

CHARACTERIZATION AND TREATMENT OF LABORATORY WASTEWATERS BY FENTON OXIDATION

Cláudia Telles Benatti

Universidade Estadual de Maringá, Departamento de Engenharia Química - 87020-900 - Maringá-PR - Brazil
claudiatb@deq.uem.br

Célia Regina Granhen Tavares

Universidade Estadual de Maringá, Departamento de Engenharia Química - 87020-900 - Maringá-PR - Brazil
celia@deq.uem.br

Terezinha Aparecida Guedes

Universidade Estadual de Maringá, Departamento de Estatística - 87020-900 - Maringá-PR - Brazil
taguedes@uem.br

Mateus Pinatto Gaspar

Universidade Estadual de Maringá, Departamento de Engenharia Química - 87020-900 - Maringá-PR - Brazil

Rafael Gustavo Schreiner

Universidade Estadual de Maringá, Departamento de Engenharia Química - 87020-900 - Maringá-PR - Brazil

Abstract. Characterizing and establishing a treatment process for practical and economic disposal of laboratory wastewaters has become an urgent environmental concern of the Department of Chemical Engineering of the State University of Maringá – Brazil. The studies initiated at the Control Pollution Laboratory, whose wastes has been packaged and later on characterized. These wastes showed to have seasonal characteristics according to laboratory work. During the period of June-September of 2001, the main characteristics of these wastes were $pH < 1$, total phenols of 785 mg/L and chemical oxygen demand (COD) of 4363 mg O_2 /L and those during the period of August-September were $pH < 1$, total phenols of 28 mg/L and COD of 2847 mg O_2 /L. Fenton and related reactions are potentially useful oxidation processes for destroying toxic organics compounds in water. In these reactions, hydrogen peroxide (H_2O_2) is combined with ferrous or ferric iron (Fe^{2+} or Fe^{3+}) in the presence or absence of light to generate hydroxyl radicals ($OH\cdot$). This study investigated the feasibility of Fenton system (Fe^{2+}/H_2O_2) at room temperature to treat laboratory wastewaters. The ratio of $[phenol]:[H_2O_2]$, $[H_2O_2]:[Fe^{2+}]$ and pH were set as variables. Percent of total phenols removal was investigated as a response. A response surface technique was used with the aim of searching the optimum condition for the ratio $[phenol]:[H_2O_2]:[Fe^{2+}]$ and pH for the Fenton process.

Keywords. Fenton's reagent, laboratory wastewater, characterization, oxidation.

1. Introduction

In the last years the worldwide understanding of a need of an effective treatment or an appropriate disposal of any type of residues has grown in chemical industries, academics institutions and governmental organs (Amaral et al., 2001). The waste, that is generated during the Control Pollution Laboratory operations of the Department of Chemical Engineering of the State University of Maringá – Brazil, has been held for many years at the laboratory site until acceptable modes of disposal are developed. Because of the lack of specific legislation to regulate the treatment of waste chemicals, this was a common situation in many Brazilian institutions, as in the Chemistry Department of the Federal University of Paraná (Cunha, 2001).

Waste chemicals from academic laboratories are generated fundamentally by small amounts of different wastes (National Research Council - U.S., 1995). These wastes are constituted of great diversity of substances, including new compounds of unknown toxicity (Micaroni et al., 2002). The ultimate destination of waste is usually a treatment, storage, and disposal facility. The characteristics that involve these residues do not allow a unique solution. According to National Research Council - U.S. (1995), the treatment of these wastes is typically via chemical action or incineration. In this work, the Fenton oxidation of chemical analysis wastes is investigated as an advanced oxidation process.

Advanced oxidation processes are based on the generation of very reactive species such as hydroxyl radical ($OH\cdot$) that oxidize a broad range of organic pollutants quickly and non-selectively (Arslan and Balcioglu, 1999). Fenton's reagent which involves homogenous reaction and is environmentally acceptable (Bham and Chambers, 1997), is a system based on the generation of very reactive oxidizing free radical, especially hydroxyl radicals, which have a

stronger oxidation potential than ozone, 2.8 V for $\text{OH}\bullet$ and 2.07 V for ozone (Heredia et al., 2001). The classic Fenton's reaction involves the addition of dilute hydrogen peroxide to a degassed, acidic ferrous iron solution, which generates hydroxyl radicals (Eq. 1). The degradation of organic chemicals by hydroxyl radicals then proceeds via hydroxylation, hydrogen atom abstraction, or dimerization (Walling, 1975).



Some environmental applications of Fenton's reagent involve reaction modifications, including the use of high concentrations of hydrogen peroxide, the substitution of different catalysts such as ferric iron and naturally occurring iron oxides, and the use of phosphate-buffered media and metal-chelating agents. These conditions, although not as stoichiometrically efficient as the standard Fenton's reactions, are often necessary to treat industrial waste streams and contaminants in soils and groundwater (Büyüksönmez et al., 1999).

The main purpose of this work was to examine the feasibility and the efficacy of using Fenton's reagent as a treatment method for chemical laboratories wastes. Prior to treatment, the laboratory wastes were characterized through physicochemical analysis. This paper illustrates the use of variance analysis and factorial design of experiments to provide insight into the Fenton oxidation process. That is, the significance of the effect of three main experimental variables, ratio of $[\text{phenol}]:[\text{H}_2\text{O}_2]$, $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$ and pH, on the percent of total phenols removal, which has been selected as a representative parameter of process efficiency.

2. Materials and Methods

2.1. Laboratory Effluent Characterization

All chemical analysis residues generated in the laboratory were retained in clearly marked containers and their source was defined in a notebook record. Later on they were characterized in terms of pH, chemical oxygen demand (COD), total phenols, real and apparent colors, turbidity, settleable solids (Imhoff cone) and metals content (Cu, Fe, Zn, Al, Co, Cr, Mn, Mg, K and Ca).

2.2. Experimental Procedure

Wastewater generated during July-September/2001 from the chemical laboratory were collected and mixed to obtain a composite sample that was used in the experiments of Fenton oxidation.

Prior to the experiments, the pH was adjusted to the desired value using NH_4OH (30%). A 1N $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ stock solution was prepared and standardized (Pavan et al., 1992) just before the experiments. H_2O_2 (~33% w/w) was standardized using permanganate titration (Vogel, 1992) and directly transferred from the original bottle to the reaction mixture.

Experiments were carried out in 250 ml beakers. The reaction mixture consisted of laboratory effluent without solids separation in a final volume of 150 ml. The effluent was continuously mixed (100 rpm) in a jar test apparatus at room temperature ($23 \pm 2^\circ\text{C}$). The wastewater samples were centrifuged at 2500 rpm by 5 minutes and the initial concentration of total phenols in supernatant (S_0) was measured. The required amount of reagents was then determined. The definite volume of FeSO_4 was first added to the reaction mixture. The Fenton reaction was then initiated by sequential addition of the required amount of H_2O_2 , in three steps of equal volumes added in intervals of 20 minutes, to moderate the rise in temperature that occurs as the reaction proceeds. The Fenton reaction time was initiated by the addition of the first required amount of H_2O_2 to the reaction mixture. There was no pH control throughout the oxidation process. After reactions have completed (4h), precipitation of the oxidized iron as $\text{Fe}(\text{OH})_3$ was performed by adjusting the pH to 8.0 and then about 20 h of clarification at quiescent conditions. Final samples of supernatant were taken for total phenols measurements (S_E). Control experiments were done in the absence of both Fe^{2+} and H_2O_2 . All experiments including controls were performed in duplicate.

The percent of total phenols removal was then determined through the following equation:

$$\eta = \left(\frac{S_0 - S_E}{S_0} \right) * 100 \quad (2)$$

2.3. Experimental Design

Fenton oxidation experiments were based on a factorial design using a response surface technique, as outlined by Werkema and Aguiar (1996) and Kuehl (2000), to decrease the number of experiments while increasing the statistical significance of the results. Table 1 shows the levels of factors used in this experiment. The percent of total phenols removal, obtained in Eq. 2, was the response measured.

Frequently, the initial estimate of the optimum operating conditions for the system will be far from the actual optimum. In such circumstances, the experimenter's objective is to move rapidly to the general vicinity of the optimum, based on a simple and economically efficient experimental procedure (Montgomery, 1993).

According to Werkema and Aguiar (1996), the response surface technique is a sequential procedure that includes the following steps: (1) relate the factors that might affect an interest response variable; (2) plan an experiment that can identify the influent factors among those related in (1); (3) eliminate the factors detected as non-influent at the former step and evaluate the need of including new factors in the study; (4) carry out a more detailed experiment, involving only the significant effects over the response variable; (5) based on the adjusted model obtained in (4), normally presented as a first order model, accomplish analyses that will allow the determination of the optimum operating conditions for the system; (6) walk sequentially to the general vicinity of the optimum; (7) adjust an advanced order model in the vicinity of the optimum that will allow the determination of the optimum operating conditions for the system.

According to Annadurai et al. (2002), the advantages of this method are: (1) all experimental units are used in evaluating effects, resulting in the most efficient use of resources; (2) the effects are evaluated over a wider range of conditions with the minimum of resources; (3) a factorial set of treatments is optimized for estimating main effects and interactions.

The design matrix that indicates the combination of factor levels to be tested is shown in Tab. 2. This design involves 14 tests, based on a 2^3 factorial augmented by six center points. Repeated observations at the center were used to estimate the experimental error. The design was centered at the optimum condition for the Fenton process: ratio of $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}] = 6:1$ w/w, according to Tang and Huang (1996); and $\text{pH} = 3.5$, according to Bishop et al. (1968).

Table 1. Factors and levels for the optimization experiment

Factor	Notation	Level		
		Low (-)	Center (0)	High (+)
$[\text{phenol}]:[\text{H}_2\text{O}_2]$	X1	1:20	1:60	1:100
$[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$	X2	2:1	6:1	10:1
pH	X3	2	3.5	5

Table 2. Experimental design and results of the Fenton oxidation of laboratory effluent

Expt no.	Natural Variable			Coded Variable			% total phenols removal		Design location
	$[\text{phenol}]:[\text{H}_2\text{O}_2]$	$[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$	initial pH	X1	X2	X3	Y1	Y2	
1	1:20	2:1	2	-	-	-	81.4	81.6	Factorial design
2	1:20	2:1	5	-	-	+	85.9	85.4	
3	1:20	10:1	2	-	+	-	15.6	12.5	
4	1:20	10:1	5	-	+	+	69.9	70.3	
5	1:100	2:1	2	+	-	-	87.2	87.5	
6	1:100	2:1	5	+	-	+	90.3	89.2	
7	1:100	10:1	2	+	+	-	83.4	83.2	
8	1:100	10:1	5	+	+	+	85.8	85.8	
9	1:60	6:1	3.5	0	0	0	84.1	84.1	Center
10	1:60	6:1	3.5	0	0	0	84.0	85.1	
11	1:60	6:1	3.5	0	0	0	84.5	84.7	
12	1:60	6:1	3.5	0	0	0	83.4	83.5	
13	1:60	6:1	3.5	0	0	0	84.3	84.9	
14	1:60	6:1	3.5	0	0	0	84.5	84.4	

2.4. Analytical Methods

Measurements of chemical oxygen demand (COD), pH and settleable solids (Imhoff cone, $t=24\text{h}$) followed Standard Methods (APHA, 1998). Total phenols were measured according to the colorimetric method of Folin-Ciocalteu reagent (Scalbert et al., 1989). Real and apparent colors and turbidity were measured by an analytical method developed by HACH Company. Metal concentrations (Cu, Fe, Zn, Al, Co, Cr, Mg, Ca, K and Mn) were determined in the filtrate by atomic absorption spectroscopy (Varian SpectrAA- 10 Plus).

3. Results and Discussion

The main characteristics of wastewater produced by the chemical laboratory during the period of study are listed in Tab. 3 and 4. These wastes showed to have seasonal characteristics according to laboratory work. These wastes were collected and mixed to obtain a composite sample that was used for the experiments of Fenton oxidation.

Table 3. Main characteristics of wastewater from chemical laboratory

Period	pH	Apparent color (Pt/Co)	Real color (Pt/Co)	Turbidity (FAU)	Settleable solids (ml/L)	COD (mg O ₂ /L)	Total phenols (mg/L)
Jul. to Aug.	< 1	7650	1200	1350	96.0	4363	784.6
Aug. to Sep.	< 1	8350	320	2900	4.3	2847	27.9

Table 4. Metal concentrations on wastewater from chemical laboratory

Period	Fe (mg/L)	Cr (mg/L)	Cu (mg/L)	Zn (mg/L)	Co (mg/L)	Al (mg/L)	Na (mg/L)	Mn (mg/L)	Mg (mg/L)	Ca (mg/L)	K (mg/L)
Jul. to Aug.	2.5	589.6	1.0	2.9	0.9	27.2	2226.6	0.1	2.3	4.9	22.4
Aug. to Sep.	0.4	382.0	3.1	0.4	0.1	16.2	3163.0	0.0	0.6	22.4	380.4

A statistical analysis software package (SAS Institute, Inc., Cary, N.C. – version 6.12) was used to analyze the results, provide estimated percent of total phenols removal on a first order model fit to the data (Tab. 2), and provide the next steps to generate response surface plots.

The analysis of variance (Tab. 5) indicates that the model can be satisfactorily used ($R^2 = 0.9991$, $P\text{-value} < \alpha$).

Table 5. Analysis of variance

Source	Degree of freedom	Sum of square	Mean square	F-value	P > F
Model	8	9531.34	1191.42	2641.67	0.0001
Error	19	8.57	0.45		
Corrected total	27	9539.91			

$R^2 = 0.9991$

Mean percentage of total phenols removal= 78.8

Level of confidence (α)=0.05

The analysis of variance for main factors and interactions (Tab. 6) indicates that the main effects of the variables X1, X2 and X3 are significant ($P\text{-value} < \alpha$). Furthermore, there is a significant interaction between the variables X1, X2 and X3 ($P\text{-value} < \alpha$). Thus, all factors (ratio of [phenol]:[H₂O₂], [H₂O₂]:[Fe²⁺] and pH) significantly affect the efficiency of total phenols removal.

Table 6. Analysis of variance for factors and interactions

Run	Degree of freedom	Sum of square	Mean square	F-value	P > F
X1 = [phenol]:[H ₂ O ₂]	2	2884.01	1442.00	3197.28	0.0001
X2 = [H ₂ O ₂]:[Fe ²⁺]	1	2070.25	2070.25	4590.27	0.0001
X3 = pH	1	1059.51	1059.50	2349.18	0.0001
X1.X2	1	1406.25	1406.25	3118.01	0.0001
X1.X3	1	764.52	764.52	1695.14	0.0001
X2.X3	1	676.00	676.00	1498.86	0.0001
X1.X2.X3	1	670.81	670.81	1487.35	0.0001

Level of confidence (α)=0.05

According to Tukey's test, there is a difference between the means of the two levels of the factors X1, X2 and X3. Table 7 shows the estimated effects of the three main factors and their interaction on the percent of total phenols removal.

Table 7. Estimated effects from a 2³ factorial design augmented by six center points

Effects	Estimated effect ± standard error
Mean	78.804 ± 0.1269
X1 = [phenol]:[H ₂ O ₂]	23.725 ± 0.2538
X2 = [H ₂ O ₂]:[Fe ²⁺]	- 22.750 ± 0.2538
X3 = pH	16.275 ± 0.2538
X1.X2	18.750 ± 0.2538
X1.X3	- 13.825 ± 0.2538
X2.X3	13.000 ± 0.2538
X1.X2.X3	- 12.950 ± 0.2538

Figure 1 shows the effect of factor levels on the total phenols removal efficiency. As can be seen in Fig. 1, a change in the levels of each factor produces a different variation in the process efficiency. An increase on the ratio of [phenol]:[H₂O₂] from 1:20 to 1:100 caused an increase in process efficiency of 23.7%. The same can be observed on the pH, on which an increase from 2 to 5 caused an increase in process efficiency of 16.2%. On the other hand, an increase on the ratio of [H₂O₂]:[Fe²⁺] from 2:1 to 10:1 decreased the process efficiency in 22.8%. Thus, considering that the model is suitable, the maximum efficiency of total phenols was obtained for the following combination of factor levels: (+ - +), or, X1 (ratio [phenol]:[H₂O₂]), 1:100; X2 (ratio [H₂O₂]:[Fe²⁺]), 2:1; and X3 (pH), 5.

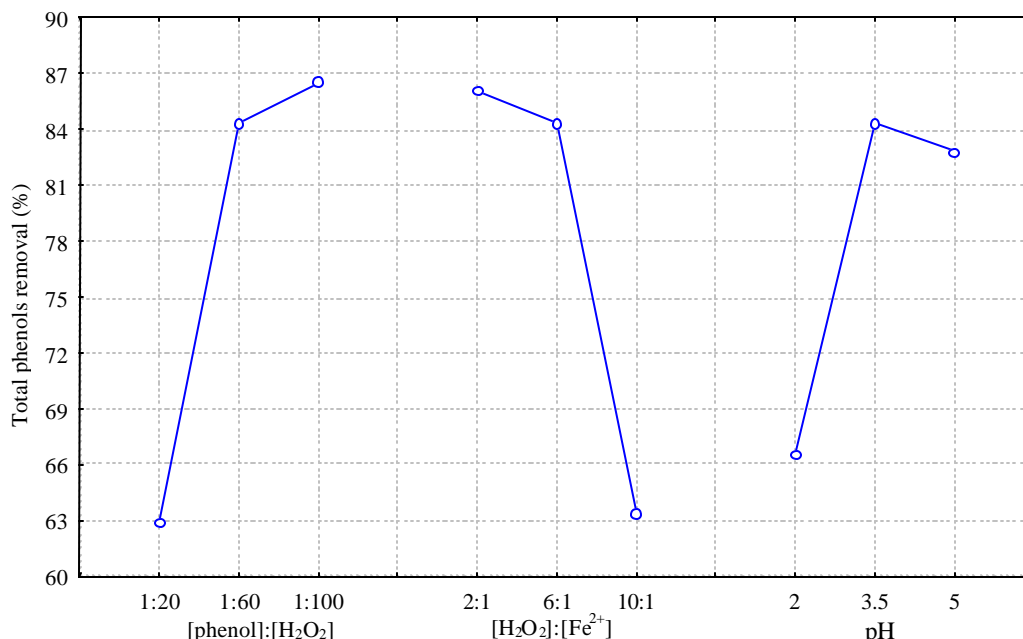


Figure 1. Effect of the factor levels on the percentage of total phenols removal mean response.

The results showed that the efficiency of the iron/peroxide systems increased with higher Fe²⁺ and H₂O₂ concentrations. In previous works (Benatti et al., 2002), no treatment of the laboratory effluent was observed when low concentrations of peroxide were added to the wastewater (ratio phenol:H₂O₂<1:20 w/w).

The iron/peroxide systems also showed to be pH sensitive, and acidic conditions were necessary for iron solubility. Vella and Munder (1993) used Fe²⁺/H₂O₂ for the degradation of phenolic compounds in water. Again, acidic conditions (pH=4) were used. Kwon et al. (1999) showed in their study that the decomposition of *p*-chlorophenol by Fenton oxidation progressed at higher rates at pH 2.4 and at a pH above 4, the decomposition rate significantly decreased as the pH was raised. According to Kim and Vogelpohl (1997) apud Kwon et al. (1999) this is probably because the dissolved fraction of iron species decreases at a pH above 4.

In the factorial design of experiments, it is useful to consider the factor response relationship in terms of a mathematical model such as a response function. Based on Eq. 3, it is possible to fit an adequately regression model to the data and obtain a first order polynomial equation (Eq. 4), so that the response at intermediate factor levels can be predicted.

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_1 X_2 + \beta_5 X_1 X_3 + \beta_6 X_2 X_3 + \beta_7 X_1 X_2 X_3 + \varepsilon \tag{3}$$

$$\hat{Y} = 78.804 + 11.863 X_1 - 11.375 X_2 + 8.137 X_3 + 9.375 X_1 X_2 - 6.913 X_1 X_3 + 6.500 X_2 X_3 - 6.475 X_1 X_2 X_3 \tag{4}$$

The measured and the predicted data are shown in Fig. 2, revealing a reasonably good agreement.

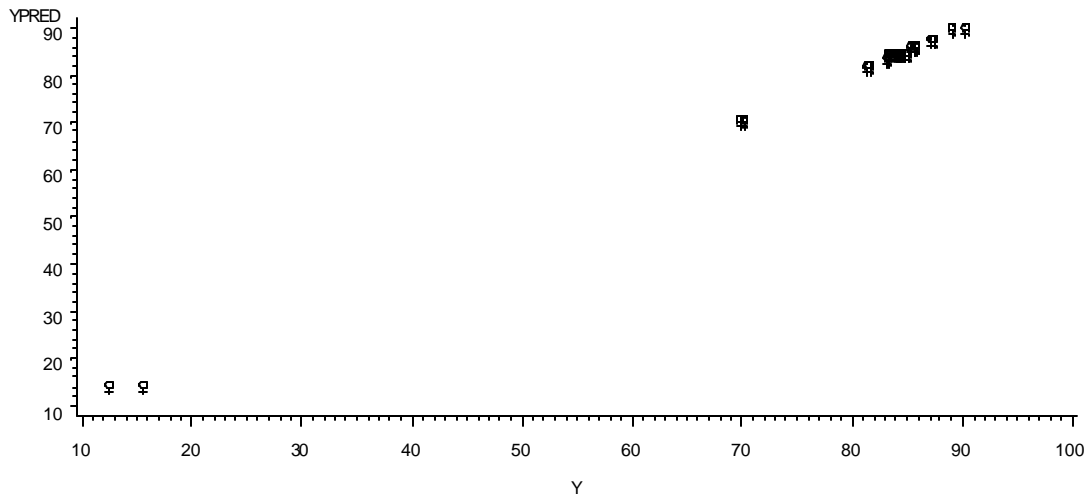


Figure 2. Measured data against predicted values from the factorial design 2^3 including center points.

The first order response surface, that is, the contours of Y , is a series of parallel lines that indicates the direction in which Y increases more rapidly. Figures 3 to 5 show the contour curves to the percent of total phenols removal. According to Werkema and Aguiar (1996), this direction is parallel to the normal to the fitted response surface. It can be taken as the path line through the center of the region of interest and normal to the fitted surface. Thus, the steps along the path are proportional to the regression coefficients (β) shown in Eq. 4 and based on the experimenter's experience.

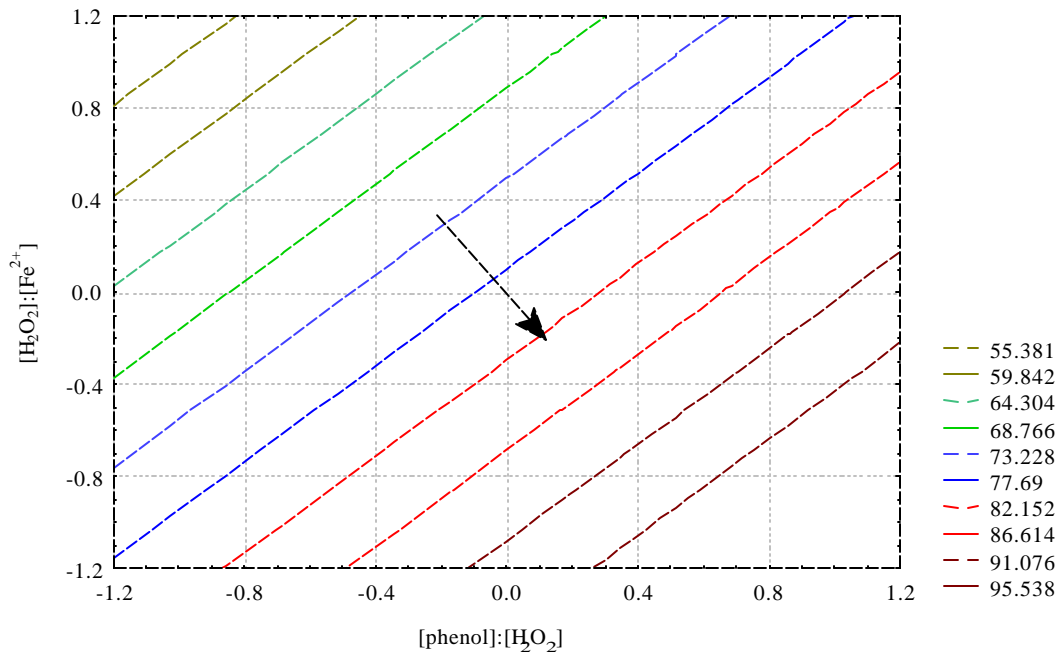


Figure 3. Contour curves to the percent of total phenols removal in function of the ratio $[\text{phenol}]:[\text{H}_2\text{O}_2]$ and $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$

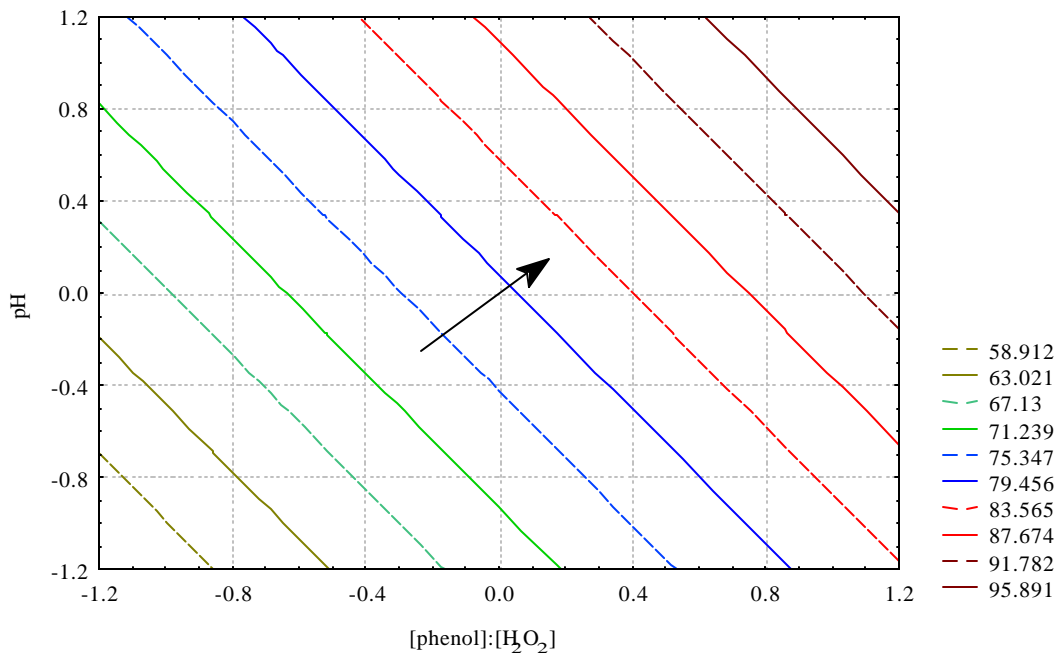


Figure 4. Contour curves to the percent of total phenols removal in function of the ratio [phenol]:[H₂O₂] and pH

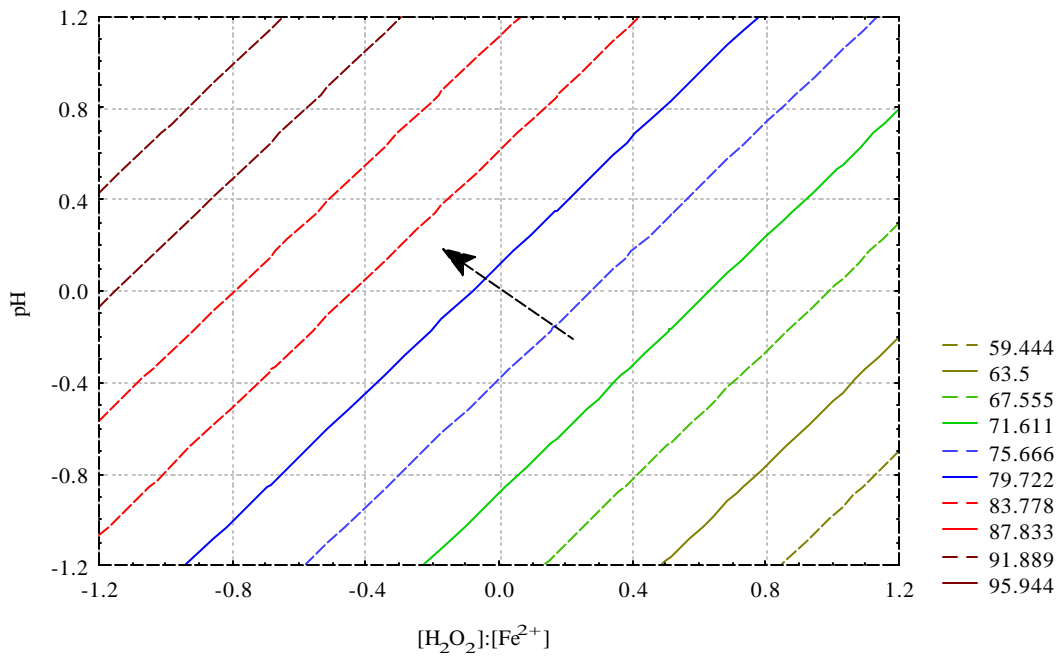


Figure 5. Contour curves to the percent of total phenols removal in function of the ratio [H₂O₂]:[Fe²⁺] and pH.

The new operational condition proposed is represented by the following equation:

$$(1:60+\Delta X_1, 6+\Delta X_2:1, 3.5+\Delta X_3) = (1:60+10, 6-1:1, 3.5+0.5) = (1:70, 5:1, 4.0) \quad (5)$$

Thus, experiments must be conducted along this path until no further increase in response is observed. Then a new model must be fitted in the vicinity of the optimum in order to achieve the optimum operating conditions for the Fenton oxidation in treating laboratory effluents.

4. Conclusions

The overall results of this study showed high potential for Fenton oxidation to treat complex residues generated from chemical laboratories.

The factorial design of experiments for Fenton oxidation of laboratory wastewaters was studied. The effects of three factors, the ratio of [phenol]:[H₂O₂], [H₂O₂]:[Fe²⁺] and pH, on percent of total phenols removal were identified. According to the significance effect obtained in variance analysis, the ratio [phenol]:[H₂O₂] was the most significant factor in this process, followed by the ratio [H₂O₂]:[Fe²⁺] and pH. The statistical analysis for each case confirmed that the polynomial equation (Eq. 4) gave a reasonably good fit. The contour curves to the percent of total phenols removal indicated the next steps for searching the optimum operating conditions for the process.

5. Acknowledgement

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