materials proceedings

MDPI

Proceeding Paper

Application of Ferrocene in the Treatment of Winery Wastewater in a Heterogeneous Photo-Fenton Process †

Nuno Jorge [1,2,*], Ana R. Teixeira [2], Leonilde Marchão [2], Pedro B. Tavares [2], Marco S. Lucas [2] and José A. Peres [2]

1 Escuela Internacional de Doctorado (EIDO), Campus da Auga, Campus Universitário de Ourense, Universidade de Vigo, As Lagoas, 32004 Ourense, Spain
2 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.); leonilde.mar@gmail.com (L.M.); ptavares@utad.pt (P.B.T.); mlucas@utad.pt (M.S.L.); jperes@utad.pt (J.A.P.)
* Correspondence: njorge@uvigo.es

† Presented at the 3rd International Online-Conference on Nanomaterials, 25 April–10 May 2022; Available online: https://https://iocn2022.sciforum.net.

Abstract: Recent studies in the literature have shown successful applications of the nanomaterial precursor ferrocene (Fc) as a catalyst in heterogeneous photo-Fenton; however, ferrocene has never been used for the treatment of winery wastewater (WW). Therefore, the aim of this work is to: (1) characterize Fc by Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM); (2) optimize heterogeneous photo-Fenton in WW treatment; and (3) study the kinetic rate and regeneration of Fc. The FTIR analysis confirmed the presence of Fe^{2+} in its composition and SEM images showed that Fc is a porous compound. Under the best operational conditions—[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—significant TOC removal was achieved (82.7%). The results showed that the Fc catalyst decreased its stability across three consecutive cycling processes, with the TOC removals decreasing to 82.7, 76.2 and 63.9% for the first, second and third cycles. Fermi's non-linear kinetic model was applied, observing a k_{TOC} of 4.77×10^{-2} min^{-1}. In conclusion, ferrocene is a suitable compound for the treatment of WW with the heterogeneous photo-Fenton process.

Keywords: ferrocene; FTIR; nanomaterial; winery wastewater

Citation: Jorge, N.; Teixeira, A.R.; Marchão, L.; Tavares, P.B.; Lucas, M.S.; Peres, J.A. Application of Ferrocene in the Treatment of Winery Wastewater in a Heterogeneous Photo-Fenton Process. *Mater. Proc.* **2022**, *9*, 12. https://doi.org/10.3390/materproc2022009012

Academic Editor: Jian-Gan Wang

Published: 24 April 2022

1. Introduction

Winery wastewater (WW) is a major waste stream resulting from a number of activities including tank cleaning, washing floors and equipment, rinsing transfer lines, barrel cleaning, off wine and product losses, bottling, filtration, and the management of rainwater diverted into or captured in the wastewater management system. The effluent produced contains various contaminants, such as ethanol, sugars, organic acids, phenolic compounds, etc. [1,2]. To treat this type of wastewater, several methods can be applied, such as thermocatalytic [3], ozone [4], homogeneous Fenton [5], and heterogeneous photo-Fenton processes [6]. The homogeneous Fenton process has several disadvantages, such as: (1) a low pH is needed to prevent metal precipitation; (2) the homogeneous catalyst needs to be recovered from the treated wastewater; and (3) the resulting wastewater needs to be neutralized to meet the legal discharge limits imposed (pH 6.0–9.0) [6]. To overcome these disadvantages, in this work, we performed the treatment of WW with heterogeneous photo-Fenton with the application of ferrocene. Ferrocene has several advantages, such as high stability, a special structure, and strong ultraviolet absorbance [7]. In addition, in the work of Nie et al. [8], it was observed that ferrocene could be reused in four cycles. Therefore, the aim of this work is: (1) to characterize ferrocene by FTIR and SEM; (2) to optimize the heterogenous photo-Fenton process; and (3) to study the kinetic rate and regeneration of ferrocene.

2. Materials and Methods

2.1. Reagents and Winery Wastewater Sampling

Ferrocene was supplied by Alfa Aesar (Haverhill, MA, USA), and hydrogen peroxide (H_2O_2 30%) was supplied by Sigma-Aldrich (St. Louis, MO, USA). For pH adjustment, sodium hydroxide (NaOH) was used from Labkem, Barcelona, Spain, as well as sulphuric acid (H_2SO_4, 95%) from Scharlau, Barcelona, Spain. Deionized water was used to prepare the respective solutions. The winery wastewater was collected from a cellar located in the Douro region (Northern Portugal).

2.2. Analytical Determinations

Different physical–chemical parameters were determined to characterize the WW, including turbidity, total suspended solids (TSS), chemical oxygen demand (COD), biological oxygen demand (BOD_5), total organic carbon (TOC), and total polyphenols. The main winery wastewater characteristics are shown in Table 1.

Table 1. Characterization of winery wastewater.

Parameters	Winery Wastewater	Portuguese Decree Law No. 236/98
pH	4.0	6.0–9.0
Conductivity (µS/cm)	62.5	
Turbidity (NTU)	296	
Total suspended solids (mg/L)	750	60
Chemical Oxygen Demand—COD (mg O_2/L)	2145	150
Biochemical Oxygen Demand—BOD_5 (mg O_2/L)	550	40
Total Organic Carbon (mg C/L)	400	
Total polyphenols (mg gallic acid/L)	22.6	0.5
Ferrous iron (mg Fe/L)	0.05	2.0
Biodegradability—BOD_5/COD	0.26	

2.3. Heterogeneous Photo-Fenton Experimental Set-Up

The heterogeneous photo-Fenton experiments were performed in a batch cylindrical photoreactor (600 cm^3) equipped with a UV-C low-pressure mercury vapour lamp (TNN 15/32) with a working power of 15 W (795.8 W/m^2) and a λ_{max} of 254 nm (Heraeus, Germany). The optimization of the heterogeneous photo-Fenton process was performed in a 500 mL stirred glass reactor under UV-C radiation, the temperature was maintained constant to 298 K for 240 min, and the WW samples were treated as follows: (1) variation of pH (3.0–7.0); (2) variation of H_2O_2 addition (single and multiple dosing steps); (3) variation of H_2O_2 concentration (97–291 mM); (4) variation of Fc concentration (0.25–1.0 g/L); (5) performance of 3 recovery cycles.

After the reaction had started, 20 mL of solution was withdrawn and filtrated with a 0.20 µm filter for TOC measurements at different reaction times, completing a total period of 240 min. The percentage of organic carbon removed through adsorption was calculated according to Equation (1) [9]:

$$TOC_{rem.}(\%)\frac{TOC_i - TOC_t}{TOC_i} \times 100 \quad (1)$$

where TOC_i is the initial TOC content (mg C/L) and TOC_t corresponds to the TOC value at instant t (mg C/L).

2.4. Statistical Analysis

All the experiments were performed in triplicate and the observed standard deviation was always less than 5% of the reported values. The statistical analysis was performed with OriginLab 2019 software (Northampton, MA, USA).

3. Results

3.1. Characterization of Ferrocene

Ferrocene, an organometallic compound with the formula $Fe(C_5H_5)_2$, has a chemical assembly of two cyclopentadienyl rings bound to a central iron atom in a "sandwich" or "double-cone"-type structure. By the performance of FTIR analysis (Figure 1), it was observed that the main bands exhibited by ferrocene were associated with C–H stretching at 3093 cm^{-1}, C=C stretching at 1631 cm^{-1}, C–C stretching at 1404.18 and 1105.21 cm^{-1}, C–H deformation at 999.13 and 812.03 cm^{-1} [10], and the Fe peak at 476 cm^{-1}. The iron center in ferrocene should be assigned the (+2) oxidation state. Each cyclopentadienyl (Cp) ring should then be allocated a single negative charge. Thus, ferrocene could be described as iron(II) bis(cyclopentadienide), $Fe^{2+}[C_5H_5]_2$ [11].

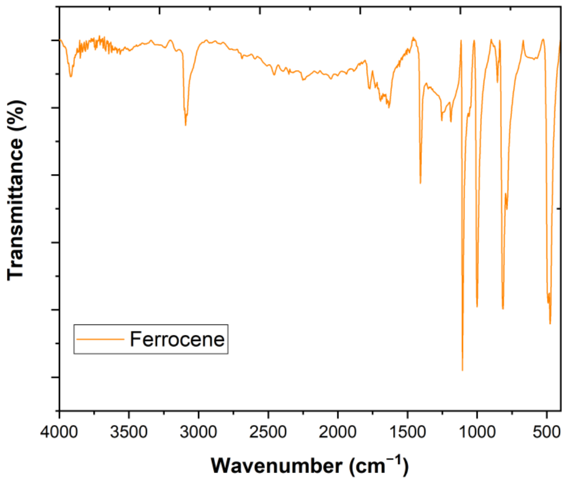

Figure 1. FTIR spectra of ferrocene.

In Figure 2, the SEM images of the ferrocene can be observed. The ferrocene catalyst in its initial form has an irregular shape with a lot of free space in between the particles; thus, the Fc catalyst has adsorption capacity.

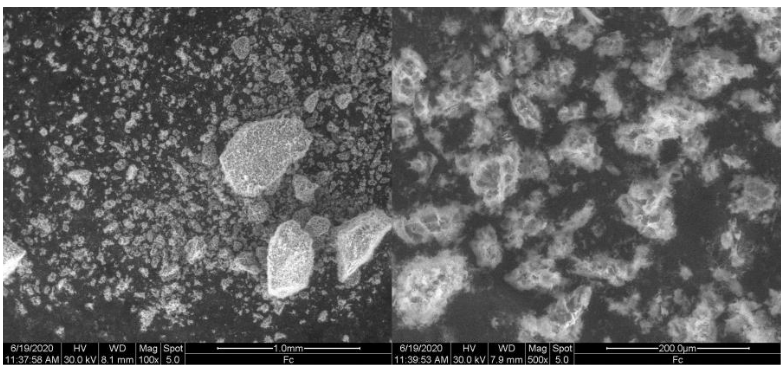

Figure 2. Scanning electron microscopy (SEM) images of ferrocene (100 and 500×).

3.2. Heterogeneous Photo-Fenton Optimization

To achieve maximum TOC removal from the WW, the heterogeneous photo-Fenton process was optimized. The pH varied from 3.0 to 7.0, and the results showed that the heterogeneous photo-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 (240 min). In the work of Wang et al. [12], it was observed that ferrocene had a complete degradation of methylene blue (MB) at pH 3.0 (Equations (2) and (3)), but at a higher pH (4.0 and 5.0) the ferrocene had a decrease in its efficiency, which could be explained by the fact that Fc achieved a higher dissolution at pH 3.0, decreasing as the pH increased, thus decreasing the heterogeneous photo-Fenton efficiency, as observed in Equation (4), as follows:

$$Fc + H_2O_2 \rightarrow Fc^{+} + HO^{\bullet} + HO^{-} \quad (2)$$

$$Fc^{+} + H_2O \rightarrow Fc + HO^{\bullet} + H^{+} \quad (3)$$

$$2Fc^{+} + H_2O_2 \rightarrow 2Fc + O_2 + 2H^{+} \quad (4)$$

The manner of addition of H_2O_2 was varied (single and multiple addition) to evaluate the TOC removal. The final TOC values after 240 min of treatment were 82.7% using multiple dosing and 53.3% using a single dose. The same effect was also observed by Rodríguez-Chueca et al. [13] in the treatment of WW by multiple dosage steps. By the application of multiple dosing steps, the H_2O_2 concentration was varied from 97 to 291 mM, and the results showed a TOC removal of 48.5, 82.7 and 81.4% for 97, 194 and 291 mM H_2O_2, respectively. Clearly, increasing the H_2O_2 concentration above 194 mM led to radical scavenging by the excess of H_2O_2 present in solution, as observed in Equation (5), as follows:

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \quad (5)$$

The ferrocene catalyst concentration was varied (0.25 to 1.0 g/L) and the results showed a TOC removal of 83.1, 82.7 and 54.2% for 0.25, 0.50 and 1.0 g/L Fc, respectively (Figure 3a). These results showed that the application of 0.50 g/L was ideal because more hydroxyl radicals were produced; however, increasing to 1.0 g/L may have contributed to increasing the solution turbidity, hampering the UV radiation penetration, as previously observed by Guimarães et al. [6]. Without the penetration of UV radiation, there was a lower reduction of ferric iron to ferrous iron, decreasing the heterogeneous photo-Fenton efficiency, which explains the decrease in TOC removal with the application of 1.0 g/L Fc.

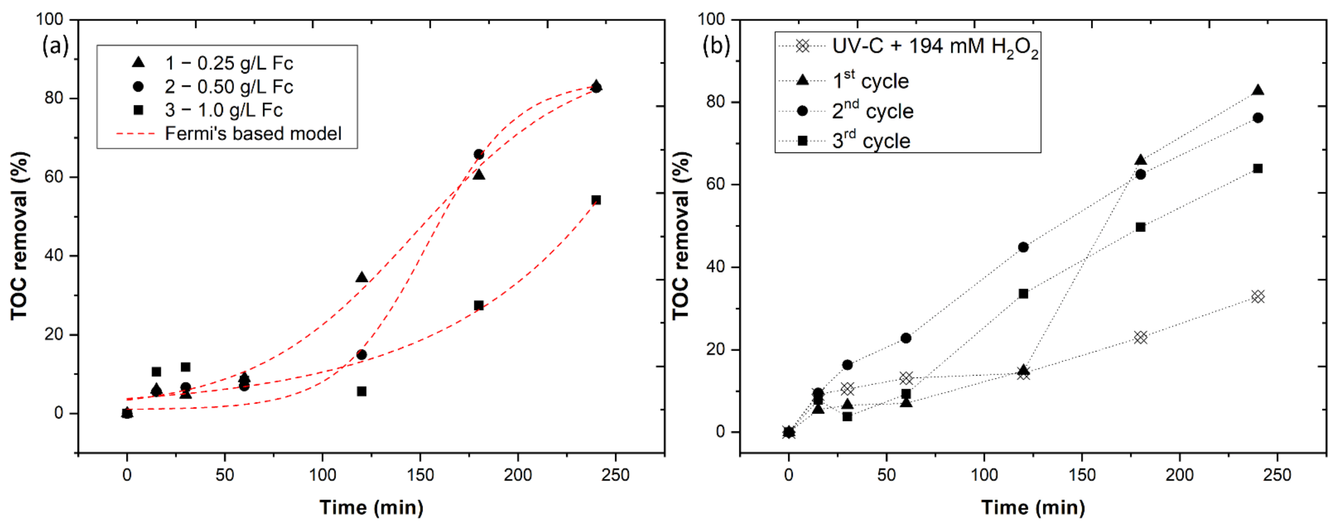

Figure 3. (**a**) TOC removal with variations in Fc concentration (0.25–1.0 g/L); (**b**) regeneration cycles from the ferrocene catalyst along the 3 consecutive cycles of the heterogeneous photo-Fenton process ([Fc] = 0.50 g/L, [H_2O_2] = 194 mM, pH = 3.0, agitation = 350 rpm, T = 298 K, radiation UV-C, t = 240 min).

Finally, 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 three consecutive cycles. The results showed a TOC removal of 82.7, 76.2 and 63.9% for the first, second and third cycles, respectively (Figure 3b). Therefore, the FC catalyst can be reused.

3.3. Kinetic Analysis

Fermi's non-linear kinetic model was used to determine the behavior of the ferrocene catalyst. Fermi's model provides a single fit for experimental results showing a transition between the induction period (slow degradation) and the subsequent rapid degradation step of an organic compound (inverted S-shaped transient curve), as observed in Equation (6) [14,15], as follows:

$$\frac{TOC}{TOC_0} = \frac{1 - X_{TOC}}{1 + \exp[k_{TOC}(t - t^*_{TOC})]} + X_{TOC} \quad (6)$$

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 following operational conditions: pH 3.0, Fc dosage 0.50 g/L, H_2O_2 concentration 194 mM (addition in six steps) (k_{TOC} = 4.77 × 10^{-2} min^{-1}; 82.7% TOC removal).

4. Conclusions

Considering the results obtained in this work, it is concluded that:

(1) Ferrocene can be used as a source of iron in heterogeneous catalysis in winery wastewater treatment;
(2) Under the optimal conditions, the heterogeneous photo-Fenton achieves an 82.7% TOC removal;
(3) Fermi's kinetic model shows the best operational condition at k_{TOC} = 4.77 × 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% for the first, second and third cycles, respectively.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/materproc2022009012/s1.

Author Contributions: Conceptualization, N.J., A.R.T. and L.M.; methodology, N.J.; software, N.J.; validation, N.J., P.B.T., M.S.L. and J.A.P.; formal analysis, N.J.; investigation, N.J., A.R.T. and L.M.; resources, N.J.; data curation, N.J.; writing—original draft preparation, N.J., A.R.T. and L.M.; writing—review and editing, N.J. and J.A.P.; visualization, N.J., P.B.T., M.S.L. and 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, operation nº NORTE-01-0145-FEDER-000041, and to the Fundação para a Ciência e a Tecnologia (FCT) for the financial support provided to CQVR through UIDB/00616/2020. Ana R. Teixeira also thanks the FCT for the financial support provided through the doctoral scholarship UI/BD/150847/2020.

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. 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. [CrossRef] [PubMed]
2. Petruccioli, M.; Duarte, J.C.; Federici, F. High-Rate Aerobic Treatment of Winery Wastewater Using Bioreactors with Free and Immobilized Activated Sludge. *J. Biosci. Bioeng.* **2000**, *90*, 381–386. [CrossRef]

3. Jorge, N.; Teixeira, A.R.; Guimarães, V.; Lucas, M.S.; Peres, J.A. Treatment of Winery Wastewater with a Combination of Adsorption and Thermocatalytic Processes. *Processes* **2022**, *10*, 75. [CrossRef]
4. 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. [CrossRef] [PubMed]
5. 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. [CrossRef] [PubMed]
6. Guimarães, V.; Teixeira, A.R.; Lucas, M.S.; Silva, A.M.T.; Peres, J.A. Pillared Interlayered Natural Clays as Heterogeneous Photocatalysts for H_2O_2-Assisted Treatment of a Winery Wastewater. *Sep. Purif. Technol.* **2019**, *228*, 115768. [CrossRef]
7. Dąbrowski, M.; Misterkiewicz, B.; Sporzyński, A. Solubilities of Substituted Ferrocenes in Organic Solvents. *J. Chem. Eng. Data* **2001**, *46*, 1627–1631. [CrossRef]
8. Nie, Y.; Hu, C.; Qu, J.; Hu, X. Efficient Photodegradation of Acid Red B by Immobilized Ferrocene in the Presence of UVA and H_2O_2. *J. Hazard. Mater.* **2008**, *154*, 146–152. [CrossRef] [PubMed]
9. Amor, C.; Fernandes, J.R.; Lucas, M.S.; Peres, J.A. Hydroxyl and Sulfate Radical Advanced Oxidation Processes: Application to an Agro-Industrial Wastewater. *Environ. Technol. Innov.* **2020**, *21*, 101183. [CrossRef]
10. De Souza, A.C.; Pires, A.T.N.; Soldi, V. Thermal Stability of Ferrocene Derivatives and Ferrocene-Containing Polyamides. *J. Therm. Anal. Calorim.* **2002**, *70*, 405–414. [CrossRef]
11. Zhang, L.; Chen, H.; Zhao, X.; Zhai, Q.; Yin, D.; Sun, Y. The Marriage of Ferrocene and Silicotungstate: An Ingenious Heterogeneous Fenton-like Synergistic Photocatalyst. *Appl. Catal. B Environ.* **2016**, *193*, 47–57. [CrossRef]
12. Wang, Q.; Tian, S.; Cun, J.; Ning, P. Degradation of Methylene Blue Using a Heterogeneous Fenton Process Catalyzed by Ferrocene. *Desalin. Water Treat.* **2013**, *28*, 5821–5830. [CrossRef]
13. Rodríguez-Chueca, J.; Amor, C.; Silva, T.; Dionysiou, D.D.; Li, G.; Lucas, M.S.; Peres, J.A. Treatment of Winery Wastewater by Sulphate Radicals: HSO5-/Transition Metal/UV-A LEDs. *Chem. Eng. J.* **2017**, *310*, 473–483. [CrossRef]
14. Rache, M.L.; García, A.R.; Zea, H.R.; Silva, A.M.T.; Madeira, L.M.; Ramírez, J.H. Azo-Dye Orange II Degradation by the Heterogeneous Fenton-like Process Using a Zeolite Y-Fe Catalyst—Kinetics with a Model Based on the Fermi's Equation. *Appl. Catal. B Environ.* **2014**, *146*, 192–200. [CrossRef]
15. 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: Switzerland, 2021; pp. 291–294, ISBN 978-3-030-59320-9.