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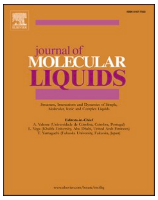

Short Communication

The glycerol/water mixture is an effective deep eutectic solvent for the extraction of bioactive components from food waste matrices

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ABSTRACT

Deep Eutectic Solvents (DESs) are a novel class of liquid systems that are increasing their relevance in the literature for their green and environmentally friendly features, for their catalytic properties and for their structural features. In this work, the mixture glycerol/water at 1/2.55 M ratio was demonstrated to be a DES thanks to the comparison of the experimental melting points with the theoretical melting curves. This DES was used as extracting agent on different food waste matrixes: onion, tomato and apple peels, spent coffee grounds and grape pomace. The results were compared with those obtained with water and with glycerol, showing a superior capability of the DES in the extractions, as well as superior antioxidant properties of the extracts. This promotes the use of this DES at the eutectic point and promotes a novel approach about the direct use of the extracts without further purification procedures considering the food grade of the DES components.

1. Introduction

Deep Eutectic Solvents (DESs) are a class of organic liquids that are rapidly increasing in their importance in the literature thanks to their environmentally-friendly features, as well as to their peculiar structural characteristics and to their catalytic capabilities [1,2,3]. These liquids are formed via weak interactions, mainly H-bonds, between two species: a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA). The interactions occurring between the two different species (HBD-HBA), as well as the ones occurring between the same species (HBA-HBA and HBD-HBD) lead to an non-regular crystal lattice formation, therefore to a substantial lowering in the melting points of the mixtures [4–6]. The environmentally-friendly features of this class of liquids relies on their low or absent toxicity; their low or absent vapor pressure; their realization in absence of any other solvent; their easy recycle capabilities and so on [7–9]. The need for reduction of the human being impact on the environment for the climate emergency is pushing forward for the application of DESs in many different areas as substitutes to common volatile organic compounds (VOCs). In organic synthesis, DESs can also have acid, basic, reductive, organocatalytic catalytic properties and in the extraction/preconcentration of valuable molecules from food or vegetal matrixes they show better results than VOCs in a large number of cases [10,11]. In particular in the latter, DESs are finding excellent results because of their affinity with aromatic, in particular phenolic, molecules [12]. Thanks to the richness of this class of valuable molecules in food and vegetal matrixes, to the effectiveness of this class of liquids superior by far to the VOCs, and to their environmental friendly features, DESs represent an advantageous choice in this subject [13].

In order to clearly recognize the DES' identity of a liquid mixture, a comparison of the experimental melting points at different molar fractions with the theoretical melting curves is mandatory to define a liquid as a DES and to identify its eutectic point [14–16]. The experimental curves of a DES, in fact, show an experimental eutectic point with a lower melting point and a shift in the molar fraction compared to the theoretical one. Also, the activity coefficients of the components show a non-ideal behavior. This is important also considering that when one of the components is already a liquid, it is impossible to define the system as a simple solution or an ideal mixture rather than a DES without the

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use of these quantitative curves. With this approach, recently *aquo*DESs mixtures were realized, characterized and identified as DESs [17,18]. These are mixtures in which water, thanks to its widely known capabilities as H-bonds acceptor and donor, is part of a binary mixture. However, nothing has been reported yet in the literature about possible DESs mixtures realized with both liquid components at room temperature. This could seem redundant as the resulting system is obviously a liquid, but the DES' properties, even if are relatable to the ones of the components, are different from the formers and, in many cases, better.

In this work the mixture glycerol/water in 1/2.55 M ratio (GLY/H_2O) was undoubtedly defined as a deep eutectic solvent thanks to the comparison of the experimental melting points with the theoretical melting curves and thanks, consequently, to the analysis of the experimental activity coefficients. Glycerol/water mixture is widely characterized in literature in its chemical-physical properties in all the composition ranges; still nothing has been reported with this novel approach considering it as a DES [19,20]. This mixture is a well-known industrial product, widely produced and used in a high number of different applications such as: antifreeze agent; liquid for electronic cigarettes; liquid for cryopreservation of living cells; preservation of proteins; artificial smoke production and so on [21–24]. Because of the safety of the components [25] and because of the above-mentioned advantageous properties with food or vegetal products of the DESs, GLY/H_2O DES was tested in extraction procedures in five different food waste matrixes: onion; tomato and apple peels; spent coffee grounds and grape pomace. The superior capabilities of this DES were demonstrated by comparing the results with the ones of the single components water and glycerol in terms of extracted phenols amounts and of antioxidant activity of the extracts, underlining the importance of the DES' identity of this liquid.

2. Experimental

2.1. Reagents, food matrixes, DES realization

Glycerol (10 % w/w water content) and 1,2-propanediol (>99 %) were purchased from Merck and Carlo Erba suppliers. Folin–Ciocalteu reagent and sodium carbonate (Na_2CO_3) were purchased from Sigma-Aldrich (St. Louis, MO, USA). DPPH (2,2-diphenyl-1-picrylhydrazyl) was bought from Glentham Life Sciences (Corsham, UK). Water was bidistilled grade. Metrohm 684 KF Coulometer Karl Fischer titrator was used to determine the glycerol starting water amount.

DES was prepared adding bidistilled water to the glycerol considering the starting amount of water in the glycerol, this was made in each batch prepared for each experimental set for avoiding any change in the composition for water absorption from air. The mixtures were prepared in closed screw-capped vials then shaking with vortex and gently heating with a heating gun the samples. With the same procedure the 1,2-propanediol/water mixtures were realized at the different molar fractions.

Onions, tomatoes and apples were purchased from local market and spent coffee grounds was taken from local coffee producers. Grape pomace wastes were provided by a regional winery located in Morro D'Alba (AN, Italy).

2.2. Theoretical/experimental melting curves

The melting points of 1,2-propanediol/water mixture were obtained by measuring the different samples at different molar ratios with a thermometer via immersion of the samples in liquid nitrogen in a Dewar. The melting temperatures were evaluated in triplicate in order to avoid any kinetic effect on the melting of the mixtures. The values showed a standard deviation <1 °C in the triplicates.

The melting theoretical curves were determined by using the following Formula (1) that represents the solid–liquid equilibrium curve in a eutectic mixture:

$$ln(\chi_i \bullet \gamma_i) = \frac{\Delta_m h_i}{R} \bullet \left(\frac{1}{T_{m,i}} - \frac{1}{T}\right) + \frac{\Delta_m Cp_i}{R} \bullet \left(\frac{T_{m,i}}{T} - ln\frac{T_{m,i}}{T} - 1\right) \quad (1)$$

where χ_i is the molar fraction and γ_i is activity coefficient of component i in the liquid phase, $\Delta_m h_i$ and $T_{m,i}$ are its melting enthalpy and temperature, respectively, $\Delta_m Cp_i$ is its heat capacity change upon melting, R is the ideal gas constant, and T is the absolute temperature of the system. Glycerol $\Delta_m h = 18280$ J/mol, $T_m = 290.9$ K; 1,2-propanediol $\Delta_m h = 8400$ J/mol, $T_m = 213.15$ K; water $\Delta_m h = 6007$ J/mol, $T_m = 273.15$ K [26]. Considering the heat capacity change upon the melting of a substance as negligible, this equation can be simplified. Therefore Eq. (2) was used:

$$ln(\chi_i \bullet \gamma_i) = \frac{\Delta_m h_i}{R} \bullet \left(\frac{1}{T_{m,i}} - \frac{1}{T}\right) \quad (2)$$

The theoretical melting temperatures T were calculated in Microsoft Excel with Eq. (2) at each molar fraction considering the activity coefficients $\gamma_i = 1$. The eutectic points were defined as the minimum in the experimental curves and they were compared to the theoretical ones.

The experimental γ_i values were determined via Eq. (3) by using the experimentally observed melting temperatures:

$$\gamma_i = \frac{\exp\left[\frac{\Delta_m h_i}{R}\left(\frac{1}{T_{m,i}} - \frac{1}{T}\right)\right]}{\chi_i} \quad (3)$$

2.3. Extraction procedures

The extractions were made via heating/ultrasonication procedures at 59 kHz (FALC ultrasonic bath, Treviglio, Italy) following protocols already optimized and published in the literature. The matrices were put in 3 mL Eppendorf tubes containing the extracting liquids and the shredded and dried (40 °C for 48 h) solid matrixes. The detailed extraction procedures are reported in Table 1:

Table 1
Food matrices analyzed; references for the procedures adopted, correspondent solvent/solid ratios (mg/ml), Temperatures (°C) and times (mins) used.

Matrix	Reference	Solid/Solvent ratio, mg/ml	Temperature, °C	Time, minutes
Onion peels	[27]	1/30	50	45
Tomato peels	[28]	1/20	65	60
Grape pomace	[29]	1/10	45	30
Spent coffee ground	[30]	1/38	60	10
Apple peels	[31]	1/30	40	40

After heating/sonication, the samples were centrifuged for 20 min at 5000 rpm (Thermo Scientific IEC CL10 Centrifuge, Thermo Electron Industries SAS) and the supernatants were diluted in water for the subsequent UV–Vis analysis (see further). The dilutions were made in order to have the maximum of the absorbances between 0.1 and 1 A.U., proper values for TPC and DPPH analysis (dilutions spanning from 1/1 to 1/10 of supernatant/water). The same procedures with the same matrixes were replicated with GLY/H_2O DES, water and glycerol respectively. All the experiments were made in triplicates with standard deviations determined via these replicates.

2.4. Total phenolic contents determination (TPC)

The TPC: Total Phenolic Content was determined spectrophotometrically using an Agilent Cary 8454 UV–Vis spectrophotometer, with the procedure described by Santanatoglia et al. [32], with some modifications: 0.5 mL of each water diluted sample was added, followed by 2.5 mL of Folin–Ciocalteu reagent and 7 mL of a 7.5 % w/w Na_2CO_3 water solution. The reaction mixture was left in the dark for 2 h at room temperature, then absorbance was measured at 765 nm. TPC was quantified using a gallic acid calibration curve and expressed as mg gallic acid equivalents (GAE) per g of food matrix.

2.5. DPPH radical scavenging activity

The antioxidant activity was assessed via the DPPH method, which involves spectrophotometric measurement of the reduction by antioxidant compounds of the 2,2-Diphenyl-1-Picrylhydrazyl radical. An Agilent Cary 8454 UV–Vis spectrophotometer was used for the measures. This evaluation was performed by adapting the methodology outlined by Santanatoglia et al. [32] 0.5 mL of each water-diluted sample was mixed with 4.5 mL of a 0.1 mM ethanolic DPPH solution. The mixtures were left in the dark for 30 min at room temperature. The decrease in DPPH radical concentration was then measured at 517 nm. The results were expressed in terms of mg Trolox equivalents (TE) per g of food matrix, with Trolox as the reference antioxidant.

3. Results and discussion

The first step of this work was the glycerol/water mixture DES identity demonstration. With this purpose, the theoretical melting points curves of the two components were drawn according to Eq. (2) and compared with the experimental melting points taken from literature data [20]. The graphs, comprehensive also of the activity coefficient profiles calculated with Eq. (3), are reported in Fig. 1.

As it can be clearly seen from Fig. 1, glycerol/water mixture is a deep eutectic solvent. The mixture shows a eutectic point at the molar ratio glycerol/water 1/2.55 and a melting point of −46.5 °C (226.65 K). This point shifts from the crossing point of the theoretical curves of the two components both in terms of the melting point value (that is lowered by about 20 degrees) and of the molar ratio, that is theoretically observed at about −27 °C and at 1/3 GLY/H_2O molar ratio. The activity coefficients of both components, obtained from these melting points, were calculated and reported in the same Fig. 1. The values are all below the value of 1, reaching a minimum at the experimental eutectic point. According to the literature, these are clear and sufficient evidences of the DES' identity of this mixture. Glycerol itself is a really hygroscopic liquid that can easily absorb water from the air, so we measured the water content of our batch in order to see how behaves under this point of view. The glycerol has an amount of starting water (measured to be 10 % w/w, corresponding to $\chi_{glycerol} = 0.64$) that corresponds to a part of the curve where it behaves almost as an ideal mixture. This can be easily detected also from the activity coefficients, slightly below 1 in this region. The non-ideal behavior of this mixture is more significant in the range of $\chi_{glycerol}$ from 0.25 to 0.45, closer to the eutectic point.

To strengthen these data, another water mixture was realized by mixing 1,2-propanediol with water and measuring the melting points at the different molar fractions. This diol has a structure very similar to the glycerol (lacks of just one –OH group compared to glycerol which has three). The theoretical/experimental melting points graphs and the

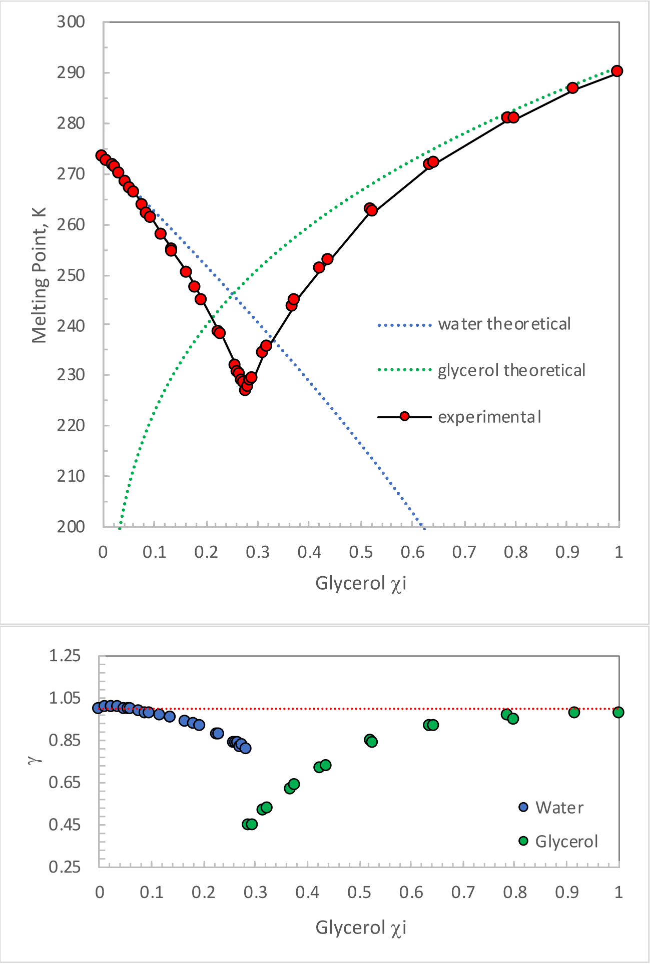

Fig. 1. DES identity of glycerol/water mixture: UPPER PART comparison of theoretical melting curves of water (blue dashed line) and glycerol (green dashed line) with experimental melting points (red dots) [20]; LOWER PART activity coefficients of water (blue dots) and of glycerol (green dots).

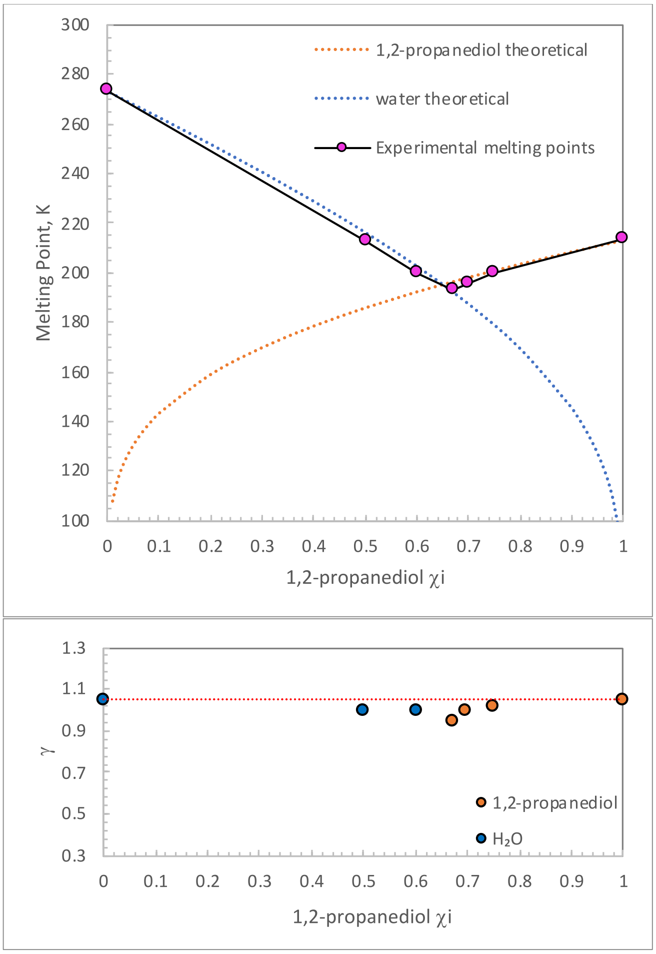

Fig. 2. 1,2-propanediol/water mixture: UPPER PART comparison of theoretical melting curves of water (blue dashed line) and 1,2-propanediol (orange dashed line) with experimental melting points (purple dots); LOWER PART activity coefficients of water (blue dots) and of 1,2-propanediol (orange dots).

activity coefficients are reported in Fig. 2.

1,2-propanediol/water mixture behaves in an ideal way in all the composition range, showing an almost perfect overlap of the theoretical melting curves, except of a really slight lowering at 1/1 M ratio and at the eutectic point, maybe due to the slight uncertainties of the measures via thermometer. The activity coefficients calculated from the experimental melting points are very close to 1. This indicates that even if these two molecules are reciprocally soluble, the interactions occurring between them are not so strong to determine a DES with the presence of HBD-HBA, HBA-HBA and HBD-HBD domains responsible of the disorganization of the crystal lattice of the mixture. The difference of only one hydroxyl group of 1,2-propanediol compared to the glycerol underlines again the singularity of GLY/H_2O mixture.

Considering the suitability of glycerol and, of course, of water in food applications [33], the next step of this work was the application of GLY/H_2O DES in food matrices extractions. In this experimental design, the results coming from the DES extractions were compared with the ones made in same identical conditions with the same food batches made with water and with glycerol only. The food matrixes analyzed were onion; tomato and apple peels; spent coffee grounds and grape pomace. The extraction capabilities were determined by measuring the total phenolic contents (TPC), avoiding any chromatographic analysis of the extract such as HPLC. This was made because the TPC value can give with a single number an evaluation of the overall capacity of extraction of a solvent for this class of compounds. Any chromatographic study can lead to difficult comparisons of different molecules amounts and they also need standard calibrations of their chromatograms. Moreover, in this paper the overall efficiency of the GLY/H_2O DES was made by analyzing five different food matrixes, therefore this should increase by much the number of experiments, standards and so on. In Fig. 3 the histograms of the TPC values observed for the extractions on the five matrixes with the DES compared to the water and to the glycerol components are reported.

As it can be clearly seen from the histograms in Fig. 3, GLY/H_2O DES showed a greater extraction efficiency of phenolic compounds from all tested matrixes compared to the use of glycerol and water components alone. Based on the literature data, the mainly phenolics compounds belong to phenolic acids and flavonoids classes [33]. In the spent coffee matrix, a slightly better extraction capability was observed with water as the extraction solvent. However, this may be due to the matrix that is properly realized for water extractions, and some target compounds are hydrophilic [34]. This data underlines the importance of the eutectic composition of the DES in these processes, showing results that are not related to the ones of the single components of the DES mixture itself. Spent coffee grounds matrix was extracted also with choline chloride/water mixture as a proof-of-concept comparison with other water-based systems. The results in this case were worse than the ones observed with GLY/H_2O DES that showed about twice the UV–Vis absorbance of the supernatant liquids with the same batch (see the spectrum in supporting Information section, Fig. S1).

The DESs extracts from various matrixes are known for their antioxidant activity [35], and this is particularly relevant for the extraction of phenols. Therefore, we tested the antioxidant activity of the DESs extracts with the DPPH radical scavenging method, once again comparing the data with those obtained with the same extracts in water and in glycerol (Fig. 4).

In general, the highest extraction of bioactive compounds with the DPPH method was observed in all matrices' extracts obtained by using DES. Water showed a moderate antiradical activity in all the extracts, with the exception of the ones from grape pomace wastes. Indeed, the antioxidant activity results were well confirmed by the TPC, which highlight a similar trend for all extracts.

4. Conclusions

Glycerol/water mixture is widely produced in the industry for various applications and purposes. Because of the lack of application of the theoretical/experimental melting curves comparison, it was not yet demonstrated to be a deep eutectic solvent. In this work it was demonstrated to be a DES thanks to this quantitative approach. GLY/H_2O (1/2.55 M ratio) DES was applied for the extraction of phenols from five different food matrixes, showing superior results compared to its components, underlining the validity of this mixture at the eutectic point. The antioxidant activity of DES extracts showed better results also for the preservation from oxidation compared to the water and to the glycerol.

Because of the food-grade, the safety and the suitability for food applications of the components in all the concentrations, GLY/H_2O DES represents a highly promising mixture for the possible direct use of the extracts in food and food supplements applications, opening for an innovative approach to the extraction procedures avoiding further purifications. Undoubtedly, cytotoxicity studies are needed, and they are currently undergoing in our laboratories. These will define any synergic/antisynergic effect between the components that could impact on their toxicity in the same way they impacted on their non-ideal melting points. All of the above-mentioned studies are mandatory to develop a new regulation that could consider using GLY/H_2O DES with this approach.

CRediT authorship contribution statement

Francesca Pompei: Methodology, Investigation, Data curation. **Elison Lepore:** Methodology, Investigation, Data curation. **Alejandro Torregrosa-Chinillach:** Investigation, Conceptualization. **Francesco Catalini:** Investigation. **Diego A. Alonso:** Writing – review & editing, Validation, Funding acquisition. **Rafael Chinchilla:** Writing – review & editing, Validation, Funding acquisition. **Serena Gabrielli:** Writing – review & editing, Validation, Methodology, Formal analysis. **Cinzia Mannozzi:** Writing – original draft, Methodology, Data curation. **Sauro Vittori:** Writing – review & editing, Supervision, Resources, Funding

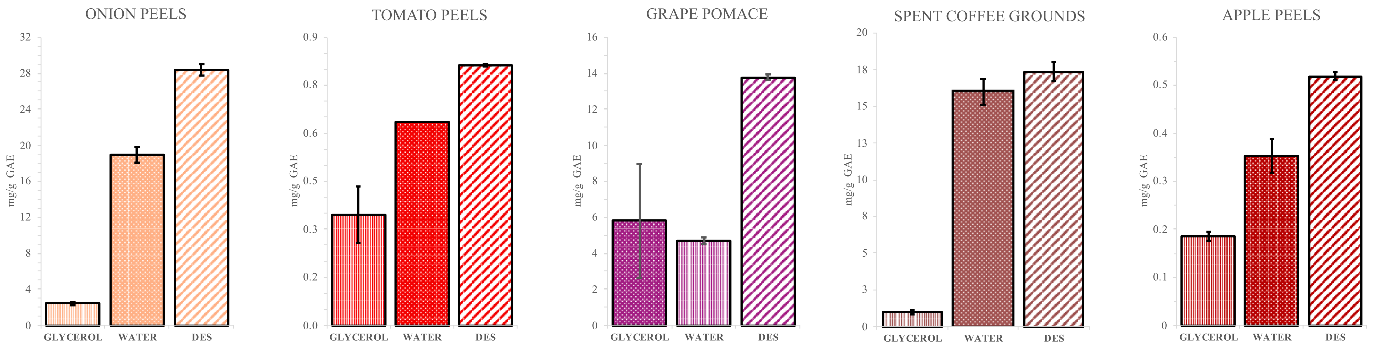

Fig. 3. Total polyphenolic contents (TPC, mg Gallic Acid Equivalent (GAE)/g) of the extracts from onion peels, tomato peels, grape pomace, spent coffee grounds and apple peels with glycerol, water and glycerol/water DES respectively.

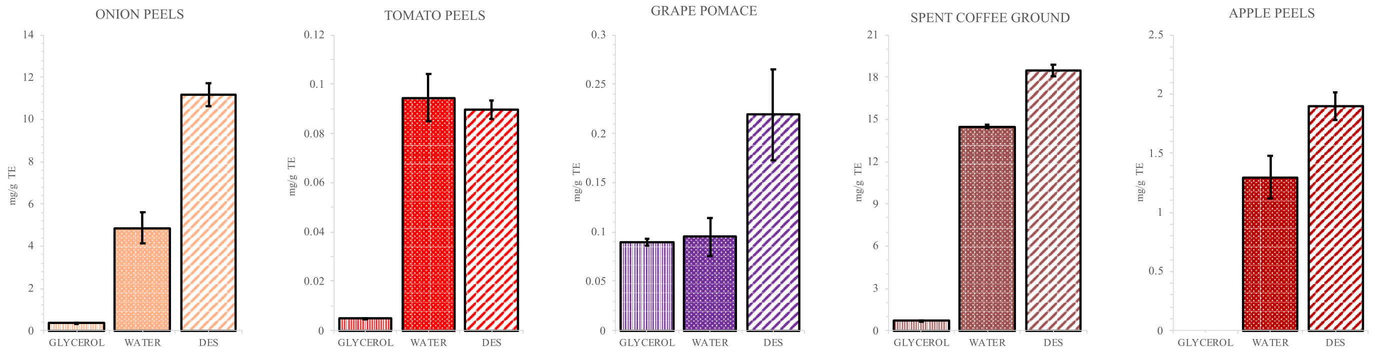

Fig. 4. Radical scavenging method (DPPH, mg Trolox Equivalent (TE)/g) of the extracts from onion peels, tomato peels, grape pomace, spent coffee grounds and apple peels with glycerol, water and glycerol/water DES respectively.

acquisition, Formal analysis. **Matteo Tiecco:** Writing – original draft, Visualization, Validation, Supervision, Software, Project administration, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2025.127416.

Data availability

Data will be made available on request.

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