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Emilie Isidore, Gaëlle Willig, Fanny Brunissen, Christian Magro, Charles Monteux, et al.. Selective recovery of glycosylated phenolic compounds from nectarine tree branches (*Prunus persica* var. *nucipersica*). *Food Chemistry Advances*, 2024, 4, pp.100585. 10.1016/j.focha.2023.100585 . hal-04431326

HAL Id: hal-04431326

<https://hal.science/hal-04431326>

Submitted on 1 Feb 2024

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Selective recovery of glycosylated phenolic compounds from nectarine tree branches (*Prunus persica* var. *nucipersica*)

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Abstract:

Nectarine tree branches, by-products from the arboriculture, contain phenolic compounds. Six main components were revealed by LC-MS and divided into 3 aglycones (A) (catechin, chlorogenic acid, naringenin) and 3 glycosylated (G) (rutin, isoquercetin and prunin) molecules. To maximize their content in nectarine tree branches extract, the extraction process was optimized. The optimum conditions were found at 55% ethanol and 90 °C, leading to 9.05 ± 0.80 mg/g_{DM} of catechin, 3.17 ± 0.31 mg/g_{DM} of chlorogenic acid, 1.15 ± 0.01 mg/g_{DM} of naringenin, 1.56 ± 0.08 mg/g_{DM} of rutin, 0.57 ± 0.02 mg/g_{DM} of isoquercetin, and 1.73 ± 0.11 mg/g_{DM} of prunin. The glycosylated-aglycone ratio is equal to 0.276 ± 0.006 , meaning that aglycones are predominant. Purification of the extract was carried out by adsorption. A screening of several resins led to the choice of the XAD-7 resin that provides a recovery rate of 66-84% of glycosylated compounds and 9-46 % of aglycones. The effect of the adsorption process on the evolution of the G/A ratio was studied. Under the studied conditions, this parameter increased by 123%, mainly due to a good performance of the XAD-7 towards glycosylated components and a low recovery rate of chlorogenic acid.

Keywords: Nectarine tree branches, glycosylated components, extraction, adsorption, phenolic compounds

Nectarine (*Prunus persica* var. *nucipersica*) is a variety of peach (*Prunus persica*), a species native from China. The culture of peach trees, including nectarine trees, represented 11,700 ha in France in 2021. The nectarine fruit is usually smaller than that of the conventional peach with the particularity of having a smooth skin. They are intended for human nutrition and generate many by-products during cultivation, harvest (leaf, twig) or after processing (kernel, stem) (Agreste, *La Statistique Agricole*, n.d.; Siddiq et al., 2012; Sodeifian & Sajadian, 2021). Although very few studies have been published on the valorization of *Prunus persica* by-products, peach leaves and stems, as well as nectarine kernel oil, represent an interesting source of natural molecules with antioxidant activity and thus a great potential for the food, pharmaceutical or cosmetics industries (Maatallah et al., 2020; Murata et al., 2022; Sodeifian & Sajadian, 2021).

Tree pruning is performed to obtain fruits of better quality and facilitate the harvest. The wood coming from pruning, produced in large volumes, are often sent back on the land or burned (Aliaño-González et al., 2022; Siddiq et al., 2012). For example, the annual pruned biomass of Croatian nectarine trees has been estimated to 2.9 T/ha, which represents a significant amount of underutilized biomass (Bilandzija et al., 2012). Branches of arboriculture, whatever the fruit production, are rich in bioactive secondary metabolites. Phenolic acids, flavonoids have been identified in peach by-products, and several studies have shown the existence of bioactivities from peach branch extracts (Aliaño-González et al., 2022; Maatallah et al., 2020; Nakagawa et al., 2018; Yi et al., 2008). Therefore, *Prunus Persica* var. *nucipersica* branches seems an interesting source of phenolic compounds and it is worth considering studying a potential valorization of this biomass. To that end, a more in-depth knowledge of the phenolic compounds profile is necessary. The extraction of these molecules from their matrix remains a mandatory step for their identification and quantification. Conventional extraction process was mainly used to achieve this goal (Maatallah et al., 2020; Raturi et al., 2012; Yi et al., 2008). The process used in this study is an accelerated solvent extraction based on the use of a pressure fixed at 100 bar. In such working condition, it is possible to exceed the saturation pressure of the solvent and speed up the extraction. The process is fully automated, and the extract is filtered in-line at the end of the extraction process, allowing a quick and efficient screening of the extraction conditions (Mendiola et al., 2007).

However, phenolic compounds are often recovered at low concentrations in a complex mixture and the selectivity of the extraction process with respect to these molecules remains low (Kühn et al., 2014). Among the various purification technologies, our attention has focused on adsorption process. Indeed, synthetic resins have been successfully used to separate and/or concentrate phenolic compounds from crude vegetal extracts. Moreover, adsorption is economic, scalable, simple to operate, and the adsorbent can be regenerated (Conde et al., 2013; Kammerer, Kammerer, Jensen, et al., 2010; Kühn et al., 2014; Soto et al., 2011). This technology offers high yields after optimization which makes it popular (Kammerer, Kammerer, Jensen, et al., 2010; Kinoshita et al., 2015; Soto et al., 2011). Adsorption is impacted by the physical characteristics of the resin (Conde et al., 2013; dos Santos et al., 2022; Kinoshita et al., 2015; Silva et al., 2007) and the operating conditions such as the temperature or the pH of the solution (Conde et al., 2013; Kammerer, Kammerer, Jensen, et al., 2010; Tomás-Barberán et al., 1992). However, the large variety of molecules (phenolic compounds, sugars, proteins) present in the crude extract may affect the affinity of a given compound with the adsorbent, and even compete for adsorption (Conde et al., 2013; Kammerer, Kammerer, & Carle, 2010; Silva et al., 2007). For this reason, a follow-up of each target component is mandatory to assess the process efficiency.

Therefore, the objective of this work is to selectively recover phenolic compounds from nectarine tree branches. A first part is dedicated to the identification and quantification of the phenolic compounds present in the raw extract of nectarine tree branches. Then, a second part will be devoted to the study of the impact of the extraction process on the molecules of interest. The last part will be focused on the recovery of phenolic compounds using the adsorption technology, where the behavior of each single component will be studied.

2. Material and Methods

2.1. Plant material and chemicals

Nectarine tree branches var CARENE® Monecar cov, harvested in March 2020 were kindly provided by the company ChestNut (Valence, France). The plant material was dried outside at ambient temperature before shipment, which is beneficial for the extraction of phenolic compounds (Babiker et al., 2021). Nectarine tree branches' preparation consisted in a grinding step with a SM300 Retsch cutting mill (Retsch, Haan, NRW, Germany). The equipment was set at 1500 rpm and the nectarine tree branches were continuously crushed and sieved at 4 mm particle size. The ground sample was stored in the dark at room temperature. The dry matter of the plant material was $90.2 \pm 0.1\%$.

The standards catechin and isoquercetin were purchased from Sigma Aldrich (Saint-Louis, Missouri, USA) while chlorogenic acid and rutin were supplied from Fischer Scientific (Illkirch, France). Naringenin and prunin are provided by VWR (Radnor, Penn., USA) and Carbosynth (Berkshire, United Kingdom), respectively. For HPLC analysis, acetonitrile was purchased from VWR (Radnor, Penn., USA) and formic acid was from Fischer Scientific (Illkirch, France) as well as the 3 Amberlite resins XAD-4, XAD-7 and XAD-16. Ethanol for the extractions was supplied from VWR (Radnor, Penn., USA). The ultrapure water used in this study was produced with a water filtration equipment (MilliQ Integral 5, Millipore, Burlington, Massachusetts, USA).

2.2. Identification and quantification of phenolic compounds

2.2.1. Phenolic compounds identification by LC-MS

The composition in phenolic compounds of nectarine tree branches extract was investigated by LC-MS. The extract sample was diluted in ethanol then filtered with a 0.2 μ m RC filter. The LC-MS equipment was an Agilent 1290 coupled with a 6545 Q-TOF mass spectrometer (Wilmington, DE, USA) and a PDA UV detector. The Dual Agilent JetStream ESI source was run at atmospheric pressure in positive ionization mode. The Zorbax Eclipse plus C18 column (50 mm \times 2.1 mm, 1.8 μ m, Agilent, Santa Clara, CA, USA) was heated at 40 °C and the injection volume was fixed at 1 μ L. The mobile phase was composed of 0.1% (v/v) formic acid in water (solvent A) and 0.1% (v/v) formic acid in acetonitrile (solvent B). The elution gradient, flow rate, acquisition wavelength and MS source were defined as described by (Willig et al., 2022). MassHunter software (version 8.0.0, Agilent, Santa Clara, CA, USA) was used to process the results. The most responding phenolic compounds were identified with an internal database as well as NIST and Metlin commercial databases. The resulting propositions were then validated with commercial standards.

2.2.2. Phenolic compounds quantification by HPLC

The preparation of the extract samples consisted in a suitable dilution in ethanol followed by a filtration with 0.2 μ m RC filters prior HPLC analyses. The phenolic compounds were quantified with a Dionex Ultimate 3000 (Dionex Corporation, Sunnyvale, Californie, USA) system equipped with a diode array detector (DAD). The Halo 90 Å AQ-C18 column (150 mm \times 2.1 mm \times 2.7 μ m, Advanced Material Tech, Wilmington, DE, USA) was heated at 48 °C. A volume of 1 μ L was injected, the phenolic compounds were eluted with a mobile phase composed of 1%

(v/v) formic acid in water (solvent A) and acetonitrile (solvent B). The elution gradient lasted 16 min at a flow rate of 0.6 mL/min as followed: 2 to 20% of solvent B from 0 to 6 min, 20% of (B) from 6 to 8 min, 20 to 50% of (B) from 8 to 11 min, 50% of (B) from 11 to 12 min, 50 to 2% of (B) from 12 to 12.5 min, and 2% of (B) from 12.5 to 16 min. UV detection was set at (i) 285 nm to detect catechin, naringenin and prunin, (ii) 254 nm to detect rutin and isoquercetin, and (iii) 325 nm for chlorogenic acid. Chroméléon software (version 7.3) was used to record chromatograms and related data. Stock solutions of chlorogenic acid, catechin, naringenin, rutin, isoquercetin and prunin were prepared in ethanol as well as the corresponding dilutions to draw proper calibration curves. The yield of individual phenolic compounds was determined in mg/g_{DM}.

A distinction between glycosylated (G) and aglycone (A) phenolic compounds appeared interesting because these two types of compounds might have different behaviors during the extraction and purification processes. Thus, the G/A ratio parameter, representing the ratio between the glycosylated and aglycone forms was defined in order to monitor the effect of the extraction and purification on the two classes of molecules throughout the study (Equation 1).

$$\text{Equation 1: } G/A = \frac{\sum_{i=1}^n C_i}{\sum_{j=1}^n C_j}$$

Where G/A is the glycosylated-aglycone ratio (no unit), and C_i and C_j are the respective yields or concentrations of glycosylated and aglycone phenolic compounds, respectively, extracted from nectarine tree branches (mg/g_{DM} or mg/L).

2.3. Study of the operating conditions on the selectivity of the extraction process

2.3.1. Optimization of the extraction of phenolic compounds

The extraction of phenolic compounds was studied using response surface methodology. A D-optimal design of experiment was set with MODDE software (version 12.0.1, Sartorius, Goettingen, Germany). Accelerated solvent extractor (ASE 350, Dionex Corporation, Sunnyvale, Californie, USA) is used to extract phenolic compounds from nectarine tree branches. Ten milliliter extraction cells were used. Time (including a 5 min heating period) and sample mass were fixed parameters respectively set at 35 min and 2 g. The pressure is fixed at 100 bar. The extract is filtered online at the end of the extraction. After each extraction, the samples were stored at -20 °C.

The first factor studied (X₁) is the ethanol concentration in water (0-30-70-100%, v/v) and the second factor (X₂) is the temperature (40-65-90 °C). Y_i are the responses, expressed in mg/g_{DM} and the glycosylated-aglycone ratio (G/A). The design of experiments, showed in table A.1 (supplementary material), consisted in 12 assays including 3 centered points.

The experimental results were used to model the responses with a second order polynomial equation as described in Equation 2.

$$\text{Equation 2: } Y_i = a_0 + a_1 \cdot X_1 + a_2 \cdot X_2 + a_{11} \cdot X_1^2 + a_{22} \cdot X_2^2 + a_{12} \cdot X_1 \cdot X_2 + e$$

Where Y_i are the responses (Y₁ to Y₇), a₀ is the constant, a_i the linear (a₁ and a₂), quadratic (a₁₁ and a₂₂) and interaction (a₁₂) coefficients of the model respectively, X₁ is the variable "ethanol concentration", X₂ is the variable "temperature" and e is the lack of fit.

The extraction parameters were optimized using the software optimizer tool and validated through experimental assays carried out in the optimal conditions.

2.3.2. Kinetic study of the extraction in optimal conditions

A kinetic study was conducted at 90 °C and 55% ethanol, these conditions are the optimum defined by the aforementioned design of experiments. Different 10 mL extraction cells were filled with 2 g of nectarine tree branches and loaded in the ASE. An extraction was performed on every cell and stopped after the heating time (5 min), and 10, 20, 25 and 35 min including the 5 min heating time. It is not recommended to heat more than 30 minutes with the ASE because of the potential degradation of the phenolic compounds. Y_t were determined by HPLC and plotted according to the extraction time.

The extraction kinetics were drawn for each phenolic compound and different mathematical models were applied and compared to find the best fit with the experimental data:

- 1st order kinetic model (Poojary & Passamonti, 2015)

$$\text{Equation 3: } Y_t = Y_{eq} \cdot (1 - e^{-kt})$$

Where Y_t and Y_{eq} are the phenolic compound's concentrations at time t and at equilibrium (mg/g_{DM}), k the extraction rate constant (min⁻¹), and t the time of extraction (min).

- Peleg's model (Peleg, 1988)

$$\text{Equation 4: } Y_t = Y_0 + \frac{t}{k_1 + k_2 \cdot t}$$

Where Y_0 and Y_t (mg/g_{DM}) are the phenolic compound's concentrations at time $(t) = 0$ and time t (min), k_1 Peleg's rate constant (min g_{DM}/mg), k_2 Peleg's capacity constant (g_{DM}/mg). Y_0 is assumed to be 0 at $t = 0$ min. Equation 4 is thus simplified as follows:

$$\text{Equation 5: } Y_t = \frac{t}{k_1 + k_2 \cdot t}$$

It should be noted that Peleg's model is very close to a 2nd order kinetic model. For this reason, the latter is not presented in this study.

- Logarithmic model (Anbalagan et al., 2019)

$$\text{Equation 6: } Y_t = b + a \cdot \log(t)$$

Where Y_t is the phenolic compound's concentration at time t , a and b are the logarithmic model parameters.

- Two-sites kinetic model (Karacabey et al., 2013)

$$\text{Equation 7: } Y_t = Y_{eq} \cdot [1 - f \cdot e^{-k_1 t} - (1 - f) \cdot e^{-k_2 t}]$$

The two-sites kinetic model is a succession of two 1st order terms, that describe the fast release of components in a first step, then the slow diffusion in a second step. In Equation 7, Y_t is the phenolic compound's concentration at time t (min), f is the fraction of the component during the 1st step, k_1 is the corresponding extraction rate constant (min⁻¹); while $(1 - f)$ is the fraction of the component during the 2nd step, and k_2 the corresponding extraction rate constant (min⁻¹).

Every model was tested thanks to Excel's Solver tool. Model fitting was evaluated by calculation of the coefficient of determination, R^2 and the root mean square error, RMSE.

2.4. Study of the extract's fractionation by adsorption

2.4.1. Preparation of an aqueous extract concentrate

ASE is an interesting extraction technique with many advantages such as time reduction or operating at pressure above solvent's boiling point. However, ASE has also drawbacks since it produces small volumes of extract (around 100 mL). For this reason, hot maceration is preferred to scale-up the process. The optimal temperature of phenolic compound's extraction with ASE is 90 °C, above ethanol boiling point. This condition cannot be respected with maceration, thus a temperature of 70 °C and an ethanol concentration of 70% v/v are chosen for this technique.

Hot maceration was performed in erlenmeyers. The nectarine tree branches were soaked during 6 h with a solvent composed of 70% ethanol in water (v/v). The solvent to material ratio was 30 mL/g and the temperature was set at 70 °C. A magnetic stirrer was used for the agitation; the power was adjusted to create a vortex and observe the mixture in motion. The final extract is separated from the plant material by filtration through a 20 µm nylon filter and stored at -20 °C.

An aqueous extract is preferred to study the fractionation by an adsorption process. The hydroalcoholic solvent of nectarine tree branches extract has been evaporated under vacuum and solubilised in a volume of water in order to concentrate 4 times the final extract. A smaller volume is used to get a higher phenolic compound concentration in the solution and to save solvent with negligible loss of the target molecules. This aqueous extract concentrate (AEC) is used as starting solution for adsorption assays.

2.4.2. Selection of macroporous resin

The three amberlite resins XAD-4, XAD-7 and XAD-16, described in table A.2, are employed to separate phenolic compounds from AEC. Prior their use, resins were soaked in methanol then rinsed with ultrapure water in order to activate the resins and eliminate chemical conservatives. Dry weight of wet resins was measured with moisture analyser (MB23, OHAUS, Parsippany, New Jersey, USA). The adsorption is studied in a static mode. A volume of 50 mL of AEC is introduced in a beaker with an equivalent of 1 g_{DW} resin at room temperature (22 °C). After 120 min, the resin is separated from the extract with a nylon filter and rinsed with ultrapure water. Phenolic compounds are desorbed with 50 mL of 70% ethanol in water (v/v) during 2 h at ambient temperature. The phenolic compounds contained in the extract after adsorption and in the desorption eluent were quantified by HPLC. Adsorption and desorption rates, as well as adsorption capacity and recovery rate, were calculated for each phenolic compound according to the following equations:

$$\text{Equation 8: } A_i = \left(1 - \frac{C_t}{C_0}\right) \times 100$$

$$\text{Equation 9: } D_i = \frac{C_d \times V_d}{(C_0 - C_t) \times V_{AEC}} \times 100$$

$$\text{Equation 10: } Q_{a,i} = \frac{(C_0 - C_t) \times V_{AEC}}{W}$$

$$\text{Equation 11: } R_i = \frac{C_d \times V_d}{C_0 \times V_{AEC}} \times 100$$

With A_i , D_i , $Q_{a,i}$, and R_i the adsorption rate, desorption rate, adsorption capacity, and recovery rate of individual phenolic compound (%), C_0 the initial phenolic compound's concentration in AEC (mg/L), C_t the phenolic compound concentration in AEC after 120 min adsorption (mg/L),

C_d the phenolic compound concentration in eluent after 120 min desorption (mg/L), V_d and V_{AEC} the eluent and AEC volumes (L), and W the mass of resin (g) on a dry matter basis.

The best resin was selected based on A, D and R, but also on the evolution of the G/A ratio after the process. The most satisfying resin was used to study the impact of the desorption solution, where different ethanol concentrations (30, 50, 70 and 90%) were tested.

2.4.3. Modelling of adsorption kinetic

The adsorption kinetic corresponds to the adsorption capacity plotted according to the adsorption time. This one is studied using the resin chosen previously (XAD-7 resin), in the same conditions as described above. The samples are collected after 5, 15, 30, 45, 60, 90 and 120 min. The adsorption capacity is calculated for each phenolic compound according to Equation 10, and is plotted against time. Pseudo-first order and pseudo-second order kinetic models were applied to determine the best fit to the experimental data:

- Pseudo 1st order kinetic model (Shen et al., 2022; Yu et al., 2020)

$$\text{Equation 12: } Q_t = Q_{eq} \cdot (1 - e^{-k_1 t})$$

- Pseudo 2nd order kinetic model (Shen et al., 2022; Yu et al., 2020)

$$\text{Equation 13: } Q_t = \frac{k_2 \cdot t \cdot Q_{eq}^2}{1 + k_2 \cdot t \cdot Q_{eq}}$$

With Q_t and Q_{eq} the adsorption capacities at time t and at equilibrium (mg/g_{DM} resin), k_1 and k_2 the adsorption rate constants (min⁻¹) of the pseudo 1st and pseudo 2nd order kinetic models respectively, and t the time of adsorption (min).

2.5. Statistical analysis

Experiments related to the design of experiments were treated with MODDE software (version 12.0.1, Sartorius, Goettingen, Germany).

All other experiments were conducted in triplicate. Means and standard deviations were calculated with Excel. The analyses of variance (ANOVA) were performed using R software (version 4.0.2). First, the normal distribution of data was validated with a Shapiro test, then a Bartlett test was used to check the variance equality. After validation, the differences in means were tested by a Tukey test. Student tests were also carried out to show the non-significant differences between two means. All the risks used are equal to 5%.

3. Results

First, the phenolic compounds of extracts from nectarine tree branches were identified and quantified. The operating conditions of the extraction process were then optimized and the extraction kinetic was monitored and modelled. In a third part, an adsorption process was applied to separate the phenolic compounds from the extract. Glycosylated-aglycone ratio was monitored along this study to define a potential selectivity of the processes on these classes of phenolic compounds.

3.1. Phenolic compounds identification and quantification

The phenolic compound composition of nectarine tree branches was determined by LC-MS. Thirteen components were identified with databases according to their fragment mass. The corresponding standards allowed to confirm their presence. The results are presented in table A.3.

Although the composition in phenolic compounds in nectarine branches had never been studied before, there are a number of studies on fruit trees of the genus *Prunus*. (Willig et al., 2022) have identified from cherry tree branches the same phenolic compounds as found in this study. Other studies dealing with *Prunus persica* branches have identified chlorogenic and neochlorogenic acids, catechin, epicatechin, naringenin, prunin, quercetin and derivatives, and anthocyanins (Aliaño-González et al., 2022; Maatallah et al., 2020; Murata et al., 2022; Raturi et al., 2012). To the best of our knowledge, genistein, apigenin and chrysin were identified for the first time in *Prunus persica* branches.

According to a first quantification on LC-MS (table A.4), 6 major compounds were identified. Then, a quantification method has been developed on an UHPLC. The resulting chromatogram is shown in figure A.1 and their respective formula are visible in figure 1.

In this study, the most abundant phenolic compounds of nectarine tree branches are divided in 2 categories: the aglycone components (catechin, chlorogenic acid and naringenin) and the glycosylated phenolic compounds (rutin, isoquercetin and prunin). Among the compounds identified, there are two glucosides (prunin and isoquercetin) and one rutinoside (rutin), the latter bearing a disaccharide (rhamnose-glucose). It is also interesting to note that prunin is a glycosylated form of naringenin, whereas rutin and isoquercetin are glycosylated forms of quercetin.

The interest in glycosylated components lies in their higher solubility in water and higher bioavailability in comparison with their corresponding aglycone, the glycoside moiety inducing a higher polarity and a better hydrophilicity. They are also more stable and are assumed to be the storage form of their corresponding aglycone molecules. However, their bioactivities are usually decreased compared to aglycone forms, and the different sugars and linkages involved can modulate their bioactivities (Johnson et al., 2021; Slámová et al., 2018).

3.2. Optimization of the phenolic compounds' extraction

A D-optimal design was performed to find the operating conditions affecting the extraction of phenolic compounds from nectarine tree branches. For this, the extraction yield of the 6 main phenolic compounds and the G/A ratio (Equation 1) were modelled according to the ethanol concentration (X_1) and the extraction temperature (X_2). Values obtained for the 7 responses are shown in table A.5.

The extraction yields differ widely between each phenolic compound. Catechin, varying from 1.35 to 7.84 mg/g_{DM}, is the most abundant component among the phenolic compounds investigated in nectarine tree branches. This result is supported by other works, where catechin was found to be abundant in *Prunus persica* and *Prunus avium* stems (Maatallah et al., 2020; Willig et al., 2022). On the opposite, naringenin and isoquercetin show the lowest yields, in the range 0-0.84 mg/g_{DM} and 0.14-0.58 mg/g_{DM}, respectively. The aglycone molecules, particularly catechin and chlorogenic acid, are predominant. Glycosylated phenolic compounds are found in a lower quantity, thus leading to a G/A ratio below 1.

For all components, the lowest yields are reached at low temperature (40 °C) with a solvent composed of pure water (N1) or pure ethanol (N3). Ethanol mixed with water (70% (v/v)) is the solvent of choice to obtain the highest yields. The minimum values are thus obtained in very close operating conditions, independently of the phenolic compounds. This is also the case for the maximum values. The G/A ratio does not change significantly between each run (0.237 to 0.287). The minimum and maximum values are obtained with water, at 65 °C (N4) and 40 °C (N1), respectively.

3.2.1. Modelling of the extraction yield of phenolic compounds

From experimental data, coefficients of the polynomial equations were determined by MODDE software. The analysis of their significance enables to determine the effect of the extraction temperature, the ethanol concentration, their quadratic and interaction terms on the responses.

For each response Y_i , the relevant terms are kept in the prediction equations of the results and to shape the response surfaces (figure A.2). Table A.6 gathers the coefficients calculated by MODDE for the reduced models.

The adjusted coefficients of determination, p -values of the regressions and p -values for lack of fit of all phenolic compounds indicate a good fit of the models to the experimental data. In the case of G/A ratio, the adjusted R^2 is very low and the p -value exceeds 0.05 suggesting that the model is not satisfactory. This means that in the studied conditions, ethanol concentration and temperature do not allow a selectivity of a category of components over another.

Ethanol (X_1) has a significant positive effect on naringenin and prunin yields and a significant negative effect on chlorogenic acid. This term has also non-significant effects on catechin, rutin and isoquercetin yields. As the quadratic term of ethanol (X_1^2) negatively impacts the extraction of every phenolic compounds, the variable ethanol must be kept in the models. The quadratic term of ethanol has the highest effect on the extraction of phenolic compounds from nectarine tree branches. According to (Barwick, 1997), it is difficult to predict the solubility of a given compound in a solvent. Nevertheless, polarity is used to explain this parameter because this is the most influential factor. Rohrschneider polarity scale or Hildebrand solubility parameter are recommended to calculate solvents' polarity (Barwick, 1997). In the work of (Muhamad et al., 2014) and (Rahman et al., 2013), the Rohrschneider polarity scale is used to demonstrate that the addition of water modifies the polarity of a solvent like ethanol and offers a better solubility thus favoring the extraction of phenolic compounds. Indeed, solvent and solute must be in the same polarity range to obtain a good solubility although other interactions influence the solubility of phenolic compounds (Barwick, 1997; Muhamad et al., 2014; Rahman et al., 2013). In the design of experiment, the influence of the water/ethanol mixture varies according to the phenolic compounds, probably due to their own polarity range and interactions with the solvent. These results prove the necessity to use a solvent composed of ethanol and water to increase the extraction yield of phenolic compounds from nectarine tree branches instead of the sole ethanol or water.

Temperature (X_2) is the second factor investigated in this study. Temperature has a positive effect on all the phenolic compounds studied indicating that an increase of this parameter benefits the recovery of every phenolic compound. Despite the non-significance for the extraction of chlorogenic acid, rutin and isoquercetin, equations including the temperature's coefficients result in a stronger model. An increase of temperature improves the solubility of phenolic compounds and thus their diffusion from the plant matrix to the solvent (Muhamad et al., 2014). However, a temperature too high may result in compounds degradation and lower recovery. This phenomenon is not observed in the tested conditions. The extraction duration chosen in this work, 35 min, is indeed quite short. Such extraction period is thus not long enough to observe phenolic compound degradation even at the higher temperatures tested. Only prunin is affected by the quadratic term of temperature (X_2^2), indicating a potential degradation of this molecule to a small measure that is not noticeable on the responses' values (table A5).

The interaction between the factors ($X_1 \cdot X_2$) has a significant positive impact on naringenin recovery. The best yields are obtained at highest temperatures and ethanol concentrations. The ethanol-temperature interaction does not have such effect on the other responses.

The effect of ethanol concentration and temperature described above can be observed on the response surfaces presented in figure A.2.

All extraction yields, except that of naringenin, follow the same trend as the ethanol concentration changes in the solvent. As shown in table A.6, this factor has a great impact on the recovery of phenolic compounds, with an optimal concentration around 50%. Naringenin extraction benefits most from higher ethanol concentrations in the solvent, especially at high temperatures. Temperature has a lower impact than the ethanol concentration on the recovery of phenolic compounds. The maximum values of extraction yields were obtained for temperatures above 70-75 °C. As the extraction temperature is limited to 90 °C in this work, studying the effect of temperatures superior to 90 °C could be interesting to possibly reach higher recovery in phenolic compounds.

3.2.2. Validation of the prediction models

The optimal extraction conditions were determined with MODDE software to recover efficiently the phenolic compounds from nectarine tree branches. All the phenolic compounds, except naringenin, have their maximum predicted yield in the same ranges of temperature and ethanol concentration, meaning that they are in close polarity ranges. Furthermore, as mentioned before, the G/A ratio is not affected by the variables. A selection of glycosylated or aglycone phenolic compounds during the extraction is thus not possible. For this reason, the chosen scenario for optimizing the extraction conditions is the maximisation of all the phenolic compounds. A separation step will be performed in the following sections to attempt the fractionation of the glycosylated and aglycone phenolic compounds. The MODDE optimizer tool was used to define the optimum conditions, an ethanol concentration of 55% v/v and an extraction temperature of 90 °C. To validate the design of experiments, these extraction conditions were applied on nectarine tree branches to compare the observed and predicted values (table 1). The observed values are 9.05 ± 0.80 mg/g_{DM} of catechin, 3.17 ± 0.31 mg/g_{DM} of chlorogenic acid, 1.15 ± 0.01 mg/g_{DM} of naringenin, 1.56 ± 0.08 mg/g_{DM} of rutin, 0.57 ± 0.02 mg/g_{DM} of isoquercetin, and 1.73 ± 0.11 mg/g_{DM} of prunin. A solvent composed of 55% ethanol gives the best solubility for most phenolic compounds from nectarine tree branches, and a temperature of 90°C is better to enhance their solubility.

According to a Student's test, the observed catechin, chlorogenic acid, naringenin, rutin and isoquercetin yields are equivalent to the predicted values (p -value > 0.05). Only the extraction yield of the prunin is not correctly predicted by the model. Acquisition of supplementary data would be useful to increase the prediction precision of this model. After the optimisation of the extraction, G/A ratio is 0.276 ± 0.006 . This value is in the range of results obtained in the design of experiments.

3.3. Modelling the extraction kinetic in optimal conditions

The evolution of phenolic compound yields was investigated during the extraction in the optimal conditions (90 °C, 55% EtOH). The kinetics for each phenolic compound are shown in figure 2.

Different kinetic models (Peleg's model, first order model, logarithmic model, 2-sites kinetic model) were used to explain the extraction kinetics of every phenolic compounds. The R^2 and RMSE were used to evaluate the model adequacy. Table A.7 gathers these parameters for each model and each phenolic compound.

A model is assumed to describe properly the kinetic when the calculated R^2 is close to 1 and the RMSE is low. In table A.7, all the tested models lead to a high R^2 and a low RMSE meaning that they give a good description of the extraction of the phenolic compounds from nectarine tree branches. However, the best kinetic description is achieved with the 1st order and the 2-sites kinetic models for the extraction of catechin, chlorogenic acid, naringenin and rutin. The 2-sites kinetic model described better the extraction of isoquercetin and Peleg's model was better for prunin. It should be noted that 1st order kinetic model and 2-sites kinetic model gave very close or equivalent results. As described in Equation 7, the 2-sites kinetic model is composed of two 1st order terms, corresponding to a fast washing of the phenolic compounds from the plant material followed by a slow diffusion. According to (Dias et al., 2017), when the washing does not occur, only the slow diffusion is considered. Equation 7 is simplified and becomes a pseudo 1st order kinetic. An absence of washing step can be thus assumed when 1st order kinetic and 2-sites kinetic models give very close evaluation parameters. For this reason, the 2-sites kinetic model is preferred to describe the extraction of phenolic compounds from nectarine tree branches.

According to figure 2, the extraction of phenolic compounds from nectarine tree branches is fast, 90% of the theoretical equilibrium yield (C_{eq}) is obtained in less than 10 min for all the phenolic compounds except prunin. The extraction kinetic of the latter is slower and 17 min are needed to achieve 90% of C_{eq} . The 2-sites model predicts an equilibrium reached in 12 to 34 min during the ASE extraction for all phenolic compounds except prunin, whose equilibrium yield is expected to be reached in 64 min. The observed values of C_{eq} reach the predicted C_{eq} after 35 min of extraction for each phenolic compound.

3.4. Selective recovery of glycosylated phenolic compounds by adsorption

As we have shown, the phenolic compounds from nectarine tree branches are successfully extracted but the extraction is not selective towards glycosylated or aglycone components. By the implementation of adsorption technology, the following step focuses on increasing the G/A ratio. Prior adsorption, the extract solvent was evaporated, and the extract was dissolved in water to decrease the solubility of the target molecules in the extract and increase their affinity with the resin. There is indeed a competition between the two phenomena (Kammerer, Kammerer, Jensen, et al., 2010; Silva et al., 2007). A selection is performed among 3 resins available in the laboratory. The concentration of ethanol in the desorption solvent was then studied on the most satisfying resin.

3.4.1. Screening of resins

An adsorption process has been used to separate glycosylated and aglycone phenolic compounds from the aqueous extract concentrate (AEC). Macroporous resins XAD-4, XAD-7 and XAD-16 have been screened to find the most suitable one. Adsorption, desorption and recovery rate of each phenolic compound were calculated with equations 8, 9, 11, and are given in figure 3 (A, B, C).

The material, pore size and surface area of a given resin affect the molecules' affinity and result in different adsorption rates, as it can be observed with phenolic compounds from nectarine tree branches after 120 min in contact with the 3 resins (Conde et al., 2013; dos Santos et al., 2022). Chlorogenic acid is the component with the lowest adsorption rate on all resins ($\leq 33\%$) while naringenin has a good affinity with resins XAD-7 ($96 \pm 2\%$) and 16 ($94 \pm 2\%$) and is one of the best adsorbed molecules with XAD-4 ($51 \pm 3\%$). In general, XAD-7 offers the best adsorption rates except for chlorogenic acid that is better adsorbed with XAD-16. On the opposite, XAD-4 has a poor performance, with low adsorption of phenolic compounds compared to the other resins. XAD-7, made of acrylic resin, is more polar than XAD-4 and

XAD-16, composed of styrenedivinylbenzene, and has higher affinity with glycosylated compounds. However, XAD-16 allows a good adsorption of these molecules as well. A reason for this observation could be the higher pore size of XAD-16 (100 Å) compared to XAD-4 (50 Å) as shown in table A.2, inducing a better penetration of the molecules into the resin. The larger molecules, such as glycosylated phenolic compounds, might also have more chance to be adsorbed. A similar observation was made by *Um et al.* (2017), who compared XAD-4 and XAD-16 during the adsorption of phenolic compounds from yellow poplar hydrolysate (Um et al., 2017).

Furthermore, the average adsorption rate is higher for glycosylated than for aglycone compounds with XAD-7 and 16. However, glycosylated molecules should have a higher solubility in water than the aglycone ones, resulting in a lower affinity with the resins. Indeed, hydrophobicity is important to induce the adsorption, but this parameter does not seem to predominate. This phenomenon has already been described before (Kammerer, Kammerer, & Carle, 2010; Kammerer, Kammerer, Jensen, et al., 2010; Pompeu et al., 2010). Other interactions, such as hydrogen bounds, might explain the higher binding of glycosylated phenolic compounds. In particular, the low adsorption rate of chlorogenic acid can be explained by the pH of AEC. The pKa of this phenolic acid has been estimated at 3.95 ± 0.50 by Kammerer et al. (2010) and is lower than the pH of AEC (4.85 ± 0.14). Indeed, chlorogenic acid was better adsorbed at pH = 1-3, where the neutral form of the molecule predominates (Kammerer, Kammerer, & Carle, 2010; Rodriguez-Lopez et al., 2021; Soto et al., 2011). The pH might have a lower effect on other target phenolic compounds that does not display carboxylic acid moiety. The higher pKa of flavonoids makes it possible to operate in a wider pH range (Kühn et al., 2014). For example, the pKa of rutin and catechin have been estimated at 6.84 ± 0.60 and 9.54 ± 0.10 , respectively (Kammerer, Kammerer, & Carle, 2010). It should be noted that, probably because they are more hydrophilic, rutin (being described as an isoquercetin with a rhamnose) and prunin (as a naringenin with a glucose) exhibit lower adsorption rates than isoquercetin and naringenin, respectively. Other compounds from the AEC might also affect the adsorption, however they are not studied here. For example, the adsorption of phenolic compounds is influenced by the presence of sugars or amino acids (Kammerer, Kammerer, & Carle, 2010).

The phenolic compounds from the 3 resins have good desorption rates for glycosylated molecules (> 80%) and variable desorption performances for aglycones. Glycosylated compounds have a greater affinity with the eluent than their aglycone or mono-glycosylated homologs, but this affinity is not the only factor affecting the rate of desorption. Indeed, the small molecules could have diffused into the smallest pores of the resin and they would be less accessible during desorption (Ferri et al., 2011; Kinoshita et al., 2015). However, prunin shows a better desorption rate than its aglycone (naringenin) with all the resins, while rutin has a better desorption than isoquercetin with XAD-4 and XAD-16 and an equivalent value with XAD-7. Thus, the polarity of phenolic compounds is the predominant factor in explaining the results observed during the desorption.

The recovery rate results from the combined efficiency of the adsorption and desorption steps. The XAD-7 and XAD-16 resins exhibit a recovery of aglycone phenolic compounds ranging from 9 to 69% while that of glycosylated compounds can reach 84%. XAD-4 resin offers less than 50% of recovery rate for each phenolic compound. The aglycone phenolic compounds are less recovered under the tested conditions.

The evolution of the G/A ratio at the different steps of the adsorption process is presented figure 3 (D).

The G/A ratio of AEC before the adsorption is 0.304 ± 0.022 . After the adsorption step, the G/A ratio on XAD-7 and XAD-16 resins increased significantly to 0.483 ± 0.077 and 0.522 ± 0.016 , respectively. Since both values are significantly different from G/A ratio in AEC, the adsorption is considered to be selective for glycosylated phenolic compounds. This result can be explained by the good binding of these molecules due to hydrogen bonds, and on the lower adsorption of aglycones, especially chlorogenic acid. On the contrary, XAD-4 resin has a G/A ratio similar to AEC (0.288 ± 0.030) because the phenolic compounds have similar adsorption rates. The desorption rates with this resin are also quite close, resulting in a slight but not significant increase in the G/A ratio after elution. Concerning the XAD-7 and XAD-16 resins, the G/A ratios increase after the desorption going from 0.483 ± 0.077 and 0.522 ± 0.016 after the adsorption step to 0.678 ± 0.028 and 0.544 ± 0.020 after desorption, respectively. In addition, XAD-7 has very good recovery rates of phenolic compounds and the best increase in G/A ratio. This increase is significant, showing a selective desorption of glycosylated phenolic compounds. The use of XAD-7 resins allows to increase the selectivity of the purification process with respect to glycosylated phenolic compounds. This resin was thus selected to study the adsorption kinetics and the desorption solution in the following chapters.

3.4.2. Modelling of adsorption kinetics

Pseudo 1st and pseudo 2nd order models are empirical models that consider adsorption as a pseudo chemical reaction. They are frequently used to describe the adsorption kinetics and are employed to fit the adsorption kinetic of each phenolic compound obtained from nectarine tree branches with XAD-7 resin (dos Santos et al., 2022; Soto et al., 2011). The R^2 and RSME parameters were used to assess the model adequacy; they are presented in table A.8 as well as the equilibrium adsorption capacities and the adsorption rate constants.

The pseudo 2nd order model provides the best fit to the adsorption kinetics of all phenolic compounds. The R^2 and RMSE parameters are indeed more satisfactory with this model. For this reason, the adsorption kinetics of phenolic compounds from nectarine tree branches were modelled with the pseudo 2nd order equation (figure 4).

The adsorption of aglycone phenolic compounds is very fast (figure 4 A, B, C). Indeed, the XAD-7 resin reaches 90% of its equilibrium adsorption capacity in less than 20 min. Concerning glycosylated phenolic compounds, 90% are reached in 27 to 107 min. The adsorption kinetics of hydrophobic compounds has already been described and seems to indicate a weaker competition between the aqueous extract and the resin, which would explain why the adsorption of aglycone compounds is fast (Campone et al., 2020). It should be noted that the adsorption of chlorogenic acid is instantaneous with a low rate (table A.8). As explained above, the ionic form of this component is predominant under the working pH, which induces a high solubility in water, and thus a lower affinity with the resin. The predicted equilibrium adsorption capacities are reached at very long times (more than 100 h), however, 120 min is a satisfactory duration for obtaining an efficient adsorption of the phenolic compounds.

3.4.3. Effect of the elution solvent

Hydroalcoholic solutions have been widely used to elute phenolic compounds from resins (dos Santos et al., 2022; Soto et al., 2011). Different concentrations of ethanol in water (30 to 90%, v/v) were tested during the desorption step with XAD-7 resin. Indeed, the 6 phenolic compounds could have different affinities according to the ethanol concentration and induce a change of the G/A ratio. The desorption rates of each phenolic compound and the G/A ratio are given, in figure 5, for all the eluent solutions.

The desorption rate increases with higher ethanol concentrations up to 70% and then decreases for catechin, chlorogenic acid, isoquercetin and prunin. A higher ethanol

concentration (90%) is needed to solubilize efficiently naringenin during the elution. In the case of rutin, 50, 70 and 90% ethanol give the same desorption performance. All phenolic compounds are desorbed with the lowest ethanol concentration, a partition of the molecules with different eluents is thus not possible. It has been demonstrated that phenolic compounds can be desorbed from acrylic resins with high quantity of water which is in accordance with the results of this study (Tomás-Barberán et al., 1992).

The G/A ratio after an elution with 30% ethanol is 0.361 ± 0.017 , which represents a significant decrease compared to the value obtained after the adsorption step. Eluents composed of 50 to 90% ethanol desorb glycosylated compounds at a higher rate compared to the aglycone ones which results in higher G/A ratios. The elution with 70% ethanol offers the highest G/A ratio, meaning that the glycosylated phenolic compounds are well recovered while some of the aglycone compounds component remains on the resin after desorption. Some authors have already showed the best elution of phenolic compounds with 70% ethanol among mixtures of ethanol in water ranging from 0% to 95% ethanol (Campone et al., 2020; Jiao et al., 2017). This eluent composition is therefore the best solvent for an efficient recovery and separation of phenolic compounds from AEC.

4. Conclusion

The selective recovery of phenolic compounds from nectarine tree branches has been studied. A preliminary extract allowed the identification of 13 phenolic compounds including 6 major ones. Some components were identified for the first time in this work. The 6 main phenolic compounds were tracked during the extraction and purification. The extraction process is efficient, however there is no selectivity towards glycosylated or aglycone components. An adsorption process was thus applied to the extract and XAD-7 was found to be the best resin to separate them with an elution with 70% ethanol. After the purification process, the G/A ratio increased significantly from 0.304 ± 0.022 in AEC to 0.678 ± 0.028 in the eluent. The glycosylated phenolic compounds are well recovered while a part of the aglycone component (mainly chlorogenic acid) was lost during the adsorption step. The extraction and adsorption kinetics were successfully modelled by the 2-sites and pseudo 2nd order models respectively. An extraction step followed by adsorption is thus an efficient and scalable process to selectively recover a fraction of glycosylated phenolic compounds from nectarine tree branches. A deeper study on purification by adsorption would be necessary to observe the results in dynamic mode and determine the isotherms of adsorption, thus allowing the determination of the adsorption mechanism of each phenolic compound.

Authors contributions

Emilie ISIDORE: investigation, statistical and HPLC analyses, writing-original draft. Gaëlle WILLIG: investigation. Fanny BRUNISSEN: LC-MS analyses, development of HPLC analyses. Christian MAGRO: resources, writing-review and editing. Charles MONTEUX: resources, writing-review and editing. Irina IOANNOU: conceptualization, supervision, writing-review and editing.

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729 *Figure 1: Chemical structure of the 6 main phenolic compounds found in nectarine tree*
730 *branches.*

731

732 *Figure 2: Extraction kinetics of the different phenolic compounds (55% ethanol – 90 °C – 35*
733 *min). A: catechin. B: chlorogenic acid. C: naringenin. D: rutin. E: isoquercetin. F: prunin.*
734 *Dashed lines correspond to the models while dots are the observed values.*

735

736 *Figure 3: Comparison of macroporous resins performances. A: Adsorption rates. B: Desorption*
737 *rates. C: Recovery rates. For a given phenolic compound, values with different letters mean a*
738 *significant difference ($p < 0.05$). D: G/A ratio at different adsorption steps. For each step,*
739 *different letters mean a significant difference in the values ($p < 0.05$).*

740

741 *Figure 4: Adsorption kinetic of phenolic compounds from nectarine tree branches with XAD-7*
742 *resin (2h – room temperature). A: catechin. B: chlorogenic acid. C: naringenin. D: rutin. E:*
743 *isoquercetin. F: prunin. Dashed lines correspond to the models while dots are the observed*
744 *values.*

745

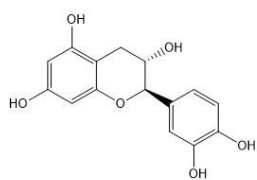
746 *Figure 5: Desorption rate of phenolic compounds from nectarine tree branches using different*
747 *eluent solutions (XAD-7 – 2h adsorption – room temperature – 2h desorption). For a given*
748 *phenolic compound, different letters mean a significant difference in the values ($p < 0.05$).*

749

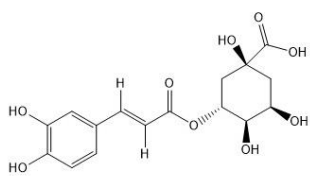
750 *Table 1: Experimental validation of the prediction models of the phenolic compounds'*
751 *extraction yield.*

752

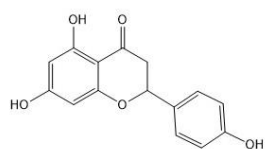
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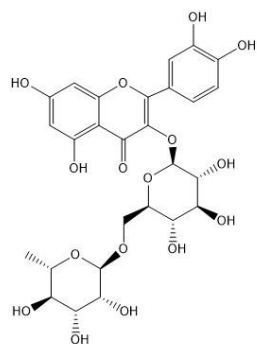
Catechin



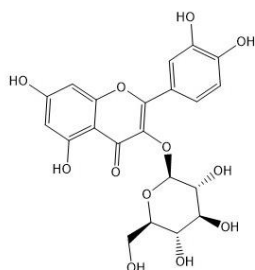
Chlorogenic acid



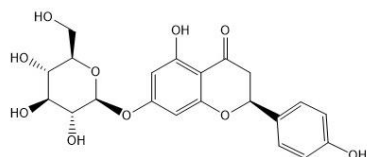
Naringenin



Rutin



Isoquercetin



Prunin

Figure 1

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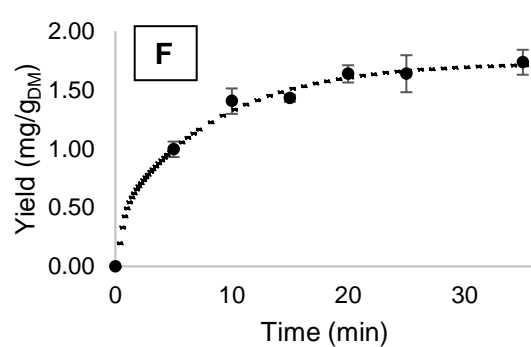
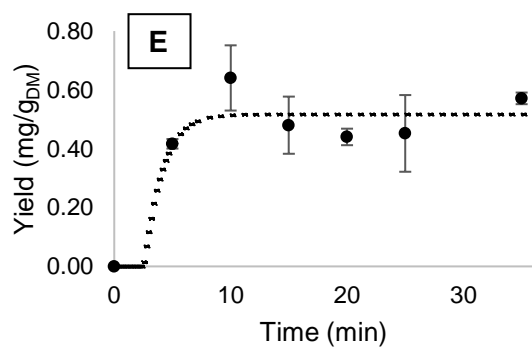
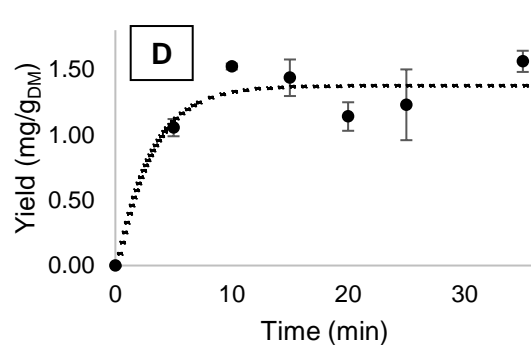
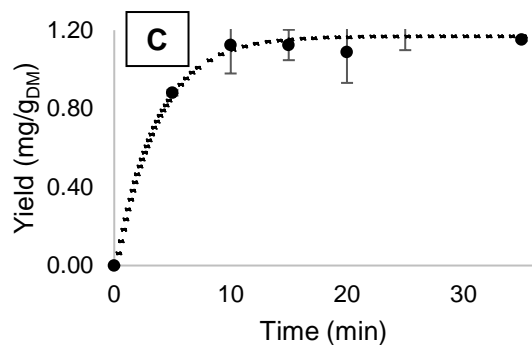
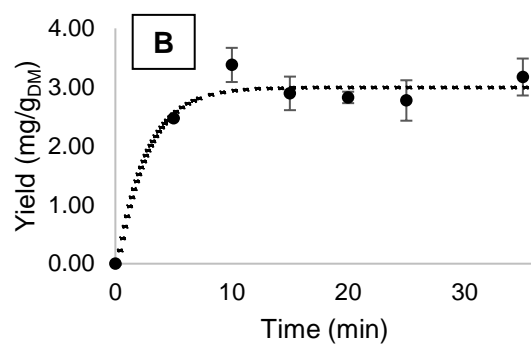
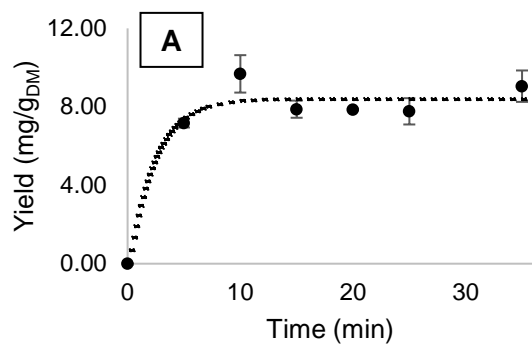
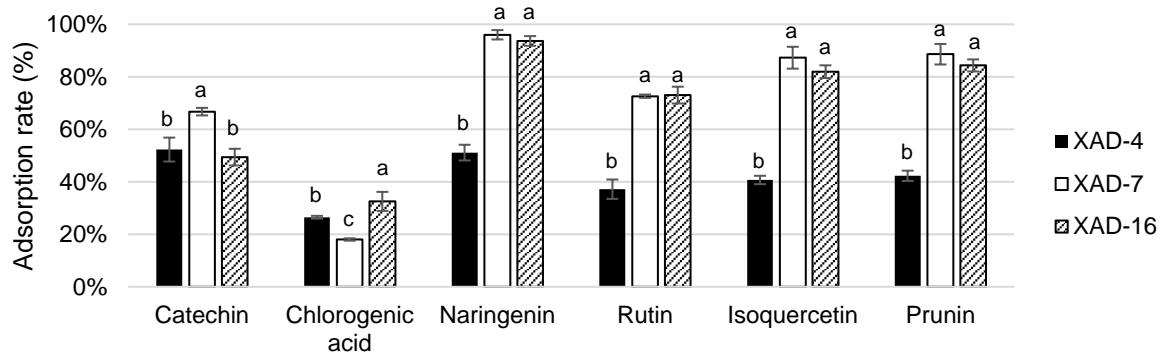
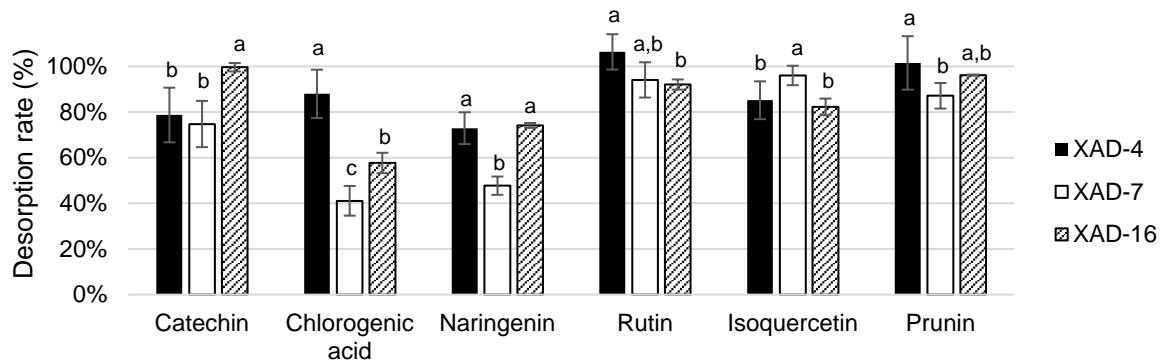


Figure 2

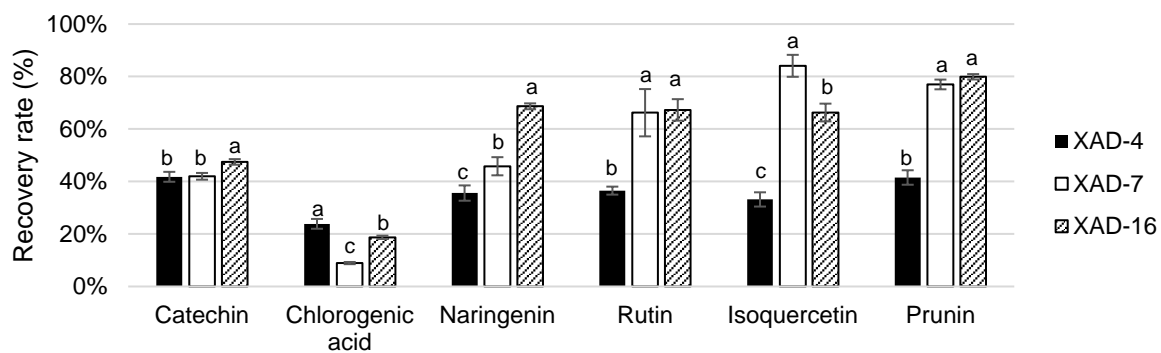
A



B



C



D

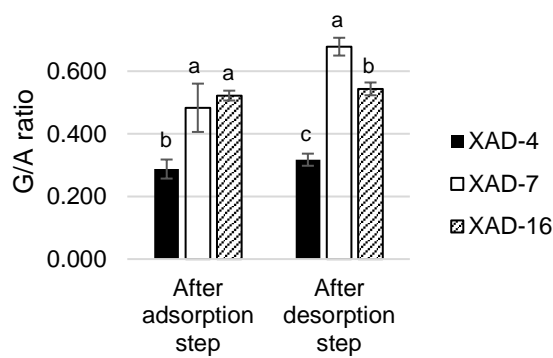


Figure 3

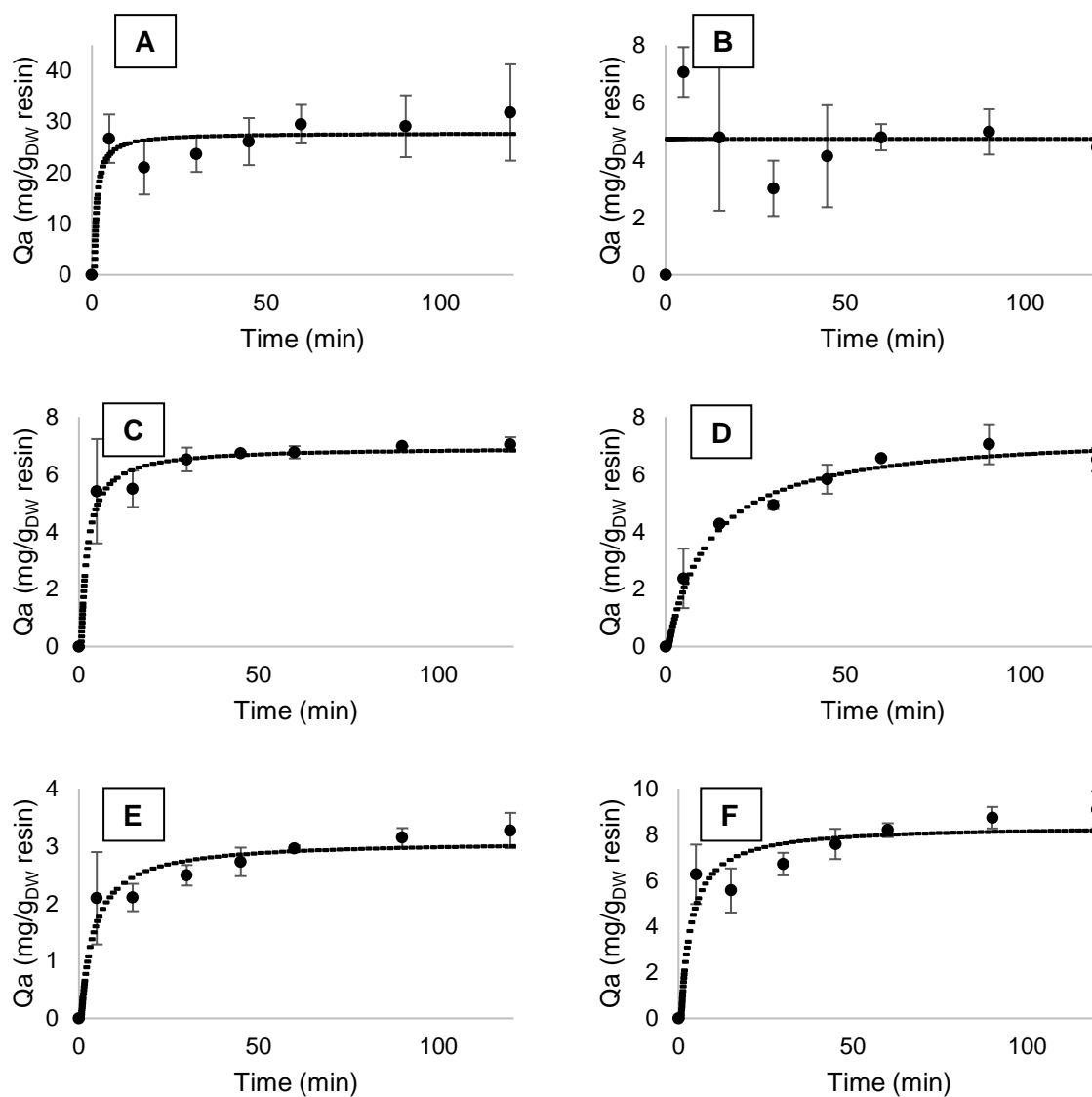


Figure 4

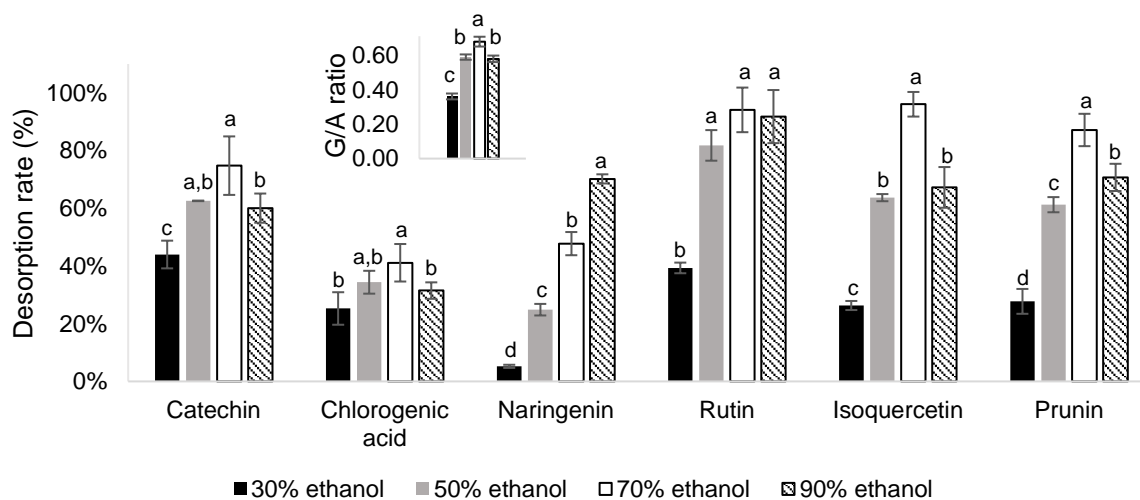


Figure 5

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Table 1

	Catechin (mg/g _{DM})	Chlorogenic acid (mg/g _{DM})	Naringenin (mg/g _{DM})	Rutin (mg/g _{DM})	Isoquercetin (mg/g _{DM})	Prunin (mg/g _{DM})
Predicted values	8.01 ± 0.61	3.15 ± 0.38	1.02 ± 0.06	1.35 ± 0.20	0.58 ± 0.06	1.13 ± 0.02
Observed values	9.05 ± 0.80	3.17 ± 0.31	1.15 ± 0.01	1.56 ± 0.08	0.57 ± 0.02	1.73 ± 0.11
p-value	0.15	0.93	0.14	0.30	0.83	0.01

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