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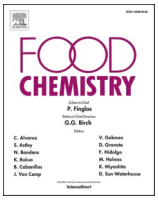

Combining eutectic solvents and food-grade silica to recover and stabilize anthocyanins from grape pomace

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ABSTRACT

Concentrated in the skins of red grapes are the anthocyanins, the primary colorants responsible for the fruits' reddish-purple color. These colorants are recognized for their significant antioxidant properties and potent nutraceutical and pharmaceutical ingredients. Nevertheless, their widespread use is compromised by the (i) need for more efficient yet sustainable downstream processes for their recovery and (ii) by the challenges imposed by their poor stability. In this work, these drawbacks were overcome by applying eutectic solvents and stabilizing agents. Besides, the anthocyanins were successfully loaded into a solid host material (approved in both food and pharmaceutical sectors) based on silicon dioxide (SiO_2, loading capacity: $1_{extract}$:7_{silica} m/m). Summing up, with the process developed, the extraction yield (21 $mg_{anthocyanins}.g^{-1}_{biomass}$) and the stability (under 55, 75, and 95 °C) of the recovered anthocyanins were over three times better than with the conventional process. Finally, the raw materials and solvents were recycled, allowing an economical and environmentally friendly downstream process.

1. Introduction

Globally, 1.3 billion tons of food per year are wasted or lost, representing around 30 % of the total produced (Tsegaye et al., 2021), accounting for an economic loss estimated at S$2.6 trillion annually (Esteve-Llorens et al., 2021; Jones et al., 2022). Food waste repurposing provides an alternative waste management strategy to meet Goal #12 of the United Nations Sustainable Development Goals (Kumar & Agrawal, 2020). The industrial need to replace some of the synthetic compounds for their natural congeners is associated with the problem of food waste, where natural colorants are typical examples. Besides, some European restrictions towards synthetic pigments are associated with the need for waste valorization (EU, 2020), stimulating the search for new sources of natural colorants even more.

Indeed, the natural colorants market is relevant and expected to reach an annual growth of 6.22 % (Cortez et al., 2017). However, despite the high dyeability and stability of the synthetic dyes (increased half-life time), they are nocive to the environment and, in some cases, also to humans (Dey & Nagababu, 2022). Their synthesis requires high energy costs and volatile organic solvents (VOS), besides chemical stabilizers (also synthetic), which contribute to a high carbon footprint (de Souza Mesquita et al., 2021). Furthermore, their harmful impacts on the consumer's health and contamination of the water resources make their replacement an urgent need (Ardila-Leal et al., 2021). An alternative is, as previously mentioned, to repurpose the food wastes by extracting their colorants. This strategy follows the principles of Green Chemistry, but it also answers the Circular Economy concept by using discarded biomass to create new products (Schanes et al., 2018). So far, despite the best resource-efficient strategy for food waste valorization is maintaining it for human consumption (Lavelli, 2021), other strategies include the valorization of those wastes, namely for (i) energy production, (ii) reprocessing food waste by making functional materials, and (iii)

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reprocessing food waste by making new products and extracts (Fig. S1).

This work investigated a strategy to develop efficient and sustainable processes for extracting anthocyanins from grape pomace while maintaining color thermal stability. Grape pomace is the waste produced by the winery industry, the biggest consumer of grapes, at circa 74 million tons annually. 20–30 % per grape is considered residue and consists of the remaining pulp, seeds, stalks, and skins (Bender et al., 2017; García-Lomillo & González-SanJosé, 2017). Concentrated in the skins are the anthocyanins, primary colorants from grapes' wastes responsible for the natural reddish-purple color (Khoo et al., 2017). These colorants are recognized for their significant antioxidant properties, relevant to reducing the risks of several diseases, and as potent nutraceutical and pharmaceutical ingredients (Liu et al., 2021). Nevertheless, their use in a broader range of applications is still compromised by the challenges concerning their color instability, especially during food processing, temperature variations, storage, and commercialization (Cortez et al., 2017).

Aiming to develop a more efficient and sustainable process of extracting anthocyanins from the grape pomace, we have investigated the performance of eutectic solvents. Eutectic solvents (ESs) are formed by mixing a hydrogen bond acceptor (HBA) with at least a hydrogen bond donor (HBD) and limited water content (Smith et al., 2014). Many components can be used to formulate eutectic solvents. These are recognized by their "design solvent" nature (Hessel et al., 2022), which means that some characteristics, like their solvent performance, toxicity, viscosity, and stability, can be modulated to a specific application (Smith et al., 2014). Behind the credentials of sustainability and efficiency, the extraction processes need to be compatible with the products extracted. Thus, the process and solvents must maintain their color and chemical stabilities for colorants. Several approaches have been considered regarding the maintenance of the colorants' stability. Examples are (i) the removal of the solvents at the end of the processes but also (ii) their loadings in solid host materials, like gums, starches, sugars, and silicas (Yang et al., 2020). Aiming to achieve a high-performance loading, some works report the use of microencapsulation techniques. However, these are costly, energy-demanding, and exigent in terms of specialized labor (Mohammadalinejhad & Kurek, 2021). In addition, these often cause anthocyanins' degradation, which generally means low chemical stability, high sensitivity to oxidation, and low dyeing uniformity (Mohammadalinejhad & Kurek, 2021). This work investigated silicon dioxide (SiO_2), a non-toxic adsorbent material approved to be applied in food and pharmaceutical formulations. SiO_2 can convert any liquid into powders with high bulk density and excellent flow properties.

Summing up, in this work, the anthocyanins from grape pomace were extracted by using several aqueous solutions of eutectic mixtures (Fig. S2; Table S1). The eutectic solvents were experimentally tested after a predictive study performed with the Conductor-like Screening Model for Real Solvents (COSMO-RS) to identify the best options for extracting the anthocyanins. The best solvent was selected, and the operational conditions [solid–liquid ratio ($R_{(S/L)}$, in $g_{biomass}.mL_{solvent}^{-1}$), water content (wt%, the amount of water in the eutectic solvent solution), and static time (t_{stat}, in min)] were optimized. After achieving the best extraction conditions, the anthocyanins' purification was performed using solid-phase extraction (SPE) to remove contaminants and simultaneously separate the colorants from the eutectic solvent. Then, the colorants were incorporated into the SiO_2. Their thermal stability was evaluated at three temperatures, providing information about their application even at high temperatures. All raw materials' recovery and recycling steps were considered and proved advantageous in decreasing the environmental and economic impacts.

2. Materials and methods

2.1. Materials

The grape pomace was donated by a local industry at Limeira (São Paulo, Brazil). It was subjected to autoclaving (121 °C, 15 min, 5 bar) for sterilization, then powdered in a knife mill, and finally sieved through a #50 mesh. To prepare the eutectic mixtures, the starting materials were all purchased at *Dinâmica* (Campinas, Brazil); namely, proline – Pro-(>99 %), glycine – Gly-(>99 %), alanine – Ala-(>99 %), nicotinamide – Nic – (vitamin B3) (>99 %), ammonium acetate – AmmAc – (>95 %), sodium acetate – NaAc – (>95 %), glycerol – Glyce – (>98 %), 1,4-butanediol – But –, 1,2-ethylene glycol – Ety – (>98 %), xylitol – Xyl – (>99 %), sorbitol – Sor – (>99 %), citric acid – CA –, acetic acid – AA – (>99 %), and lactic acid – LA – (>85 %). Ethanol absolute (EtOH) was purchased from Synth (Diadema, Brazil). The ultra-pure water was provided by a Purelab Flex 3 purifying system (ElgaVeolia, High Wycombe, United Kingdom). Acetonitrile was used in the chromatographic analysis, purchased from J.T Baker. The chromatographic standard cyanidin-3-*O*-glucoside was purchased from Sigma-Aldrich (>99 %). The adsorbent used to perform the solid-phase extraction, Sepra C_{18}-E (particle size: 50 μm, pore size: 85 Å), was acquired from Phenomenex. Silicon dioxide (SiO_2 – specific surface area 190 $m^2.g^{-1}$, particle size 320 μm) was kindly assured by EVONIK (São Paulo, Brazil).

2.2. COSMO-RS model

Conductor-like Screening Model for Real Solvents (COSMO-RS) calculations was performed in a two-step procedure. First, using the software Turbomole (TmoleX19 software package), the geometry of each molecule (HBA, HBD, and anthocyanins models) was optimized using the COSMO-BP-TZVP. Then, using these designed molecules, the polarization charges (σ) and the surface composition functions, p(σ), were calculated and plotted *via* COSMOtherm® software. For this, the COSMOtherm® package with the parameterization BP_TZVP_21.ctd was used (Eckert & Klamt, 2002). The COSMO-BP-TZVP model includes a base set of def-TZVP, DFT with the theory functional level B-P83, and the COSMO solvation model. Then, the chemical potential from eutectic solvents components (HBA and HBD) and anthocyanins models (Malvidin-3-*O*-glucoside and Peonidin-3,5-*O*-diglucoside), *i.*e., σ-potentials, were calculated considering the thermodynamics of their molecular interactions. This data set discussed the anthocyanins models' solubility affinity into eutectic solvents, represented by p(σ) and μ(σ) curves.

2.3. Eutectic solvents preparation

Eutectic solvents were prepared using a method adapted from Abbott and collaborators (Abbott et al., 2004). Briefly, the eutectic solvents formed by two-component mixtures (HBA and HBD) were accurately weighed into a closed glass flask. The water content was adjusted to 15 wt% (considering the initial water content of each starting material). For the screening assay, all eutectic solvents were formulated using a molar ratio 1:2. The mixtures were stirred in an oil bath at 60 ± 2 °C at 500 rpm until a homogenous and transparent liquid was obtained. The pH of all aqueous solutions was measured at 27 ± 2 °C using Bel Engineering PHS3BW equipment with an uncertainty of ±0.01. The mixtures were stored for less than 24 h until use.

2.4. Solid − liquid extraction using eutectic solvents and conventional solvents

The extraction capacity of different aqueous solutions of eutectic solvents was evaluated by determining the yield of anthocyanins extracted from the grape pomace ($mg_{anthocyanins}.g_{biomass}^{-1}$). All extraction systems were performed in triplicate, and the results were expressed as the mean ± standard deviations. The eutectic solvents were initially

formed with 15 wt% of water content. The first extractions were performed by an ultrasonic-assisted extraction (UAE), using an ultrasonic bath (P60H, Elmasonic, Singen, Germany, 2.75 L, 37KHz, 135W) under the operational conditions fixed at $R_{(S/L)}$ 0.05 $g.mL^{-1}$ for 120 min. Afterward, to separate the biomass debris from the colored extract, a centrifugation step was performed in an Eppendorf 16R centrifuge at 4 °C, 12000 rpm for 10 min. The anthocyanins-rich supernatant was collected and analyzed by ultra-performance liquid chromatography coupled with a photodiode array detector (UHPLC-PDA – Waters).

After the first screening, the most efficient eutectic solvent was selected to be employed in the extraction process optimization. The extraction method based on an ultrasonic bath was replaced with an ultrasonic probe (Ultronique, 800 W, 20 kHz) to maximize the extraction yield. Firstly, the ultrasonic power was studied step-by-step to determine the power required to improve the extraction yield of anthocyanins. The variation of temperature under the extraction process for 5 min was recorded, being the power values 160, 240, 320, and 400 W initially selected for this study. After selecting the most appropriate ultrasonic power, the molar ratio of the selected eutectic solvent was studied. For this study, the molar ratio 1:2 (initially used in the screening assay), 2:1, 1:1, 1:3, were studied. The effect of the aqueous solutions of HBA and HBD (500 mM - no eutectic solvent formation) was also evaluated for comparison purposes. After selecting the appropriate ultrasonic power and the molar ratio able to increase the extraction performance of the anthocyanins from grape pomace, the process optimization was done using a central composite rotatable design (CCRD 2^3 plus axial), with six central points performed as replicates, with a total of 20 assays (Table S2). At this point, the extraction time was fixed at 5 min (t_{ext} in min) since this variable influences the extraction temperature and consequently could degrade the thermosensitive colorants. The operational variables studied were the solid–liquid ratio ($R_{(S/L)}$ in $g_{biomass}.mL_{solvent}^{-1}$), water content (wt% in %), and the static time (t_{stat} in min), which represents the time the biomass was put in contact with the solvent but without cavitation. The responsive variable used as a model to guide the optimization of the extraction process was the total anthocyanin content ($mg_{anthocyanins}.g_{biomass}^{-1}$). The extraction conditions representing the optimum process were validated in triplicate, with the respective variation coefficient expressed in %. In addition to the 5 min initially tested as extraction time, other times were investigated, namely 2, 4, 6, 8, 10, and 12 min, in order to determine the time promoting the higher extraction yield of anthocyanins ($mg_{anthocyanins}.g_{biomass}^{-1}$).

Ethanol and water were tested as conventional solvents, and the results obtained compared with the data achieved using the alternative process based on UAE-eutectic solvent after optimization. Additionally, the effect of different mechanical methods was evaluated for the best eutectic solvent and the optimum process conditions. The mechanical processes selected were static maceration (24 h), agitation under magnetic stirring (12 h, 500 rpm), and agitation under ultra-dispersion (5 min, 15000 rpm). The experiments were performed in triplicate, and the results obtained were expressed as $mg_{anthocyanins}.g_{biomass}^{-1}$.

2.5. Statistical analysis

After selecting the best operational condition by CCRD, an Analysis of variance (ANOVA) followed by the Bonferroni post-hoc test was applied to compare the extraction yield between the different extraction techniques and select the best extraction time. The significance level selected was set at 95 % ($p < 0.05$, $n = 3$). All analyses were performed using the JAMOVI software.

2.6. Anthocyanin quantification and identification

Ultra-high performance liquid chromatography coupled with a photodiode array detector (UPLC-PDA) was performed in an Acquity UHPLC H-Class system (Waters, Milford, MA, USA), and used to quantify the extracted anthocyanins from the grape pomace. The extracts were diluted in acidified water (0.1 $mol.L^{-1}$ of citric acid) in a proportion of 1.5×, to avoid experimental difficulties in the UHPLC analysis due to the high viscosity of the eutectic solvent. After that, the solution was mixed in a vortex and filtered using a nylon syringe filter (particle diameter 0.22 μm – Analitica, São Paulo, Brazil). Finally, the obtained samples were injected into the UHPLC-PDA system. The separation was performed on a Kinetex C_{18} column (150 × 4.6 mm, 2.6 μm, Phenomenex Torrance, CA, USA), maintained at 45 °C with a mobile phase flow of 0.7 $mL.min^{-1}$. The mobile phase was composed of two solvents: (A) acidified water (phosphoric acid 5 %) and (B) acidified acetonitrile (phosphoric acid 4 %). The gradient used was as follows: 0 min (97 % A), 1 min (87 % A), 2 min (85 % A), 2.5 min (85 % A), 3 min (82 % A), 3.50 min (80 % A), 4 min (75 % A), 4.5 min (73 % A), 5 min (72 % A), 6 min (70 % A), 7 min (70 % A), and 9 min (97 % A). The absorbance was monitored at 280, 350, and 500 nm, and the peaks were processed at 500 nm. The injection volume was 4 μL, and the conditioning time was set at 4 min (until re-equilibration of the initial conditions ($\Delta_{pressure} < 19$ psi), a total of 13 min of analysis). The total anthocyanin content was calculated using an external analytical curve for cyanidin-3-*O*-glucoside as an external standard (1.6–195 ppm).

The primary identification of the extracted anthocyanins was performed by UHPLC coupled with a mass spectrometer detector (MS). MS analyses were carried out in a Thermo Finnigan (San Jose, CA, USA) LCQ mass spectrometer equipped with an electrospray ionization source (ESI), ion-trap (IT) analyzer, and Xcalibur software for data processing. Briefly, the MS analysis was acquired in the positive ion mode, the capillary temperature fixed at 300 °C; 85 arbitrary units of nitrogen and gas assist with 5 arbitrary units. Additionally, a comparison with the literature data regarding the elution order of the extracted anthocyanins, retention times, UV–vis spectra of the separated compounds, and the co-elution with authentic standards was performed to allow precise identification.

2.7. Isolation of anthocyanins and eutectic solvents

Solid-Phase Extraction (SPE) was adopted to separate the extracted anthocyanins from the solvent and consequently recover the eutectic solvents, allowing their reuse. Firstly, the commercial C_{18} adsorbent material was activated with ethanol ($1_{adsorbent}$:$5_{ethanol}$ w/w) and conditioned with water in the same proportion. After that, the anthocyanin-rich extract obtained by the ES-mediated process was loaded in the C_{18} ($1_{adsorbent}$:$4_{extract}$ w/w) and washed with 30 mL of water to recover the eutectic solvent from the extract. After removing the eutectic solvent, 30 mL of ethanol (>50 % v/v) was added to allow the colorants' desorption from the adsorbent material. Then, the recycling of the same adsorbent was evaluated in new extraction cycles. Finally, a new SPE step was briefly studied by applying a fresh batch of eutectic solvent to the same adsorbent material after the colorants' elution. After the polishing step, the anthocyanin extract and the water used to remove the eutectic solvent from the adsorbent were analyzed through UHPLC-PDA to estimate the eutectic solvent's recovery rate. This analysis was done by monitoring the HBA maximum peak (processing at 260 nm).

2.8. Anthocyanin load to SiO_2

The obtained extracts rich in anthocyanins were loaded in SiO_2, a silica-based material approved for food and pharmacological formulations. Briefly, 35 mL of anthocyanin extract was added to 5 g of SiO_2, manually stirring the system. The system was stirred until all the extract was loaded in the SiO_2 material. The colorants loaded in the SiO_2 were then evaluated regarding their thermal stability. Besides, the water activity (a_w) of the obtained material (SiO2 + pigments) was evaluated using a dew point hygrometer (Aqualab, 168 Decagon Devices, Pullman, WA, USA) equipment at two moments: (i) immediately after loading the extract in the SiO_2, and (ii) after storing the obtained material in the

oven (50 °C, 120 min).

2.9. Thermal stability

The thermal stability of anthocyanins obtained using eutectic solvent, ethanol, and water as solvents was studied at three temperatures (55 °C, 75 °C, and 95 °C). Vials containing 1.5 mL of anthocyanin extract were heated in an oven for up to 48 h (Memmert GmbH, UF55, Buechenbach, Germany), collected at different times, and immediately cooled in an ice bath to stop any reaction occurring in the samples. After that, each collected vial was analyzed by UHPLC-PDA. The degradation rate constant (K_d, min^{-1}) was calculated by a semi-natural logarithmic plot of the anthocyanin concentration vs time. In addition, the thermal kinetics parameters, half-life time ($t_{1/2}$, h), and thermal activation energy (E_a, $kJ.mol^{-1}$) were calculated. Additionally, the colorants loaded in the food-grade silica (SiO_2) were also evaluated regarding thermal stability. Here, 1.5 g of the colored silica was placed in conic tubes (15 mL) and heated at 95 °C for 24 h (this describes the worst scenario studied for the extracts). The tubes were collected and immediately cooled in an ice bath. In order to analyze the concentration of the pigments remaining in the SiO_2 after heating, the anthocyanins from the SiO_2 were extracted using an ethanolic solution (70 % v/v acidified with citric acid 0.25 $mol.L^{-1}$), filtered using a nylon syringe filter (particle diameter 0.22 μm), and analyzed by UHPLC-PDA.

2.10. Environmental analysis

A life cycle assessment (LCA) was performed according to ISO 14,040 standard to quantify the environmental impacts *per* mg of anthocyanins extracted from grape pomace (Arvanitoyannis, 2008). In the analysis, the following scenarios were analyzed: (i) **Scenario 1** – extraction and polishing of anthocyanins and recycling of the eutectic solvent; (ii) **Scenario 2** – extraction and polishing of anthocyanins, recycling of the eutectic solvent, C_{18} adsorbent, ethanol, and water; (iii) **Scenario 3** – similar to scenario 2, however considering the anthocyanins adsorbed into SiO_2 material; (IV) **Scenario 4** – similar to scenario 2, but with the anthocyanins dried by spray drying.

A cradle-to-gate approach was adopted, comprising the impacts associated with the production of chemicals, water, and electricity. No impacts were allocated to grape pomace as it is considered waste from the food industry. The anthocyanins' input and output flows are presented in Table S3 for each scenario. The amounts of chemicals and water were obtained during the experimental methods. The amount of electricity consumed in the solid–liquid extraction, polishing, and recycling was estimated based on the equipment's power, use, and capacity. In Scenario 4, data on electricity and natural gas consumed in spray drying were derived from the World Food LCA Database available in SigmaPro software. The impacts associated with the production of the remaining inputs were retrieved from ecoinvent 3.7.1 (Wernet et al., 2016). The impact assessment was based on the ReCiPe 2016 method (Huijbregts et al., 2017) for the following impact categories: global warming, ozone formation - human health, terrestrial acidification, mineral resource scarcity, and fossil resource scarcity.

2.11. Economic analysis

The economic analysis was conducted considering a laboratory-scale process. That's why, costs regarding energy and machinery are not considered in this analysis. Nevertheless, it is possible to make some projections considering a hypothetical selling price of the extract obtained. Thus, Eq. (1) was applied to determine the production costs *per* mg of anthocyanin extracted from the grape pomace, while Eq. (2) estimates the return of the process (adapted from Martins and co-workers) (Martins et al., 2021).

$$\frac{Productioncost}{mg_{anthocyanins}} = \frac{\sum_{i=1} n \frac{useofmaterial}{batch} \times \frac{priceofmaterial_i}{unitofmaterial_i}}{\frac{mg_{anthocyanin}}{unit_{biomass}} \times mass_{biomass}} \quad (1)$$

$$Return\left(\frac{\$}{g_{biomass}}\right) = \left[C_{prod} \times \$_{prod}\right] - \$_{biomass} - \left[\alpha \times \frac{productioncost}{g_{biomass}}\right] \quad (2)$$

Eq. (1) allows the cost evaluation of goods *per* mg of anthocyanin extracted, $CoG.mg^{-1}$. First, the cost of each raw material was tabulated (Table S4). Then, Eq. (2) uses five variables to estimate the possible profit (Return), considering the recycling of the raw materials (especially the adsorbent material and eutectic solvent) in new extraction cycles. The C_{prod} represents the concentration of the anthocyanin *per* mg of biomass (extraction yield obtained in the optimized condition – $mg_{anthocyanin}.g_{biomass}^{-1}$). The $\$_{prod}$ is the market price of the grape anthocyanin extract. However, up to now, no anthocyanin extracts commercialized have been obtained with eutectic solvents. Thus, for the estimation of the $\$_{prod}$, the mean of an equivalent anthocyanins' commercial extract sold today ($0.32 *per* mg of extract) was considered. The $\$_{biomass}$ characterizes the costs to obtain the grape pomace, fixed at $42 *per* ton. Moreover, since the price of raw materials frequently changes according to the market tendencies or the purity of the pigment extract, a multiplier factor ($\alpha = 0.1$, 1, and 10) was used to express different price scenarios, representing a decrease or increase by 10-fold.

3. Results and discussion

3.1. Biomass characterization regarding anthocyanins

First, the grape pomace biomass was characterized in terms of anthocyanins by UHPLC-PDA-MS/MS (Fig. S3, Table S5), using an aqueous extract prepared at pH 3. We identified the presence of delphinidin, malvidin, and peonidin derivatives (anthocyanins aglycones). The most abundant compounds are represented by Peonidin-3,5-*O*-diglucoside (*m/z* 625; peak 4) and by the acylated anthocyanin Malvidin-3-*O*-(*trans*-6-*O*-coumaroyl)-glucoside-5-glucoside (*m/z* 801; peak 13).

3.2. Screening of eutectic solvents

To represent the target anthocyanins obtained, the sigma profiles of the malvidin-3-*O*-glucoside and peonidin-3,5-*O*-diglucoside and the sigma profiles of the HBA and HBD, were determined (Fig. S4). It is possible to better evaluate and understand the polarity differences between the molecules through the obtained profiles. The σ-profile graph can be separated into three areas according to the molecule's affinity: the hydrogen bond donor area ($\sigma < -0.01$ e/Å2), the non-polar area (-0.01 e/Å2 $< \sigma <$ 0.0084 e/Å2), and H-bonding acceptor area ($\sigma >$ +0.01 e/Å2). Malvidin-3-*O*-glucoside and Peonidin-3,5-*O*-diglucoside present a similar profile, with a peak in the H donor area related to the contribution of H atoms and a notable peak in the H-acceptor region, related to the hydroxyl groups of the molecules. However, most of the peaks are in the non-polar region due to the contribution of the molecule's carbon chain. On the other hand, the different HBAs and HBDs studied show different trends due to the groups composing the molecules (Fig. S5). Among all HBAs and HBDs evaluated, the highest affinities in the polar region (H-bond donor and H-Bond acceptor area) were presented by sodium acetate and citric acid, respectively. This fact is related to the high acceptor capacity of the H-bonds of these molecules. Instead, Glycine and 1,4-butanediol showed a notable peak in the non-polar region, corresponding to the carbon chain. In general, some relevant differences were observed in the affinity behavior of HBAs and HBDs, which depend on the molecules' molecular structure.

The activity coefficient at infinite dilution ($\ln\gamma\infty$) of two anthocyanin model molecules (Malvidin-3-*O*-glucoside and Peonidin-3,5-*O*-diglucoside) for the combinations of 29 HBA and 59 HBD totalizing 1711 eutectic mixtures are represented in Fig. 1 and Table S6. The horizontal

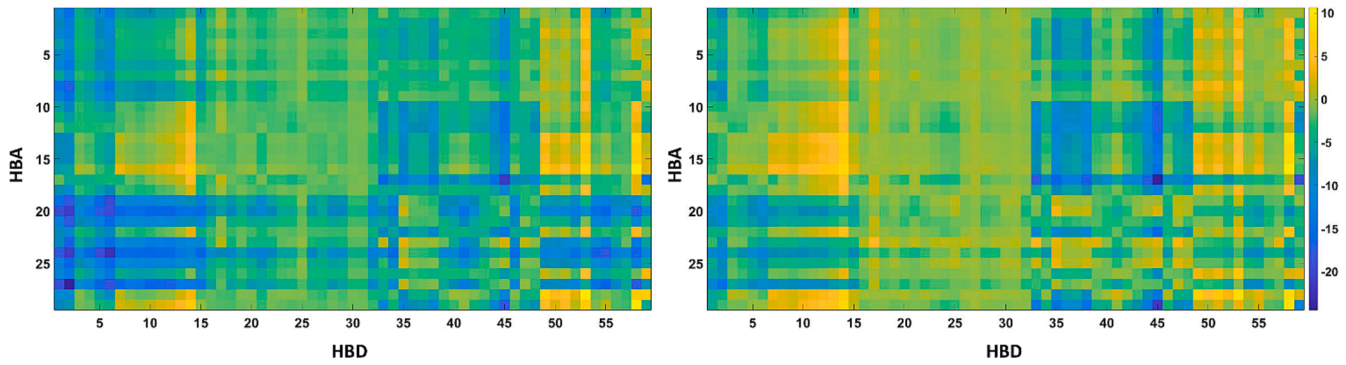

Fig. 1. The activity coefficients at infinite dilution (ln$\gamma\infty$) of Malvidin-3-*O*-glucoside (left) and Peonidin-3,5-*O*-diglucoside (right) in eutectic solvents (1:2) at 308.15 K.

axis represents the HBD in each graph, and the vertical axis represents the HBA. The lower value of ln$\gamma\infty$ represents the greater solvating capacity of the solvent (Huggins, 1951). Fig. 1 shows that the eutectic solvent with the highest dissolution capacity to anthocyanins model molecules is located in the blue areas and low dissolution capacity in the yellow areas. As it can be seen, the trends obtained for the two anthocyanin models are similar, choline chloride, nicotinamide, and sodium acetate being the HBAs with the highest dissolution potential when combined with polyalcohol's (glycerol, ethylene glycol, 1,2-propanol, 1,4-butanediol, 1,6-Hexanediol) or carboxylic acids (citric, acetic, and lactic, formic) as HBDs.

On the other hand, the eutectic solvents formed by sugars (xylitol, sorbitol, and sucrose) and fatty acids (octanoic acid, nonanoic acid) have the highest value of ln$\gamma\infty$ and, consequently, the lowest dissolution capacity. With this approach, it was possible to carry out a rapid qualitative assessment of solute solubility without experimental tests. Additionally, although cholinium chloride-based eutectic solvents have a remarkable extraction performance to recover many phenolic compounds, like anthocyanins (Vannuchi et al., 2022), tannins (Neto et al., 2020), coumarins (Wang et al., 2020), are considered environmentally friendly and biodegradable, they do not display equally health benefits. This was the reason to opt for not using cholinium-chloride-based eutectic solvents in the set to be experimentally tested. In this work, we highlighted the use of eutectic solvents with potential health benefits, such as those based on vitamins.

Based on the trends obtained with the COSMO-RS predictions, 54 different aqueous solutions of eutectic solvents were tentatively prepared using 15 % water and an HBA:HBD molar ratio fixed at 1:2 (Fig. 3). However, only 35 eutectic solvents were applied to extract anthocyanins from grape pomace by UAE-bath ($R_{(S/L)}$ 0.05 $g.mL^{-1}$ for 120 min) since those were the ones becoming liquid at these conditions. Despite water and ethanol (acidified or not) being considered excellent solvents (Prat et al., 2015), their performance in extracting anthocyanins was the worst (extraction efficiency ~6–7 $mg_{anthocyanins}.g^{-1}_{biomass}$) (Fig. 2). In general, and contrarily to the results obtained for the conventional solvents, the eutectic mixtures demonstrated similar or higher (almost the double) extraction ability. The results obtained in Fig. 2 show that the best solvents to extract the anthocyanins are the

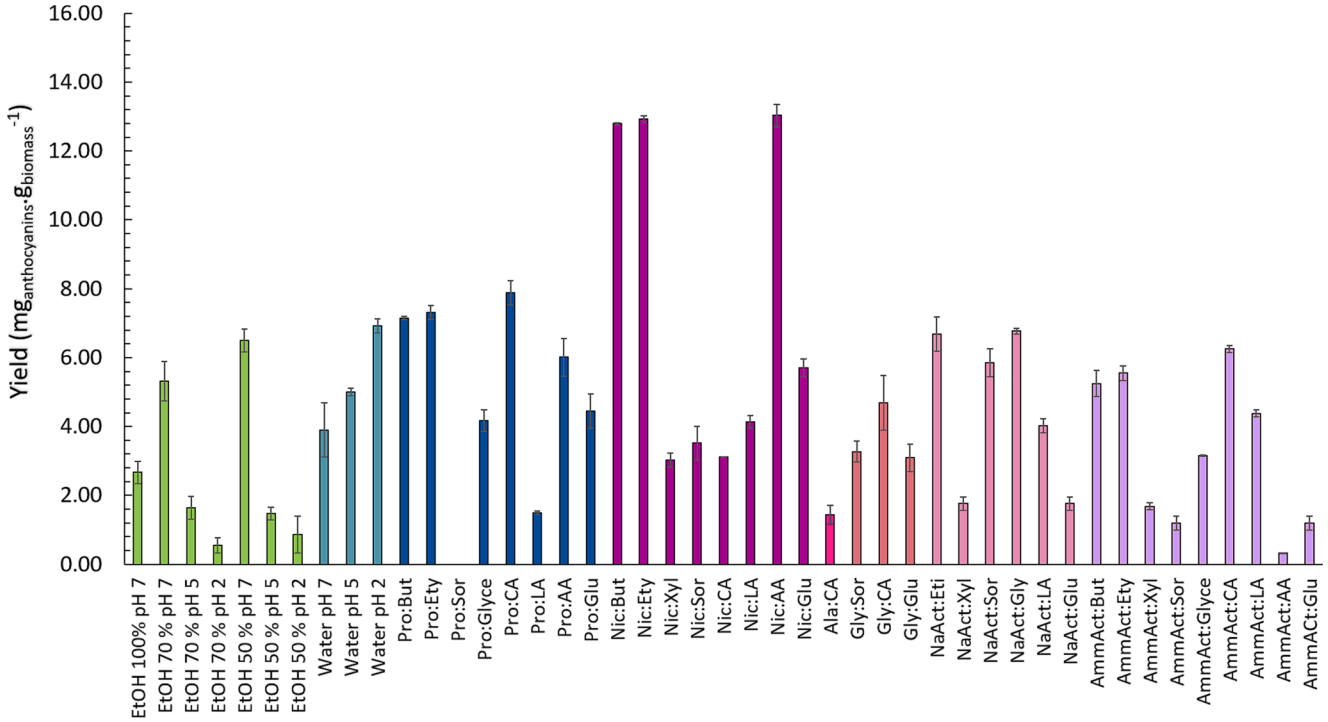

Fig. 2. Screening of aqueous solutions of different eutectic solvents on the extraction of anthocyanins from grape pomace by UAE (135 W, $R_{(S/L)}$ 0.05 $g.mL^{-1}$ for 120 min). The yields of extraction obtained for water and ethanol, used as controls (pH 2, 5, and 7), are also presented.

nicotinamide-based eutectic solvents, mainly Nic:But, Nic:Ety, and Nic:AA, with extraction yields around 13 $mg_{anthocyanins}.g^{-1}_{biomass}$. Nicotinamide is a form of vitamin B3, also known as niacinamide or nicotinic acid amide, which has a high anti-inflammatory effect, mainly when used to treat acne, atopic dermatitis, rosaceae, and other inflammatory skin conditions. Furthermore, when ingested in specific amounts, nicotinamide prevents non-melanoma skin cancer (Rolfe, 2014). Thus, associating an extract rich in anthocyanins and nicotinamide seems to be an excellent system for envisioning cosmetic and food applications. Although promising results were obtained for Nic:But, Nic:Ety, and Nic:AA, only the eutectic solvent-based in acetic acid as HBD was able to guarantee the best pH conditions (optimum pH between 3 and 3.5) for the color maintenance (Table S1).

An optimization study was conducted with the most appropriate eutectic solvent to maximize its extraction capacity. For that, the solvent composition (molar ratio: 1:1, 1:3, 2:1 with 15 % water each) was investigated, using the same operational conditions fixed before (UAE-bath at $R_{(S/L)}$ 0.05 for 120 min). Additionally, aqueous solutions of the starting materials, nicotinamide and acetic acid (500 mM) were tested to investigate the relevance of using the eutectic solvent instead of the starting materials. As depicted in Fig. S6, the best molar ratio was 1:1 (ANOVA $p < 0.05$), with an extraction yield of 16.2 ± 0.9 $mg_{anthocyanins}.g^{-1}_{biomass}$. It is also possible to note that the aqueous solution of acetic acid presented worst results than nicotinamide and the eutectic solvent at different molar ratios. The results suggest an effect of synergism between the nicotinamide and acetic acid, allowing excellent extraction performance.

The COSMO-RS predictions reveal that the addition of water contributes to the increase the dissolution in the slightly diluted region (0.1–0.4) (Fig. S7). Still, for fractions higher than 0.5, the addition of water demonstrates a negative influence, decreasing the power of the solvent, which is corroborated by the experimental data. This behavior may be related to the fact that the system, with increasing water content, is changing from a hydrated eutectic solvent to an aqueous solution of eutectic precursors with significant differences in terms of capacity for the dissolution of anthocyanin. Indeed, the eutectic solvents' solubilization and extraction capacity may be correlated with molecular interactions between extract/solute and solvent. This aspect can be assessed by studying the molecular structure of the solvents and solutes (target compounds) by evaluating the sigma profiles of molecules (Cao et al., 2019).

After the preliminary solvent screening, the UAE-bath (135 W) was replaced by a UAE-probe (operational capacity between 200 and 800 W), aiming to reduce the extraction time (120 min). The ultrasonic power was studied at 160, 240, 320, and 400 W; the results are depicted in Fig. S8. Moreover, the temperature variation during the extraction procedure was also recorded, considering the ultrasonic power effect on temperature and the thermo-sensitivity nature of anthocyanins. As expected, the potency of 160 W promoted both the lowest extraction yield (3.3 ± 0.1 $mg_{anthocyanins}.g^{-1}_{biomass}$) and the lowest temperature variation ($\Delta T = 33$ °C), even compared to the extraction efficiency of the screening assay. However, at 240 W, the extraction yield increased to 10 ± 2 $mg_{anthocyanins}.g^{-1}_{biomass}$ ($\Delta T = 73$ °C), representing an extraction yield statistically equivalent to the one obtained at 320 W (11 ± 2 $mg_{anthocyanins}.g^{-1}_{biomass}$, $\Delta T = 91$ °C). For 400 W, the extraction yield diminished to 8.4 ± 0.7 $mg_{anthocyanins}.g^{-1}_{biomass}$ with $\Delta T = 96$ °C, suggesting that powers higher than 320 W are not a good strategy to perform the extraction. Thus, since higher powers demand more energy expenditure and, consequently, higher operational costs, and there was no statistical difference between extractions performed at 240 and 320 W (ANOVA; $p > 0.05$), the potency of 240 W was selected.

3.3. Optimization of the solid–liquid extraction step

After selecting the best solvent (Nic:AA), the molar ratio (1:1) and mechanical approach (UAE-probe), the optimization of the solid–liquid ratio ($R_{(S/L)}$), water content (wt%), and static time (t_{sta}, i.e. biomass/solvent contact without any stirring force) was performed – Table S2. Thus, the extraction process was optimized using 5 min as dynamic time (i.e. when ultrasound energy is applied in the process). The yield of extraction of anthocyanins was the dependent variable guiding the predictive model represented by Eq. (3). The yield of extraction of each assay performed in the CCRD planning is shown in Table S2. A total of 20 assays/extractions were performed following the CCRD matrix's stipulated levels (8 linear points, 6 axial points, and 6 central points). According to Eq. (3) (considered a high-predictive model), all the variables tested had statistical relevance and helped define the predictive model at 95 % (p-value < 0.05) (Fig. S9). However, no interaction between the variables was identified.

$$\left(\boldsymbol{Y}_{\boldsymbol{anthocyaninsyield}}\right) = 17.88 + 1.46(\boldsymbol{x}_1) - 3.30(\boldsymbol{x}_1)^2 + 2.68(\boldsymbol{x}_2) - 2.63(\boldsymbol{x}_2)^2 + 1.23(\boldsymbol{x}_3) - 3.23(\boldsymbol{x}_3)^2 \quad (3)$$

Thus, interpreting the predictive model depicted in Fig. 3, the optimum operational conditions chosen to follow the process were: $R_{(S/L)}$ 0.03, t_{sta} 25 min, and wt% 40 %. Then, the model was validated by performing three independent extractions in the optimum operational conditions. The model' accuracy and precision (Eq. (3)) were checked by comparing the experimental and predicted data (Table S7 and Fig. S10). As a last step of optimization, the time of extraction was studied by applying the optimum conditions previously defined, where it was concluded that, instead of the 5 min initially used in the optimization assays, 4 min was enough to promote the extraction (Fig. S11), obtaining even higher yields of extraction (21 ± 1 $mg_{anthocyanins}.g^{-1}_{biomass}$), probably caused by the slight temperature increase from the ultrasound cavitation (Gadioli Tarone et al., 2021).

After optimization, the yields of extraction of the alternative (eutectic solvent combined with UAE) and conventional (with water or ethanol) methods were compared (Fig. S12). The results indicate that the eutectic solvent-based process is the most efficient, with an extraction yield higher by 2.5-fold. In addition, the data also shows the need for the eutectic solvent instead of just water or ethanol. Otherwise, the yields obtained were lower (2.93 and 3.30 times lower considering ethanol and water, respectively).

3.4. Isolating anthocyanins from the eutectic solvent using SPE

As important as developing a feasible extraction step is optimizing the purification and isolation steps to ensure that the final product (the anthocyanin' extract) meets the necessary demands considering production costs and final application (Chemat et al., 2020). After optimizing the solid–liquid extraction step, it was attempted to separate the anthocyanins from the eutectic solvent, enabling solvent recycling and reuse in other extraction' cycles. This is an essential strategy to address the concerns associated with Circular Economy and responsible consumption and industrial production (SDG #12) (Clark et al., 2016; Erythropel et al., 2018). However, when the solvent applied is designed to be safe (i.e., devoid of toxicity; and the application envisioned does not require a high purity for the extract), the product obtained after the solid–liquid extraction may be adequate for further use, saving costs of

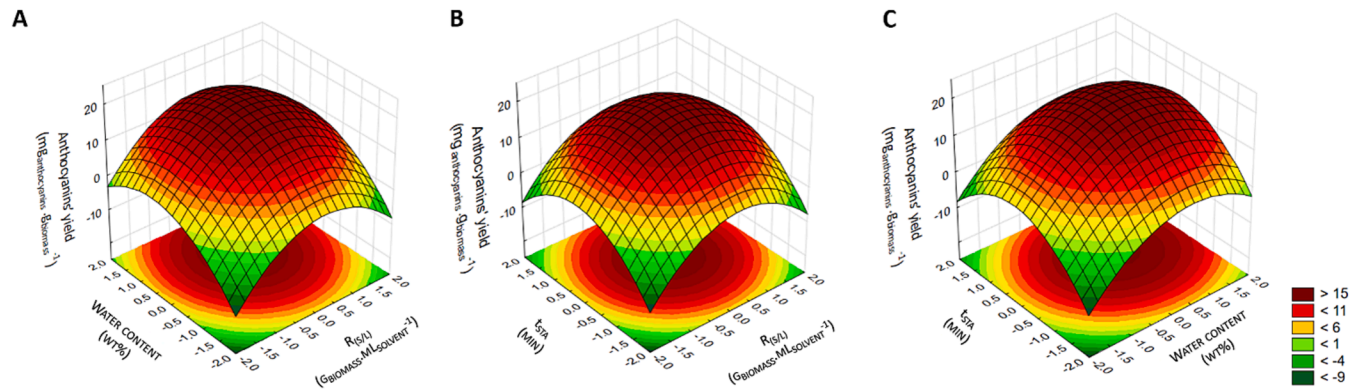

Fig. 3. Response surface plots obtained from the CCRD predictive model for anthocyanins' extraction yield, considering $R_{(S/L)}$ ($g_{biomass}.mL_{solvent}^{-1}$), t_{sta} (min), and wt% (%) as independent variables. The combination between the independent variables was performed 2 by 2 as follows: wt% (%) vs $R_{(S/L)}$ (A); t_{sta} vs $R_{(S/L)}$ (B); t_{sta} vs wt% (%) (C).

energy and raw materials usually required to carry out the polishing step (de Souza Mesquita et al., 2021). Frequently, three methods are employed to separate the eutectic solvents from the target compounds, namely, (i) liquid–liquid extraction using an additional solvent, (ii) an antisolvent with different chemical characteristics from those initially applied in the extraction process, and (iii) a solid-phase extraction, performed using resins with high-adsorbent capacity (Grillo et al., 2020). Despite the anthocyanins being considered hydrophilic molecules, their chemical structure also has a significant hydrophobic part (as shown in Fig. S4), making the use of SPE with a hydrophobic adsorbent an excellent alternative to isolating the anthocyanins from the eutectic solvent.

In this study, after loading the anthocyanin extract into the C_{18}, 30 mL of water was added to the colored adsorbent, enabling the recovery of 92 ± 4 (%) of eutectic solvents, which can be reused in new extraction processes. Subsequently, when 30 mL of ethanol 50 % (v/v) is added to the pigmented C_{18} resin (already free of eutectic solvent), 100 % of the anthocyanins are recovered. So, after recovering the colorants from the adsorbent material, the resin recyclability was addressed to mitigate the operational costs of the process once an industrial application is envisioned. The study of the recyclability of the C_{18} material was conducted to monitor the recycled resin's capacity to adsorb a new anthocyanin extract. In Fig. S13, we observe that after the initial cycle (fresh – 100 % recovery), the same resin can be reused up to 8 new cycles [maximum possible to achieve, since in cycle 9 the recovery rate drops to 35.1 ± 0.2 (%)] with an average recovery rate of 96 ± 10 (%), calculated as the average between cycle 1–8. In the end, only 3.3 % of the eutectic solvent remained in the final anthocyanin' extract and a total of 4.8 % in the C_{18} resin (after 9 cycles).

3.5. Anthocyanins' thermal stability – load anthocyanins in SiO_2

One of the consequences of anthocyanins degradation is their color change, which is usually associated with alterations in their biological potential (Murador et al., 2019). Thus, it is imperative to search for stabilization strategies to guarantee their successful application. It is well known that some degradation reactions may happen even at lower temperatures when a colorant is maintained in a liquid state (Oancea, 2021), and therefore, low temperatures (<0 °C), with higher energetic impacts, are required to store the colorant correctly. Our first step was to investigate the thermal stability of anthocyanins-rich extract obtained from the solid–liquid extraction step at three temperatures, 55 °C, 75 °C, and 95 °C. The extracts obtained from the extraction with the aqueous solution of Nic:AA, ethanol (100 % v/v) and pure water were analyzed by monitoring the anthocyanins' concentration with time. Based on the data and, independently of the temperature setpoint, the anthocyanins degradation followed a first order kinetics (semilog-plot fit, R2 > 0.9) (Fig. S14). Table 1 shows the kinetic parameters calculated using the fitted data from the linear model. As expected, and independently of the extraction solvent, the higher temperature leads to a more significant decrease in the anthocyanin half-life time. This decrease is smaller for the extracts produced by the eutectic solvent, which is more significant for extracts obtained with ethanol (Table 1). These results are also confirmed by the kinetic parameters determined. For example, at 55 °C, using the eutectic solvent allows increasing the half-life time of anthocyanins (from 5.77 h using ethanol to 9.62 h using water and to 38.51 h using the alternative solvent). Although less pronounced, the same trend is observed at 75 °C and 95 °C. This trend reflects the highest thermal activation energy obtained for the colorants extracted with the eutectic solvent (76.50 $kJ.mol^{-1}$). However, and despite the half-life time data, the thermal activation energy of the dyes extracted with water was lower compared to those with ethanol. This aspect demonstrates that, although water promotes a better half-life time than ethanol, lower initial energy caused by heating is sufficient to start the degradation kinetics of the colorants.

Despite the dual role of the eutectic solvent (as a solvent and as a stabilizing agent) for anthocyanins, depending on the final application, the half-life time of the colorants recovered from the grape pomace may still require improvements. One of the ways of doing that is to pass them from a liquid to a solid state (Cai et al., 2019). This work investigated the approach of loading the anthocyanins obtained after SPE into a highly adsorbent material constituted mainly of SiO2. The choice was justified

Table 1
Influence of the extraction solvent (water, ethanol, and eutectic solvent) on the anthocyanins' thermal stability (55 °C, 75 °C, and 95 °C).

Extraction solvent	55 °C		75 °C		95 °C		Ea ($kJ.mol^{-1}$)
	K_d (min^{-1})	$t_{(1/2)}$ (h)	K_d (min^{-1})	$t_{(1/2)}$ (h)	K_d (min^{-1})	$t_{(1/2)}$ (h)	
Water (pH 3)	0.0012	9.62	0.0023	5.02	0.0114	1.04	55.93
Ethanol (pH 3)	0.002	5.77	0.0043	2.69	0.0238	0.48	61.58
Eutectic solvent (pH 3)*	0.0003	38.51	0.0018	6.42	0.0063	1.83	76.50

K_d = Thermal degradation constant (min^{-1}); $t_{(1/2)}$ = Half-life time (h); Ea = Thermal activation energy.
* Extract obtained under the optimum operational conditions.

since this adsorbent is widely applied in several fields, especially food and as excipients in the pharmaceutical and cosmetic sectors. Additionally, silica-based materials are often used for biomedical applications, primarily due to their inert chemical composition and non-toxicity (Chen et al., 2018). Since the SiO_2 is white, no color damage was observed after adding the extract. Briefly, the liquid extract of anthocyanins obtained after extraction with Nic:AA was added to the SiO_2 under manual shaking until a purple powder was obtained. After that, the purple silica was submitted to the highest temperature tested for the liquid extracts, 95 °C, and the concentration of anthocyanins was monitored over time. This temperature was selected to represent the worst-case scenario previously investigated for the extracts obtained after the solid-phase extraction step. As described for the liquid extracts, a linear model of anthocyanins' degradation was obtained after being loaded in the silicon material (95 °C, R2 = 0.9793) – Fig. S15. However, the half-life time achieved was 3.5 times (6.42 h) higher when compared to the liquid eutectic solvent-anthocyanin extract when heated at 95 °C (1.83 h). Besides, the water activity of the product (SiO_2 + pigments) was 0.74 ± 0.00. This value was acquired immediately after loading the pigments and is not satisfactory, concerning that some microorganisms can grow in this condition (Allen, 2018). An alternative, which allows the reduction of the a_w, without compromising the original color of the pigments (and consequently its application), is storing the product for 120 min at 50 °C, which possibilities a lower a_w (0.58 ± 0.00) with a same initial pigments concentration. As discussed by (Lavelli et al., 2017), a_w levels below 0.85 aid in preserving the material and consequently increasing its shelf-life. Therefore, applying the SiO_2 as a solid host to store anthocyanins could be a more efficient alternative to replace long microencapsulation approaches like lyophilization (which demands substantial energy costs and long-processing times) or spray-drying (which often causes the browning of the anthocyanins) (Mohammadalinejhad & Kurek, 2021).

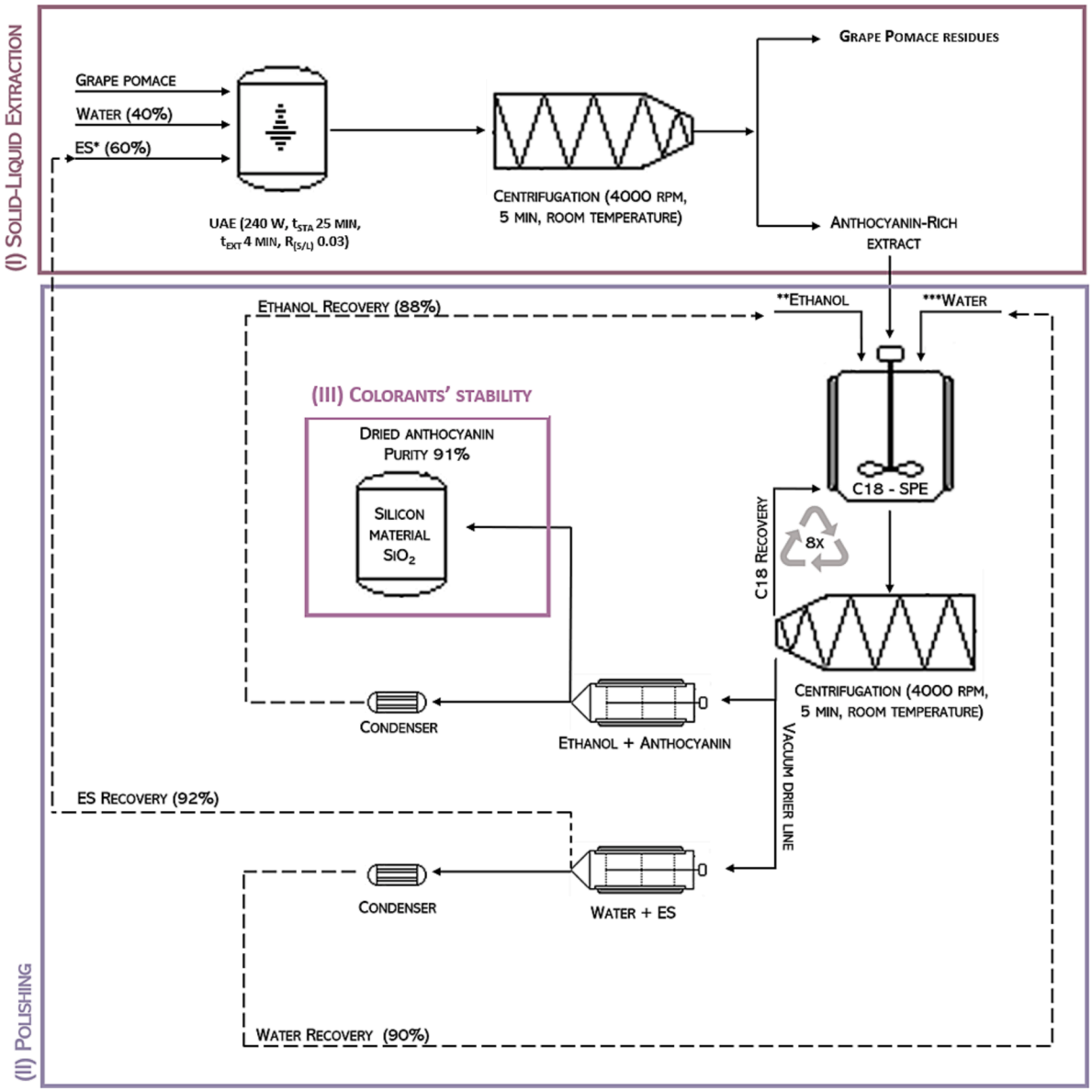

Fig. 4. Schematic representation of the integrated process: Step I – solid–liquid extraction by ultrasound-assisted extraction (UAE), Step II – separation of colorants from eutectic solvent through Solid-Phase Extraction (SPE – with C_{18} adsorbent material); and Step III – loading in SiO_2 to stabilization of the anthocyanins (drying without energy dependence). *Eutectic solvent (ES) formed with nicotinamide: acetic acid (1:1, 40% of water). **Ethanol used in SPE; ***Water used in SPE. Dashed lines are hypothetical routes that were not experimentally studied in this work. Abbreviations: t_{STA}: static time (min), t_{EXT}: extraction time (min), $R_{(S/L)}$: Solid-liquid ratio.

These results open new perspectives concerning storing natural colorants without spending (too much) energy. Besides, the colorants loaded in the SiO_2 material can be used directly in several applications. For example, this material can be used to color other solutions, or it can also be applied as part of a cosmetic or food formulation.

Fig. 4 represents the final process diagram. All materials, especially the C_{18} resin with a high cost (around $2 *per* g) compared to the other raw materials, were recycled, optimizing the use of the raw materials and consequently lowering the economic impact of the developed process. The final process is divided into three main steps, (i) solid–liquid extraction, (ii) polishing, and (iii) colorants' stability. As depicted in Fig. 4, two options may be followed depending on the demands of the application envisioned, and these are the use of the colorants purified (meaning after step ii) or the extract rich in both anthocyanins and nicotinamide (vitamin B_3) (after step i). In this latest scenario, the extract obtained after the solid–liquid extraction can be subjected to vacuum evaporation to eliminate water and acetic acid, and then obtaining a rich extract in anthocyanins and nicotinamide (vitamin B_3), a very desirable product to cosmetic sectors (high biological activity summing the nicotinamide and anthocyanin potential together).

3.6. Environmental analysis.

Table S8 presents the total environmental impacts associated with the four scenarios analyzed, and Fig. 5 illustrates the relative contributions to those impacts. The comparison of Scenario 1 (which includes both extraction and polishing with just the recycling of the eutectic solvent) with Scenario 2 (which differs from Scenario 1 because it includes additional recycling of ethanol, water, and C_{18}) demonstrates that recycling of ethanol, water, and C_{18} leads to a reduction of the total impacts ranging from 23 % for global warming to 69 % for mineral resource scarcity. In global warming, mineral resource scarcity and fossil resource scarcity are mainly due to C_{18} savings, whereas for ozone formation and terrestrial acidification, the leading cause is ethanol saving. Ethanol is assumed to be produced from sugar cane. Hence, the importance in these two impact categories relates mainly to sugar cane cultivation, in particular emissions from fertilizer application and straw burning in the field.

The loading with food-grade silica (SiO_2) evaluated in Scenario 3 increases impacts concerning Scenario 2 by only 0.01–0.06 % because of the relatively small impacts of manufacturing the SiO_2. Comparing the effects of Scenarios 3 and 4 (where spray drying is used instead of loading with food-grade silica) highlights that loading with food-grade silica is more environmentally sustainable than spray drying (high-energy dependence). Indeed, the impacts of Scenario 4 are 3 % (in terrestrial acidification) to 53 % (in fossil resource scarcity) higher than those of Scenario 3. The main reason for this difference relates to heat consumption during spray drying obtained from natural gas.

Electricity consumption during polishing is essential to most of the impact categories, particularly relevant in global warming and fossil fuel scarcity. However, it is noteworthy that electricity consumption was determined for the laboratory-scale process and, thus, could be potentially much decreased at an industrial scale. Besides, the impacts were estimated considering electricity production in the Brazilian grid, which incorporates electricity produced based on fossil fuels (natural gas, fuel oil, and hard coal). If the electricity production had been calculated based on impacts from photovoltaic electricity, the impacts would decrease significantly. However, the relative ranking of scenarios would remain the same because electricity consumption during polishing is equal in all scenarios.

3.7. Economic analysis

In this work, since all the raw materials are recycled in new extraction cycles, the economic impact of each operation was reduced. For this analysis, the C_{18} adsorbent was recycled nine times. In Table S9, the costs of each raw material are presented and normalized for 1 g of grape pomace. From the results obtained, the higher costs associated with the final process are represented by the cost of the C_{18} ($ 7.29) followed by the eutectic solvent, totalizing 89 % and 6.3 % of the total costs, respectively. These results highlight the need to recycle both materials. In the case of the eutectic solvent, considering that *at least* circa 92 % is recycled and that each new cycle of extraction only requires around 8 % of fresh solvent, it is possible to say that each new cycle only represents a cost increment of $ 0.04 (Table S9). UAE-mediated extractions are recognized as energy-demanding techniques. However, its impact in this process was reduced by optimizing the process conditions, with the total energy cost of only $ 0.24 (Table S9).

When considering the optimum yield of 21 ± 1 $mg_{anthocyanins} \cdot g_{biomass}^{-1}$ extracted in the process design, the cost of goods *per* mg of extracted

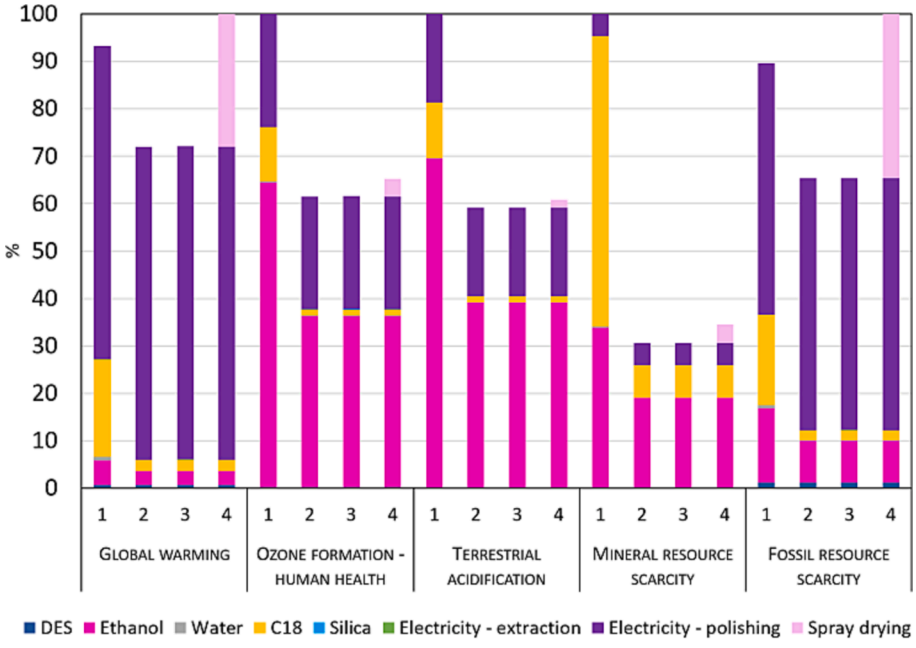

Fig. 5. The relative contribution of the inputs for the LCA results obtained in Scenarios 1, 2, 3, and 4.

anthocyanin ($CoG.mg^{-1}$) in the first extraction cycle was $ 0.38 (calculated according to Eq. (1)). However, since the raw materials are recycled, especially the C_{18} adsorbent material, the $CoG.mg^{-1}$ decreases proportionally (Table S9). In the second successive extraction, we achieved double the yield of anthocyanins. However, the extraction cost decreased to $ 6.88, representing a $CoG.mg^{-1}$ of $ 0.35, which decreased by 44.7 % in the ninth cycle ($CoG.mg^{-1}$ is $ 0.21) (Table S9).

The return ($\$.g_{biomass}^{-1}$) obtained in each extraction cycle was calculated (Eq. (2)). The product market price was estimated *per* mg of extracted anthocyanin (based on the price of anthocyanin extracts already commercialized). However, this value of $ 0.32 is underestimated due to the differences in the solvent used and purity obtained in this study (91 %). Thus, to create a more realistic simulation, the market price and the α scenarios (multiplicator factor; α = 0.1, 1, and 10) were varied, increasing, and decreasing by 10-fold. In Fig. S16, if the market price is ten times lower than the actual market price ($ 0.032), none of the α scenarios will guarantee profit. Similarly, the raw materials' recyclability is not justified when the actual market price for conventional extracts is considered ($ 0.32), and α is 10 (raw material costing 10-fold higher than the current value). Otherwise, when α is in line with the actual production costs (α = 1) or lower (α = 0.1; cheaper than the current one), the market price of $ 0.32 means profit. In the end, when the market price of the extracted colorants is 10-fold higher than those initially proposed, which is acceptable considering the beneficial potential of an extract rich in *anthocyanins* + *nicotinamide*, all α scenarios are positive, representing a win–win relation between recyclability and profits. The latest scenario will represent the production of purer anthocyanins with high stability like those produced with the process developed in this work.

4. Conclusions

In this work, anthocyanins were successfully recovered from grape pomace using aqueous solutions of the eutectic solvent composed of nicotinamide and acetic acid. The developed process extracted high amounts of anthocyanins (maximum yield of 21 ± 1 $mg_{anthocyanins}.g_{biomass}^{-1}$) with low environmental impacts and economic costs compared with those performed using conventional solvents. Moreover, this approach also improved the colorants' stability at high temperatures. When the colorants were loaded in a silicon material approved for use in the pharmaceutical and food sector was further improved.

CRediT authorship contribution statement

Leonardo M. de Souza Mesquita: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision. **Filipe H.B. Sosa:** Methodology, Formal analysis, Investigation. **Letícia S. Contieri:** Methodology, Formal analysis, Investigation. **Priscilla R. Marques:** Methodology, Investigation, Resources. **Juliane Viganó:** Methodology, Investigation. **João A.P. Coutinho:** Resources, Data curation, Methodology, Supervision. **Ana C.R.V. Dias:** Formal analysis, Investigation. **Sónia P.M. Ventura:** Resources, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration. **Maurício A. Rostagno:** Conceptualization, Resources, Visualization, Supervision, Project administration, Funding acquisition, Investigation, Writing - original draft.

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.

Data availability

No data was used for the research described in the article.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2022.135093.

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