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# **Green extraction of polyphenols from grapefruit peels using high voltage electrical discharges, deep eutectic solvents and aqueous glycerol**

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## Abstract

Deep eutectic solvents (DES) and aqueous glycerol were proposed as green alternatives to conventional solvents for the extraction of polyphenols from grapefruit peels. In order to increase the extraction kinetics and yields of polyphenols, high voltage electrical discharges (HVED) were used as a pre-treatment technology (energy varied between 7.27 and 218 kJ/kg). Results showed that the HVED energy input can be reduced, when the subsequent solid-liquid extraction was performed in 20% (w/v) aqueous glycerol or in DES (lactic acid: glucose) instead of water. The addition of glycerol has reduced the energy of the pre-treatment by 6 times. The same diffusivity of polyphenols ( $4 \times 10^{-11} \text{ m}^2/\text{s}$ ) was obtained in water from HVED pre-treated peels at 218 kJ/kg and in aqueous glycerol from pre-treated peels at 36 kJ/kg. The solubility of naringin, the main flavonoid compound of grapefruit peels in the solvents, was investigated through a theoretical modelling of its Hansen solubility parameters.

**Keywords:** High Voltage Electrical Discharges, Green Extraction, Deep Eutectic Solvents, Aqueous Glycerol, Polyphenols, Grapefruit peels

## 1. Introduction

Grapefruits are among the most important citrus crops. They are highly appreciated by the consumers, for containing many nutrients and phytochemicals that contribute to a healthy diet. They are consumed by both fresh market and for processing (Zheng, Zhang, Quan, Zheng, & Xi, 2016). The processing of grapefruits results in juice that accounts for about half of the fruit weight, and the rest are by-products consisting of peels, seeds and pulps (Wilkins, Widmer, Grohmann, & Cameron, 2007). Peels remain as the primary by-product and are a rich source of natural antioxidants (Ahmad & Langrish, 2012). Polyphenols have attracted much attention due to their use in food industries to prevent the rancidity and oxidation of lipids. They are also beneficial against many diseases related to the oxidative stress such as cancer (Hajj, Debs, Nguyen, Maroun, & Louka, 2013; Khan, Abert-Vian, Fabiano-Tixier, Dangles, & Chemat, 2010).

Among the polyphenols present in grapefruit peels, naringin is the most abundant flavonoid. It has many pharmacological activities. It is also used as a food additive to treat obesity and diabetes (Liu, Qiao, Gu, Yang, & Yang, 2017; Raafat et al., 2018). Therefore, it is advantageous to extract polyphenols and specifically naringin from grapefruit peels.

Conventional extraction techniques are usually associated with long extraction times, important amount of organic solvent consumption and the possible thermal degradation of polyphenols (Azmir et al., 2013). Most organic solvents are flammable, volatile, explosive, toxic and are responsible for environmental pollution and the greenhouse effect (Chemat, Vian, & Cravotto, 2012). Therefore, they are incompatible with the principle of the “green” extraction process, and their elimination from the extracts is mandatory. The development of green solvents with low toxicity and cost, as alternatives to hazardous organic solvents has been receiving increasing attention.

Deep eutectic solvents (DES) are promising alternatives to traditional organic solvents. They are mixtures of natural, renewable, readily available and non-toxic components (Cunha & Fernandes, 2018). The preparation of DES is easy and cheap. It consists in mixing a hydrogen bond acceptor (e.g. choline-chloride) with a hydrogen bond donor (natural plant-based organic ions, such as amino acids, carboxylic acids, sugars). The components associate by hydrogen bonding to form an eutectic mixture, that has a lower melting point than that of each individual component. DES are liquid at low temperatures, miscible with water, non-flammable and highly viscous (Bajkacz & Adamek, 2017; Bakirtzi, Triantafyllidou, & Makris, 2016; Dai, Verpoorte, & Choi, 2014; García, Rodríguez-Juan, Rodríguez-Gutiérrez, Rios, & Fernández-Bolaños, 2016). DES have been recently used in many applications such as the stabilization of natural pigments (Dai et al., 2014), and the delignification (Malaeké, Housaindokht, Monhemi, & Izadyar, 2018). Also, there is a number of studies on the extraction of bioactive compounds including rutin (Huang et al., 2017), isoflavones (Bajkacz & Adamek, 2017) and flavonoids (Bakirtzi et al., 2016) with DES.

Glycerol is a non-toxic and inexpensive substance that occurs naturally in foods. It can be used as an efficient co-solvent to change the polarity of water, increasing thus, the recovery of polyphenols (Karakashov, Grigorakis, Loupassaki, & Makris, 2015).

Pre-treatments are generally applied to enhance the extraction kinetics and yields during the subsequent solid-liquid extraction. Among the non-conventional pre-treatment methods, high voltage electrical discharges (HVED) have been applied to improve the extraction of biomolecules (Gros, Lanoisellé, & Vorobiev, 2003; Rajha, Boussetta, Louka, Maroun, & Vorobiev, 2015). This technology is based on the electrical breakdown in water. When an electric field is applied, an avalanche of electrons called streamer is created. When the electric field is intense, the streamer propagates from the positive to the negative electrode, and an electrical breakdown in water occurs.

The electrical breakdown is accompanied by a number of secondary phenomena (high amplitude shock waves, bubbles cavitation, turbulence of liquid) that cause particle fragmentation and cell damage (Boussetta, Lesaint, & Vorobiev, 2013).

To the best of our knowledge, there is still no report on the evaluation of the potential and effectiveness of DES and glycerol for the extraction of polyphenols from citrus peels. This work is devoted to study the effect of HVED pre-treatment on the subsequent solid-liquid extraction of polyphenols from grapefruit peels, with green solvents. The main objective is to find alternative green solvents for the extraction of polyphenols from grapefruit peels.

## **2.Materials and Methods**

### **2.1.Citrus peels**

Grapefruits were purchased at a local supermarket (Compiègne, France) and stocked at 4°C. Those without any damage were washed and peeled. Fresh peels were cut into squares of 1 cm<sup>2</sup> and stored at 4°C until use. The dry matter content, measured by drying 20 g of fresh orange peels at 100°C to constant weight, was 25 wt%.

### **2.2. Preparation of the deep eutectic solvents**

DES with choline-chloride and lactic acid as hydrogen bond donors, were used in this study. The synthesis of all DES was based on previously reported methodologies (Bubalo, Čurko, Tomašević, Kovačević Ganić, & Radojic Redovnikovic, 2016). Choline-chloride (hydrogen bond donor) was mixed with lactic acid and tartaric acid. Lactic acid (hydrogen bond donor) was mixed with sodium acetate, ammonium acetate, glucose and glycine. Components were directly weighed at predetermined molar ratios (Supplementary Table 1) and the mixtures were heated at 80°C for 2 to 6 h under stirring, until a perfectly transparent liquid was formed. Incorporation of 30% water

was necessary to reduce the viscosity of the DES and facilitate polyphenols diffusion. DES were kept in sealed glass flasks in the dark, at ambient temperature. The codes of the DES used in this study are given in the Supplementary Table 1.

Water and 50% (v/v) ethanol/water were used for comparison. Preliminary experiments showed that ethanol concentration of 50% is optimal for the extraction of polyphenols from grapefruit peels. At concentrations higher than 50% the polyphenol yields decreased. Therefore, an intermediate (optimal) solvent polarity, can give the highest polyphenol extraction.

### 2.3. Extraction experiments

The general scheme of experiments is shown in the supplementary Figure 1. After the selection of the most efficient solvents, fresh grapefruit peels were pretreated with HVED, in water at different number of pulses. After HVED pre-treatment, the solvents were added to the solution (pre-treated peels + water) for the subsequent solid-liquid extraction.

#### 2.3.1. High voltage electrical discharges pre-treatment

Fresh grapefruit peels (20 g) and water (180 mL) were introduced in a Teflon cylindrical treatment chamber (Innovaltech, Saint Quentin) between two electrodes: needle ( $d = 10$  mm) and plane ( $d = 35$  mm). The distance between the electrodes was 5 mm. The treatment chamber was connected to a generator that provided the maximum voltage  $U$  of 40 kV and current of 10 kA. Pulses had a frequency of 0.5 Hz and an average energy of 160 J/pulse. In this study, the number of pulses  $n$  was varied between 10 and 300. The HVED energy input  $W_{HVED}$ , varied between 7.27-218 kJ/kg, was calculated as shown in Eq. (1):

$$W_{HVED} = \frac{W_i \times n}{m} \quad (1)$$

where  $W_i$  is the energy per pulse (kJ/pulse),  $n$  is the number of pulses, and  $m$  is the mass of the suspension (kg).

### 2.3.2. Solid-liquid extraction

For the experiments without HVED pre-treatment, the solid-liquid extraction was conducted in water, 50% (v/v) ethanol/water or in the prepared DES. The liquid to solid ratio was 10, and the extraction was conducted at 50°C for 60 min, under stirring at 160 rpm. For the experiments with HVED, the diffusion was conducted in water, aqueous glycerol (10, 20 and 30% (w/v) glycerol/water) or with the most efficient DES (lactic acid: glucose). HVED pre-treatment was carried in water, then DES or glycerol were added at the beginning of the diffusion process. The final liquid to solid ratio was 10. Following extraction, samples were filtered and the extracts were submitted to further analysis.

## 2.4. Analysis

### 2.4.1. Polyphenols extraction index $Z_p$

In order to evaluate the efficiency of the HVED pre-treatment, the normalized polyphenol content was calculated as follows:

$$Z_p = \frac{[C] - [C_i]}{[C_{max}] - [C_i]} \quad (2)$$

Where  $C$  is the polyphenol concentration after the HVED,  $C_i$  is the polyphenol concentration in the extraction medium without HVED pre-treatment (fresh intact peels) and  $C_{max}$  is the maximal value of polyphenol concentration obtained from milled peels without HVED pre-treatment.

### 2.4.2. Total polyphenol content

The amount of total polyphenol content in the extracts was determined through the reducing capacity of the Folin-Ciocalteu reagent (Singleton, Orthofer, & Lamuela-Raventós, 1998). The extract (0.2 mL) was mixed with 1 mL of ten-fold diluted Folin–Ciocalteu reagent (Merck, Darmstadt, Germany). Then 0.8 mL of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) (75 g/L) (Prolabo, Fontenay-sous-Bois, France) was added. The mixture was incubated at 60°C for 10 min. After cooling at



room temperature, the absorbance was measured at 750 nm by the UV-Vis spectrophotometer (Thermo Spectronic Genesys 20, Thermo Electron Corporation, MA, USA). Gallic acid (Sigma-Aldrich, St-Quentin Fallavier, France) was used for the calibration curve. The results were expressed as g of Gallic acid equivalent (GAE) per 100 gram of dry matter (g GAE/100 g DM).

#### 2.4.3. High performance liquid chromatography analysis

High performance liquid chromatography (HPLC) was used to identify the phenolic compounds extracted from grapefruit peels. Ultimate 3000 (Dionex, Idtsein, Germany) liquid chromatography apparatus coupled to a diode array detector was used. The chromatography column C18 capillary column 100 × 4.6 mm (Hypersil Gold, Thermo Scientific, USA), was used for all experiments. The temperature of the column was maintained at 30°C. 0.1% trifluoroacetic acid (solvent A), 3% acetonitrile (solvent B) (HPLC grade, Sigma-Aldrich, St-Quentin Fallavier, France) and 97% water were used as solvents. A flow rate of 1.250 mL/min was applied. The elution profile of solvent B was as follows: 10 min, 2% ; 25 min, 6% ; 40 min, 15% ; 52 min, 20% ; 70 min, 40%. The injection volume of the sample was 100 µL. Chromatograms were recorded using the photodiode array detector at 280 nm. The flavonoid was identified according to its retention time in comparison to the commercial standard. Naringin (Sigma-Aldrich, St-Quentin Fallavier, France) was used as standard. It was solubilized in 50% ethanol-water. Extracts were also diluted in 50% ethanol-water. Prior to analyses, samples and standards were filtered through 0.2 µm syringe filters (VWR, France). The external standard method was used for quantification. A linear regression of the peak area vs. concentration (0.03 to 1 mg/mL) was used and the final concentrations were expressed in g per 100 g dry matter (g/100 g DM).

#### 2.4.4. Diffusion coefficients

The diffusivity of polyphenols was studied using Fick's second law (Crank, 1975).

The geometry of orange peels was considered as plane for the experiments without and with HVED pre-treatment.

The diffusion in a plane sheet, with agitation, in a limited volume follows the following formula (Crank, 1975):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(\alpha+1)\exp(-Dq_n^2 t/l^2)}{1+\alpha+q_n^2 \alpha^2} \quad (3)$$

Where  $M_t$  is the polyphenol concentration in the extract after time  $t$ ,  $M_\infty$  is the maximal concentration of polyphenol after an infinite time,  $\alpha$  is the liquid-solid ratio (10),  $D$  is the coefficient of diffusion ( $\text{m}^2/\text{s}$ ),  $l$  is the thickness of the particles,  $n=5$ ,  $q_1=1.5708$ ,  $q_2=4.7124$ ,  $q_3=7.854$ ,  $q_4=10.9956$  and  $q_5=14.1372$ .

#### 2.4.5. Hansen solubility parameters

The Hansen solubility parameter is divided into 3 components:  $\delta_d$  for dispersion (van der Waals),  $\delta_p$  for polarity and  $\delta_h$  for hydrogen bonding. For naringin and solvents, Hansen's solubility parameters are calculated using the method of Hoftyzer and Krevelen (Van Krevelen & Nijenhuis, 2009):

$$\delta_d = \Sigma F_{di} / V \quad (5)$$

$$\delta_p = \sqrt{\Sigma F_{pi}^2} / V \quad (6)$$

$$\delta_h = \sqrt{\Sigma E_{hi}} / V \quad (7)$$

Where  $F_{di}$  and  $F_{pi}$  are the group contributions to the dispersion and polar components per structural group to the molar attraction constant,  $E_{hi}$  is the hydrogen bonding energy per structural group, and  $V$  is the molar volume of the molecule. The numerical values of  $F_{di}$ ,  $F_{pi}$ , and  $E_{hi}$  of common structural groups are taken from the literature (Van Krevelen & Nijenhuis, 2009).

The calculated solubility parameters can be placed on three axes x, y, and z ( $\delta_d$ ,  $\delta_p$ , and  $\delta_h$ ). A sphere can then be plotted. The center of the sphere corresponds to the solubility parameters of naringin. The radius of the sphere is determined experimentally by testing the solubility of naringin in different solvents. Effective and suitable solvents for solubilization of naringin are those within the sphere. Solvents that are not appropriate for the solubilization of naringin will therefore be outside the sphere. The sphere is drawn using the Matlab 2015b program. The distance  $R_i$  between the naringin (center of the sphere) and every solvent is calculated as follows (Li, Fabiano-Tixier, Ginies, & Chemat, 2014):

$$R_i^2 = 4 [\delta_d(A) - \delta_d(B)]^2 + [(\delta_p(A) - \delta_p(B))]^2 + [(\delta_h(A) - \delta_h(B))]^2 \quad (8)$$

Where  $A$  refers to the solute (naringin) and  $B$  to the solvent.

## 2.5. Statistical analysis

All experiments and measurements were repeated at least three times. One-way analysis of variance (ANOVA) was used for statistical analysis of the data using SPSS (Statistical Package for the Social Sciences) version 24.0. ANOVA is a parametric statistical test, used to compare three or more mean values, in order to check if the differences are significant (Granato, de Araújo Calado, & Jarvis, 2014). In order to specify exactly the pairs of means that differ statistically, the post hoc Fisher's Least Significant Difference (LSD) was conducted for all the analysis. For each analysis, significance level of 5% was assumed. The error bars presented on the figures correspond to the standard deviations.

### 3. Results and discussions

#### 3.1. Solid-liquid extraction in green solvents

Figure 2 shows the relative total polyphenols increase  $C/C_0$  as a function of the solvent nature. According to the LSD test, only DES-6 (Lactic acid: glucose) and 20% (w/v) aqueous glycerol significantly improved the extraction of polyphenols up to 1.3 and 1.4 times, respectively, in comparison with water. The efficiency of DES for the recovery of polyphenols was previously reported in the literature. For example, DES containing choline-chloride and oxalic acid allowed 5 and 2-fold higher extraction of anthocyanin from grape peels, than water and methanol, respectively (Bubalo et al., 2016). The concentration of herein extracted from Greek medicinal plants with a DES containing lactic acid, glycine and water, was 1.7 times higher than that achieved with 80% ethanol (Bakirtzi et al., 2016). DES have the capacity to donate and accept protons and electrons, which allows the formation of hydrogen bonds between the polyphenols and the DES molecules, thus enhancing their dissolution capacity (Radošević et al., 2016; Shishov, Bulatov, Locatelli, Carradori, & Andruch, 2017). No statistical difference was obtained between DES-1 to 5. Their efficiency was similar to ethanol. The polarity of these DES may be close to that of ethanol. Note that the polarity of DES may be affected by the addition of water. So the solubilizing capacity of the same DES can increase by varying the percentage of water according to the target compounds. For example, rutin was more soluble in choline chloride: glucose with 5% water, but carthamin showed the highest solubility in the same DES with 10% water (Dai, van Spronsen, Witkamp, Verpoorte, & Choi, 2013). In this study, the percentage of water that must be added to DES has not been optimised and the extraction conditions were adjusted by adding 30% of water (Bajkacz & Adamek, 2017). It has been shown that low water concentrations (10-15%) can decrease the extraction efficiency because of the high viscosity of the DES. Also high water

concentrations (40-75%), can limit the interactions between DES and the target compounds by affecting the hydrogen bonding interactions (García et al., 2016).

Previous studies also showed the efficiency of using glycerol as a co-solvent to improve the extraction of bioactive compounds. Using 10% glycerol in water increased the yields of polyphenols from the plant *Hypericum perforatum* from 71 mg GAE /g DM (with pure ethanol) to 86 mg GAE /g DM. Glycerol can change the dielectric constant of water. The polarity of the medium would therefore be modified, which can improve the extraction of certain bioactive compounds (Karakashov et al., 2015).

### 3.2. Efficiency of the solvents on the extraction of naringin

The HPLC was realised for the extracts obtained from milled grapefruit peels, after the solid-liquid extraction with the conventional solvents (water and 50% (v/v) ethanol/water) and with the proposed green solvents (aqueous glycerol and DES-6), without HVED pre-treatment (results not shown). The analysis revealed that naringin is the major flavonoid in grapefruit peels. Similar chromatograms (Supplementary Figure 3) were obtained for all the extracts, but with different surfaces of the peaks. This result shows that there is no selectivity in the extraction of some polyphenols when using these different solvents. The only difference is the concentration of the extracted polyphenols. Table 2 shows the concentrations of naringin obtained using different solvents and the improvement of naringin extraction compared to water. Aqueous glycerol and DES-6 improved the extraction of naringin by 3 times compared to water, and their effectiveness is approximately similar to that of ethanol. Therefore, they allowed a clear improvement in the extraction of naringin compared to water, while the improvement of the extraction of total polyphenols was limited. This shows the selectivity of the proposed solvents for the extraction of naringin. The obtained result is interesting, since naringin molecule has many pharmacological

properties such as hepatoprotective, anti-diabetic and cardioprotective. Naringin has also a therapeutic role in various neurological disorders such as Parkinson disease (Viswanatha, Shylaja, & Moolemath, 2017). Due to the interesting properties of this molecule, many studies aimed to increase the solubility of the naringin such as its complexation with beta-cyclodextrin (Cui, Zhang, Sun, & Jia, 2012).

The solubility of naringin in the proposed solvents is investigated through a theoretical modelling of its Hansen Solubility Parameters (HSP). Figure 4 shows the three dimensional Hansen solubility sphere for naringin in different solvents. The green diamonds in the sphere correspond to the Hansen solubility parameters ( $\delta_d$ ,  $\delta_p$ ,  $\delta_h$ ) of the solvents that were used as references to determine the radius of the sphere ( $R_s=22.1$ ). The solubility of naringin in these solvents was already studied (Zhang et al., 2015). The red squares represent the solubility parameters of the solvents that were used for the extraction of polyphenols. The HSP for solvents and naringin were calculated from their structures according to Hoftyzer and Krevelen method, and their calculated and theoretical values are presented in the supplementary Table 3 (Van Krevelen & Nijenhuis, 2009). They were used in plotting a 3D HSP sphere for theoretical characterization of naringin solubility in each solvent. The diamonds and squares located inside the sphere are generally considered as good solvents and those located outside the sphere have relatively poor capacity to dissolve naringin. The smaller the  $R_i$  is, the greater is the affinity between naringin and the solvents. The organic solvents (butanol, isopropanol, ethyl acetate and ethanol) have the smallest  $R_i$ . However, the objective is to replace these solvents with green solvents, efficient for the solubilization of naringin. DES-6 and aqueous glycerol are placed inside the HSP sphere, so they are good solvents for naringin solubilisation. However, 50% ethanol-water and DES-6 were closer to the HSP centre than the aqueous glycerol. Previous HPLC results have shown that the efficiency of aqueous

glycerol and DES-6 is comparable to that of 50% ethanol-water. Therefore, a slight divergence exists between the final extraction yield of naringin obtained by aqueous glycerol and the value of the HSP for the same solvent. 20% (w/v) glycerol-water had relatively high  $\delta_h$  value due to the presence of relatively high amount of water. This divergence can be explained by the fact that the HSP value can only predict the capacity of the solvents to dissolve naringin, but will not affect the diffusion process and the final extraction yields (Li et al., 2014).

### 3.3. Intensification of polyphenols extraction in green solvents by HVED pre-treatment

Aqueous glycerol and DES are green solvents that can be used as alternatives to hazardous organic solvents in the conventional solid-liquid extraction. To enhance the yields and the kinetics of polyphenols extraction during the solid-liquid extraction, grapefruit peels were pre-treated with HVED in water. The use of HVED is in correspondence with the green extraction concept. This concept is based on using renewable plant material and green solvents as alternative to hazardous solvents. It includes also the use of technologies or extraction processes, that will reduce the energy consumption and allow the obtention of high quality extracts (Chemat et al., 2012).

Supplementary Figure 5 presents the effect of the HVED energy input on the polyphenols extraction index  $Z_p$ . The value of  $Z_p$  is related to the release of polyphenols from the treated cells. It increases gradually with the increase of the HVED energy input. According to statistical analysis, the variation of the energy from 7.27 to 72 kJ/kg, significantly enhanced the liberation of polyphenols and the value of  $Z_p$  increased from 0.36 to 0.72, respectively where it reached a plateau. The disintegration of grapefruit peels could be visually observed during HVED pre-treatment (photos in Figure 4). For  $W=7.27$  kJ/kg, peels are still intact. The fragmentation of the product increases with the HVED energy input, and the size of grapefruit peels significantly decreased when the energy varied from 7.27 to 72 kJ/kg.

Similar results were observed earlier on flaxseed cake (Boussetta et al., 2013). The values of  $Z_p$  increased gradually with the treatment duration and the maximal value was obtained after 5 ms of treatment. Additional discharges did not increase the extraction of polyphenols and the optimal treatment duration was fixed at 5 ms (Boussetta et al., 2013).

Figure 6 shows the effect of the HVED energy input on the polyphenols content during the subsequent solid liquid extraction in water. An ANOVA analysis was performed to evaluate if there were significant differences in the total polyphenol content of grapefruit peels extracts after the HVED pre-treatment at different energies. The LSD test has shown which HVED energy pre-treatments have significantly increased the extraction of polyphenols. After the HVED pre-treatment, before the diffusion process (at 0 min), a significant improve in the polyphenol content was observed, when the HVED energy pre-treatment was increased from 7.27 to 36 and to 72 kJ/kg. These results are in agreement with those obtained by other authors who found an improvement in the extraction efficiency of the biomolecules by increasing the number of pulses during HVED pre-treatment (Almohammed et al., 2017; Moubarik, El-Belghiti, & Vorobiev, 2011). The explosion of cavitation bubbles and the propagation of shock waves during HVED pre-treatment, cause the fragmentation of the particles which increases the surface area and improves the diffusion of biomolecules (Boussetta, Lesaint, et al., 2013; Rajha, Boussetta, Louka, Maroun, & Vorobiev, 2014; Rajha et al., 2015). Since the fragmentation of the peels during HVED pre-treatment is the main factor that improves the subsequent diffusion, we compared the HVED to a conventional grinding pre-treatment of grapefruit peels (data not shown). The same concentration of polyphenols (1.8 g/100 g DM) was obtained with HVED with an energy consumption 4 times lower (218 kJ/kg with HVED compared to 900 kJ/kg with the grinder). HVED can thus be proposed as an alternative, innovative, green technology for the pre-treatment of fresh grapefruit



peels in water, in order to improve the extraction of polyphenols. However, more studies should be performed to develop this technology at the industrial scale.

After 10 min of diffusion in water, the concentration of polyphenols has increased from 1.33 g/100 g DM from untreated peels (0 kJ/kg) to 1.55, 1.63, 1.67, 1.72 and 1.88 g/100 DM from HVED pre-treated peels at respectively 7.27, 36, 72, 145 and 218 kJ/kg. These values were comparable to those previously reported by Garcia-Castello et al. (2015) when they obtained between 0.4 and 5.5 g/ 100 g DM of polyphenols from grapefruit peels at different diffusion time, temperature and ethanol concentration.

Figure 7 presents the effect of the HVED energy input on the polyphenols content during the subsequent solid liquid extraction in 20% (w/v) aqueous glycerol. Without HVED pre-treatment, after 10 min of diffusion, the concentration of polyphenols obtained with 20% (w/v) water/glycerol (1.53 g/100 g DM) was higher than that obtained in water (1.33 g/100 g DM). This efficiency could be attributed to the extraction of more polar compounds with water/glycerol mixtures. After 10 min of diffusion, the same concentration of polyphenols ( $\approx 1.9$  g/100 g DM) was obtained for W=72 kJ/kg followed by solid-liquid extraction in aqueous glycerol and for W=218 kJ/kg followed by solid-liquid extraction in water. Combining HVED pre-treatment with extraction in aqueous glycerol had a very marked effect. The cell disintegration and product fragmentation during HVED increase the exchange surface and enhance the solvent transport into cells. Similar results were observed in the literature. The HVED pre-treatment of grape pomace (Boussetta et al., 2011) or grape stems (Brianceau, Turk, Vitrac, & Vorobiev, 2016) has increased the aqueous extraction of polyphenols, but in the presence of ethanol, polyphenols extraction was significantly better.

Insert in Figure 7 shows the effect of the HVED energy input on the diffusion coefficient  $D$  ( $\text{m}^2/\text{s}$ ) of polyphenols. Without HVED pre-treatment, the diffusivities of polyphenols were  $2.3 \times 10^{-11} \text{ m}^2/\text{s}$

and  $2.9 \times 10^{-11}$  m<sup>2</sup>/s in water and aqueous glycerol, respectively. This difference can be attributed to the solubility of polyphenols, which is higher in the glycerol-water mixture than in water only. The intracellular polyphenols diffusivities were higher after the application of HVED pre-treatment. For  $W=72$  kJ/kg, the value of  $D$  increased from  $4 \times 10^{-11}$  m<sup>2</sup>/s (in water) to  $6 \times 10^{-11}$  m<sup>2</sup>/s (in glycerol-water). Moreover, the same diffusivity of polyphenols ( $4 \times 10^{-11}$  m<sup>2</sup>/s) is attained for  $W=218$  kJ/kg followed by S-L extraction in water and for  $W=36$  kJ/kg followed by S-L extraction in aqueous glycerol. Therefore, the addition of glycerol has reduced the energy of the HVED pre-treatment by 6 times. Hence the advantage of using 20% (w/v) aqueous glycerol instead of only water during the S-L extraction, is to reduce the duration and consequently the energy of the HVED pre-treatment.

Figure 8 shows the effect of glycerol percentage and DES-6 on the extraction of polyphenols from HVED pre-treated grapefruit peels. According to the previous result (Figure 5) and for avoiding long time of treatment and high energy consumption, the HVED energy input was fixed at 72 kJ/kg. Moreover, the ANOVA analysis showed a significant increase in the polyphenol content when the energy of HVED increased from 0 to 72 kJ/kg. No significant differences were observed for energies above 72 kJ/kg (Figures 6 and 7). The increase in glycerol percentage from 10 to 30% has increased the yields of polyphenols from 1.77 g/100 DM to 1.93 g/100 g DM. This can be attributed to the polarity of glycerol, which has a dielectric constant (44.38) lower than that of water (80.1) and can decrease the polarity of the mixture, allowing thus the solubilisation of higher amounts of polyphenols (Katsampa, Valsamedou, Grigorakis, & Makris, 2015). The glycerol percentage of 30% has not been exceeded, because the viscosity of water / glycerol mixture (at 50 °C) became very high. According to the LSD test, both glycerol 30% and DES-6 improved significantly the yields of polyphenols in comparison with water, 10% and 20% (w/v)

glycerol/water. Insert in Figure 8 shows the increase in the diffusion coefficients as a function of the content of glycerol in water, with and without HVED. Without HVED, the values of  $D$  increased from  $2.32 \times 10^{-11} \text{ m}^2/\text{s}$  to  $3.57 \times 10^{-11} \text{ m}^2/\text{s}$  when the glycerol % was varied from 0 to 30%. With HVED, the increase in the values of  $D$  was more pronounced (from  $4 \times 10^{-11} \text{ m}^2/\text{s}$  to  $6.64 \times 10^{-11} \text{ m}^2/\text{s}$ ). Therefore, there is a synergetic effect between HVED pre-treatment and the diffusion in aqueous glycerol.

## 4. Conclusions

This study has shown that deep eutectic solvents or aqueous glycerol are the green solvents that could replace the conventional solvents for the extraction of polyphenols from grapefruit peels. They significantly enhanced the extraction of polyphenols and especially the flavonoid naringin from grapefruit peels, in comparison with water. The Hansen solubility parameters can be used as a theoretical method to predict the solubilisation of naringin in the solvents. This modelling can reduce the number of experiments by selecting the appropriate solvents for the solubilization of the molecule of interest. The HVED pre-treatment of grapefruit peels allowed a significant enhancement of the extraction kinetics and the yields of polyphenols during the subsequent solid-liquid extraction. The effect of the HVED energy input on the polyphenols extraction was estimated through the calculation of the polyphenols extraction index. The calculation of the diffusion coefficients showed that the energy of the HVED pre-treatment can be reduced by 6 times, if the subsequent solid-liquid extraction is conducted in aqueous glycerol instead of water.

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## Conflict of Interest

None.

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## Table

**Table 2.** The concentrations of naringin extracted with aqueous glycerol and DES in comparison with water and ethanol.

Solvent	Concentration of naringin (g/100 g DM)	Improvement of naringin extraction, in comparison with water
Water	0.575 +/- 0.040	1
50% (v/v) ethanol/water	2.092 +/- 0.088	3.64
20% (w/v) aqueous glycerol	1.9695 +/- 0.087	3.42
DES-6 (lactic acid: glucose)	1.864 +/- 0.079	3.24

## Figure Captions

**Supplementary Figure 1.** Experimental setup

**Figure 2.** Effect of the solvent nature on the relative extraction of total polyphenols,  $C/C_0$ . (C corresponds to the total polyphenols content after a 1 h extraction in a selected solvent,  $C_0$  corresponds to the total polyphenols content after extraction in water in the same conditions)

**Supplementary Figure 3.** The HPLC chromatogram obtained from grapefruit peels extracts in water. Similar chromatograms were obtained for grapefruit peels extracts in 50% ethanol/water, aqueous glycerol and DES-6 with different surfaces of the peaks

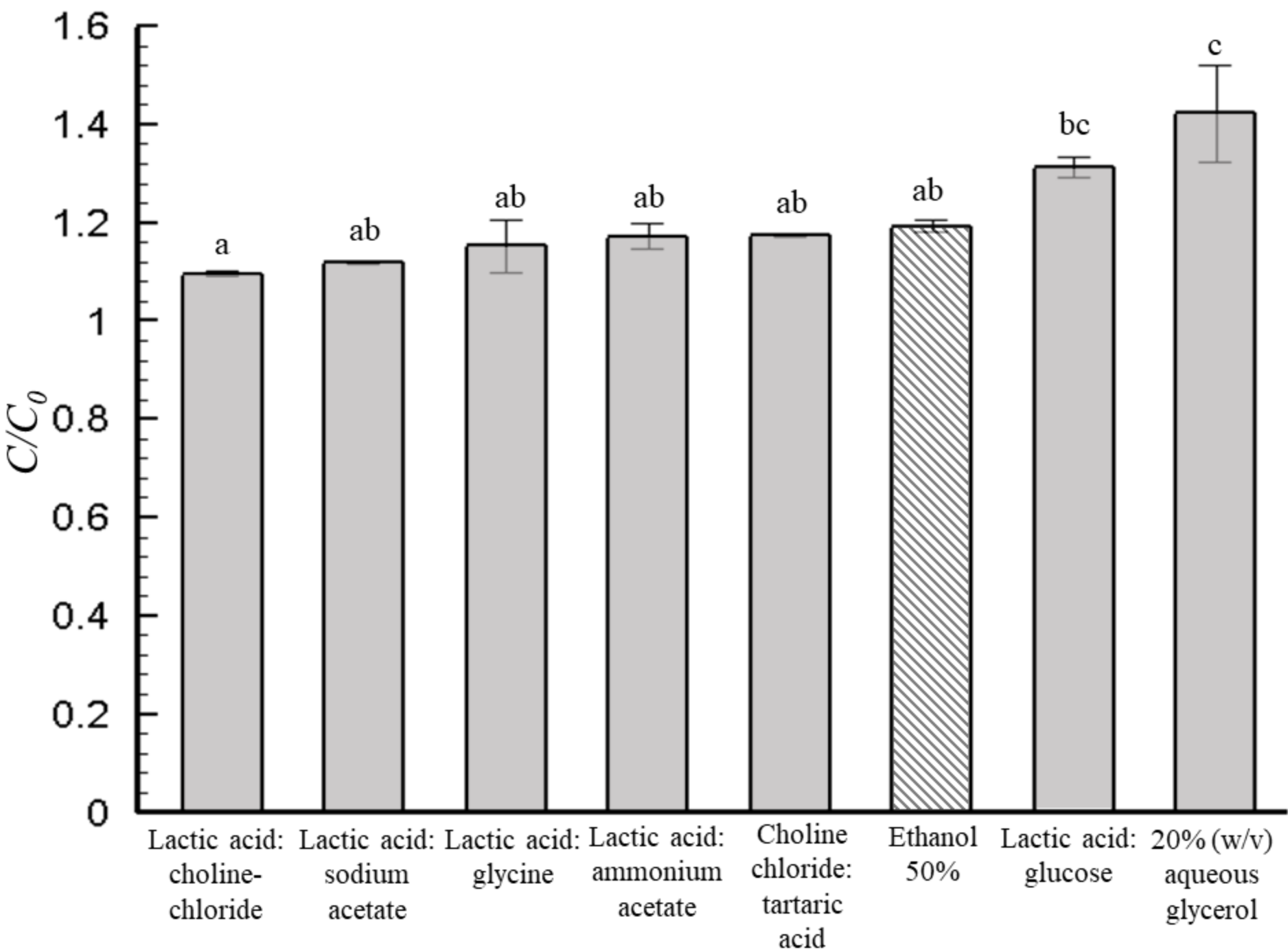
**Figure 4.** Three dimensional Hansen solubility sphere ( $R_s=22.1$ ) of all solvents and naringin

**Supplementary Figure 5.** The variation of the polyphenols extraction index  $Z_p$  as function of the HVED energy input. Insert shows the photos of grapefruit peels after HVED pre-treatment at different energy inputs

**Figure 6.** Effect of the HVED energy input on the polyphenols content during the subsequent solid liquid extraction in water

**Figure 7.** Effect of the HVED energy input on the polyphenols content during the subsequent solid liquid extraction in 20% (w/v) aqueous glycerol. Insert shows the effect of the HVED energy input on the diffusion coefficient  $D$  ( $m^2/s$ ) of polyphenols

**Figure 8.** Effect of the glycerol content and the DES-6 on the polyphenols content during solid-liquid extraction from HVED pre-treated samples ( $W=72$  kJ/kg). Insert shows the corresponding diffusion coefficient  $D$  of polyphenols as function of the glycerol % for untreated ( $W=0$  kJ/kg) and treated ( $W=72$  kJ/kg) grapefruit peels



$\delta_H$ 

■ Used solvents

◆ Unused solvents

● Naringin

■ Water (16;16;42);  $R_i=24$

■ 20% (w/v) aqueous glycerol  
(16;15;39);  $R_i=21$

■ 50% (v/v) ethanol-water (17;12;30);  $R_i=12$

■ 100% glycerol (17;12;29);  $R_i=13$

■ Lactic acid: glucose (17;11;28);  $R_i=11$

(13;5;21);  $R_i=0$

◆ 100% ethanol (15;7;16);  $R_i=6$

◆ Isopropanol (15;7;16);  $R_i=6$

◆ Butanol (16;5;15);  $R_i=8$

◆ Ethyl acetate (15;5;8);  $R_i=13$

◆ Hexane (15;12;30);  $R_i=22$

0  
20  
40  
 $\delta_D$

-20

0

20  
 $\delta_P$

