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Response surface method and Taguchi Orthogonal Array applied to phenolic wastewater by advanced oxidation process (AOP)

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Abstract: The advanced oxidation process was conducted using the Design of Experiments in this work. Initially, Taguchi's Orthogonal Array L_{16} (Photo-Fenton and Ozone) was applied, with which it was obtained 29.07% TOC removal. Then, the process was optimized with the Photo-Fenton RSM, thus it was achieved the highest percentage of TOC removal= 54.68%. This condition is associated with a mass ratio of hydrogen peroxide and ferrous ions of eight, which corresponds to 47,8g H_2O_2 and 5,95g Fe^{+2}.

Keywords: Advanced Oxidation Process, Taguchi, RSM

1. Introduction

Currently, the evolution of industrial processes and the emergence of several products helped highlight industrial activity, therefore, those responsible for environmental contamination phenomena. The contributing factors to pollution are: the accumulation of raw materials, inputs and the inefficiency of conversion processes [1].

According to [2], this worldwide problem is due to about two million tons of household and commercial waste being generated daily, which is equivalent to an average of about 0.7 kg/day^{-1} per inhabitant of urban areas.

Thus, in this context, solid, gaseous and liquid waste is quite harmful to ecosystems and humans [3].

According to [4], there is a need for developing new effluent treatment processes that ensure a low level of contaminants.

A promising alternative for the treatment of this effluent are Advanced Oxidation Processes (AOPs), mainly due to having features as high capacity and degradation speed [5].

The present work specifically approaches the application of the design of experiments (Taguchi's Orthogonal Array and Response Surface Methodology) in the treatment of phenolic effluents.

2. Literature Review

2.1. Advanced Oxidation Processes

Advanced oxidation processes; UV/TiO_2, UV/H_2O_2, $UV/H_2O_2/Fe$, O_3, O_3/Fe, O_3/TiO_2, $UV\text{-}O_3/H_2O_2/Fe$; are characterized by the generation of free radicals that degrade organic matter, thus polluting compounds are mineralized into other compounds with lower toxicity [6].

AOPs are based on the generation of reactive species, which are hydroxyl radicals (OH •) and are characterized by quickly degrading a wide variety of organic pollutants, being unstable and generated continuously through chemical or photochemical reactions in situ [7]. Table 1 presents the reduction potential of various compounds and, it can be observed that after the fluoride, the hydroxyl radical is the species that presents the greatest potential for oxidation [8].

Table 1. *Reduction potential of some compounds*

Species	E^0 Reduction (V, 25 °C)1
Fluoride (F2)	3,03
Hydroxyl radical (•OH)	2,80
Atomic oxygen (O2)	2,42
Ozone (O3)	2,07
Hydrogen peroxide (H2O2)	1,78
Perhydroxyl radical (HO2•)	1,70
Chlorine dioxide	1,57
Hypochlorous acid (HCLO)	1,49
Chloride (Cl2)	1,36
Bromine (Br2)	1,09
Iodine (I2)	0,54

Source: DOMÈNECH et al. (2001)
1 The potentials refers to a standard hydrogen electrode

2.2. Photo-Fenton Process

The Photo-Fenton process is highly efficient in the study of effluents containing high organic load [9; 10; 11]. The oxidation of organic compounds under UV irradiation in the presence of ferric ion in an acidic medium was verified in the 50's, when it had been postulated that the electronic transfer initiated by irradiation resulted in the generation of • OH radicals that are responsible for oxidation reactions [12].

The Photo-Fenton reaction is an effective technology for the treatment of organic compounds in wastewater through advanced oxidative processes. The interest in these oxidation processes has increased recently, due to being able to destroy a large variety of toxic organic compounds.The main reactants, the catalyst of iron and hydrogen peroxide, are also less costly and relatively easier and safer to be handled than other oxidants or chemical products [13].

[14;15].The Fenton process produces hydroxyl radicals from the H_2O_2 reaction with iron ions. A simultaneous emission of photons increases the speed of the reaction and it reaches complete mineralization, even for recalcitrant organic acids. This degradation is attributed to ferrous ion regeneration (Fe^{+2}), as shown in Equation 1. The ferric ions (Fe^{+3}) are irradiated, and the promotion of an electron that is bound to the metal occurs, which implies the reduction of Fe^{+3} to Fe^{+2} and the oxidation of the ligand, as Equation 2[14, 15].

$$Fe^{+3}(HO)_2 + h\nu \rightarrow Fe^{+2} + 2\,OH\bullet \quad (1)$$

$$Fe^{+3}(RCO_2)_2 + h\nu \rightarrow Fe^{+2} + CO_2 + R\bullet \quad (2)$$

2.3. Taguchi's Method

According to [16], Taguchi's method is characterized as a robust mathematical tool which is capable of finding out significant parameters of ideal processes through multiple quality aspects.

According to [17], the application of Taguchi's Method consists in:

-Selecting the response variables to be optimized;

-Identifying the factors (input variables) and choosing their levels;

-Selecting a suitable orthogonal array according to literature [18];

-Conducting the experiments randomly to avoid the incorporation of systematic errors;

-Analyzing the results using the signal-to-noise ratio (S/N) and the analysis of variance (ANOVA);

-Determining the optimum parameter adjustment.

Taguchi's method uses orthogonal arrays that allow studying several factors with a reduced number of experiments [19]. Moreover, the method is able to offer other advantages such as: reducing the variability of the process, compliance that is close to the desired result and, consequently, a reduction of operating costs [20].

[21] defines the analysis of variance (ANOVA) as being applied in a statistical study of Taguchi's method, in order to evaluate the significance of the parameters used in the process. The results of the ANOVA are presented in a table that determines the most relevant parameters for the process through the following values, as equations 3, 4, 5 and 6:

-SS: quadratic sum of factors

$$SS = \sum_{i=1}^{n} (y_i - \overline{y})^2 \quad (3)$$

-gl: degrees of freedom for each factor (gl)

$$gl = (\text{Number of levels for each factor} - 1) \quad (4)$$

-MS: quadratic average

$$MQ = SS/gl \quad (5)$$

-Test F: evaluates the significance of each factor

$$F = MS\,effect/MSerror \quad (6)$$

2.4. Response Surface Methodology

The response surface methodology (RSM) is a set of mathematical and statistical techniques that are used to model and analyze the response variable of interest, in order to optimize it. (MONTGOMERY, 2001).

It is an optimization technique based on the use of factorial experimental designs, and which have been widely used in industrial process modeling ever since. This study consists of two stages; modeling and displacement; it is sought to achieve an optimal region (maximum or minimum) of the investigated area [22].

Modeling and displacement consist of analyzing the behavior of the input variables as decision variables regarding the response variable. The variables present correlations, therefore, they are obtained by second-order models by the least squares method (equation 7), in which Y is the response variable, βo is the constant and βi, βii and βij are the linear, quadratic and interaction effect coefficients, respectively [23].

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{i \neq j=1}^{i} \beta_{ij} x_i x_j + \varepsilon \quad (7)$$

The response surface design can be enlarged, thus forming the Central Composite design or star design [24].

According to [25], the degradation of azo dyes was carried out using the Photo-Fenton treatment (AOPs) via the response surface methodology. The optimization of input variables allowed 98% color degradation, 78% of chemical oxygen demand (COD) and 59% of total organic carbon (TOC) in this process.

3. Materials and Methods

3.1. Characteristics of the Design of Experiments

Table 2 presents the variable with its respective selected levels. Figure 1 depicts a linear graph with 7 factors and 8 interactions, being that the distribution of factors in it is made with the intention of obtaining the interactions that could be the most significant [26].

Table 2. *Control factors and levels for the exploratory study on the phenolic effluent treatment*

Factor	Symbol	Level 1	Level 2
* Hydrogen peroxide (g)	A	38,7	46,5
*Ferrous Ions (g)	B	1,26	1,55
pH	C	3	5
Ozone ($L\ h^{-1}$)	D	3	5
Temperature (ºC)	E	30	35
Lamp power	F	16	28

* Fenton Reagent

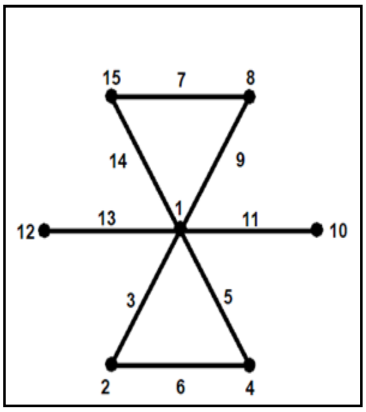

Figure 1. *LinearGraph of the Orthogonal Array L_{16} (CARNEIRO, 2007)*

Both H_2O_2 and Iron II were used in solutions, whose concentrations were: $[H_2O_2]$=30%m/m and $[Fe^{2+}]$=0,82 mol L-1; These values are proportional to 3L of treated effluent.

The used values were based on literature, and most of the studies were conducted with Fenton, an optimal pH for the treatment is the one that is in the range of 2 to 5, since it avoids the hydrolysis of iron salts. A catalytic ozonation also features good results in acidic media in some experimental conditions and with certain effluents.

In Taguchi's design, which is used for the degradation of organic matter from the effluent, was chosen to be used in a pH range of 3 to 5 in order to evaluate the effluent's behavior. The selected temperatures were determined through data from literature, in which temperatures ranging between 25° C and 40° C present optimum conditions for the degradation for effluents submitted to AOPs.

Tables 3 and 4 present the variables with their selected levels and the response surface methodology of the treatment optimization with the AOP, respectively.

Table 3. *Control factors and levels for the optimizationstudy (Photo-Fenton RSM)*

Factor	Symbol	Level 1	Level 2	Level 3
* Ferrous Ions (g)	A	2,6	5,95	9,3
* Hydrogen peroxide (g)	B	38,7	42,6	46,5

* Fenton Reagent

Table 4. *Response Surface Methodology for the Photo-Fenton process*

Experiment	Ferrous Ions (A)	Hydrogen Peroxide (B)
1	-1	-1
2	1	-1
3	-1	1
4	1	1
5	0	0
6	0	0
7	0	0
8	-(2)1/2	0
9	0	(2)1/2
10	(2)1/2	0
11	0	-(2)1/2

4. Results and Discussions

4.1. Taguchi's Orthogonal Array L_{16} for Total Organic Carbon (TOC) Removal

Table 5 shows the percentage variation in the TOC for the experiments conducted in the design of experiments L_{16}. Experiments 13 and 15 had a higher percentage of TOC removal for the advanced oxidative process (O3/UV and Photo-Fenton).

Table 5. *Taguchi's Orthogonal array L_{16} with TOC removal percentage*

Taguchi Orthogonal Array Experiments (L_{16})	TOC Reduction %
1	18,28
2	23,82
3	9,83
4	15,74
5	23,72
6	22,48
7	15,89
8	15,55
9	25,71
10	23,74
11	22,88
12	21,07
13	29,07
14	26,78
15	28,68
16	21,82

The statistical analysis of Taguchi's design L_{16} (Figure 2) showed the most significant parameters for degrading the effluent's organic matter, which correspond to pH = 3 and set on a low level, and the adjusted maximum level factors are: 46.5 g hydrogen peroxide, 1.55 g ferrous ions and UV lamp power of 28W.

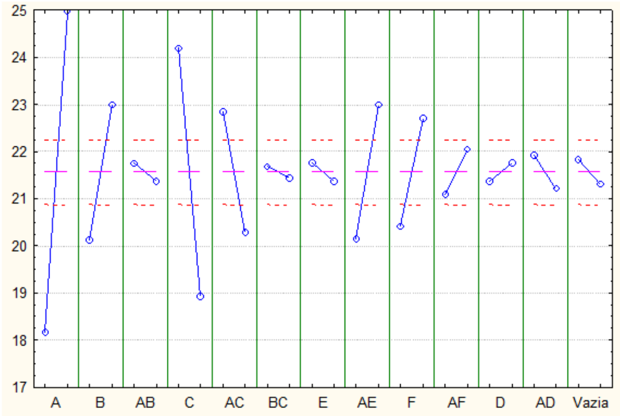

Figure 2. *Main effects of percentage variation measures of TOC in the treatment of phenolic effluent from the L_{16}design*

In the utilized design of experiments, the interactions between factors were also evaluated, in which those that werethe most significant for the process are: hydrogen peroxide and pH adjusted for level 1, and hydrogen peroxide and temperature for level 2.

The statistical significance of the factors and their interactions towards the TOC reduction for the treatment ofthe phenolic effluent was confirmed by the analysis of variance (ANOVA), as shown in Table 6.

Table 6. *Analysis of variance of Taguchi's orthogonal array L_{16}*

Factors	*(SS)	*(gl)	*(SMQ)	F	P
A	185,2321	1	185,232	195,6	0,005
B	32,8329	1	32,8329	34,684	0,02
AB	0,555	1	0,555	0,5863	0,52
C	110,9862	1	110,986	117,24	0,00
AC	26,1121	1	26,1121	27,584	0,03
BC	0,2304	1	0,2304	0,2434	0,67
E	0,5852	1	0,5852	0,6182	0,51
AE	32,49	1	32,49	34,321	0,02
F	21,16	1	21,16	22,353	0,04
AF	3,6672	1	3,6672	3,874	0,18
D	0,6162	1	0,6162	0,651	0,50
AD	2,0164	1	2,0164	2,1301	0,28
Empty	1,1025	1	1,1025	1,1647	0,39
Residual	1,8933	2	0,9466		

*SS (Sum of squares), gl (Degrees of freedom), SMQ (Average Sum of Squares)

The statistical analysis; at 95% reliability level; showed the most significant factors for removingthe organic load. According to Array F whosecritical value is 18.51 and for a p-value which is less than 5%, the most important factors to the degradation of the organic matter of the phenolic effluent were H_2O_2, Fe^{+2}, pH, UV, and interactions H_2O_2/pH and H_2O_2/temperature.

Hydrogen peroxide was the most significant factor, with F=195.6 and a p-value of 0.5%, andthe other factors are pH (F = 117.2441 and p-value =0.84%), ferrous ions (F = 34.6842 and p-value = 2.76%)lamp power (F = 22.3531 and p-value = 4.19%) and the interactions of H_2O_2/pH (F = 27.5844 and p-value =3.44%) and H_2O_2/temperature (F = 34.3219 and p-value = 2.79 percent). The values obtained by the analysis of variance confirm the significance shown by themain effects graph.

The best experiment for the degradation of the organicload of the phenolic effluent was experimentalcondition13, with 29.07% removal. It has 46,5g hydrogen peroxide, 1,55g of ferrous ions, pH = 3, ozone flow of 3L/h, temperature of 30ºC and28W ultraviolet lamp power.

4.2. Results of the Response Surface Methodology (Fe^{+2}/H_2O_2) for Removing the Total Organic Carbon (TOC)

The percentage of Total Organic Carbon removal for theexperiments conducted by the Response Surface Methodology (Fe + 2/H2O2) is described in Table 7. Experiment10 presents the greatest percentage of organicloadremoval, i.e. 54.68%.

Table 7. *Photo-Fenton Response Surface Methodology*

Experiment	Fe^{+2}	H_2O_2	TOC
1	-1	-1	12,14
2	1	-1	15,28
3	-1	1	33,66
4	1	1	42,35
5	0	0	49,58
6	0	0	51,26
7	0	0	52,69
8	$-(2)^{1/2}$	0	47,6
9	0	$(2)^{1/2}$	44,53
10	$(2)^{1/2}$	0	54,68
11	0	$-(2)^{1/2}$	1,44

Estimates of the effects of the TOC removal percentage are depictedin a Pareto chart,taking into account that the terms whose $t_{calculated}$(represented by the bars in the Pareto graph) values are higher than the t_{tabled} (represented by the dashed line on the chart) values for Student's arrayt, at 95% reliability, as shown in Figure 3.

On the Pareto chart analysis, the addition of hydrogen peroxide to the quadratic model was of paramount importance for the process of organic load removal from the phenolic effluent. The relevance of thequadratic peroxide addition to a significance level of0.05% is confirmed by the values of Student t, in which $t_{calculated}$= 3.29 and the $t_{critical}$ equals 2.5706.

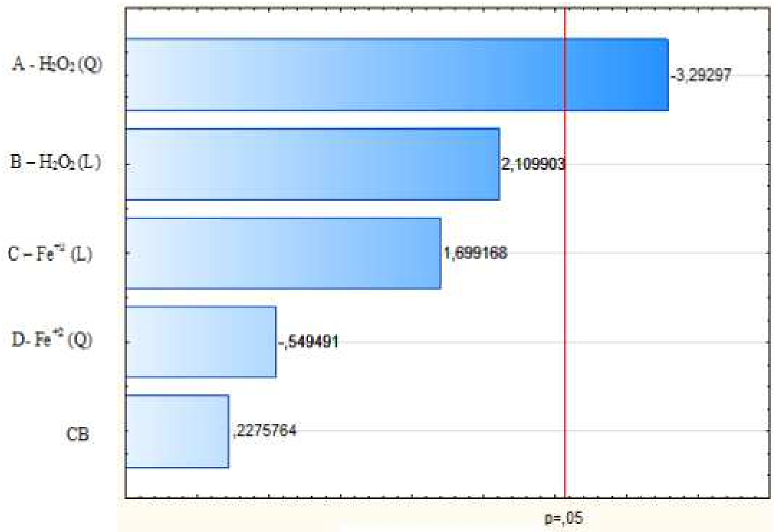

Figure 3. *Estimate of the effects by the pareto chart*

In table 8, it is presented the analysis of variancefor the linear and quadratic model proposed to explainthe response of the TOC reduction, based on significantterms of the Pareto chart and on the variance analysis of the effects. The analysis of variance (ANOVA), with 95% reliability, F critical that equals 6.61 and a p-value which is less than 5%; showed that the significant factor for the removal of the Total Organic Carbon was the addition of hydrogen peroxide to the quadratic model (F = 10.8436 and p-value= 2.16 percent).

In Figure 4, the percentage of TOC removal increases as the mass amount of H_2O_2 e Fe^{+2} is increasing. It is possible to observe a significant dropin the quadratic model Response Surface Methodology when the Fenton reagent is at a lowlevel (-1).

Table 8. *Analysis of variance of RSM Photo-Fenton*

Factors	*(SS)	*(gl)	*(SMQ)	F	P
A- H_2O_2(Q)	1612,300	1	1612,300	10,8436	0,0216
B- H_2O_2(L)	661,906	1	661,906	4,4517	0,0886
C- Fe^{2+}(L)	429,284	1	429,284	2,8872	0,1500
D- Fe^{2+}(Q)	44,894	1	44,894	0,3019	0,6063
CB	7,701	1	7,701	0,0518	0,8289
Error	743,432	5	148,686		
Total SS	3483,202	10			

*SS (Sum of Squares), gl (Degrees of freedom), SMQ (Average Sum of Squares)

The greatest reduction of TOC (54.68%) was observed for level0 of hydrogen peroxide and ferrous ions at a high level (+1.5), which corresponds to experimental conditionnumber 10 of the response surface chart. In Figure 4 b, it is observed that the greatest majority of experimental data is distributed in the optimal region, which is indicated in light and dark red colors.

The parameters used in the optimization of organic matter degradation of the phenolic effluent for a better experimental condition were: 48.3 g hydrogen peroxide and 5.95 g ferrous ions. Experimentalcondition number 10, with 54.68% removal of theorganic load of the effluent, was the most significant forthe process.

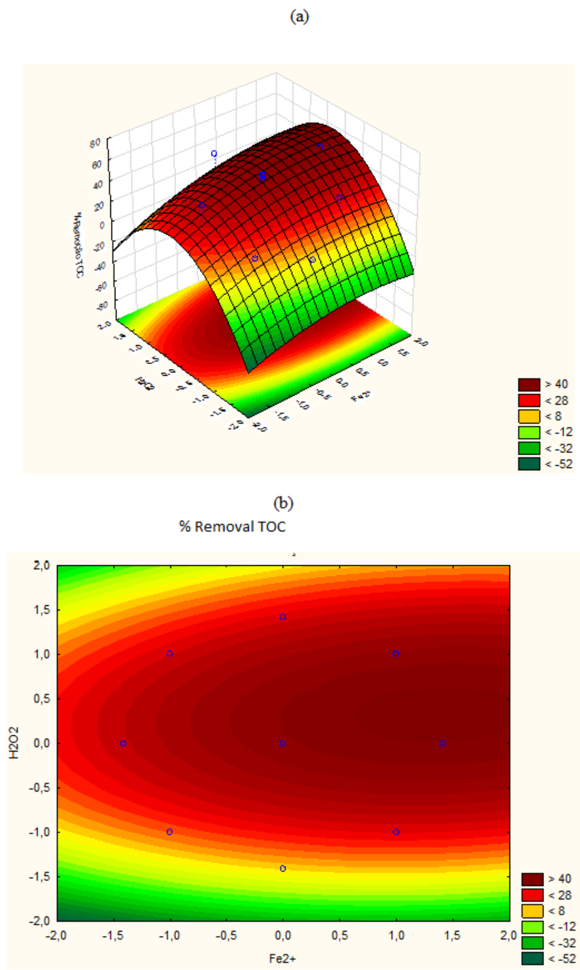

Figure 4. *Response surface (a) and (b) level curves*

5. Conclusions

On this work, advanced oxidativeprocesses (Photo-Fenton andO_3/UV) were evaluated with Taguchi's design, in which the values were not significant for the removal of organic load. In this design of experiment, it was found that the greatest reduction of TOC (%) is related to an increase in the concentration of $Fe^{2+}$and H_2O_2, and to the absence of ozone in the reaction medium.

The Photo-Fenton response surface methodology has demonstrated that optimum conditions of treatment werewithin the studied region, since the conducted experiment had reached a significant curvature, making it necessary forthe accomplishment of the star experiment. The obtained resultswere significant for the removal of the TOC (%).

In the process optimization; RSM Photo Fenton; it was achieved the highest percentage of TOC removal =54.68%, which corresponds to experimentalcondition number 10. This condition is associated with the mass ratio of hydrogen peroxide and ferrous ions being equal to eight, which corresponds to 47,8 g of $H_2O_2$and 5,95g of Fe^{+2}. It is concluded that the Photo-Fenton is the most effective process for the phenolic effluent treatmentused in this work.

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