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Research article

# Eco-friendly solvent-based liquid-liquid extraction of phenolic acids from winery wastewater streams

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A B S T R A C T

This study proposes liquid-liquid extraction (LLE) for the recovery of phenolic acids from winery wastewater replacing common volatile organic compounds (VOCs) with environmentally friendly solvents. On one hand, terpenes (α-pinene and p-cymene) and terpenoids (eucalyptol and linalool) were selected as green solvents and compared to common VOCs (ethyl acetate or 1-butanol). On the other hand, gallic acid (GA), vanillic acid (VA), syringic acid (SA) and caffeic acid (CA) were selected as phenolic acids to be recovered. The extraction performance was evaluated under different operation conditions: solvent-to-feed ratio, initial concentration of phenolic acids and temperature.

This work also evaluated the back-extraction whole process global recovery and solvent regeneration, by means of aqueous NaOH solution. Eucalyptol has shown the highest overall global extraction performance (21.07 % for GA, 93.21 % for VA, 78.79 % for SA, and 80.57 % for CA) and lower water solubility compared to the best performing VOC solvent (1-butanol). Therefore, eucalyptol can be a potential eco-friendly solvent to replace VOCs for sustainable phenolic acid recovery from winery wastewater. Finally, to ensure a clean water stream after the LLE, the traces of solvent were completely removed by electrooxidation with boron-doped diamond anode at a current density of 422.54 A/m$^2$.

## 1. Introduction

The agrifood industry faces the challenge of satisfying the growing need for food via sustainable, eco-friendly, and cost-effective methods. Food loss is estimated to be one third of the edible parts (Food and Agriculture Organization of the United Nations, 2017), yielding detrimental effects on the economy and causing considerable wastage of resources and pollution, for instance, 24% of the entire fresh water for crop cultivation and 23% of global fertilizer usage (Kummu et al., 2012), as well as to 3.3 gigatonnes of $CO_2$ emission (Food and Agriculture Organization of the United Nations, 2013). Therefore, the agri-food sector must progress towards zero waste processes (Irfanoglu et al., 2014). Complete waste valorization not only contributes to reducing waste generation, but also to decreasing natural resource consumption. In this regard, the wine industry stands out for its significant impact on society, the global economy and environment. Worldwide wine production in 2022 amounted to 258 million litres resulting from the processing of 33.6 million tonnes of wine grapes (OIV, 2023). The processing of one tonne of wine grapes produces 0.13 t of pomace, 0.06 t of lees, 0.03 t of stems, and 1.65 m$^3$ of wastewater (Oliveira and Duarte, 2016). This output raises environmental and economic concerns due to the seasonal and highly pollutant nature of this type of waste (Albergamo et al., 2020; Bustamante et al., 2008). However, waste generated by the winery industry and its by-products contain abundant bioactive compounds such as polyphenols, which are characterized by the presence of more than one phenolic group per molecule and have antioxidant, anticancer, antihypertensive and anticholesterol properties (Barba et al., 2016; Cassano et al., 2017; Kumar et al., 2017; Montenegro-Landívar et al., 2021). However, they also have the potential to cause microbial dormancy. Thus, prior to biological treatment, it is necessary to remove polyphenols from wastewater (Nayak et al., 2018; Rosenkranz et al., 2013). Polyphenol recovery is of great interest due to its high value in industries such as pharmaceuticals, cosmetics and food (Castro;Muñoz et al., 2016). This is evidenced by the size of the market, which reached $1.6 billion in 2021 and is expected to grow at a compound annual growth rate of 7.4% between 2022 and 2030 (Grand View Research, 2023).

In order to achieve the valorization of polyphenols, liquid-liquid

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extraction (LLE) has been considered as an alternative process due to its economy, simplicity and feasibility in terms of operating conditions and applicability to dilute streams (Silva et al., 2018). Additionally, LLE has been reported for heat sensitive products such as polyphenols (Silva et al., 2018).

Solvent selection is key to LLE processes. For polyphenol extraction, the solvent must provide selectivity, extraction capacity, high solute mass transfer ratio (Silva et al., 2018), hydrophobicity and low water solubility to avoid solvent losses and water pollution, which is undesirable from a wastewater treatment perspective (Larriba et al., 2016). Volatile organic compounds (VOCs) are frequently used to extract polyphenolic compounds from aqueous matrices, with ethyl acetate serving as a reference solvent for both olive mill wastewater (Gueboudji et al., 2021; Kalogerakis et al., 2013; Larriba et al., 2016; Posadino et al., 2021) and winery aqueous streams (Cañadas et al., 2021a, 2022). For example, literature of LLE with ethyl acetate showed 57 % extraction of phenolics concentration from real olive mill wastewater (6 g/L) (Kalogerakis et al., 2013); 74 % and 94 % extraction of hydroxytyrosol from synthetic olive mill wastewater (1 g/L) at a solvent-to-feed ratio (S/F) of 1.0 and 5.0, respectively (Larriba et al., 2016); 64 %–100 % extraction of phenolic acids from simulated agri-food wastewater (50–500 mg/L) at S/F of 1.0 (Cañadas et al., 2021a). In addition, LLE with ethyl acetate at a S/F of 1.0 was reported to extract gallic acid from both synthetic winery wastewater prepared from diluted wine and synthetic solution, both of 2350 mg/L, achieving recoveries of 48 % and 92 %, respectively (Cañadas et al., 2022). These works show the potential of LLE due to the high extraction yields of phenolic compounds from agri-food wastewater with a simple and well-known process. Nonetheless, VOCs have adverse qualities such as low volatility, flammability, petrochemical origins, non-renewability, and atmospheric accumulation. These factors demonstrate the need to replace VOCs, reduce their use or establish alternative sustainable techniques for their production. In this framework, studies have indicated that bioethanol processes can be used to produce ethyl acetate Clark et al. (2015) and 1-butanol (Landau et al. (2021); Wang et al. (2019)). In addition, many efforts have been made to replace conventional solvents with more environmentally friendly solvents for extraction processes on agrifood wastewaters such as ionic liquids (Fan et al., 2017a, 2017b; Larriba et al., 2016), deep eutectic solvents (Cañadas et al., 2021b; Rodríguez-Llorente et al., 2023b) and bio-based solvents like 2-methyltetrahydrofurane, cyclopentyl methyl ether (Cañadas et al., 2021a, 2022), terpenes and terpenoids (Rodríguez-Llorente et al., 2023b).

Terpenes, which are hydrocarbon solvents consisting of isoprene units, are characterized by their hydrophobic nature. They are obtained from biomass resources and are therefore considered renewable solvents with minimal environmental and health impacts (Boutekedjiret et al., 2014; Zwenger and Basu, 2008). Terpenoids are terpenes modified with substituent groups (e.g: hydroxyl groups, oxygen atoms) that are potential alternatives to conventional solvents (Zwenger and Basu, 2008). Among the more than 80,000 terpenes and terpenoids (Christianson, 2017), only a minority number have been studied as polyphenolic extracting agents. For example, limonene, α-pinene, and p-cymene terpenes were reported as effective solvents for extracting compounds from agricultural products (lipids, carotenoids, and aroma compounds) to replace n-hexane (Rodríguez;Llorente et al., 2020a). Eucalyptol has been found to be a successful LLE extraction agent for phenolic compounds (phenol, p-cresol) from both microalgae and water streams (Hamiche et al., 2018; Li et al., 2017). Citral, eugenol, geraniol and linalool for LLE has been tested for the extraction of $C_2$, $C_3$, $C_4$ and $C_5$ acids (Rodríguez;Llorente et al., 2020b). Eucalyptol, citronellol, lavandulol, and geraniol for phenolics contained in olive mill wastewater (tyrosol, catechol and caffeic acid) (Rodríguez-Llorente et al., 2023b). However, the extraction of the main phenolic compounds (gallic, vanillic, syringic, ferulic, protocatechuic, cinnamic acids) from wine industry water streams has only been addressed with limonene (Cañadas et al., 2021a), and eucalyptol, citronellol, lavandulol and geraniol in the case of caffeic acid (Rodríguez-Llorente et al., 2023b), to the authors' knowledge. Due to the limited literature available on the use of terpenes and terpenoids in LLE as extraction agents for main phenolic acids (gallic, vanillic, syringic and caffeic acids) from wine industry water streams, this work is focused on their recovery by means of LLE with terpenes and terpenoids that have been tested in literature for other purposes listed above.

It is worth noting that, although the solvents used in LLE processes for water streams are mainly hydrophobic, to some extent they are soluble in water, leading to water stream contamination. Recently, boron-doped diamond (BDD) anodes have been used in advanced oxidation techniques to degrade organic compounds contained in winery wastewater (Baía et al., 2022; Candia-Onfray et al., 2018; Martínez-Cruz et al., 2020) as well as organics solvents (alcohols and carboxylic acids such as ethanol, 2-propanol, butyric acid and chloroacetic acid) (Cañizares et al., 2008), demonstrating high removal efficiencies. Electrooxidation (EO) with a BDD anode demonstrated superior removal of organic compounds compared to alternative methods such as ozonation and Fenton (Cañizares et al., 2008).

This work aims to recover polyphenols present in synthetic wastewater streams by an LLE process. Given the high concentration of phenolic acids contained in wine industry wastewater (Tapia;Quirós et al., 2022), the recovery of caffeic acid, vanillic acid, syringic acid and gallic acid will be evaluated using VOCs (ethyl acetate and 1-butanol), terpenes (α-pinene and p-cymene) and terpenoids (eucalyptol and linalool) as solvents. In addition, the influence of the S/F, the concentration of phenolic acids in the raw wastewater and the process temperature will be evaluated. To assess the feasibility of this LLE process, tests including solvent regeneration, recovery of phenolic acid from the extract phase, and removal of the solvents present in the wastewater after the LLE by EO will be carried out.

## 2. Materials and methods

### 2.1. Chemical products

The suppliers and properties of the solvents (1-butanol, ethyl acetate, α-pinene, p-cymene, eucalyptol and linalool) and phenolic acids (gallic acid, vanillic acid, syringic acid and caffeic acid) used in this work are shown in Tables S1 and S2, respectively. NaOH pellets (>98.0 % wt) for both solvent regeneration and phenolics recovery and $Na_2SO_4$ (>99.0 % wt) for solvent degradation were acquired from Panreac AppliChem. HR COD Vials K7365 were purchased from Chemetrics. All aqueous solutions were prepared with deionized water (8 μS/cm).

### 2.2. Phenolic acids liquid-liquid extraction (LLE) methodology

Aqueous phenolic acid solutions were prepared by weighing the solid phenolic acids on a Mettler Toledo XS205 balance with a deviation of $\pm 10^{-5}$ g and diluting them in flasks. LLE experiments were performed in 8 mL glass vials by combining 1.5 mL of the prepared aqueous phenolic acid solution with 1.5 mL of the solvent. This method is based on previous LLE works (Ayuso et al., 2023; Cañadas et al., 2021a, 2022; Larriba et al., 2016; Rodríguez-Llorente et al., 2023b). Both the aqueous and organic phases were mutually saturated prior to LLE tests, ensuring the volumetric stability of both phases during LLE due to the mutual solubilities of the water and organic solvents (Cañadas et al., 2022) while avoiding dissolution between the phases. LLE experiments were carried out at the following base operating conditions: a S/F of 1.0, an initial concentration of phenolic acid in the wastewater of 100 mg/L, controlled temperature of 298 K and a stirring speed of 900 rpm (Labnet Vortemp 1500, precision of ±0.1 K) for 4 h to facilitate optimal mixing and equilibrium. The phases were separated using a Labnet Accublock dry bath (precision of ±0.1 K) for 16 h, after which the organic phase (extract) was carefully removed, and samples of the aqueous phase (raffinate) were collected for further analysis.

The influence of operating conditions, except stirring speed and operation time, was independently evaluated at the base operating conditions described and modifying only the one under study: i) S/F: 0.25, 0.5, 1.0, 2.0 and 4.0; ii) initial concentration of phenolic acids in wastewater: 500, 250, 100, 50, 25 and 10 mg/L; and iii) process temperature: 298 K, 308 K and 318 K.

### 2.3. Extraction performance determination

The Orion Aquamate 7100 UV–Vis spectrophotometer (precision of ±0.001 AU) was used to determine the extraction performance (EP) by analyzing the phenolic content of both the stock solutions that simulate the wastewater and the LLE raffinate phase samples, that are related to the non-recovered phenolic acid. For this purpose, wavelength sweeps of standards were performed, determining the maximum absorption wavelength and calibration curves (Fig. S1) for each phenolic acid, detecting gallic acid at 269 nm, vanillic acid at 259 nm, syringic acid at 275 nm and caffeic acid at 324 nm. The extraction performance can be calculated according to Eq. (1):

$$EP\ (\%) = \frac{C_{PA,0}^{aq} - C_{PA}^{aq}}{C_{PA,0}^{aq}} \cdot 100 \tag{Eq. 1}$$

Where $C_{PA,0}^{aq}$ (mg/L) represents the phenolic acid content in the wastewater (initial aqueous phase) before LLE while $C_{PA}^{aq}$ (mg/L) is the phenolic acid content in the raffinate phase after LLE. The reproducibility of the method was studied on triplicate, and standard deviations (SD) were determined according to Eq. (2):

$$SD = \sqrt{\frac{\sum (x - \bar{x})^2}{(n-1)}} \tag{Eq.2}$$

Where x is the value of each sample, $\bar{x}$ is the mean value of the three samples, and n is the number of replicates. In addition, one-factor ANOVA (significance level of $\alpha = 0.05$) followed by a post-hoc Tukey test was carried out to check the results obtained from the study of the influence of the initial concentration of phenolic acids in raw wastewater in the EP.

### 2.4. Phenolic acids recovery and solvent regeneration

To ensure that the process is economical and sustainable, phenolic acid recovery and solvent regeneration were evaluated.

The recovery of phenolic acids can be carried out with a NaOH solution, as high pH values promote the dissociation of hydroxyl and carboxyl groups when their $pK_a$ values (Table S2) are exceeded, leading to a loss of solvent affinity and a back-extraction into the aqueous phase (Fan et al., 2017a, 2017b). However, it is crucial to operate under non-degradative conditions during the back-extraction process as gallic and caffeic acids degrade under basic conditions (Fan et al., 2017b, 2017a; Friedman and Jürgens, 2000). To perform phenolic acids back-extraction, 1,5 mL of LLE extract phases obtained by operating at the base operating conditions (Section 2.2) were mixed with 1.5 mL of $10^{-5}$ M, $10^{-4}$ M or $10^{-3}$ M aqueous NaOH solution. After liquid-liquid equilibrium, samples were taken from the raffinate phase and neutralized with 85% w/w $H_3PO_4$. The phenolic recovery yield or back-extraction performance (BEP) was calculated according to Eq. (3):

$$BEP\ (\%) = \frac{m_{PA}^{aq,NaOH}}{m_{PA}^{O}} \cdot 100 \tag{Eq. 3}$$

Where $m_{PA}^{aq,NaOH}$ is the phenolic acid mass content in the resulting neutralized extract phase sample after NaOH back-extraction determined by UV–Vis spectrophotometry, and $m_{PA}^{O}$ is the phenolic acid mass content in the extract phase obtained after LLE determined by mass balance.

In order to calculate the global recovery (GR), which is the percentage of phenolic acids recovered on the back-extract phase compared to the initial phenolic acids present in the raw wastewater, Eq (4). was employed:

$$GR(\%) = \frac{BEP \cdot EP}{100} \tag{Eq. 4}$$

Although back-extraction of phenolic acids can be used to regenerate the solvent, it is crucial to ensure a complete regeneration of the resulting solvent so it can thus be reused for a new LLE process, which is known as cycle. Some authors have reported the use of 0.1 M NaOH solutions for solvent regeneration to obtain organic solvents free of phenolic compounds, following the same procedure as explained on the back-extraction process (Cañadas et al., 2021a; Larriba et al., 2016). Therefore, after the LLE process at the base operating conditions described in Section 2.2, a 0.1 M NaOH solution was used for solvent regeneration. The solvents selected for this study were the most effective solvents according to LLE results (1-butanol and eucalyptol). To carry out this procedure, 1.5 mL of the organic solvent obtained from an LLE cycle is mixed with 1.5 mL of NaOH solution at base operating conditions given in section 2.2. Following this, it is crucial to ensure that the residual NaOH in the solvent is completely removed for further extraction cycles to be successful. To do this, the solvent was neutralized with 50 μl of 85% w/w $H_3PO_4$, resulting in a ready-to-use solvent (Cañadas et al., 2021a; Larriba et al., 2016).

The LLE experiments were performed in triplicate, and the solvent was regenerated between each cycle with 0.1 M NaOH. The extraction performance in each cycle was determined by Eq. (1) by measuring the raffinate phase obtained after each LLE cycle.

### 2.5. Solvent removal from wastewater streams

Although the chosen solvents are highly hydrophobic, the wastewater was contaminated with them after LLE due to their solubility, as shown in Table S1. To remove the solvent contained in the wastewater, an electrooxidation (EO) process was carried out in galvanostatic mode (applied current densities (j): 422.54 $A/m^2$ and 634.92 $A/m^2$) employing a boron doped diamond (BDD) electrode as anode (100 × 50 × 2 mm) and a stainless steel cathode (120 × 50 × 1.5 mm) separated by 30 mm and both immersed in a 650 mL jacketed batch reactor connected to a thermal bath (Thermo Scientific Haake DC30-K20 Digital Control Bath, 115VAC 60 Hz) to ensure room temperature conditions (298 K). To simulate wastewater conditions after LLE, deionized water was saturated with the best performing solvents (VOC solvent: 65,000 mg/L 1-butanol; terpenoid solvent: 3400 mg/L eucalyptol) at concentrations close to saturation values and $Na_2SO_4$ was added as supporting electrolyte (0.083 M). The solvent degradation was monitored by COD determination using HR COD Vials K7365 and Orion Aquamate 7100 UV–Vis spectrophotometer at 600 nm according to ASTM Standard Method D 1252-06 (American Society for Testing and Materials, 2020).

## 3. Results and discussion

### 3.1. Effect of solvent-to-feed ratio and solvent molecular structure on the extraction performance

To study the phenolic acid extraction capacity of the selected solvents (1-butanol, ethyl acetate, α-pinene, p-cymene, eucalyptol and linalool), volumetric S/F values of 0.25, 0.5, 1.0, 2.0 and 4.0 were evaluated, considering an initial phenolic acid concentration in the wastewater of 100 mg/L and performing the LLE process at 298 K.

The relationship between the extraction performance (EP) of phenolic acids and S/F for the afore-mentioned solvents is illustrated in Fig. 1. The EP data can be found in more detail in Table S3. Firstly, it can be observed that the extraction capacity of the terpene solvents, namely

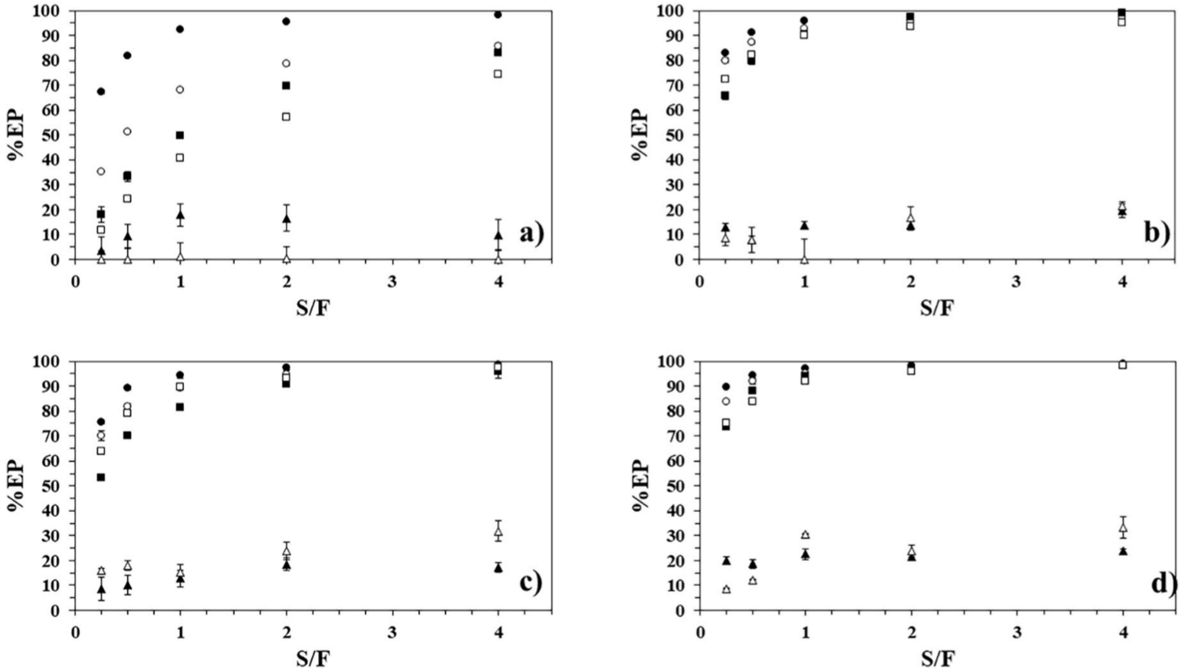

**Fig. 1.** Relation of the extraction performance of phenolic acids a) gallic acid, b) vanillic acid, c) syringic acid, d) caffeic acid with S/F ratio for LLE at process with different solvents: (●) 1-butanol, (○) ethyl acetate, (■) eucalyptol, (□) linalool, (▲) p-cymene, (Δ) α-pinene. Conditions: $[\text{Phenolic acid}]_0$: 100 mg/L; T: 298 K.

α-pinene and p-cymene, is limited over the whole S/F range studied compared to VOCs (1-butanol and ethyl acetate) and terpenoids (eucalyptol and linalool), which show higher EP rates. These results agree with those of Cañadas et al., who unsuccessfully studied the terpene limonene as solvent (Cañadas et al., 2021a). Additionally, Rodríguez-Llorente et al. performed molecular simulations of terpenes and terpenoids for LLE of caffeic acid, catechol and tyrosol from olive mill wastewater, concluding that terpenes without heteroatoms (e.g.: α-pinene, limonene) have low affinity for solutes, while terpenoids (e.g.: eucalyptol, verbenone) show the highest affinities, aligned with the EP trend of this work (Rodríguez-Llorente et al., 2023b). Thus, α-pinene and p-cymene solvents will be excluded in the following studies due to their limited performance for this application.

VOCs and terpenoids show moderate to high EP values in LLE of vanillic acid (65.84–82.99 %), syringic acid (53.1–75.42 %) and caffeic acid (73.71–89.80 %) at the lowest S/F of 0.25. This S/F is related to the low solvent usage, that is a positive aspect considering the large volume of wastewater produced by winery industries (>$10^8$ $m^3$/year) (Flores et al., 2023). The balance between solvent usage and moderate-high EP values can result in S/F of 0.25 as the optimal S/F. However, low-moderate EPs are obtained in LLE of gallic acid: 35.38% with ethyl acetate, 18.07 % with eucalyptol, 11.72 % with linalool and 67.29 % with 1-butanol. As expected, an increase in S/F results in moderate to high EPs, being noticeable at the intermediate S/F of 1.0 for all the phenolic acids. In this context, a relevant improvement in the EP is observed for the gallic acid, which is the most problematic phenolic acid, compared to S/F of 0.25: 92.36 % for 1-butanol, 68.19 % with ethyl acetate, 49.62 % with eucalyptol and 40.89 %. All other phenolic acids show a high EP regardless of the solvent: >90.25 % for vanillic acid, >81.37% for syringic and >91.87% for caffeic acid. Therefore, S/F of 1.0 faces the low EP of gallic acid. It can be observed that the EP do not increase greatly above S/F of 1.0 in the cases of vanillic, syringic and caffeic acids, as the EP values obtained for this S/F are already high: EP>94.24 % after 1-butanol LLE, EP>89.43 % after ethyl acetate LLE, EP>81.38 % after eucalyptol LLE and EP>89.67 % after linalool LLE. The benefit of up to a 4-fold increase in S/F is mainly for gallic acid extraction with 1-butanol, ethyl acetate, eucalyptol and linalool solvents.

Regarding the solvent usage, the producing costs of terpenoids are higher than those of VOCs (8–10$/kg for eucalyptol and 5–8$/kg for linalool (Kirk;Othmer, 2013), against 1.19$/kg for 1-butanol and 0.94 $/kg for ethyl acetate (Business Analytiq, 2024a, 2024b)). However, terpenoids come from biomass and their hydrophobicity is higher compared to VOCs (3.5 g/L for eucalyptol, 1.59 g/L for linalool, 68 g/L for 1-butanol and 80 g/L for ethyl acetate). These aspects leads to lower environmental impact and solvent losses, which reduces the subsequent equipment and treatment costs (Cañadas et al., 2020). Moreover, retrofitting of this LLE process with terpenoid solvents remains a challenge. On one hand, the principal physical properties (density and viscosity) of terpenoids have close values to those of VOCs. On the other hand, the lower EP values for terpenoids compared to VOCs would require large equipment sizes to achieve similar performances (Green and Perry, 2008). Conversely, smaller equipment would be required for downstream treatment due to the lower water solubility of terpenoids (Green and Perry, 2008).

On one hand, considering the highest EP for all phenolic acids, the best S/F to operate the system is 4.0. However, high S/F ratios are related to the dilution of phenolic acids in the solvent, that would result in a lower performance on the back-extraction step (Rodríguez-Llorente et al., 2023b). This would imply higher equipment requirements and operating costs in both the LLE process and downstream operations due to higher flow rates. Therefore, from an industrial point of view, lower S/F ratios are more practical if they provide relevant EP in this process. On the other hand, a proper balance between solvent use and EP is obtained with an S/F of 0.25. However, the extraction of gallic acid in this case is limited. Taking all these factors (EP values obtained, solvent usage and dilution of phenolic acids) into account, the intermediate S/F of 1.0 is selected for the following experiments, ensuring relatively high EP rates for all phenolic acids, while avoiding a high solvent use and the dilution of phenolic acids. It is important to highlight that further techno-economic analysis would be needed to determine an optimal S/F for large scale processes employing this methodology, as the performance of LLE processes can also be improved by the multi-stage countercurrent extractors, reducing the S/F while reaching high EP values Rodríguez-Llorente et al., 2023a.

The overall trend of the solvent EP was observed to be as follows: 1-

butanol > ethyl acetate > eucalyptol > linalool > p-cymene ~ α-pinene. This trend can be attributed to the polarity and hydrogen bonding capacity of the solvents. The polarity of the solvents, which can be verified in Table S1 based on the dielectric constants, favours the EP, as the dielectric constants of the solvents follow the suggested order. In literature, a phenolic acids extraction study with D-limonene, which is a terpene solvent similar in structure to p-cymene and α-pinene, suggests that the extraction capacity of the solvents is mainly limited by the presence of hydrophobic functional groups (Cañadas et al., 2021a). This can explain the lower EP values of p-cymene and α-pinene, which do not exceed 33.37% for the phenolic acids studied, as they are strongly apolar solvents.

It can be noted that the EP could be affected by other factors, such as steric hindrance. Complex solvent structures may not promote solvent-phenolic acid interactions (Deng et al., 2018; König et al., 2018; Leelaphiwat et al., 2018; Wang et al., 2021). The importance of this parameter for terpenoids is highlighted by the change of eucalyptol - linalool EP order for different phenolic acids. Comparing the values obtained at S/F 1.0, the EP order is eucalyptol > linalool for gallic acid, eucalyptol ~ linalool for vanillic acid and caffeic acid, and linalool > eucalyptol for syringic acid, suggesting that steric hindrance might be significant in these particular solvents.

### 3.2. *Effect of phenolic acid concentration and structure on the extraction performance*

After selecting an S/F ratio of 1.0 and discarding the terpene solvents α-pinene and p-cymene due to their low performance, tests were conducted to study the effect of the concentration of phenolic acid in the wastewater on the EP using the solvents 1-butanol, ethyl acetate, eucalyptol and linalool. The concentrations of each phenolic acid studied in the raw wastewater were 10 mg/L, 25 mg/L, 50 mg/L, 100 mg/L, 250 mg/L, 500 mg/L. These values were selected to be in the range of the total phenolic concentration found in winery wastewater, which varies between 0.51 and 1450 mg/L (Zacharof, 2017). The relationship between the EP values and the initial concentration of phenolic acids in the wastewater is shown in Fig. 2. For more details of the EP values, see Table S4.

On one hand, a constant trend for the EP of VOCs is obtained throughout the initial phenolic acid concentration range. This finding is confirmed by an ANOVA (Table S6), in which all solvent-phenolic acid combinations did not show significant differences ($p > 0.05$) for all the concentration range, except for a few specific cases that showed significant differences: 1-butanol-gallic, 1-butanol-syringic acid, and ethyl acetate-caffeic acid. For these solvents, a variable trend within the 10–100 mg/L range and a constant EP trend between 100 and 500 mg/L was confirmed by the Tukey test results (Table S7), excepting 1-butanol-gallic acid for the 100–500 mg/L range. The obtained EP trend is similar to the results obtained by Fan et al. (Fan et al., 2017a, 2017b) with ionic liquids for the extraction of phenolic acids, where the phenolic acid concentration had practically negligible effect on the EP in the range of 1–100 mg/L for caffeic acid and 10–200 mg/L for gallic, vanillic and syringic acids. On the other hand, for terpenoids, the trend observed is different from that of the VOCs. Fig. 2 shows an increasing EP trend in the 10–100 mg/L phenolic acid concentration range and a constant EP trend in the 100–500 mg/L phenolic acid concentration range. The different trend as a function of the initial phenolic acid concentration is confirmed for most of the terpenoid-phenolic acid combinations by the ANOVA and Tukey test performed (Tables S6 and S7), with a few exceptions: a constant EP for the whole range of initial concentrations for eucalyptol-gallic acid from ANOVA; and, a constant trend in the range 10–100 mg/L concentration for eucalyptol-caffeic acid and non-constant trend in the range 100–500 mg/L concentration for linalool-vanillic acid, that showed significant differences through this range, both from Tukey test. In this context, the EP reduction at low concentrations of phenolic acid was generally observed for terpenoid solvents (eucalyptol and linalool). This could be due to their more hydrophobic nature compared to VOCs, which can result in both mass transfer and kinetic limitations, together with the lower driving force at lower solute concentrations (Rodríguez;Llorente et al., 2021).

Based on the results, the EP of the phenolic acids can be established as follows, from highest to lowest one: caffeic acid > vanillic acid >

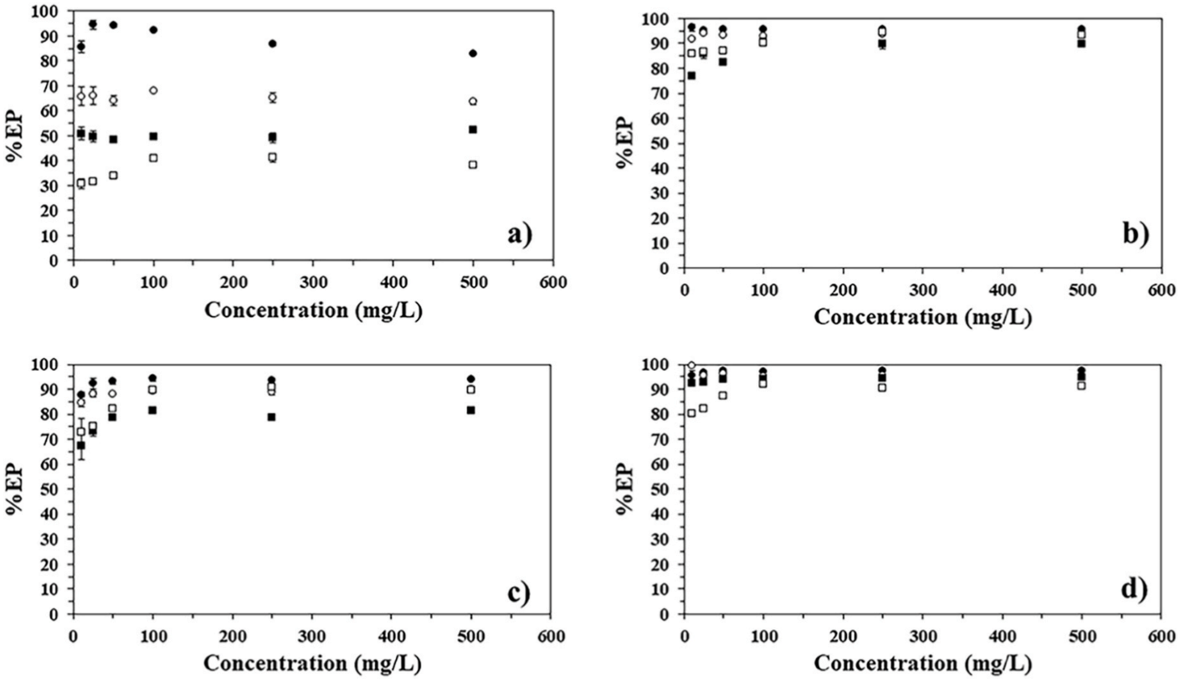

**Fig. 2.** Relation of extraction performance of phenolic acids a) gallic acid, b) vanillic acid, c) syringic acid, d) caffeic acid with initial phenolic acid concentration in wastewater for LLE process with different solvents: (●) 1-butanol, (○) ethyl acetate, (■) eucalyptol, (□) linalool, (▲) p-cymene, (Δ) α-pinene. Conditions: S/F: 1.0; T: 298 K.

syringic acid > gallic acid. The molecular structure of the phenolic acids is responsible for this as well as their polarity and hydrophobicity, as indicated by their Log $K_{ow}$ and water solubility (Table S2). Gallic acid has the lowest Log $K_{ow}$ and the highest water solubility because of the existence of three polar -OH groups, which increase the polarity of this molecule and its interaction with water, reducing the extraction performance. The EP values of vanillic and syringic acid are similar; however, vanillic acid exhibits slightly higher values due to its greater non-polarity compared to syringic acid, as evidenced by its Log $K_{ow}$ value (1.42 for vanillic acid and as 1.13 for syringic acid). This difference in polarity is due to the presence of an additional $-OCH_3$ group on the phenolic ring of syringic acid. The water solubility of both molecules aligns with this trend, demonstrating that vanillic acid (solubility: 1.50 g/L) is more hydrophobic than syringic acid (solubility: 5.78 g/L). Furthermore, the Log $K_{ow}$ of the caffeic acid is 1.29, lower than vanillic acid value. It can therefore be assumed that caffeic acid is the most polar molecule. However, the hydroxycinnamic acid structure of the molecule results in a more non-polar molecule due to the addition of a 3-carbon chain to the acid functional group instead of the 1-carbon chain of the acid functional group typical of hydroxybenzoic acids. Furthermore, the solubility of caffeic acid in water, which is the lowest of all studied phenolic acids (0.98 g/L), show the highest hydrophobicity compared to the rest of the molecules, resulting in the highest EP.

Finally, the best performing VOC and terpenoid were chosen as solvents for the following studies. In particular, 1-butanol showed a superior EP compared to ethyl acetate, irrespective of the extracted phenolic acid. As for terpenoids, eucalyptol resulted in higher extraction of gallic acid, which proved to be the limiting phenolic acid when extracting with terpenoid solvents.

### *3.3. Effect of temperature on the extraction performance*

The effect of the temperature on the phenolic acid extraction capacity was evaluated in Fig. 3. To do this, LLE tests were carried out at 298 K, 308 K and 318 K using 1-butanol and eucalyptol as solvents at the base operating conditions detailed in Section 2.2.

According to Fig. 3 (detailed data in Table S5 in the Supplementary Data), an increase in temperature does not lead to an improvement in EP, as the best EP values were obtained at 298 K in all cases. Fan et al. (2017a) studied the extraction of gallic, vanillic, syringic and caffeic acids using ionic liquids (Fan et al., 2017a, 2017b). They established that the LLE process is exothermic as the enthalpy values obtained were below 0 in all cases. It is also important to take into account operation costs and solvent losses to water, as an increase in temperature favours the solvent solubility (Larriba et al., 2016). Fig. 3 reveals a negative impact on the LLE thermodynamic equilibrium with increasing temperature. Based on these results, 298 K is selected as the optimum temperature for the extraction of phenolic acids from wastewater by LLE with VOCs and terpenoids.

### *3.4. Regeneration of the extraction solvents and recovery of phenolic acids*

The recovery of phenolic acids from the extract phase (1-butanol and eucalyptol) into a basic aqueous solution was evaluated with $10^{-5}$ M, $10^{-4}$ M and $10^{-3}$ M NaOH solutions according to Section 2.4. Table 1 shows the EP results of the back-extraction and the global recovery.

Table 1 shows that, regardless of the solvent used under basic conditions, the recovery of caffeic, syringic and vanillic acids from the extract phase increases with increasing NaOH concentration. This is because the increase in pH causes the dissociation of the carboxyl and hydroxyl groups of the phenolic acids when their $pK_a$ values are exceeded, and a decrease in their solvent affinity. As a result of these phenomena, the phenolic acids returned to the aqueous phase (Fan et al., 2017a, 2017b). As for gallic acid and caffeic acid, both were observed to show irreversible degradation when exposed to pH 10.5 for 2 h and then neutralized to pH 7 (Friedman and Jürgens, 2000). As for caffeic acid, an increase in NaOH concentration had no appreciable negative effect, as the highest back-extraction recovery performance was achieved at the highest value of $10^{-3}$ M NaOH concentration for both solvents, and so no degradation effect could be observed in this case. However, there is a significant decrease in gallic acid back-extraction performance from eucalyptol at $10^{-3}$ M NaOH. The back extraction performance decreases from 78.73% at $10^{-4}$ M NaOH to 37.54% at $10^{-3}$ M NaOH, which may be due to degradation under high pH conditions. No degradation of gallic acid was observed in the

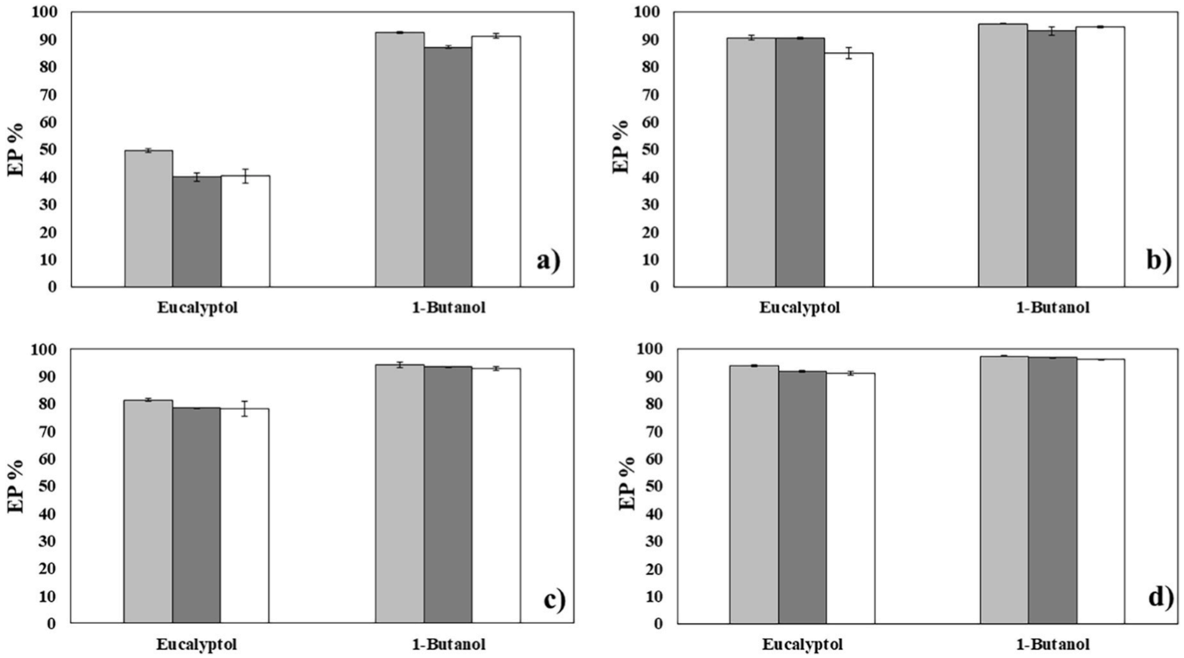

**Fig. 3.** Relation of the extraction performance of phenolic acids: a) gallic acid, b) vanillic acid, c) syringic acid and d) caffeic acid, with temperature (■) 298 K, (■) 308 K, (□) 318 K during a LLE process with eucalyptol and 1-butanol solvents. Conditions: [Phenolic acid]$_0$: 100 mg/L; S/F: 1.0.

**Table 1**
NaOH back extraction and global recovery EP after LLE and back-extraction for phenolic compounds: GA (Gallic acid), VA (Vanillic acid), SA (Syringic acid), CA (Caffeic acid), for the solvents 1-butanol and eucalyptol. Conditions: [Phenolic acid]$_0$: 100 mg/L; S/F: 1.0; T: 298 K.

| Solvent | Phenolic Acid | Back Extraction (%) | | | Global Recovery (%) | | |
|---|---|---|---|---|---|---|---|
| | | [NaOH] (M) | | | [NaOH] (M) | | |
| | | $10^{-5}$ | $10^{-4}$ | $10^{-3}$ | $10^{-5}$ | $10^{-4}$ | $10^{-3}$ |
| 1-Butanol | ***GA*** | 27.46 | 33.65 | **73.24** | 23.32 | 28.34 | **60.40** |
| | ***VA*** | 8.64 | 12.09 | **59.57** | 8.22 | 11.56 | **56.45** |
| | ***SA*** | 13.32 | 17.64 | **71.34** | 12.51 | 16.67 | **66.78** |
| | ***CA*** | 9.44 | 13.67 | **54.28** | 9.19 | 13.19 | **52.81** |
| Eucalyptol | ***GA*** | 77.94 | **78.73** | 37.54 | 36.85 | **37.76** | 21.07 |
| | ***VA*** | 41.55 | 52.94 | **100** | 35.36 | 47.97 | **93.21** |
| | ***SA*** | 65.18 | 68.93 | **100** | 52.80 | 55.92 | **78.79** |
| | ***CA*** | 30.51 | 37.97 | **85.49** | 28.80 | 35.89 | **80.57** |

1-butanol back-extraction, implying the solvent impact on the pH of the aqueous NaOH phase, since higher pH values favour this degradation. To test this hypothesis, saturated aqueous solutions of the solvents used were prepared and their pH was measured, showing that the pH of the water saturated with eucalyptol was 5.17, while for 1-butanol it was 4.61, suggesting then that the resulting pH of the aqueous NaOH solutions used, mixed with eucalyptol, is higher than that of the aqueous NaOH solutions mixed with 1-butanol, thus promoting the degradation of gallic acid with eucalyptol, while working under a higher NaOH concentration range.

It should be noted that when a $10^{-3}$ M aqueous NaOH solution was used with eucalyptol, almost complete back-extraction of vanillic and syringic acids and a high back-extraction recovery of caffeic acid (85.49 %) were achieved. However, to recover gallic acid from eucalyptol, it is advisable to avoid high NaOH concentrations.

In order to develop a sustainable process, it is essential to assess the recyclability and regeneration of solvents. Although terpenoids have not been used on an industrial scale, and their lifetime has not been tested over a large number of cycles, some works has shown their chemical stability and constant performance over repeated cycles of solvent extraction and regeneration, pointing out their potential in the industry. (Rodríguez-Llorente et al., 2020b; Rodríguez-Llorente et al., 2021; Rodríguez-Llorente et al., 2023a; Rodríguez-Llorente et al., 2023b). The results of the extraction performance over three LLE cycles, with regeneration cycles between LLE, are shown in Fig. 4. After regeneration with 0.1 M NaOH solution and neutralization with 85 % w/w $H_3PO_4$, the solvents maintain their EP, regardless of the phenolic compound and solvent tested. The results suggest that the process using 1-butanol and eucalyptol is feasible for repeated extraction cycles.

### *3.5. Degradation of solvents present in water after extraction by electrooxidation*

From the perspective of circular wastewater treatment, the recovery of phenolic compounds is crucial. Nevertheless, the proposed LLE process must deal with solvent contamination of the wastewater due to its solubility (Table S1). Therefore, this section evaluates an electro-oxidation process with BDD as anode as described in Section 2.5. Fig. 5 shows the evolution of solvent removal (1-butanol and eucalyptol) in terms of COD removal with the applied electric charge at operating current densities of 422.54 A/m$^2$ and 634.92 A/m$^2$. For eucalyptol, almost complete COD removal can be observed at a similar applied electric charge regardless of the current density: 99.48% of COD removed at an applied electric charge of 28.62 A h/dm$^3$ at a current density of 422.54 A/m$^2$ and 98.79% for an applied electric charge of 28.48 A h/dm$^3$ at a current density of 634.92 A/m$^2$. When wastewater is

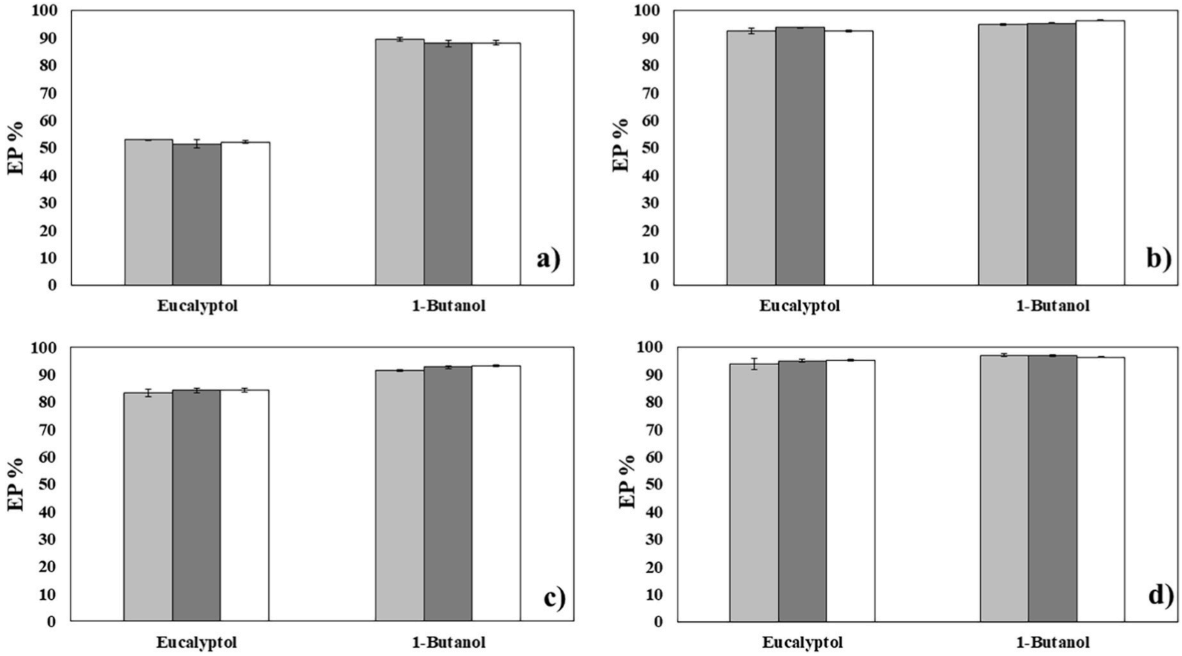

**Fig. 4.** Extraction performance of phenolic acids: a) gallic acid, b) vanillic acid, c) syringic acid and d) caffeic acid, over 3 LLE cycles with regeneration between cycles with eucalyptol and 1-butanol: (■) Cycle 1, (■) Cycle 2, (□) Cycle 3. Conditions: [Phenolic acid]$_0$: 100 mg/L; S/F: 1.0; T: 298 K; [NaOH]: 0.1 M.

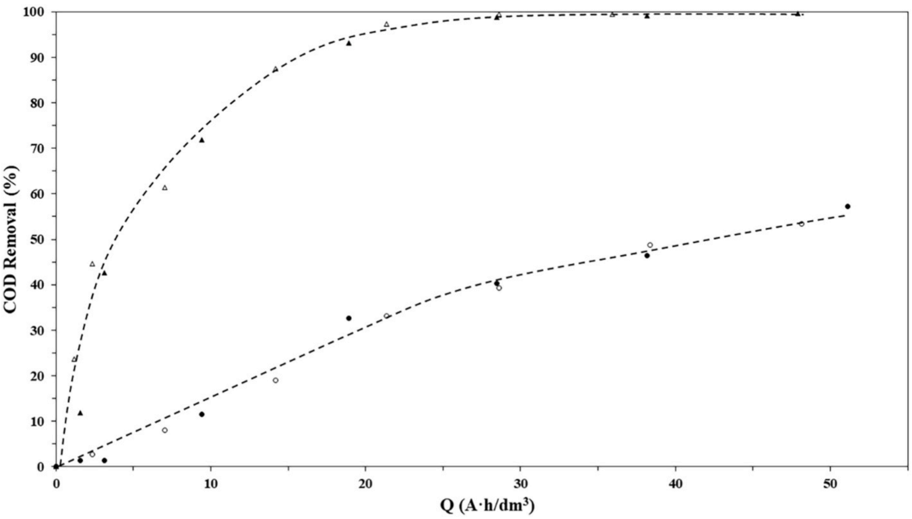

**Fig. 5.** Evolution of the COD removal with the applied electric charge during the treatment of wastewater contaminated with LLE solvents. Symbols correspondence: (○) Solvent: 1-butanol, j: 422.54 A/m$^2$; (●) Solvent: 1-butanol, j: 634.92 A/m$^2$; (Δ) Solvent: eucalyptol, j: 422.54 A/m$^2$; (▲) Solvent: eucalyptol, j: 634.92 A/m$^2$.

contaminated with 1-butanol, the COD removal performance at similar conditions of applied electric charge was 39.27% and 40.22% at a current density of 422.54 A/m$^2$ and 634.92 A/m$^2$, respectively. These results are promising as the wastewater contaminated with 1-butanol has a solvent concentration 20 times higher (65,000 mg/L) than that of the system with eucalyptol (3400 mg/L).

## 4. Conclusions

The aim of this study is to evaluate the performance of traditional solvents (1-butanol and ethyl acetate), as well as terpenes (α-pinene and p-cymene) and terpenoids (eucalyptol and linalool) for the extraction of phenolic acids (gallic acid, vanillic acid, syringic acid, caffeic acid) contained in winery wastewater. The study evaluated crucial variables such as solvent to feed ratio (S/F), concentration of phenolic acids in raw wastewater and temperature. Solvent contamination in the wastewater stream was also considered and an electrooxidation process was proposed to degrade the solvents. The findings yielded the following conclusions:

- 1-butanol and eucalyptol were identified as the most suitable conventional and green solvents, respectively, according to their EP. 1-butanol allows EP of 92,36 % for GA, 95,74 % for VA, 94,24 % for SA and 97,20 % for CA while eucalyptol usage results in 49,62 % for GA, 90,94 % for VA, 81,38 % for SA and 93,80 % for CA.
- Eucalyptol can be a potential substitute for VOCs in LLE of phenolic acids from agri-food wastewater.
- The low polarity and the significant hydrophobicity of terpene solvents (α-pinene and p-cymene) results in low EP.
- A solvent to feed ratio of 1.0 shows high EP values, regardless of the phenolic acid and the solvent, balancing the solvent consumption and the ease of the back-extraction stage.
- The EP remains constant regardless the initial concentration of phenolic acid in the range studied (10–500 mg/L) for VOCs while an increasing trend was observed when increasing the initial concentration of phenolic acid in the concentration range 10–100 mg/L for terpenoids, followed by a constant EP trend for higher concentration values.
- The extraction performance of each phenolic acid is related to its structure, polarity, log $K_{ow}$ and solubility.
- Eucalyptol achieves lower EP rates compared to conventional solvents, but its lower water solubility and environmental impact can benefit this process in terms of lower subsequent treatment needs and lower environmental costs.
- An increase in the temperature does not enhance the phenolic acid extraction, being 298 K the most suitable temperature for this LLE application.
- Phenolic acids can be back-extracted into a NaOH aqueous phase ($10^{-3}$, $10^{-4}$ and $10^{-5}$ M). For gallic acid, a low concentration of NaOH is recommended to avoid its degradation.
- 1-butanol and eucalyptol solvents can be regenerated and reused with a 0.1 M NaOH solution without losing extraction capacity.
- Electrooxidation with BDD as anode is a technically feasible technology to remove LLE solvents from the wastewater due to its contamination after the possible LLE.
- Given the positive results, it is encouraged to carry out studies focused on the potential scalability of the process, technoeconomic and environmental impact analyses, as well as parameter optimizations and exploring other types of green solvents.

## CRediT authorship contribution statement

**Ismael Martín:** Writing – original draft, Visualization, Methodology, Investigation, Conceptualization. **Claudia López:** Writing – original draft, Visualization, Investigation. **Julián García-González:** Writing – review & editing. **Sara Mateo:** Writing – original draft, Visualization, Supervision, Methodology, 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.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2024.121969.

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