



Tartaric acid recovery from winery lees using cation exchange resin: Optimization by Response Surface Methodology



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ABSTRACT

A crucial first step in developing a novel cost-effective and environment-friendly process for recovering tartaric acid and bioactive polyphenolic compounds from wine lees involves tartrates dissolution by mild means, aiming to maximize tartaric acid recovery, while minimizing the concentration of undesirable potassium. Such a processing step, using cation exchange resin, has been systematically assessed to obtain a set of near-optimum values of the key variables (i.e. pH, water dosage and cation exchange resin dosage). An experimental design was carried out based on Central Composite Design (CCD) with Response Surface Methodology (RSM) to evaluate the effects of process parameters and their interaction towards the attainment of optimum conditions. All three variables considered were found to be significant; however, the most influential factor for maximum tartaric acid concentration was the volume of added water, whereas for potassium removal the cation exchange resin dosage. A quadratic model was developed that fitted well to the experimental data confirmed by the high R^2 values, greater than 0.98. A set of optimum values of the three main variables was determined to be pH = 3.0, water dosage 10 ml/g dry lees and resin dosage 3.5 g/g dry lees. Under these optimum conditions, the predicted tartaric acid and potassium concentration were 43,143 ppm and 178 ppm, respectively, which correspond to 74.9% tartaric acid recovery and 98.8% potassium removal. Furthermore, the corresponding experimental values, from the validation experiment, fitted well to these predictions. This work clearly shows that the recovery of tartaric acid from wine lees can be achieved using cation exchange resin, under mild conditions (ambient temperature) avoiding the waste calcium sulfate sludge of the conventional process.

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1. Introduction

Tartaric acid is a white crystalline diprotic organic acid ($C_4H_6O_6$), which finds many applications as an acidification agent, antioxidant, taste enhancer etc. in the winery, food industry, bakery and pharmaceutical industry. Other uses include the production of emulsifiers, in cement and gypsum as a retardant, as a chelating agent in soil fertilizers, for polishing and cleaning in the metal industry, and in the chemical industry [1]. The estimated world market of tartaric acid is approx. 50,000–70,000 tons per year [2]. Tartaric acid occurs naturally in many plants and can be recovered from various natural products, mainly from winery by-products [1]; other sources of tartaric acid are bio-technological processes [3–6] or synthesis via the peroxidation of maleic anhydride [7].

The winemaking process generates a significant amount of residues whose management and disposal raise serious environmental concerns [8–10]. However, the winery residues are major starting materials for the production of TA; such residues include wine lees, i.e. the deposits of dead yeasts, particulates and other precipitates to the bottom of wine vats after fermentation or stabilization, together with wine tartars i.e. the crystalline deposits on the walls of the wine vats during ageing and/or cold stabilization of wine [1]. The concentration of tartrate species is reported to be 100–150 kg/ton of wine lees [11] or 190–380 kg/ton of lees [1], whereas in wine tartars the concentration of tartrate species may be as high as 80–90% w/w [1]. Differences in the reported values may be attributed to the variety and maturity of the grapes, the cultivation techniques, the soil and climate conditions, and the winemaking process. Wine lees also contain a significant amount of bio-active compounds (i.e. polyphenolic substances, anthocyanins, etc.), whose health benefits have attracted the interest of researchers, food and nutraceutical industry [8,10,12]. Polyphenolic substances in wine lees have been quantified, varying

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between 1.9 and 16.3 g/kg on a dry basis [8] and 1895 ± 239 mg/L on a wet basis [13].

Tartaric acid in wine lees exists mainly in the form of the sparingly soluble potassium bitartrate and, to a lesser extent, calcium tartrate crystals, together with dead yeast, particulate solids and other organic substances. The traditional method of recovery comprises drying and grinding of wine lees, followed by dilution of potassium bitartrate with hot water (70 °C), separation from particulate residues, and the addition of calcium salts or lime to precipitate as calcium tartrate. The latter is separated from the mother liquor containing the potassium ions and decomposed with sulfuric acid yielding tartaric acid solution and insoluble sludge of calcium sulfate, discharged as a waste. The tartaric acid solution is further purified with activated carbon for decolorization and with ion-exchange for the removal of excess sulfuric anions. Finally, the tartaric acid solution is concentrated under vacuum and passed to a crystallizer to obtain the solid tartaric acid [1]. The traditional processes lead to high recovery ratios of tartaric acid (80–85%) [14]; however they are complicated, costly, labor intensive, and environmentally offensive, due to the significant quantities of obnoxious calcium sulfate sludge [15,16].

Development of alternative methods for the recovery of tartaric acid is of great interest and include electrodialysis [17–19], organic extraction [20,21], and adsorption of tartaric ion on anion exchange resins [22–24]. These processes are applicable to aqueous streams containing dissolved tartaric acid or tartaric salts (i.e. wastewater from juice industry or washing waters from wineries); however, a preparatory step for tartaric acid dissolution is required in the case of wine lees that contain tartaric acid in solid form. Furthermore, in the case of anion exchange adsorption, regeneration of saturated resins would result in a liquid stream containing a tartaric salt that would need further treatment to obtain tartaric acid in its acid form.

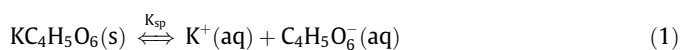
Pressure-driven membrane technologies in their many configurations are widely used throughout the food processing and wine making industry. Membranes in food industries can be used for a variety of processes including selective separation of specific compounds, clarification of liquid streams as well as concentration of dissolved substances [25]. The success of membrane technology in the food and beverage market is due to the inherent advantages of this technology, that include: gentle product treatment at low to moderate temperatures, high selectivity, low energy consumption compared to conventional technologies (e.g. condensers and evaporators) and modular design that permits adaptation to a broad range of plant [26]. To the best of the authors' knowledge, there are no reported data on the use of pressure-driven membrane operations for the separation and recovery of tartaric acid from wine lees and tartrates. Considering the physical state of these winemaking by-products (watery sludge or crystals), a preparatory step is necessary for the dissolution of the tartaric acid and the implementation of a membrane-based recovery method.

The objective of the work reported herein is the development and optimization of a cost-effective and environment friendly process for the dissolution of tartaric acid from wine lees, which could be used as a pre-treatment step in the context of a membrane-based methodology for the recovery and separation of tartaric acid. This process step aims to minimize the use of chemicals and eliminate obnoxious waste streams, to permit the simultaneous recovery of the co-existing bio-active compounds, and to be easily implemented (e.g. at ambient temperature and pressure) in wineries. Considering that various factors may affect the efficiency of such a process, and that there may be interactions between the analyzed factors, difficult to assess, a Response Surface Methodology (RSM) has been applied as an appropriate experimental design tool that can greatly reduce the number of necessary experiments,

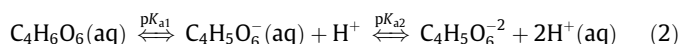
and provide a set of mathematical equations for the theoretical process optimization [27].

2. Process background

Tartaric acid in wine lees exists mainly in the form of the sparingly soluble potassium bitartrate ($\text{KC}_4\text{H}_5\text{O}_6$), which has a low solubility compared to that of tartaric acid; the respective solubilities, at 20 °C, are 0.57 and 147 g/100 g H_2O [1]. Potassium bitartrate equilibrium in water is as follows:



According to LeChatelier principle, the dissolution of potassium bitartrate is favored when the concentration of the potassium and bitartrate ions decrease. Furthermore, tartaric acid is a diprotic acid that has two dissociation constants $\text{p}K_{\text{a}1} = 2.98$ and $\text{p}K_{\text{a}2} = 4.34$; the relative concentration of each of the three tartaric acid forms, i.e. free acid, bitartrate or tartrate anion is given by the following equilibria:



Considering that the relative concentration of bitartrate ion is dependent on H^+ concentration, adjustment of pH value can be used to reduce the bitartrate concentration in the solution and thus increase the solubility of potassium bitartrate. In the usual pH values of wine, the relative concentration of bitartrate varies between 50 and 70%, whereas at lower (i.e. <2.0) and higher (i.e. >5.0) pH values the relative concentration drops to less than 10% [28].

The dilution with water, and pH adjustment through the addition of HCl have been studied [29] for the dissolution of tartrates from white and red wine lees. The volume of HCl, temperature and reaction time have been optimized, to maximize dissolution of potassium bitartrate, through a factorial design experimental procedure. The optimum values concerning temperature, HCl addition and dissolution time have been determined to be 20 °C, 8–10 ml HCl (37%) per 100 ml of wet white or red lees, and 5.0–9.0 min, respectively. Approximately, the same conditions have been used [30] for dissolution of tartaric acid from dried red wine lees; i.e. 3.15 L H_2O per kg of dry lees, together with 0.361 L HCl (37%) for 10 min, at 20 °C. Dissolution of potassium bitartrate has been also achieved through the adjustment of pH to higher values through the addition of KOH [11,31]. An aqueous solution of KOH is added until reaching a pH value 8 [11] or 7–8 [31], and heated at approx. 60–80 °C.

Another approach to facilitate potassium bitartrate dissolution, while minimizing the addition of acids or bases, is the removal of K^+ from the solution using strong cation exchange resins. According to Eq. (1), reduction of K^+ concentration promotes the dissolution of potassium bitartrate, whereas at the same time K^+ are separated from the other valuable compounds (i.e. polyphenolic substances, anthocyanines etc.) of the wine lees, which can be exploited further. Many factors, such as dissolution time and temperature, water dosage, pH and ion-exchange resin dosage can influence the aforementioned dissolution process. The conventional approach for the optimization of a multivariable system is usually to deal with one variable at a time. This can be very time-consuming, especially with multi-parameter systems; moreover, when interactions exist between the variables, it is unlikely to find the true optimum processing conditions. As a package of statistical and mathematical techniques employed for process development, and optimization, RSM can be effectively used to evaluate the effects of multiple factors and their interaction on one or more response variables [32]. One of the advantages of this method is its capability to take into account the interactions

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