperature.

3.2. Fitting kinetic models.

The model proposed by Peleg was adapted for the extraction and used in the form:

$$C_t = t/(a+bt) \quad (1)$$

where: C_t is concentration of total polyphenols at time t (g GAE/g db), t– extraction time (min); a – Peleg's rate constant (min gdb/g GAE), b – Peleg's capacity constant (gdb/g GAE). The Peleg rate constant a relates to the extraction rate at the very beginning ($t = t_0$): The Peleg capacity constant b relates to maximum extraction yield, i.e., equilibrium concentration of total polyphenols extracted (y_e) when $t \to \infty$.

Eq. (1) gives the relation between equilibrium concentration and b constant: (y_e) = 1/b

Fitting the experimental data with this model we found:

$$a= 0.257020651624709 \pm 0.0114050284115597$$

$$b= 0.0324376964703313 \pm 0.000933316267541642$$

$$C_t= t/(0.2570207+0.0324377*t)$$

From this equation equilibrium concentration of polyphenols is equal to 1/0.0324377=30.82 %

Goodness of fit of Peleg's model was very high (Table 2, Fig.2), but equilibrium concentration of polyphenols was much higher than that of experimental value.

Table 2 Goodness of fit of Peleg's model

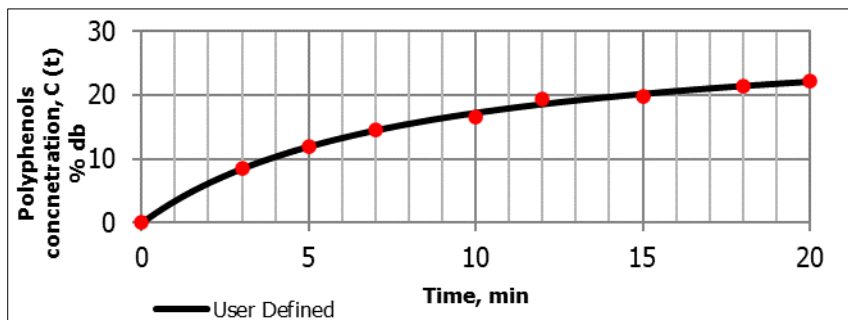| Goodness of Fit Measure	Value
R^2	0.997443255193699
aR^2	0.996712756677613
P	8.45095549095731E-010
SE	0.38854923110137
SSE	1.05679353492626
F	1365.42817436226
AIC	10.2630266111741
BIC	10.6574757658465
DoF	7
AICc	12.2630266111741

Figure 2 Polyphenols concentration vs time, Peleg's model

3.3. First-order model

The leaching rate is expected to be directly proportional to a driving force, which is represented as $(C_s - C_t)$, where C_s (g/g db) and C_t (g/g db) denote the concentrations of water-soluble polyphenolic compounds at saturation and at any given time t, respectively. To determine the extraction order and rate constant, experimental measurements are necessary. The first-order model equation, as presented by Harouna-Oumarou et al. [12] (2007), can be expressed in its differential form as: $dC_t/dt = k (C_s - C_t)$ where C_s represents the concentration of polyphenolics achieved at equilibrium, C_t is the concentration of polyphenolics at time t, k stands for the first-order rate constant (min^{-1}), and t denotes the time at the specific instant.

Upon integrating this differential equation and applying the boundary conditions $C_t = 0$ at $t = 0$ and $C_t = C_t$ at $t = t$, the resulting equation is: $C_t = C_s (1 - e^{-kt})$

Fitting the experimental data with this model we found:

$$C_s = 23.0927763747484 \pm 0.554472907861848$$

$$k = 0.141826443080166 \pm 0.00878882515336818$$

$$C_t = 23.09278*(1-e^{-0.1418264*t}) \quad (2)$$

From Eq.2 polyphenols concentration at equilibrium is 23.09278 %, which is very close to the experimental value 22.2 %. Measures of fitness of good was also, very high, which indicated on that a First Order Model describes extraction process very well.

Fitting curve is shown on Fig.3, Measures of goodness of fit is given in Table 3.
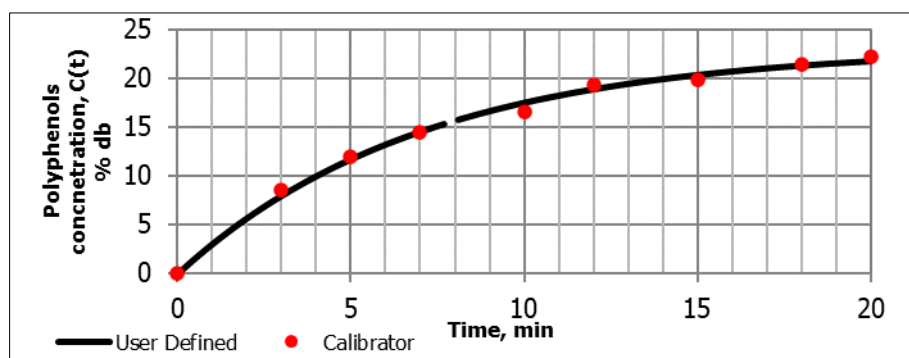

Figure 3 Polyphenols concentration vs time, First Order Model

Table 3 Goodness of fit of the First Order Model

Measures of goodness of fit	Value
R^2	0.995583846346832
aR^2	0.994322088160213
P	5.72340674853677E-009
SE	0.510651310114398
SSE	1.82535332365086
F	789.044887447312
AIC	15.1818345343264
BIC	15.5762836889988
DoF	7
AICc	17.1818345343264

3.4. Effect of temperature

In the assessment of the impact of extraction temperature on kinetic models, Agu et al. [18] (2021) employed the Arrhenius equation. This equation served to elucidate the correlation between the extraction rate constant (k) and the temperature (T). Equation (2) presents the Arrhenius equation

$$Ln\ k = Ln\ k_0 - E_a/(R \times T)\ (2)$$

Rearranging the above Equation (2), results to Equation (3).

$$k = k_0 e^{-E_a/RT}\ (3)$$

From the first-order model at 70°C k= 0.141826443080166 min^{-1}. By the same way we found k value at 40°C, k=0.127755102040816

Thus, we got system of two equations with two unknown parameters, k_0 and Ea:

$$Ln\ 0.140368337719762 = Ln\ k_0 - E_a/(8.31 \times 343)\ (4)$$

$$Ln\ 0.127755102040816 = Ln\ k_0 - E_a/(8.31 \times 313)$$

Solving this system of equations, we got k_0= 1.7365 and E_a=2798 j/mol. In this particular model, the activation energy exhibited a positive value, indicating that the extraction of polyphenols is characterized as an endothermic process. Dependance of polyphenols concentration in tea extract on extraction temperature is shown in Table. 4.

Table 4 Effect of temperature on the polyphenols concentration in tea infusion*

Temperature of extraction, ^{0}C	Polyphenols concentration, % db
30	16 ± 0.1
40	18 ± 0.2
45	19 ± 0.2
50	20 ± 0.2
55	21 ± 0.2
60	21.3 ± 0.3
65	21.8 ± 0.3
70	22.5 ± 0.3
75	21 ± 0.2
80	20.5 ± 0.2
85	20 ± 0.3
90	± 0.2

*Extraction time 20 min.

3.5. Thermodynamic parameters

The Van't Hoff Equation (Atkins and De Paula 2006) [19] was applied to compute the thermodynamic parameters, namely the enthalpy change (ΔH) and entropy change (ΔS), associated with the extraction of polyphenols from green tea.

$$Ln\ K = -\Delta H/RT + \Delta S/R\ (5)$$

Equation (5) can be re-written to include the Gibbs free energy change in the form of Equation (6).

$$Ln\ K = \Delta G/RT = -\Delta H/RT + \Delta S/R\ (6)$$

The Gibbs free energy change was calculated using Equation (7).

$$\Delta G = \Delta H - T \cdot \Delta S\ (7)$$

$$K = Y_T/Y_u = m_L/m_S\ (8)$$

where K is equilibrium constant, Y_T is the yield of polyphenols at temperature T, Y_u is the percentage of the un-extracted polyphenols, m_L is amount of polyphenols in liquid at equilibrium temperature T, m_s is amount of polyphenols in solid at equilibrium temperature T, R is gas constant (8.314 J (molK)$^{-1}$), while ΔH (Jmol^{-1}), ΔS (Jmol^{-1} K^{-1}), and ΔG (Jmol^{-1}) are enthalpy, entropy, and Gibbs free energy changes, respectively.

According to Table 5 dependance of Ln k vs 1/T was plotted (Fig. 4) and values of and ΔH and ΔS were calculated from this plot.

Table 5 Effect of temperature on extraction process and equilibrium constant values

Extraction temperature, K	M_l, polyphenols in solution, g	M_s, polyphenols in solid phase, g	K, equilibrium constant
303	1.6	1.9	0.84
313	1.8	1.7	1.06
318	1.91	1.59	1.20
323	2	1.5	1.33
328	2.1	1.4	1.50
333	2.13	1.37	1.55
338	2.18	1.32	1.65
343	2.25	1.25	1.80

From Fig.4 we found that entropy change (ΔS) of this process was equal to 52 (J, (mol, K^{-1})), and enthalpy change (ΔH) was equal to 16304 (Jmol^{-1}).
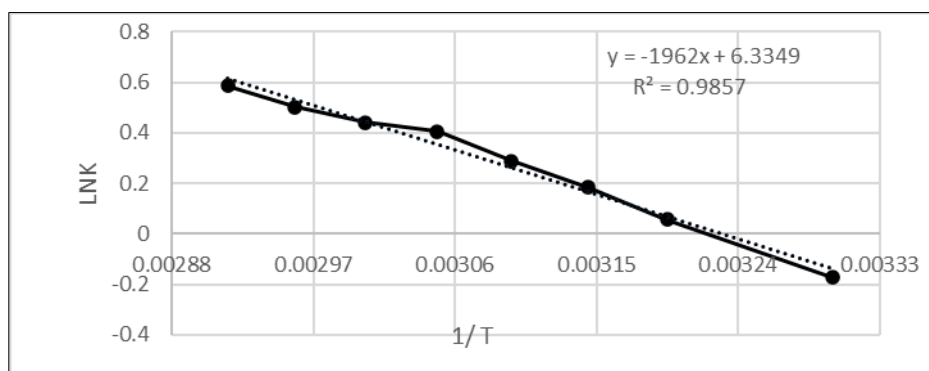
Figure 4 Plot of Lnk vs 1/T

The fact that the enthalpy change displayed a positive value suggested that the process of extracting polyphenols was endothermic. Likewise, the entropy change of the process was also positive. Change of Gibbs free energy at different temperature is given in Table 6.

Table 6 Change of Gibbs free energy at different temperature

Extraction temperature, K	ΔG, kJmol^{-1}
303.00	0.548
313.00	0.028
318.00	-0.232
323.00	-0.492
328.00	-0.752
333.00	-1.012
338.00	-1.272
343.00	-1.532

For the Gibbs free energy change values of the process at temperatures 303 and 313 K were though positive but very near to zero, all other values were negative. Therefore, this indicates that the process is feasible and occurs spontaneously. As the extraction temperature increased, the ΔG value progressively decreased, implying that higher temperatures facilitate easier extraction.

4. Conclusion

First Order Model of tea polyphenols extraction was shown to be well describing the process.

The most useful conditions for polyphenols extraction from green tea leaves were $70\,^0C$ and 20 min. At these conditions equilibrium constant of the extraction process was equal to 1.8.

Activation energy of the process $E_a=2798$ j/mol. The positive value of the enthalpy change was an indication that polyphenols extraction process was endothermic. Similarly, the entropy change of the process was also positive. The ΔG value gradually decreased as the extraction temperature increased, indicating that increasing the extraction temperature can make the extraction easier.

Compliance with ethical standards

Disclosure of conflict of interest

The authors declare no conflict of interest.

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