VIII Encontro sobre Aplicações Ambientais de Processos Oxidativos Avançados
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Escola de Engenharia-UFMG - Belo Horizonte – MG - Brasil

HYDROXYL RADICAL PRODUCTION BY HETEROGENOUS FENTON REACTION SUPPORTED IN INSOLUBLE TANNIN BARK OF *PINUS RADIATA*

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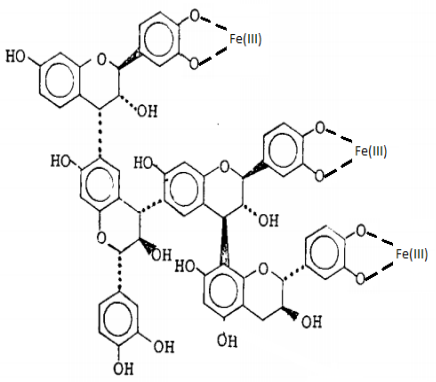
ABSTRACT

In this work we made a modification of the conventional Fenton reaction for increase the hydroxyl radical production with a heterogeneous system employing hydrogen peroxide and a solid iron container with dihydroxybenzenes, as the literature indicates that amplify Fenton reaction. The measure of hydroxyl radical was made by Electron Paramagnetic Resonance (EPR) in differents systems. The advantage of this approach is the use of a water insoluble solid, which drive Fenton reaction but prevents contamination of the effluent with phenolic compounds and also have an important environmental value to be obtained from forest bark waste, specifically *Pinus radiata*.



INTRODUCTION

Currently, Chile has an area of forest resources of about 15.6 million hectares. An important part of wood resources available in the country are discarded as waste (chips, bark, sawdust, etc.) generated during the forest production chain, from the production of wood in the forest to the processing plant. It is estimated to be approximately 3 million cubic meters of wood residues. The bark is part of these wood residues; about one tenth of the mass of lumber is bark. Currently, this bark is removed prior to mechanical processing and burned to obtain process energy. The bark of *Pinus radiata* contains about 60% phenolic compounds, which are soluble in 8-12% water and 15-20% soluble in methanol. Polyphenols from the bark of *Pinus radiata* correspond to condensed tannins, which consist of polymers of flavonoids with various degrees of condensation.

At present, the tannins are widely used in adhesives for wood panels, which is required for the tannin is totally soluble in water to obtain a strong cross-linking with formaldehyde, otherwise a brittle resin is obtained.

In this work is used the portion of insoluble tannins from bark. The advantage of this portion, is it free from sugars, furfural and other compounds that bark have in native form. They must be separated to improve the availability of phenolic groups. Recent analysis of micro pyrolysis of these tannins have shown that catechol is a major product of thermal decomposition and also molecules of methyl catechol in less proportion. From these results we can see that insoluble bark tannins are composed mainly of units condensed dihydroxybenzenes.

METHODOLOGY

The direct detection of some free radicals is very difficult or impossible in solution at room temperature. Spin trapping is a technique developed at late 1960s where a nitrone compound reacts with a target free radical to form a stable and distinguishable compound to be detectable by EPR. The hydroxyl radicals produced by the different systems were detected by spin-trapping method consisting in forming a paramagnetic radical adduct between this radical and 5,5-dimethyl-1-pyrroline N-oxide(DMPO). The DMPO/•OH adduct has a characteristic signal that is detectable by electron paramagnetic resonance, EPR.

Production of OH • radical was determined at pH 3.40 and 7.00.

The reaction was initiated by adding the corresponding aliquot of iron. Once the reaction started, the samples were transferred to a capillary located inside Bruker ESP 300, in order to acquire the first spectrum corresponding to the signal of the adduct DMPO / • OH, in the shortest time possible. The magnetic field was set in the peak spectrum adduct had higher intensity in order to record the variation in the height of this peak over time.

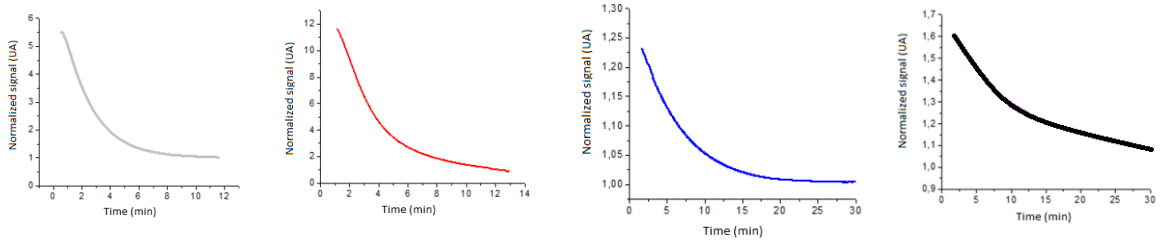
The profiles obtained by EPR, corresponding to changes in signal adduct DMPO / • OH in time, are the result of two processes: adduct formation by production of • OH radicals by Fenton reaction and decomposition of the same by H_2O_2 present in the system, which oxidizes the paramagnetic nitroxide adduct group to non-radical products by pseudo first order kinetics. The profiles obtained by EPR systems studied exhibit a complex equation speed and not yet known, containing variables involved in both processes. In order to simplify the analysis, the data were fitted to equations to obtain valid comparative parameters. Where the standard signal is obtained dividing the raw signal by the limit value when the time tends to infinity. In this way, the function is obtained when the data fit an exponential decay curve.

After that, it´s necessary graph natural logarithm against the time (min) to obtain the values of the slope. The variations observed in the decay of the adduct profiles, reflected in the values of b, were interpreted as a relative difference in the production of • OH radical.

RESULTS AND DISCUSSION

When we comparing the results between systems Fenton without modifying and systems driven Fenton noted that systems catechol driven have a significant decrease of the slope b ($p < 0.01$) indicating that the presence of these species promotes sustained production of OH • radical by Fenton systems. Notably, the profile corresponding to the Fenton

system driven by catechol also showed an increase in the value of the initial signal recorded with respect to unmodified Fenton system.



a b c d

Figure 1. Production of hydroxyl radical in the time at pH=3.4 in these systems: a) Non-modified Fenton reaction; b) Fenton driven by catechol; c) Fenton driven by catechine; d) Fenton driven by tannin.

This implies that these system not only maintain • OH radical production time, but also are able to increase the amount of • OH radicals from the start of the reaction. As mentioned previously the most quantity of • OH radical, in the Fenton system is produced at the start of the reaction because it is the only time when the iron is in entirety as Fe (II). The reduction of Fe (III) can happens slowly occur then by reaction with H_2O_2, or be accelerated by reaction with 1, 2-DHB. Catechol reduces Fe (III) faster than catechine and tannin but for a short period of time (2 min), explaining that this present compound the largest initial signal value and the highest value recorded in b. For catechine and tannin the low initial signal may be related to the low rate at which both compounds reduce Fe (III), and low slope values can be associated with both compounds reduce Fe (III) greater time than that observed for the catechol.

CONCLUSIONS

Is important to say that the systems with catechine and tannin driven Fenton showed decreasing slope values 6 times than that determined for systems Fenton conducted by catechol, this reduction means that this compounds are able to extend the production of • OH radical for longer than the catechol.

ACKNOWLEDGEMENTS

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CONTRERAS, D., J. RODRIGUEZ, J. FREER, B. SCHWEDERSKI, AND W. KAIM, Enhanced hydroxyl radical production by dihydroxybenzene-driven Fenton reactions. *Journal of Biological Inorganic Chemistry*, 12(7): p. 1055-1061, 2007.

ACCEPTANCE LETTER

Dear Researcher,

It is our pleasure to anounce that the work entitled "HYDROXYL PRODUCTION BY HETEROGENOUS FENTON REACTION SUPPORTED IN INSOLUBLE TANNIN BARK OF PINUS RADIATA" submitted by **Romina Romero; David Contreras; Cristina Segura; Brigitte Schwederski and Wolfgang Kaim** has been accepted to be presented at the VIII Meeting on Environmental Application of Advanced Oxidation Processes and II Iberoamerican Congress of Advanced Oxidation Technologies which will be held in Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brazil, on November 3rd to 6th, 2015.

Your abstract has been reviewed by the Scientific Committee and the following observation(s) have been made by the referee:

There are no comments and/or modifications suggested

If you wish to make any changes on the revised abstract we ask you to send the updated version within 10 days from this receiving date. The submission of the updated version should be done by the submission link in our website: http://www.epoa8.desa.ufmg.br/en/sub_trab.php.

Please, name the updated document as: FEN_035

Belo Horizonte, 31 de agosto de 2015.

Vitor Vilar

Vitor Jorge Pais Vilar
Chairman of II CIPOA

Asunto **VIII EPOA II CIPOA_Decision Notification**

Remitente VIIIEPOA-Encontro sobre Aplicações Ambientais de Processos Oxidativos Avançados – IICIPOA <epoa8@desa.ufmg.br>

Destinatario <rominaromero@udec.cl>

Fecha 2015-08-31 20:01

- FEN_035.pdf (~449 KB)

Dear researcher,

It is with great pleasure that we announce that your abstract to be presented at the VIII EPOA & II CIPOA has been accepted. Attached follows the letter of acceptance with comments from a member of the Scientific Committee. In case you need to edit your document, please, resubmit the updated version using the same link you have used in the first submission. Please, save your second submission with the same code used in the acceptance letter (XX_##). The presentation form: poster. We are pleased to remind you that registration is already available in: http://www.epoa8.desa.ufmg.br/partbrasil.html (for Brazilian participants) or http://www.epoa8.desa.ufmg.br/partestrangeiro.html (for international participants). The deadline for registration with discounts is 15/08. We are offering especial rates for group registration. For further informations: http://www.epoa8.desa.ufmg.br/en/tabelapreco.html It will be a pleasure to welcome you in Belo Horizonte. Do not hesitate to contact us if you have any questions.

Sincerely,

Caro pesquisador,
É com grande satisfação que informamos que o seu resumo foi aceito para apresentação no VIII EPOA e II CIPOA. Segue anexa a carta de aceite, que apresenta os comentários do revisor do Comitê Científico. Caso seja necessário realizar qualquer alteração em seu resumo, pedimos que submeta a versão atualizada pelo site do evento, no mesmo link em que foi realizada a primeira submissão, nomeando o arquivo com o código utilizado na carta de aceite (XX_##). A forma de apresentação será no formato pôster. Aproveitamos a oportunidade para lembra-lo que as inscrições já podem ser realizadas no nosso site (http://www.epoa8.desa.ufmg.br/partbrasil.html) para participantes brasileiros, e para os estrangeiros (http://www.epoa8.desa.ufmg.br/en/partestrangeiro.html). O prazo de inscrição com descontos vence em 15/08. Excepcionalmente estamos oferecendo descontos para grupos de participantes. Maiores informações http://www.epoa8.desa.ufmg.br/tabelapreco.htmlAgradecemos sua participação no VIII EPOA e II CIPOA. Em caso de dúvidas, não hesite em nos contatar.
Atenciosamente,

Comitê Organizador
VIII EPOA-Encontro sobre Aplicações Ambientais de Processos Oxidativos Avançados
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03 a 06 de novembro de 2015.
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Asunto **8EPOA Special Issue Invitation Letter**

Remitente VIIIEPOA-Encontro sobre Aplicações Ambientais de Processos Oxidativos Avançados – IICIPOA <epoa8@desa.ufmg.br>

Destinatario <rominaromero@udec.cl>

Fecha 2015-09-17 22:03

Dear Author,

The abstract FEN_035 HYDROXYL PRODUCTION BY HETEROGENOUS FENTON REACTION SUPPORTED IN INSOLUBLE TANNIN BARK OF PINUS RADIATA, to be presented at VIIIEPOA/IICIPOA, has been selected for the Special Issue in Environmental Science and Pollution Research (ESPR).

In the year 2015, the journal Environmental Science and Pollution Research (ESPR) will be featuring a collection of innovative papers highlighting AOPs: Recent Advances to Overcome Barriers in the Treatment of Water, Wastewater and Air (special issue of VIII EPOA-II CIPOA). As the Guest Editor of this collection of papers, I am writing to invite you to contribute a paper on your current research activities in the area of AOPs.

The special issue will feature both critical reviews and research papers. Here are some further details on the different paper types. A review is expected to present a critical overview of the state-of-the-art of a topic, with critically selected examples (not only from your own work), to point the reader to trends and likely future developments and to give a selection of important references to the current literature. As a guideline, for a critical review the manuscript is expected to be around 35 000 characters in length, plus figures and tables. For a research paper, paper length must be appropriate to content. There is no strict page limit, but ESPR advises a maximum length of up to 25 000 characters including 20-30 references, plus 4-6 figures and 1-3 tables. You will find the journal's instructions for authors on the ESPR homepage at www.springer.com/environment/journal/11356.

Furthermore, I am pleased to announce that color figures will be printed in color free-of-charge to the author, both in the online and print versions of the journal.
The submission deadline for papers has been set as 30th November 2015. Earlier submissions are encouraged, and papers will be published online as soon as they have been accepted for publication. All invited papers will be subject to the same rigorous peer-review process as regular submissions to the journal, and upon publication each author team will be provided with a free pdf file of the printed article. We ask that you submit your manuscript directly to the ESPR editorial office by online submission at http://www.editorialmanager.com/espr/.

We would very much appreciate your participation in this special issue and hope that you are able to accept this invitation. I kindly request your response by 23th September. Please let us know whether you are able to contribute a critical review or whether you would prefer to contribute a research paper, and indicate the names of the coauthors and the provisional title of your paper.

More information http://www.epoa8.desa.ufmg.br/en/specialissue.html
We look forward to your response with great interest.

With best regards,

Vítor Vilar