engineering proceedings

MDPI

Review Proceeding

Winery wastewater: challenges and perspectives †

Nuno Jorge*, Ana R. Teixeira, Ana Gomes, José A. Peres and Marco S. Lucas

Centro de Química de Vila Real (CQVR), Departamento de Química, Universidade de Trás-os-Montes e Alto Douro (UTAD), Quinta de Prados, 5001-801 Vila Real, Portugal; ritamourateixeira@gmail.com (A.R.T.); ana.filipa111@hotmail.com (A.G.); jperes@utad.pt (J.A.P.) and mlucas@utad.pt (M.S.L.)

* Correspondence: njorge@uvigo.es (N.J.)

† Presented at the 4th International Electronic Conference on Applied Sciences, will be held online from 27 October to 10 November 2023

Abstract: In this review it was aimed to study in detail the characterization of the winery wastewater (WW), the problems cause 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 in 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 effective for biodegradable WW, with the possibility to store biogas with anaerobic treatments. To complement biologic treatments, physical-chemical processes based in 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

Citation: Jorge, N.; Teixeira, A.R.; Gomes, A.; Peres, J.A.; Lucas, M.S. Winery wastewater: challenges and perspectives. **2023**, *5*, x. https://doi.org/10.3390/xxxxx

Academic Editor(s):

Received: date
Accepted: date
Published: date

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]. The wine production is a complex process which 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 [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 leads to the production of large volumes of a wastewater which varies in accordance with the volume 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 spent at least 2 L of water per liter of wine produced [6], it is observed annually the generation of large volumes of a 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.

2. Characterization of the winery wastewater

Portuguese legislation under the Decree Law nº 236-98, stated that the wastewater can be discharged in natural water bodies, if reached 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.

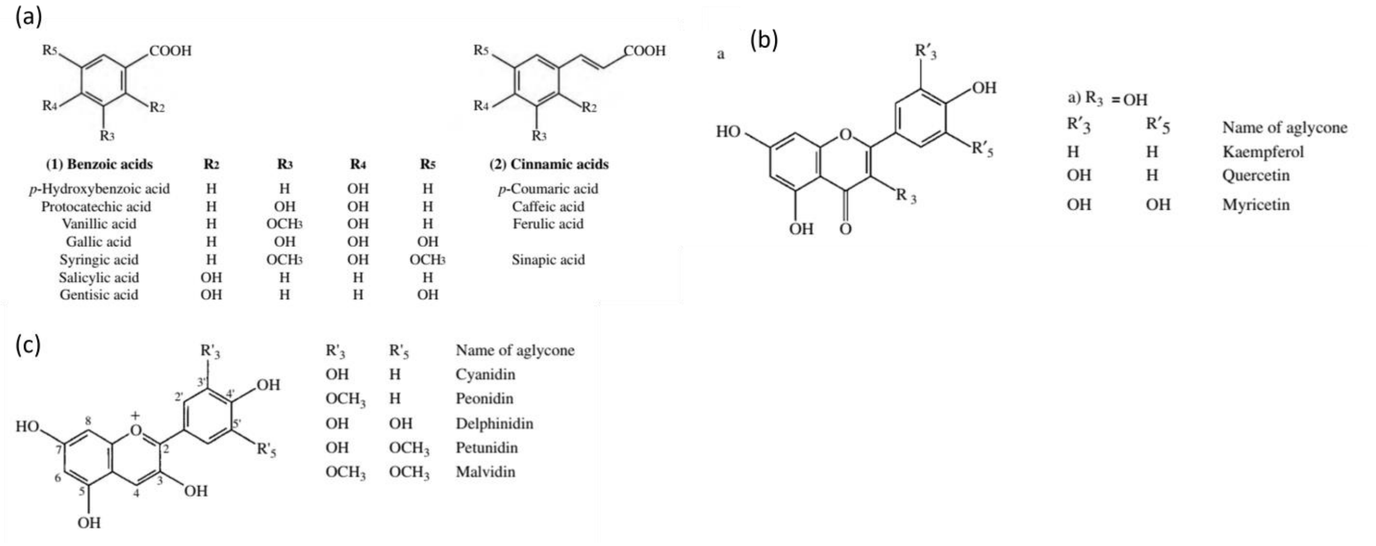

Figure 1. (a) Phenolic acids in grape and wine; (b) flavonoids: a - flavone (R3 = H) and flavonol (R3 = OH); (c) structure of anthocyanidins in grapes and wine.

However, several studies indicated that WW typically reaches a pH of 3 – 4, and a COD range of 800 – 12800 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 integrant 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.

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 eutrophication of water bodies (rivers, wetlands, natural streams, rivers), due to the fast consumption of the dissolved oxygen, which causes the lack of oxygen of aquatic and amphibious life. Although the WW can be applied as irrigation, thus becoming reusable, without a 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 the 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 to cause 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].

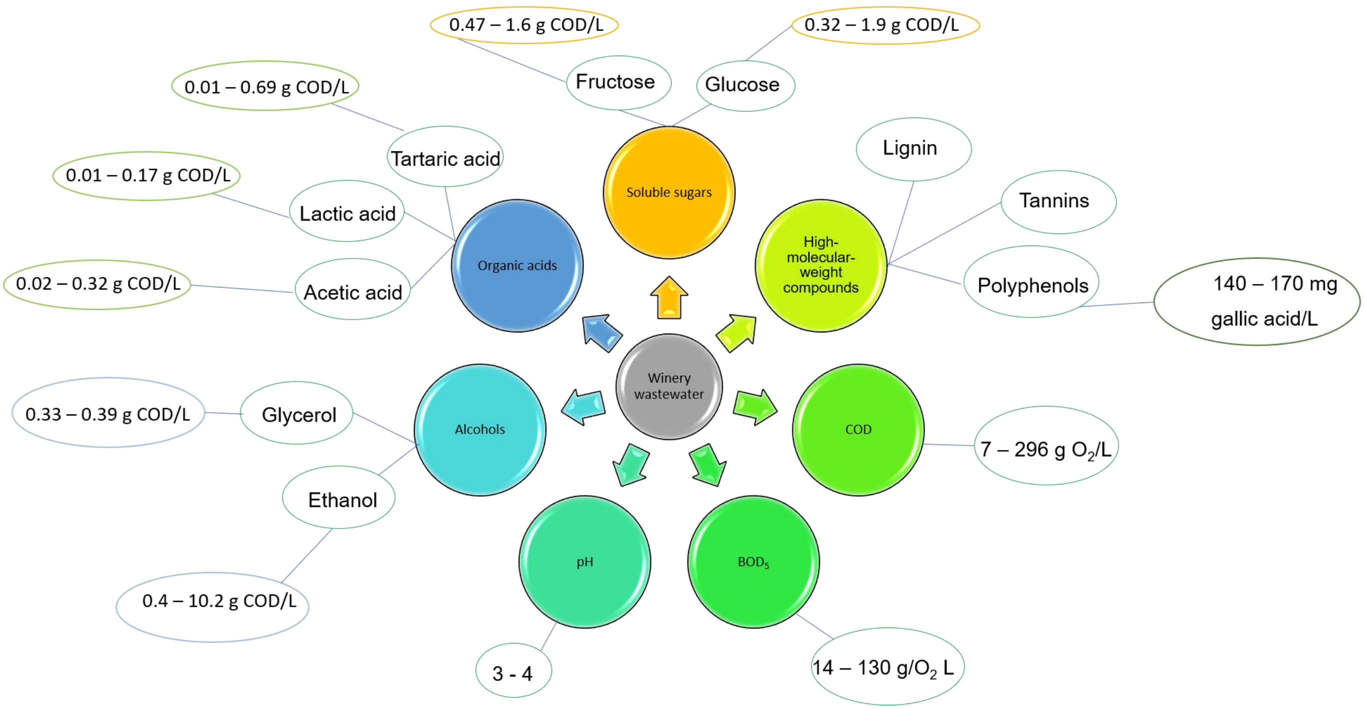

Figure 2. Chemical composition of the winery wastewater.

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, are proposed several processes that can be adapted with success to maximize the WW treatment, with the possibility to obtain several gains.

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 are 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 pilot scale. This process was selected considering the high biodegradability (BOD_5/COD = 0.55). The COD removal results showed 64% after biologic process (11 weeks). Application of 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 biologic 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 by 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 to apply the anerobic digestor for the treatment of the WW is also a possibility. During the 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 application of 100 mg/L of fly ash improved biogas production up to 79%.

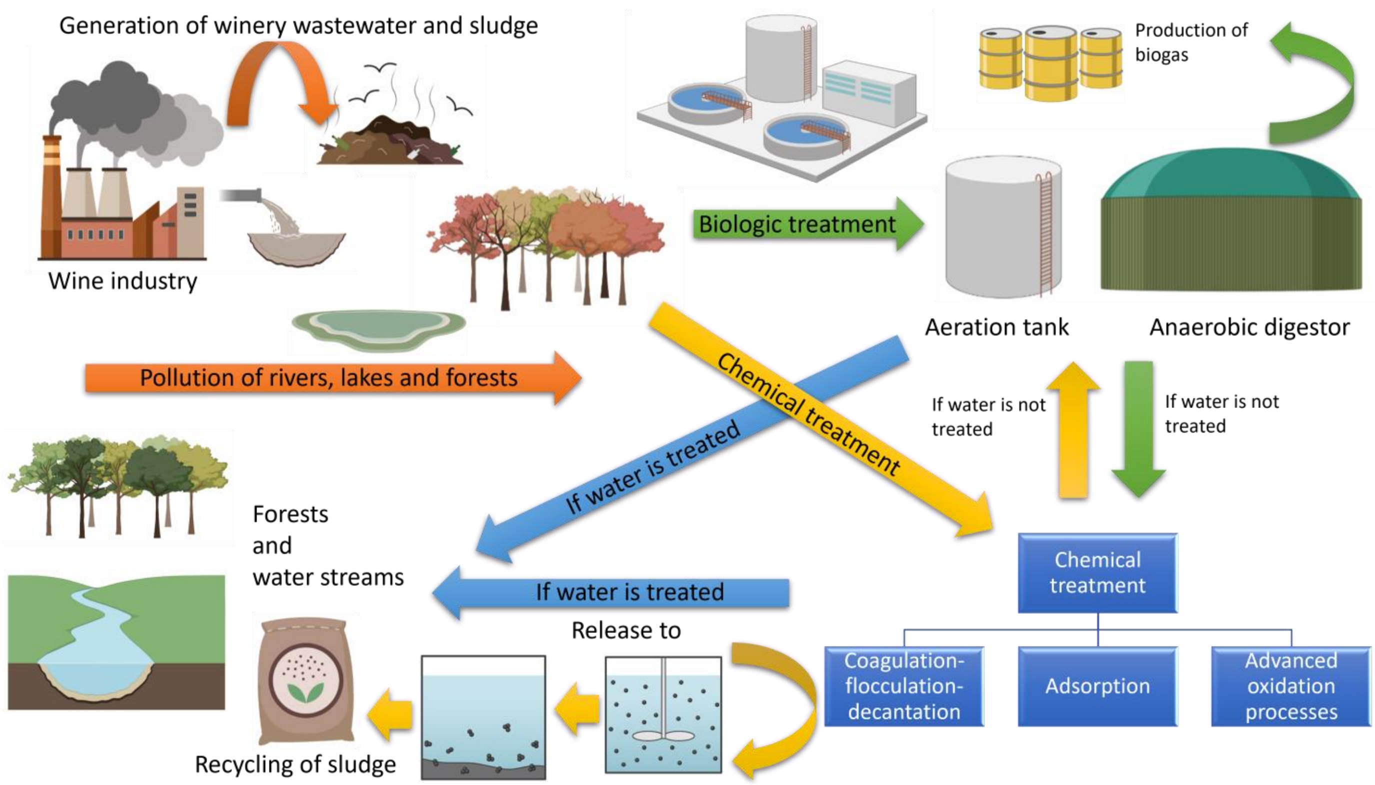

Figure 3. General scheme for WW generation and treatment: wine production, biologic treatment with biogas, chemical treatments (CFD, adsorption, AOPs), sludge recycling and water reuse.

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 the adsorption lies 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 efficient was related with 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 of 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 can´t be degraded by biologic processes, thus chemical treatments, such as AOPs can be applied. Among the AOPs it was observed the successful application of hydroxyl-based AOPs [23,26,27], sulfate-radical-based AOPs [25] and ozone-based AOPs [28] 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 allows the removal of recalcitrant matter and at the same time reuse the water and recycle the sludge. Based in the review of several works, it was shown that the WW is a very complex matrix with the 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 in the literature, it is concluded that several mechanisms can be employed to treat the WW, which includes degradation of organic matter, water reuse and sludge recycling. The processes suggested in this review shows high efficiency in COD removal, with low energy consumption, thus they can be adapted for pilot scale WW treatment.

Author Contributions: Conceptualization, N.J., A.G. and A.R.T.; methodology, N.J.; software, N.J.; validation, N.J., A.G., M.S.L., and J.A.P.; formal analysis, N.J.; investigation, N.J.; resources, M.S.L. and J.A.P.; data curation, N.J.; writing—original draft preparation, N.J.; writing—review and editing, M.S.L. and J.A.P.; visualization, J.A.P.; supervision, M.S.L. and J.A.P.; project administration, J.A.P.; funding acquisition, J.A.P. All authors have read and agreed to the published version of the manuscript."

Funding: The authors are grateful for the financial support of the Project AgriFood XXI NORTE-01-0145-FEDER-000041 and Fundação para a Ciência e a Tecnologia (FCT) to CQVR (UIDB/00616/2020). Ana R. Teixeira also thanks the FCT for the financial support provided through the doctoral scholarship UI/BD/150847/2020. This work was also financially supported by project "Vine and Wine Portugal – Driving Sustainable Growth Through Smart Innovation" with reference number C644866286-011, co-financed by the Recovery and Resilience Plan (RRP) and NextGeneration EU Funds.

Institutional Review Board Statement: "Not applicable".

Informed Consent Statement: "Not applicable."
Data Availability Statement: "Not applicable."

Conflicts of Interest: "The authors declare no conflict of interest."

References

1. OIV State of the World Vine and Wine Sector 2021 2022, 1–20.
2. Jorge, N.; Santos, C.; Teixeira, A.R.; Marchão, L.; Tavares, P.B.; Lucas, M.S.; Peres, J.A. Treatment of Agro-Industrial

Wastewaters by Coagulation-Flocculation-Decantation and Advanced Oxidation Processes—A Literature Review. *Eng. Proc.* **2022**, *19*, 33, doi:10.3390/ECP2022-12665.

3. Ribéreau-Gayon, P.; Glories, Y.; Maujean, A.; Dubourdieu, D. *Handbook of Enology Volume 2 The Chemistry of Wine Stabilization and Treatments 2nd Edition*; 2 nd.; England, 2006; Vol. 2; ISBN 9780470010396.
4. Spennati, E.; Casazza, A.A.; Converti, A. Winery Wastewater Treatment by Microalgae to Production Purposes. *Energies* **2020**, *13*, 2490, doi:10.3390/en13102490.
5. Kyzas, G.Z.; Symeonidou, M.P.; Matis, K.A. Technologies of Winery Wastewater Treatment: A Critical Approach. *Desalin. Water Treat.* **2014**, *57*, 3372–3386, doi:10.1080/19443994.2014.986535.
6. Kara, S.; Gürbulak, E.; Eyvaz, M.; Yüksel, E. Treatment of Winery Wastewater by Electrocoagulation Process. *Desalin. Water Treat.* **2013**, *51*, 5421–5429, doi:10.1080/19443994.2013.770223.
7. Agustina, T.E.; Ang, H.M.; Pareek, V.K. Treatment of Winery Wastewater Using a Photocatalytic/Photolytic Reactor. *Chem. Eng. J.* **2008**, *135*, 151–156, doi:10.1016/j.cej.2007.07.063.
8. Cañadas, R.; Díaz, I.; Rodríguez, M.; González, E.J.; González-Miquel, M. N Integrated Approach for Sustainable Valorization of Winery Wastewater Using Bio-Based Solvents for Recovery of Natural Antioxidants. *J. Clean. Prod.* **2022**, *334*, 130181, doi:10.1016/j.jclepro.2021.130181.
9. Chatzilazarou, A.; Katsoyannos, E.; Gortzi, O.; Lalas, S.; Paraskevopoulos, Y.; Dourtoglou, E.; Tsaknis, J. Removal of Polyphenols from Wine Sludge Using Cloud Point Extraction. *J. Air Waste Manage. Assoc.* **2010**, *60*, 454–459, doi:10.3155/1047-3289.60.4.454.
10. Ioannou, L.A.; Puma, G.L.; Fatta-Kassinos, D. Treatment of Winery Wastewater by Physicochemical, Biological and Advanced Processes: A Review. *J. Hazard. Mater.* **2015**, *286*, 343–368, doi:10.1016/j.jhazmat.2014.12.043.
11. Strong, P.J.; Burgess, J.E. Treatment Methods for Wine-Related and Distillery Wastewaters: A Review. *Bioremediat. J.* **2008**, *12*, 70–87, doi:10.1080/10889860802060063.
12. Nair, C.I.; Jayachandran, K.; Shashidhar, S. Biodegradation of Phenol. *African J. Biotechnol.* **2008**, *7*, 4951–4958, doi:https://doi.org/10.5897/AJB08.087.
13. Lucas, M.S.; Mouta, M.; Pirra, A.; Peres, J.A. Winery Wastewater Treatment by a Combined Process: Long Term Aerated Storage and Fenton's Reagent. *Water Sci. Technol.* **2009**, *60*, 1089–1095, doi:10.2166/wst.2009.555.
14. Souza, B.S.; Moreira, F.C.; Dezotti, M.W.C.; Vilar, V.J.P.; Boaventura, R.A.R. Application of Biological Oxidation and Solar Driven Advanced Oxidation Processes to Remediation of Winery Wastewater. *Catal. Today* **2013**, *209*, 201–208, doi:10.1016/j.cattod.2012.08.037.
15. Marchão, L.; Fernandes, J.R.; Sampaio, A.; Peres, J.A.; Tavares, P.B.; Lucas, M.S. Microalgae and Immobilized TiO2/UV-A LEDs as a Sustainable Alternative for Winery Wastewater Treatment. *Water Res.* **2021**, *203*, 117464, doi:10.1016/j.watres.2021.117464.
16. Ngwenya, N.; Gaszynski, C.; Ikumi, D. A Review of Winery Wastewater Treatment: A Focus on UASB Biotechnology Optimisation and Recovery Strategies. *J. Environ. Chem. Eng.* **2022**, *10*, 108172, doi:10.1016/j.jece.2022.108172.
17. Lauzurique, Y.; Fermoso, F.G.; Sánchez, N.; Castillo, A.; Salazar, R.; García, V.; Huiliñir, C. Biogas Production from Winery Wastewater: Effect of the Substrate-Inoculum Ratio on Fly Ash Addition and Iron Availability. *J. Water Process Eng.* **2022**, *47*, 102826, doi:10.1016/j.jwpe.2022.102826.
18. Akhtar, J.; Amin, N.A.S.; Shahzad, K. A Review on Removal of Pharmaceuticals from Water by Adsorption. *Desalin. Water Treat.* **2016**, *57*, 12842–12860, doi:10.1080/19443994.2015.1051121.
19. Jorge, N.; Teixeira, A.R.; Lucas, M.S.; Peres, J.A. Combination of Adsorption in Natural Clays and Photo-Catalytic Processes for Winery Wastewater Treatment. In *Advances in Geoethics and Groundwater Management : Theory and Practice for a Sustainable Development*; Abrunhosa, M., Chambel, A., Peppoloni, S., Chaminé, H.I., Eds.; Springer, Cham, 2021; pp. 291–294 ISBN 978-

3-030-59320-9.

20. Guimarães, V.; Lucas, M. S.; Peres, J. A.. Combination of adsorption and heterogeneous photo-Fenton processes for the treatment of winery wastewater. *Environ. Sci. Pollut. Res* **2019**, *26*, 31000-31013, doi:10.1007/s11356-019-06207-6.
21. Rytwo, G.; Lavi, R.; Rytwo, Y.; Monchase, H.; Dultz, S.; König, T. N.. Clarification of olive mill and winery wastewater by means of clay–polymer nanocomposites. *Sci. Total Environ.* **2013**, *442*, 134-142, doi:10.1016/j.scitotenv.2012.10.031.
22. Braz, R.; Pirra, A.; Lucas, M.S.; Peres, J.A. Combination of Long Term Aerated Storage and Chemical Coagulation/Flocculation to Winery Wastewater Treatment. *Desalination* **2010**, *263*, 226–232, doi:10.1016/j.desal.2010.06.063.
23. Jorge, N.; Teixeira, A.R.; Lucas, M.S.; Peres, J.A. Combined Organic Coagulants and Photocatalytic Processes for Winery Wastewater Treatment. *J. Environ. Manage.* **2023**, *326*, 116819, doi:10.1016/j.jenvman.2022.116819.
24. Jorge, N.; Teixeira, A.R.; Lucas, M.S.; Peres, J.A. Agro-Industrial Wastewater Treatment with Acacia Dealbata Coagulation/Flocculation and Photo-Fenton-Based Processes. *Recycling* **2022**, *7*, 54, doi:10.3390/recycling7040054.
25. Rodríguez-Chueca, J.; Amor, C.; Silva, T.; Dionysiou, D. D.; Puma, G. L.; Lucas, M. S.; Peres, J. A.. Treatment of winery wastewater by sulphate radicals: HSO5−/transition metal/UV-A LEDs. *J. Chem. Eng* **2017**, *310*, 473-483, doi:10.1016/j.cej.2016.04.135.
26. Johnson, M. B.; Mehrvar, M.. Treatment of Actual Winery Wastewater by Fenton-like Process: Optimization to Improve Organic Removal, Reduce Inorganic Sludge Production and Enhance Co-Treatment at Municipal Wastewater Treatment Facilities. *Water* **2021**, *14*, 39, doi:10.3390/w14010039.
27. Jorge, N.; Teixeira, A.R.; Lucas, M.S.; Peres, J.A. Enhancement of EDDS-Photo-Fenton Process with Plant-Based Coagulants for Winery Wastewater Management. *Environ. Res.* **2023**, *229*, 116021, doi:10.1016/j.envres.2023.116021.
28. Jorge, N.; Teixeira, A.R.; Matos, C.C.; Lucas, M.S.; Peres, J.A. Combination of Coagulation–Flocculation–Decantation and Ozonation Processes for Winery Wastewater Treatment. *Int. J. Environ. Res. Public Health* **2021**, *18*, 8882, doi:10.3390/ijerph18168882.

Disclaimer/