

Fenton like systems in a non-aqueous medium for oxidation of a lignin model molecule

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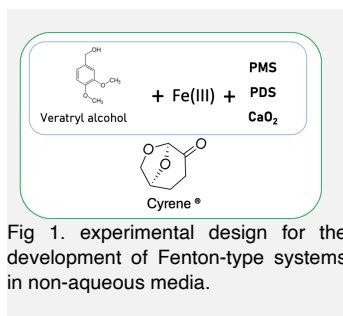
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The Fenton reaction is restricted to aqueous media, which limits its effectiveness on water-insoluble molecules such as lignin, which has great potential for obtaining chemicals. This study developed a Fenton-type reaction in the green solvent Cyrene, using calcium peroxide, peroxymonosulfate and peroxydisulfate as oxidizing agents. Radical formation was verified by electron paramagnetic resonance (EPR) spectroscopy, and quantification of oxidation products was performed by HPLC. The results show that Fenton-type systems in Cyrene generate radical species and allow the degradation of veratryl alcohol, a model lignin, highlighting the feasibility of this approach to valorize lignin in non-aqueous media.

Introduction

The Fenton reaction uses an oxidizing agent, such as hydrogen peroxide (H_2O_2), in combination with an iron source that acts as a catalyst. This reaction has been widely used and investigated for the degradation of pollutants. It is carried out in aqueous media because the hydroxo aqueous complexes are the reactive centers that interact with H_2O_2 [1]. Recently, the oxidation and depolymerization of organic compounds of natural origin by advanced oxidation process has begun to be explored to obtain higher value-added products in order to replace the petroleum derived building blocks [2]. The most widely used advanced oxidation process reported in the literature is the Fenton reaction, however this system is limited to aqueous systems. Therefore, its effectiveness is very limited for apolar, water-insoluble molecules such as lignin. Lignin, one of the main components of biomass, is structurally characterized by its abundance of phenol groups. It can be valorized by depolymerization and oxidation processes of its functional groups, allowing the production of commercial products of higher value, such as biofuels[2], [3].

In this context, the present work develops a Fenton-type reaction by replacing the aqueous medium with the green solvent Cyrene, which has a high capacity to dissolve lignin and lignin model compounds. For simplicity of the study and due to the structural complexity of lignin, veratryl alcohol (3,4-dimethoxybenzyl alcohol), a lignin model widely used in related research, was used [4]. The feasibility of Fenton type systems formed by the peroxides CaO_2 , peroxymonosulfate (PMS) and peroxydisulfate (PDS), peroxides of solid nature (non-aqueous) that are used in advanced oxidation processes, and as a source of anhydrous $FeCl_3$ iron,

was evaluated. The formation of radicals that could form in the systems was detected by Electronic Spin Paramagnetic Resonance (EPR) spectroscopy and the oxidation of veratryl alcohol was evaluated.

Material and Methods

Calcium peroxide, peroxymonosulfate, and peroxydisulfate were used as oxidizing agents. The peroxide solutions were prepared in Cyrene, filtered, and the peroxide concentration in Cyrene was verified using the spectrophotometric vanadate oxidation method.

For the radical detection, POBN was used as spin traps at a concentration of 20 mM. The sample was measured in a flat quartz cuvette, using an EPR spectrometer (Bruker, EMX micro).

The quantification of veratryl alcohol in the reaction was performed using a Flexar HPLC system with a diode array detector. A RP-18 column was used. The mobile phase used was Type I water with 1% formic acid and acetonitrile. A gradient method with three steps was used for the separation.

Results and Discussion

The peroxides presented low solubility in Cyrene, CaO_2 was able to dissolve up to 7%, PMS 15%, and PDS could not be determined. Cyrene in the determination of peroxides by the vanadate method because it produces the oxidation of vanadium from the +5 to the +7 state. The peroxide generated by PDS was lower detection limit by vanadate method but was detected by reflectometry by peroxyquant strip (Merck).

The oxygen and carbon centered radicals were determined by EPR using POBN as spin trapping. The radicals generated by the $CaO_2/Fe(III)$ system were determined by a spectrum showing a triplet. This signal was weak (figure 2 A). On the other hand,

the PMS/Fe(III)/POBN and PDS/Fe(III)/POBN systems show a clearer signal which corresponds to a triplet (Figure 2A), which intensifies with time, being at 30 min its highest intensity. When performing reaction controls, Cyrene alone, POBN dissolved in Cyrene and a system in the absence of peroxide showed non-significant signal (Figure 2A). The coupling constant for the $\text{CaO}_2/\text{Fe(III)}/\text{POBN}$ systems are $a_N=14,5$, $\text{PMS}/\text{Fe(III)}/\text{POBN}$ $a_N=14,0$ y $\text{PDS}/\text{Fe(III)}/\text{POBN}$ $a_N=14,5$. The EPR spectra simulation for the identification of this radicals are in progress.

Because the VA oxidation is possible by the radicals generated in the Fenton-like systems, this was determined by HPLC. The PMS/Fe(III)/AV system shows the highest percentage of VA oxidation, reaching 29.9%, and for the system with CaO_2 the oxidation was 18.3%(Fig. 3). For the PDS/Fe(III)/AA system, the oxidation was 20.9%, considering that the concentration of PDS is unknown.

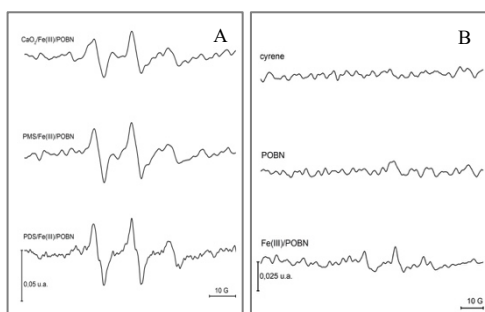


Figure 2: EPR spectra of A) systems with peroxide. The conditions were 5 mM peroxide, 40 $\mu\text{Fe(III)}$, 15 mM POBN after 30 minutes of reaction. B) control of the systems.

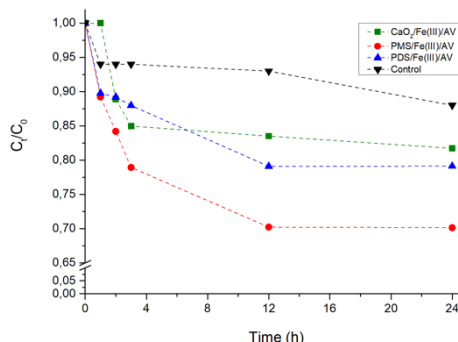


Figure 3: AV oxidation using Fenton-like systems. The conditions were 5 mM peroxide, 40 $\mu\text{Fe(III)}$, 500 $\mu\text{M AV}$.

Conclusions

The results demonstrate the feasibility of performing a Fenton-type reaction in the non-aqueous solvent Cyrene, which allows the generation of radical species and the oxidation of water-insoluble organic molecules. Although the oxidation efficiency was low, it is possible to improve the degradation of veratryl alcohol by adjusting the peroxide and Fe(III) concentrations and optimizing other reaction factors. To confirm the effectiveness on lignin, it is recommended to apply these systems to model lignin molecules with higher complexity.

Acknowledgments

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References.

- [1] B. Ensing, F. Buda, and E. J. Baerends, "Fenton-like chemistry in water: Oxidation catalysis by Fe(III) and H_2O_2 ," *Journal of Physical Chemistry A*, vol. 107, no. 30, pp. 5722–5731, Jul. 2003, doi: 10.1021/jp0267149.
- [2] J. Kang, S. Irmak, and M. Wilkins, "Conversion of lignin into renewable carboxylic acid compounds by advanced oxidation processes," *Renew Energy*, vol. 135, pp. 951–962, May 2019, doi: 10.1016/j.renene.2018.12.076.
- [3] C. Chio, M. Sain, and W. Qin, "Lignin utilization: A review of lignin depolymerization from various aspects," Jun. 01, 2019, *Elsevier Ltd*. doi: 10.1016/j.rser.2019.03.008.
- [4] C. W. Lahive, P. C. J. Kamer, C. S. Lancefield, and P. J. Deuss, "An Introduction to Model Compounds of Lignin Linking Motifs; Synthesis and Selection Considerations for Reactivity Studies," Sep. 07, 2020, *Wiley-VCH Verlag*. doi: 10.1002/cssc.202000989.