

Article

Kinetics of Ultrasound-Assisted Flavonoid Extraction from Agri-Food Solid Wastes Using Water/Glycerol Mixtures

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Abstract: Red grape pomace (RGP) and onion solid wastes (OSW) were used as raw material to produce flavonoid-enriched extracts, using ultrasound-assisted solid-liquid extraction. The extraction medium used was composed of water and glycerol and under the conditions used the extraction of flavonoids from both materials was shown to obey first-order kinetics. Maximum diffusivities (D_e) values were 4.01×10^{-11} and $2.35 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$, for RGP and OSW extraction, respectively, while the corresponding activation energies (E_a) were 14.00 and 15.23 $\text{kJ} \cdot \text{mol}^{-1}$.

Keywords: extraction kinetics; flavonoids; glycerol; onion solid wastes; red grape pomace

1. Introduction

In spite of the variety of phytochemicals that may be encountered in agri-food by-products and wastes, significant attention has been given to polyphenols. This particular family of secondary metabolites includes an enormous number of compounds with diverse structures and bioactivities, including antioxidant, anti-inflammatory and anti-cancer properties [1,2]. Hence, there is an on-going research pertaining to the effective recovery of such substances, with the aim of utilizing them in food, pharmaceuticals and cosmetics [3,4].

The valorization of waste biomass for the recovery of polyphenolic compounds should include processes that generate far less or even zero further waste; otherwise no concept of “green” or “sustainable” could be substantiated. Thus, research on such a field should focus on the discovery and design of extraction processes, which will allow the use of alternative solvents and renewable natural products, and ensure a safe and high quality extract/product [5]. This challenge strongly suggests that technological innovations in the direction of utilizing novel extraction media and techniques are imminent.

The recovery of polyphenolic compounds from plant food industry wastes is currently a major concept towards the development of efficient techniques and a much research has been focused on efficient methodologies dealing with solid-liquid extraction. The utilization of a suitable solvent in combination with treatments, such as microwave heating, ultrasounds and high pressure (pressurized liquids), have become the state-of-the-art, displaying high recovery yields [6]. On the other hand, several extraction processes developed on a laboratory scale are characterized by significant shortcomings and the prospect of industrial implementation is rather particularly limited. This is owed to the toxicity of solvents frequently used and the need for recycling (acetone, methanol), strict control by State laws (ethanol), as well as increased cost and questionable efficiency (pressurized liquids, supercritical fluids) [5].

Glycerol is a material that has not been extensively used for extraction purposes, despite the fact that it possesses attractive characteristics, such as lack of toxicity, lack of flammability, volatility and

reactivity, as well as low cost, as it is a biodiesel industry by-product. Previous studies demonstrated that water/glycerol mixtures may be very effective in extracting polyphenols [7,8], but the information available to date is rather poor to fully evaluate glycerol's potency for efficient polyphenol recovery from plant material. Such an evaluation would embrace kinetic studies [9], to ascertain the efficacy and rapidity of extraction, carried out with a given solvent system. With regard to water/glycerol mixtures, polyphenol extraction has been shown in some instances to follow second-order kinetics [10,11], yet results from the extraction of various plant materials demonstrated that polyphenol extraction may follow first-order kinetics as well [12,13]. Furthermore, the ultrasound-assisted extraction of either red grape pomace (RGP) or onion solid wastes (OSW) was never been previously reported and thus no data are available in the relevant literature. Hence a kinetic examination becomes imminent in order to generate detailed data, which could be used for comparison of the efficiency of various extraction methodologies and for the engineering of improved extraction processes.

To this purpose, this study was performed to examine the kinetics of ultrasound-assisted flavonoid extraction from two agri-food residues, red grape pomace and onion solid wastes. Both solid wastes contain mainly flavonoid compounds, and the test employed to assess the total flavonoid yield is very specific, as opposed to the widely used Folin-Ciocalteu for total polyphenol determination, which determines the totality of polyphenols and not only flavonoids. Thus the data provided allowed for a more accurate and reliable determination of the extraction kinetics.

2. Results and Discussion

To identify the model that better described flavonoid extraction from both RGP and OSW, Y_{TFn} values were plotted as a function of t (Figures 1 and 2). The model best fitted to the extraction kinetics using non-linear regression was a 2-parameter, single exponential rise-to-maximum, described by the equation:

$$y = a(1 - e^{-bx}) \quad (1)$$

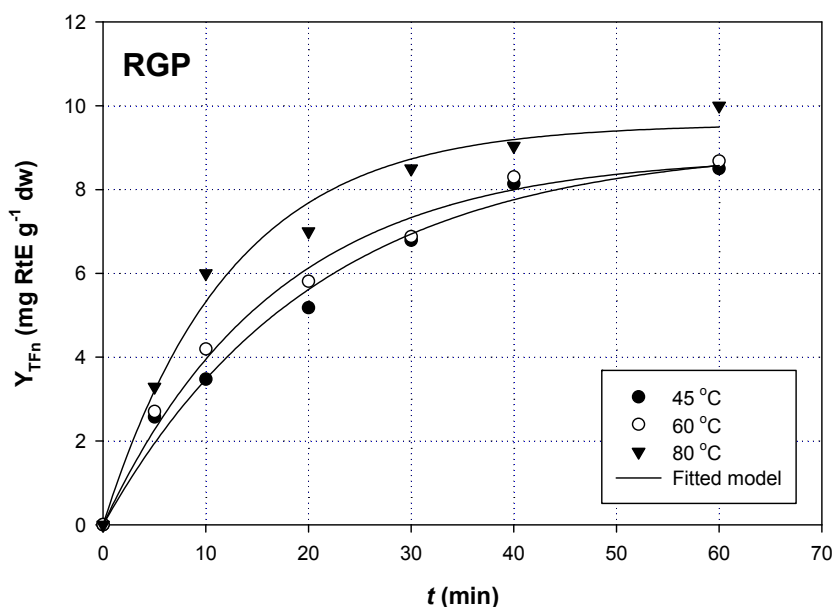


Figure 1. Non-linear regression between Y_{TFn} and t values during extraction of RGP; $R_{L/S} = 90 \text{ mL} \cdot \text{g}^{-1}$ and $C_{gl} = 90\% (w/v)$. Extractions were carried out under sonication (140 W, 37 kHz, $35 \text{ W} \cdot \text{L}^{-1}$).

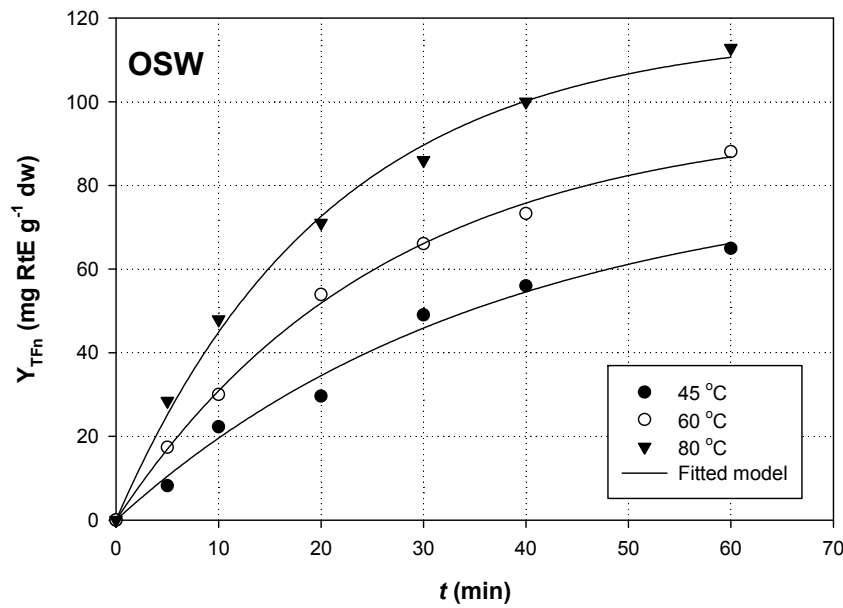


Figure 2. Non-linear regression between Y_{TFn} and t values during extraction of OSW; $R_{L/S} = 90 \text{ mL} \cdot \text{g}^{-1}$ and $C_{gl} = 90\% (w/v)$. Extractions were carried out under sonication (140 W , 37 kHz , $35 \text{ W} \cdot \text{L}^{-1}$).

For both RGP and OSW extractions, and for all temperatures tested, correlation was high and statistically significant ($R^2 > 0.98$, $p < 0.0001$). This suggested that extraction yield for total flavonoids as a function of t can be adequately predicted by the Equation (1), which represents first-order kinetics, considering the boundary conditions $t = 0$ to t and $Y_{TFn(t)} = 0$ to $Y_{TFn(t)}$:

$$Y_{TFn(t)} = Y_{TFn(s)}(1 - e^{-kt}) \quad (2)$$

The above considerations regarding diffusion were admitted, assuming that:

1. Flavonoids were uniformly distributed within the solid particles.
2. The particles were considered to be spherical.
3. Diffusivity remained constant throughout the extraction process.
4. The solution was perfectly mixed upon the energy dissipated by the ultrasonic waves.
5. Resistance to mass transfer was negligible in the liquid phase.
6. The transport of flavonoids from the solid particles into the liquid phase occurred through diffusion.

where $Y_{TFn(t)}$ is the extraction yield at any time t ; $Y_{TFn(s)}$ the extraction yield at saturation (equilibrium); and k the apparent first-order extraction rate constant. Both $Y_{TFn(s)}$ and k values were calculated by non-linear regression, using SigmaPlot™ 12.0 [14].

Rearrangement of Equation (2) would give:

$$\ln \left(\frac{Y_{TFn(s)}}{Y_{TFn(s)} - Y_{TFn(t)}} \right) = kt \quad (3)$$

$$\log \left(Y_{TFn(s)} - Y_{TFn(t)} \right) = \log \left(Y_{TFn(s)} \right) - \frac{k}{2.303} t \quad (4)$$

A plot of $\log(Y_{TFn(s)} - Y_{TFn(t)})$ as a function of t would yield a straight line with slope $= -k$ (Figures 3 and 4).

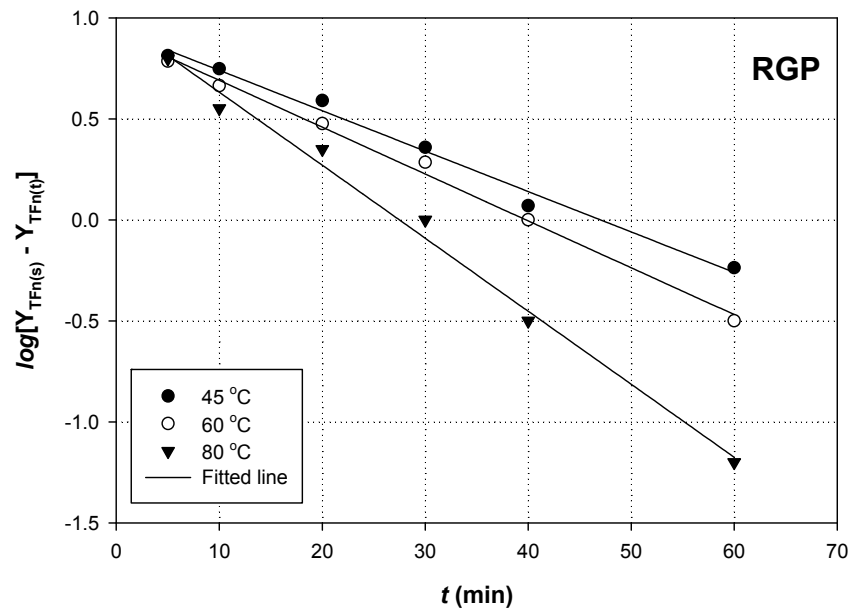


Figure 3. First-order kinetics of flavonoid extraction from RGP, using 90% (*w/v*) glycerol. Extractions were carried out with $R_{L/S} = 90 \text{ mL} \cdot \text{g}^{-1}$ and $C_{gl} = 90\% \text{ (} w/v \text{)}$, under sonication (140 W, 37 kHz, $35 \text{ W} \cdot \text{L}^{-1}$).

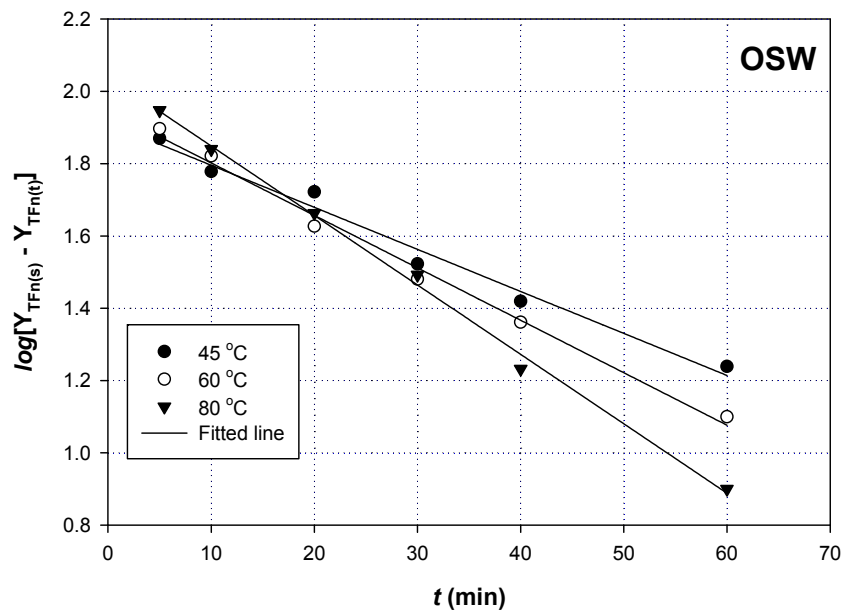


Figure 4. First-order kinetics of flavonoid extraction from OSW, using 90% (*w/v*) glycerol. Extractions were carried out with $R_{L/S} = 90 \text{ mL} \cdot \text{g}^{-1}$ and $C_{gl} = 90\% \text{ (} w/v \text{)}$, under sonication (140 W, 37 kHz, $35 \text{ W} \cdot \text{L}^{-1}$).

Based on Fick's second law, the mathematical expression that links Y and the effective diffusion of the solute (polyphenols/pigments) can be described as follows [15]:

$$\frac{Y_{TFn(t)}}{Y_{TFn(s)}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-\frac{D_e n^2 \pi^2 t}{r^2}} \quad (5)$$

where D_e is the diffusivity ($\text{m}^2 \cdot \text{s}^{-1}$); and r the radius of the solid particles (m). However, after the elapse of a short extraction period, only the first term of the series solution is considered significant, hence Equation (5) can be written as:

$$1 - \frac{Y_{TFn(t)}}{Y_{TFn(s)}} = \frac{6}{\pi^2} e^{-\frac{D_e \pi^2 t}{r^2}} \quad (6)$$

The linearized form of Equation (6) would be:

$$\ln \left(\frac{Y_{TFn(s)}}{Y_{TFn(s)} - Y_{TFn(t)}} \right) = \ln \frac{\pi^2}{6} + \frac{D_e \pi^2 t}{r^2} \quad (7)$$

The D_e coefficient can then be calculated graphically from the slop of the straight line, obtained after plotting $\ln \left(\frac{Y_{TFn(s)}}{Y_{TFn(s)} - Y_{TFn(t)}} \right)$ against t .

The kinetic parameters deriving from engineering the extraction process for both RGP and OSW were determined and analytically presented in Table 1. Raising the temperature from 50 to 80 °C had a positive effect on $Y_{TFn(s)}$ for the extraction from both materials, although for RGP a slight decrease was recorded by increasing temperature from 45 to 60 °C. The effect of temperature on the extraction of RGP in several instances is positive [16,17], since higher temperatures facilitate both polyphenol diffusion and increase solubility in polar solvents [18,19]. By contrast, total polyphenol extraction from OSW has been shown to decline at temperatures higher than 40 °C [20]. Furthermore, it has been demonstrated that solubilization of catechin, an abundant RGP constituent, is endothermic and, thus, thermodynamically favored at higher temperatures [21]. Similar phenomena may hold true for other RGP constituents too. On the other hand, temperature cannot be increased beyond certain limits, as this has been proven detrimental to anthocyanins, inducing their thermal degradation [22,23].

Table 1. Kinetic parameters determined for the Y_{TFn} at the temperatures tested, using first-order kinetic model. All extractions were performed with 90% (w/v) glycerol at a $R_{L/S}$ of 90 mL \cdot g $^{-1}$, under sonication (140 W, 37 kHz, 35 W \cdot L $^{-1}$).

Kinetic Parameters				
T (°C)	k (min ⁻¹)	Y _{TFn(s)} (mg RtE· g ⁻¹ dw)	D _e (m ² · s ⁻¹) × 10 ⁻¹¹	E _a (kJ· mol ⁻¹)
RGP				
45	0.0482	9.08	0.17	14.00
60	0.0594	8.82	2.69	
80	0.0813	9.57	4.01	
OSW				
45	0.0272	82.30	1.11	15.23
60	0.0387	96.28	1.74	
80	0.0484	117.06	2.35	

The maximum $Y_{TFn(s)}$, achieved at 80 °C, was 9.57 mg RtE \cdot g $^{-1}$ dw for RGP and 117.06 RtE \cdot g $^{-1}$ dw for OSW. Regarding the kinetics of TF_n extraction, k was found to increase in response to raising the temperature, reaching 0.0813 and 0.484 min $^{-1}$ at 80 °C, for RGP and OSW, respectively. These values are lower than 0.130 min $^{-1}$ reported for polyphenol extraction from grape juice bagasse using 50% ethanol [12] and 0.088 min $^{-1}$ reported for UAE (ultrasound-assisted extraction) of polyphenols from apple peels at 40 °C using water [13], but higher than 0.012 min $^{-1}$ found for water extraction of *Tilia* sapwood polyphenols at 80 °C [9]. Furthermore, the outcome from previous studies on the extraction

of anthocyanins from RGP with 50% ethanol yielded k values between 0.034 and 0.157 min^{-1} , within a temperature range of 25–60 °C [24].

In order to obtain quantitative data pertaining to the effect of temperature on the extraction rate, the Arrhenius equation was used:

$$k = k_0 e^{-\frac{E_a}{RT}} \quad (8)$$

where k_0 is the temperature-independent factor (min^{-1}); R the universal gas constant ($8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$); T the absolute temperature (K); and E_a the activation energy ($\text{J} \cdot \text{mol}^{-1}$). Transformation of Equation (8) allows obtaining a linear relationship between the first-order extraction rate constant and the inverse of T :

$$\ln k = \ln k_0 + \left(-\frac{E_a}{R}\right) \frac{1}{T} \quad (9)$$

Therefore, E_a could be determined graphically, since the straight line obtained by plotting $\ln k$ as a function of $1/T$ would have a slope $= -\frac{E_a}{R}$ (Figure 5).

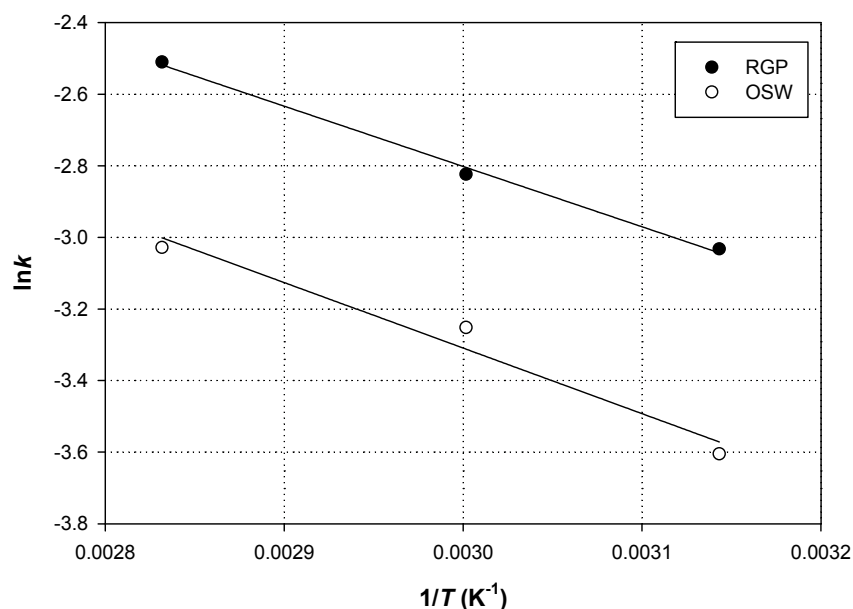


Figure 5. Relationships between temperature and the first-order extraction rate constant, $\ln k$, for extraction of flavonoids from RGP and OSW. Extractions were carried out with $R_{L/S} = 90 \text{ mL} \cdot \text{g}^{-1}$ and $C_{gl} = 90\% \text{ (w/v)}$, under sonication (140 W, 37 kHz, $35 \text{ W} \cdot \text{L}^{-1}$).

The E_a determined for TFn extraction for RGP and OSW were 14.00 and 15.23 $\text{kJ} \cdot \text{mol}^{-1}$, respectively. These values are almost 3–3.5 times higher than 4.6 $\text{kJ} \cdot \text{mol}^{-1}$, determined for the UAE of TP (total polyphenols) from RGP [25], employing 50% ethanol and almost 2.2 times higher than 6.34 $\text{kJ} \cdot \text{mol}^{-1}$ found for the UAE of orange peel polyphenols with 75% ethanol [26]. It should be emphasized that E_a determined for the extraction of polyphenols from various plant sources varied from 0.5 $\text{kJ} \cdot \text{mol}^{-1}$ [18] to as high as 97.1 $\text{kJ} \cdot \text{mol}^{-1}$ [27], depending on the solvent system and the conditions used. In general, the sufficient amount of E_a for polyphenol extraction lies from 14.54 [28] to 56.00 $\text{kJ} \cdot \text{mol}^{-1}$ [15].

In both cases E_a were positive, which is in agreement with endothermic process. E_a may be associated with both medium and matrix resistance, which the solute should overcome. If $E_a < 20 \text{ kJ} \cdot \text{mol}^{-1}$, then extraction is managed by diffusion [25]. Ultrasounds can assist with extraction processes both through cell disruption and by enhancing mass transfer in the boundary layer surrounding the solid matrix [29]. The relatively low E_a levels found for both extractions of RGP

and OSW indicated that ultrasonication is an effective means of assisting extraction, by providing the appropriate energy dissipation for efficient mass transfer. The ultrasonic energy is thought to accelerate the diffusional process by enhancing the solid particle permeability by the solvent, hence facilitating polyphenol release [30]. It could also be argued that the lower energy barrier required to initiate diffusion is provided by ultrasonic energy, which may contribute in overcoming solute-solute and solute-matrix interactions, thus decreasing E_a of the extraction process.

To support this hypothesis, the diffusivity (D_e) for both extractions were also calculated (Table 1). As can be seen, flavonoid extraction from RGP and OSW attained a D_e level of $4.01 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ and $2.35 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ at 80°C , respectively, which are higher than 0.14×10^{-12} to $1.57 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ reported for extraction of lignans from flaxseed [15] and $1.05 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ for polyphenols extraction from RGP with 50% ethanol [31] and 12.3×10^{-12} to $15.0 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ achieved in the extraction of polyphenols from RGP using 60% ethanol [32]. D_e as high as $12.3 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ and 1.2×10^{-11} to $25.0 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ were also determined for polyphenol and anthocyanin extraction from milled berries with 67% ethanol, respectively [33].

3. Experimental Section

3.1. Chemicals and Reagents

Rutin (quercetin 3-O-rutinoside) was from Sigma Chemical Co. (St. Louis, MO, USA). Aluminium chloride (AlCl_3) was from Merck (Darmstadt, Germany). Glycerol was obtained from Fisher Scientific (Pittsburgh, PA, USA).

3.2. Agri-Food Wastes

Red-skinned onions, with no apparent damages and infections, were purchased from a local grocery store (Myrina, Lemnos, Greece). The bulbs were transferred to the laboratory and peeled immediately using a sharp cutter, so as to remove the outer dry and semi-dry layers, as well as the apical trims (onion solid wastes-OSW). Red grape pomace (RGP) originating from vinification of Agiorgitiko variety (*Vitis vinifera* spp.) was kindly provided by the Department of Food Science and Human Nutrition, Agricultural University of Athens. The materials were placed in an oven set at 65°C for 48 h and then pulverized to a fine powder in a laboratory mill (approximate mean particle size 0.3 mm for RGP and 1 mm for OSW). The pulverized material was kept at -20°C until used. This powder was used for all extraction processes.

3.3. Ultrasound-Assisted Extraction

A previous methodology was employed [34], with slight modifications. Extractions were carried out in plastic containers, using 100 mL of 90% (*w/v*) aqueous glycerol and an amount of pulverized material to provide a liquid-to-solid ratio ($R_{L/S}$) of $90 \text{ mL} \cdot \text{g}^{-1}$. The mixture was vortexed for a few seconds to form slurry and ultrasound-assisted extractions were performed in a temperature-controlled, sonication bath (Elma P70, Singer, Germany), at a fixed power of 140 W, a frequency of 37 kHz, and an acoustic energy density (AED) of $35 \text{ W} \cdot \text{L}^{-1}$, for 60 min, at 45, 60 and 80°C . Sampling was accomplished at predetermined intervals. Samples were placed in 1.5 mL Eppendorf tubes (Hamburg, Germany) and centrifuged in a table centrifugator (Hermle, Wehingen, Germany) at 10,000 rpm for 10 min. The clear solution was used for further analysis.

3.4. Determination of Total Flavonoid Yield (Y_{TFn})

A previously published protocol was used [35], with modifications. An aliquot of 0.25 mL sample was mixed with 0.75 mL AlCl_3 reagent (0.16% (*w/v*) AlCl_3 in 5% (*v/v*) acetic acid in methanol) and allowed to stand for 30 min, at room temperature. The absorbance was obtained at 415 nm (A_{415}) and the total flavonoid concentration (C_{TFn}) was calculated from a calibration curve, constructed with rutin

(quercetin 3-*O*-rutinoside) as the calibration standard. Yield in total flavonoids (Y_{TFn}), expressed as mg rutin equivalents (RtE) per g of dry weight, was determined using Equation (10):

$$Y_{TFn} \left(\text{mg RtE g}^{-1} dw \right) = \frac{C_{TFn} \times V}{m} \quad (10)$$

where V is the volume of the extraction medium (L); and m the dry weight of the plant material (g).

3.5. Kinetics and Statistical Analyses

All determinations were carried out at least in triplicate and values were averaged and given along the standard deviation (\pm S.D.). Kinetics was performed by carrying out non-linear regression between Y_{TFn} and t values. Kinetics and linear and non-linear correlations were established at least at a 95% significance level ($p < 0.05$). For all statistics, SigmaPlot™ 12.0 and Microsoft Excel™ 2010 were used.

4. Conclusions

This examination provided for the first time concrete evidence that a solvent system composed of 90% (*w/v*) aqueous glycerol can efficiently extract flavonoids from RGP and OSW, with the assistance of ultrasonication. In both cases, extraction yield increased in response to raising the temperature up to 80 °C, a phenomenon ascribed to higher diffusion. The relatively low activation energies for the extraction of flavonoids were attributed to the effect of ultrasounds, which were assumed to provide the appropriate dissipation energy for such a process. The satisfactory extraction yields achieved, confirmed such a hypothesis. This is a significant outcome, considering that glycerol is an inexpensive, abundant and non-toxic bio-material. Hence the adoption of similar methodologies by the industry would be anticipated to form the basis for the development of green processes, aimed at the valorization of food industry waste streams and the sustainable production of value-added commodities, such as food additives, food supplements, pharmaceutical formulations, and cosmetics.

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Conflicts of Interest: The author declare no conflict of interest.

Nomenclature

AED	acoustic energy density ($\text{W} \cdot \text{L}^{-1}$)
C_{TFn}	total flavonoid concentration ($\text{mg RtE} \cdot \text{L}^{-1}$)
D_e	diffusivity ($\text{m}^2 \cdot \text{s}^{-1}$)
E_a	activation energy ($\text{kJ} \cdot \text{mol}^{-1}$)
k	first-order extraction rate constant (min^{-1})
$R_{L/S}$	liquid-to-solid ratio ($\text{mL} \cdot \text{g}^{-1}$)
t	time (min)
T	temperature (°C or K)
Y_{TFn}	yield in total flavonoids ($\text{mg RtE} \cdot \text{g}^{-1}$)
$Y_{TFn(s)}$	yield in total flavonoids at saturation ($\text{mg RtE} \cdot \text{g}^{-1}$)

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