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Degradation of disrupter regulateur dietilphtalate by (AOP)-UV-C/H_2O_2 using response surface methodology

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ABSTRACT

In this study, the performance the treatment for the degradation of the pollutant diethyl phthalate (DEP) in synthetic effluent by the application of advanced oxidative process (AOP)-UV-C/H_2O_2 was verified. The study of oxidation kinetics followed a factorial design of eleven trials to understand the oxidation phenomena of DEP by AOP under experimental planning conditions. In this way, the influence of the H_2O_2 concentration, pH, temperature, and its effects were verified. The highest results were in the K9, K10 and K11 tests, which presented approximately 99.91; 96.18; 98.17% DEP degradation percentage (%), at pH 7, with 20 mM of H_2O_2 at 30°C in 120 min, respectively. For the DEP degradation percentage (%) there was a significant difference for pH with ($p < 0.5$) and the central points presented the results repeatability. Therefore, AOP as a treatment proposal for the degradation of DEP in agro-industrial effluent is efficient.

Keywords: Effluent; Diethyl phthalate; Advanced oxidation process; UV-C/H_2O_2

1. Introduction

There is a growing imposition of regulations by environmental regulatory bodies due to the uncontrolled emission of organic micro-pollutants. In Europe, the objective is to minimize the emission of emerging organic pollutants (EOPs) by industries. Thus, strategies have been developed for the treatment of agro industrial effluents, especially, in reducing the effluents released into the receiving bodies without first receiving efficient treatment [1].

Among the EOPs, the phthalate esters are widely used by industry to give flexibility to rigid polymers, such as polyvinyl chloride (PVC), to fix or maintain color or fragrance and to provide film brightness [2,3]. Due to the fact that they are not bound in their matrix, the phthalate esters elute to the environment and are among the most abundant micro-pollutants [2,4]. Phthalates are considered to be hazardous pollutants, with several effects being attributed: fetal deformities, cancers and endocrine disorders [5].

The European Union (EU) has classified phthalates as priority hazardous substances and has determined that these micro-pollutants will be reduced in aqueous industrial effluents at 30% by 2020. Except that, the concentration of phthalates allowed is 1.3 μg L^{-1} in effluents released into the receiving water bodies [6]. In Brazil, the Ministry of the Environment through the National Environment Council (CONAMA) has not yet established the maximum permitted limit for the phthalates. Although Resolution 430/2011 did not establish effluent conditions and standards in Brazil for these compounds, the Ministry of Health through Ordinance nº2914, dated 12/12/2011, established the standard for human consumption of drinking water and defined the limit at which chemical substances represent a risk to health with the concentration limit for only one type of phthalate, di (2-ethylhexyl) as 11.7 to 81.7 μg L^{-1} [7].

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(PVC), to fix or maintain color or fragrance and to provide film brightness [2,3]. Due to the fact that they are not bound in their matrix, the phthalate esters elute to the environment and are among the most abundant micro-pollutants [2,4]. Phthalates are considered to be hazardous pollutants, with several effects being attributed: fetal deformities, cancers and endocrine disorders [5].

The main source of contamination occurs in aquatic sources through effluent releases after treatment but still charged with phthalates. According to the Environmental Quality Standards (EQS) [8], DEP, toxicological regulations and values, and the lethal concentration (CL) for aquatic organisms [9] are 200 µg L^{-1} (NQA) and 4.21–102 mg L^{-1} (LC50).

For the alternative efficient treatment of dangerous and/or toxic pollutants, advanced oxidation processes (AOPs) based on the formation of reactive species, hydroxyl radicals ($HO^•$) have been used for the treatment of organic and inorganic pollutants found in air, soil and water at acceptable rates and operating costs [10].

The control of and the optimal reduction of EOP(s) remains a serious challenge, particularly for industrial wastewater treatment applications. Therefore, DEP, a pollutant model found in different types of industrial effluents [10] and which has been ranked among the priority hazardous compounds by the EU, may be a candidate for treatment.

In this context, the objective of this work was to study (AOP) (UV-C/H_2O_2) process in the DEP degradation percentage (%). A factorial design of eleven trials with three independent variables (H_2O_2 concentration, pH, temperature) was applied with to evaluating the impacts of the variables and their effects on the micro-pollutant degradation percentage (%), as well as the oxidation time, through a kinetic study and statistical analysis using the response surface methodology.

2 .Materials and methods

2.1. Photo degradation pilot equipment

The photo-degradation tests were developed as in Fig. 1. The photo-degradation pilot equipment in which the AVANT 125 W UV light bulb with average light intensity (UV-C) of 20.41 W m^2 is coupled perpendicular to the 12 L capacity metal vessel, where the reactor is inserted inside a wooden box.

2.2. Determination of oxidation kinetics by AOP - UV-C/H_2O_2

The oxidation kinetic was performed as follows: by varying the H_2O_2 concentration which was added to a reactor containing 250 mL of the effluent with a DEP micro-particle concentration of 0.2 g L^{-1}. This was chosen as the standard (the concentration was chosen from the results of preliminary studies). Experimentation started when H_2O_2 was introduced into the reactor. The reactor was placed in a magnetic stirrer (NOVATÉCNICA) with the agitation control set at 150 rpm, and at a given temperature, in accordance with the experimental design (Table 1). Eleven tests were performed in a complete factorial design 2^3, replicated three times at the central point. Three factors were studied H_2O_2 concentrations (10, 20, and 30 mM) beginning with 30% peroxide PA; the pH of the solution (3, 7, 11) and the temperature (15, 30, 45°C as set forth in Table 1.

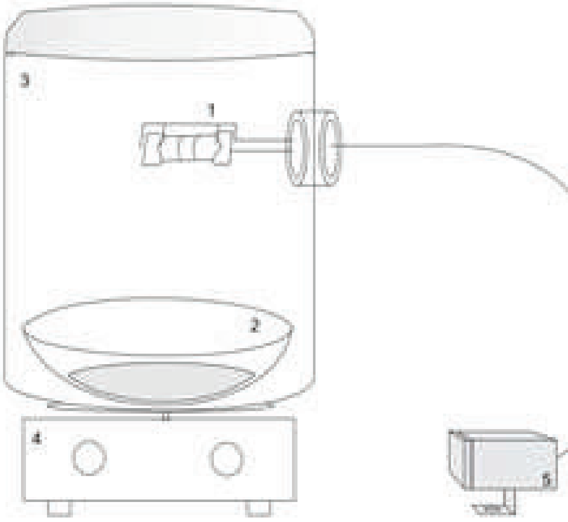

Fig. 1. Advanced Oxidative Process (AOP) pilot scheme: (1) Mercury vapor lamp; (2) glass parabolic cell; (3) metallic cylindrical cell; (4) magnetic stirrer; (5) lamp reactor.

Table 1
Influencing factors investigated, inferior levels (–1), central (0) e superior (+1) varying the following factors: H_2O_2 concentrations (10, 20, and 30 mM), pH (3, 7 and 11) and temperature (15, 30 and 45°C)

Factors	Code	–1	0	1
H_2O_2 (mM)	x_1	10	20	30
pH	x_2	3	7	11
Temperature (°C)	x_3	15	30	45

During the advanced oxidation processes, aliquots of 10 mL were collected at the following time intervals: 0, 6, 12, 24, 36, 48, 60, 80, 80, 100 and 120 min. After each collection, 5 mL of sodium sulfite (0.1 mol L^{-1} Na_2SO_3) was added to stop the oxidation reaction and it was then analyzed by a chromatograph (HPLC–UV/Vis) at 228 nm. The samples were conditioned in test tubes wrapped in foil, thereby eliminating the possibility of light degradation after collection.

2.3. Micro-pollutant analysis

The level of the DEP concentration in samples were quantified by high performance liquid chromatography HPLC (SCHIMADZU C202047; model LC-8A) equipped with a Hypersil C18 column (250 mm long × 4.6 mm) i.d, Thermo Scientific) at a temperature of 20°C and a Spectra Physics 200 UV detector (228 nm). The mobile phase was a mixture of acetronitrile/water (70:30, v:v) delivered at a flow rate of 1 mL min^{-1}. In these experimental conditions, the retention time was 7.0 min. Analyses were performed in triplicate, and the standard deviation of results was <5%. The DEP degradation percentage (%) was calculated by Eq. (1).

$$ta_1 = \frac{[DEP]_0 - [DEP]_t}{[DEP]_0} \cdot 100 \quad (1)$$

where $[DEP]_0$ and $[DEP]_t$ = the concentrations in diethyl phthalate (DEP), respectively, at the initial and time instants t (g L^{-1}); ta_t = the DEP degradation percentage (%) over time.

2.4. Statistical analysis

The data obtained were analyzed using Statistica 7.0 (StatSoft Inc., Tulsa, Oklahoma, USA), with significance level ($p < 0.05$), to determine the response surfaces.

3. Results and discussion

3.1. DEP oxidation kinetics by AOP-UV-C/H_2O_2

Fig. 2 illustrates the variations between the oxidation kinetics of DEP in the different experimental conditional studied. The results show that from the beginning of the treatment was a rapid decrease in the DEP concentration. After, the development of AOP is attenuated, until it achieves DEP elimination, in the initial molecular form and certainly presents itself in the form of intermediate products of photo-oxidation [11]. It is observed in Fig. 2 that the differences that were regarded as necessary to eliminate DEP therefore depend on the experimental conditional applied. Thus the independent variables or factors, H_2O_2 concentration, pH and temperature that influenced and impacted in the treatment studied differently.

The results obtained in Fig. 2 also show that the highest DEP degradation percentage, and the shortest times required for photo-oxidation of DEP. For in the K9 condition, (pH 7–20 mM H_2O_2 - 30ºC) was observed a degradation of 99.92%. For, K6, (pH 3–30 mM H_2O_2 - 45), 98.42% degradation was achieved after 100 min. The repeatability of K9, K10 and K11 responses (standard deviation less than 5%) could be verified, the central points of the design, with DEP degradation percentage (%) of 96.18 and 98.17%, for K10 and K11, respectively, and photo-oxidation times of 100 min for both. The highest degradation percentage are at pH 3 and pH 7.

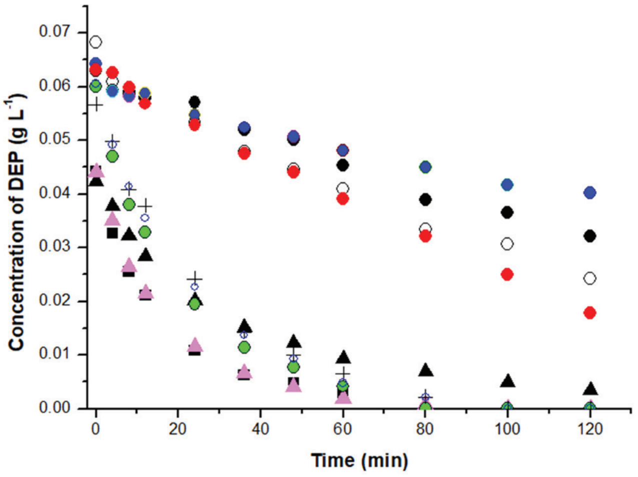

Fig. 2. Comparison between DEP oxidation kinetics curves by AOP are obtained by plotting the DEP concentration (g L^{-1}) as a function of time (minutes) of C1 (■) pH 3, 10 mM H_2O_2, 15ºC; C2 (●) pH 3, 30 mM H_2O_2, 15ºC; C3 (○) pH 11, 10 mM H_2O_2, 15ºC; C4 (▲) pH 11, 30 mM H_2O_2, 15ºC; C5 (▲) pH 3, 10 mM H_2O_2, 45ºC; C6 (●) pH 3, 30 mM H_2O_2, 45ºC; C7 (●) pH 11, 10 mM H_2O_2, 45ºC; C8 (●) pH 11, 30 mM H_2O_2, 45ºC; C9 (-) pH 7, 20 mM H_2O_2, 30ºC; C10 (+) pH 7, 20 mM H_2O_2, 30ºC; C11 (○) pH 7, 20 mM H_2O_2, 30ºC.

Table 2 shows the responses obtained in the AOP treatment, the DEP degradation percentage (%) (Y_1), and the total photo-oxidation time (min) for 100% of the micro-pollutant (Y_2).

The K7 condition at pH 11, 10 mM H_2O_2, 45ºC had the lowest DEP degradation per AOP 37.36%, and in 120 min it was unable to eliminate the DEP having lower process efficiency at alkaline pH, showing that the pH is an influential parameter for degradation of DEP when compared to other studied variables such as H_2O_2 concentration and temperature. Thus, it can be confirmed we found that the K8 test, at pH 11, 30 mM H_2O_2, 45ºC, had a DEP degradation percentage of 71.66%. It was therefore observed that at the same temperature, the H_2O_2 concentration was more influential in the degradation, as was also the temperature, and so had a lower impact than the pH factor.

Studies using the 2,4-chlorophenol micro-pollutant (2.4 DCP), revealed only 15% removal in 90 min, and no mineralization occurred under these experimental conditions, 40 mM H_2O_2 at pH 7 and an absence of UV-C irradiation, but 91% of 2.4 DCP could be removed by UV-C photolysis in 90 min. However, the mineralization efficiency at the end of the treatment was only 16%, indicating that the use of UV-C treatment alone was not sufficient in the effective degradation of intermediate products by photolysis 2.4 DCP [10].

For other studies, [12], was observed that there are no ionizable functional groups in lindane (γ-hexachlorocyclohexane), H_2O_2 ionizes at higher pH values (pka = 11.7). The reduction of the reaction rate as a function of pH may reflect a less efficient production of HO$^{\bullet}$ due to the acid-based chemical reaction of H_2O_2. In this connection, for

Table 2
Response rates for DEP degradation in percentages (%); and the photo-oxidation time of DEP by AOP (min)

Kinetics	DEP degradation percentage (%)	Photo-oxidation time (in min)
K1	91.57	120
K2	94.13	80
K3	49.05	120
K4	64.45	120
K5	91.62	120
K6	98.42	100
K7	37.36	120
K8	71.66	120
K9	99.92	100
K10	96.18	100
K11	98.17	100

DEP, anincomplete mineralization by AOP was observed in pH 11. Probably, because it did not present ionizable functional groups with high pH values (pH 11), and thus the ionizing H_2O_2 did not produce enough $HO^•$ for the efficient treatment. Fig. 3 shows the degradation time with the highest micro-pollutant degradation percentage (K9) and the lowest degradation percentage (K7).

Similar studies by Nienow et al. [12] were performed on aqueous solutions of γ-hexachlorocyclohexane (lindane) at initial concentrations of H_2O_2 and lindane ranging from 0 to 20 mM and 0.21 to 0.22 µM, respectively, with varying pH from 3 to 11, and with various proportions of the concentration of humic acid (from the Suwannee River, southern United States) and fulvic acid dissolved in the irradiated solutions. Lindane compound reacted rapidly at pH 7 and an initial H_2O_2 concentration of 1 mM. Thus, 90% of lindane were destroyed in approximately 4 min under these conditions. Additionally, within 15 min, all chlorine atoms were converted to chloride ions, indicating that the chlorinated organic by-products did not accumulate. The reaction was characterized by the measurement of the photon flux (7.04 × 10^{-6} E s^{-1}) and the cumulative production of $HO^•$ during irradiation. Similar results were found by Nienow et al. [12], where the cumulative $HO^•$ production during irradiation was the fastest when an initial H_2O_2 concentration of 5 mM (k = 0.77 µM s^{-1}) was used. Although lindane exposures occur at very slow rates of direct photolysis, it reacted rapidly through indirect photolysis under photo-etching conditions [14].

In this study [13–15], the use of the phthalates DEP and dimethyl phthalate (DMP), report that the efficiency of the process is affected by the concentration of H_2O_2, UV radiation and pH. H_2O_2 concentration and intensity of UV radiation are directly related to the process efficiency to increase the production of hydroxyl radicals [13]. According to literature increasing the pH also increases phthalate degradation through further hydroxyl radical formation, however an additional increase in pH may have a deleterious effect on the hydroxyl radicals due to the self-decomposition of H_2O_2 [Eq. (2)] or its decomposition by anion hydroperoxide [Eq. (3)] [16].

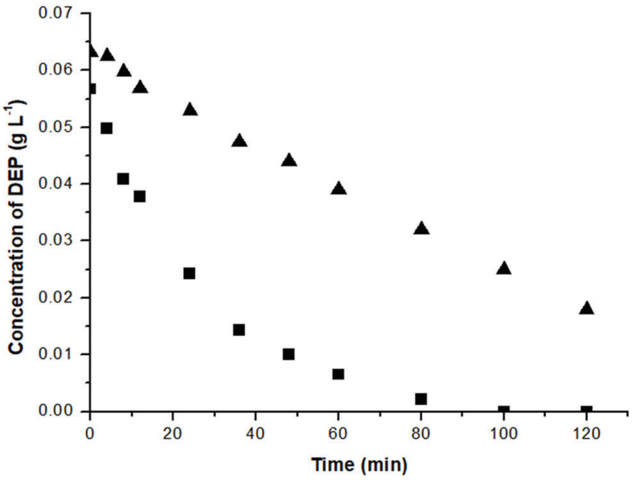

Fig. 3. Evolution of AOP kinetics by plotting DEP concentration (g L^{-1}) as a function of time (min) compared to positive results for DEP degradation percentage as in C9 (■) pH 7, 20 mM H_2O_2, 30); and negative as in C7 (▲) pH 11, 10 mM H_2O_2, 45°C).

$$H_2O_2 \xrightarrow{h\nu} 2\ HO \tag{2}$$

$$H_2O_2 + {}^{•}HO_2 \rightarrow HO^{•} + H_2O + O_2 \tag{3}$$

Xu et al. [17] reported an increase in the rate of the first-order constant for dimethyl phthalate (DMP) degradation from 0.04 min^{-1} to 0.1 min^{-1} when the pH was increased from 2.5 to 4, while it still decreased to 0.02 min^{-1} at pH of 11.

The use of H_2O_2 as a UV oxidizing agent has showed several advantages, since it is a chemical that can be stored easily and has more thermal stability [18]. In addition the hydroxyl radical is two per H_2O_2 molecules and commercially H_2O_2 is readily and it requires a minimum capital investment in the operation of the reactor system. In this context of the applicability of AOPs, just as in treating the effluent by UV/H_2O_2, AOPs based on ozonation, also have hydroxyl radicals reduced by the organic matter in the solution, which decreases the efficiency of the process.

Medellin-Castillo et al. [14], reported that by applying UV/H_2O_2 100% the removal of DEP from ultrapure water was 60 min, while removal was 37% in surface water and 21% in wastewater. This may suggest the use of such a process in the post-treatment phase in a wastewater treatment plant after removal of much of the organic content in the secondary treatment stage. With O_3/H_2O_2 application, 100% removal of DEP from ultrapure water occurred in 60 min, while removal was 43% in waste water.

3.2. Statistical analysis: response surfaces

Table 3 shows the response surfaces that are presented in Fig. 4. The results showed that the regression coefficient was significant at the significance level of 5% ($p < 0.05$) for pH factor. Analyzing Table 3 for Y_1 response (DEP degradation percentage), we found that the regression coefficient showed a significant difference, being <0.05 for the mean, ($p = 0.00103$), as shown in the Pareto Diagram of the standardized effects presented in Fig. 5, and the determination of coefficient whit variation (R^2) of 74.96% explained.

The response surfaces (Fig. 4) confirm the data obtained experimentally, since the higher values for the DEP degradation percentage (%) per AOP occurred for the lower pH values and higher values of H_2O_2 concentration. The effect is positive, for this variable, that is, directly proportional, when there is an increase in H_2O_2 concentration, there is an increase in the rate of degradation of DEP per AOP. The pH, however, has a negative effect, even more impacting than the H_2O_2 concentration, and even more shocking than the temperature. Both the H_2O_2 concentration and the effect of the H_2O_2 concentration and temperature together have positive effects on the rate of degradation with differentiated action. Although the temperature between the main variables has a negative effect, its impact is much lower.

However, Medellin-Castillo et al. [14] described that the decay data of the experimental concentration ranged from 4.5–10^{-5} to 4.5 × 10^{-4} M (10–100 mg L^{-1}) by photodegradation

Table 3
Regression coefficients for Y_1 response (DEP degradation percentage)

Factors	Regression coefficients	Standard error	t(4)	p-value	Interval estimation (95%)	
					Lower limit	Upper limit
Mean	81.1403	5.2636	15.41519	0.000103	66.5261	95.75459
(x_1) [H_2O_2]	7.3826	6.1721	1.19611	0.297708	–9.7541	24.51935
(x_2) pH	–19.1521	6.1721	–3.10297	0.036117	–36.2889	–2.01536
(x_3) Temperature	–0.0161	6.1721	–0.00261	0.998042	–17.1529	17.12063
x_1 e x_2	5.0432	6.1721	0.81708	0.459754	–12.0936	22.17991
x_1 e x_3	2.8910	6.1721	0.46839	0.663889	–14.2457	20.02775
x_2 e x_3	–1.1023	6.1721	–0.17859	0.866942	–18.2390	16.03447

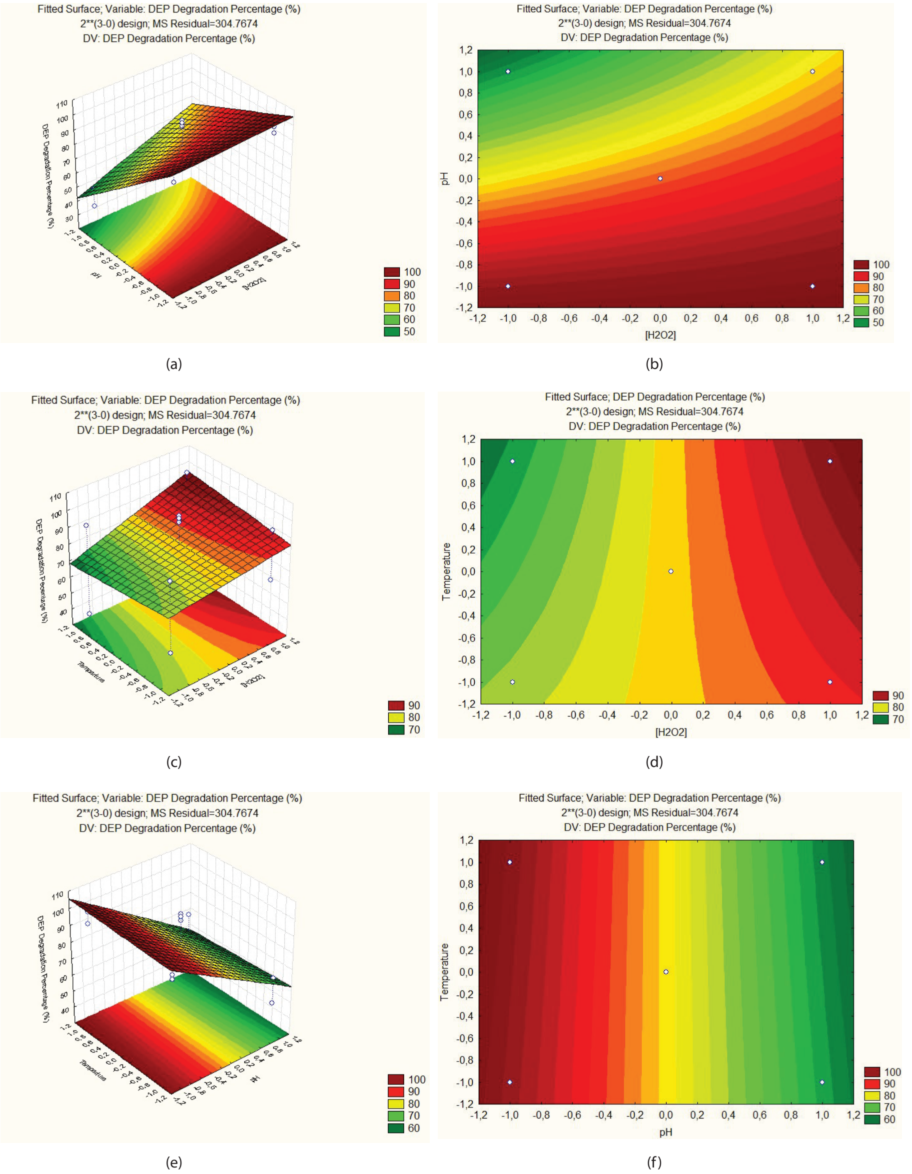

Fig. 4. (a) Response surface and (b) contour curve for DEP degradation percentage (%) per AOP (Y_1) as a function of pH and H_2O_2 concentration (mM); (c) Response surface and (d) contour curve for DEP degradation percentage (%) per AOP (Y_1) as a function of temperature (°C) and H_2O_2 concentration (mM); (d) Response surface and (e) contour curve (c) DEP degradation percentage (%) per AOP (Y_1) as a function of temperature (°C) and pH.

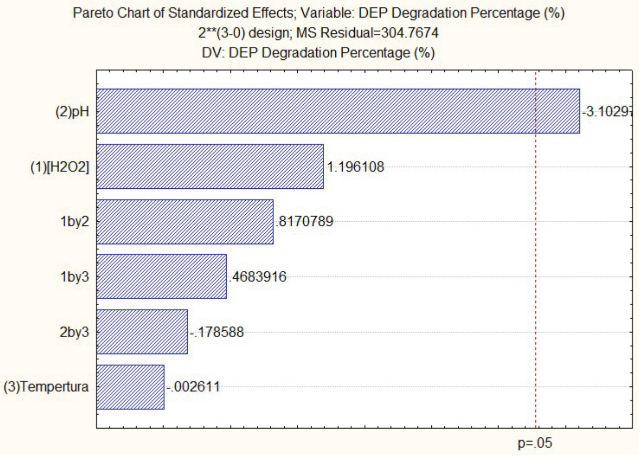

Fig. 5. Pareto diagram of the standardized effects for Y_1 response (DEP degradation percentage (%) per AOP).

of DEP with a low pressure UV mercury lamp (TNN 15/32 Heraeus 15 W), at a wavelength of 254 nm, at pH values of 2.3, 3.4, 6.2 and 8.1 and in an H_2O_2concentration in the reaction solution varying from 0.15 to 3 mM, and while they almost overlapped each other independently of the pH of the solution, the pH did not significantly affect the degradation kinetics of DEP. Thus, it can be deduced that the interaction between the pH and the concentration of H_2O_2 is affected by a reduction in the H_2O_2 concentration. So, the effect of the concentration has a positive impact, while the pH is negative for the photodegradation of DEP and for the interaction between these variables, the H_2O_2 concentration had a more relevant impact.

The degradation of DEP was considerably increased by the addition of H_2O_2 to the reaction solution, according to a study by [13,19], where an initial H_2O_2 concentration of 0.15 mM had a DEP degradation rate given by the coefficient (k_{DEP}) of the value of 6.34×10^{-4} s^{-1}, which was 15 times higher than that of k_{DEP} by direct photodegradation of DEP. This increase can be attributed to the generation of HO radicals, which break down DEP molecules into lower molecular weight by-products. HO radicals were generated by the decomposition of H_2O_2 by UV light.

According to Barakat, Tseng and Huang [20], the study of photo-catalytic oxidation with the H_2O_2/UV/TiO_2 system is much more effective than UV/TiO_2 or UV/H_2O_2alone. They state that the efficiency of photo-catalytic degradation of phenol has been improved from 30 to 97% due to the presence of H_2O_2. As for DEP, it can be verified that in this comparative study of photo-catalytic oxidation with the H_2O_2/UV/TiO_2, UV/TiO_2 and UV/H_2O_2 systems of phenolic compounds, correlated AOP systems with both heterogeneous and homogeneous phases, and as the H_2O_2 concentration increases, more hydroxyl radicals are produced and the oxidation rate of the phenol increases. With high H_2O_2 concentration (≥10–2 M), the O_2 or N_2 atmospheres are not important factors for the phenol oxidation in the H_2O_2/UV/TiO_2 system.

Due to concern over chlorinated by-products from wastewater treatment and the publication by the US Army Center for Health Promotion and Preventive Medicine [21], the removal of 3-chloro-1,2-propanediol (3-MCPD) from samples of water was by hydrolysis and photolysis methods. From the methods examined, UV/H_2O_2 was the fastest way to remove 3-MCPD from water, the AOP makes almost complete conversion in a few minutes, whereas reasonable temperature hydrolysis takes several months [22].

Lau, Chu and Graham [23] studied degradation by UV photolysis (254 nm) of dibutyl phthalate (DBP) (laboratory scale with synthetic solution and ultrapure water), and observed that the removal of DBP (4 µM) occurred completely in 90 min; the reaction pathways of DBP degradation are different at different pH values, the reaction mechanisms are acid catalysis at pH 3, hydrolysis and oxidation/reduction reaction of the butyl chain at pH 5 and basic catalysis at pH > 7. Already in an AOP study performed by, [17], (DMP) (in laboratory scale with synthetic solution and ultrapure water), observed that direct oxidation with H_2O_2 does not oxidize DMP (reaction time 3 h); the first order rate constant increases with increasing initial H_2O_2 concentration (2.5–40 mg L^{-1}), however, a higher concentration causes the elimination of OH radicals; the degradation of DMP decreases with increasing concentration in an exponential trend; The first order rate constant increased with increasing pH (2.5–4), but decreased with higher pH.

Chung and Chen [24], in a study of the application of AOP UV/TiO_2 for degradation of di-2-ethylhexyl phthalate (DEHP) (laboratory scale with synthetic solution and ultrapure water), confirm that the photo-catalytic degradation of DEHP followed first order kinetics (constant rate of 0.0198 h^{-1} and $t_{1/2}$ = 0.58 h of 75 µg L^{-1} (DEHP) and 100 µg L^{-1} TiO_2); the degradation efficiency decreased with increasing concentration (25–300 µg L^{-1}); the optimal removal was 95.2% at 75 µg L^{-1}; however, degradation of DEHP increased with higher and lower pH due to acidic and basic catalytic hydrolysis, respectively; and also the amount of photo-catalyst increased the degradation to the optimum amount (100 µg L^{-1}) due to surface saturation in excess of dosage; and also for AOP in degradation of DEP with UV/H_2O_2, the non-significant effect of temperature (20–40°C) on degradation.

4. Conclusion

According to the results, a rapid degradation of DEP was observed in the tests at pH 7 (C9 - pH 7, 20 mM) and pH 3 (C6 - pH 3, 30 mM) with medium and high temperatures, of 30 and 45ºC used, and which according to the factorial planning, varied between 15, 30 and 45ºC. The complete degradation of DEP, however, does not occur at pH 11 (basic), so it can be deduced that the mineralization was incomplete under these experimental conditions. Statistical analysis confirms that pH is the variable that presents the most significant difference for the treatments ($p > 0.05$). The level of impact of the variables are in the following decreasing order: pH > H_2O_2 concentration > temperature.

During AOP applications, an immediate release of intermediates was evident, as soon as the treatment processes were started, as verified by the peaks in the chromatograms. Thus, we suggest an investigation of these compounds to be completed in later studies, as the evolution of the toxicity of these compounds, until their complete mineralization at the end of the treatments, is not known. Therefore, it can be concluded that in general the UV-C/H_2O_2 AOP tests proved to be effective and rapid in lowering the DEP degradation percentage in the synthetic effluent containing significant concentrations of DEP. These are well above those of the European community levels recommended - 1.3 µg L^{-1} in effluent released into the recipient body, as DEP is already classified as a priority substance for elimination.

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