Mass transfer modeling of the antioxidant extraction of roselle flower (*Hibiscus sabdariffa*)

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Abstract The aim of this study was to analyze the equilibrium and dynamic periods for mass transfer during the antioxidant solid–liquid extraction of dry roselle flower (*Hibiscus sabdariffa*). Extraction kinetics for total phenolic compounds (TPC), total flavonoids (TFL) and total antioxidant capacity (TAC) were obtained at different temperatures (50, 60, 70 or 80 °C) and solvent-to-product mass ratios (100:1, 200:1 or 300:1 g/g) under stirring (220–230 rpm). An analytical solution for unsteady-state mass transfer based on Fick’s second law of diffusion was used to mathematically describe solid–liquid extraction curves and for the simultaneous estimation of diffusion coefficients and the final amount of extracted bioactive compounds, which were further related to experimental conditions by a second order model. The amount of extracted bioactive compounds at equilibrium were in the ranges of 30.8–89.8 g GAE/kg d.m. for TPC (0.154–0.373 g GAE/L extract), 40.0–131.6 g catechin/kg d.m. for TFC (0.269–0.559 g catechin/L extract) and 37.5–227.0 g trolox/kg d.m. for TAC (0.346–0.865 g trolox/L extract). On the other hand, diffusion coefficients for TPC, TFC and TAC were in the ranges of $0.72\text{--}2.66 \times 10^{-11}$, $0.25\text{--}2.37 \times 10^{-11}$ and $1.19\text{--}5.79 \times 10^{-11}$ m²/s, respectively.

Keywords Bioactive compounds · Diffusion coefficient · Equilibrium point · Solid–liquid extraction

Abbreviations

GAE Gallic acid equivalents
TPC Total phenolic compounds
TFL Total flavonoids
TAC Total antioxidant capacity

List of symbols

A Denotes product surface
C Concentration of a given component in solution (g/l solution)
D Apparent diffusivity (m²/s)
K Equilibrium partition coefficient (kg solid/kg solution)
k_c Convective mass transfer coefficient (m/s)
L Characteristic length for diffusion (m)
n Normal unit vector
R Solvent-to-product mass ratio (kg/kg)
X, $\bar{X}$ Mass fraction of a given component in product (kg/kg product): local and average, respectively
Y Mass fraction of a given component in solution (kg/kg solution)
t Time (s)
T Temperature (°C)
V Denotes product volume
z Axial coordinate (m)
 ΔX Extracted amount of a given component in product (kg/kg product)

Subscripts

e At equilibrium
i At the solid–liquid interphase
l For liquid
s For solid

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Greek letters

ρ	Density (kg/m ³)
ψ, Ψ	Dimensionless concentration: local and average, respectively

Introduction

Roselle (*Hibiscus sabdariffa* L.) flower is a natural source of red–purple compounds with antioxidant properties (Ochoa-Velasco et al. 2017). This plant is commonly used in several countries against diseases such as diarrhea, dysentery, hypertension, hypercholesterolemia and urinary tract infections because is rich in compounds like phenolics (mainly anthocyanins), polysaccharides and organic acids (Riaz and Chopra 2018). Roselle flower is consumed as hot infusion or as cold beverage due to their pleasant flavor and therapeutic properties; however, several factors affect the extraction of its phytochemical compounds during the drink preparation (Cissé et al. 2012).

Solid–liquid extraction is the preferred method for the isolation of bioactive compounds with antioxidant capacity from plant materials (Garcia-Perez et al. 2010; Linares et al. 2010; Qu et al. 2010; Alara et al. 2018). The extraction process is affected by several variables whose effect should be experimentally determined and several models have been formulated to analyze extraction data, including empirical and theoretical ones (Pinelo et al. 2006). Empirical models mainly include response surface equations, which are used to describe the effect of processing variables (temperature, time, solvent-to-solute ratio) on selected performance indices of the extraction operation, such as the amount or yield of the isolated substances (Xu et al. 2017; Alara et al. 2018); however, these models do not provide information about the dynamic or mass transfer properties.

Extraction curves are very often modeled by an unsteady-state diffusion model based on Fick's second law (Garcia-Perez et al. 2010; Linares et al. 2010; Cissé et al. 2012; Krishnan et al. 2015; Castillo-Santos et al. 2017). However, literature data on the characterization of dynamic (diffusivity values) and equilibrium (partition coefficients) periods for mass transfer during solid–liquid extraction are scarce. In addition, diffusion coefficients and equilibrium properties during solid–liquid extraction are very often characterized in terms of total (bulk) extracted solutes (Linares et al. 2010; Krishnan et al. 2015; Castillo-Santos et al. 2017), instead of the observed antioxidant activity (Garcia-Perez et al. 2010) or the real diffusing substances or chemical groups (Winitsorn et al. 2008). Thus, “there is a need for mathematical modeling, which readily facilitates optimization, simulation, design, and process control, while also contributing to the effective utilization of

energy, solvent and time” as highlighted by some authors (Krishnan et al. 2015).

The mass transfer properties of anthocyanins from grounded roselle flower have been investigated (Cissé et al. 2012). Nevertheless, equilibrium characteristics and partition coefficients were not reported, as well as other useful measurements related with bioactive compounds, such as TAC, or the effect of solvent-to-solid ratio on mass diffusivities. Therefore, the aim of this study was to evaluate the effect of process temperature and solvent-to-product mass ratios on the equilibrium and dynamic periods for mass transfer during the antioxidant solid–liquid extraction of roselle flower, characterized in terms of TFC, TFL and TAC as measured by DPPH method (*Hibiscus sabdariffa*).

Methods and materials**Raw material**

Dehydrated Roselle (*Hibiscus sabdariffa* L.) calyces were obtained from Chiautla de Tapia, Puebla, Mexico. Roselle was ground, sieved (425 μ m) and stored in a hermetic bottle in dark environment and room temperature until use.

Solvents and reagents

Ethanol was purchased from J.T. Baker (Mexico City, Mexico). Folin–Ciocalteu reagent, gallic acid, catechin, 6-hydroxy-2, 5, 7, 8 tetramethylchroman-2-carboxylic acid (trolox), 2,2-diphenyl-1-picrylhydrazyl (DPPH), sodium carbonate, sodium nitrite, aluminum chloride and sodium hydroxide were purchased from Sigma–Aldrich (St. Louis, MO, USA).

Extraction experiments

One gram of Roselle (*Hibiscus sabdariffa* L.) was placed in a glass vessel and mixed with distilled water (100, 220 or 300 mL) at different temperatures (50, 60, 70 or 80 °C) and stirred at 220–230 rpm. Samples were obtained at different extraction times (0, 2, 4, 8, 15 and 30 min). Roselle infusion was filtered through a Whatman No. 1 paper and immediately used for the bioactive compounds and antioxidant capacity quantification.

Analytical methods**Total flavonoids**

TFL were analyzed following the methodology proposed by Hernández-Carranza et al. (2016). One mL of an adequate dilution of Roselle infusion was mixed with 1 mL of

NaNO₂ (1.5%) in an amber glass tube, the mixture was vortexed and let stand for 5 min. Afterward, 1 mL of AlCl₃ (3%) was added and mixed for 1 min; then, 0.5 mL of NaOH (1 N) was added. The mixture was let to stand for 1 min and the absorbance was recorded at 490 using a Jenway UV–Vis spectrophotometer (model 6405, Staffordshire, UK). Water was used as blank of the sample. Result was expressed as g of catechin per kg of roselle using a standard curve of catechin (slope: 0.0045, intercept: – 0.0123 and R²: 0.997). Initial TFL in product were determined as 469.2 g catechin g/kg d.m.

Phenolic compounds

Phenolic compounds were evaluated according to the Hernández-Carranza et al. (2016) methodology. One mL of an adequate dilution of Roselle infusion was mixed with 1 mL of Folin–Ciocalteu reagent (0.1 M) in an amber glass tube; afterward 3 min, 1 mL of Na₂CO₃ (0.5%) solution was added. Mixture was incubated during 30 min in dark condition at room temperature; total phenolic compounds were recorded at 765 nm using a UV–Vis spectrophotometer. Water was used as blank of the sample. Result was expressed as g of Gallic acid equivalents (GAE) per kg of roselle using a standard curve of Gallic acid (slope: 0.0126, intercept: – 0.0481 and R²: 0.991). Initial TPC in product were determined as 306.0 g GAE/kg d.m.

Antioxidant capacity

Antioxidant capacity of Roselle infusion was analyzed according to the Hernández-Carranza et al. (2016) method. One mL of an adequate dilution of Roselle infusion was collocated in an amber glass tube and mixed with 1 mL of DPPH (0.004%) solution. The mixture was vortexed and let stand in dark environment and room temperature for 30 min. Absorbance was recorded at 517 nm using a UV–Vis spectrophotometer. Results was expressed as g of Trolox per kg of Roselle using a standard curve of Trolox (slope: 9.2811, intercept: – 0.7289 and R²: 0.989). Initial TAC in product was determined as 541.4 g trolox/kg d.m.

Modeling of solid–liquid extraction data

The extraction of soluble materials from solids with a liquid can be described by the unsteady state mass transfer equation by diffusion with a convective boundary (Castillo-Santos et al. 2017):

$$\frac{\partial(\rho_s X)}{\partial t} = \nabla \cdot [D \nabla(\rho_s X)] \quad \text{in } V \quad (1)$$

$$-\mathbf{n} \cdot D \nabla(\rho_s X_i) = k_c \rho_l (Y_i - Y) \quad \text{in } A \quad (2)$$

By assuming that: (1) changes in solid density are negligible, (2) solute diffusivity is constant, (3) product geometry can be approximated by a sphere and (4) product surface reaches instantaneously the mass transfer equilibrium, the corresponding extraction model becomes

$$\frac{\partial \psi}{\partial \tau} = \frac{\partial^2 \psi}{\partial \xi^2} \quad (3)$$

$$\psi = 0 \quad \text{for } \tau > 0, \quad \xi = 1 \quad (4)$$

where

$$\psi = \frac{X_t - X_e}{X_0 - X_e}; \quad \tau = \frac{Dt}{L^2}; \quad \xi = \frac{z}{L} \quad (5)$$

The analytical solution of this model for average concentration of diffusing substance under uniform initial distribution of extractable material within the solid is the well-known equation (Crank 1975)

$$\Psi = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp[-n^2 \tau] \quad (6)$$

At any time, the total amount of extracted material ($\Delta \bar{X}_t$, kg/kg) is related with the amount of solute that can be extracted from solid at equilibrium ($\Delta \bar{X}_e$, kg/kg) and the amount of solute that can be extracted but still remains inside the solid ($\bar{X}_t - \bar{X}_e$, kg/kg).

$$\Delta \bar{X}_t = \Delta \bar{X}_e - (\bar{X}_t - \bar{X}_e) \quad (7)$$

Combination of Eqs. (6) and (7) and definitions for dimensionless concentration (Ψ) and Fourier number for mass transfer (τ) produces

$$\Delta \bar{X}_t = \Delta \bar{X}_e \left(1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 Dt}{L^2}\right) \right) \quad (8)$$

Equation (8) can be fitted to the experimental data to simultaneously estimate parameters $\Delta \bar{X}_e$ and D by non-linear regression.

Finally, the equilibrium distribution coefficient K (kg solid/kg solution) for studied responses between the liquid and solid phases was calculated as (Pacheco-Angulo et al. 2016; Castillo-Santos et al. 2017)

$$K = \frac{Y_e}{\bar{X}_e} \quad (9)$$

Data analysis

Nonlinear regression (based on ordinary least squares) was used to estimate the diffusion coefficient (D) and equilibrium point ($\Delta \bar{X}_e$). The product was considered to have a radius of half the size of the mesh sieve; thus, a value of 212.5 μm was used for all calculations. The effect of

temperature and solvent-to-product ratio on diffusivities and the amount of extracted bioactive compounds at equilibrium was further described by a second order model with main, interaction and quadratic terms, which can describe possible curvature of the response:

$$y = b_0 + b_1x_1 + b_2x_2 + b_{12}x_1x_2 + b_{11}x_1^2 + b_{22}x_2^2 \quad (9)$$

where x_1 and x_2 represent the coded levels for the temperature (T) and solvent-to-product mass ratio (R), respectively, and y denotes either the diffusion coefficients or equilibrium points. Here, $x_1 = \{-1, -1/3, 1/3, 1\}$ for $T(^{\circ}\text{C}) = \{40, 50, 60, 80\}$, and $x_2 = \{-1, 0, 1\}$ for $R(\text{kg/kg}) = \{100, 200, 300\}$. The fitness quality of the identified models was quantified by the generalized determination coefficient (R^2) and statistical significance of parameter estimates was evaluated through their 95% confidence intervals (95% CI). Nonlinear and linear regression procedures as well as statistical analysis were performed using the software Matlab R12a and its Statistics Toolbox 7.3 (MathWorks Inc., Natick, MA, USA).

Results and discussion

Diffusion coefficients

The unsteady state diffusion equation achieved a satisfactory reproduction of all extraction curves ($R^2 > 0.94$). Selected experimental and fitted extraction curves of TPC, TFC and TAC are shown in Fig. 1 for the lowest solvent-to-product mass ratio (100:1). Table 1 summarizes the estimated diffusion coefficients, the amount of extracted bioactive compounds at equilibrium and the partition coefficients. TPC, TFC and TAC diffusivities were between $0.72\text{--}2.66 \times 10^{-11}$, $0.25\text{--}2.37 \times 10^{-11}$ and $1.19\text{--}5.79 \times 10^{-11} \text{ m}^2/\text{s}$, respectively. Diffusivity values are comparable to those found for anthocyanins ($3.9 \times 10^{-11}\text{--}1.35 \times 10^{-10} \text{ m}^2/\text{s}$, $25\text{--}90^{\circ}\text{C}$) in *Hibiscus sabdariffa* (Cissé et al. 2012) and other bioactive compounds in vegetable matrices during solid–liquid extraction such as vanilla pods (total solids; $1.2\text{--}2.4 \times 10^{-11} \text{ m}^2/\text{s}$; ethanol–water 60% v/v; $30\text{--}50^{\circ}\text{C}$; 10:1 mL solvent/g product) and yerba mate (water soluble solids; $6.1\text{--}9.5 \times 10^{-11} \text{ m}^2/\text{s}$; water; $40\text{--}70^{\circ}\text{C}$) and hot ($40\text{--}115^{\circ}\text{C}$) and freeze dried grape stalks (antioxidant activity as measured by trolox method; $0.2\text{--}14.2 \times 10^{-12} \text{ m}^2/\text{s}$; ethanol–water 80% v/v, 60°C , 22:1 mL solvent/g product) (Garcia-Perez et al. 2010; Linares et al. 2010; Castillo-Santos et al. 2017). Krishnan et al. (2015) modeled the kinetics of antioxidant extraction of *Origanum vulgare* and *Brassica nigra* as a two-stage diffusion process. Diffusivity values for the fast period

Fig. 1 Effect of temperature on extraction of total phenolic compounds (a), total flavonoids (b) and total antioxidant capacity (c) at a solvent-to-product mass ratio of 100:1

(first stage) of total extracted solutes from *O. vulgare* and *B. nigra* were in the range $1.0 \times 10^{-11}\text{--}1.2 \times 10^{-11} \text{ m}^2/\text{s}$ and $1.0 \times 10^{-11}\text{--}1.1 \times 10^{-11} \text{ m}^2/\text{s}$, respectively (ethanol, methanol, hexane or water; 65°C ; 50:1 mL solvent/g product). Corresponding diffusivity values for the slow period (second stage) were a magnitude order higher ranging $1.7 \times 10^{-12}\text{--}3.6 \times 10^{-12} \text{ m}^2/\text{s}$ for *O. vulgare* and $2.0 \times 10^{-12}\text{--}3.2 \times 10^{-12} \text{ m}^2/\text{s}$ for *B. nigra*, respectively.

Table 1 Estimated diffusivities and equilibrium characteristics for total bioactive compounds and their antioxidant capacity during solid–liquid extraction of roselle flower (*Hibiscus sabdariffa*)

Temperature (°C)	Solvent-to-product ratio (kg/kg)	Total phenolic compounds (g GAE/kg d.m.)					Total flavonoids (g catechin/kg d.m.)					Total antioxidant capacity (g trolox/kg d.m.)				
		$D \times 10^{11}$ (m ² /s)	$\Delta\bar{X}_e$	C_e (g/L)	K	R^2	$D \times 10^{11}$ (m ² /s)	$\Delta\bar{X}_e$	C_e (g/L)	K	R^2	$D \times 10^{11}$ (m ² /s)	$\Delta\bar{X}_e$	C_e (g/L)	K	R^2
50	100	1.94 (1.52/2.36)	32.3 (31.0/33.7)	0.32	0.74	0.99	1.75 (1.25/2.26)	40.0 (37.7/42.2)	0.40	0.93	0.99	2.01 (1.38/2.64)	37.5 (35.3/39.7)	0.38	1.19	0.98
60	100	2.11 (1.68/2.54)	34.4 (33.1/35.6)	0.34	1.22	0.99	2.08 (1.39/2.77)	44.6 (41.9/47.4)	0.45	1.05	0.98	4.39 (2.63/6.16)	58.6 (55.7/61.6)	0.59	1.27	0.98
70	100	2.34 (1.66/3.03)	35.5 (33.7/37.4)	0.36	1.54	0.99	2.27 (1.55/2.98)	50.5 (47.7/53.3)	0.51	1.21	0.98	4.95 (3.49/6.42)	72.3 (69.8/74.8)	0.72	1.32	0.99
80	100	2.66 (1.67/3.66)	37.3 (35.0/39.6)	0.37	1.90	0.98	2.37 (1.65/3.08)	55.9 (53.0/58.9)	0.56	1.35	0.98	5.50 (4.06/6.95)	86.5 (84.0/88.9)	0.87	1.40	0.99
50	200	0.72 (0.49/0.95)	30.8 (28.1/33.4)	0.15	0.73	0.99	0.99 (0.76/1.21)	66.8 (63.1/70.4)	0.33	0.83	0.99	1.19 (0.46/1.92)	69.1 (59.5/78.7)	0.35	0.56	0.94
60	200	0.72 (0.51/0.94)	36.9 (34.0/39.8)	0.18	0.76	0.99	0.86 (0.41/1.31)	74.3 (64.5/84.0)	0.37	0.94	0.96	2.65 (1.82/3.48)	71.7 (68.0/75.4)	0.35	0.69	0.98
70	200	0.93 (0.64/1.22)	39.3 (36.3/42.3)	0.20	1.37	0.99	0.82 (0.54/1.11)	81.9 (74.7/89.1)	0.41	1.06	0.98	4.28 (2.23/6.33)	116.4 (109.3/123.6)	0.58	0.74	0.97
80	200	1.19 (0.80/1.58)	40.8 (37.8/43.9)	0.20	1.98	0.98	1.28 (0.86/1.70)	85.9 (79.7/92.0)	0.43	1.12	0.98	5.79 (3.92/7.67)	153.6 (148.5/158.8)	0.77	0.78	0.99
50	300	0.96 (0.32/1.61)	65.6 (54.9/76.4)	0.22	1.06	0.94	0.41 (0.27/0.54)	80.8 (72.3/89.3)	0.27	0.69	0.99	3.58 (2.44/4.73)	130.1 (124.2/136.1)	0.43	0.95	0.99
60	300	0.88 (0.39/1.38)	70.8 (60.9/80.6)	0.24	1.38	0.96	0.25 (0.07/0.43)	98.4 (72.1/124.8)	0.33	0.89	0.99	3.07 (2.00/4.14)	158.7 (150.1/167.2)	0.53	1.05	0.98
70	300	1.23 (0.56/1.89)	77.1 (67.7/86.4)	0.26	1.80	0.96	0.28 (0.14/0.42)	118.1 (96.9/139.2)	0.39	1.12	0.99	3.19 (2.32/4.06)	190.1 (182.2/197.9)	0.63	1.17	0.99
80	300	1.15 (0.65/1.64)	89.8 (81.0/98.7)	0.30	2.41	0.97	0.34 (0.19/0.50)	131.6 (111.8/151.3)	0.44	1.30	0.99	4.30 (3.31/5.28)	227.0 (220.3/233.6)	0.76	1.45	0.99

Values in parentheses indicate the 95% confidence intervals for the parameter estimates (nonlinear regression)

Table 2 Pearson's correlation coefficients for equilibrium points and diffusion coefficients

Response	Equilibrium points			Diffusion coefficients		
	TPC	TFL	TAC	TPC	TFL	TAC
TPC	1	0.8852	0.9025	1	0.8709	0.4896
TFL	0.8852	1	0.9588	0.8709	1	0.3810
TAC	0.9025	0.9588	1	0.4896	0.3810	1

TPC total phenolic compounds, TFL total flavonoids, TAC total antioxidant capacity

Bold numbers indicate a significant correlation ($p < 0.05$)

Extraction yields and equilibrium properties

Extracted amounts of bioactive substances at equilibrium were estimated in the ranges of 30.8–89.8 g GAE/kg d.m. for TPC (0.154–0.373 g GAE/L extract), 40.0–131.6 g catechin/kg d.m. for TFC (0.269–0.559 g catechin/L extract) and 37.5–227 g trolox/kg d.m. for TAC (0.346–0.865 g trolox/L extract). A similar result was obtained by Fernández-Arroyo et al. (2011) for phenolic compounds and total antioxidant capacity of *Hibiscus sabdariffa*. They reported 53.12 ± 1.9 g/kg d.m. of polyphenols in *Hibiscus sabdariffa* aqueous extract being hibiscus acid (31.12 g/kg d.m.), hydroxycitric acid (8.29 g/kg d.m.), chlorogenic acids (5.72 mg/kg d.m.), delphinidin 3-sambubioside (2.70 g/kg d.m.) and cyanidin 3-sambubioside (1.94 g/kg d.m.) the main phenolic compounds. They also informed a similar antioxidant capacity (40.04 g trolox/kg d.m.) evaluated by the TEAC assay. For other products, Garcia-Perez et al. (2010) reported extraction levels for antioxidant capacity (FRAP assay) in the range of

15–40 mmol Trolox/L (3.7–10 g trolox/L) during the extraction of hot air dried (40–115 °C) and freeze dried grape stalks (ethanol–water 80% v/v, 60 °C, 22:1 mL solvent/g product). These values are higher than those reported in this study; however, the reaction mechanisms of FRAP and DPPH assays are not comparable (Huang et al. 2005).

In this study, partition coefficients varied in the ranges 0.73–2.41 kg solid/kg solution for TPC, 0.69–1.35 kg solid/kg solution for TFL and 0.56–1.45 kg solid/kg solution for TAC. Results are similar to that found for total soluble solids (0.86 kg product/kg solvent) for total solids of vanilla pods (ethanol–water 60% v/v, 30–50 °C, 10:1 mL solvent/g product) (Castillo-Santos et al. 2017).

A significant correlation was found between the all the studied responses for equilibrium points (Table 2, $p < 0.05$); however, only diffusion coefficients for TPC and TFL were significantly correlated ($p < 0.05$). Overall, as shown in Table 1, diffusion coefficients for TAC were higher ($p < 0.05$) than those of TPC and TFL. These results might indicate that roselle flower has some components contributing to the TAC test diffusing at a different rate than those quantified as TPC and TFL.

Effect of process variables on mass transfer properties

The parameters for response surface models describing the relationship between diffusion coefficients, equilibrium points and process variables are shown in Table 3. In all cases proposed models achieved a good fit of original data ($R^2 > 0.80$). Contour plots were also generated with Eq. (3) to visually assess the effect of process variables and

Table 3 Regression coefficients of response surface models for diffusivity and equilibrium data during solid–liquid extraction of roselle flower (*Hibiscus sabdariffa*)*

Activity	Response	Parameters*						R^2
		b_0	b_1	b_2	b_{12}	b_{11}	b_{22}	
TPC	$D \times 10^{11}$ (m ² /s)	0.849	0.246	– 0.604	– 0.114	0.073	0.770	0.99
	ΔX_e^a	36.6	6.38	20.5	4.71	0.54	18.4	0.99
	K	0.686	0.149	– 0.071	0.068	0.016	0.530	0.98
TFL	$D \times 10^{11}$ (m ² /s)	0.928	0.136	– 0.898	– 0.164	0.109	0.228	0.99
	ΔX_e^b	77.9	14.5	29.7	8.86	– 1.29	0.30	0.99
	K	0.990	0.223	– 0.068	0.047	– 0.006	0.081	0.95
TAC	$D \times 10^{11}$ (m ² /s)	3.50	1.44	– 0.339	– 0.659	– 0.031	0.397	0.80
	ΔX_e^c	99.0	39.0	56.4	12.1	6.76	17.4	0.99
	K	1.134	0.631	0.156	0.051	0.140	0.294	0.98

*Bold numbers indicate significant parameter estimates ($p < 0.05$)

TPC total phenolic compounds, TFL total flavonoids, TAC total antioxidant capacity

^ag GAE/kg d.m.

^bg catechin/kg d.m.

^cg trolox/kg d.m.

Fig. 2 Effect of temperature and solvent-to-product mass ratio on diffusivities (left) and equilibrium points (right) of TPC (A, a), TFL (B, b) and TAC (C, c). Diffusivity values $\times 10^{11} \text{ m}^2/\text{s}$. Equilibrium values for TPC, TFL and TAC in g GAE/kg d.m., g catechin/kg d.m. and g trolox/kg d.m., respectively

their interactions on the diffusion coefficients and equilibrium points (Fig. 2). The use of higher temperatures led to higher diffusivities and extracted amounts of bioactive compounds ($p < 0.05$). The same trend has been found by other authors (Jokić et al. 2010; Linares et al. 2010; Qu et al. 2010; Krishnan et al. 2015; Castillo-Santos et al. 2017; Sánchez et al. 2017).

Similarly, the use of increasing solvent-to-product mass ratios led to higher amounts of extracted solute, but lower diffusion coefficients were observed for TPC and TFL ($p < 0.05$). Higher antioxidant extraction levels for

increasing solvent-to-product ratios have been also observed by other authors (Qu et al. 2010; Goula 2013; Krishnan et al. 2013). From a mass transfer standpoint, it is expected that higher amounts of solvent-to-product ratios should allow for a higher amount of extracted material. Krishnan et al. (2015) observed increasing diffusion coefficients for total extracted solutes from *Origanum vulgare* and *Brassica nigra* by increasing the solvent-to-product ratio during the fast mass transfer period (ethanol; 65 °C; 20:1–50:1 mL solvent/g product); however, they did not find a definite trend for diffusion coefficients for the slow

mass transfer stage. It should be highlighted that while the amount of extracted bioactive compounds increased in this study with the use of higher solvent-to-product ratios at a given temperature, lower concentrations were in fact obtained in the liquid phase ($p < 0.05$), and both negative and quadratic effects of solvent-to-product were identified on partition coefficients, affecting the mass transfer rates during dynamic extraction period.

Conclusion

The equilibrium and dynamic periods for mass transfer during solid–liquid extraction of bioactive compounds from roselle flower were successfully described by the unsteady-state Fickian diffusion model and response surface equations. Correlation analysis might indicate that Roselle has other bioactive compounds contributing to the TAC test, besides TPC and TFL. Moreover, identified mathematical relationships obtained can be applied for the prediction of process kinetics in a Roselle-water extraction system.

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