The use of an innovative inverse numerical modeling method for the evaluation and parameter estimation of barberry anthocyanins ultrasound assisted extraction

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ABSTRACT

There has been a significant interest to extract functional ingredients by novel methods such as ultrasound assisted extraction, recently, whereas limited engineering data are available in this regard. The aim of this study was to develop a precise and powerful technique based on inverse parameter estimation of finite volume model to estimate process coefficients of barberry anthocyanin compounds (ACs) ultrasound-assisted extraction (UAE). For this purpose, anthocyanin concentration over time was determined under different experimental conditions. Then, a new numerical model considering a complex system of dispersion, diffusion and degradation was developed and coupled with a parameter estimation code. Finally, parameters were estimated by minimizing differences between experimental and numerical data. UAE enhanced the extraction rate while degradation of the extracted barberry ACs was occurred. Therefore, it was necessary to understand the rate parameters of the process. The predicted coefficients of overall mass transfer, diffusion (D_e), dispersion (E), and degradation (k_deg) of the barberry ACs under different conditions were (1.375–2.731 × 10⁻⁷ m/s), (2.523–5.012 × 10⁻¹¹ m²/s), (1.000 × 10⁻⁷–1.000 × 10⁻³ m²/s), and (1.000 × 10⁻⁷–5.637 × 10⁻⁵ s⁻¹), respectively. A good agreement between the experimental and predicted data were obtained. Sonication was shown to affect both extraction rate and degradation rate. Higher D_e values were obtained at the presence of sonication while high duty cycles could increase degradation rates.

1. Introduction

In recent years, the application of novel extraction methods including ultrasound assisted extraction (UAE), has been evaluated and employed widely to obtain functional foods and/or ingredients from plant sources. The main focus of researches available on UAE has been providing experimental data of ultrasound efficiency, while further efforts to practical applications of this process demand engineering investigations including process simulation and modeling. Berberis vulgaris, known as barberry, contains high amounts of phenolic compounds and is known as a plant material with remarkable anti-oxidant activities. The bioactive compounds of barberry are widely used in food and pharmaceutical industries [1]. The application of this plant in the food industry is limited although its functional properties are promising. As the predominant species of phenolic compounds, anthocyanin compounds (ACs) cause development of anti-inflammatory and anti-mutagenicity properties as well as protection of the body cardiovascular diseases [2].

Solid-liquid extraction is a process used for separation and isolation of bioactive compounds from natural sources. Traditional extraction of ACs leads to high solvent and energy consumption, long process time and relatively low yield. Alternatively, the extraction has been practiced recently by assisting ultrasound, microwave, super and sub critical fluid, solid phase, etc. instead of the traditional methods to enhance the efficiency of the process [3]. Meanwhile, UAE has been considered as a well-established system because of reducing the time, energy and solvent consumption as well as increasing the efficiency of the process [4–6]. The increased efficiency is related to the cavitation phenomenon during the process, causing degradation of the plant cellular walls, and improved mass transfer process of the target compound in the solvent [7]. Therefore, it has been suggested that new parameters i.e. mass transfer, diffusion, dispersion and degradation coefficients could be

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introduced for the processes that are assisted by sonication.

Since the extraction process is affected by different physiochemical variables, precise quantitative and qualitative evaluation is difficult. Modeling of natural processes has been known as an acceptable tool for describing and predicting purposes under various environmental conditions. Mathematical modeling is one of the beneficial methods in simulating processes. Solving mass or heat transfer equations using analytical methods leads to precise calculation of the differential equations parameters. However, this method is inefficient in most nonlinear equations and can not be used for systems with complex geometries and boundary conditions. Numerical solution of partial differential equations has been considered as one of the most practical methods for complex systems [8].

In recent years, thanks to the access to high-speed computers and specialized software, application of mathematical modeling and computational simulation based on numerical analysis has been grown interests in designing, developing, optimizing, and controlling various transfer phenomena [9,10]. Knowledge of mass transfer properties plays a significant role in the design and simulation of extraction processes. The physical characteristics of foods are different in varying environmental conditions and determination of the coefficients necessitates time-consuming measurements. Furthermore, specification of these parameters using common experiments may not represent real conditions [10].

The estimation of physical characteristics using inverse method has recently attracted a great deal of attention [11–13]. Indeed, the inverse approach is a technique for estimating the model parameters applying experimental data. Unlike the direct method, which calculates the results by mathematical equations and model parameters, inverse methods involve applying general mathematical techniques to estimate the model parameters based on observing their effects [14]. In this method, the model parameters are computed by using experimental data, the general equations governing the system and suitable iterative optimization algorithms [15]. The optimum model parameters are obtained by minimizing differences between experimental and predicted results [16].

In various studies, indirect parameter estimation methods has been used for determining heat characteristics [11,17–19], moisture permeability [10,12,13], and rheological properties of foods [16,20]. However, no study has been conducted on modeling the extraction of bioactive compounds of foods using inverse method.

The aim of this study was to model the ultrasonic-assisted extraction of barberry ACs based on inverse of finite volume method and to investigate the potential of this technique for simultaneous estimation of $k_c$, $D_a$, E, and $k_{deg}$ through simulation in a complex system. Thus, the evaluations were carried out in three steps: determination of anthocyanin concentration under different extraction conditions; development of a numerical model (capable of explaining the system behavior influenced by different variables) and numerically determination of barberry ACs concentration versus time; and finally estimation of the parameters through reducing the differences between the numerical data and experimental results.

2. Materials and methods

2.1. Materials

Fresh barberries were prepared from Birjand farms in fall 2015. After separating the redundant parts, branches and leaves from the fruit and cleaning it, every 250 g of the barberries were put inside a polyethylene package and were kept in the fridge before analysis.

2.2. The extraction process

For barberry ACs extraction, the sample (barberry) and solvent (water) were mixed together with a ratio of 1:5. To prevent the effect of light on barberry ACs, the extraction container was covered by an aluminum foil. The extraction was performed using an ultrasonic bath with a frequency of 28 kHz and nominal power of 80–180 W. The total extraction time was 300 min, and sampling was performed at 2, 4, 8, 15, 30, 60, 120, 240, and 300 min intervals. In this study, the analyzed variables were temperature (20, 40 and 60°C), duration of sonication...
(60, 150 and 240 min) and the duty cycle percentage (30, 50 and 70%).

2.3. Determination of anthocyanin concentration

Anthocyanin concentration measurement was carried out using the differential pH method [21]. As mentioned previously, at certain time intervals, samples were taken from the barberry and water mixture. To remove the turbid agents and to clear the extract, the samples were centrifuged for 15 min at 7000 rpm. Then, the top phase was used for measuring the anthocyanin concentration. In practice, the extract was diluted with the potassium chloride buffer (0.025 M, pH 1.0) and sodium acetate buffer (0.4 M, pH 4.5), and concentration was calculated by the following equation:

\[
\text{Anthocyanin concentration (mg/L)} = \frac{[(A_100 - A_500) \times 10^3 - (A_100 - A_500) \times 10^3] \times MW \times DF \times 1000}{c \times L}
\]

where \(A\) is absorbance and the indices represent the wavelength, MW is molecular weight of cyaniding 3-glycoside (449.2 g/mole), DF is dilution factor, \(c\) is molar absorbance of cyaniding 3-glycoside (26,900) and \(L\) is the length of cell path (1 cm). Absorbance was measured with a UV–vis spectrophotometer (HACH-DR/4000U, USA)

2.4. Model development and numerical determination of ACs

In this study, the extraction system contained barberry particles as the solid phase along with water as the liquid phase. Microscopically, the interactions occurring during the extraction process of barberry ACs can be considered as [22]:

- Transfer of the target compound through diffusion mechanism to the external surface of the solid structure
- Transfer of the ACs to the surrounding solution through the liquid boundary layer
- Transfer of the target compound through diffusion or dispersion mechanism within the liquid phase

Many researchers assume that this process is controlled by internal diffusion of the solvent particles in the solid matrix, and thus model it using Fick’s second law of diffusion [21,23]. From another perspective, which has been examined here, this process could also be affected by mass transfer of the dissolved particles between the solid matrix and liquid phase. It is assumed that mass transfer is controlled by the concentration gradient of the solute in the liquid phase and its equilibrium concentration [24,25]. The process equilibrium depends on various factors including temperature, time, the solid-to-solvent ratio, etc.

Considering the above-mentioned points, to develop an acceptable model, the following assumptions were made for the system:

- The system is isothermal and isobaric, and its physical characteristics remain constant in the course of the process.
- The concentration profile is constant within the particles at the initial extraction time.
- The concentration of the target compound in the solvent is dependent on time.
- The solvent volume is considered constant.
- The primary liquid phase is devoid of any ACs.
- The diffusion coefficient is independent of time and space.

Based on the mentioned assumptions and the results obtained from other studies, the following differential equation was considered as mass equilibrium of ACs in the liquid phase:

\[
\frac{\partial C}{\partial t} = D \nabla^2 C - k_{cl} (C_i^* - C) + V \cdot (\nabla C) = 0
\]

Eq. 2 indicates the mass transfer of ACs in the liquid phase, in which the accumulation rate of target particles is affected by molecular and dispersion transfer along the control volume (Laplacian part of the equation).

In this equation, \(C\) is the concentration (kg/m\(^3\)), \(t\) is time (s), \(E\) represents dispersion coefficient (m\(^2\)/s), \(k_c\) denotes the mass transfer coefficient (m/s), \(a\) is the specific surface area of the particles (1/m), \(C^*\) shows the concentration of the target compound in fruit particles (kg/m\(^3\)), and \(\phi\) is the flux of particles which corresponds to the level of fluid entering the system. Since the system of interest here is a closed system with no inlet or outlet, \(\phi\) level is considered zero [24].

Eq. 3 denotes the conservation of mass and indicates that the total mass of substances within the whole system is constant. In this equation \(u\) is the velocity (m/s) and \(p\) is the density of the component (kg/m\(^3\)).

As shown in the above equations, extraction of ACs from the tissue involves different types of mass transfer processes. Therefore, the total mass transfer coefficient \(k_\text{t}\) of the system, which is indeed a combination of internal and external resistance to mass transfer, is defined as [26]:

\[
k_\text{t} = \frac{k_{cl}k_{ca}}{k_{cl} + k_{ca}}
\]

where \(k_{cl}\) and \(k_{ca}\) are the external and internal mass transfer coefficients. Fig. 1 is a schematic showing \(k_c\), \(k_{cl}\), and \(k_{ca}\). The mass transfer coefficient in fruit particles is defined as [24]:

\[
k_{ca} = \frac{60D_i}{h^3}
\]

On the other hand, the mass transfer coefficient in the liquid phase (in the boundary layer between the solid and liquid) is calculated given the dimensionless numbers of Reynolds, Schmidt, and Sherwood [15]:

\[
Sh = 0.442Re^{0.69}Sc^{0.42}
\]

![Fig. 1. Schematic of anthocyanin mass transfer from the barberry to the extract solvent (water). C, C*, k_c, k_{cl} and k_{ca} represent concentration in the solid particles (barberry), concentration in the solution (water), overall mass transfer coefficient, mass transfer coefficient in the solid particles (barberry), and mass transfer coefficient in the liquid phase (water).](image-url)
control volumes (CV) is required for the spatial part of solution domain. In these types of problems, the CVs are not overlapped, have positive finite volumes and are completely localized in the measurement domain. Finally, all variables are calculated in the centroids of CVs based on their arrangement [29,30]. An ordinary CV is presented in the Fig. 3. As shown, each CV is surrounded by flat faces and each face is only common with the one neighbor CV. As illustrated in Fig. 3, the face area vector (Sf) for each face is considered such that its direction is outward from the CV, located in the centroid, normal to the interested face and its value is identical to face area. In Fig. 3, P and N represent centroid of CVp and CVn. Distance between P and N nominate as d vector. In order to brevity, all of the faces of CV including centroid is denoted as f.

The general transport equation (Eq. (2)) pointed in the Section 2–4 can be inscribed in the specified control volume Vp as follow:

\[
\sum \left( \frac{\partial E}{\partial t} \right)_i = \int_{V_p} \nabla \cdot \hat{\mathbf{q}} \, dV + \int_{S_p} \hat{\mathbf{q}} \cdot \left( \hat{\mathbf{n}} \right) \, dS
\]

(13)

The basis of FVM is on the Gauss theorem applied in the discretization procedure for transforming volume integrals to their surface corresponds. According to the Gauss theorem, the volume integral of the divergence of vector field \( \mathbf{b} \) in the CV is equivalent with the surface integral of the outward normal flux (n) to the surface embedded CV. For the vector \( \mathbf{b} \):

\[
\int_{V_p} \nabla \cdot \mathbf{b} \, dV = \sum_{f_p} \hat{n} \cdot \mathbf{b} \, dS
\]

(14)

In this equation \( \nabla \) is the surface bounded the control volume V and ds is the microscopic surface component owning the normal n with direction toward the outside of the surface. From this point, ds is used instead of nds [30].

With respect to Gauss theorem, Eq. (13) is written as:

\[
\frac{d}{dt} \int_{V_p} C \, dV + E \int_{S_p} \mathbf{q} \cdot \left( \mathbf{n} \right) \, dS \left( \int_{V_p} C \, dV \right) - \sum_{f_p} \mathbf{q} \cdot \left( \hat{n} \right) \, dS = 0
\]

(15)

For computing integral surfaces in above equation, knowledge of Ci value transported from each face of surface control is require. But these data are not available because variables are estimated in the centroid of CV, therefore an approximation should be consider in this step. It is supposed Ci linearly change in each face f of CV and mean value of Ci is.

![Fig. 2. Schematic of barberry anthocyanin ultrasonic-assisted extraction setup.](image-url)
calculated in each centroid face. So, the surface integral is approxi-
mated by product of transported $C_i$ at centroid face $f$ (mean of $C_i$ over
the surface) and surface $[28–31]$.

For numerical solution of the temporal part (first ones) of Eq. (13), it
is discretized through forward differencing method as below:

For new value of $C_i$: (14)

Finally by Euler implicit method, $C_i$ values is obtained in different
time steps:

As obviously illustrated, as a result of spatial discretization of dif-
fusion term, face gradient $\nabla C_i$ is constructed. In the orthogonal faces
which $d$ and $S$ vectors are parallel (Fig. 3-b), gradient term is calculated
as follow:

According to above equation, $(\nabla C_i)_f$ is computed by $C_i$ values of control volumes in two sides of face $f$ ($V_p$ and $V_N$).

But in the non-orthogonal meshes (Fig. 3-c), concerned in this study,
this approach is not applicable. In these kinds of meshes, instead of non-
orthogonal vector $S$, two vectors named $L$ and $N_\perp$ is introduced that sum
of them is vector $S$. Then $C_i$ gradient is estimated by Eq. 19:

And $(\nabla C_i)_f$ of face $f$ is given by:

Fig. 3. Spatial discretization in numerical modeling. a: An illustration of control volume, b: Orthogonal mesh, c: Non orthogonal mesh.
2.6. Numerical simulation and parameters estimation

The mathematical model mentioned in the previous section was implemented in the open source computational software, OpenFOAM (Foil-Extend 3.1), according to which a solver was developed based on finite volume method (FVM). For this purpose, the model of interest was solved in an iterative loop, and the desired stability was achieved when the residuals for the concentration decreased up to $10^{-5}$. The output of the solver written in the simulator was the curve of concentration changes vs. time, which was a function of diffusion ($D_e$), dispersion ($E$), and degradation ($k_{deg}$) coefficient.

Based on the least squares error criteria, the best value for the model parameters is obtained when the minimum extent of the objective function (the difference between experimental data and simulated results), is achieved [10]. The general relation for the target function can be defined as follows:

$$\text{minimize: } f(x) = \sum_{i=1}^{n} \left( T_i(x) - T_i(x) \right)^2$$  \hspace{1cm} (31)

In this relationship, $T_i$ is the residual between the model values and experimental results at point $i$, and $x$ is a parameter that should be predicted.

To achieve this target, the simulator (OpenFOAM) was connected to an optimization software, DAKOTA (Ohio, USA). Indeed, the main goal of using the optimization software was to develop a systematic and fast instrument to achieve optimal designs using simulation-based methods. DAKOTA optimization algorithms are used to minimize the target function, which is generally calculated through the simulator code in regard to defined limitations of the variable and response. By altering the level of the model parameters, this process proceeds such that the residual value approaches zero.

In this study, the aim was to optimize three parameters including $D_e$, $E$ and $k_{deg}$ using inverse method to model the ACs extraction process. Accordingly, the objective function in this study was considered as follows:

$$\text{OF}(D_e, E, k_{deg}) = \int \left[ C_{\text{exa}}(t_i) - C_{\text{num}}(t_i, D_e, E, k_{deg}) \right]^2 dt$$  \hspace{1cm} (32)

For each of the mentioned parameters, a range was considered based on the values reported in the literature. DAKOTA and the simulator code exchange the information through reading and writing short information files. The algorithm for parameter estimation assigns values to each of the variables and applies them into the simulator code. Thereafter, it receives a set of numerical data for the concentration and compares the numerical results with experimental data. Eventually, the objective function is evaluated in DAKOTA and when the errors decrease to an acceptable level, the corresponding values are reported as the final parameters (Fig. 4). In this study, to investigate the extent of fitness between experimental data and model results, $R^2$, SSE, and RMSE statistical parameters were used, and optimal models were achieved when $R^2$ was more than 0.7, while SSE and RMSE were minimum.

The simulation code was solved on a PC (VAIO VPCCW2DGX/B, Lubuntu, 64-bit operating system) equipped with a CPU (Intel® Core™ i5, M 540 @ 2.53 GHz) and 8 GB RAM.

3. Results and discussion

The extraction diagram of barberry ACs (changes of concentration vs. time) is demonstrated in Figs. 5–7. As revealed, regardless of the type and process conditions, three separate stages were observed during the extraction process of ACs. The first stage was the primary washing phase, which involved the early moments of the extraction process. At this stage, ACs with poor attachment to the plant matrix, due to different physicochemical reasons, are separated by the solvent. In the next step, slow or molecular diffusion of the compound was occurred, when the solid phase and boundary layer between the solid and liquid governed mass transfer through diffusion mechanism. In the last stage, the curve of concentration changes reached its maximum and a steady state was achieved, suggesting that the transfer rate of ACs to the solution at the residual time is zero [23].

Furthermore, the values of $k_c$, $D_e$, $E$ and $k_{deg}$ and the statistical parameters suggesting the extent of model fitness with experimental data are provided in Table 1. As illustrated, $R^2$ values for the proposed models were larger than 0.89, while SSE and RMSE were less than 0.005, and 0.023, respectively. These results suggested suitable agreement between experimental data and predicted ones. The reported deviation can be attributed to the experimental errors (personal or instrumental), the heterogeneity of barberry, and considered assumptions for the simulation (including neglecting the changes in the plant structure during the extraction process, and the effect of extraction of other plant compounds on ACs extraction).

The optimum level of $D_e$, $E$ and $k_{deg}$ estimated by reverse method was applied in the Eq. (2) in order to forward simulation for AC concentration computation. Trends of gradual variation of simulated ACs concentration during time are presented in Fig. 8. As shown, AC concentrations are illustrated by color scales and each rectangular reveals a 2D section of a CV. In all of runs, by marching in the time, AC concentration was developed and the intensity of color was changed. Since, depending on experimental treatment, the predicted values of $D_e$, $E$ and $k_{deg}$ were different the color pattern in each sample was different specially at lower times when changes were taking place. As illustrated in each time step, 2D plot had a specific color instead of color spectra. This was because of the fact that the concerned extraction system was liquid, with low viscosity, under continuous agitation, therefore variation of concentration in each time step for any spatial area was negligible.

The range of the calculated $D_e$ in this study was $(2.52-5.01 \times 10^{-11} \text{ m}^2/\text{s})$. Based on others studies, so far no value has
been reported for $D_e$ of barberry AC during extraction. However, some values are available for other plants as well as other methods in the literature. Amor et al. [32] reported 4.62–6.11 × 10^{-11} m²/s for instant pressure drop treatment, Xu et al. [21] observed 1.39–8.65 × 10^{-10} m²/s for high pressure CO₂ method, and Bonfigli et al. [22] found 7.97–9.78 × 10^{-12} and 4.49–6.32 × 10^{-12} m²/s for diffusion coefficient of traditional and UAE extraction, respectively.

ACs are synthesized in spherical-shaped cellular organs called anthocyanoplast, which lie in the cell vacuoles [21]. The releasing facility of ACs depends on physiological (cellular wall) and chemical (composition, stereochemistry, and degree of polymerization) characteristics. Based on the general theory of mass transfer during the solid-liquid extraction process, the cellular wall is the greatest obstacle against mass transfer due to its hard and resistant structure, and the role of chemical factors as well as the resistance of the anthocyanoplasts and vacuoles membrane is trivial in comparison with it [33].

However, since the experimental conditions, variables, and the simulation method used in this work have been different with those of other researchers, comparison of the diffusion coefficient values is difficult. Indeed, in most of the studies, the simple process of fitting the experimental data (resulting from changing the concentration of target compounds in the fruit solid structure) with mass transfer equations has been performed. The problem is that under real conditions, the process is also affected by other mechanisms including convection mass transfer. In some other papers, Fick’s law has been used for estimating the diffusion coefficient. Considering the porous structure of solid food compounds, the obtained values are typically larger than the real value. On the other hand, Knudsen diffusion may be the main controlling mechanism of mass transfer in the system, and thus the diffusion coefficient obtained by Fick’s law may not represent real conditions of the system [26,34]. Therefore, in this study, after estimating the effective diffusion coefficient of AC, the total mass transfer coefficient

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Fig. 5. Experimental and predicted values of anthocyanin concentration at different temperatures: a: 20°C, b: 40°C, c: 60°C.

Fig. 6. Experimental and predicted values of anthocyanin concentration at different ultrasonic wave time: a: 1H, b: 2.5H, c: 4H.
which includes the mass transfer coefficient of AC in the solid structure and the surrounding solution was calculated and investigated.

As stated previously, the solid-liquid extraction process involves two stages: 1) the washing or rapid stage, in which the target compound is rapidly extracted from damaged and external cells; 2) the diffusion stage in which the target compounds are transferred from the internal layers through diffusion. The prevailing phenomenon in the first stage is connective which is controlled by \( E \), while the second stage is diffusion and is controlled by \( D_e \).

The estimated value of \( E \) was \( 1.000 \times 10^{-7} - 1.000 \times 10^{-3} \text{m}^2/\text{s} \). So far, in the calculations of mass equilibrium of solid liquid extraction, the dispersion coefficient has not been investigated separately. However, in very few studies the \( D_e \) of the washing stage and diffusion has been calculated separately. Bonfigli et al. [22] reported \( 8.58 - 9.78 \times 10^{-12} \) and \( 3.67 - 8.97 \times 10^{-11} \text{m}^2/\text{s} \) for \( D_{ex,\text{wash}} \) of traditional extraction and UAE of AC within the thermal range of 25–65 °C. Similarly, Tao et al. [35] reported \( 2.44 - 4.92 \times 10^{-11} \text{m}^2/\text{s} \) for UAE of phenolic compounds within the thermal range of 20–50 °C. The coefficient \( E \) value predicted by the model has a larger magnitude compared to other studies. This may because of the physical properties of the plant compound, the extent of damage of its structure, and the process characteristics.

On the other hand, if the extraction includes heat-sensitive compounds such as ACs, in the mass equilibrium equation, in addition to transfer (either dispersion or diffusion) of target compound to the solvent, thermal degradation of them should also be considered [27]:

\[
\text{Plant} \rightarrow \text{so} \text{lent Degradation} \rightarrow \text{Kdeg}
\]

In fact, with temperature elevation, the rate of all reactions including degradation of ACs as well as the non-enzymatic browning reaction increases, causing diminished stability of ACs [36]. In spite of its importance, this issue has been relatively overlooked in the extraction modeling of heat-sensitive compounds. When the extraction involves this group of compounds (as anthocyanin), the final concentration is an outcome of transferred and thermal degraded active compounds.

In this study, the \( k_{\text{deg}} \) estimated by the model was (1.000 × 10^{-7}, 5.637 × 10^{-5} \text{s}^{-1}), which is almost comparable to the values obtained by other researchers for other anthocyanin-containing products. In this regard Cissé et al. [36] reported (0.286–7.99 × 10^{-5} \text{s}^{-1}) for the degradation rate of blackberry and Roselle. Similarly, Peron et al. [37] reported (0.205–9.083 × 10^{-5} \text{s}^{-1}) for Italian grape, and Sinela et al. [38] proposed (0.083–0.427 × 10^{-5} \text{s}^{-1}) and (0.320–1.853 × 10^{-6} \text{s}^{-1}) for cyanidin and Delphinidin respectively.

### 3.1. Effect of extraction temperature on \( D_{ex}, E \) and \( k_{\text{deg}} \)

![Graph](image)

Fig. 7. Experimental and predicted values of anthocyanin concentration at different ultrasonic duty cycles: a: 30%, b: 50%, c: 70%.

### Table 1

Estimated parameters of mass balance equation during UAE of barberry anthocyanin compounds in various conditions.

<table>
<thead>
<tr>
<th>parameters</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Duty cycle (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_e )</td>
<td>T = 20°C</td>
<td>3.239E-11</td>
<td>DC = 33%</td>
</tr>
<tr>
<td></td>
<td>T = 40°C</td>
<td>5.012E-11</td>
<td>3.91E-11</td>
</tr>
<tr>
<td></td>
<td>T = 60°C</td>
<td>3.442E-11</td>
<td>3.84E-11</td>
</tr>
<tr>
<td>( k_e )</td>
<td>T = 60°C</td>
<td>9.25E-6</td>
<td>3.81E-11</td>
</tr>
<tr>
<td>( k_{\text{deg}} )</td>
<td>T = 20°C</td>
<td>1.000E-7</td>
<td>9.89E-6</td>
</tr>
<tr>
<td></td>
<td>T = 40°C</td>
<td>9.52E-7</td>
<td>1.000E-7</td>
</tr>
<tr>
<td></td>
<td>T = 60°C</td>
<td>6.73E-7</td>
<td>1.125E-5</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>T = 60°C</td>
<td>0.999</td>
<td>0.982</td>
</tr>
<tr>
<td>RMSE</td>
<td>T = 60°C</td>
<td>0.001</td>
<td>0.008</td>
</tr>
<tr>
<td>SSE</td>
<td>T = 60°C</td>
<td>0.003</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Fig. 5(a–c) demonstrates the curves of changes in the concentration of ACs over time under different temperatures. As observed, the general trend is elevation of the extraction efficiency with temperature. At the temperatures of 20 and 40 °C, there was a classic trend of mass transfer process: the extraction rate of AC diminished over time, until reaching equilibrium (Fig. 5a–b). However, at 60 °C, there was a different trend; after initial increase (up to 180 min), the ACs in the solvent was diminished (Fig. 5c). Generally, in most food industry processes, the
solubility and diffusion coefficient of the compounds under extraction is increased with temperature rise, causing a higher extraction rate. This is due to the increased internal energy of molecules and decreased dynamic viscosity of the solvent (Stock-Einstein Equation) [39]. Furthermore, the temperature rise causes denaturation of proteins, and softening and swelling of plant tissues, thus facilitating diffusion of compounds [35]. As can be seen in Table 1, the mass transfer and diffusion coefficient predicted by the model increased with temperature rise up to 40 °C, but they decreased at 60 °C. In extraction of ACs by traditional and ultrasound-assisted methods, Bonfigli et al. [22] reported ongoing increase of k_c and D_e within the thermal range of 25–65 °C. However, in this study, unlike other investigations, k_c and D_e values first increased (up to 40 °C) and then decreased.

Note that the curve of barberry ACs over time predicted by the model is affected by k_c, D_e, E, and k_{deg}, whose outcome determines the concentration at a specific time. At the beginning of the process, as shown by the Fig. 5, a dramatic increase in the concentration of the compounds was observed, where the mass transfer driving force in this part was dispersion as controlled by the dispersion coefficient. The temperature of 60 °C had the maximum level of E (Table 1). This was due to the high initial concentration of ACs and the direct effect of temperature on E, causing increased mass transfer rate and process efficiency. Subsequently, the extraction rate declined, where the main mechanism of mass transfer in this part was diffusion. Thus, the reduction of k_c and D_e values at 60 °C (in contrast with what was observed in previous studies) was affected by two principal factors. At first, the major part of the compounds has been extracted through convection mechanism, and thus due to the diminished concentration difference, the extraction rate and k_c and D_e values decreased. On the other hand, temperature rise could cause swelling and degradation of plant tissue and also it could increase the solubility of other compounds, especially pectic materials. Hence, it could slow down the diffusion of solvent to the plant structure, thereby reducing k_c and D_e.

The results presented in Table 1 suggest a direct relationship between temperature and k_{deg}. So far, in various studies, the kinetics of heat degradation of ACs has been investigated [37–39]. However, the heat degradation of barberry ACs has not been examined in the literature. The magnitude of heat degradation and k_{deg} would depend on the process conditions (the magnitude and duration of the heating period) along with the intrinsic characteristics of the plant product (the
type of anthocyanin compounds as well as interaction between the fruit components [39], so comparison of the values is difficult. Expectedly, the degradation process is accelerated by temperature rise, \( k_{\text{deg}} \) predicted by the model well reflected this fact. Indeed, heat causes degradation of ACs through oxidation and breakdown of covalent bonds. In the first stage of degradation reactions, the pyrylium ring opens and chalcones form. In the next stage, by losing their B ring, chalcones convert to coumarin glycoside derivatives. Furthermore, the hydrolysis of sugar compounds and formation of cyclic compounds and aglycones are due to heat degradation [40]. All of the above-mentioned reactions become intensified with temperature rise, with predicted \( k_{\text{deg}} \) confirming these points.

### 3.2. Effect of ultrasonic irradiation time on \( D_e \), \( E \) and \( k_{\text{deg}} \)

The effect of applying the ultrasound time on extraction of ACs along with the relevant modeling curves are shown in Fig. 6(a–c). Here, the total time of extraction was considered 300 min, but the samples were exposed to ultrasound waves for 60, 150, and 240 min. As with the effect of temperature, the results suggested increased extraction efficiency with the duration of ultrasound application. Even after disconnecting the ultrasound waves, the extent of extraction was higher than the sample with normal extraction. This is due to the fact that ultrasound waves cause tissue degradation, increased contact area between the solvent and solid tissue, and eventually increased extraction rate [41]. The anthocyanin concentration in the samples which were exposed to the waves for 60 min had an ascending trend until the end of the duration (300 min) (Fig. 6-a). The samples exposed for 150 min showed a rising extraction rate after disconnecting the waves, and then remained constant (Fig. 6-b). Eventually, the samples with 240 min irradiation time initially, had an increasing trend, but then experienced anthocyanin concentration reduction (Fig. 6-c). Therefore, ultrasound could increase extraction rate, but the maximum efficiency was observed within the first hour. Wang et al. [42], Carrera et al. [43], Mane et al. [3], and Lazare et al. [44] stated that with prolongation of ultrasound duration, at first increase and then decrease in the extraction rate was observed. This reduction in extraction rate could be affected by two factors: reduced diffusivity coefficient and increased degradation rate of the compounds. As shown in Table 1, the \( D_e \) values predicted by the model did not change with prolongation of the radiation time until 150 min. However, at the time of 240 min, \( D_e \) level was decreased while \( E \) was increased. As a justification, it can be stated that ultrasound caused the development of acoustic cavitation and degradation of plant cells [45]. Collapse of bubbles caused improved transport of solvent into the plant cells and dissolution of the target components. With prolongation of the extraction time, a high number of plant cells were broken, whereby the extraction efficiency increased. Nevertheless, when plant cells were degraded, various compounds including insoluble and cytosol compounds enter the extraction liquid, causing diminished diffusivity of the solvent [42]. On the other hand, the target compounds were absorbed onto the broken plant components due to their relatively high surface area, resulting in diminished \( D_e \) levels. Meanwhile, at 240 min, the maximum \( E \) level was observed, which was possibly due to further damage to the barberry tissue during the early stages of extraction and immediate dissolution of ACs from the protective walls. Elevation of \( E \) levels could be considered as another reason for \( k_e \) and \( D_e \) reduction: a high percentage of compounds were extracted through dispersion mechanism, thus causing diminished \( k_e \) and \( D_e \) levels. In addition, the \( k_{\text{deg}} \) values predicted by the model were increased over time at constant temperature. This was owing to the both the heating effect resulting from the ultrasound waves and the local high pressures induced by bubble collapses [46,47]. It has been proven that ultrasound could cause degradation of ACs via formation of hydroxyl radicals inside cavitation bubbles due to the high collapsing pressures. Oxidation of ACs could cause the production of chalcones, opening of aromatic ring, development of smaller organic molecules, eventually \( k_{\text{deg}} \) was increased and the efficiency was reduced [3].

On the other hand, a comparison between the results of irradiation time in the samples under ultrasonic treatment and the samples extracted by the conventional method at 20 °C (Table 1) illustrated that acoustic waves resulted in enhanced values of \( D_e \). This was because of cavitation effects which led to the increase of cell destruction levels and facilitation of perforation of solvent to dipper inward sections of solid matrix. There was not any significant difference between the ultimate ACs levels in samples extracted at 40 °C (with highest \( D_e \) value) and those extracted under ultrasonic treatment for 60 min. These results suggested that acoustic-assisted extraction improved extraction efficiency at lower temperatures. Nevertheless, \( k_{\text{deg}} \) in all samples under ultrasonic treatments was higher than those extracted by conventional method at 20 °C. These results may arise from ultrasonic effects mentioned previously, and operation of ultrasonic in higher duty cycles.

### 3.3. Effect of ultrasound duty cycle on \( D_e \), \( E \) and \( k_{\text{deg}} \)

To investigate the effect of duty cycle, the extraction was conducted at three levels of duty cycles including 33, 50, and 70%. The experimental and modeling results of concentration changes versus time are demonstrated in Fig. 7(a–c). As can be seen in this figure, with the increase in the duty cycle from 33 to 50%, the extraction rate was risen, while at 70% it was decreased. Similar results were reported in other studies [41,48,49]. UAE can be done in continuous and pulsed modes. Various studies have indicated that extraction with pulsed mode could benefit a higher efficiency compared to the continuous extraction [50]. This method has various advantages including reduced process time, saving energy, and higher efficiency. In addition, the extraction rate in this method could increase along of easier destruction of the cellular walls in response to applying pulse, alteration of environmental conditions, and non-steady state mass transfer [5].

According to the results related to predicting the parameters of mass balance equation (\( k_e, D_e, E, k_{\text{deg}} \) (Table 1), with the increase in duty cycle, first \( k_e, D_e \) and \( E \) levels increased and then declined. Since the difference between the dispersion coefficient of 33% and 50% duty cycles was far greater than that of the diffusion coefficient, it can be concluded that the effect of duty cycle on the primary and rapid extraction phase is far greater than that of the slow or diffusion stage. At low duty cycles, there was likely not enough time for the development and collapse of cavitation bubbles and tissue fragmentation, thus reducing \( k_e, D_e \) and \( E \) levels [41,42]. However, at high duty cycles, reduction of mass transfer rate was possibly due to the diminished cavitation activity at high bubble densities. Indeed, the interaction between the bubbles could transform the bubbles, develop non-spherical bubbles, and diminish efficiency of the energy resulting from their breakdown. On the other hand, the increase in the number of bubbles produced at high duty cycles resulted in lessen energy transfer to the surrounding environment, which is known as saturation effect [49,50].

The \( k_{\text{deg}} \) value was constant at 33% and 50% levels, while it increased at 70%. This is due to the development of thermal and high pressure effects in continuous state or high ultrasound cycle duties. At high cycle duties, the interval between the two pulses could function as a resting time, through which small bubbles and instable cavities developed in response to breakdown of bubbles. The breakdown of bubbles causes the development of local pressure and temperature, which promote destruction of heat-sensitive compounds [49].

The results of ACs extraction at 33% and 50% duty cycles and conventional method at 20 °C revealed that ultrasound increased \( D_e \) levels. Additionally, the final concentration of ACs extracted at 40 °C exhibited no significant difference with those extracted at 33% and 50% duty cycle of ultrasound. Furthermore, the results of Table 1 showed that \( k_{\text{deg}} \) values at 20 °C and 50% were similar, therefore in these conditions (50% duty cycle), ACs destruction due to ultrasonic waves is in minimum levels. Consequently, these conditions can be introduced as the optimum state of ACs extraction.
4. Conclusion

The coefficients of mass transfer, diffusion, dispersion, and degradation were estimated by modeling the ultrasound assisted extraction of ACs by barberry through inverse numerical technique based on finite volume method. The concentration values versus time obtained by the model were then compared with experimental ones. The results indicated suitable congruence between the experimental and simulation data. Thus, this method can be utilized to predict the concentration of ACs during extraction under different predetermined conditions. Further, this technique is suitable for determining mass transfer, diffusion, dispersion, and degradation coefficient of ACs under different experimental conditions. Accordingly, inverse numerical simulation is an accurate and robust approach to investigate transport properties of food processes. With the aid of this method it was possible to investigate and analyze a complex process of ultrasound assisted extraction considering different phenomena occurring during the process. Parameter studies in the literature are usually based on simple kinetic models or accomplish significant assumptions while the inverse method could consider the full transport equation and simultaneously determine the parameters with an acceptable accuracy.

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References