Tertiary Treatment of Wine Distillery Wastewater at Near-Neutral pH using the Chelate-modified Fenton Process

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INTRODUCTION & AIM

- Wine distilleries produce high amounts of strongly polluted wastewater (WDW), wasting a valuable hydrological resource in drought-prone climates.
- Economically motivated incorporation of grape lees and pomace increase recalcitrancy secondary treatment, rendering the final effluent unsuitable for reutilization, namely in the European Union (EU).
- The Fenton process can be used to refine such effluents via hydroxyl radical generated by H_2O_2 decomposition (Eq. 1) under acidic conditions (pH 2.5 – 3). Although this pH adjustment prevents iron catalyst precipitation (Eq. 2), it raises operational costs and limits feasibility

$$H_2O_2 + Fe^{2+} \rightarrow HO^{\bullet} + Fe^{3+} + HO^- \quad (1)$$

$$Fe^{3+} + 3\,OH^- \rightarrow Fe(OH)_3\downarrow \quad (2)$$

This study investigates the application of **chelating agents** (CAs) as a means to stabilize the iron catalyst at near-neutral pH (Eq. 3 and Eq. 4), thus achieving a **cost-effective** tertiary treatment for reutilization goals.

$$Fe^{2+} + CA \leftrightarrow Fe^{2+}\text{- }CA \quad (3)$$

$$Fe^{3+} + CA \leftrightarrow Fe^{3+}\text{- }CA \quad (4)$$

METHODS

1. Effluent Preparation and Collection

An oriented dillution of a synthetic, lees-based, raw WDW formulation was carried out to simulate a previous secondary treatment step

Table 1. Estimation of the composition of a biologically treated synthetic WDW

Component	Raw Effluent (mg/L)	Relative Biodegradability	Dilution (%)	Final Effluent (mg/L)
Succinic acid	11500	1.26	82.5	2010
Fructose	5000	1.39	89.7	515
Glucose	4800	1.47	95	240
Tartaric acid	2460	1.14	84.4	383
Caffeic acid	800	0.75	47.0	424
Gallic acid	800	1.15	75.8	194
Syringic acid	800	1.06	74.8	202
Protocatechuic acid	800	0.98	78.7	171
Mallic acid	100	1.04	74.8	25

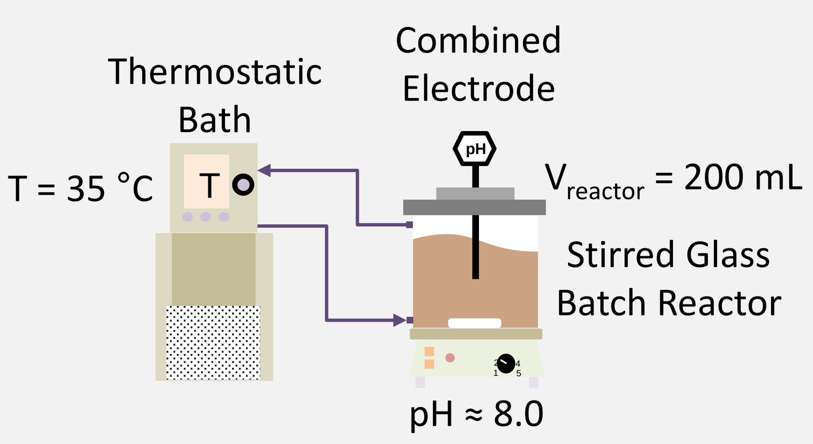
2. Chelating Agent Selection

Preliminary screening was done based on commercial availability, toxicity of the ligand and ability to chelate at the desired WDW pH range (6.0 – 8.0)

Table 2. Chelating agents employed in the study

Sodium Pyrophosphate (PPP)	Ethylenediamine dissuccinicacid (EDDS)	Tartaric Acid (TA)	Oxalic Acid (OA)

3. Parametric Study



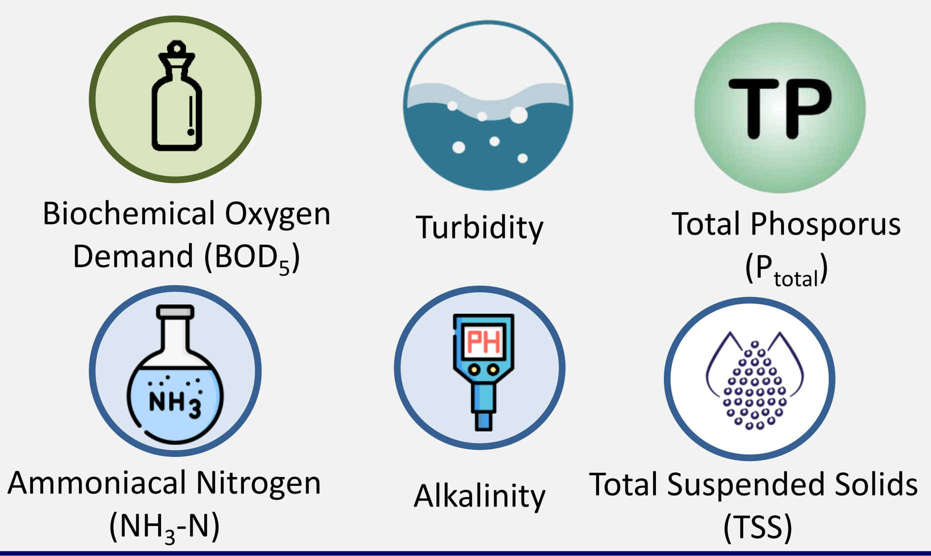
$[H_2O_2]$ = 0.2 - 3.0 g/L (Stoichiometric with COD)

$[Fe^{2+}]$ = 0.2 - 0.3 g/L (1:10 mass ratio with H_2O_2)

$[CA]:[Fe^{2+}]$ = 1.0 - 2.0 (CA-to-catalyst molar ratio)

4. Effluent Characterization

EU Regulation 2020/741 on Water Reutilization



https://sciforum.net/event/ECWS-9

RESULTS & DISCUSSION

1. Performance Analysis

TOC net effect was assessed at different $[CA]:[Fe^{2+}]$ at pH = 8.0. Best performer ($[PPP]:[Fe^{2+}]$ = 1) was then tested at an initial pH = 6.0, where no significant effect on TOC reduction was found between the run and the blank.

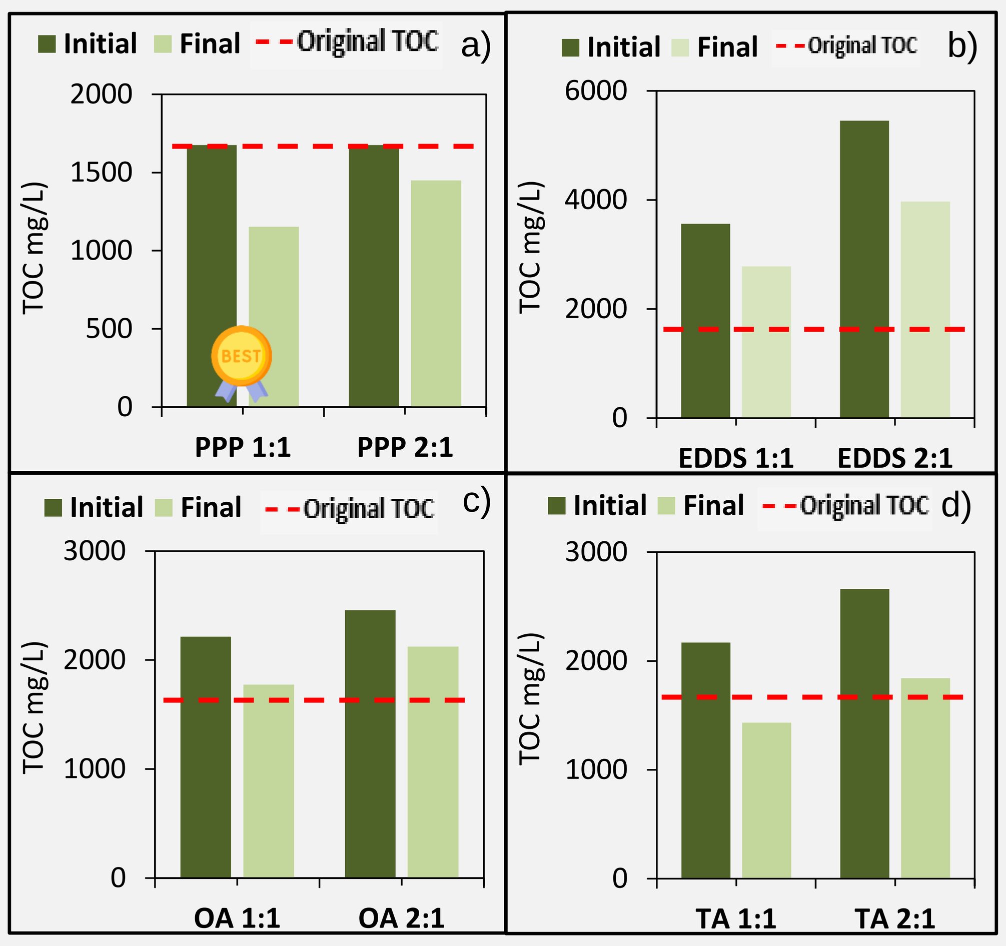


Figure 1. Initial and final TOC levels after treatment with PPP (a), EDDS (b), OA (c), and TA (d) at different CA-to-catalyst molar ratios for the synthetic effluent along the reaction (t = 2 h, pH = 8.0, T= 35 °C; $[H_2O_2]$ = 8.7 g/L and $[Fe^{2+}]$ = 0.87 g/L).

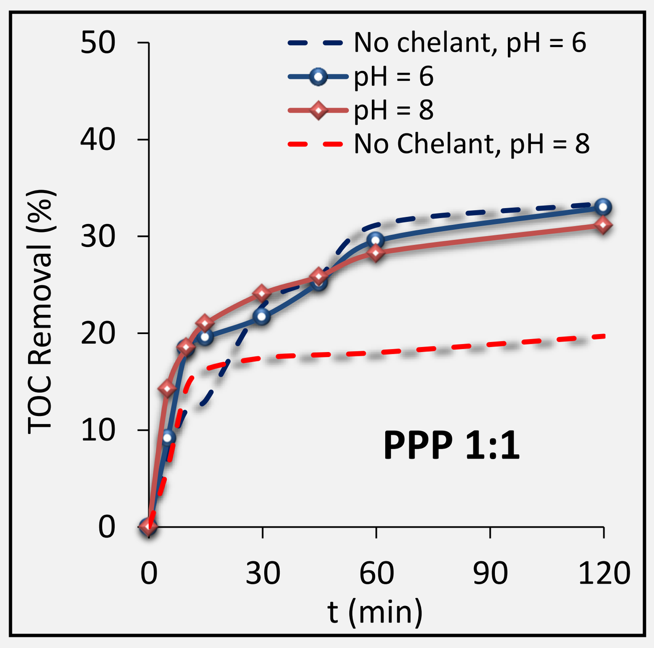


Figure 2. Influence of pH on the TOC removal for the synthetic effluent along the reaction (T= 35 °C; $[H_2O_2]$ = 8.7 g/L and $[Fe^{2+}]$ = 0.87 g/L).

2. Legislation Compliance and Cost Analysis with Real WDW

Real WDW was collected from an aerobic SBR (sequential batch reactor) at a local distillery and used for an extended run (t = 5h) with the best run ($[PPP]:[Fe^{2+}]$ = 1) whose results are summarized in Table 2.

Table 3. Characterization of real, biodigested WDW before and after treatment with pH = 8.1; T= 35 °C; $[H_2O_2]$ = 2.0 g/L, $[Fe^{2+}]$ = 0.2 g/L)

Parameter	Pre-Fenton	Post-Fenton	Requirements*
BOD_5 (mg O_2/L)	90	< 1	< 25
Turbidity (NTU)	16	12	-
TSS (mg/L)	< 1	< 1	< 35
N_{total} (mg N/L)	11.97	14.41	< 15[a]
P_{total} (mg P/L)	21.5	253.0	< 2[a]
pH	8.1	6.7	6.0 – 9.0

*EU Regulation 2020/741 for class B reclaimed water for agricultural irrigation; [a] optional parameters - applicable to some irrigation projects to minimize the risks of biofilm formation and obstruction of irrigation systems

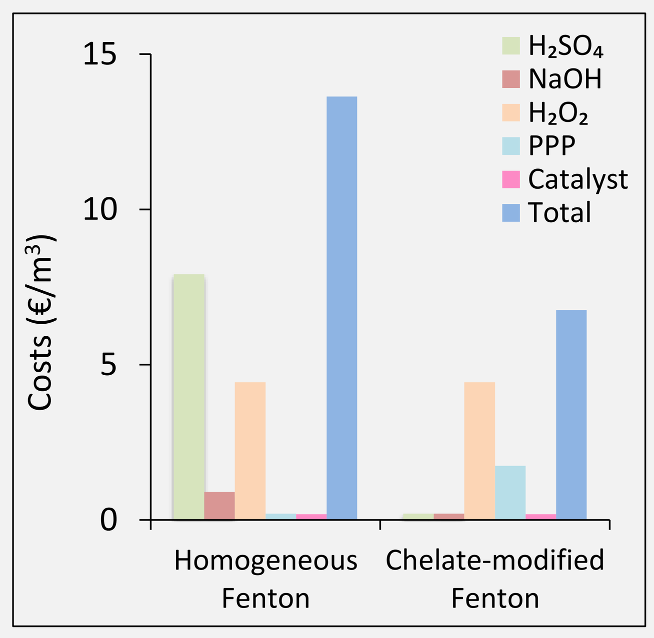


Figure 3. Costs analysis for Fenton's reaction at standard conditions (pH 3.0) and the chelate-modified version (pH = 8.1; [PPP] = 1.05 g/L).

CONCLUSIONS

- PPP demonstrated the best affinity for iron in WDW at 1:1 ratio with Fe^{2+}. Compared to a blank run with no CA at pH 8.0, TOC removal was increased by 12%.
- The final effluent complies with the Class B limits imposed but can only be used for irrigation when raw plants are not in contact with the irrigation water, processed food crops or non-food crops.
- Nonetheless, this approach significantly reduced reagent costs (53.7%) compared to the standard acidic conditions, which is a promising feature.

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