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Evaluation of efficiency of advanced oxidative process in degradation of 2-4 dichlorophenol employing UV-C radiation reator

Avaliação da eficiência de processo oxidativo avançado na degradação de 2-4 diclorofenol empregando reator com radiação UV-C

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Abstract

The study accomplished to analyze, identify and quantify 2,4-dichlorophenol employing high efficiency chromatography with a previously validated analytical methodology. The validation was made by using some analytical parameters: linearity, precision, accuracy, quantification limit (LOQ) and detection limit (LOD). The analytical curve was linear for the studied range of concentration (10 up to 100 mg.L-1) presenting a linear regression coefficient (R^2) above 0,99. Regarding the methodology accuracy, a repeatability analysis was performed by observing a coefficient of variance (CV) below 20% for each of the concentrations used. The LOD and LOQ were adequate for the analyzed compound, showing the values of 1.42 mg.L-1 and 4.30 mg.L-1, respectively. The tests to verify the accuracy, by the recovery method provided values above 79%, thus resulting in specific, sensitive, precise, linear and accurate methodology in the studied concentration range. In the advanced oxidative process UV/H_2O_2, the compound was degraded to 88.04% under the following experimental conditions: [H_2O_2] = 1016.0 mg·L-1 in 120 minutes. Therefore, it can be affirmed that the treatment employed can be used as an alternative for industrial effluent treatment with phenolic compounds.

Keywords: Chromatography; 2,4-dichlorophenol; Photo-Fenton

Resumo

O presente estudo analisou, identificou e quantificou o 2,4-diclorofenol via cromatografia líquida de alta eficiência, através de metodologia analítica previamente validada. A validação foi realizada utilizando os seguintes parâmetros analíticos: linearidade, precisão, exatidão, limite de quantificação (LQ) e limite de detecção (LD). A curva analítica mostrou-se linear na faixa estudada (10 a 100 mg.L-1) e com coeficiente de regressão linear (R^2) superior a 0,99. Quanto à precisão da metodologia, empregou-se a análise da repetibilidade observando-se um coeficiente de variância (CV) abaixo de 20%, para cada uma das concentrações empregadas. Os LD e LQ foram adequados para o composto analisado, apresentando os seguintes valores 1,42 mg.L-1 e 4,30 mg.L-1, respectivamente. Os ensaios para verificação da exatidão, pelo método de recuperação, forneceram valores acima de 79%, resultando assim numa metodologia específica, sensível, precisa, linear e exata na faixa da concentração estudada. No processo oxidativo avançado (UV/H_2O_2), obteve-se uma degradação do composto analisado em até 88,04%, nas seguintes condições experimentais: [H_2O_2] = 1016,0 mg·L-1; num período de 120 minutos. Desse modo, pode-se afirmar que o tratamento empregado pode ser utilizado como alternativa para tratamentos de efluentes industriais.

Palavras-chave: Cromatografia; 2,4-diclorofenol;. Fhoto-Fenton

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INTRODUCTION

The 2,4-dichlorophenol (Figure 1) is a compound employed in the production of 2,4-dichlorophenoxyacetic acid (2,4-D) e 2,4-dichlorophenoxy propionic acid (2,4-DP). This type of substance is found in aquatic matrices often derived from conventional wastewater treatment plants, which utilize biological or physico-chemical processes that do not degrade or partially degrade molecules such as phenol (LIU, et al., 2017).

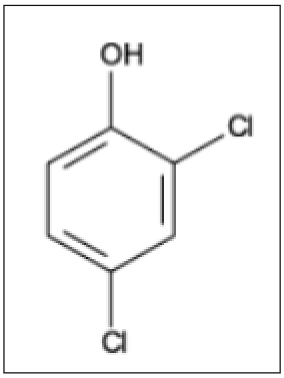

Figure 1 – 2,4 dichlorophenol chemical structure
Fonte: RESENDE, 2011

Since conventional treatments are not capable of degrading substances considered as persistent, it is necessary to use alternative treatments, such as advanced oxidative processes. Among all types of compounds that need to be studied to remove them from environmental matrices are chlorophenols, compounds present in disinfectants, effluents from petroleum refineries, rubbers, plastics and steel industries. Tauchert (2006) states that 2,4-DP is reported as one of the first 2,4-D reaction intermediates, so it is necessary to find ways to promote the degradation of this compound, which is persistently present in the environment.

AOP have been utilized to promote the degradation of different compounds considered persistent and refractories as they are capable of mineralize them, converting it to carbon monoxide and water. The advanced oxidative processes occur in the presence of a strong oxidizing agent, usually hydrogen peroxide, which is responsible for the release of hydroxyl radicals. These types of processes can be divided into two systems: those involving homogeneous reactions, such as photolysis, UV/H_2O_2 action, Fenton and photo-Fenton (BORTOTI, et al., 2016); and those that comprise heterogeneous reactions (photocatalytic processes), with or without radiation assistance (KLAMERTH *et al.,* 2010).

Among the most utilized POA, are those that involve homogeneous processes, which have been efficient degrading different types of persistent organic pollutants, such as pharmaceuticals (AZIZ *et al.*, 2017), dyes (BILIŃSKA; GMUREK; LEDAKOWICK, 2017), hormones (DIETRICH *et al.,* 2017; GIANNAKIS *et al.,* 2017), aromatic polycyclic hydrocarbon (LABIADH *et al.,* 2015; CLEMENTE; PALMA; PEÑUELA, 2014), among others compounds. Furthermore, it can be observed in the literature that the degradation of the refractory compounds, such as phenol, is also realized through POA, which employs heterogeneous photo catalysis using $BiPO_4$ e TiO_2 as photo catalysts (ZAIDAN *et al.,* 2017; ZHANG *et al.*, 2014; NAEEM *et al.*, 2013).

UV/H_2O_2 action, also known as photoassisted peroxidation, is based in a combination between direct photolysis employing ultraviolet radiation (UV) and H_2O_2, being considered the most appropriated to degrade organic substances of high toxicity. By the presence of UV radiation, the hydrogen peroxide molecule breaks releasing hydroxyl radicals capable of promote oxidation of organic pollutant (ARAÚJO; YOKOYAMA; TEIXEIRA, 2006; KATSUMATA, 2014).

According to Brito and Silva (2012), the production of the hydroxyl radical involves a homolytic break, which occurs from the rupture of a sigma type bond. This type of bonding requires high energy and also requires considerable potency of ultraviolet radiation from the absorbed photons to promote the formation of the radical. This mechanism is described in Equation 1.

$$H_2O_2 + h\nu \rightarrow 2OH^{\cdot} \tag{1}$$

Day by day, the environmental preoccupation increases in terms of water, soil and atmosphere quality. The phenols and their derivatives have been found in superficial water from industrial effluents disposal of a variety of industrial processes such as glue, rubber, resin, steel, among others (ROSA; KIST; MACHADO, 2013).

A study of intermediary products of reaction for chlorophenols is necessary because of the persistence and identification of those compounds in aqueous matrices, which have a slow degradation kinetics promoting difficulties in biodegradation process (QU; TIAN; LIAO, 2010; AGHAV; KUMA; MUKHERJEE, 2011). For efficiency evaluation of AOP, safe and selective analytic techniques must be utilized having as an example the chromatographic technique (CUNHA; AGUIAR, 2014).

In the last decade, extraction techniques were developed in order to perform chromatographic analysis that helps to identify different compounds even when they are in lower concentration in the environment (SODRÉ et al., 2010). High efficiency liquid chromatography (HPLC) has been used to detect phenolic compounds and their intermediaries such as catechol, hydroquinone, resorcinol and p-benzoquinone (ZAIDAN et al., 2013). Thus, HPLC stands out for identification and quantification of phenolic compounds (VRSALJKO et al., 2012). The present study had an aim of employ HPLC methodology to evaluate the 2,4-dichlorophenol degradation using advanced oxidative processes with an UV-C bench reactor.

MATERIAL AND METHODS

HPLC analysis

The 2,4-dichlorophenol was detected and quantified in high efficiency chromatograph (Shimadzu). It was used an ULTRA C18 column operating in reverse phase (5µm; 4,6mm x 250mm) and UV detection (SPD-20A) for wavelength equal to 215 nm, the temperature of HPLC oven was maintained in 35ºC. The equipment operated with 1 mL.min-1 flux, with 105 kgf.C-1 of pressure, being methanol and deionized water (60:40) the mobile phase, with isocratic elution. The 2,4-dichlorophenol standard (Sigma Aldrich) employed in the present work presents high purity content, 99%.

Methodology evaluation

For the process validation, 7 analytical curves were plotted with 7 different concentrations each (10, 20, 30, 40, 50, 60, 70, 80 e 100 mg.L-1). Then, were analyzed the following parameters: linearity, precision, accuracy, detection limits and quantification. The determination of linearity was made based on the linear regression coefficient (R2).

Furthermore, the method precision was determined based on variation coefficient (CV) – Equation 2. Grubb's test was applied to guarantee value dispersion for 95% of trust level through G< e G> determination, Equation 3.

$$CV\ (\%) = (s / X_m)\cdot 100 \tag{2}$$

$$G_< = (X_m - X_{i<}) / s \quad \text{and} \quad G_< = (X_{i>} - X_m) / s \tag{3}$$

Where Xm is the average of the obtained values for the peak areas of the different concentrations; s is the estimated standard deviation for n=7; G< and G> are the obtained Grubbs values for the lowest and highest measured value, respectively, and Xi< and Xi> are the lowest and highest, respectively, values of peak area of a given concentration.

Regarding the accuracy determination, a sample fortification process was utilized in three different concentrations (10+20, 10+30, 10+50 mg.L-1), and the analysis occurred in triplicate, obeying the concentration range given by the analytic curve, according Equation 4.

$$R(\%) = [(C_1 - C_2) / C_3]\cdot 100 \tag{4}$$

Wherein, C1 is the concentration determined in the sample with addition of the standard, C2 is the concentration determined in the sample without addition of the standard and C3 is the concentration of the added standard.

Ultimately, through Equations 5 and 6, limits of detection (LOD) and quantification (LOQ) were determined, respectively, which consider the absolute standard deviation (s) and the value of the slope of the analytic curve (S).

$$LOD=3{,}3\cdot(s/S) \tag{5}$$

$$LOQ = 10 \cdot (s/S) \tag{6}$$

It is important to emphasize that a validation methodology was proceeded to guarantee the reliability of the obtained results. This option was performed since the final values are expressed in terms of percentage of degradation, which is calculated based on the results of the areas obtained in the chromatogram.

Degradation by AOP

A bench reactor with UV-C radiation composed with three lamps (PHILIPS) in parallel of 30W each, operating with a temperature between 10 and 50ºC e frequency of 50Hz. It was utilized to perform the degradation using an aqueous solution containing 2,4- dichlorophenol, 200 mg.L-1 (Figure 2).

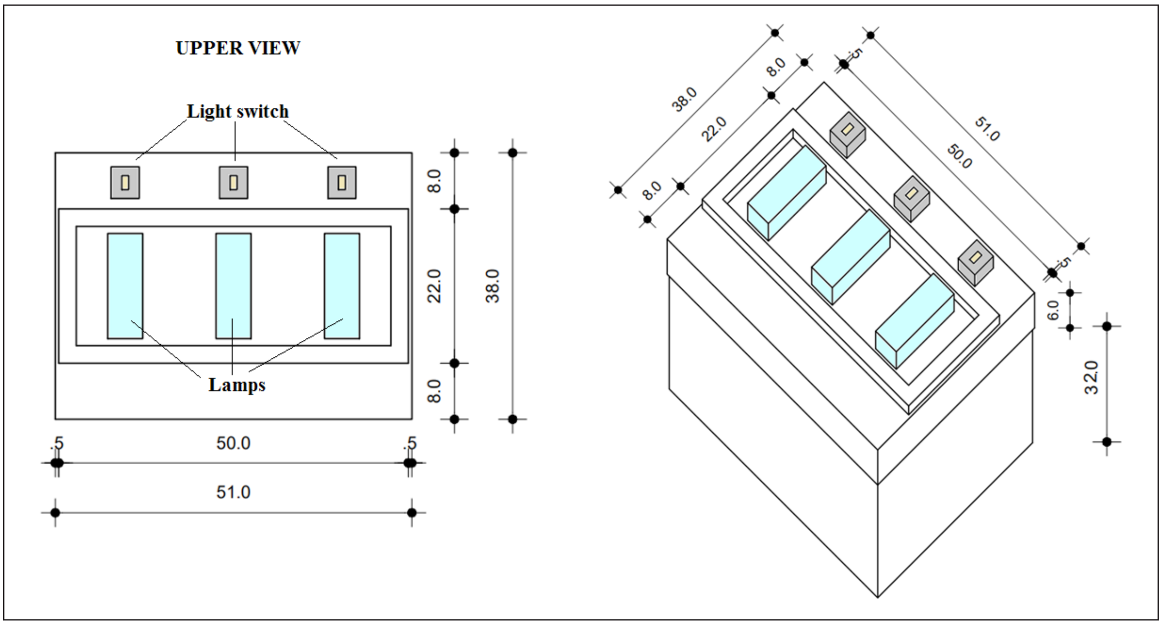

Figure 2 - Schematic bench reactor using UV-C radiation

Aliquots of 50 mL of aqueous solution containing 2,4-diclorophenol, 100 mg.L-1, were degraded according a factorial design 2^3 plus central point (in triplicate), with hydrogen peroxide, iron and time as the process variables. For the present study the natural pH of the solution was maintained (5.5), since previous studies obtained similar results varying pH of the Fenton reaction (3-4) and pH between 6 and 7 (Napoleão et al., 2015). The description of the factorial design is presented in the Table 1, which the tests of 1 to 4 refer to UV/H2O2 and 5 to 11 treat the photo-Fenton process.

Table 1- Factorial design matrix 2³ with center point (in triplicate) to study the degradation of 2-4 dichlorophenol

Test	[H2O2]	Time	[Iron]
1	- 1 (338.7 mg.L-1)	-1 (60 min)	-1 (sem adição)
2	+ 1 (1016.0 mg.L-1)	-1 (60 min)	-1 (sem adição)
3	- 1 (338.7 mg.L-1)	+1 (120 min)	-1 (sem adição)
4	+ 1 (1016.0 mg.L-1)	+1 (120 min)	-1 (sem adição)
5	- 1 (338.7 mg.L-1)	-1 (60 min)	+1 (2.02 mg.L-1)
6	+ 1 (1016.0 mg.L-1)	-1 (60 min)	+1 (2.02 mg.L-1)
7	- 1 (338.7 mg.L-1)	+1 (120 min)	+1 (2.02 mg.L-1)
8	+ 1 (1016.0 mg.L-1)	+1 (120 min)	+1 (2.02 mg.L-1)
9	0 (677.3 mg.L-1)	0 (90 min)	0 (1.01 mg.L-1)
10	0 (677.3 mg.L-1)	0 (90 min)	0 (1.01 mg.L-1)
11	0 (677.3 mg.L-1)	0 (90 min)	0 (1.01 mg.L-1)

The amount of H2O2 used in the photo-Fenton system was performed according the function of reaction stoichiometry (FAGNANI et al., 2013), according to Equation 7.

$$C_6H_4Cl_2O + 13\,H_2O_2 \rightarrow 6CO_2 + 15H_2O + Cl_2 \qquad (7)$$

However, preliminary studies have shown that this amount was not sufficient to obtain good degradations of the compound. Therefore, the [H2O2] was gradually increased until a significant degradation was achieved. The residual H2O2 concentration was then evaluated by means of identification tapes of this compound (Merck).

RESULTS AND DISCUSSION

HPLC detection of 2,4-dichlorophenol

2,4-dichlorophenol was detected at a wavelength equal to 215 nm and at a retention time between 9.6 and 9.8 minutes, which is in agreement with the results described by Sbano (2013). The methodology validation step was carried out once the compound was detected.

The methodology validation procedure was performed according to the requirements of two Brazilian regulatory agencies: National Health Surveillance Agency (ANVISA) and National Institute of Metrology (INMETRO). According to ANVISA, a validated method must guarantee the reliability of the results, which can be assured by determining parameters such as linearity, precision, accuracy, LD and LQ.

An analytical curve was constructed with a concentration range of 10 to 80 mg.L-1, followed by the determination of the chromatographic peaks areas. The seven replicates of each concentration, the standard deviation and the dispersion of the data were calculated. The dispersion analysis was performed using Grubb's test. The data of the areas and respective means are presented in Table 2, while in Table 3 the results of the standard deviation, Grubb's test and coefficient of variance are described.

Table 2- Values of the areas obtained for the seven curves in seven different concentration

Concentration (mg.L-1)	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6	Area 7
10	286479	286903	263251	290473	280271	292908	278085
20	510438	469118	467564	486849	471315	512536	487618

Table 2 - Continuetion

Concentration (mg.L-1)	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6	Area 7
30	666698	656116	660832	623006	636685	662911	680778
40	877712	855021	863267	884387	950815	933173	821409
50	1187770	1119273	1067418	1191318	1232740	1163720	1178948
60	1269112	1293333	1292676	1368299	1438970	1432806	1450906
70	1637139	1595031	1546699	1497497	1833744	1835249	1790968
80	1728238	1715070	1730767	1669977	2106527	2102278	2130921

Table 3- Values of area averages, standard deviation, Grubb's test and coefficient of variance

Concentration (mg.L-1)	Mean	Standard deviation	Grubb's Test 95 % of confidence (*)		CV (%)
			G<	G>	
10	282624.10	10016.51	1.03	1.93	3.54
20	486491.12	18901.33	1.38	1.00	3.89
30	655289.34	19397.80	1.31	1.66	2.96
40	883683.50	44923.03	1.49	0.64	5.08
50	1163026.66	54132.38	1.29	1.77	4.65
60	1363728.99	78538.61	1.11	0.90	5.76
70	1676618.16	141484.35	1.12	1.27	8.44
80	1883396.70	216107.97	1.15	0.99	11.47

(*) For an equivalent number of eight measures with a confiability of 25%. $G_<$ e $G_>$ must be below 2,126.

The linearity test was evaluated regarding the analytical curve construction through regression linear coefficient (R2) analysis. Thus, the linearization test analysis indicated that the area of the chromatographic peak is proportional to the concentration (Figure 3).

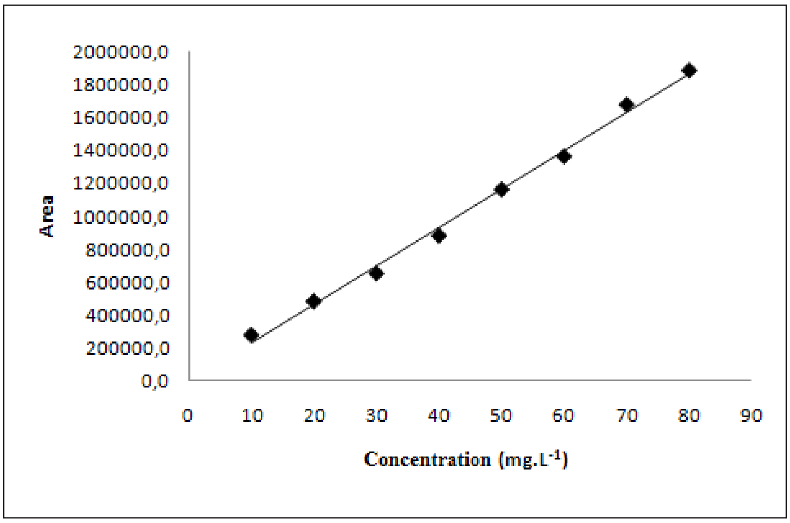

Figure 3- Analytical curve of 2,4-dichlorophenol

Once the analytical curve was constructed, it was possible to find the equation that represents it (Equation 8) and the linear regression coefficient (R2= 0.9953). The value obtained for this coefficient shows that the method meets the standards required by the Brazilian regulatory agencies ANVISA (2003) (values equal to or greater than 0.99) and INMETRO (2011) (values greater than 0.90).

$$y=23.287x + 1462.4 \tag{8}$$

After verifying the linearity of the method, the precision was analyzed based on the coefficient of variance (CV), presented in Table 3. The CV values obtained were lower than 20% for all the analyzed concentrations. These values are in agreement with that required for complex samples, such as drugs (RIBANI et al., 2004). The accuracy test was performed, as described in the methodology, through recovery trials, whose experiments were done in triplicate. The results are reported in Table 4.

Table 4 - Results of recovery trials

Concentration (mg. L-1)	Area	Area average	Standard deviation	Percentage of Recovery (R%)
10	-	282624.1 (*)	10016.51	-
20	-	486491.1 (*)	18901.33	-
30	-	655289.3 (*)	19397.80	-
50	-	1163026.7(*)	54132.38	-
10+20	639180.2	669808.1	41023.15	79.59
10+20	653827.6			
10+20	716416.6			
10+30	892829.4	801551.8	83036.25	79.19
10+30	730490.2			
10+30	781335.8			
10+50	1298259.0	1414317.3	103832.70	97.31
10+50	1446287.4			
10+50	1498405.6			

(*)Values obtained from the linearity analysis of the method.

The data presented in Table 4 indicate that the method under analysis is accurate, since according to the literature, it is necessary that the recovery percentage is between 50 and 120% (Perlatti *et al.*, 2012), or in a range of 70 To 120%, according to Ribani *et al.* (2004). Finally, the detection limits (LOD) and quantification (LOQ) were determined, which were respectively 1.42 $mg.L^{-1}$ and 4.30 $mg.L^{-1}$.

2,4 - DICHLOROPHENOL DEGRADATION USING AOP

After the submission to the AOP of the aqueous solution containing 100 $mg.L^{-1}$ of 2,4- dichlorophenol, the degradation of the compound was evaluated employing a UV-C reactor with photons emission equal to 1,45 $mW \cdot cm^{-2}$. Furthermore, aliquots were collected and submitted to HPLC analysis obtaining the compound concentration and the percentage of degradation reached. The percentage of the compound degradation and its final concentrations are shown in Table 5. It is important to note that to ensure that all the added hydrogen peroxide was consumed during the reaction, at the end of the exposure period of the solution to the radiation, H_2O_2 measurements were made. After the end of the experiments, a self-decomposition of the hydrogen peroxide was observed, not being observed a residual amount.

The analysis of Table 5 shows that the percentage of degradation of 2,4-dichlorophenol obtained was satisfactory, reaching 88.04%. The Table 5 analysis, for tests 2, 4, 6 and 8 (higher concentration of hydrogen peroxide), allows to verify that although the hydroxyl radical generations is favored by the presence of iron in the sample, the percentage values of degradation obtained were similar, presenting values of 76.76 to 88.04%. These values indicate that the presence of iron was not relevant to the process, which can be better analyzed from the following statistical study.

Table 5 - AOP degradation using UV-C reactor

Experiment	Concentration of 2,4 DP (mg. L-1)	% Degradation
1	62.73	37.27
2	23.24	76.76
3	35.66	64.34

Table 5 - Continuetion

Experiment	Concentration of 2,4 DP (mg. L-1)	% Degradation
4	11.96	88.04
5	48.25	51.75
6	17.88	82.12
7	35.24	64.76
8	17.86	82.14
9	29.99	70.01
10	38.69	61.31
11	30.49	69.51

According to Brito and Silva (2012), the Fenton process presents higher or lower efficiency as a function of the medium pH once it depends of the chemical form of the iron present in the sample. The pH of the solution in the present study was maintained at 5.5 (natural solution pH) the UV/H2O2 process presented higher efficiency, which is in agreement with the review carried out by these authors, who affirm that the UV/H2O2 process is favored at less acid pH values, because in these the H2O2 photolysis process is more efficient. This happens because at acidic pH a capture of the hydroxyl radicals occurs. The authors further claim that for chlorinated hydrocarbons, such as 2,4-DP, this capture process, also called hydrogen abstraction, needs to be disadvantageous for electron transfer reactions to become possible, leading to degradation of the interest. Therefore, this type of abstraction needs to be reduced, as it may lead to the formation of undesirable intermediate compounds, as can be observed in Figure 4.

In order to better observe the efficiency of the AOP, the chromatogram of the solution before degrading it and after the experiment 4, shown in Figure 4, could be analyzed, in which there is a decrease in the peak intensity of 2,4- dichlorophenol and formation of intermediate compounds. In order to be better identified a mass spectrometry analysis would be required. It is known that phenol and some phenolic compounds present as intermediates substances such as catechol, resorcinol, hydroquinone, p-benzoquinone, which are generally observed and quantified at a wavelength of 270 nm (ZAIDAN et al, 2013), requiring further studies to investigate which intermediate compounds have been formed.

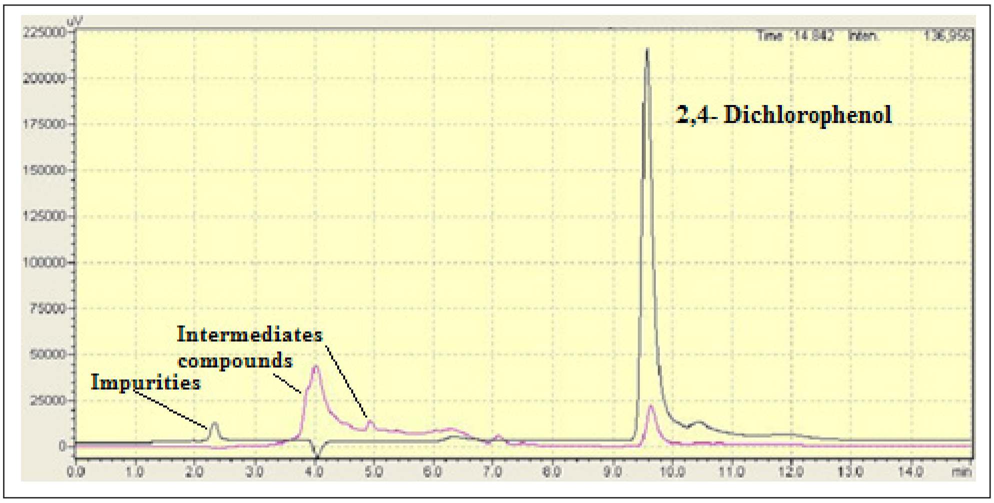

Figure 4 - Chromatogram of the solution before degrading and after the AOP

Can be verified from Figure 3 that the peak obtained for 2,4-dichlorophenol after the degradation presented a concentration of 11.96 mg.L-1. The observed intermediate compounds had a retention time range between 2.0 and 5.5 min. For a better comprehension of the results shown in Table 5, were evaluated the utilized parameters (H2O2 concentration, time and iron concentration) and their interactions with the aid of the Statistica StatSoft program. Thus, Pareto Chart was constructed and is shown in Figure 5.

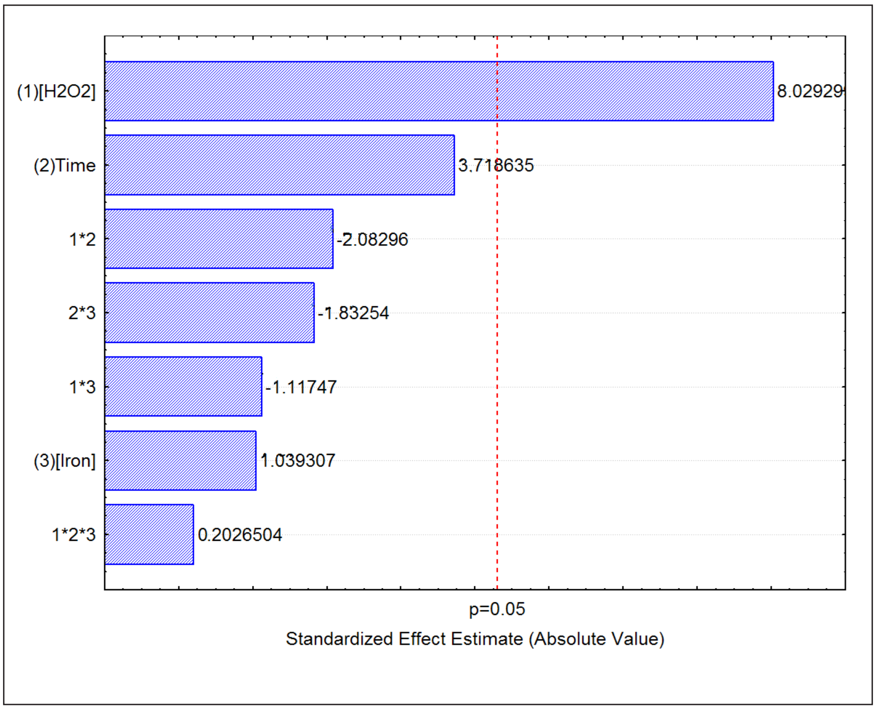

Figure 5 - Pareto's chart of 2,4-dichlorophenol degradation

Figure 4 analysis indicate that no interaction effect was significant. Nevertheless, among the main effects only the peroxide concentration was statistically significant at 95% confidence. This effect exhibits a positive value indicating that a higher percentage of degradation is observed when the factor level is increased, then, when the employed concentration of H2O2 is equal to 1016.0 mg·L-1. It is possible to observe that the test that presented a greater efficiency employed the AOP (UV/H2O2) combination, once the experiment was carried out in absence of iron.

Thus, the percentage of degradation obtained for 2,4-dichlorophenol could be considered efficient for (UV/H2O2) AOP combination, since the exposure time to radiation was only 120 min, which indicates that UV/H2O2 is better than the photo-Fenton, once the first one does not use iron causing lower environmental impact and a lower process cost. When analyzing the Pareto chart, the effect of the main time, although it has not been statistically significant for 95% confidence, presents a positive value, which indicate that a greater degradation of the component will be observed, being close to 100% degradation, when the level of this factor is increased.

CONCLUSION

The proposed method for the detection of 2,4-dichlorophenol using HPLC/UV can be considered reliable, since it was validated according to the requirements of the Brazilian regulatory agencies (ANVISA and INMETRO), and can be applied in the analysis of the compound present in aqueous matrices, which contribute to the improvement of wastewater control before being disposed of in the environment. The present study also allowed to verify that the UV/H2O2 advanced oxidative process using UV-C radiation was efficient when using a [H2O2] of 1016 mg.L-1 for a period of 120 minutes, degrading 88.04% of the compound analyzed.

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