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The 3rd International Online-Conference on Nanomaterials

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Application of ferrocene for the treatment of winery wastewater in a heterogeneous photo-Fenton process

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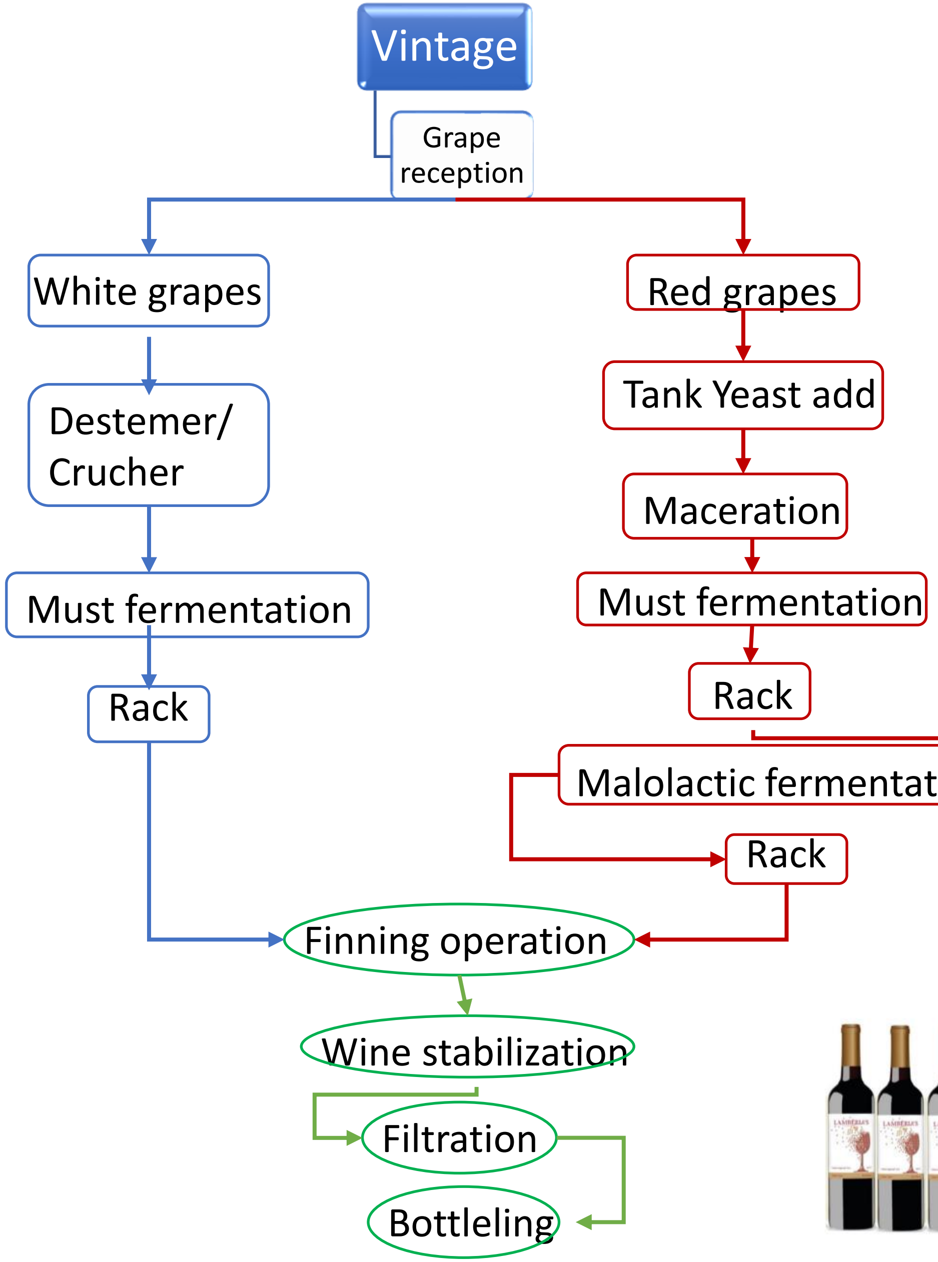
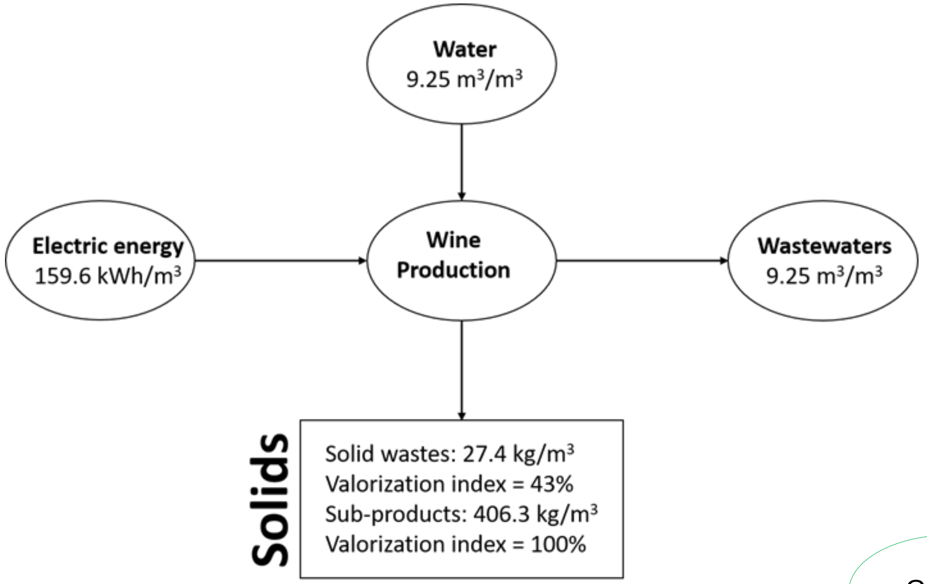
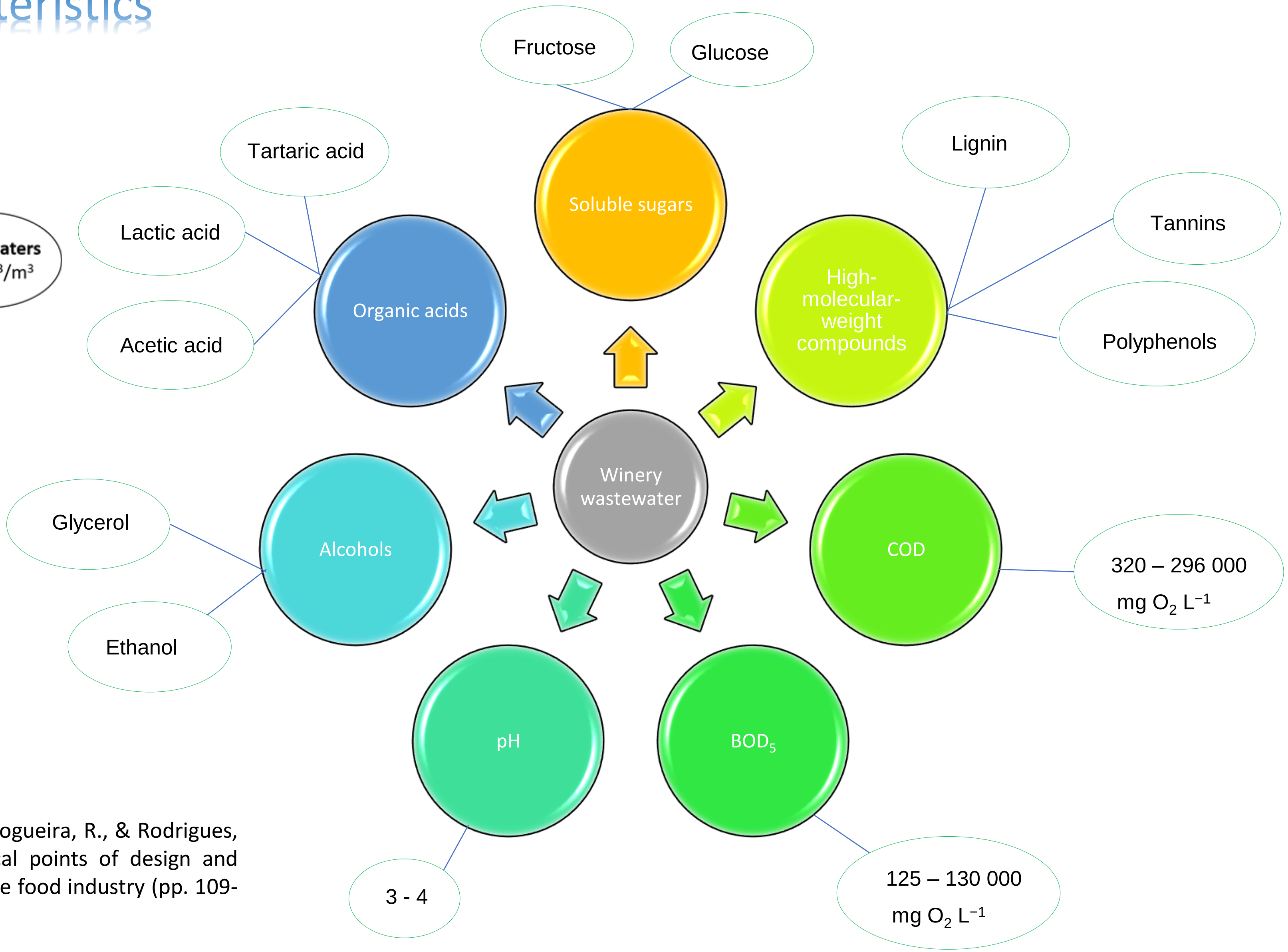


- In the vintage, the grapes are collected
- In the grape reception, the grapes are selected and separated
- In white wines the grapes are crushed and the must is fermented
- In red wines, the grapes are marecerated and the must is fermented with the grapes
- After must fermentation and wine stabilization, the wine is filtrated
- Finally, the wine is bottled

Winery wastewater main characteristics



Mass balance applied to ACPB winery representing specific values, i.e., values per cubic meter of produced wine. Losses of water by evaporation were neglected [1].



[1] Brito, A. G., Peixoto, J., Oliveira, J. M., Oliveira, J. A., Costa, C., Nogueira, R., & Rodrigues, A. (2007). Brewery and winery wastewater treatment: some focal points of design and operation. In Utilization of by-products and treatment of waste in the food industry (pp. 109-131). Springer, Boston, MA.

AOPs

HR-AOP

Fenton/ photo-Fenton

- Homogeneous
  - Oxalate
  - EDDS
  - EDTA
  - NTA
- Heterogeneous
  - Clay
  - Zeolite
  - Fly ash
  - Ferrocene
- Electro-Fenton

SR-AOP

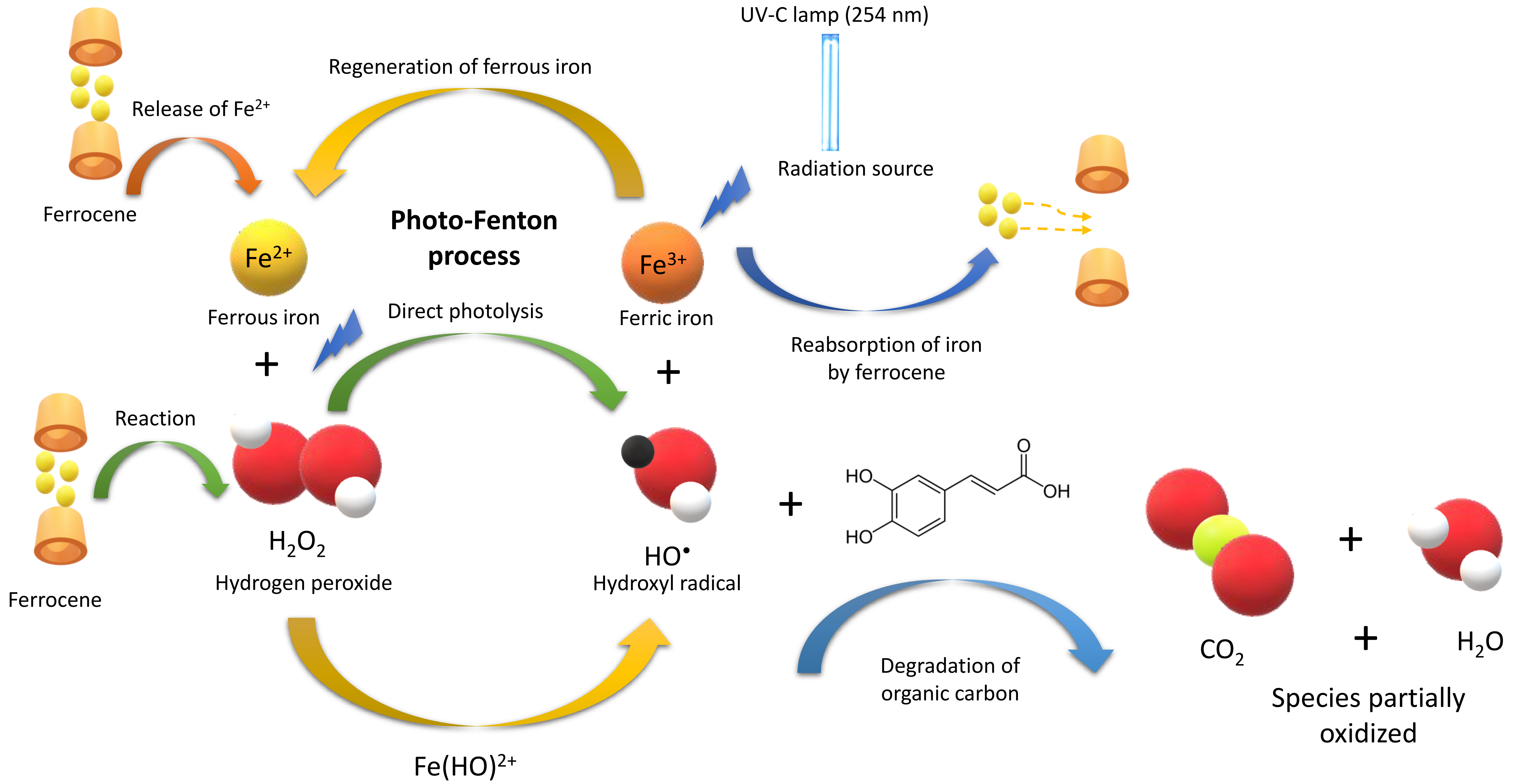
Activation processes

- Thermal activation
- Alkaline activation
- Radiation activation

Ozone

Ozone treatments

- HO^-/O_3 process
- O_3/H_2O_2 process
- UV/O_3 process
- O_3/biological treatment



UV-C lamp (254 nm)
Regeneration of ferrous iron
Release of Fe^{2+}
Radiation source
Ferrocene
Photo-Fenton process
Fe^{2+}
Fe^{3+}
Ferrous iron
Direct photolysis
Ferric iron
Reabsorption of iron by ferrocene
+
+
Reaction
HO
O
OH
HO
H_2O_2
Hydrogen peroxide
$HO^{\bullet}$
Hydroxyl radical
+
+
Ferrocene
Degradation of organic carbon
CO_2
+
H_2O
Species partially oxidized
$Fe(HO)^{2+}$

Considering the low information regarding the treatment of winery wastewater by heterogeneous photo-Fenton, catalyzed by ferrocene, the aim of this work is:

(1) To characterize ferrocene by FTIR and SEM

(2) to optimize heterogenous photo-Fenton

(3) to study the kinetic rate and regeneration of ferrocene

Winery wastewater collection and storage

Winery wastewater characterization

Main chemical characteristics of winery wastewater (WW)

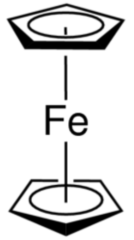
Parameters	Portuguese Law Decree nº 236/98	WW
pH	6.0-9.0	4.0
Biochemical Oxygen Demand - BOD_5 (mg O_2/L)	40	550
Chemical Oxygen Demand - COD (mg O_2/L)	150	2145
Biodegradability – BOD_5/COD		0.26
Total Organic Carbon – TOC (mg C/L)		400
Turbidity (NTU)		296
Total suspended solids – TSS (mg/L)	60	750
Electrical conductivity (µS/cm)		62.5
Total polyphenols (mg gallic acid/L)	0.5	22.6
Iron (mg/L)	2.0	0.05

Winery wastewater used in this work

Storage in small containers

Conservation at -40ºC

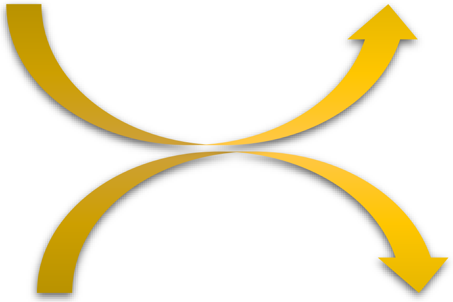
Equipment used in the heterogeneous photo-Fenton process



Ferrocene (Fc)

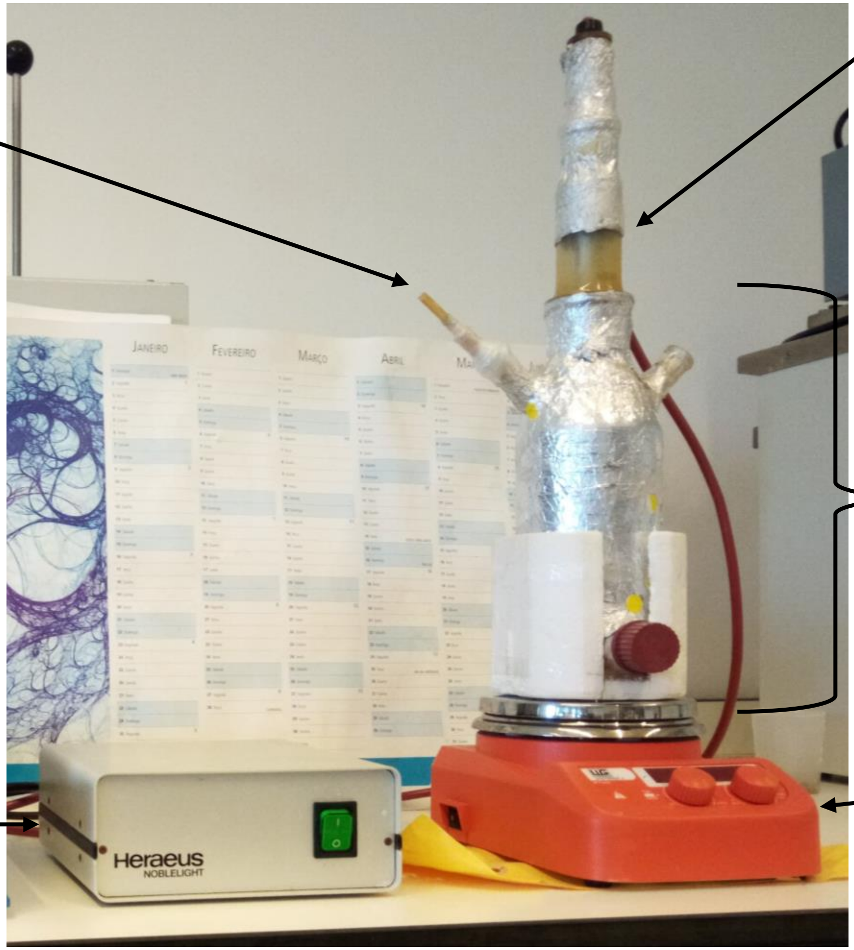
+

H_2O_2



Sample retriver

UV-C Mercury lamp
λ =254 nm

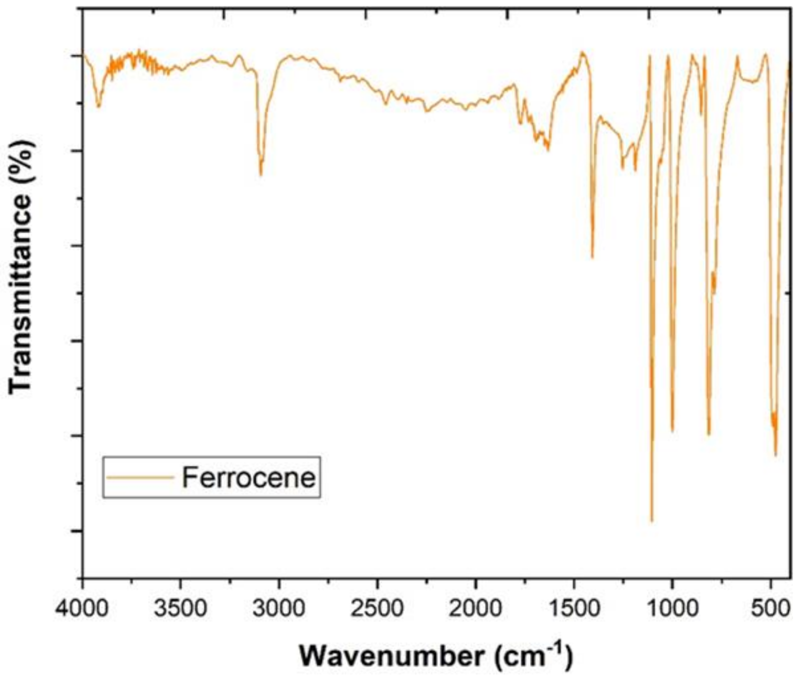


Cylindrical photoreactor
V = 500 mL

Power generator

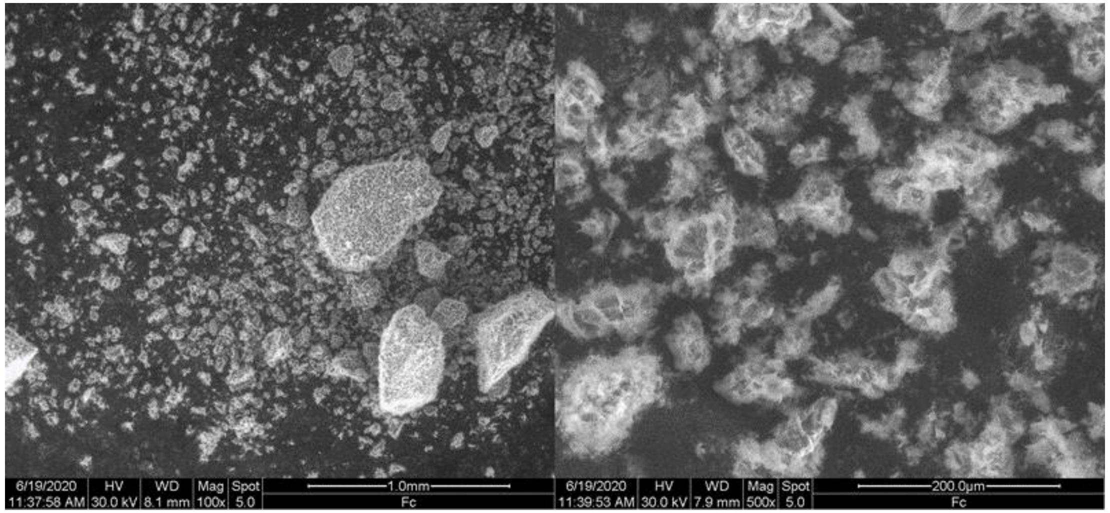
Stirrer

Characterization of Ferrocene



FTIR spectra of ferrocene.

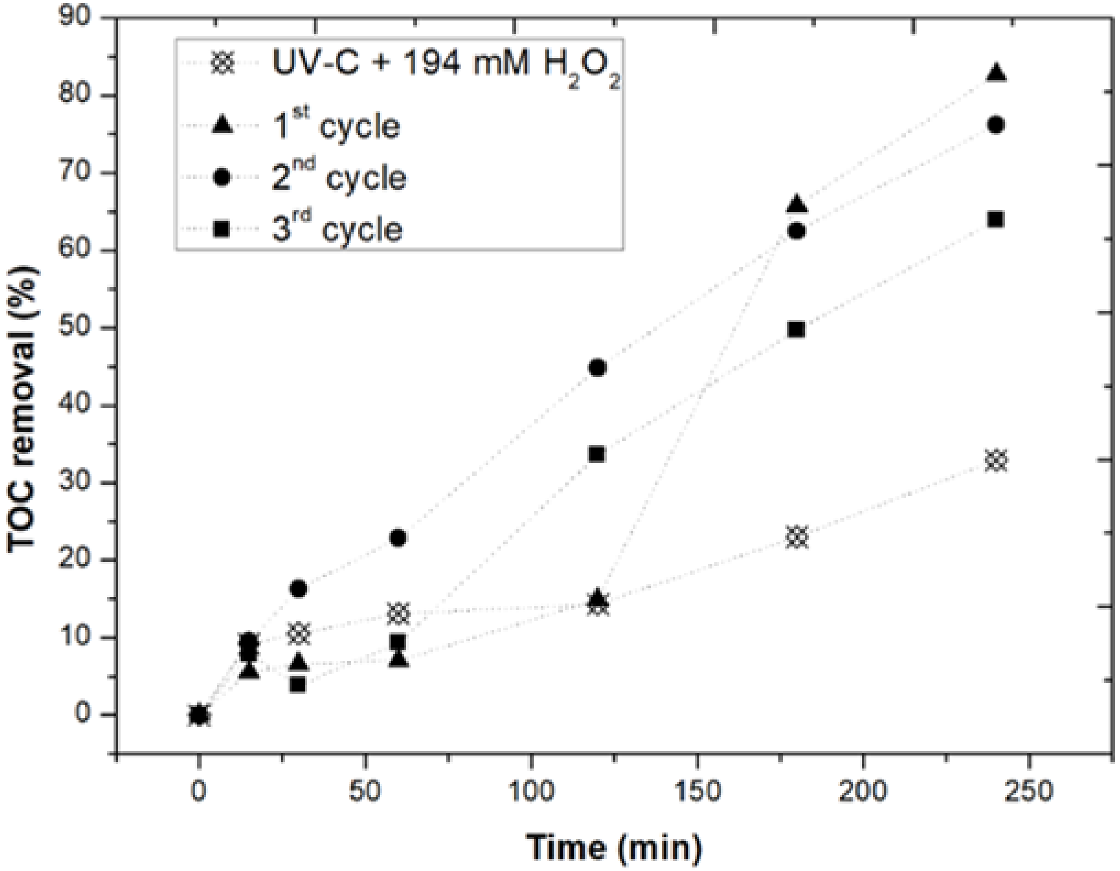
- C–H stretching at 3093 cm^{-1}
- C=C stretching at 1631 cm^{-1}
- Fe peak at 476 cm^{-1}



Scanning Electron Microscopy (SEM) images of ferrocene (100 and 500x).

- The ferrocene catalyst in its initial form has an irregular shape
- The ferrocene has a lot of free space in between the particles
- The ferrocene has adsorption capacity

Heterogeneous photo-Fenton optimization



Regeneration cycles from ferrocene catalyst along the 3 consecutive cycles of the heterogeneous photo-Fenton process ([Fc] = 0.50 g/L, $[H_2O_2]$ = 194 mM, pH = 3.0, agitation = 350 rpm, T = 298 K, radiation UV-C, t = 240 min).

- The pH was varied from 3.0 to 7.0, and results showed that heterogeneous pho-to-Fenton process was highly dependent on pH (3.0 > 4.0 > 6.0 > 7.0) with 53.3, 42.1, 35.0 and 22.8% respectively

- The H_2O_2 concentration was varied from 97 to 291 mM, and results showed a TOC re-moval of 48.5, 82.7 and 81.4%, respectively, for 97, 194 and 291 mM H_2O_2

- The ferrocene catalyst concentration was varied (0.25 to 1.0 g/L) and results showed a TOC removal of 83.1, 82.7 and 54.2%, respectively, for 0.25, 0.50 and 1.0 g/L Fc

- The durability of the Fc catalyst was examined by recovering the material and re-using it under the best operational conditions, as follows: [Fc] = 0.50 g/L, $[H_2O_2]$ = 194 mM, pH = 3.0, agitation = 350 rpm, T = 298 K, radiation UV-C, t = 240 min, for 3 consecutive cycles
- The results showed a TOC removal of 82.7, 76.2 and 63.9%, respectively for the 1st, 2nd and 3rd cycles, therefore, the FC catalyst can be reused

Kinetic analysis

The Fermi's non-linear kinetic model was used to determine the behavior of the ferrocene catalyst.

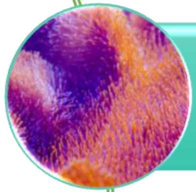
$$\frac{TOC}{TOC_0} = \frac{1 - X_{TOC}}{1 + \exp[k_{TOC}(t - t^*_{TOC})]} + X_{TOC}$$

- where k_{TOC} corresponds to the apparent reaction rate constant; t^*_{TOC} represents the transition time related to the TOC content curve's inflection point, and x_{TOC} corresponds to the fraction of non-oxidizable compounds that are formed during the reaction;

- The results showed that a higher k_{TOC} was obtained under the operational conditions pH 3.0, Fc dosage 0.50 g/L, H_2O_2 concentration 194 mM (addition in six steps) (k_{TOC} = 4.770x10^{-2} min^{-1}; 82.7% TOC removal).

Based in the results, it is concluded

(1) The ferrocene can be used as source of iron in heterogeneous catalysis in winery wastewater treatment



(2) Under the optimal conditions, the heterogeneous photo-Fenton achieves a 82.7% TOC removal

(3) Fermi's kinetic model shows that under the best operational condition a $k_{TOC} = 4.770 \times 10^{-2}$ min^{-1}

(4) Ferrocene can be reused for three consecutive cycles, with a TOC removal of 82.7, 76.2 and 63.9%, respectively, for the 1st, 2nd and 3rd cycles

Acknowledgements

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Thank you for your attention