Analysis of Efficiency of Lignin Degradation Via Fenton Reaction: Study of the Synergistic Catalytic Action and Reaction Kinetics

POSTER

Ph.D. Student: N

Journal: I&EC Research; I.F = 4.2

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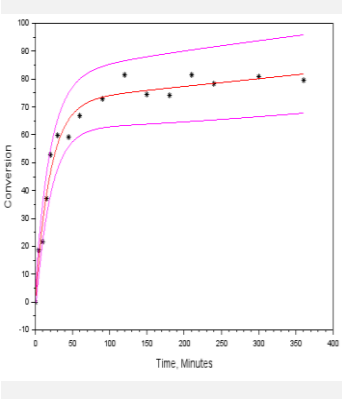

Pulp and paper industries generates highly polluted wastewater containing high levels of COD and toxic organic compounds such as lignin. Lignin is a complex macromolecule present in plants, that is highly resistant to biodegradability. Alternative methods that can be applied to lignin degradation are Advanced Oxidation Processes (AOPs). We proposed several experimental conditions that explore different proportions of H_2O_2 and catalytic agents' dosages with the aim of assessing the synergistic catalytic action of Fe^{2+} and Fe^{3+} and evaluating the reactions kinetics. An optimized condition for the Fenton reaction was predicted, which adopts a molar ratio of H_2O_2/Fe^{2+} = 9.0 and H_2O_2/Fe^{3+} = 6.0. The optimum condition presented a decrease of 79.7% absorbance at UV_{280} and a coherent reduction curve, with a correlation coefficient for the model (R^2) of 0.976. The model presented an average R^2 of 0.950. The treated organic compound was later used as a carbon source for lignin degrading microorganisms.

Introduction

In the past decades, the pulp and paper industry has been making use of 10 – 300 m^3 of water per ton of product, and produces, globally, over 400 million tons of paper commodities every year [1]. During the pulping processes, lignin compounds, such as black liquor, are extracted and discarded as highly toxic effluents, known for their dark color and their ability to inhibit photosynthesis in bodies of water [1].

Lignin has a characteristically high resistance to enzymatic attacks by microorganisms. For this reason, conventional wastewater treatment methods based on the activity of microbial cultures are found to be ineffective, leading to the discharge of poorly treated effluents into water streams and rivers [2].

In this context, Advanced Oxidation Processes (AOPs), defined as processes that involve the generation of highly reactive species (e.g., OH•, $•SO_4^-$), are presented as a promising alternative to lignin degradation. With a relatively low cost and the ability to transform pollutants into less harmful compounds, these processes are mainly used in the degradation of organic and inorganic substances [3].

Fenton process is an AOP that extends the longevity of hydroxyl radicals through the addition of catalytic ions Fe^{2+} [3,4]. The catalyst improves the process effectiveness by activating the H_2O_2 molecule, increasing the rate of radical formation [4].

Previous studies have explored Fenton reactions and their associated variables [1,3,4,5], such as H_2O_2 dosage, pH, and Fe^{2+} concentration, but few have observed the synergistic catalytic action of different iron catalysts (Fe^{2+} and Fe^{3+}) or the reaction kinetics.

In this study, we explored the efficiency of lignin degradation via Fenton reactions under acidic conditions (pH = 3). For this, a simple batch processing was employed, with the aim of investigating the effect of catalyst synergism and evaluating the reactions kinetics in a 6-hour process. Ten experimental conditions were proposed that make use of different H_2O_2/Fe^{2+} and H_2O_2/Fe^{3+} molar ratios (Table 1), in order to elaborate an optimized and economically viable condition.

Material and Methods

Lignin solution (black liquor) was provided by Brazilian company Suzano Pulp & Celulose, from the unit of Limeira–SP. Gravimetric analysis of lignin was performed to determine the concentration of solids in the sample, and the concentration of soluble lignin was determined through spectrophotometry, by measuring total aromatic compounds. (λ =280 nm).

All experiments were conducted in a bench top reactor powered by a vacuum pump, under room temperature (25 ºC) and local air pressure of 1 atm in simple batch processing. For pH adjustments, HCl 4M and 30% w/v NaOH solutions were used. Fenton reagents used were hydrogen peroxide (H_2O_2) 30% w/w, iron (II) sulfate heptahydrate ($FeSO_4.7H_2O$) and iron (III) chloride hexahydrate ($FeCl_3.6H_2O$).

The sample was diluted a thousand times and had its pH adjusted to the optimum value (pH = 3), where the catalytic action is most effective [5]. The average lignin concentration of the sample was 105.2 mg/L.

Samples were taken over the course of 6 hours, and the reactions were neutralized by elevating the pH level to 12 using the NaOH solution. All samples were frozen immediately after. The readings of the concentration of soluble lignin present in the samples were carried out using a spectrophotometer (ThermoFisher Scientific), at wavelength λ=280 nm.

An optimized condition was then proposed based on the results obtained from all 10 experimental runs. The molar ratios for this condition were designed in

such a way to use the minimum concentration of reagents to make an economically viable process.
The reduction curve was obtained via the empiric stochastic modelling proposed by Siqueira, 2013 [6], that has been previously applied in other AOPs studies, such as landfill leachate treatment.

Results and Discussion

The results have shown a noticeable decrease of lignin concentration (Table 1). Eight out of the ten proposed experiments have conferred a coherent degradation curve. Experiments 5 and 7 have shown poor reduction rates and incoherent degradation curves as a result of the designated proportions.

Table 1. Experimental conditions for molar ratios and lignin reduction after 6-hour processes

Run	H_2O_2/Fe^{2+}	H_2O_2/Fe^{3+}	Reduction (%)
1	3.00	3.00	47.60
2	3.00	9.00	84.71
3	9.00	3.00	72.03
4	9.00	9.00	73.86
5	1.75736	6.00	31.91
6	10.24264	6.00	72.45
7	6.00	1.75736	50.58
8	6.00	10.24264	64.46
9	6.00	6.00	71.01
10	6.00	6.00	71.89

These results reinforce the importance of adequate reagents concentrations in the medium, as well as the impact of Fe^{2+}/Fe^{3+} ratios in Fenton reactions.
We have observed that a low dosage of H_2O_2 relative to the catalysts dosages results in an ineffective process, that presents an inconsistent reduction progress [7]. Similarly, the same irregularities are observed when the medium is subjected to a high relative concentration of catalysts. In such conditions, scavenging effects (Equation 1) are more susceptible of consuming the hydroxyl radicals, impacting directly the compound's reduction [7].

$$Fe^{2+} + HO\cdot \rightarrow Fe^{3+} + OH- \quad (1)$$

An optimized condition was proposed and experimented with molar ratios of H_2O_2/Fe^{2+} = 9.0 and H_2O_2/Fe^{3+} = 6.0. The kinetic study showed a concentration reduction of 66.7% after 60 minutes, and 79.7% after 360 minutes, as shown in the Graphical Illustration. The red line represents the average percentage reduction, and the pink lines delimit the 95% confidence range.
The curve profile is divided into two regions, one of a high reduction rate, which took place in the first 90 minutes of the reaction, and one with a low reduction rate, reaching a plateau, which takes place in the following hours. This condition presented a reduction curve that successfully adjusts to the kinetic model, with a correlation coefficient (R^2) of 0.976. The regression equation was designed, with an average correlation coefficient (R^2) of 0.950, along with its components (Equations 2-4) that describe the average behavior of the stochastic model and how the control variables influence the process.

$$a = 3.97*10^{-4} - 4.43*10^{-4}x0 + 2.23*10^{-4}x0^2 + 1.22*10^{-4}(H_2O_2/Fe^{2+})(H_2O_2/Fe^{3+}) \quad (2)$$

$$b = -0.358 + 3.96*10^{-2}(H_2O_2/Fe^{3+}) + 9.78*10^{-3}x0 - 4.87*10^{-3}(H_2O_2/Fe^{3+})^2 \quad (3)$$

$$1/k = -46.9 + 25.77(H_2O_2/Fe^{2+}) - 1.937(H_2O_2/Fe^{2+})^2 \quad (4)$$

Conclusions

Fenton process was proven to be an effective alternative to lignin degradation, presenting high percentage reductions, especially in the first 90 minutes of the oxidation process. The optimized condition obtained high levels of lignin degradation, and the kinetic study was successfully applied to the design of an accurate kinetic model. The reduction of aromatic compounds, measured at wavelength λ = 280 nm, reflects in the decrease of the toxicity levels in the matrix, and synergistic catalytic action was found to be essential for an effective degradation. The process was adequately optimized in such a way to present high efficiency reduction while making use of a reasonable amount of reagents.

Acknowledgments
We thank the technician Joaquim Brandão, who has shared his experience in equipment handling to carry out this study. G. Mendes, would like to thank the opportunity given by the scholarship PUB-USP, the Environmental Processes Research, RECABS and LCM laboratories of DEBAS & DEBIQ EEL-USP that have welcomed him. A.K. Chandel also thanks FAPESP for the research projects (JP-2020/12559-6 and 2022/13184-1).

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