

Polyphenols Recovery from Hazelnut Skin Wastes through Extraction with a Water-Ethanol Solvent Mixture: Equilibrium and Kinetic Studies

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This study delves into the principles of the Circular Economy by focusing on the extraction of polyphenols from hazelnut skin wastes. The project's innovation lies in the pioneering use of a 50% vol/vol water-ethanol mixture as a solvent for polyphenol extraction, within a custom batch set-up. The primary objective was to explore both equilibrium and kinetic aspects of this novel system. Initial experiments involved maintaining the solvent at 70°C for six hours to reach equilibrium, while varying solid/liquid ratios from 0.16 to 50 g/L. A fitting of the experimental data with an equilibrium modelling revealed values of $q_{tot} = 0.255$ g/g and $k = 0.0092$ L/g as the total amount of extractable polyphenols and the solid-liquid linear isotherm partition coefficient, respectively. Furthermore, kinetics of the extraction process was investigated across three different solid-liquid ratios (0.54, 1.00 and 2.00 g/L). Concentration measurements at different time intervals were fitted with the Linear Driving Force (LDF) kinetic model, allowing for the estimation of the LDF mass transfer coefficient ak_{LDF} for each solid-liquid dosage. Notably, the thermodynamic and kinetic parameters derived in this study are unique, since they are specifically tailored to the utilization of a 50% vol/vol water-ethanol mixture as polyphenol extraction solvent. This research underscores the potential of utilizing such solvent mixtures in polyphenol extraction from biomass wastes, thereby contributing to the advancement of sustainable practices within the Circular Economy framework.

1. Introduction

In the current historical context, the application of the traditional linear model based on the “take-make-use-dispose” principle has become unsustainable, especially in light of exponential population growth. In opposition to this linear approach, the Circular Economy represents a production paradigm designed to maximize the lifespan of products and transform production waste into valuable resources. In this regard, hazelnut skin, a byproduct resulting from various food industry processes, demonstrates considerable potential. Hazelnuts are mainly cultivated in Turkey and Italy, with costs ranging from 2.12 to 2.52 euros/kg for the Turkish product (GİRESUN) and from 9.90 to 11.10 euros/kg for the Italian variant (Camera Di Commercio Cuneo) in 2019. Hazelnut skin, accounting for approximately 2wt% of the fruit, is a rich source of polyphenols, organic compounds which are highly valued by the industry for their strong antioxidant power. As reported by Silva and Pogačnik (2020), this property plays a vital role in preventing and treating diseases associated to oxidative stress and inflammation, including cancer, cardiovascular and neurodegenerative pathologies, metabolic syndrome and type 2 diabetes.

Hence, by extracting polyphenols from discarded hazelnut skins using a liquid solvent, they can be profitably supplied to the industry. To illustrate the market potential, the quantity of extracted polyphenols reached 16,380 tons in 2015 (Adebooye et al., 2018). Among the solvents traditionally applied to the extraction of organic compounds from vegetable matrices, exclusively water, ethanol, and water-ethanol mixtures are known for

being fully green, safe, and non-toxic. Natural Green Eutectic Solvents (NADES) are also emerging as promising green solvents in recent years (Fanali et al., 2021).

In this work, various extraction tests were performed at different solid/liquid ratios in a batch set-up using 50% vol/vol water-ethanol mixture at 70 °C as solvent.

The scopes of this paper are the following:

- to study the equilibrium of the polyphenols extraction from hazelnut skins at 70 °C, in order to estimate the thermodynamic parameters; in particular, the solid-liquid partition coefficient k of the linear isotherm and the total extractable mass of polyphenols q_{tot} were evaluated from a fitting of experimental equilibrium data.
- to investigate the kinetics of the extraction process; in particular, a fitting of experimental kinetic data with the Linear Driving Force (LDF) model allowed for the estimation of the product between the overall mass transfer coefficient and the specific surface area made available by the solid matrix referred to the liquid volume αK_{LDF} .

The paper's results were compared with the outcomes of our previous works, which explored the extraction of polyphenols from the same solid matrix and using water (Bertino et al., 2023) and NADES (Mazzeo et al., 2023) as solvents.

2. Materials and Methods

2.1 Solid preparation

Extraction tests were conducted on hazelnut skins samples obtained from a local company which employs hazelnuts to create food items. Before the experiments, the solid matrix was ground and sieved in order to obtain a solid particle size < 0.5 mm.

2.2 Experimental set-up

Extraction runs were performed in a batch set-up consisting of glass Laboratory bottles of 0.2 L filled with measured amounts of liquid solvent and solid matrix under constant stirring (300 rpm). The bottles were appropriately sealed to avoid solvent loss and placed in a thermostatic bath set at 70 °C. In accordance with our previous works, this temperature was selected as it is sufficiently elevated to facilitate extraction without promoting thermal degradation of phenolic compounds, which occurs at 80 °C (Antony & Farid, 2022).

2.3 Experimental tests

A total of 18 tests were carried out by varying the solid mass and the liquid volume, and consequently the solid-liquid ratio α (Table 1). Tests 1.1-1.15 focused on studying the system's equilibrium within the α range of 0.16 to 50 g/L, while the last three tests, designated as 2.1-2.3, were dedicated to investigating the system's kinetic within the α range of 0.54 to 2 g/L. Thus, the maximum solid-liquid ratio tested was 50 g/L, as attempts to exceed this value in batch mode proved challenging due to excessive solid presence, impeding uniform liquid mixing.

Table 1: Experimental conditions ($T=70$ °C). Tests 1.1-1.15 = Equilibrium runs; Tests 2.1-2.3 = Kinetic runs.

Test	α (g/L)	M_S (g)	V_L (L)
1.1	0.16	0.008	0.050
1.2	0.31	0.016	0.050
1.3	0.62	0.031	0.050
1.4	1.24	0.062	0.050
1.5	2.50	0.125	0.025
1.6	5.00	0.125	0.025
1.7	10	0.250	0.025
1.8	15	0.375	0.025
1.9	20	0.500	0.025
1.10	25	0.625	0.025
1.11	30	0.750	0.025
1.12	35	0.825	0.025
1.13	40	1.000	0.025
1.14	45	1.125	0.025
1.15	50	1.250	0.025
2.1	0.54	0.081	0.150
2.2	1.00	0.150	0.150
2.3	2.00	0.300	0.150

Equilibrium runs (tests 1.1-1.15) lasted for 6 h, which was evaluated from preliminary tests (data not shown) to be enough time for the system to reach equilibrium conditions. At the end of each test, the supernatant of the extracted solutions was analyzed as described in Section 2.4.

During kinetic runs (tests 2.1-2.3), samples of the liquid supernatants were collected at fixed time intervals and then analyzed as described in Section 2.4 in order to determine the extraction kinetic curve. In particular, for each run, 9 total samples were collected at 0, 15, 30, 60, 90, 120, 150, 180 and 210 min. To ensure that the error introduced by removing a portion of the liquid during each sampling (leading to a gradual increase in the solid-liquid α throughout the test) remains below 1%, the following inequality should be satisfied:

$$\frac{(n_i - 1)V_i}{V_L} < 0.01 \quad (1)$$

where n_i and V_i are the number and the volume of samples collected during each kinetic run, respectively, and V_L is the volume of liquid solvent loaded at the beginning of the test. Being $n_i = 9$ and $V_L = 0.15$ L, the use of volume samples equal to $V_i = 150$ μ L allowed Eq. 1 to be automatically respected. Each test was repeated at least two times to assure the reproducibility of the results.

2.4 Analyticals

The concentration of polyphenols in the liquid samples obtained from experimental tests was measured using the Folin-Ciocalteu (F-C) assay, which involves the oxidation of phenolic compounds. The specific analytical procedure is detailed by Everette et al. (2010). In summary, 20 μ L of each experimental sample were combined with 1580 μ L of distilled water and 100 μ L of Folin-Ciocalteu's reagent ($C_{10}H_5NaO_5S$), sourced from Sigma Aldrich (Milan, Italy), without further purification. The mixture was stirred and placed in the dark for 8 min. Subsequently, 300 μ L of an aqueous solution containing 20% w/w of sodium carbonate (Na_2CO_3) was added and the mixture was returned to darkness for 2 h. Finally, 200 μ L of the prepared sample was transferred to a Greiner 96 flat transparent microplate. The absorbance of the sample was measured using the Infinite M200 PRO Tecan microplate spectrophotometer (Tecan Trading AG, Switzerland) at 765 nm. The concentration was determined by interpolating the result on a calibration curve achieved by measuring the absorbance of solutions with known gallic acid compositions, serving as the analytical standard. Therefore, the concentration of polyphenols was expressed in terms of equivalent Gallic Acid.

3. Results

3.1 Equilibrium studies

A global mass balance can be used to describe the extraction system at any time, and in particular when equilibrium is reached:

$$q_{tot} - q_e = \frac{V_L}{M_S} C_e = \frac{C_e}{\alpha} \quad (2)$$

where q_{tot} is the total amount of extractable polyphenols per mass of solid matrix, C_e and q_e are the experimental equilibrium data of polyphenols in liquid and solid phases, respectively, V_L and M_S are the liquid solvent volume and the solid mass loaded at the beginning of the test, respectively, and α is the solid-liquid ratio.

The link between q_e and C_e at 70 °C was expressed by a linear equilibrium isotherm as follows:

$$q_e = kC_e \quad (3)$$

where k is the linear partition coefficient, that gives information on how the polyphenols are distributed in the two solid and liquid phases at equilibrium.

The system composed by Eq. 2 and Eq. 3 was solved to obtain the final equilibrium model, relating C_e to α :

$$C_e = \frac{q_{tot}}{\frac{1}{\alpha} + k} \quad (4)$$

The latter expression was directly adopted to estimate both q_{tot} and k with a fitting of the experimental equilibrium data C_e obtained by varying the solid-liquid ratio α within the tests 1.1-1.15. A graphical representation of the fitting is provided in Figure 1. It is worth noting that the trend of the C_e data in Figure 1 is consistent with the use of a linear isotherm. This is particularly evident in Figure 1b, where a zoom on low concentration values is shown.

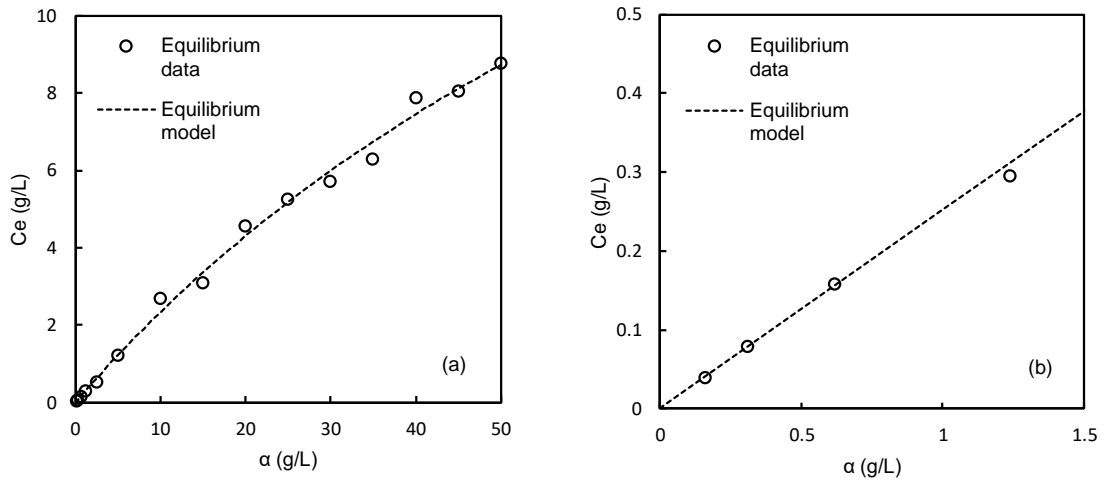


Figure 1: Equilibrium C_e versus α data at 70 °C (tests 1.1-1.15) fitting with equilibrium model (Eq. 4); (a): Fitting, (b): Fitting (zoom in)

The fitting yielded values of $q_{tot} = 0.255$ g/g and $k = 0.0092$ L/g. The q_{tot} result is consistent with the outcomes of our previous works. In particular, the total amounts of extractable polyphenols per mass of solid matrix obtained using water and NADES were $q_{tot} = 0.114$ g/g (Bertino et al., 2023) and $q_{tot} = 0.470$ g/g (Mazzeo et al., 2023), respectively.

3.2 Kinetic studies

The experimental results of the three kinetic runs (tests 2.1-2.3) are reported in Table 2.

Table 2: Experimental data (concentrations C of polyphenols in liquid solvent) for the kinetic tests 2.1-2.3 ($T=70$ °C; Test 2.1: $\alpha = 0.54$ g/L, Test 2.2: $\alpha = 1$ g/L, Test 2.3: $\alpha = 2$ g/L).

Time t (min)	C (g/L) from test 2.1	C (g/L) from test 2.2	C (g/L) from test 2.3
0	0.130	0.169	0.250
15	0.132	0.218	0.304
30	0.136	0.232	0.351
60	0.138	0.231	0.418
90	0.142	0.242	0.497
120	0.140	0.229	0.483
150	0.143	0.243	0.512
180	0.145	0.234	0.520
210	0.141	0.233	0.521

It is worth noting that the initial concentration of polyphenols in liquid solvent (at $t = 0$) is different from zero. In fact, during experimental tests, as soon as the solid was brought into contact with the solvent, a release of phenolic compounds was immediately evidenced by a rapid coloration of the liquid.

The experimental data of Table 2 were then fitted with the corresponding theoretical predictions provided by the Linear Driving Force (LDF) Model. The aim of the fitting was to obtain the product between the global mass transfer coefficient and the specific surface area made available by the solid matrix referred to the liquid volume aK_{LDF} . In the LDF model, the mass balance equation for the liquid phase is (Bucić-Kojić et al., 2013):

$$\frac{dC}{dt} = aK_{LDF}(C^* - C) = aK_{LDF}\left(\frac{q}{k} - C\right) = aK_{LDF}\left[\frac{q_{tot}}{k} - \left(1 + \frac{1}{\alpha k}\right)C\right] \quad (5)$$

where aK_{LDF} accounts for two resistances in series: the resistance offered by the liquid film according to the film theory and the hypothetical linear resistance offered by a film inside the solid where the q gradient is considered to be concentrated. In Eq. 5, the theoretical liquid concentration C^* in equilibrium with the solid phase was expressed with the linear Eq. 3. Finally, the variable q was eliminated using the global mass balance provided by Eq. 2, evaluated at a generic time t . By integrating Eq. 5 with the initial condition $C(t = 0) = C^0$, the following prediction of C over time was obtained:

$$C(t) = \frac{\alpha q_{tot}}{1 + \alpha k} \left[1 - \left(1 - C^0 \left(\frac{1 + \alpha k}{\alpha q_{tot}} \right) \right) \exp \left(- \frac{1 + \alpha k}{\alpha k} aK_{LDF} t \right) \right] \quad (6)$$

where α and C^0 are the solid-liquid ratio and the initial polyphenol concentration in liquid for the specific test under consideration, respectively, and the thermodynamic parameters q_{tot} and k are taken from Section 3.1. The predicted concentration C provided by the LDF Model, as described by Eq. 6, was used to fit the experimental data C obtained from the three runs 2.1-2.3. In particular, a graphical representation of the fitting is provided in Figure 2. The good agreement between the experimental data and the model predictions shows the efficacy of the LDF model in describing the kinetic behaviour of the system.

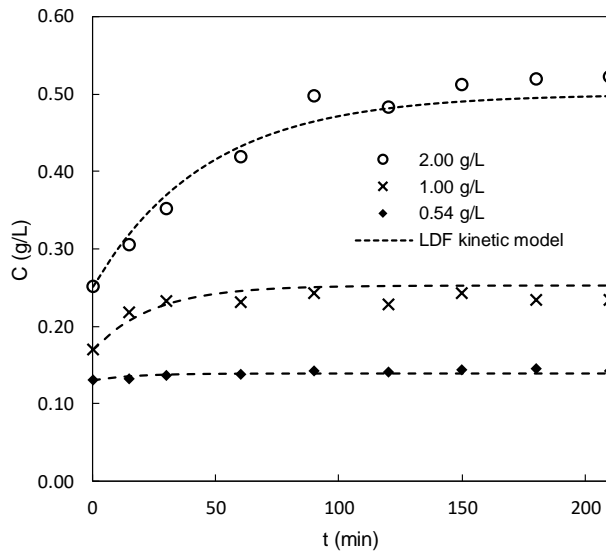


Figure 2: Kinetic curve of C versus t data fitted with the LDF kinetic model (Eq. 6).

These results shows that the process is very fast, reaching a plateau within the first hour. This is in line with what we observed in our previous experimental studies regarding polyphenols extraction with water and NADES (Bertino et al., 2023; Mazzeo et al., 2023). Finally, the aK_{LDF} values estimated for each run are reported in Table 3. It is possible to observe that the aK_{LDF} values increase accordingly to the increase in the solid-liquid ratio which is well-known to be proportionally related to the specific surface area.

Table 3: Estimated aK_{LDF} values for the various kinetic runs 2.1-2.3.

Test	α (g/L)	aK_{LDF} (1/s)
2.1	0.54	0.00030
2.2	1.00	0.00037
2.3	2.00	0.00039

4. Conclusions

This article is part of a research line focusing on evaluating the efficacy of different green solvents for extracting polyphenols from waste hazelnut skins. Specifically, it explores the feasibility of using a 50% vol/vol water-ethanol mixture. Experimental tests were conducted in a batch set-up, varying the solid-liquid ratio from 0.16 to 50 g/L while maintaining a constant temperature of 70°C, to investigate both equilibrium and kinetic aspects. Equilibrium tests lasted 6 hours to ensure reaching equilibrium conditions, and an equilibrium model combining global mass balance and a linear equilibrium isotherm was employed. Experimental equilibrium data were fitted with the model, yielding $q_{tot} = 0.255$ g/g and $k = 0.0092$ L/g as the total amount of extractable polyphenols in solid mass of hazelnut skins and the linear partition coefficient, respectively. By comparing the q_{tot} value obtained in this paper with the values presented in our previous works, it is worth noting that the 50% vol/vol water-ethanol mixture has a higher extraction efficiency than water ($q_{tot} = 0.114$ g/g, (Bertino et al., 2023)), but a lower extraction efficiency than NADES ($q_{tot} = 0.470$ g/g, (Mazzeo et al., 2023)). However, the higher viscosity of NADES makes it less suitable for plant-use scale.

Kinetic runs involved collecting liquid samples at fixed intervals, with results fitted to the Linear Driving Force Model to estimate the LDF mass transfer coefficient, showing an increase with solid-liquid ratio. Rapid extraction reaching maximum polyphenol concentration within the first hour was consistent with our previous findings. Future research will involve investigating the application of water-ethanol mixtures in a continuous set-up, enabling an expansion of the investigated solid-liquid ratios range. Moreover, employing a closed-loop fixed bed set-up will enable precise calculation of total extractable mass of polyphenols, allowing for a comparison with the q_{tot} value fitted in this paper. Finally, ongoing research will delve into exploring diverse water-ethanol mixtures with varying %vol compositions. Nevertheless, it is important to highlight that the particular 50% vol/vol water-ethanol mixture employed in this study has already proven to be an effective solution for recovering polyphenols from hazelnut skins.

Nomenclature

aK_{LDF} – Linear Driving Force mass transfer coefficient, 1/s	q – concentration of polyphenols in solid mass of hazelnut skins, g/g
C – concentration of polyphenols in solvent, g/L	q_e – equilibrium concentration polyphenols in solid mass of hazelnut skins, g/g
C^* – theoretical concentration of polyphenols in solvent in equilibrium with solid, g/L	q_{tot} – total amount of extractable polyphenols in solid mass of hazelnut skins, g/g
C_e – equilibrium concentration of polyphenols in solvent, g/L	t – time, min
C^0 – concentration of polyphenols in solvent at $t = 0$, g/L	V_i – volume of each sample collected during kinetic runs, μL
k – linear partition coefficient, L/g	V_L – volume of liquid solvent, L
M_S – mass of solid matrix, g	α – solid-liquid ratio, g/L
n_i – number of samples collected during each kinetic run, -	

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