Phenol removal via advanced oxidative processes (O₃/photo-Fenton) and chemometrics

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Abstract: Taguchi's L₁₆ orthogonal array in the study of removal of total phenols using advanced oxidation processes was efficient. In the statistical assessment, the input variables obtained as significant through ANOVA were: hydrogen peroxide (F = 10.0924 and p-value = 5.02) and ozone (F = 3.8686 and p-value = 14.39). In this assessment, the best experimental condition for the removal of total phenols is 100%. The following factors must therefore be adjusted: hydrogen peroxide = 38, 7g and ozone flow = 3 L/h.

Keywords: Taguchi Method, Advanced Oxidation Processes

1. Introduction

The chemical characteristics of effluents from textile industries involve concerns for the society, as for public health, and it is also a matter of great scientific interest [1].

The phenolic effluents are characterized by presenting high toxicity and low biodegradability [2,3].

Phenol is a compound that has high solubility, stability and toxicity in water, thus widely used as a parameter in assessment studies of water and wastewater treatment [4]. According to [5], this compound is produced from compounds of phenolic resins, processes of organic synthesis, combustion of wood, petroleum products, and natural degradation of organic compounds, waste and compounds containing benzene.

Phenol produces many adverse effects on the aquatic ecosystem, even at small concentrations [6]. This compound at concentrations exceeding 2 mg L⁻¹ is toxic to fish, and at concentrations in the range of 10-100 mg L⁻¹ result in the death of aquatic plants within 96 h [7]. It is also characterized by causing DNA modifications and mutations in mammals and microorganisms' cells [8]. The oxidation of phenolic compounds is a viable alternative for the treatment of wastewater with a high organic load [9].

It gives off a detectably annoying sweet odor for most people in concentrations of 40 ppb in air, and between 1 and 8 ppm in water. Phenolic compounds are characterized as being highly polluting substances and some of their physico-chemical properties are presented in table 1 [10].

Table 1. Physico-chemical properties of phenol. Source EPA 2002

Properties	Characteristics
Synonyms	hydroxybenzene, hydrated phenyl, mono phenol, benzenol, oxibenzene and phenylic acid
Solubility in water in g/L at 25 °C	84
Vapor Pressure at 25°C	0.3513
Empirical Formula	C ₆ H ₆ O

Phenols are toxic compounds to microorganisms, and can be difficult to be removed from the system through biological treatments or by natural processes in an aquatic environment [11]. It is one of the most common organic compounds and is found as effluent in many industries, such as oil refining, petrochemical, pharmaceuticals, pesticides, paints, textile industries, manufacture of organic chemicals, among others [12].

The diverse composition of phenolic effluents may limit the efficiency of many conventional treatment processes. In textile industries, it is common to see the presence of EDTA, surfactants, enzymes, dyes, metals and other organic compounds that can affect the proliferation of micro-organisms and hamper biological treatments [13].

The treatment of hazardous residues and the presence of organic pollutants in water have increased the use of alternatives to environmental matrices, such as the use of Advanced Oxidative Processes (AOP) for wastewater treatment [14].

The AOP's are considered as a highly competitive water treatment technology, thereby contributing to the removal of organic pollutants that are non-treatable with traditional methods. Advanced oxidation processes are highly competitive techniques for the removal of polluting organic compounds, the phenols. The AOP's can be applied in stages of pre or post treatment of effluents, in order to reduce the recalcitrance of these compounds [15].

The AOP's and the electrochemical methods are developed to treat the contaminants of drinking water and industrial effluents. The oxidation processes are based on the generation of reactive species, such as hydroxyl radicals ($\bullet\text{OH}$). These radicals degrade a wide variety of organic pollutants, in a quick and non-selective manner. The radical $\bullet\text{OH}$ is unstable, and should be continuously generated in situ through chemical or photochemical reactions [16].

The organic matter (OM) present in the system is etched by the hydroxyl radical on the precise moment in which it is generated and, as a result of this process, the effluent is degraded to other intermediate products, as described in Equation 1 [17].

Figure 1. Tubular reactor used for the photochemical treatment

In Taguchi's experimental planning L₁₆ with the oxidative process (O₃/UV and Photo-Fenton), it was used 3.0 liters of raw effluent, previously homogenized and

According to [18], a high potential reduction standard of the hydroxyl radical enables the oxidation of a wide variety of organic compounds to CO₂, H₂O, and inorganic ions from heteroatoms.

In the treatment of phenolic effluents, advanced oxidation processes are highly applied and pretty efficient [19].

The application of ozone as a pre-treatment in the oxidative process was conducted in order to assess the biodegradability of the 4-cresol, 4-nitrophenol and 2-chlorophenol compounds in which, with the experimental analysis, it was not only assessed the reaction time for the composites degradation, but also the reaction intermediates were studied [20]. Ozone is efficient in the degradation of dyes because it assists in removing the coloring of these compounds [21].

The Fenton Process is an advanced oxidative process that generates highly reactive $\bullet\text{OH}$ radicals. This reaction is of great interest in the remediation of contaminated water by toxic pollutants [22].

In recent decades, the Fenton reaction was introduced in wastewater treatment processes, and degradation through this process has been proven. A variety of refractory organic compounds can be effectively degraded, and do not produce toxic substances in the aquatic environment [23].

In this work, it was conducted the study of advanced oxidative process (O₃/H₂O₂/Photo-Fenton) in treating phenolic effluents through an experimental planning: Taguchi's L₁₆ orthogonal Array.

2. Materials and Methods

The oxidation reaction of the phenolic effluent is accomplished in a tubular reactor Germetec (model GPJ-463/1), with nominal volume of approximately 1 L and that receives irradiation from a low-pressure mercury lamp of type GPH-463T5L, emitting UV radiation in 254 nm, and with 16 W and 28 W of power (with two power levels planning), protected by a quartz tube, as shown in Figure 1.

conditioned to room temperature. Then, it was added the volume of the iron solution (0.82 mol L⁻¹) during the first 30 minutes of the beginning of the reaction, and the volume

of H_2O_2 (30 % m/v) was added during 50 minutes of the total reaction time of 1 hour and 30 minutes. The introduction of a gas mixture (O_2 and O_3) inside the chemical reactor was performed through an ozone distribution chamber. The reaction medium temperature throughout the photocatalysis process was controlled by means of a thermostatic bath UNITEMP (MOD. 112D at Fanem). The measurement of the reaction pH was accomplished through a combined glass electrode adapted to the reservoir, with the same connected to a Digimed digital potentiostat. The effluent circulation between the tubular reactor and the storage tank was carried out by means of a centrifugal pump.

3. Results and Discussions

The statistical planning was conducted and is represented by Taguchi's L_{16} orthogonal array, for which the analyzed response variable was the Total Phenols removal percentage for a reaction time of 90 minutes. The independent variables - factors - proposed for this stage were: pH, temperature, Fenton's reagent, UV radiation power and O_3 flow. Tables 2 and 3 present the variables with their according selected levels, and the orthogonal array L_{16} , respectively, of the treatment with AOP.

Table 2. Control Factors and levels for the exploratory study of the phenolic effluent treatment

Factor	Symbol	Level 1	Level 2
* H_2O_2 (g)	A	38.7	46.5
*Ferric Ions (g)	B	1.26	1.55
pH	C	3	5
Ozone (L h^{-1})	D	3	5
Temperature ($^{\circ}\text{C}$)	E	30	35
Lamp Power (W)	F	16	28

* Fenton's Reagent

Table 3. Taguchi's L_{16} orthogonal array in 2 levels for the study of phenolic effluent treatment with the Photo-Fenton and Ozone process.

Exp	A	B	AB	C	AC	BC	*	E	AE	F	AF	D	AD	*	*
	H_2O_2	Fe^{+2}	$\text{H}_2\text{O}_2/\text{Fe}^{+2}$	pH	$\text{H}_2\text{O}_2/\text{pH}$	Fe^{+2}/pH	7	Temp	$\text{H}_2\text{O}_2/\text{Temp}$	UV	$\text{H}_2\text{O}_2/\text{UV}$	O_3	$\text{H}_2\text{O}_2/\text{O}_3$	14	15
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	1	1	1	2	2	2	2	2	2	2	2
3	1	1	1	2	2	2	2	1	1	1	1	2	2	2	2
4	1	1	1	2	2	2	2	2	2	2	2	1	1	1	1
5	1	2	2	1	1	2	2	1	1	2	2	1	1	2	2
6	1	2	2	1	1	2	2	2	2	1	1	2	2	1	1
7	1	2	2	2	2	1	1	1	1	2	2	2	2	1	1
8	1	2	2	2	2	1	1	2	2	1	1	1	1	2	2
9	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
10	2	1	2	1	2	1	2	2	1	2	1	2	1	2	1
11	2	1	2	2	1	2	1	1	2	1	2	2	1	2	1
12	2	1	2	2	1	2	1	2	1	2	1	1	2	1	2
13	2	2	1	1	2	2	1	1	2	2	1	1	2	2	1
14	2	2	1	1	2	2	1	2	1	1	2	2	1	1	2
15	2	2	1	2	1	1	2	1	2	2	1	2	1	1	2
16	2	2	1	2	1	1	2	2	1	1	2	1	2	2	1

Variables 7, 14 and 15 are empty columns

Both H_2O_2 , and iron II were used in the solutions whose concentrations were: $[\text{H}_2\text{O}_2] = 30\% \text{ m/m}$ and $[\text{Fe}^{2+}] = 0.82 \text{ mol L}^{-1}$. These values are proportional to the volume of treated effluent of 3L.

The percentage of Total Phenols removal for the experiments performed by the Taguchi's L_{16} Orthogonal Array is described in Table 4. The used method for determining it was the colorimetric 4-amino antipyrine.

Experimental data show that most experienced conditions presented highly significant values for the percentage of Total Phenols removal.

[24] studied the kinetics of phenolic pollutants' catalytic oxidation, and the determination of phenols was performed through the 4-amino antipyrine method. The monitoring of phenolic compounds degradation; phenol, 2-chlorophenol, chlorophenol and 4 dichlorophenol 2.4; was performed by this method. The used method was highly significant to the kinetic accompaniment of the phenolic compounds and their derivatives.

Table 4. Taguchi's L16 orthogonal array for Total Phenols removal (%)

Taguchi's Orthogonal Array Experiments (L ₁₆)	% Total Phenol Reduction
1	100.0
2	100.0
3	100.0
4	98.7
5	100.0
6	100.0
7	100.0
8	100.0
9	96.91
10	68.43
11	97.51
12	93.56
13	99.32
14	85.08
15	69.82
16	91.89

Significant factors for the removal of Total Phenols are demonstrated in the effects graphic (Figure 2). The most

significant parameters for the process of organic matter degradation of the phenolic effluent are hydrogen peroxide (level 1 = 38.7 g), ozone flow equals to 3 L/h and lamp power of 16W. Ferric ions interactions/pH H₂O₂/O₃ and H₂O₂/UV set in level 2 demonstrated their relevance for the removal of Total Phenols.

Figure 2. Main effects of the percentage variation measures of Total Phenols in effluent treatment of L16 design

These factors must be adjusted: hydrogen peroxide = 38.7 g, ozone flow = 3 L/h and UV lamp power equal to 16 watts, according to the effects graph.

The analysis of variance (ANOVA) with $F > 2$ demonstrated the significant factors for the removal of total phenols. The significant factors for this process were hydrogen peroxide ($F = 10.0924$) and ozone ($F = 3.8686$). The O₃/H₂O₂ interaction ($F = 4.2083$) was significant for the oxidative process. According to Phadke [25], an F value statistically that is greater than 2 is considered as a significant effect (factor), according to Table 5.

Table 5. Analysis of variance obtained from Taguchi's L16 orthogonal array for the removal of Total Phenols (%)

Factors	Sum of Squares (SS)	Degrees of Freedom (df)	Average Sum of Squares (ASS)	F	p-value
1 – A	578.4025	1	578.4025	10.0924	0.0502
2 – B	5.0850	1	5.0850	0.0887	0.7852
3 – AB	8.3810	1	8.3810	0.1462	0.7276
4 – C	0.1936	1	0.1936	0.0034	0.9573
5 – AC	1.1664	1	1.1664	0.0203	0.8956
6 – BC	138.8862	1	138.8862	2.4234	0.2174
7 – E	41.8609	1	41.8609	0.7304	0.4556
8 – AE	33.9889	1	33.9889	0.5931	0.4973
9 – F	107.8482	1	107.8482	1.8818	0.2637
10 – AF	94.9650	1	94.9650	1.6570	0.2883
11 – D	221.7121	1	221.7121	3.8686	0.1439
12 – AD	241.1809	1	241.1809	4.2083	0.1326
13 – Empty Residual	171.9315	3	57.3105		

4. Conclusions

The phenolic effluent is toxic to most organisms and requires a chemical treatment. In this work, Taguchi's planning was assessed for the study of advanced oxidative processes (Photo-Fenton and O₃). In the statistical assessment, the best experimental condition for the removal

of total phenols is 100% which can be validated by the effects chart. These factors must be adjusted: hydrogen peroxide = 38.7 g, ozone flow rate = 3 L/h. The process of ozonization for the removal of Total Phenols is highly efficient, thus it contributes to the increase in effluent biodegradability and the absence of ozone in the reaction medium.

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