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Superheated Water Extraction of Catechins from Green Tea Leaves: Modeling and Simulation

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Abstract. *Catechins from fresh green tea leaves as potential sources of anticancer and antioxidant components were target materials in this work. Superheated water extraction, which is a kind of leaching operation, and solvent partition with chloroform and ethyl acetate were utilized to recover Catechins from tea leaves. Then, a mathematical model was developed to simulate the superheated water extraction of Catechins. The unsteady state mass balance of the solute in solid and superheated water phases led to two partial differential equations. The model was solved numerically using a linear equilibrium relationship. The model parameters were predicted applying existing experimental correlations. An intraparticle diffusion coefficient was used as the model tuning parameter. The model is able to show the influence of different process parameters, such as time of extraction, particle size and the ratio of water/leaves (v/w), on Catechin recovery.*

Keywords: *Superheated extraction; Modeling; Mass transfer; Diffusion; Catechins.*

INTRODUCTION

Recently, the demand for green tea has increased, due to human health concerns and preference. The main components in green tea are polysaccharides, flavonoids, vitamins B, C and E, R-amino butyric acid, Catechin compounds and fluoride. Among them, Catechin compounds have been of focus for an anticancer function. The pharmaceutical activities of the components have been studied. The main Catechin compounds found in green tea are: (-) epigallocatechin (EGC), (-) epicatechin (EC), (-) epigallocatechin gallate (EGCG), (-) epicatechin gallate (ECG) and other compounds. These Catechin compounds have been proven to have a variety of physiological functions, such as those affecting duodenum, colon, skin, lung, breast, esophageal, pancreatic and prostate cancer. EGCG exhibits stronger sulfated effects 20 of 30 and 2-4 times higher than vitamins C, E, and BHA or BHT, respectively, when used as sulfated agents in general cosmetics. Sulfated agents protect vital cells by combining free radicals before they react with other vital cells. Therefore, the high sulfated effect of Catechin compounds will become more important in the future of the cosmetic industry [1]. For the quality control of green tea preparation and for in-depth investigation of the biological and pharmacological properties of green tea polyphenols, reference compounds of certified purity are required in milligram to multigram quantities [2]. Yoshida et al. [3] studied the effects of various experimental conditions that may affect the extraction efficiency of green tea Catechins using aqueous buffers. They extracted tea samples with 100 ml of either buffer or distilled water at 80°C with constant shaking for 20 min [3]. In another study, crude Catechin extracts from the shoots of tea cultivars were extracted with boiling aqueous 70% Methanol, concentrated on a rotavapor (40°C) and partitioned with an equal volume of light petroleum (40-60). The aqueous layer was portioned with Ethyl Acetate and the Ethyl Acetate layer was concentrated on a rotavapor (< 40°C). The sticky residue obtained was dissolved in water and freeze dried to obtain the Catechin extracts as pale yellow solids [4]. Ho Row and Jin [1] used the methodologies of solvent extraction and partition to recover Catechin compounds from Korean tea at 80°C and 40 min. Perva-Uzunalic et al. [5] studied the effects of different extraction set-

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ups that influence the extraction efficiency of Catechins and caffeine from green tea leaves using different aqueous and pure solvents (acetone, ethanol, methanol, acetonitrile and water), different temperatures (60, 80, 95 and 100°C) and times (5-240 min) [5]. Extraction of Catechin and epicatechin from tea leaves and grape seed with four different pure solvents (water, methanol, ethanol and ethyl acetate) at 1×10^7 Pa and at high temperatures (100-200°C) was studied by Pineiro et al. [6]. Separation of Catechins from green tea using carbon dioxide extraction has been reported by Chang et al. [7].

With an increasing interest in avoiding organic solvents in the extraction of active or marker compounds from medicinal plants, superheated water extraction has been shown to be a feasible alternative approach. The equipment required can be relatively simple and avoids the need for the high pressures (3.1×10^7 Pa) [7] employed in supercritical fluid extraction. Even with the additional sample preparation steps, methods using superheated water extraction have been shown to give good repeatability and recovery [8].

In this work, Catechins were leached from fresh green tea leaves by superheated water (100-130°C, 3×10^6 Pa). Also, a mathematical model based on differential mass balances in two phases was developed. The model can be used to study the effect of different parameters on extraction efficiency and scaling up the superheated water extraction process.

MATERIALS AND METHODS

Materials

The fresh green tea leaves used in this experiment were collected from plants growing in Lahijan, Iran in May and June. Chloroform and ethyl acetate were HPLC grade and from the Merck Co. (Germany). Twice distilled water was used.

Extraction System

All extractions were performed using the apparatus shown schematically in Figure 1. The extraction system consisted of:

- A 30 mL extraction cell made of stainless steel, with four layers of filter paper in the outlet to filter the extraction product.
- A 27 L insulated paraffin bath with heater, mixer and temperature controller to keep the system at constant temperature.
- A pressure gauge.
- A nitrogen gas cylinder to keep the system at constant pressure and purge the extraction product after the extraction is finished.

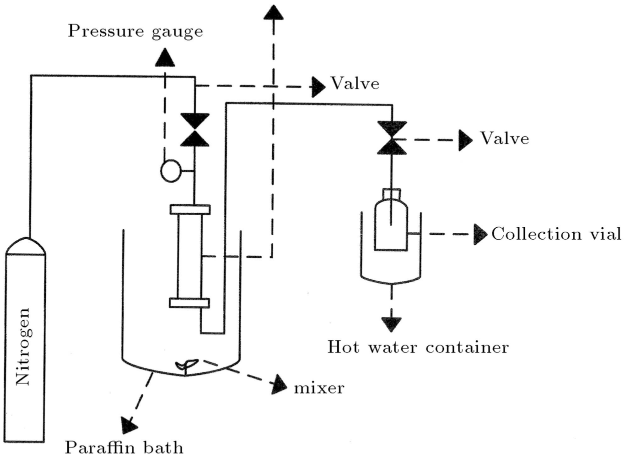

Figure 1. Superheated water extraction system.

- Valves in the inlet and outlet of the extraction cell.
- Connecting tubes.
- Collecting vial.

EXTRACTION OF CATECHINS FROM TEA LEAVES

The extraction of Catechin was done in three steps:

1. 5 g of grounded fresh leaves were extracted with 25 ml pure water at four different temperatures (100, 110, 120 and 130°C), and different times (0, 5, 10, 15, 20, 25 and 30 min). The pressure was kept constant (3×10^6 Pa) to keep the water in a liquid phase. In all extractions, the cell was filled with 5 g of ground leaves. Then, 25 ml pure water was added to the cell. The extraction cell was then assembled in the paraffin bath. The valve connected to the nitrogen cylinder was opened until achieving the required pressure. Then, the system was heated to the desired temperature. After around 20-25 min. (depending on the temperature selected to perform the extraction), the system achieved the required temperature and the extraction time was set to zero. After each extraction time, the outlet valve was opened and the extracts were collected in the vial. To separate the tea leaves from the water extract, four layers of filter paper were inserted in the outlet of the extraction cell.
2. The water extract was partitioned with water/chloroform (1:1 vol. %). Using the water/chloroform partition, caffeine and related impurities were extracted into the chloroform. The water phase which contained Catechin was collected and the chloroform phase was discarded. As a second partitioning, water/ethyl acetate (1:1 vol. %) was used. Catechins moved into the ethyl acetate layer. Each partitioning was done three times [1].

3. Compressed air was used to evaporate ethyl acetate. Then, dried crude Catechins were weighed.

MODEL DESCRIPTION

A two-phase model, comprising solid and superheated water phases, was used. The extraction vessel was cylindrical. The ground leaves were considered to be mono-sized spherical solid particles. Chemical reactions, usually the oxidation and epimerization of Catechins, may take place during extraction. Therefore, the operating temperature and extraction time should be taken into account. To develop a kinetic model, two main factors were taken into account: mass transfer and the thermal degradation of Catechins in both solid and superheated water phases.

Main assumptions of the model were:

- Catechins are assumed as a single component and the effect of other components on the extraction process at extraction temperature and pressure is negligible.
- Extraction temperature and pressure is constant during the process.
- The physical properties of superheated water and Catechins are constant.
- Concentration of Catechins in the solid phase is a function of r (distance from the center of the particle) and time and is independent of coordinates ϕ and θ.
- At a certain time, the concentration of Catechins in the superheated water is uniform in the extractor.
- All the Catechins were extracted with superheated water, transferred to the ethyl acetate layer and weighed.
- The degradation of Catechins follows first-order kinetics and the rate constants of the reaction are equal in both phases.

The governing partial differential equations and their associated initial and boundary conditions for each phase are as follows:

Solid phase:

$$\frac{\partial C_s}{\partial t} = \frac{1}{r^2} D_s \frac{\partial r^2 \frac{\partial C_s}{\partial r}}{\partial t} - KC_s, \tag{1}$$

$$t = 0, \quad 0 \le r \le R, \qquad C_s = C_{s0}, \tag{2}$$

$$t > 0, \quad r = 0, \qquad \frac{\partial C_s}{\partial r} = 0, \tag{3}$$

$$t > 0, \quad r = R,$$

$$-D_s \frac{\partial C_s}{\partial r} = K_f (C_{fs} - C_f). \tag{4}$$

A linear equilibrium relationship between concentrations in the solid phase and superheated water phase at the interface can be assumed as follows [9]:

$$C_{fs} = K_p C_{ss}, \tag{5}$$

where C_{fs} is Catechins concentration in the water at the particle surface, C_{ss} is the solute concentration in the solid phase in equilibrium with the water phase and K_p is the volumetric partition coefficient of the solute between the solid and the liquid phase.

Substituting $U = rC_s$ and Equation 5 in Equations 1-4 [9] the following are obtained:

$$\frac{\partial U}{\partial t} = D_s \frac{\partial^2 C_s}{\partial r^2} + KU, \tag{6}$$

$$t = 0, \quad 0 \le r \le R, \qquad U = r \times C_s, \tag{7}$$

$$t > 0, \quad r = 0, \qquad U = 0, \tag{8}$$

$$t > 0, \quad r = R,$$

$$\frac{\partial U}{\partial r} = \left(\frac{1}{R} - \frac{K_f K_p}{D_s} U + \frac{K_f R}{D_s} C_f \right). \tag{9}$$

Superheated water:

$$\frac{\partial C_f}{\partial t} = K_f \frac{6(1-\varepsilon)}{\varepsilon d_p} (C_{fs} - C_f) - KC_f, \tag{10}$$

$$t = 0, \qquad C_f = C_{f0}. \tag{11}$$

Equations 6 and 9 can be solved simultaneously for C_f and C_s.

Solution Technique

The equations obtained were solved numerically. The Crank-Nicolson implicit method was used to find the concentration profile in the solid phase. The time derivation in Equation 6 was substituted by a forward difference approximation. In the boundary condition (Equation 9), the spatial derivative was substituted by a backward difference approximation. The time derivation in Equation 10 was substituted by a backward difference approximation. The finite difference form of the governing equations is as follows:

Solid phase:

$$\begin{aligned} &-D_s \frac{\Delta t}{\Delta r^2} U_{k+1,i+1} + \Bigg(2 + \frac{2D_s \Delta t}{\Delta r^2} + \\ &\qquad K\Delta t \Bigg) U_{k+1,i} - D_s \frac{\Delta t}{\Delta r^2} U_{k+1,i-1} = \\ &\qquad D_s \frac{\Delta t}{\Delta r^2} U_{k,i+1} + U_{k,i} + D_s \frac{\Delta t}{\Delta r^2} U_{k,i-1}, \\ &\qquad 1 \le i \le N, \end{aligned} \tag{12}$$

$$U_{0,i} = r_i C_{s0}, \quad k = 0, \quad 0 \leq i \leq NR, \tag{13}$$

$$U_{k,0} = 0, \quad k > 0, \quad i = 0, \tag{14}$$

$$U_{k,NR} = \frac{4U_{k,NR-1} - U_{k,NR-2} + \frac{2K_f \Delta r}{D_s} C_{fk}}{3 - 2\left(\frac{1}{R} - \frac{K_f K_p}{D_s}\right) \Delta r U_{k,NR}},$$

$$k > 0, \quad i = NR. \tag{15}$$

Superheated water phase:

$$\begin{aligned} C_{f_{k+1}} &= 6(1-\varepsilon)\Delta t \frac{K_f K_p}{\varepsilon d_p} C_{s_{NR}} \\ &+ \left(-6(1-\varepsilon)\Delta t \frac{K_f}{\varepsilon d_p} + 1\right) C_{f_k} \\ &- K \Delta t C_{f_k}, \quad k > 0, \end{aligned} \tag{16}$$

$$C_f = 0, \quad k = 0. \tag{17}$$

As seen from Equations 12-17, a set of simultaneous linear algebraic equations must be solved. The mass of Catechins extracted was calculated by Equation 18.

$$\text{mass of extracted catechins} = M_s V_f C_f, \tag{18}$$

where V_f is the water volume at the extraction temperature, M_s is the Catechins molecular weight and C_f is the Catechins concentration in superheated water.

Parameters Identification and Correlations

There is no flow past solid spheres in the extractor. Therefore, the mass transfer coefficient in the liquid phase was estimated using an empirical correlation, which is shown in the following equation [10]:

$$\text{Sh}_m = \frac{K_f d_p}{D_f} = 2. \tag{19}$$

The diffusivity in the water (D_f) was estimated with the Wilke-Chang method [11].

$$D_f = \frac{7.4 \times 10^{-8} (\varphi M_f)^{1/2} T}{\mu_f V_s^{0.6}}, \tag{20}$$

where M_f is the water molar mass, ϕ is equal to 2 and μ_f is the water viscosity supposed to be independent of pressure. The values of the viscosity and density of water were the same as values reported by Holman [12]. The molar volume of solute (V_s) was calculated with Equation 21. In this equation, V_j is the molar volume and Y_j is the mole fraction of each Catechin. The molar volume of each Catechin was estimated with the Le Bas method [11].

The molecular weight and content of major Catechins on a dry mass basis are shown in Table 1 [5,13].

The molecular weight of Catechins was calculated with Equation 22. In this equation, M_j is the molecular weight and Y_j is the mole fraction of each Catechin. Table 2 contains the calculated molar volume and mole fraction of each Catechin.

The value of the activation energy (E_a) and the frequency factor (A) of the degradation of Catechins, were assumed to be the same as the values reported by Wang et al. [14]. K_p was estimated to be 0.55 [15].

$$V_s = \sum\nolimits_{j=1}^{4} Y_j V_j, \tag{21}$$

$$M_s = \sum\nolimits_{j=1}^{4} M_j Y_j. \tag{22}$$

Table 1. Molecular weight and content of major Catechins on dry mass basis [5,14].

Catechins	Content (g/kg Dry Leaves)	Molar Weight (gr/mol)
Epicatechingallate	15.2	290
Epigallocatechin	46.0	458
Epigallocatechin gallat	129	306
Epicatechin	0.9	442

Table 2. Calculated molar volume and mole fraction of each Catechin.

Component Name	Mole Fraction	Molar Volume (cm^3/mol)
Epicatechin	0.006511	276.7
Epigallocatechin gallat	0.590212	424.3
Epigallocatechin	0.331863	276.7
Epicatechingallate	0.071414	416.9

The initial concentration of Catechins was calculated with Equation 23.

$$C_{s0} = \frac{\left(1 - \frac{\text{water content}}{\text{mass of leaves}}\right) \times \rho_s \times \left(\frac{\text{Catechins content}}{\text{mass of leaves}}\right)}{M_s}. \quad (23)$$

Bed porosity, the density of tea leaves, the water content of fresh leaves, the initial concentration of Catechins in superheated water (C_{f0}) and the particle mean diameter were determined experimentally.

Using a diffusion coefficient in the solid phase as a model parameter, the best fit to the experimental data has been obtained employing the least-squares method.

RESULTS AND DISCUSSION

Table 3 shows the input parameters of the model. Results obtained from the model and experiments are shown in Figures 2-5. Each experiment was done twice. Relative errors which were calculated with Equation 24 show that the maximum relative error is 7.14%. This error value occurs at 120°C and 30 min.

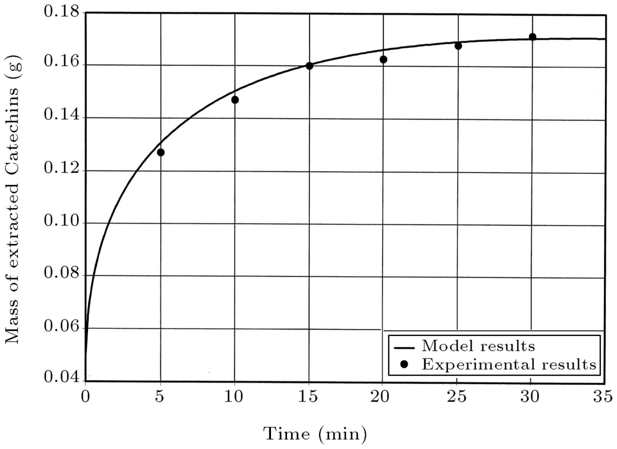

Figure 2. Mass of Catechins extracted at 100°C.

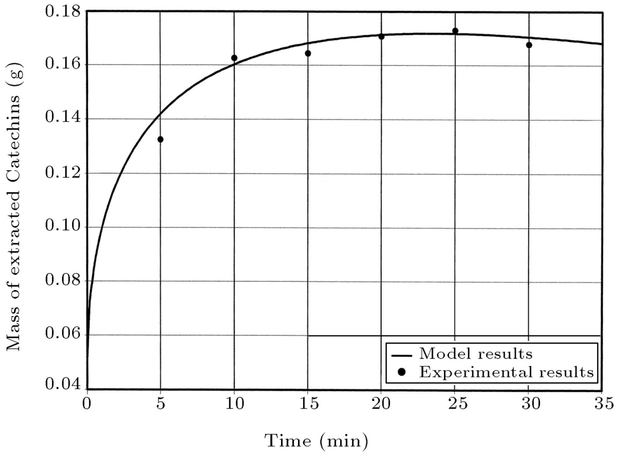

Figure 3. Mass of Catechins extracted at 110°C.

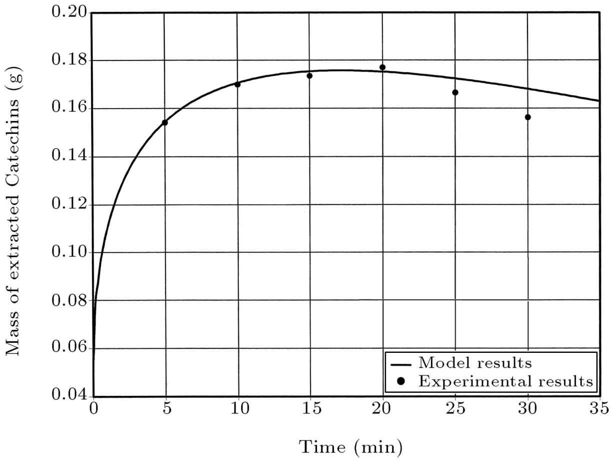

Figure 4. Mass of Catechins extracted at 120°C.

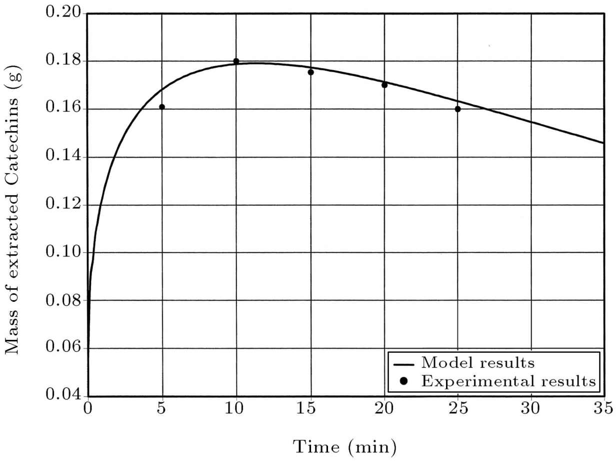

Figure 5. Mass of Catechins extracted at 130°C.

$$\delta = \frac{|\text{experimental value} - \text{model result}|}{\text{experimental value}} \times 100. \quad (24)$$

Results show that as the extraction time increased the mass of Catechins extracted increased, reached a maximum value and then decreased. Maximum values occurred at different extraction times at different temperatures. At higher temperatures, the extraction time related to the maximum value of the extracted Catechins is shorter.

The Catechins concentration profile in the solid phase, at different times at 130°C is shown in Figure 6.

The effects of particle diameter and ratio of water/leaves (v/w) on extraction efficiency at 130°C were calculated and shown in Figures 7 and 8, respectively. Here, efficiency is defined as the percent of the amount of Catechins extracted per the initial amount of Catechins in the solid phase. As seen from Figures 7 and 8, efficiency decreases with particle diameter and increases with the ratio of water/leaves.

As can be seen in the figures, the amount of

Table 3. Model parameters.

Parameter	Value
P (Pa)	3×10^6
ε (-)	0.75
d_p (m)	5×10^{-4}
K_p (-)	0.55
C_{s0} (mol/m^3)	93.51
A (min^{-1})	2.56×10^3
E_a	42.78
M_s (g/mol)	401
Δ r (m)	5×10^{-6}
Δ t (s)	10
C_{f0} (mol/m^3) at 100°C	4.95
C_{f0} (mol/m^3) at 110°C	5.17
C_{f0} (mol/m^3) at 120°C	5.36
C_{f0} (mol/m^3) at 130°C	5.61

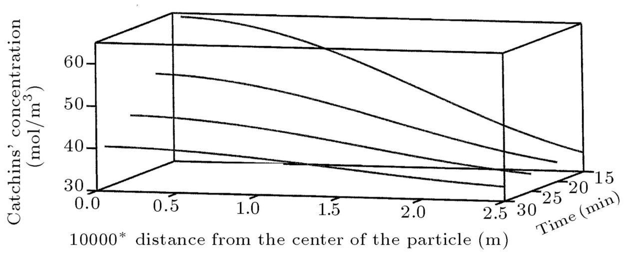

Figure 6. Catechins concentration profile in solid phase at 130°C.

extracted Catechins and therefore, the extraction efficiency increases with time reaches a maximum value and then decreases. This behavior can be attributed to the superposition of two different effects. The first of these effects is the diffusion of Catechins into the water. The second effect in this case of contrary consequences is the degradation of these compounds at high temperatures. It was shown that the epimerization and degradation of tea Catechins followed first-order reactions and the rate constants of reaction kinetics followed the Arrhenius equation [14].

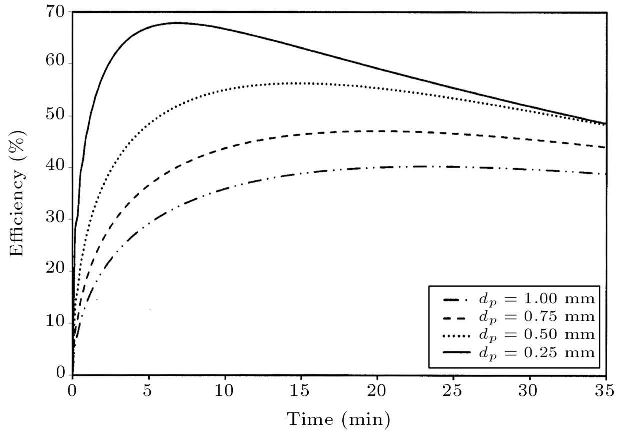

Figure 7. Effect of particle diameter on extraction efficiency at 130°C.

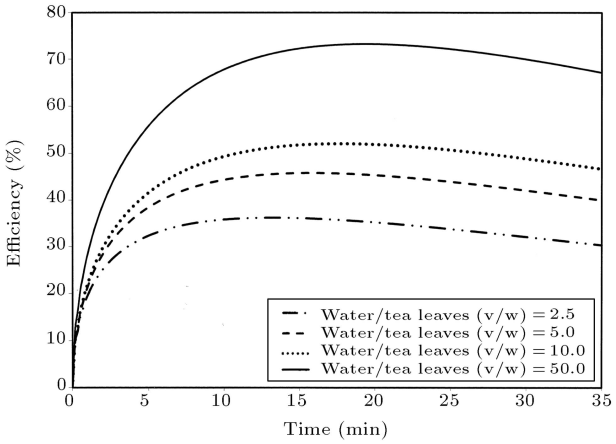

Figure 8. Effect of ratio of water/leaves (v/w) on extraction efficiency at 130°C.

Both degradation and diffusion affect the amount of extracted Catechins. Therefore, any parameter which affects the diffusion or degradation, such as particle size, temperature, extraction time etc., affects the extraction efficiency too.

Diffusion coefficients in the solid phase obtained versus temperature are shown in Figure 9. Exponential and linear fittings were used to find the relationship between diffusion coefficients in the solid phase and temperature. Equations are shown in the figure.

As seen in Figure 9, the exponential model fits the data better. The equation was used to overestimate the extraction efficiency at higher temperatures. The results are shown in Figure 10.

If different values were assumed for A, K_p and the Catechin content of leaves, different values should

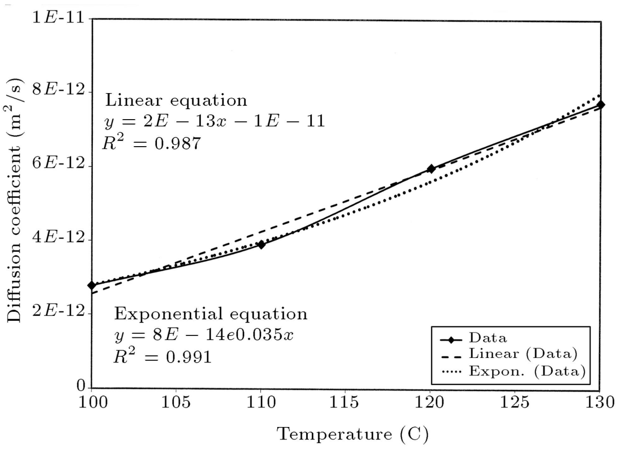

Figure 9. Diffusion coefficients in solid phase vs. temperature.

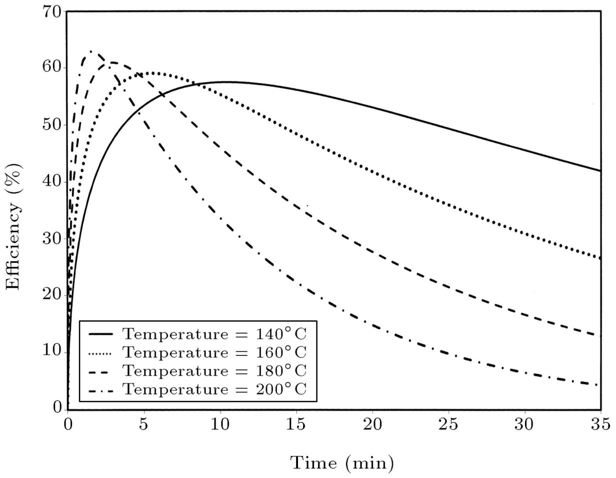

Figure 10. Extraction efficiency at temperatures higher than 130°C.

be considered for the intraparticle diffusivity to obtain the best fit with the experimental data. Intraparticle diffusivity for different values of A, K_p and the Catechin content of leaves, were calculated and are shown in Tables 4 to 6, respectively. As seen from the tables, to obtain the best fit with experimental data, the values of diffusion coefficients in the solid phase increase with A and decrease with K_p and Catechin content.

CONCLUSION

Catechins were extracted with superheated water in a batch system at constant pressure (3×10^6 Pa), different temperatures (100, 110, 120, 130°C) and different extraction times (0.5-3 min). A mathematical two-phase model was developed to simulate Catechins extraction under different operating conditions. The

Table 4. Intraparticle diffusivity for different values of A at different temperatures.

A	**$Ds \times 10^{12}$ $(\mathrm{m}^2/\mathrm{s})$ at 130°C**	**$Ds \times 10^{12}$ $(\mathrm{m}^2/\mathrm{s})$ at 120°C**	**$Ds \times 10^{12}$ $(\mathrm{m}^2/\mathrm{s})$ at 110°C**	**$Ds \times 10^{12}$ $(\mathrm{m}^2/\mathrm{s})$ at 100°C**
100	2.824	2.62	2.135	1.9
500	3.2	2.86	2.285	1.945
1000	3.728	3.18	2.485	2.08
1500	4.336	3.5418	2.705	2.215
2000	5.104	3.9443	2.94	2.305
2500	6.008	4.3916	3.19	2.45
3000	7.012	4.8804	3.47	2.585
3500	8.16	5.4129	3.76	2.765
4000	9.392	5.988	4.07	2.9
4500	10.672	6.6	4.406	3.08
5000	11.968	7.25	4.756	3.215

Table 5. Intraparticle diffusivity for different values of K_p at different temperatures.

K_p	**$Ds \times 10^{12}$ $(\mathrm{m}^2/\mathrm{s})$ at 130°C**	**$Ds \times 10^{12}$ $(\mathrm{m}^2/\mathrm{s})$ at 120°C**	**$Ds \times 10^{12}$ $(\mathrm{m}^2/\mathrm{s})$ at 110°C**	**$Ds \times 10^{12}$ $(\mathrm{m}^2/\mathrm{s})$ at 100°C**
0.8	3.6797	2.775	2.2	1.775
0.75	3.8759	2.94	2.3295	1.865
0.7	4.1702	3.25	2.4265	1.955
0.65	4.5626	3.45	2.6205	2.09
0.6	5.1512	3.813	2.873	2.225
0.5	7.309	5.268	3.649	2.765
0.45	9.6638	6.7715	4.425	3.26
0.4	14	9.365	5.686	4.025
0.35	22	15.215	8.0555	5.465
0.3	42.65	26.37	12.705	8.525

Table 6. Intraparticle diffusivity for different values of Catechin contents of leaves at different temperatures.

Weight Fraction of Catechins	**$Ds \times 10^{12}$ (m^2/s) at 130°C**	**$Ds \times 10^{12}$ (m^2/s) at 120°C**	**$Ds \times 10^{12}$ (m^2/s) at 110°C**	**$Ds \times 10^{12}$ (m^2/s) at 100°C**
15%	36	24.714	11	9.035
25%	4	1.987	1.987	1.005
30%	1.26	0.98	0.8	0.67

maximum mass of extracted Catechins was 0.1800 g at 130°C and 10 min. Model results show that at 130°C, extraction efficiency increases from 40% in 20-25 min to 68% in 7 min, when the particle diameter decreases from 1 to 0.25 millimeters. It also shows that at the same temperature extraction efficiency increases from 42% in 12 min to 72% in 17 min. Extraction efficiency was calculated at 140, 160, 180 and 200°C. The maximum value was obtained at 200°C and 2.5 min. The model obtained here can be used in scale-up studying and in predicting the effect of different extraction conditions on extraction efficiency.

ACKNOWLEDGMENT

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NOMENCLATURE

Δ	difference operator
ϕ	spherical coordinate
θ	spherical coordinate
ε	void fraction
μ_f	water viscosity (Pa s)
A	frequency factor (min^{-1})
C_f	Catechins concentration in water phase (mol/m^3)
C_{f0}	initial Catechins concentration in water phase (mol/m^3)
C_{fs}	Catechins concentration in the water phase at the particle surface (mol/m^3)
C_s	Catechins concentration in the solid phase (mol/m^3)
C_{s0}	initial Catechins concentration in the solid phase (mol/m^3)
C_{ss}	Catechins concentration in the solid phase at the particle surface (mol/m^3)
D_f	diffusivity in the water phase (m^2/s)
d_p	particle diameter (m)
D_s	ddiffusivity in the solid phase (m^2/s)
Ea	activation energy (kJ/mol)
i	space index in the solid phase
j	component index
K	Catechins degradation reaction constant (S^{-1})
k	time index
K_f	mass transfer coefficient (m/s)
K_p	volumetric partition coefficient
M_f	water molecular weight
M_j	molecular weight of each Catechins (g/mol)
M_s	Catechins molecular weight
NR	number of subdivisions in the particle
P	pressure (Pa)
r	radial distance (m)
Sh	Sherwood number
T	temperature (°C)
t	time (s)
U	dependent variable in Equation 6
V_f	water volume (m^3)
V_j	molar volume of each Catechin (cm^3/mol)
V_s	solid molar volume (m^3)

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