HEAVY METAL IDENTFICATION IN WINERY WASTEWATER

IDENTIFICAREA METALELOR GRELE ÎN APELE UZATE DIN CRAMĂ

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Abstract.
Wastewater is generated at every stage of wine production, mostly from cleaning equipment, floors, tanks, barrels and bottles. Wastewater contains heavy metals and other toxic compounds that can pose environmental hazards risks. This study quantified the concentrations of key heavy metals (lead, chromium, manganese, copper, and iron) in wastewater from a winery at different stages of the winemaking process. The results showed that all heavy metal concentrations were consistently below the maximum permitted limits, in compliance with environmental regulations. Lead concentrations decreased significantly from 24.03 µg/L after pressing stage to 9.44 µg/L after bottling stage. Manganese showed fluctuations throughout the process, while copper concentrations decreased significantly, indicating effective removal of residues. Overall, the findings suggest that the winemaking process effectively reduces heavy metal concentrations in wastewater, ensuring compliance with environmental standards.
Key words: wastewater, heavy metals, winemaking stages, environmental impact.

Rezumat.
Apele uzate sunt generate în fiecare etapă a vinificației, în special în urma spălării echipamentelor, podelelor, tancurilor de oțel, baricurilor și a sticlelor. Apele uzate conțin metale grele și alți compuși toxici care pot prezenta riscuri pentru mediu. În acest studiu s-au cuantificat concentrațiile principalelor metale grele (plumb, crom, mangan, cupru și fier) din apele uzate provenite dintr-o cramă, în diferite etape ale procesului de vinificație. Rezultatele au arătat că toate concentrațiile de metale grele au fost constant sub limitele maxime permise, în conformitate cu reglementările de mediu. Concentrațiile de plumb au scăzut semnificativ de la 24,03 µg/L după etapa de presare la 9,44 µg/L după etapa de îmbuteliere. Manganul a prezentat fluctuații pe parcursul procesului de vinificație, în timp ce concentrațiile de cupru au scăzut semnificativ, indicând o îndepărtare eficientă a urmelor de metale. În

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general, rezultatele sugerează că procesul de vinificație reduce eficient concentrațiile de metale grele din apele uzate, contribuind astfel la respectarea standardelor de mediu

Cuvinte cheie: ape uzate, metale grele, etapele vinificației, impact asupra mediului

INTRODUCTION

The wine industry plays a vital role in many countries, contributing significantly to the economy, local communities, and tourism. The winery industry plays a major role in the global food-processing sector, with the wine market valued at \$340 billion in 2020 and anticipated to grow to \$460 billion by 2028.

The winemaking process involves several stages, like as: grape harvesting, destemming and crushing, pressing, fermentation, clarification, ageing, filtration, and bottling. Throughout these stages, large amounts of wastewater, also known as winery wastewater or process effluent, are generated. Wine production uses a considerable amount of resources, which in turn leads to the creation of large quantities of wastewater (from 0.2 to 4 liters per liter of wine produced) [Holtman et. al., 2022]. This wastewater includes spilled wine or juice, wash water, cooling water, cleaning chemicals and leachate from solid byproducts.

Winery effluent concerns include heavy metals, biodegradable organics, solids and nitrogen. While the land application of winery wastewater can improve soil fertility and nutrient availability for plants, excessive application may lead to nitrate leaching, groundwater contamination, unpleasant odors, and anaerobic conditions, which can release metals like iron and manganese under acidic conditions. The quality of winery wastewater varies depending on the stage of winemaking (vintage, racking, bottling), the winemaking techniques employed (such as producing red, white, or special wines), the operation of the winery, and the cleaning chemicals used [Amor et al., 2019].

Given the significant environmental impact associated with the improper disposal of winery wastewater, it is essential to monitor its quality throughout the winemaking process. The purpose of this study is to investigate the concentrations of heavy metals in winery wastewater at various stages of the winemaking process, with the aim of enhancing wastewater management practices and contributing to the sustainability of the wine industry.

MATERIAL AND METHOD

For this study, red wine was collected from the 2023 vintage at the Iasi vineyard in Romania. The grapes were hand-harvested at optimal maturity and under ideal sanitary conditions. Standard winemaking procedures were followed at the pilot scale at the "Ion Ionescu de la Brad" Iasi University of Life Sciences. The complete winemaking process, along with wastewater sample collection, occurred after the following stages: pressing, aging, filtration, and bottling. The study focused on five key heavy metals: manganese (Mn), iron (Fe), copper (Cu), lead (Pb), and chromium (Cr).

The procedure for determining heavy metals was based on methods previously described by Dumitriu Gabur et al. [2021].

RESULTS AND DISCUSSIONS

The quality of winery wastewater depends on various factors, including the operational setup of the winery, water management practices, sanitation protocols, seasonal changes, and the winemaking stage. These variables lead to a wide range of wastewater characteristics. Winery wastewater is typically acidic and contains high levels of total solids (TS), volatile solids (VS), dissolved solids (DS), 5-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), and total phosphorus (TP) (Table 1). The low pH is primarily due to the acidic nature of grape juice, alcoholic compounds, and organic acids released from the crushed fruit and fermentation by-products. The elevated BOD concentration is attributed to biodegradable components such as alcohols (mainly ethanol), sugars (glucose and fructose), organic acids (such as lactic, tartaric, citric, malic, and succinic acids), and glycerin. In contrast, COD reflects more persistent organic substances, including polyphenols, tannins, and lignins.

Improper discharge or land application of winery wastewater into receiving waters can lead to several environmental issues. Oxygen depletion may occur due to the microbial breakdown of organic carbon and nitrogen, resulting in a decrease in dissolved oxygen levels, which can harm aquatic and amphibious life. Additionally, this process can cause odor issues, increase concentrations of nitrites and nitrates, promote eutrophication, and lead to higher emissions of nitrous oxide as ammonia is oxidized and nitrate is reduced. Releasing untreated wastewater can cause significant harm to ecosystems, including water contamination, soil degradation, and damage to vegetation [Chatzilazarou et al., 2010]. Uncontrolled wastewater discharge contributes to the eutrophication of water bodies (such as rivers, wetlands, and natural streams) by rapidly consuming dissolved oxygen, which depletes oxygen levels and threatens aquatic life.

While winery wastewater can be reused for irrigation, improper monitoring can alter soil properties, such as pH, color, and electrical conductivity, due to the release of inorganic and organic ions. The high acidity of the wastewater can negatively affect plant growth by reducing essential nutrients like calcium and phosphorus and by decreasing the population of beneficial microbes. Additionally, previous studies have shown that winery wastewater contains high concentrations of phenolic compounds, which can cause significant environmental damage. These compounds can be toxic to animals, humans, and microorganisms even at low concentrations and are highly resistant to biodegradation [Strong et al., 2008].

In most treatment cases, the presence of heavy metals in winery wastewater is often overlooked, with the focus primarily on reducing the organic load. This is because, in many instances, the concentrations of heavy metals in winery wastewater are relatively low.

Table 1

Properties of winery wastewater

Parameters	**Johnson and Mehrvar [2020]**	**Remmas [2022]**	**Ngwenya et al. [2022]**	**Vlotman et al. [2022]**	**Latessaa et al. [2023]**
pH	2.80 - 11.0	3.6 - 4.9	3.4 - 6.9	3.0 - 12.9	2.50 - 9.38
Total solids (TS), g/L	0.75 - 188	-	0.03 - 154	1.60 - 79.6	0.00 - 82.0
Volatile solids (VS), g/L	0.3 - 128	-	0.01 - 130	0.13 - 55.0	0.00 - 69.0
Total suspended solids (TSS), g/L	0.007 - 84.4	0.08 - 2.4	0.14 - 65.6	0.1 - 30.3	0.00 - 9.00
Conductivity, mS/cm	0.36 - 1.17	-	-	-	-
Chemical oxygen demand (COD), g/L	0.04 - 360	0.5 - 15.9	2.60 - 273	0.34 - 296	0.15 - 45.6
5-day biochemical oxygen demand (BOD_5), g/L	0.15 - 96.0	0.15 - 8.0	-	0.13 - 130	0.12 - 16.5
Total nitrogen (TN), mg/L	-	60 - 200		10 - 415	1.4 - 328
Total Kjeldahl nitrogen (TKN), mg/L	0.51 - 14300	-	6 - 1350	-	3.2 - 374
Ammonia-N, mg/L	0.20 - 395	-	-	-	0.22 - 24.0
Total phosphorus (TP), mg/L	0.70 - 1120	10 - 55	7.0 - 250	3.3 - 188	0.29 - 106
Phenols, mg/L	-	30 - 200	-	-	0.19 - 268
Na, mg/L	1.0 - 1160	-	-	29 - 460	0.2 - 396
K, mg/L	12.4 - 8000	-	-	7 - 1000	205 - 1445
Ca, mg/L	1.8 - 1910	-	-	-	-
Mg, mg/L	1.1 - 530	-	-	-	-
Fe, mg/L	0.17 - 335	-	-	-	-

The concentrations of the main heavy metals in the wastewater collected from a winery were quantified, and the results are summarized in Table 2. All concentrations of heavy metals identified in the wastewater from winemaking were below the maximum permitted limits, in compliance with legislative requirements.

The concentrations of lead (Pb) decrease consistently from 24.03 µg/L after pressing to 9.44 µg/L after bottling. This suggests a reduction in lead contamination throughout the winemaking process, which is good, as it is significantly below the maximum permitted limits for wastewater discharges.

Chromium (Cr) concentrations are relatively low throughout the process, with a slight decrease from 0.60 µg/L after pressing to 0.27 µg/L after filtration, followed by a sharp increase to 3.17 µg/L after bottling. This behavior could indicate the accumulation of chromium in the wine during last stage, possibly from contamination sources that were not fully removed. However, the concentration is low, below the maximum allowed limit.

Manganese (Mn) shows large fluctuations during the winemaking process, from 521.12 µg/L in pressing to 534.61 µg/L in bottling. These fluctuations may suggest that manganese is both absorbed and released during the different winemaking stages.

Table 2

Heavy metal concentrations in wastewater at different stages of winemaking

Parameters	Pressing	Aging	Filtration	Bottling
Pb (µg/L)	24.03 ± 0.39	16.67 ±0.18	13.54 ± 0.13	9.44 ± 0.04
Cr (µg/L)	0.60 ± 0.03	0.47 ± 0.01	0.27 ± 1.67	3.17 ± 0.01
Mn (µg/L)	521.12 ± 0.86	156.39 ± 0.06	310.04 ± 2.86	534.61 ± 5.48
Cu (µg/L)	629.85 ± 0.63	95.30 ± 0.44	44.24 ± 2.52	82.38 ± 0.29
Fe (µg/L)	169.23 ± 0.68	209.29 ± 0.72	236.36 ± 9.84	254.75 ± 0.63

Copper (Cu) concentrations decrease significantly from 629.85 µg/L after pressing to 82.38 µg/L after bottling. The reduction of copper over the stages of winemaking suggests that some impurities are removed, which likely benefits the wine's quality and environmental safety.

Iron (Fe) concentrations slightly increase from 169.23 µg/L after pressing to 254.75 µg/L after bottling. This could indicate a gradual accumulation of iron in the wine as it passes through various stages, which could affect the taste and stability of the wine, as iron is involved in oxidation processes.

The maximum allowable concentrations of heavy metals in wastewater discharges in Romania are 0.2 mg/L for copper (Cu), 1 mg/L for nickel (Ni), 0.3 mg/L for cadmium (Cd), 1.5 mg/L for chromium (Cr), and 0.5 mg/L for lead (Pb) when discharging into the sewerage system, and 0.1 mg/L for copper (Cu), 0.5 mg/L for nickel (Ni), 0.2 mg/L for cadmium (Cd), 1 mg/L for chromium (Cr), and 0.2 mg/L for lead (Pb) when discharging into rivers, as per NTPA002/2002 and NTPA001/2002 regulations.

CONCLUSIONS

Winery wastewater is generated in large volumes due to the need for sanitation of the facilities in order to maintain wine quality. The concentrations of heavy metals in wastewater decrease during most stages of winemaking, with some fluctuations observed, particularly in manganese and iron levels. The final concentrations at the bottling stage remain low, well below the maximum allowable limits for wastewater discharges. This indicates that the winemaking process effectively reduces the environmental impact, making the wastewater safe for disposal and minimizing potential harm to the environment.

Future efforts should focus on monitoring wastewater flow rates and pollutant concentrations, as these are essential for accurately assessing pollutant mass loading, optimizing treatment processes, designing efficient wastewater management systems, and ensuring the sustainability of the winery.

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