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Recovery of Tartaric Acid and Added-Value Phenolics from Wine Wastes Towards an Integrated Treatment and Commercial Valorisation

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Abstract. Grapes are among the largest fruit crop in the world, of which ~80% is used for wine making. The recovery of natural antioxidants from wine industry by-products is of great importance, not only because of their aforementioned significant properties, but also because it could exploit a large amount of the wine industry wastes, which are mainly used today as cattle feed or for soil conditioning or they are trucked away to disposal sites. The objectives of this study were to determine and isolate phenolic compounds with high antioxidant activity from grape pomace extracts, using sorption-desorption methods and recover tartaric acid from red and white tartar wastes.

Keywords: Antioxidant activity, phenolics, sorption, tartaric acid

1. Introduction

In the last few years diminishing the environmental impact of industrial wastes has been a subject of increasing concern. Grapes are one of the world's largest fruit crops, and wine-making wastes are rich in phenols. These compounds considerably increase biochemical and chemical oxygen demands, while in solid residues used as fertilizers may inhibit germination. On the other hand, grapes, wine, grape seeds and skins extracts are reported to exert favourable effects on human health due to their phenolic content [1].

Literature is rich of examples of recovery of antioxidant compounds from natural sources such as oil seeds, nuts, cereals, legumes, vegetables, fruits e.t.c. Phenolic compounds can be considered as high added-value by-products and the employment of low-cost industrial wastes could greatly reduce the production costs and increase the margin profit of the products. However, most of the reports started from fresh raw material, utilizing directly whole grape [2]. Although the organic solvents provide the extraction of the metabolites from plants, further purification in order to obtain concentrated specific components selectively, may be necessary. For the selective recovery of target plant metabolites from the crude solvent extracts, adsorption is mostly preferred by many of the researchers, as a low-cost separation technique [3].

Tartaric acid is a valuable product for many industries [4]. However, it lowers the quality of wine due to its precipitation forming calcium tartrate and potassium hydrogen tartrate. These tartar wine wastes can be further processed for the recovery of tartaric acid, a valuable by-product, which can be subsequently used in food, chemical and cosmetics industries [5].

The objectives of our research were: (1) to recover the tartaric acid from red and white tartar wastes and (2) to isolate the polyphenolic compounds from the wine wastes using sorption/desorption techniques and to evaluate their free radical scavenging activity.

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2. Materials and Methods

2.1. Materials

Grape pomace (red and white) was kindly provided by Gerovassiliou Domaine a wine-making factory in Epanomi (Thessaloniki, Greece) in the vintage of 2013. Methanol and ethanol were used for the extraction of phenolics from grape marc and tartar wastes respectively in a sonicator (35 ^{0}C, 3 cycles x 20 min, 1 g of sample /30 ml of solvent).

2.2. Recovery of tartaric acid

The process for the recovery of tartaric acid from red and white tartar wastes is shown in Fig. 1.

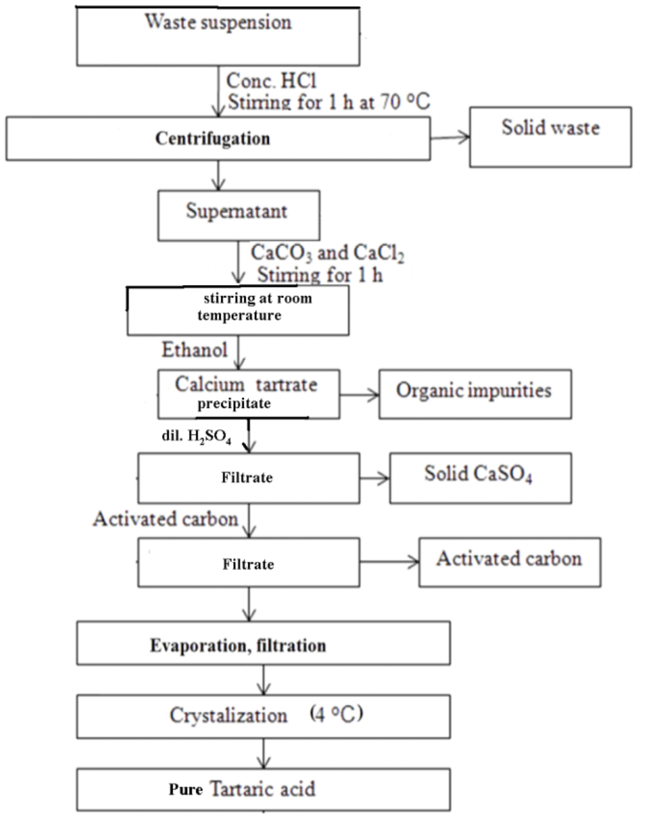


Fig. 1: Recovery of tartaric acid from red and white tartar wastes

2.3. FTIR and Ion Chromatography analysis

Potassium bromide disks were prepared by mixing 1 mg of lyophilized tartaric acid crystals with 200 mg KBr, and the spectra were recorded from 400 to 4000 cm^{-1} with a resolution number 2 cm^{-1} using Fourier Transform Infrared Spectrophotometer (Equinox 55, AXS Bruker, USA).

Tartaric acid was also analyzed by ion chromatography (Dionex series 4500i, USA) using column (PRD × 300, 25 × 4.1 mm). The mobile phase was 0.001 N H_2SO4 at a flow rate of 0.8 ml/min. The detection wavelength was set at 210 nm.

2.4. Isolation of phenolic compounds using adsorption and desoprtion techniques

Various materials were tested for their ability to adsorb phenolic compounds from mixtures including ash, non-ionic resin XAD-7, agar, zeolite and aluminium oxide.

Batch sorption experiments were conducted by stirring 20 ml of grape marc extract with 0.5 g of sorbent at ambient temperature. Samples were centrifuged (4500 rpm, 10 min) and the supernatant was further analysed for phenolics and sugar content. After equilibrium sorption, the phenolics loaded material was agitated with 0.1 M HCl.

2.5. Extract analysis

2.4.1. Total phenolics

Total phenolics content was determined using the Folin-Ciocalteu method and measuring the absorbance of the blue complex formed at 745 nm [6]. Total phenols were expressed as mg/g of gallic acid.

2.4.2. Total sugars

Total sugars were determined using DNS method at 575 nm [7].

2.4.3. Antioxidant activity

Antioxidant activity was estimated using the DPPH method. A DPPH• blank sample (containing 10 mg DPPH with 100 ml ethanol) was prepared and measured daily. The DPPH• solution was freshly prepared daily, stored in a dark coloured bottle at 4 ℃ between measurements. The percent decrease in absorbance was recorded for each concentration, and percent quenching of DPPH• radical was calculated on the basis of the observed decrease in absorbance of the radical.

$$\% \text{ inhibition} = [(A_{DPPH} - A_{Extr})/A_{DPPH})] * 100 \qquad \text{(eq. 1)}$$

where A_{DPPH} is the absorbance value of the DPPH• blank sample and A_{Extr} is the absorbance value of the test solution [8].

3. Results and Discussion

3.1. Tartaric acid recovery

The recovery of calcium tartrate and its free acid is very important, since it can also be used as food preservative and acidity regulator.

Fourier Transform Infrared (FTIR) analysis was used for identification of tartaric acid isolated from red and white tartar waste samples (data obtained but not shown) [9].

Tartaric acid was also identified, by ion chromatography. The elution time was 4.0 min for tartaric acid recovered from both red and white tartar wastes (Fig. 2a) and for commercial available sample (Fig. 2b).

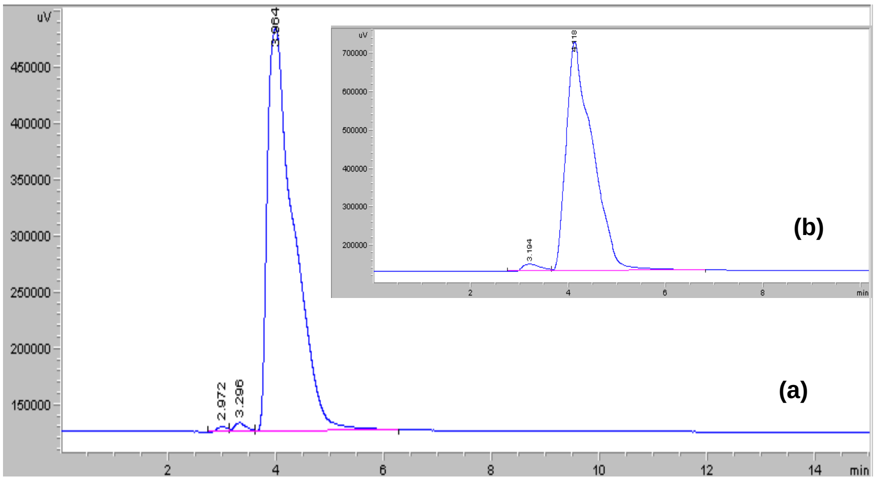


Fig. 2: Ion chromatography of (a) tartaric acid recovered from white tartar wastes and (b) standard compound

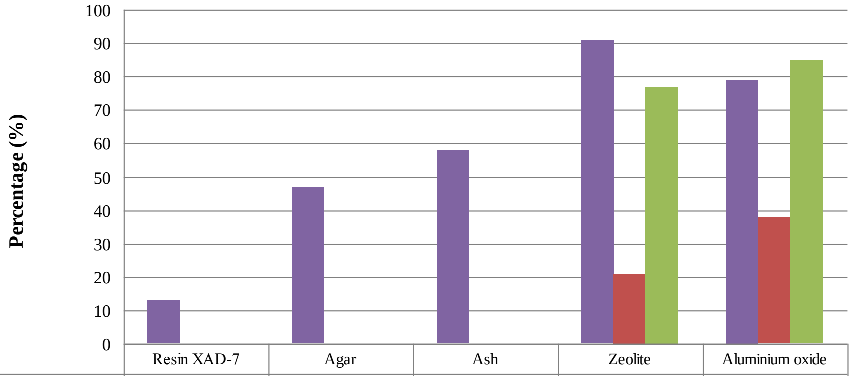
Tartaric acid in crystal form was recovered at 4.48 and 3.57 g/100 g-dry mass of red and white tartar wastes respectively.

3.2. Separation of phenolics using sorption techniques

Total phenolics, sugars and antiradical scavenging activity were determined in all samples of wine wastes obtained from Gerovasileiou wine industry.

It was found that red and white marc are good sources of natural antioxidants (25.10 and 14.16 mg phenolics/g d.w. possessing 94 and 89% of the antiradical scavenging activity). Mildner-Szkudlarz et al. (2010) reported approximately 20 mg phenolics/g d.w. using ethanolic extracts from grape marc, whereas Lafka et al. (2007) found that methanolic axtracts from red white wastes (grape skin and seeds) possess 91.4% of antiradical scavenging activity which is comparable with our results [10], [11].

A methanolic extract from white grape marc was used for sorption studies with various adsorbent materials in order to separate phenolics from sugars. Recovery of phenolics by desorption and estimation of their antioxidant activity was performed with most of the sorbents examined (Fig. 3).



	Resin XAD-7	Agar	Ash	Zeolite	Aluminium oxide
Adsorption	13	47	58	91	79
Desorption	0	0	0	21	38
Antiradical activity	0	0	0	77	85

Fig. 3: Comparison of sorption and desorption efficiency of phenolic compounds using different sorbent materials (initial concentration of phenolics 12 mg/g d.w.)

As it can be seen in Fig. 3 the most promising results are those obtained using aluminum oxide and zeolite, due to the higher desorption percentage and antiradical scavenging activity recorded. More specifically zeolite was found to selectively adsorb phenolics only, comparing to aluminium oxide that adsorded sugars also (42%). However desorption of phenolics was higher in the case of aluminium oxide showing its possible use for the isolation of phenolic compounds from these wastes.

Desorption of phenolic compounds is limited in most of the cases studied. Soto et al. (2008) used charcoal for the adsorption of phenolic compounds from grape pomace and found that only 20% of the adsorbed amount could be recovered [12]. The limited percentage of eluted adsorbed phenolics may suggest chemisorption at the carbon surface. In our study, aluminium oxide seems to be more promising for use in added-value phenolics isolation, not only due to the higher percentage of elution but also due to the high antioxidant activity maintained.

4. Conclusions

Wine wastes could be considered a good source of natural antioxidants. The radical scavenging activity is high due to the content of total polyphenols.

Sorption can be used as an alternative method for the separation of phenolic compounds from natural mixtures.

Desorption experiments resulted in selective elution of phenolics possessing 85% of the total antiradical scavenging activity.

Red and white tartar wastes can be used for the recovery of tartaric acid, another added value wine by-product in relatively good yields.

5. Acknowledgements

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