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Statistical study of the influence of H^2O^2 and Fe^{2+} concentration on treatment by photo-Fenton process of wastewater resulting from biodiesel wash

Estudo estatístico da influência da concentração de H^2O^2 e Fe^{2+} no tratamento pelo processo foto-Fenton de águas residuais resultantes da lavagem do biodiesel

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Content

ABSTRACT:
In this study, an evaluation was carried out of the efficiency of photo-degradation of effluents resulting from biodiesel purification by photo-Fenton process with the help of factorial design 22, having as variables the concentrations of H^2O^2 and Fe^{2+}. The results suggest that the two variables are significant for treatment. However, they can be optimized in an independent manner, since variable H^2O^2 resulted in a relative increase of 36 % in reducing the spectral area when its concentration varied from 150 mg L^{-1} to 250 mg L^{-1}. In the case of variable Fe^{2+}, there was a relative increase of 5% on the reduction of spectral area when concentration varied from 5 mg L^{-1} to 15 mg L^{-1}.

RESUMO:
Neste trabalho foi avaliada a eficiência de fotodegradação do efluente proveniente da purificação do biodiesel por processo foto-Fenton com o auxilio de planejamento fatorial 22, tendo como variáveis a concentração de H^2O^2 e de Fe^{2+}. Os resultados sugerem que as duas variáveis são significativas no tratamento. No entanto, as mesmas podem ser otimizadas de forma independente, sendo que a variável H^2O^2 implicou num aumento relativo de 36 % na redução da área espectral quando variou sua concentração de 150 mg.L^{-1} para 250 mg.L^{-1}. Tratando-se da variável Fe^{2+}, ocorreu um aumento relativo de 5 % na redução da área espectral quando variou-se a

Keywords: ANOVA; biofuel; factorial design; photo-degradation

concentração de 5 mg.L^{-1} para 15 mg.L^{-1}.

Palavras-chave: ANOVA, biocombustíveis, planejamento fatorial, fotodegradação

1. Introduction

Data recently surveyed by World Energy Outlook (IEA, 2015) state that oil (a non-renewable natural resource) is the main global energy matrix. Pollution generated during its drilling, transportation, processing, and burning its products (especially CO2 emissions, which is responsible for intensifying greenhouse effect) are considered the greatest disadvantages of using this energy source. Within this context, new sources have been sought, especially renewable ones (Mesaric and Krajcar, 2015).

A possible alternative to oil is the use of biodiesel. In addition to coming from renewable resources and thus contributing to decreased CO2 emissions into the atmosphere, this fuel is easily degradable when compared to oil products (Palomino-Romero et al., 2012).

Biodiesel is produced from vegetable oils, animal fats, and even residues, such as frying oil. In regards to oilseeds, the most used are soybeans, jatropha, castor beans, palm, sunflower seeds, and canola, these raw materials present efficiency in terms of fatty acids, as well as being easy to cultivate and extract oil (Kligerman and Bouwer, 2015).

Regardless of the raw material it results from, biodiesel is defined as a mix of alkyl esters of fatty acids, usually obtained through trans-esterification reaction (Knothe, 2006). This reaction takes place in the presence of a catalyst (acidic, basic, or enzymatic) in an alcoholic environment, resulting in biodiesel as the main product and glycerin as byproduct (Fukuda, Kondo and Noda, 2001).

Due to the use of catalysts in biodiesel synthesis, neutralization and purification are necessary before it is employed, since the absence or inefficiency of biodiesel purification process may result in damages in the engine such as obstruction of filters, nozzles, wear of the engine and its parts, among other mechanical problems (Atadashi et al., 2011; Demirbas, 2009 and Stojković, 2014). Among the many biodiesel purification processes, one of the most used is the adding of aqueous solutions or distilled water to it. In addition, according to these authors, this process presents the disadvantage of generating wastewater that must be separated from biodiesel and treated later (Stojković, 2014).

According to Veljkković (2014) wastewater resulting from "wash water" purification is comprised of oils and non-trans-esterified fatty acids, catalysts, salts, soaps, and organic impurities, and it presents high SS, COD, and BOD values and concentration of other organic compounds, a fact that grants it low biodegradability. Therefore, this wastewater is harmful to the environment and cannot be discharged into wastewater collection and transportation systems or bodies of water without a proper treatment (Daud, 2014)

In regards to treatment of wastewater originating from biodiesel washing, there are many Technologies that may be employed, including biological, chemical, and physical processes (Pitakpoolsil and Hunsom, 2014). Within this context, Advanced Oxidation Processes (AOPs), which are based on the formation of hydroxyl (OH), which presents a high reduction potential (E0= 2.8 V), that presents high instability, capable of react with a great range of organic compounds, promoting their mineralization, even CO2 and H2O (Nogueira and Jardim, 1998; Nogueira et al., 2007). Among the several types of AOPs, Fenton and photo-Fenton processes stand out because of their high efficiency and operational simplicity (Nogueira et al., 2007).

Fenton process is characterized by the reaction between ferrous ion (Fe^{2+}) and hydrogen peroxide (H^2O^2), resulting in hydroxyl (Nogueira et al., 2007, Wu et al., 1999). Even though the Fenton process is an alternative in the degradation of several environmental pollutants, its efficiency can be significantly improved if it is assisted by ultraviolet (UV) radiation sources or Visible (Vis), thus characterizing the process as photo-Fenton (Freire et al,. 2000). Photo-

Fenton process is one of the most efficient advanced oxidation processes when a high decrease is needed of organic matter content in wastewater from biodiesel washing (Veljković et al., 2014). The application is also emphasized of photo-Fenton process in the treatment of several types of wastewater from textile industry, dairy, and paint industry, among others (Martins et al., 2011; Punzi et al., 2015; Villa, Silva and Nogueira, 2007).

Even though it Has Been little explored, the application of photo-Fenton in the treatment of wastewater from biodiesel washing has already Been investigated in studies by Hincapié-Mejia (2011), Veljković, Stamenković and Tasić (2014) with removal efficiency in COD for wastewater (with different chemical features).

The greatest advantage of the presence of radiation (either artificial or natural) is that regeneration of ferrous species takes place, reacting with H^2O^2 from the environment, thus closing the catalytic cycle and resulting in two hydroxyl radicals for each mole of initially decomposed H^2O^2 (Nogueira et al., 2007; Ghaly et al., 2001).

In the face of both the high pollution potential by wastewater from biodiesel purification, especially regarding hydric resources, and the simplicity and efficiency of some chemical treatment processes applied to this type of wastewater, the goal of this study is to verify the influence of variation of hydrogen peroxide and Fe^{2+} concentrations in the efficiency of the degradation process by photo-Fenton of pollutants present in wastewater from biodiesel washing. A 22 factorial planning was applied to this end.

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2. Experimental stage

2.1. Wastewater

For photo-degradation essays by photo-Fenton, a sample of wastewater from biodiesel washing was collected in an industrial plant that produces bio-fuel by mixing soybean oil and tallow (via methyl route), which is located in the town of Marialva, state of Paraná.

2.2. Method

Photo-Fenton process

Treatment essays of wastewater from biodiesel washing, using photo-Fenton process, were carried out according to the methodology proposed in literature (Oliveira, Nogueira and Neto, 2001). As a source of radiation for the photo-Fenton process, a 125 W mercury vapor lamp was used, coupled to a bench photochemical reactor with volume of 250 mL which was kept in magnetic stirring. A scheme of the bench photochemical reactor used in this study is presented in Figure 1.

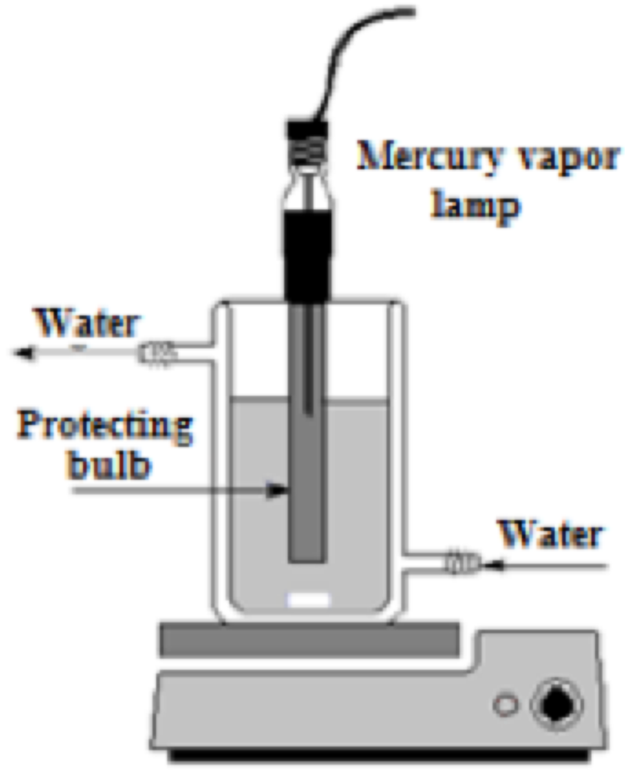

Figure 1 Schematic representation of the photochemical reactor, which is operated with artificial radiation from the mercury vapor lamp

The adopted period of time for wastewater treatment was 30 minutes, similar to that used in the study by Grangeiro et al., (2014). For analysis of treatment efficiency, spectroscopic scan assays within the ultraviolet and visible range in the 200-750 mm wavelength for raw wastewater and treated (a spectrophotometer HACH/DR6000 was employed for that end), according to the methodology adopted by Brito (2012); Marmitt (2010). The speed, low-cost, non-use of chemical reagents and the absence of generation of residues are some of the advantages of using this methodology.

With aid from *Origin 8.0* software, the area corresponding to each curve obtained in spectroscopic assays was calculated, which relates directly to the concentration of pollutants in the sample and thus the results were analyzed in terms of its decrease in percentage.

2.3. Factorial Design

The influence of the figures of hydrogen peroxide (H^2O^2) concentration and ferrous ions (Fe^{2+}) in the process of degradation in biodiesel samples was investigated by a 22 factorial design, each factor was studied at two levels (Neto, Scarminio and Bruns, 2010). The photo-degradation assays (performed in duplicate) were carried out in a random fashion for all combinations of factor levels presented in Table 1.

Table 1 Factors and levels of 22 factorial design for decreasing pollutants from biodiesel washing water by photo-Fenton process

Factor	Level (-)	Level (+)
(1) H^2O^2 concentration (mg L^{-1})	150	250
(2) Fe^{2+} concentration (mg L^{-1})	5	15

The effects of the factorial design factors (Ef) were calculated according to Equation 1:

$$Ef = (R+) - (R-) \qquad \textbf{(Equation 1)}$$

In which R+ and R- are the differences between the averages of levels (+) and (-), respectively, of the factors involved.

The effects of variables in the decrease of spectral area were tested for the statistical significance to the 95 % level, by the calculation of standard error. The statistical analysis of the data was carried out using the "Minitab 17" application.

3. Results and discussion

The photo-degradation process of biodiesel wash water by photo-Fenton studied in the factorial design made it evident a significant decrease in organic compounds over a 30-minute span, and its results are presented in Table 2, and the calculations of the effects in Table 3.

Table 2 Calculation of the effects and their respective standard deviations for 22 factorial design to determine the percentage of degradation of pollutants in wastewater from biodiesel wash through photo-Fenton process

$[Fe^{2+}]$	$[H^2O^2]$	% Decrease averages ± standard deviation
(-) 5	(-) 150	31.76 ± 0,032
(+) 15	(-) 150	44.14 ± 0,027
(-) 5	(+) 250	34.65 ± 5,049
(+) 15	(+) 250	45.35 ± 0,478

By F-test and T-test analysis at 95 % of confidence, it was found that the two variables of the design (H^2O^2 concentration and Fe^{2+} concentration) were considered as significant, however, a significant interaction effect was not observed between the two variables investigated in the process (Table 3 and Figure 2). Therefore, the H^2O^2 concentration and Fe^{2+} concentration variables may be independently optimized.

Table 3 Calculation of the average effects and their standard errors for 22 factorial design to determine the percentage of degradation of pollutants in wastewater from biodiesel wash through photo-Fenton process

Effects	Estimate ± standard error*
Global average	38,97 ± 0,11
Efeitos principais:	
$[H^2O^2]$ (1)	20,40 ± 0,21

$[Fe^{2+}]$ (2)	11,55 ± 0,21
Interaction between two factors: (1) x (2)	-0,8377 ± 0,21

* the standard error of the effects was calculated based on the standard deviations presented in Table 2.

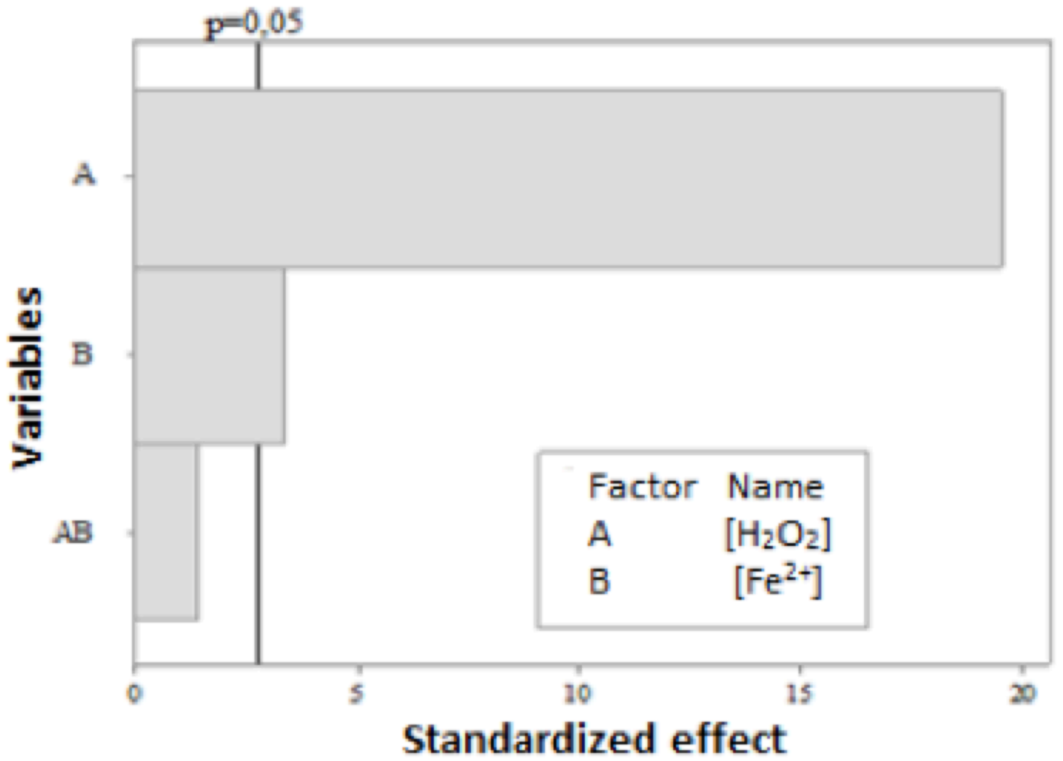

Figure 2 Pareto chart for the standardized effects of 22 factorial design at a 95 % confidence level

The change of the level of the H^2O^2 concentration variable from 150 mg L^{-1} to 250 mg L^{-1} resulted in a relative increase of approximately 36 % in decreased pollutants in the sample, regardless of the level of the Fe^{2+} concentration variable (Figure 3). This fact may be explained due to wastewater from biodiesel washing presenting high methanol concentrations, which acts as abductor of hydroxyl resulting in decreased efficiency of the process in low H^2O^2 concentrations (Nogueira, 2007). However, higher Fe^{2+} concentrations (15 mg L^{-1}) regardless of the adopted H^2O^2 concentration (150 or 250 mg L^{-1}), presented a relative reduction percentage of approximately 5,0 % higher when compared to lower Fe^{2+} levels. Even though the result presents an increase in reduction percentage, from an environmental standpoint the use of lower concentrations of iron is more appropriate, since 15 mg L^{-1} is the maximum concentration allowed for discharge into bodies of water according to CONAMA resolution 357/2005 in addition to being more economically feasible. Therefore, lower iron concentrations are suggested for the due treatment without any significant losses in the efficiency of the treatment.

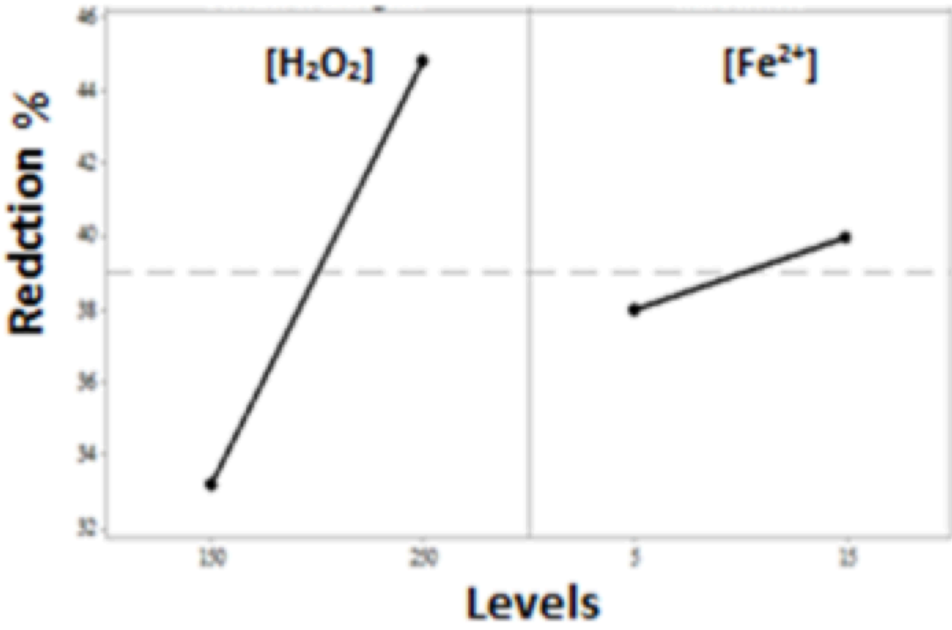

Figure 3 Diagram for the interpretation of the effects of 22 factorial design to determine degradation percentage of pollutants present in wastewater from biodiesel washing through photo-Fenton process

In addition to the main effects, no interaction effects were observed between the significant factors (Fe^{2+} and H^2O^2) as shown in Figure 3, which confirms the results presented in Table 2.

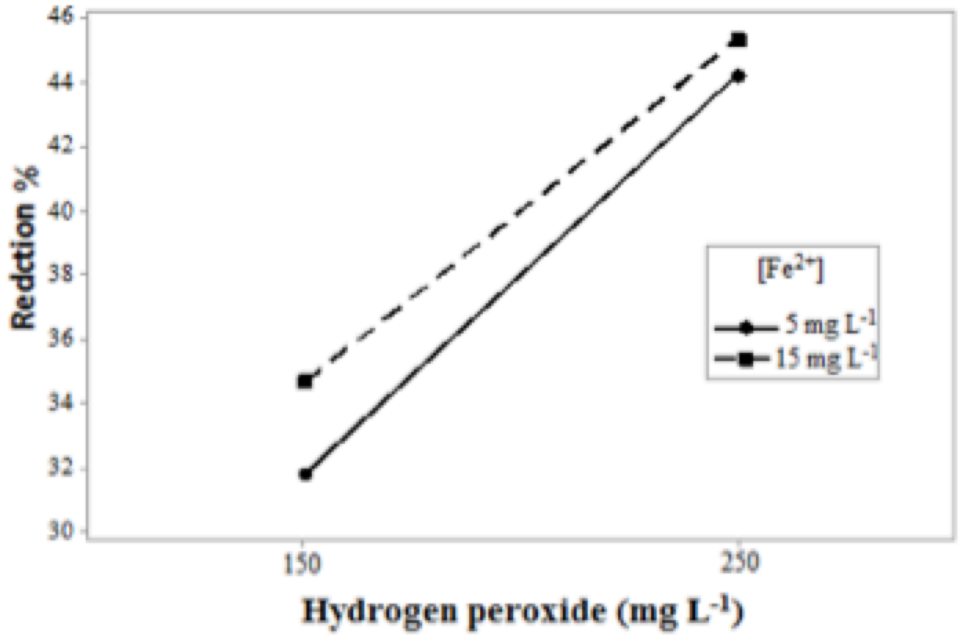

Figure 4 Graph of the effect of the interaction between H^2O^2 and Fe^{2+} concentrations for 22 design

By way of Figure 4, one can also notice that the factors may be analyzed separately, because their effects do not depend on the levels of the other variables.

4. Conclusions

Results from factorial design suggest that the variables investigated of H^2O^2 and Fe^{2+}concentrations influence the photo-degradation process of the photo-Fenton type of water resulting from biodiesel purification. However, the influence of H^2O^2 concentration is more significant than that of Fe^{2+}. The results also show that no significant interaction effects were observed between the two variables; therefore, they may be analyzed separately.

It is suggested that in order to perform a more complete analysis of the photo-degradation process optimization, an increase of other variables that might directly affect its efficiency, such as treatment time, types of radiation sources, and geometry of the reactor.

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