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Proceeding paper

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

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Abstract: Recent studies in the literature showed successful applications of nanomaterial precursor ferrocene (Fc) as a catalyst in heterogeneous photo-Fenton, however, ferrocene was never used for the treatment of winery wastewater (WW). Therefore, the aim of this work is (1) characterize Fc by Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM), (2) optimize heterogeneous photo-Fenton in WW treatment, (3) study the kinetic rate and regeneration of Fc. The FTIR analysis confirms the presence of Fe^{2+} in its composition and SEM images showed that Fc is a porous compound. 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, it was achieved a significant TOC removal (82.7%). The results showed that the Fc catalyst decreased its stability along 3 consecutive cycling processes with the TOC removals decreasing from 82.7 to 76.2 and 63.9% from the 1st, 2nd and 3rd cycle. Fermi's non-linear kinetic model was applied, and it was observed a $k_{TOC} = 4.77 \times 10^{-2}$ min^{-1}. In conclusion, ferrocene is a suitable compound to perform the treatment of a WW by heterogeneous photo-Fenton process.

Keywords: ferrocene; FTIR; nanomaterial; winery wastewater

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1. Introduction

The winery wastewater (WW), is a major waste stream resulting from a number of activities that includes cleaning of tanks, washing of floors and equipment, rinsing of transfer lines, barrel cleaning, off wine and product losses, bottling facilities, filtration units and 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 processes [3], ozone [4], homogeneous Fenton [5] and heterogeneous photo-Fenton [6]. The homogeneous Fenton process have several disadvantages such as: (1) a low pH is needed to prevent metal precipitation; (2) the homogeneous catalyst should be recovered from the treated wastewater; and (3) the resulting wastewater should be neutralized to meet the legal discharge limits imposed (pH 6.0–9.0) [6]. To overcome these disadvantages, in this work, it was performed the treatment of WW by heterogeneous photo-Fenton, with application of ferrocene. The ferrocene has several advantages, such as high stability, 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 was (1) to characterize ferrocene by FTIR and SEM, (2) to optimize 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

The ferrocene was supplied by Alfa Aesar, Haverhill, Massachusetts, USA and hydrogen peroxide (H_2O_2 30%) was supplied by Sigma-Aldrich, Missouri, USA. For pH adjustment, it was used sodium hydroxide (NaOH) from Labkem, Barcelona, Spain and 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)—working power = 15 W (795.8 W/m^2) and λ_{max} = 254 nm (Heraeus, Germany). The optimization of 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 has started, 20 mL of solution was withdrawn, and filtrated by 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]:

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

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

The 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 performance of FTIR analysis (Figure 1), it was observed that the main bands exhibited by ferrocene, are 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} and C–H deformation at 999.13 and 812.03 cm^{-1} [10] and 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].

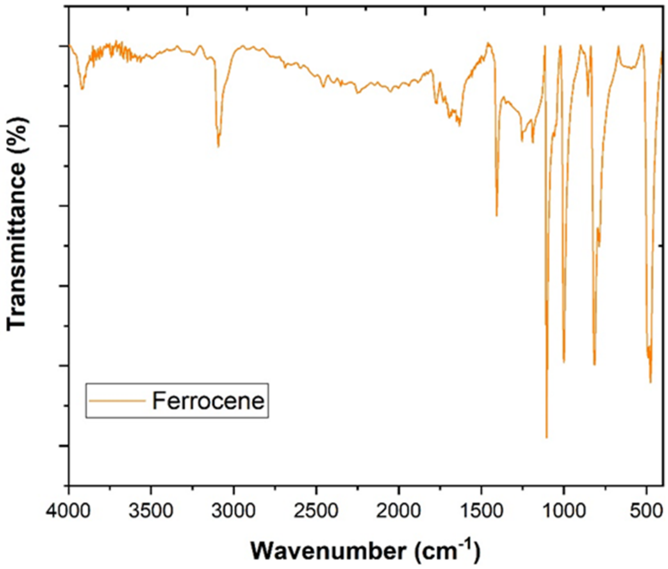

Figure 1. FTIR spectra of ferrocene.

In Figure 2, it is observed the SEM images of ferrocene. 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.

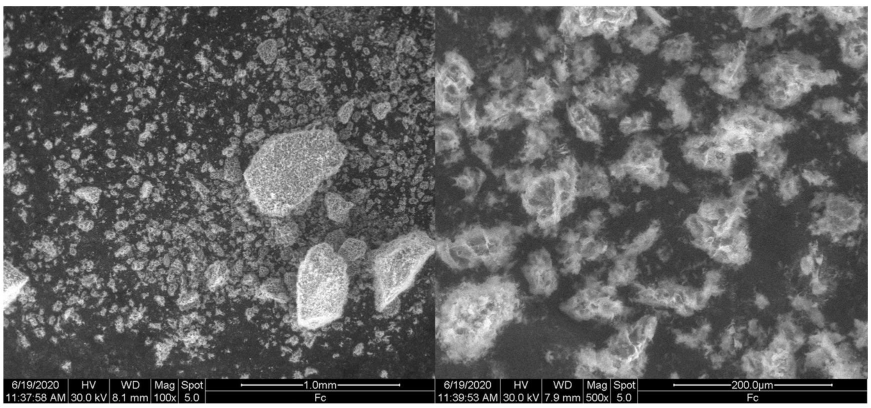

Figure 2. Scanning Electron Microscopy (SEM) images of ferrocene (100 and 500×).

3.2. Heterogeneous Photo-Fenton Optimization

To achieve a maximum TOC removal from the WW, the heterogeneous photo-Fenton process was optimized. The pH was varied from 3.0 to 7.0, and results showed that 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 higher pH (4.0 and 5.0) ferrocene had a decrease in its efficiency which could be explained, by the fact that Fc achieves a higher dissolution at pH 3.0, decreasing as the pH increases, 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 application of multiple dosing steps, the H_2O_2 concentration was varied from 97 to 291 mM, and results showed a TOC removal of 48.5, 82.7 and 81.4%, respectively, for 97, 194 and 291 mM H_2O_2. Clearly, increasing the H_2O_2 concentration above 194 mM lead to a 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 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 (Figure 3a). These results showed that 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 increase 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 of TOC removal with application of 1.0 g/L Fc.

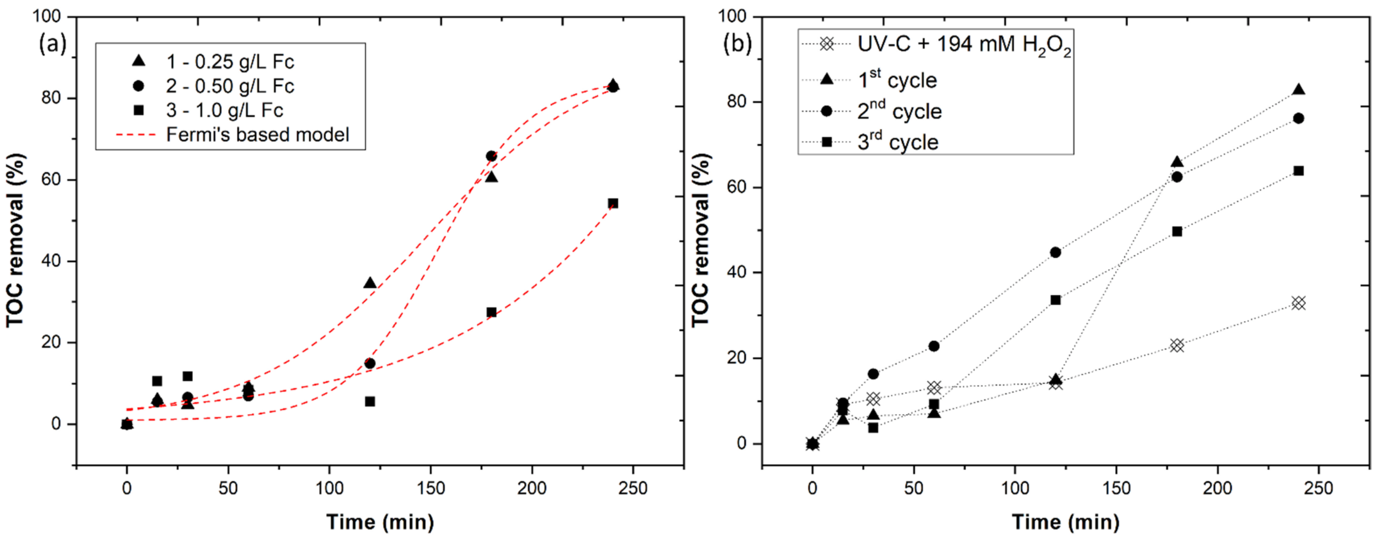

Figure 3. (**a**) TOC removal with variation of Fc concentration (0.25–1.0 g/L), (**b**) regeneration cycles from ferrocene catalyst along the 3 consecutive cycles of the heterogeneous photo-Fenton process

([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).

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 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 (Figure 3b), therefore, the FC catalyst can be reused.

3.3. Kinetic Analysis

The Fermi's non-linear kinetic model was used to determine the behavior of the ferrocene catalyst. The Fermi's model provides a single fit to 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:

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

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 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).

5. Conclusions

Considering the results obtained in this work, 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 under the best operational condition a 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%, respectively, for the 1st, 2nd and 3rd cycles.

Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used "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." Please turn to the CRediT taxonomy for the term explanation. Authorship must be limited to those who have contributed substantially to the work reported.

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