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Multivariate Analysis in Advanced Oxidation Process

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Additional information is available at the end of the chapter

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1. Introduction

Environmental degradation is attributable to improper industrial wastewater disposal, a situation that has caused serious contamination problems in many countries worldwide. Global consumption of potable water doubles every twenty years due to an exponential increase in world population (Han et al., 2009).

Industrial processes can create a wide variety of chemicals that pollute the air and water, with adverse impacts to ecosystems and humans. These impacts are caused by the polluting compounds that have toxic, carcinogenic, and also mutagenic properties (Busca et al., 2008). The treatment of wastewater containing phenolic compounds can be accomplished using applied principles of chemical oxidation, settling, membrane filtration, osmosis, ion, precipitation, and coagulation among other methods (Lin; Juang, 2009).

The treatment of hazardous wastes and reducing the presence of aqueous organic pollutants have placed focus on the use of alternatives to the standard environmental practices, such as the use of Advanced Oxidation Processes (AOPs), especially for the wastewater treatment (Segura et al., 2009).

AOPs are considered a highly effective means of water treatment contributing to the effective removal of organic pollutants that, otherwise, are untreatable whether are adopted the traditional methods (Oller; Malato; Sanchez-Pérez, 2011).

The study of riverine water quality by countries has recently become problematic due to the progressive scarcity of resources (Ongley, 1998). The monitoring water quality and making-



decisions based on qualitative data is a challenge for field researchers engaged in sample collection, storage, analysis, and the interpretations of results (Lermontov et al., 2008).

This study demonstrates the application of Multivariate Analysis (MA) in effluent treatment of polyester resin by using advanced oxidation processes (heterogeneous photocatalysis - UV/TiO₂). Exploring the relationship between methodologies and computational chemistry, the use of MA can modify the industrial processes and simplify experimental conditions, with a consequent improvement of processes, products, and the resolution of environmental issues.

2. Polyester resin

Polyesters and alkyd resins represent a class of polymers used in the manufacture of solvent-based paints due to the reduced cost and its versatility. These resins are the condensation products of polyols (e.g., glycerol, pentaerythritol), polybasic acids or their anhydrides (most phthalic anhydride) and monobasic fatty acids or oils. The term is typically restricted to polyester resins with acid or hydroxyl functional groups, which are relatively free of oil mixtures. The alkyd resins, a type of polyester resin, can be synthesized from renewable resources, i.e., vegetable oils as soybean oil, but most oils are coming from non-renewable sources (Abrafati, 1995; Weiss, 1997).

3. Dye industry

Effluents from industries are highly complex dyes so they are not treated by conventional methods. Alternative matrices; AOPs; have been used to minimize the environmental impact of these industries on ecosystems (Nedhi; Sumner, 2003).

Industrial waste is classified into three main categories: wastewater, solid waste and air pollutants. Greater attention is given to wastewater since studies revealed content of significant amount of solvents (Metcalf; Eddy, 1991).

4. Advanced oxidation process

Advanced oxidation processes UV/TiO₂, UV/H₂O₂, UV/H₂O₂/Fe, O₃, O₃/Fe, O₃/TiO₂, UV-O₃/H₂O₂/Fe, are widely used in the degradation of effluents. These processes are characterized by the generation of free radicals in the organic matter degraded, and so are the polluting compounds mineralized or they are converted into a lower-chain or a less harmful process, in order to be subjected to a biological treatment subsequently (Thiruvenkatachari et al., 2007).

Oxidation processes are based on the generation of reactive species such as hydroxyl radical (OH). These radicals are highly reactive, non selective and may be used to degrade a wide range of organic pollutants. The OH radical is unstable and must be continuously generated *in situ*, by chemical or photochemical (Oliver; Hyunook; Pen-Chi, 2000). Table 1 shows reduction potential of various chemicals, and it can be observed that after fluorine, the hydroxyl radical is the one with higher oxidation potential (Domènech et al., 2001).

The treatment of hazardous waste and the presence of organic pollutants in water have increased the use of alternatives to environmental matrices such as the use of advanced oxidation processes (AOPs) in the treatment of wastewater (Segura et al., 2009).

According to Kusic, and Koppivanac Srsan (2007), the high standard reduction potential of the hydroxyl radical enables the oxidation of a wide variety of organic compounds to CO2, H2O and inorganic ions from heteroatoms.

According to Domenech et al. (2001), hydroxyl radicals can be produced by various advanced oxidation processes and heterogeneous and homogeneous systems, divided into two groups: non-photochemical and photochemical processes. Table 2 shows the procedures described above for the production of the hydroxyl radical.

Compound	E ⁰ Reduction (V, 25 °C) ¹
Fluorine(F2)	3,03
Hydroxyl Radical (•OH)	2,80
Atomic Oxygen (O2)	2,42
Ozone(O ₃)	2,07
Hydrogen peroxide (H2O2)	1,78
Radical Perhydroxyl (HO2•)	1,70
Chlorine dioxide	1,57
Hypochlorous acid (HCLO)	1,49
Chlorine (Cl ₂)	1,36
Bromine (Br ₂)	1,09
Iodine (I2)	0,54

¹ Potential refers to the standard hydrogen electrode. Source: Domenech et al. (2001)

Table 1. Reduction potential of some compounds

	With Irradiation	Without Irradiation
	O ₃ /UV	O3/H2O2
Llomo con cours Crustome	H2O2/UV	O ₃ /OH-
Homogeneous Systems	$H_2O_2/Fe^{2+}/UV$	H_2O_2/Fe^{2+}
	*Sc/O ₃ /UV	Eletro-Fenton
Heterogeneous Systems	*Sc/H2O2/UV	-
The end of the bystems	*Sc/UV	-

*Sc: semiconductor (ZnO, TiO2, etc.)

Source: Morais (2005)

Table 2. Exploited systems to produce hydroxyl radical

4.1. Advantages of advanced oxidation processes

AOPs have a number of advantages when compared to conventional oxidation processes (Gabardo Filho, 2005; Domènech et al., 2001):

- Able to assimilate large variety of organic compounds;
- Full Mineralization of pollutants;
- Employed in the destruction of refractory compounds resistant to other treatments, such as the biologic;
- Can be integrated with other processes such as pre or post treatment;
- Used in high toxicity wastewater that can cause some difficulty in the treatment of biological process;
- Allow *in situ* treatment;
- Develop byproducts reaction intermediates that submitted to a post treatment may be mineralized;
- Improve organoleptic properties of treated water;
- Present high power with high oxidizing reaction kinetics.

4.2. Disadvantages of advanced oxidation processes

AOPs can be applied to certain types of waste under some restrictions, as follows (Domenech et al., 2001; Moral, 2005):

- Some processes are not available at appropriate scales;
- Costs can be high due to energy consumption;
- Some types do not apply to wastewater with high organic capability, turbidity, optical or color.

5. Heterogeneous photocatalysis

The heterogeneous photocatalysis is a process based on the absorption of UV-visible by a solid semiconductor. In the interface area between the solution and the electrically excited solid, a degradation reaction or transformation of pollutants may occur, without changing the chemical structure of the semiconductor (Custo et al., 2006).

According to Nogueira and Jardim (1998), a semiconductor is characterized by:

- Valence bands, where vacancies are generated;
- Driving Bands that are generating electrons;
- A region between bands called bandgap;
- Semiconductor particles, when irradiated, absorb photons that may excite electrons from the valence band to the conduction band;

This generates vacancy electrons. The electron / vacancy pair migrates to the surface of the particle resulting in oxidation and reduction sites (Carp et al. 2004). Figure 1 illustrates schematically the behavior described above.

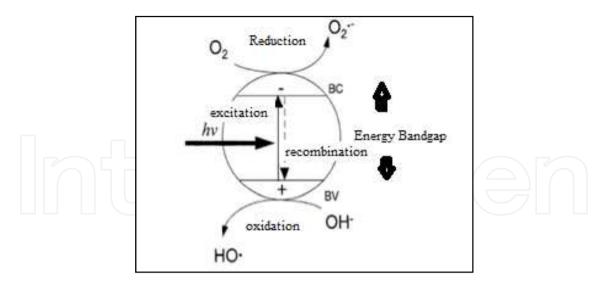


Figure 1. Electronic scheme of a photochemical process for heterogeneous photocatalysis (Ciola, 1981)

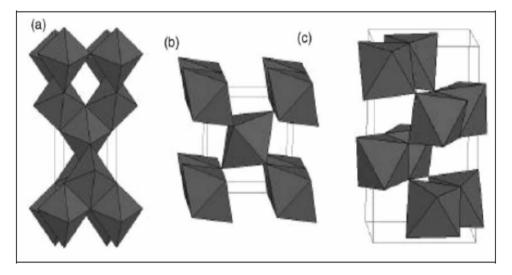


Figure 2. Crystal structures: anatase (a), rutile (b) and brookita (c)

TiO2 is a solid with a melting point of 1800 °C, and the ninth most abundant element corresponding to 0.63% of crust. The element described features 4 crystalline forms of anatase (tetragonal), brookita (orthorhombic), rutile (tetragonal) and TiO2 (B) monoclinic, as shown in Figure 2 (Carp et al., 2004).

6. Design of experiments

Design of Experiments (DOE) has been widely used in the optimization of process parameters and improving of quality products by the application of engineering concepts and Statistics (Wang, Huang, 2007).

Design of Experiments is defined as a set of statistical techniques applied to planning, conduction, analysis and interpretation of controlled tests, in order to find define factors that influence the values of a parameter or group of parameters (Bruns; Neto; Scarmínio, 2010).

According to Franceschini and Macchietto (2008), DOE is a statistical tool used to maximize the value of variable responses obtained on each experiment and also to minimize cost and time by reducing the number of experimental conditions.

Interactions between variables are considered in the experimental design and can be used for optimizing the operating parameters in multivariable systems (Ay; Catalkaya; Kargi, 2009).

According to Salazar (2009), the experimental has been studied as an important mathematical tool in the area of Advanced Oxidation Processes (Heterogeneous Photocatalysis). In this study, fractionated schedules for the degradation of organic matter and COD percentage of dairy effluent were used to obtain 93.70% of the treatment.

7. Taguchi orthogonal array

Taguchi method uses orthogonal arrays to study various factors with a small number of experiments (Sharma et al., 2005). Furthermore, the method provides other benefits, such as the reduction of process variability, low operating costs and expected results. (Barros; Bruns; Scarminio, 1995).

Rosa et al. (2009) define the Analysis of Variance (ANOVA) in the application of statistical analysis of Taguchi method in order to evaluate the significance of the parameters used in the process. A ANOVA table determines the most relevant parameters for the process according to equations 1, 2, 3 and 4:

-SS: Quadratic sum of the factors

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

- df: Degrees of freedom for each factor

$$df=N-1$$
Where N means number of level for each factor
- MS: Mean square
$$MQ=\frac{SS}{df}$$
(3)

- F Test: Assessment of the significance of each factor

$$F = \frac{MS_{effect}}{MS_{error}} \tag{4}$$

8. Multivariate analysis

- MS: Mea

The Multivariate Analysis represents a set of statistical method in which most of variables of a data set are comprise information for decision-making (Rajalahti; Kvalheim, 2011), such as Multiple Linear Regression (MLR), Principal Component Analysis (PCA), Principal Component Regression (PCR) and Partial Least Squares Regression (PLS) (Otto, 2007).

The manufacturing processes can generally have correlated variables depending on the process quality that involves a large number of characteristics (Paiva, 2006).

The field of chemometrics is a multivariate analysis defined as the application of designs and mathematical and statistical methods to solve chemical problems. It is utilized to improve data collection and to allow extraction of useful and obtained data information (Hopke, 2003).

Paiva, Ferreira and Balestrassi (2007) combined DOE with Multivariate Analysis when optimizing multiple correlated responses in a manufacturing process.

8.1. Multiple linear regression

The Multiple linear regression is a determining method of combinations of variables to achieve an optimal process or product. (Beebe; Pell; Seasholtz, 1998).

MLR property of interest relates to a linear combination of independent measurements. The modeling MRL can be represented by equation 5, where a set with n samples, i = 1 to n, Y is the response variable, X is the independent variable and i is the error estimation (Steiner et al., 2008)

$$y_{i} = \beta_{0} + \sum_{j=1}^{k} \beta_{i} X_{ij} + e_{i}$$
(5)

According to Montgomery (2001), the method of Ordinary Least Squares (OLS - Ordinary Least Squares) to determine β *i*, minimize the sum of squared errors:

$$L = \sum_{i=0}^{n} \varepsilon_{i}^{2}$$

$$= \sum_{i=1}^{n} (y_{i} - \beta_{0} - \sum_{j=1}^{k} \beta_{i} x_{ji})^{2}$$
Function L must be minimized in terms of β_{0} , β_{1} , ..., β_{k} .
$$\frac{\partial L}{\partial \beta_{j}} = -2 \sum_{i=1}^{n} (y_{i} - \beta_{0} - \sum_{j=1}^{k} \hat{\beta}_{i} x_{ji})$$

Simply stated, there is equality:

 $\hat{\beta}_0 \sum_{i=1}^n x_{ik} + \hat{\beta}_1 \sum_{i=1}^n x_{ik} x_{i1} + \hat{\beta}_2 \sum_{i=1}^n x_{ik} x_{i2} + \dots + \hat{\beta}_k \sum_{i=1}^n x_{ik}^2 = \sum_{i=1}^n x_{ik} y_i$ In matrix notation, there is $Y = \beta X + \varepsilon$, where:

$$y = \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_n \end{bmatrix}, X = \begin{bmatrix} 1 & x_{11} & x_{11} & \cdots & x_{1k} \\ 1 & x_{21} & x_{22} & \cdots & x_{2k} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 1 & x_{n1} & x_{n2} & \cdots & x_{nk} \end{bmatrix}, \beta = \begin{bmatrix} \beta_1 \\ \beta_2 \\ \vdots \\ \beta_k \end{bmatrix} e \ \varepsilon = \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \vdots \\ \varepsilon_n \end{bmatrix}$$

Then:

$$L = \sum_{i=0}^{n} \varepsilon_{i}^{2} = \varepsilon^{T} \varepsilon = (y - X\beta)^{T} (y - X\beta)$$
$$L = y^{T}y - \beta^{T}X^{T}y - y^{T}X\beta + \beta^{T}X^{T}X\beta$$
$$L = y^{T}y - 2\beta^{T}X^{T}y + \beta^{T}X^{T}X\beta$$
Minimizing the function:
$$\frac{\partial L}{\partial \beta} = -2X^{T}y + 2X^{T}X\widehat{\beta} = 0$$
Hence is obtained:

Hence, is obtained:

 $X^{T}X\widehat{\beta} = X^{T}y$

and consequently, the coefficients are determined by Equation 6:

$$\widehat{\boldsymbol{\beta}} = (\boldsymbol{X}^{\mathrm{T}}\boldsymbol{X})^{-1}\boldsymbol{X}^{\mathrm{T}}\boldsymbol{y}$$
(6)

9. Materials and methods

This work was performed at the Laboratory of the Environmental Engineering Department of the Chemical Engineering of School of Lorena EEL-USP. Polyester resin effluent was supplied by Valspar industry, located in São Bernardo do Campo, State of São Paulo. Statistical analyses were performed by Statistica version 2.0, available at the College.

Samples were stored cold chamber at EEL-USP at 4°C. The effluent from the oxidation reaction was conducted into a Germetec tubular reactor, model FPG-463/1, with a nominal volume of approximately 1 L, receiving irradiation from a GPH-463T5L mercury lamp of low pressure, which emits a UV radiation at 254 nm with a power of 15 W and 21 W and protected by a quartz tube. The manufactured reactor model is shown in Figure 3.

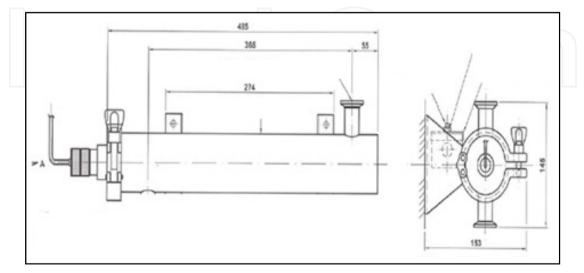


Figure 3. Tubular reactor used for photochemical treatment

Experimental design Taguchi L₉ with advanced oxidation process and heterogeneous photocatalysis were used for 1.0 liters of fresh effluent and 2 liters of distilled water, previously homogenized and conditioned at room temperature. Semiconductor titanium dioxide (TiO2), and the amount of H2O2 (30% w / v) were added during the initial 50 minutes of 1-hour total reaction, using burettes of 25 and 50 ml. The temperature of the medium reaction during the whole period of the photocatalytic process was controlled at 25 °C by using an Ophterm DC1 thermostatic bath. pH reaction was performed using a combined glass electrode adapted to the shell. This was connected to the potentiostat digital Digimed. A centrifugal pump was used for conducting the effluent from the tubular reactor to the storage tank. Ultraviolet lamps of 15 and 21 watts were used. Figure 4 presents the detailed scheme for treatment with AOP showing the experimental procedure.

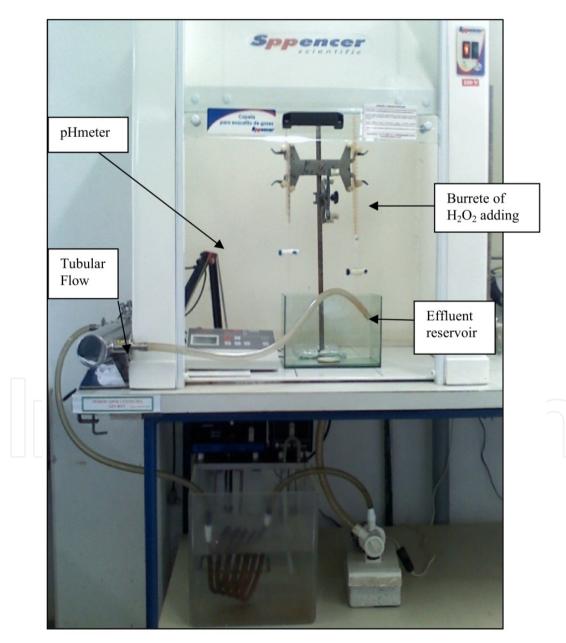


Figure 4. Layout of the process of photochemical treatment

10. Results and discussion

TOC (Total Organic Carbon) analysis of the effluent was conducted according to relevant physical-chemical aspects; that is, parameters monitored by environmental agencies (Morais, 2005). Figure 5 illustrates the appearance of the effluent polyester resin *in natura*.



Figure 5. Effluent polyester resin in natura

The statistical planning performed is represented by Taguchi L9 orthogonal array to which the response variable was TOC and independent variables as factors proposed for this stage were: pH, titanium dioxide, hydrogen peroxide and UV radiation power. Table 3 shows the variables with treatment of levels with selected AOP.

Control variables (factors)	Level 1	Level 2	Level 3		
A- pH	3,0	5,0	7,0		
B- TiO2 [g/L]	0,083	0,167	0,250		
C- H2O2*[g]	120,0	151,0	182,0		
D- UV [W]	Sem	15	21		

* [H₂O₂] = 30 % m/m

Table 3. Control variables and their levels

Initially, the mass of H_2O_2 (30% w / w) is calculated by a stoichiometric ratio that depended on the organic load of the effluent. This obtained a mass of H2O2 of 50 g per liter of effluent.

The amount of TOC of the effluent *in natura* had a mean value of 7920mg / L that was subjected to pre-treatment. For each experiment amount of TOC, a sample in a 60-minute reaction was determined. The percent reduction of TOC is calculated by equation 7.

% reduction of TOC =
$$\frac{\text{TOC}_{\text{in natura}} - \text{TOC}_{\text{t=60 min}}}{\text{TOC}_{\text{in natura}}}$$
(7)

Table 4 shows the arrangement of orthogonal Taguchi L9 for the treatment of effluent polyester resin using AOP.

	pН	TiO2	H_2O_2	UV
Experiment	Factor A	Factor B	Factor C	Factor D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6		3		2
7	3	$\neg 1 \backslash$	3	2
8	3	2	1	
9	3	3	2	1

 Table 4. L9 Taguchi Orthogonal Array with 4 factors and 3 levels each

Table 5 shows the percentage change in COT response to experiments using experimental design L9. Experiments 3 and 4 had a higher percentage of TOC removal for the advanced oxidation process (Heterogeneous Photocatalysis).

Experiment	pH Factor A	TiO2 Factor B	H2O2 Factor C	UV Factor D	Replica 1: reduction of total organic carbon (%)
1	1	1	1	1	31,970
2	1	2	2	2	34,981
3	1	3	3	3	39,489
4	2	1	2	3	37,216
5	2	2	3	1	29,962
6	2	3	1	2	30,095
7	3	1	3	2	30,549
8	3	2	1	3	33,504
9	3	3	2	1	28,182

Table 5. Results of the first replica of the percentage reduction obtained in experiments for an initial TOC of 7920mg / l.

Table 6 shows a replica of the experiment and the experimental conditions 3 and 4 that achieved significant values again.

Statistical analysis of Taguchi L9, on Figure 6, showed the most significant parameters for the degradation of organic matter in the wastewater, the latter reflecting of pH = 3, adjusted at a low level and factors set at a maximum level of: 182 g hydrogen peroxide and ultraviolet lamp power of 21 W. According to the plan performed, the level of titanium dioxide added to the process can be adjusted at low or medium level, i.e. with values 0.083g / L and 0.167g / L. According to Malik and Saha (2003), the influence of peroxide with temperature is related to the efficiency of ratio by using this compound and its rapid decomposition in the reaction.

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Experiment	pH Factor A	TiO2 Factor B	H2O2 Factor C	UV Factor D	Replica 2: reduction of total organic carbon (%)
1	1	1	1	1	31,269
2	1	2	2	2	34,498
3	1	3	3	3	36,443
4	2	1	2	3	35,720
5	2	2	3		31,648
6	2	3	1	2	30,019
7	3	1	3	2	30,739
8	3	2	1	3	33,011
9	3	3	2	1	27,481

Table 6. Results of replica 2 of the percentage reduction percentage obtained in experiments, initial TOC of 7920mg / l.

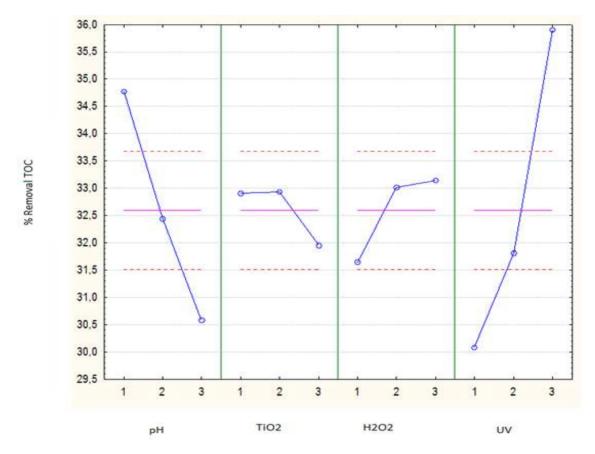


Figure 6. Main Effects in TOC percentage variation measurements in the effluent treatment of L₉ planning

Statistical analysis at a level of 95%, showed the most significant factors for the removal of organic load. According to the distribution F whose critical value is 4.26 and a p-value less than 5%, the most important factors for the degradation of organic matter in the effluent were phenolic H₂O₂, pH, UV. The most significant factor was the ultraviolet lamp power

with F of 60.65201 and a p-value less than 0.001%, and then the remaining factors are the pH (F = 30.11586; p-value = 0.10 %) and H₂O₂ (F = 4.67497; p-value = 4.053%). The values obtained by analysis of variance confirmed the significance shown in the graph of main effects.

The analysis of variance (ANOVA) with F> 2 demonstrated that the factor TiO2 is significant for TOC removal. According to Phadke (1989), an F value statistically greater than 2 is considered as a significant effect (factor). The statistical significance factor in TOC reduction in the effluent treatment was confirmed by ANOVA, as shown in Table7.

Source of					
Variation	SQ	GL	SMQ	F	P-Value
pН	53,0700	2,00	26,53499	30,11586	0,00010
TiO2	3,7711	2,00	1,88554	2,13999	0,17366
H2O2	8,2382	2,00	4,11909	4,67497	0,04053
UV	106,8806	2,00	53,44030	60,65201	<0,00001
Error	7,9299	9,00	0,88110		

Table 7. Analysis of variance	e Taguchi L16 orthogor	nal array obtained for	TOC (%) removal
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Multiple linear regressions provide another statistical approach to evaluate variables in a quantitative approach. Significant parameters to the regression analysis are shown in Table 8, where pH, UV and H₂O₂ are relevant for the degradation process of the organic load of the polyester resin effluent.

Factor	Coefficient	t-value	Coef. Beta	Probability
pН	-1,04933	-4,573584	-0,542040	0,0003
TIO2	-5,73042	-1,042771	-0,123584	0,1580
H2O2	0,0266726	1,627560	0,192891	0,0638
UV	0,245688	5,791488	0,686380	0,0000
Constant	32,2247			

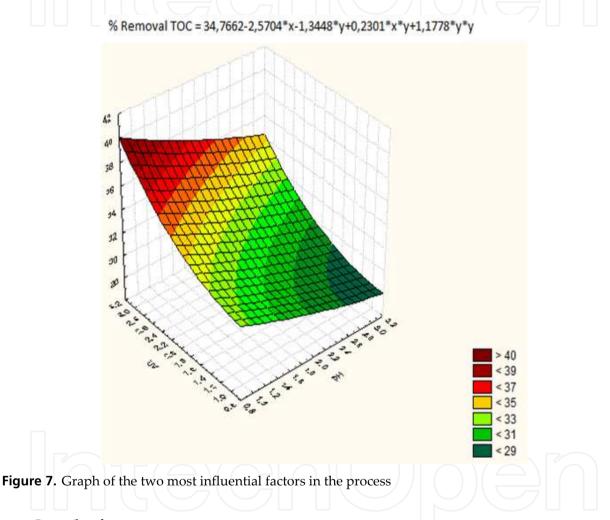
Table 8. Regression parameters

Multiple linear regression showed a coefficient of determination (R2) of 0.817404, which demonstrates the efficiency of the degradation of effluent using the polyester resin of the experimental design. An ANOVA (Table 9) was performed in order to validate the multiple linear regression equation. The significance of equation shown is for a level of significance equal to 0.0001 at 95% confidence degree.

Sources of Variation	GL	SQ	SMQ	F	P-Value
Due to Regression	4	147,0425	36,76063	14,55	0,0001
Independent	13	32,84718	2,526706		

 Table 9. ANOVA of multiple linear regression

The most influential factors in the process show the percentage removal of Total Organic Carbon in Figure 7. An increasing degradation of the organic load is observed on the surface. This is achieved by independent variables: pH and potency of the ultraviolet lamp. The percentage of the increased removal of organic load occurs when there is an increase of the power of the lamp and a decrease of the pH. The greatest percentage reduction of the organic load is equal to 39.489%, whose parameters used in this experimental condition = H2O2 were 182 g, pH = 3, TiO2 = 0.250 g / L and the lamp power of 21 W. The response variable was significant for the degradation of organic matter in the effluent.



11. Conclusions

Taguchi planning was applied to the degradation of effluent organic load. The experimental design showed that further reduction of TOC (%) is related to an increase in pH and ultraviolet intensity. The results obtained were significant for the removal of TOC (%) from polyester resin effluent treated with advanced oxidation processes, and heterogeneous photocatalysis.

In our Taguchi orthogonal array the removal-percentage achieved was COT = 39.489%, which corresponds to experimental condition number three. This condition is inclusive of

the weight ratio of hydrogen peroxide at 183g, pH = 3, TiO 2 = 0.250 g/L and the lamp intensity = 21 W. We conclude that the process of heterogeneous photocatalysis is optimally suitable for treatment of the effluent studied in this work.

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