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Winery Wastewater: Challenges and Perspectives †

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Abstract: This review aims to study in detail the characterization of winery wastewater (WW), the problems caused by its release into the environment without proper treatment, and the processes that can be applied for its treatment. Several works showed that the WW has a composition based on soluble sugars, organic acids, alcohols, and high molecular weight compounds. Among these, the phenolic compounds are considered to be very toxic, due to the difficulty of degradation by microorganisms, and also because they represent toxicity to humans and animals. To solve this issue, biologic treatments are considered to be cheaper and more effective for biodegradable WW, with the possibility to store biogas with anaerobic treatments. To complement biological treatments, physical-chemical processes based on adsorption, coagulation-flocculation-decantation (CFD), and advanced oxidation processes (AOPs) are also discussed in this review.

Keywords: adsorption; advanced oxidation processes; biogas; coagulation-flocculation-decantation

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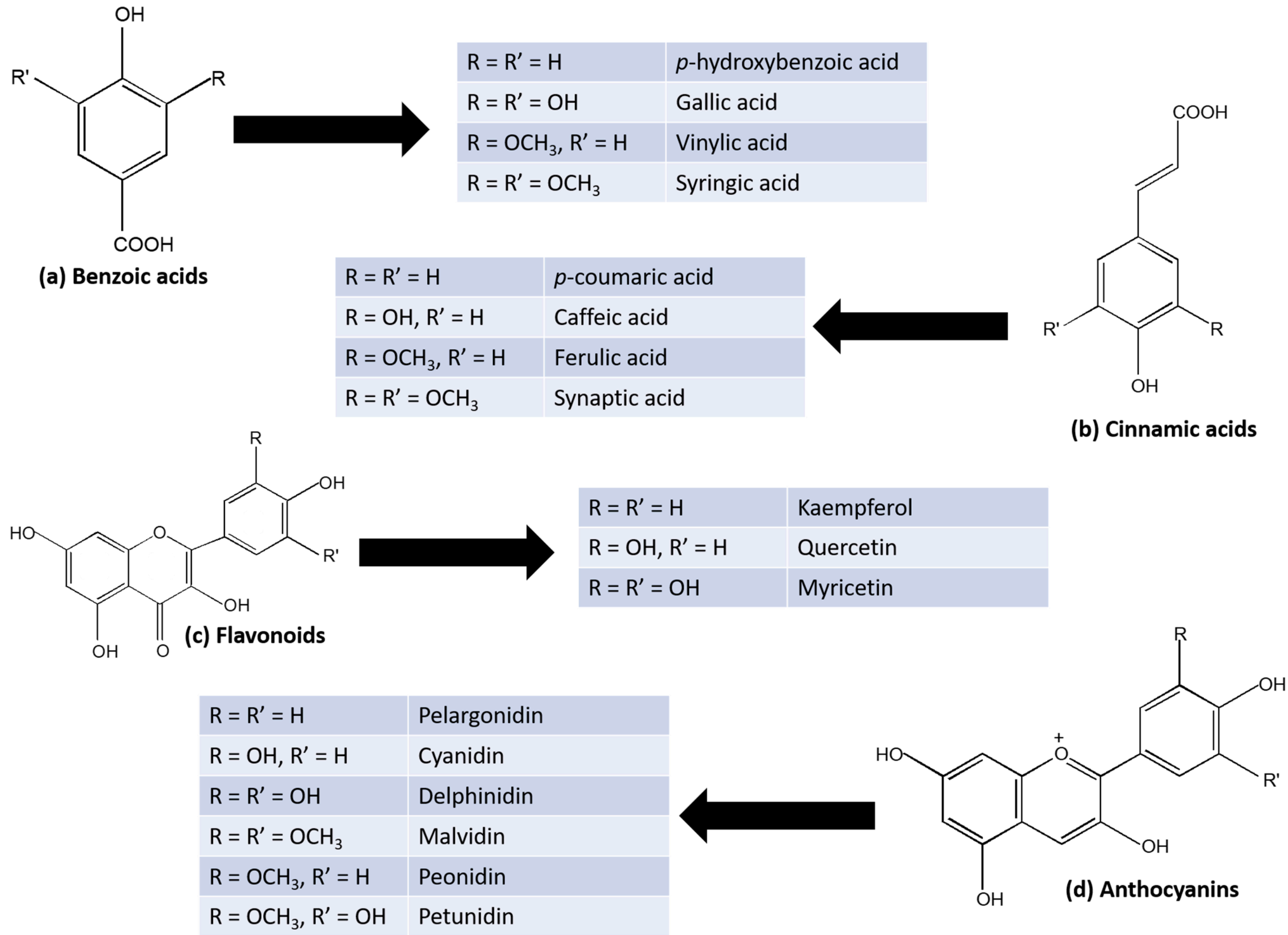
1. Introduction

The wine industry registered a steady increase in wine production. In accordance with the International Organization of Vine and Wine (OIV), the world wine production, was estimated in 2021 at 260 MhL. Among the countries inside the European Union, Portugal is the 10th highest producer with 7.3 MhL of wine produced [1]. Wine production is a complex process that begins in the harvest with grape processing, maceration, pressing, alcoholic and lactic fermentation (depending on wine type), maturation, stabilization, filtration, and bottling [2]. Among the compounds that are a part of the wine composition, the polyphenols and their derivates represent a large amount. The grapes and wine, contain (1) benzoic and cinnamic acids, in which the concentration can reach between 100–200 mg/L in red wines and 10–20 mg/L in white wines; (2) flavonoids, which are intense yellow pigments with a structure characterized by two benzene cycles bounded by an oxygenated heterocycle (the concentration can reach 100 mg/L in red wines and 1–3 mg/L in white wines); (3) anthocyanins, the red pigments present in the skin and pulp of the grapes, with a structure in the form of a flavylium cation, which included two benzene rings bonded by an unsaturated cationic oxygenated heterocycle, derived from the 2-phenyl-benzopyrylium nucleous (Figure 1) [3]. The wine is also a source of yeast and bacteria which proliferate with relative facility, thus the sanitation of tanks, pumps, hoses, walls and floors, bottles, transportation boxes, etc., is a requirement to prevent the degradation of the quality of the wine [4]. These sanitation processes lead to the production of large volumes of wastewater which varies in accordance with the volume of wine produced: (1) wineries with 5 T of grapes crushed generate 10 to 90 hL; (2) wineries with 5–20 T of grapes crushed generate 50 to 1000 hL; (3) wineries >20 T of grapes crushed generate between 400 and 2400 hL of WW per year [5]. Considering that it is necessary to spend at least 2 L of water per liter of wine produced [6], it is observed annually the generation of large volumes of wastewater.

The main aim of this work is to provide a complete review concerning the composition of the WW, its environmental consequences, and solutions to mitigate its impact.



R = R′ = H	*p*-hydroxybenzoic acid
R = R′ = OH	Gallic acid
R = OCH_3, R′ = H	Vinylic acid
R = R′ = OCH_3	Syringic acid

R = R′ = H	*p*-coumaric acid
R = OH, R′ = H	Caffeic acid
R = OCH_3, R′ = H	Ferulic acid
R = R′ = OCH_3	Synaptic acid

R = R′ = H	Kaempferol
R = OH, R′ = H	Quercetin
R = R′ = OH	Myricetin

R = R′ = H	Pelargonidin
R = OH, R′ = H	Cyanidin
R = R′ = OH	Delphinidin
R = R′ = OCH_3	Malvidin
R = OCH_3, R′ = H	Peonidin
R = OCH_3, R′ = OH	Petunidin

Figure 1. Phenolic acids in grape and wine. (**a**) benzoic acids, (**b**) cinnamic acids, (**c**) flavonoids: flavonols; (**d**) anthocyanins.

2. Characterization of the Winery Wastewater

Portuguese legislation under the Decree Law n° 236-98, stated that the wastewater can be discharged in natural water bodies if reaches a pH between 6–9, a biological oxygen demand (BOD_5) of 40 mg O_2/L, a chemical oxygen demand (COD) of 150 mg O_2/L, a total suspended solids (TSS) of 60 mg/L, an iron concentration of 2.0 mg/L and a total polyphenols (TPh) of 0.5 mg gallic acid/L.

However, several studies indicated that WW typically reaches a pH of 3–4, and a COD range of 800–12,800 mg O_2/L. Among the carbon composition, it is observed the presence of acetic, lactic, and tartaric acids, fructose, glucose, ethanol, and glycerol, as dominant organic compounds (Figure 2) [7]. In addition to these compounds, the phenolic compounds, which were observed to be an integral part of grapes and wines, also appear in high amounts in the WW. In the work of Canãdas et al. [8], a separation of compounds was performed by high-performance liquid chromatography, showing the presence of gallic acid, protocatechuic acid, 4-hydroxybenzoic acid, caffeic acid, vanillic acid, and syringic acid.

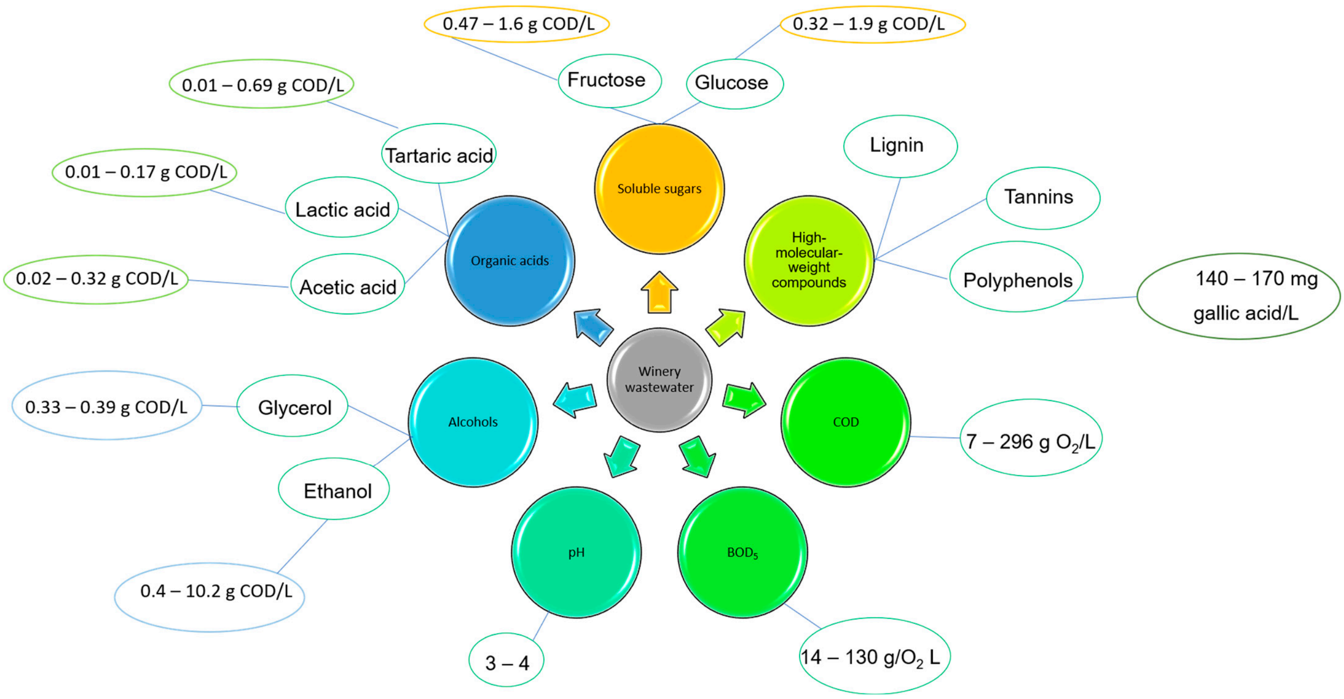


Figure 2. Chemical composition of the winery wastewater.

3. Environmental Impact of Winery Wastewater

The environmental impact caused by the release of WW without proper treatment can be problematic for the ecosystems, due to the contamination of the water, abasement of the soil and vegetation, etc [9]. The uncontrolled release of WW leads to the eutrophication of water bodies (rivers, wetlands, natural streams, rivers), due to the fast consumption of dissolved oxygen, which causes the lack of oxygen for aquatic and amphibious life. Although the WW can be applied as irrigation, thus becoming reusable, without reasonable monitoring, the properties of the soil can be altered, affecting the pH, color, and electrical conductivity, caused by the release of inorganic and organic ions. In Figure 2, it was observed that the WW has a pH between 3 and 4. This high acidity can reduce plant growth, due to the reduction of plant nutrients, such as calcium and phosphorous, decreasing the population of useful microbes [10]. It was previously observed that the WW has a high concentration of phenolics in its composition, which are capable of causing significant environmental damage since some compounds are toxic to animals, humans, and microorganisms at low concentrations, and in addition, they are very resistant to biodegradation [11,12].

4. Treatment Processes, Wastewater Reuse, and Sludge Recycling

The WW composition poses a serious problem for the environment if released without proper treatment, thus, it is necessary to create a treatment process or a combination of treatments that allows the degradation of the organic compounds. However, considering the high volumes of water consumed to produce the wine, as well as the need of the populations to obtain energy at lower costs, it is no longer sufficient to speak in wastewater treatment, it is also required to study methodologies that can be applied in the generation of biogas, reuse the water for irrigation of crops and recycle the sludge as fertilizer. In Figure 3, we proposed several processes that can be adapted with success to maximize the WW treatment, with the possibility to obtain several gains.

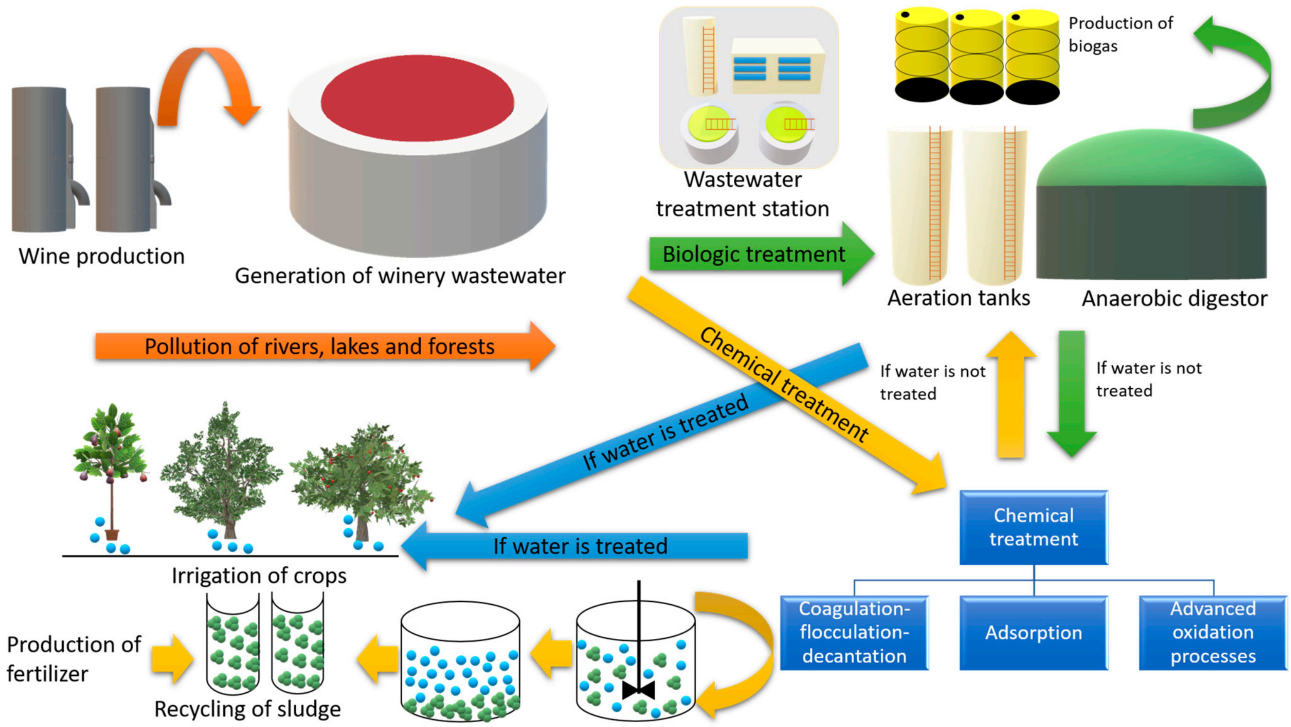


Figure 3. General scheme for WW generation and treatment: wine production, biologic treatment with biogas, chemical treatments (CFD, adsorption, AOPs), sludge recycling, and water reuse.

It is necessary to understand that due to the recalcitrant nature of some organic compounds, one treatment process may not be sufficient to treat the WW, thus a combination of processes is proposed. In the work of Lucas et al. [13], a WW with a COD = 20 g O_2/L was treated by a combined biologic/Fenton process at a pilot scale. This process was selected considering the high biodegradability (BOD_5/COD = 0.55). The COD removal results showed 64% after the biological process (11 weeks). Application of the Fenton process as a subsequent treatment allowed to reach a removal of 96%. In the work of Souza et al. [14], a WW with a COD = 2958 mg O_2/L was treated by a solar-Fenton process. The results showed that the solar-Fenton reached the Portuguese legal values for wastewater discharge and could be an alternative to biological treatments, thus accelerating the treatment of large volumes of wastewater at low cost. In the work of Marchão et al. [15], 4 different WW were treated by a primary system composed of a biological reactor, with 4 species of microalgae (*Arthrospira maxima*, *Scenedesmus obliquus*, *Auxenochlorella protothecoides*, and *Chlorella vulgaris*). The results showed that although the WW had a pH between 3–4, and the microalgae species had an optimum pH growth between 6 and 9, the microalgae increased the pH of the wastewater, thus, no costs were necessary regarding pH change. It was also shown that the concentration of organic matter had an importance in microalgae development. Results showed that WW with higher COD represented a mean with higher nutrient availability, thus the microalgae populations recorded higher development. The possibility of applying the anerobic digestor for the treatment of WW is also a possibility. During anaerobic digestion (AD), the biochemical energy is shifted metabolically to methanogenic components present in the sludge bed of the digestor, generating the biogas, which becomes a valuable energy source [16]. In the work of Lauzurique et al. [17], it was shown that a WW with a COD = 5.49 g O_2/L was treated by an anaerobic digestor, in which two substrate-inoculum ratios (0.50 and 1 g soluble COD/g VSS) and five fly ash concentrations (25, 50, 75, 100, and 150 mg/L) were tested under mesophilic conditions. The results showed that the application of 100 mg/L of fly ash improved biogas production up to 79%.

The adsorption is a physical process, in which an agent is added to the wastewater, with a property that allows the adsorption of chemical particles inside the agent. The advantages of adsorption lie in the low cost, simplicity of the reactor/adsorption design, operational simplicity, and unselective nature [18]. In several works [19–21], bentonite was used as an adsorption agent, showing great efficiency in the removal of COD from the WW. This efficiency was related to the adsorption nature of bentonites, which are porous materials that can adsorb large amounts of contaminants.

Considering the high content in turbidity and TSS, a pre-treatment of CFD can be adapted to remove the excess sediments from the WW. In the work of Braz et al. [22], traditional metallic-based coagulants (aluminium sulfate, ferric chloride, ferric sulfate) showed great efficiency in turbidity and TSS removal from WW; however, the addition of aluminum and iron creates a sludge that could be toxic for the environment. To prevent the generation of toxic sludges, plant-based coagulants can be produced and applied. In Jorge et al. [23], several invasive species (*Dactylis glomerata L.*, *Festuca ampla Hack.*, *Daucus carota L.*, and *Tanacetum vulgare L.*) were used to produce coagulants, which showed great efficiency in turbidity, TSS and COD removal. Results showed also that these coagulants had similar efficiency regarding ferric chloride, without the advantages of generating toxic sludges. The sludge generated by these coagulants was shown to be non-toxic, revealing to increase the radicular growth of plant seeds, thus it could be recycled as fertilizer [24].

Some organic compounds revel to be recalcitrant and cannot be degraded by biological processes, thus chemical treatments, such as AOPs can be applied. Among the AOPs, we observed the successful application of hydroxyl-based AOPs [23,25–27], sulfate-radical-based AOPs [28], and ozone-based AOPs [29] in the removal of organic carbon from the WW. The results obtained by these processes showed that the formation of radicals was driven by the application of catalysts (homogeneous and heterogeneous), radiation sources (UV-C, UV-A, ultrasound, and solar), pH, temperature, and COD content.

5. Conclusions

The WW is generated in large volumes by the wineries, due to the necessity for sanitation of the installations, in order to keep the quality of the wines. Considering the need to obtain reusable water, it is necessary to find methods that allow the removal of recalcitrant matter and at the same time reuse the water and recycle the sludge. Based on the review of several works, it was shown that the WW is a very complex matrix with a composition of high content of soluble sugars, organic acids, alcohols, COD, BOD_5, and low pH. If released into the environment without proper treatment, the WW causes serious environmental damage that can be irreversible. Based on the literature, it is concluded that several mechanisms can be employed to treat WW, which include degradation of organic matter, water reuse, and sludge recycling. The processes suggested in this review show high efficiency in COD removal, with low energy consumption, thus they can be adapted for pilot-scale WW treatment.

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