Optimization of phenol degradation and its derivatives using photo-Fenton and application industrial

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Abstract

In industrial effluent are common persistent organic pollutants found that even low concentrations have a high potential carcinogenic and/or mutagenic, such as phenol and derivatives thereof, which poses risks to the environment. This work has identified and measured through high-performance liquid chromatography (HPLC) and its phenol formed as intermediate and also the amount of total organic carbon (TOC). Degradation was evaluated using the same process of photo-Fenton treatment (Fe^{2+}/H_2O_2/UV) applying annular reactor and a kinetic study was carried out in terms of TOC. The experimental design was the type central composite. In the process used a photochemical reactor annular counter optimized in the following conditions: $[Fe^{2+}]$=14.15 mg L^{-1}, $[H_2O_2]$=1663.40 mgL^{-1} at pH 3 for 126.18 minutes, obtaining a mineralization 99.89% TOC and $[Fe^{2+}]$=15 mgL^{-1} $[H_2O_2]$=1800 mgL^{-1} in 120 minutes a percentage of 100% phenol degradation, respectively. The kinetic model adopted (*Lumped Kinetic Model*) allowed satisfactory way of representing (R^2=0.9892). The photo-Fenton process proved to be efficient for degradation of phenol and intermediates can be incorporated as part of the effluent treatment systems, making it an effective alternative to the complete degradation of the pollutants thereby relieving the impact on water resources and reducing contamination by-products end of the process.

Keywords: Advanced oxidation processes; Phenol, Homogeneous processes; Photo-Fenton.

1. Introduction

The industrial effluents usually consist of a number of contaminants in varying concentrations which are generally harmful to the environment and living things (El nahash *et al*., 2009). Among those pollutants, phenolic compounds pose a threat to the environment because of its toxicity and stability of bioaccumulation (Teixeira *et al*., 2015). They are considered as one of the priority pollutants by the Environmental Protection Agencies (Wang *et al*., 2012; Cravotta & Brady, 2015).

Conventional techniques applied for the treatment of these effluents are mechanical and physico-chemical properties, often associated with biological treatment, and may be formed by separation through gravity, centrifugation, application of coagulants, flotation, filtration, adsorption with activated carbon and others (Santo et al., 2012).

These techniques can remove the free and emulsified oil effluents, suspended solids, and reduce biochemical oxygen demand (BOD), when associated with biological treatment. However, when the effluent contains highly toxic and recalcitrant constituents, the implementation of more advanced techniques are needed to allow the breakdown of these compounds (Zangeneh *et al.,* 2015). Among the pollution degradation, mechanisms can be pointed out as the advanced oxidation processes (AOP), whose main advantage is the ability to degrade organic compounds, leading to reduction or even total mineralization of toxic materials organic loads in waste water. As a result, reduces the emission of pollutants in the environment or even allowing the reuse of water recovery (Giannakis *et al*., 2015).

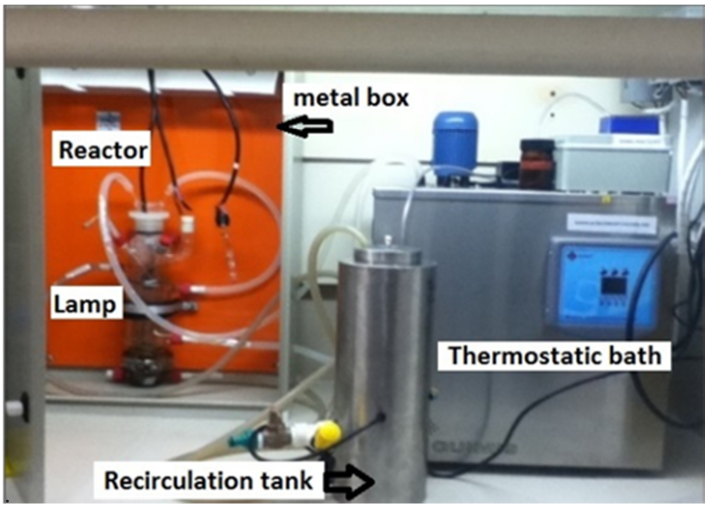
Among some kinds of AOP, the homogeneous photocatalytic degradation is considered an effective treatment, including the Fenton oxidation which is based on the Fenton reaction (hydrogen peroxide and iron salt), (Papoutsakis *et al*., 2015; Napoleão *et al*., 2015), which consists of the formation of oxidizing species, capable of degrading contaminants in waste water. This technique was used to treat both organic and inorganic compounds, laboratory scale using real effluent samples (Nogueira *et al*., 2007). When a reaction Fenton is irradiated by a light source in order to improve the formation of hydroxyl radicals, this process is called photo-Fenton. (Aljuboury *et al*., 2015; Alalm *et al.,* 2015). In order to find effective solutions to these environmental problems, it was also in this work, established methodologies for the identification, measurement and especially degradation by AOP, phenol and its derivatives when present in aqueous effluents from industries and analyzes the behaviors of the important variables that conditioned these processes. The process was optimized via central composite design rotation to maximize total organic carbon conversion (TOC), identifying the best operating conditions in relation to reaction time and initial concentrations of H_2O_2 and Fe^{2+}.

2. Materials and Methods

2.1 Configuration reactor photochemical for degradation phenol

For the fulfillment of degradation experiments, we used a photochemical reactor, consisting of an outer glass pyrex along the longitudinal axis which comprises of quartz glass tube. The reactor used is 0.7L capacity, coupled to a recirculation tank external to liquid volume 1.6L (Where the pH of the solution is controlled and the hydrogen peroxide is added in equal time intervals). The total volume of solution to be treated was therefore equal to 2,3L that recirculate at a flow rate of 1.95 L.min^{-1}. As UV radiation generator, a mercury vapor lamp (Philips HPLN) was used with medium pressure, 80W, placed inside the quartz well. The lamp has undergone a cutting process, where the housing is removed, piece of glass that protects the bulb. It was coupled to the reactor and the quartz shirts well Quimis, one thermostat bath to maintain the temperature of the system during the reaction between 20±1°C and 25±1°C. Monitoring the pH of the reaction medium was done by TECNAL brand equipment, TEC-3MP model. The reactor operated batch to recycle, and hydrogen peroxide was introduced in the middle, continuously, through a peristaltic pump PROVITEC, PM-5900 model with a flow rate of 1.75 mL min^{-1}. **Figure 1** displayed a schematic drawing of the reactor annular counter used inside a metal box which prevents radiation and exposure to external. Each of the volume of 10 mL at fixed times while each collected sample was then analyzed by HPLC to determine the concentration of phenol and a total organic carbon analyzer for measuring the TOC.

Figure 1: a) Scheme of the assembly and operation of the reactor annular



2.2 Degradation of phenol and derivatives by photo-Fenton process

The photo-Fenton process the following solutions were used: the solution of the synthetic wastewater was prepared with phenol (Dynamics, 99%) with an approximate concentration of 200 mgL^{-1}, hydrogen peroxide (Dynamics, 30%), sulphate iron heptahydrate ($FeSO_4.7H_2O$) (Nuclear), sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) for pH control (2.5 - 3). An inhibitory 0.1M solution (NaOH; KI; Na_2SO_3) was also added to complement the iron and inhibit reaction. Every single sample collected was immediately added to the inhibitor solution (15 mL of inhibitor solution to each effluent 10mL) and after 5 minutes the vacuum filtration was performed with Millipore membrane 0.22 μm to remove the iron precipitate.

2.3 Analysis by High-performance liquid chromatography (HPLC)

The quantification and identification of phenol and its derivatives were performed, using a Shimadzu HPLC equipment SS-550, equipped with Ultra C18 reverse phase column (5μm, 4.6 x 250 mm) and UV spectrophotometric detector (20A SPD). The maximum absorption of phenol, resorcinol, catechol, hydroquinone were recorded at wavelength of 270 nm while the p-benzoquinone and oxalic acids, acetic, malonic, maleic, succinic and fumaric was 254 nm. All standards were from Chem Service with purity ≥ 99.5%. We used the chromatographic system isocratic mode with a mobile phase consisting of a water solution acidified with phosphoric acid 10% (v/v) and methanol in a ratio of 90:10 isocratic mode. The temperature of the furnace equipment was maintained at 40 ± 1°C, with a flow of 0.750 mlmin^{-1} and a pressure 105 kgfcm^{-2}. The compounds were identified based on their retention times.

2.4 Analysis by Total organic carbon analysis (TOC)

For quantitative analysis of aromatics mineralization process, we used the TOC analysis using a high sensitivity equipment (4µgC·L^{-1}– 25.000 mgC·L^{-1}), Shimadzu, TOC-VCSH model, capable of quantifying the levels of TOC; subtracting the total carbon (TC), the inorganic carbon (IC). The determination of (CT) was obtained after the sample injection 680ºC and conducting the same by a flue tube containing platinum supported on alumina to a catalytic oxidation to CO_2. As regards the determination of (IC) after the sample is injected, reacted with phosphoric acid (H_3PO_4) to 25%, with complete conversion of the IC in CO_2.

2.5 Experimental design

Selected variables, was held so a factorial design consisting of five levels: -1.68, -1, 0, +1, and +1.68. As for 3 variables (n=3) and two levels (low (-1) and high (+1)), 8 factorial scores (2^3) and axial points 6(2x3) with 3 center points (rejoinders) amounting 17 experiments, which results in an orthogonal distribution. **Table 1** represented the experimental design with Central Composite Design (CCD) applied in the study.

Table 1: Experimental design with variable H_2O_2, Fe^{2+} and time.

Tests	**Fe^{2+}(mgL^{-1})**	**H_2O_2(mgL^{-1})**	**Time(minutes)**
1	-1(5)	-1(900)	-1(60)
2	1(15)	-1(900)	-1(60)
3	-1(5)	1(1800)	-1(60)
4	1(15)	1(1800)	-1(60)
5	-1(5)	-1(900)	1(120)
6	1(15)	-1(900)	1(120)
7	-1(5)	1(1800)	1(120)
8	1(15)	1(1800)	1(120)
9	-1.68 (1.59)	0(1350)	0(90)
10	+1.68(18.40)	0(1350)	0(90)
11	0(10)	-1.68(593.19)	0(90)
12	0(10)	+1.68(2106.81)	0(90)
13	0(10)	0(1350)	-1.68(39.55)
14	0(10)	0(1350)	+1.68(140.45)
15	0(10)	0(1350)	0(90)
16	0(10)	0(1350)	0(90)
17	0(10)	0(1350)	0(90)

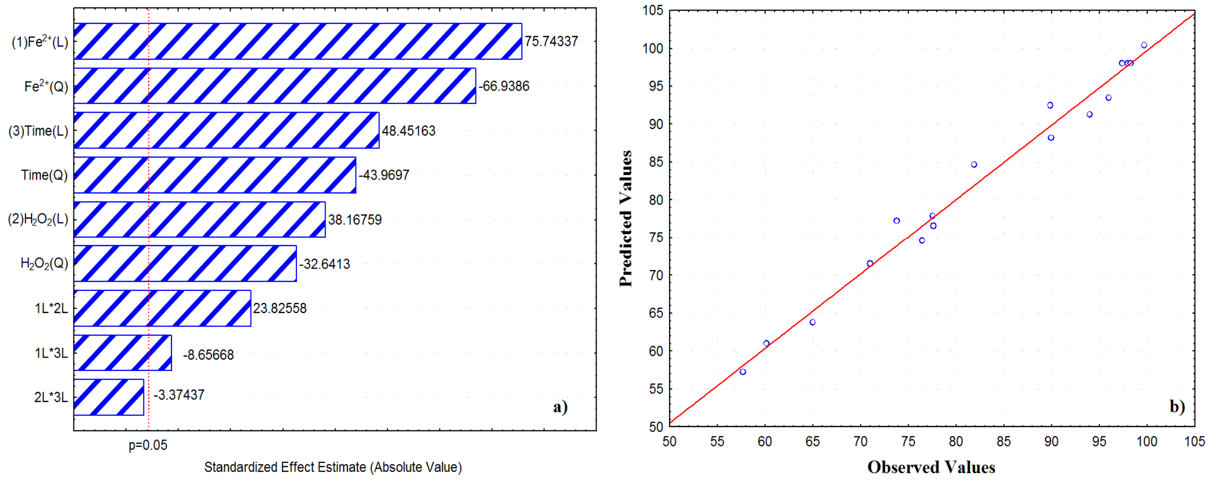
3. Results and Discussion

3.1 Degradation of phenol and intermediates by photo-Fenton process

The statistical analysis as well as the calculations of the effects of the factors and interactions between them was performed with the Statistical 6.0 program. These are identified which of the effects (initial concentrations of H_2O_2, Fe^{2+} and reaction time) were statistically significant for 95% confidence in the studied levels, as can be seen in the charter of Pareto shown in **Figure 2a**.

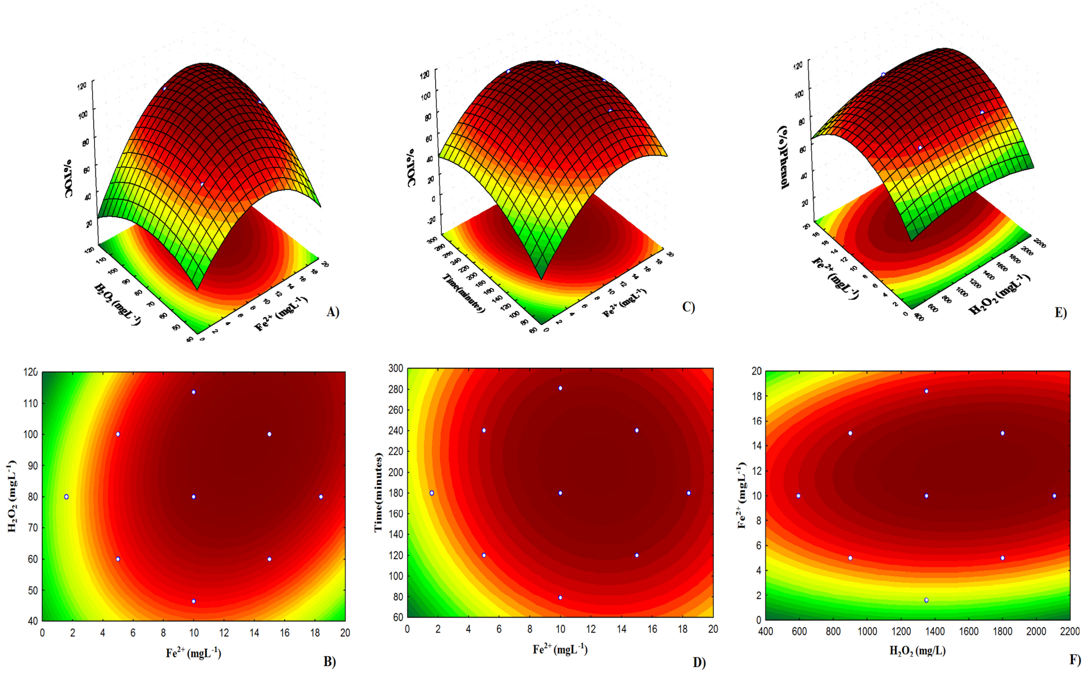
Figure 2: a) Pareto chart of the values of the effects of all the variables studied for the photo Fenton planning 2^3 central composite design of TOC conversion, b) Values predicted by the model versus values observed in the

experiment for the conversion of TOC.



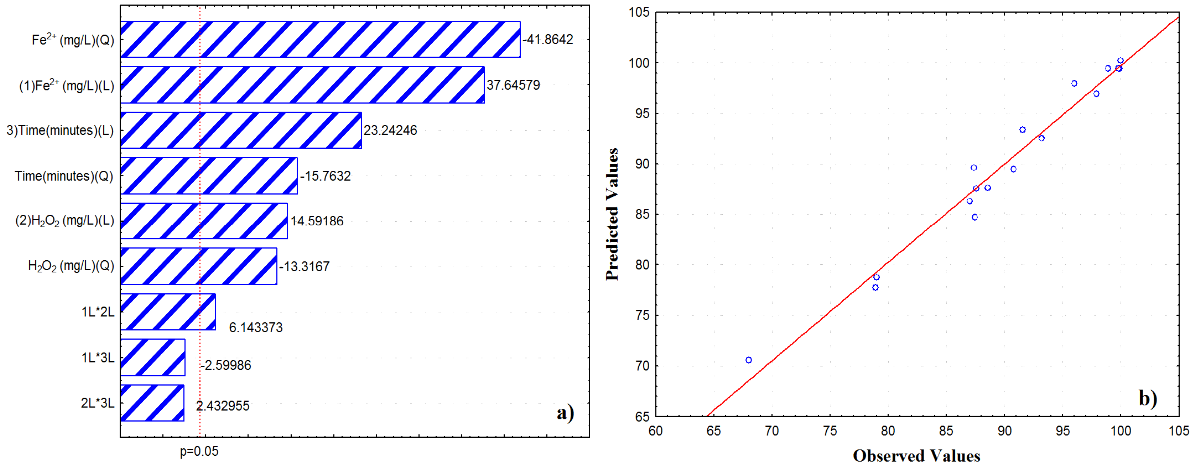
The results shown in this Figure refers to TOC conversion percentage. It was observed that the concentration of Fe^{2+} has greater influence on the photo-Fenton process. It can also be observed in the Pareto diagram interactions in the initial concentrations of Fe^{2+}/H_2O_2 and Fe^{2+}/time are relevant in using the proposed technique annular bench reactor. This planning was not only observed, the significance of the H_2O_2/time was also taking into consideration. By observing up the waste distribution chart (**Figure 2b**), it was found that the predicted values and the observed values were distributed evenly around the bend. It was found that the calculated values were, on average, closer to the red line and the gaps between them were normally distributed, positive and negative deviations were in the same proportion, without a biased behavior. The **Figures 3a and 3b** shows the contour and response surface curve, respectively, originated from the quadratic model, as stated earlier.

Figure 3: a) Response surface graphics based on %TOC mineralization; b) Curve contour for the variation of the conversion of TOC, where: X_1(concentration of hydrogen peroxide) and X_2 (concentration of ferrous ions).



It was observed that the concentration of ferrous ions initially has a positive effect on TOC percentage degraded to reach the maximum possible level, then going to present a negative result, decreasing the amount of conversion of the TOC. This is due to the excessive increase of the concentration of ferrous ions which results in increased turbidity of the solution conditioning the action of light and hence the activity of hydroxyl radicals. The same can be said in relation to the concentration of hydrogen peroxide up to a maximum value, when it begins to decrease with increasing H_2O_2 concentration. Excess H_2O_2 in the reaction medium favors self-decomposition reactions, kidnapping the radical hydroxyl radicals and generating less powerful oxidant, which corroborates the results presented by Rodrigues *et al.* (2007). In **Figure 3c,** it was found that the increase of irradiation time also had a positive effect on TOC percentage of degraded until it reaches the maximum level, from which starts to have a negative effect and degradation. The optimal conditions for the conversion of the TOC were as follows: Concentration of $[Fe^{2+}]$=14.15 mgL^{-1}, concentration $[H_2O_2]$=1663.40 mgL^{-1} 126.18 and reaction time minutes. Under these conditions, it is expected that TOC conversion percentage equal to 99.72% (**Figure 3d**), with values that confirm the excellent conditions of the curves above levels. In the Pareto chart, corresponding to the phenol degradation illustrated effect of the initial concentration of H_2O_2, Fe^{2+} and time (**Figure 4a**).

Figure 4: a) Pareto chart of the values of the effects of all the variables studied for the photo Fenton planning 2^3 of phenol degradation; b) Values predicted by the model versus values observed in the experiment for phenol degradation.

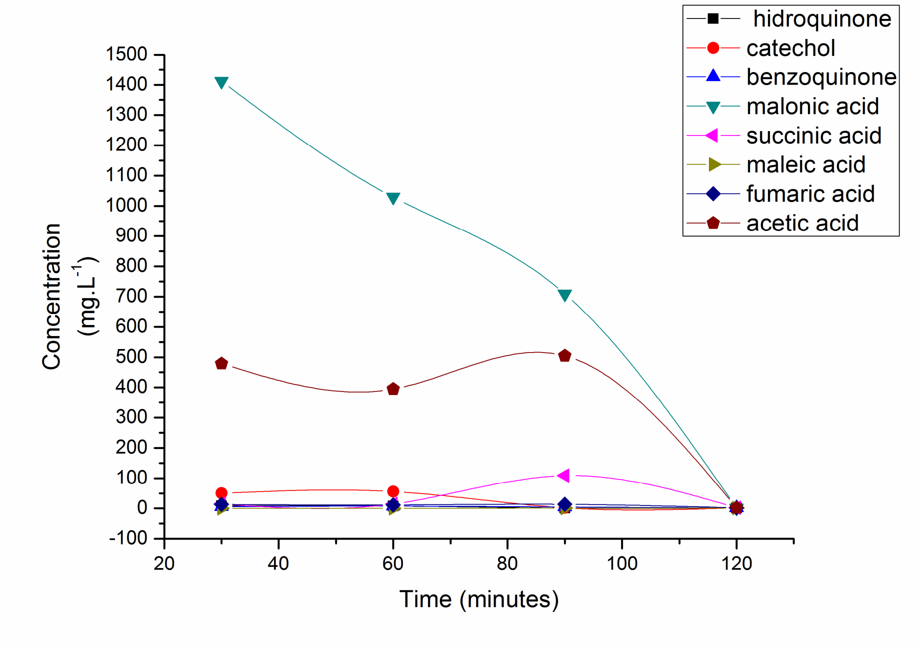


It is seen that the concentration of Fe^{2+} has greater influence on the photo-Fenton process. It can also be observed in the Pareto diagram that interacts Fe^{2+}/H_2O_2 possessed relevance. The significance between the Fe^{2+}/time and H_2O_2/time in this planning just was not observed. The waste distribution graph (**Figure 4b**), it was found that the predicted values and the observed values are distributed evenly around the red line, which confirms a good fit of the quadratic model. The differences between them are normally distributed, i.e. positive and negative deviations are in the same proportion, without a biased behavior. **Figures 3e and 3f** demonstrated the response surface and contour curve originating from the quadratic model, as to the phenol degradation. As previously mentioned, and was to be expected, it observed the same behavior as the increased concentration of ferrous ions. This initially had a positive effect on degraded phenol percentage until a maximum possible level, then moving to present a negative variation, reducing the amount of phenol. The concentration of excess ferrous ion may cause turbidity that prevents UV absorption causing the recombination of hydroxyl radicals with iron (Tokumura *et al*., 2008; Moncayo-Lasso *et al*., 2008).The optimal conditions for the phenol degradation were as follows: concentration of $[Fe^{2+}]$ = 15 $mg{\cdot}L^{-1}$, $[H_2O_2]$ = 1800 $mg{\cdot}L^{-1}$ and reaction time = 120 minutes providing a percentage of 100% phenol degradation.

3.2 Intermediate formation observed in the photo-Fenton treatment process

A major concern of degradation of organic matter by AOP is the nature and type of oxidation products that will be generated. Furthermore, in order to establish a secure degradation pathway, it is important to identify polluting products during their treatment by advanced oxidation processes. There is already, today, a set described in the literature for information on the mechanism of degradation of phenol by various AOP where the formation of aromatic products of phenolic intermediates origin, as is the case of dihidroxibenzenos (catechol and hydroquinone) and quinones, has been reported. These aromatic intermediately can undergo the subsequent aromatic ring cleavage reactions to produce carboxylic acids such as fumaric acid, muconic acid and maleic acid, and aldehydes. In order to follow the route of degradation, resulting from the proposed treatment, we tried to follow the formation of intermediate oxidation products, making chromatographic analysis of samples subjected to different treatment conditions. **Figure 5** presents the identified intermediate during oxidation degradation of phenol by the photo-Fenton process for treatment periods of 30, 60, 90 and 120 minutes.

Figure 5: Intermediates observed by applying photo-Fenton treatment



The best known and which are most frequently cited in the literature products known as dihidroxibenzenos were those that appear in greater abundance. When compared to these, the highlight was the catechol. In this figure, it is expected that the ortho-hydroxylation is the preferred route for oxidation as resorcinol, hydroquinone and p-benzoquinone occur in minor amounts. According to the analysis carried out, it also registers the presence of malonic acid as main product, maleic, fumaric, succinic and certain short chain carboxylic acids, such as acetic acid and oxalic acid (kavitha and Palanivelu, 2004). Furthermore, Zazo *et al.* (2009) evaluated the formation of the intermediate phenol degradation subjected to Fenton treatment process and verified the presence of catechol, hydroquinone and p-benzoquinone, followed by the formation of maleic, acetic, formic and oxalic acids. The degradation of aromatics, including benzene and phenol was also studied by Aranda *et al.* (2010), using AOP, the authors found that the action of •OH hydroxyl radicals on the benzene ring produces phenol, initially forming derivatives dihydroxybenzene type and then forming quinones and open chain products such as carboxylic acids.

This study verified the presence of the catechol intermediate, hidroquinonal, p-benzoquinone and malonic, succinic, maleic, fumaric and acetic which leads to suppose that the route of degradation is done in a similar way to that proposed by Aranda *et al.* (2010).

3.3 Kinetic modeling

The kinetic model used to represent the catalytic wet oxidation of organic compounds studies was called Lumped Kinetic Model (LKM) in terms of carbons contained in the liquid phase profile describing the total residual concentration. This can occur by two different pathways (Iurascu (2009) and Ayodele *et al.* (2012). The reaction pathways may be presented as **Figure 6**, where (A) means a group composed of carbon and non-refractory intermediates which can be degraded in a direct manner giving rise to CO_2 and H_2O (C), or A may form a carbon refractories group of intermediate compounds (B) and these intermediates can be converted in turn into CO_2 and H_2O. The constants k_1, k_2 and k_3 represent the rate constants for each of these reactions.

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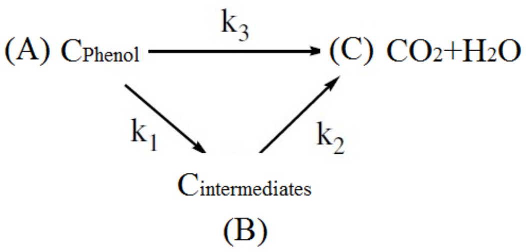
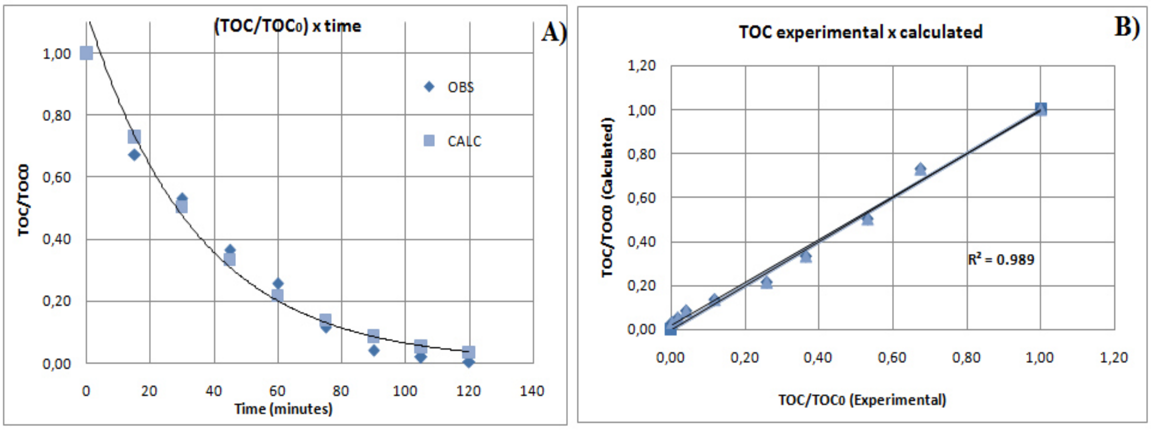
Figure 6: Reactions to convert the TOC.



The values for the rate constants k_1, k_2 and k_3 were 0.021 min^{-}1, 0.039 min^{-1} and 0.018 min^{-1}, respectively. It was shown that the mineralization of the phenol and non-refractory compounds (A) at the end substrate (C = CO_2 and H_2O) occurs at a speed (k_3=0.018 min^{-1}) which is close to the degradation of organics intermediate (B) (k_1=0.021 min^{-1}).

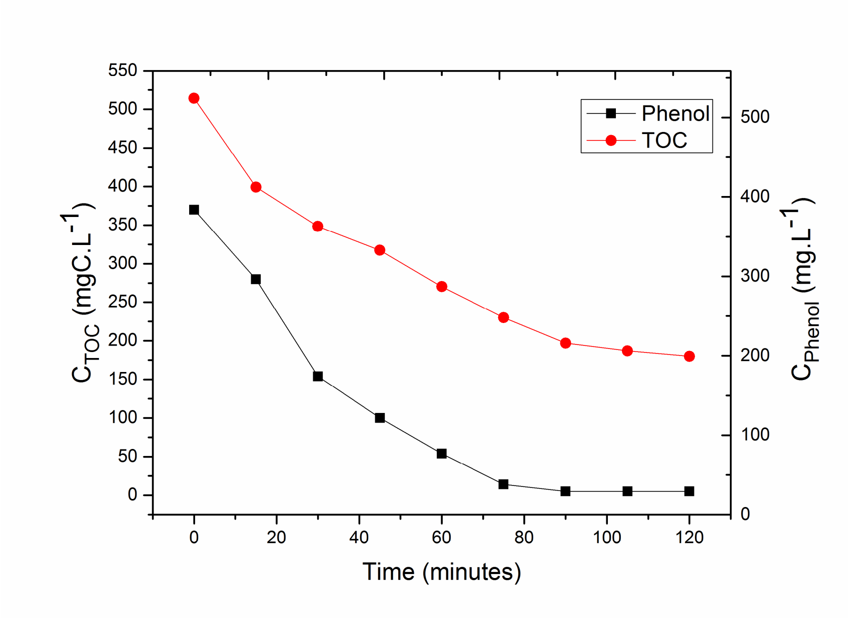
However, concerning the mineralization of refractory intermediates (B), it is characterized by its speed (k_2=0.039 min^{-1}) increased, compared to the other reactions involved in the process. **Figure 7a** shows the values of TOC/TOC_0 observed (experimental) and calculated (theoretical) for the photo-Fenton process. As can be seen the values calculated by the proposed kinetic model are close to those found experimentally.

Figure 7: a) Kinetic model of conversion of TOC the process Fe^{2+}/H_2O_2/UV in its optimum operating condition: $[Fe^{2+}]$=15mgL^{-1}, $[H_2O_2]$=1800mgL^{-1}, pH = 3, T =25°C. b) Comparison between calculated and observed values of reason TOC/TOC_0 kinetics.



The **Figure 7b** is the correlation between experimental values subject to kinetic modeling and predicted values in the theoretical model verifying a good fit for all the calculated data. The results of this step kinetic study were similar to those presented by other authors (Iurascu *et al*., 2009), who found that the phenol / intermediate reaction is about three times slower than the reaction intermediates /CO_2+H_2O once k_1 is about two to three times lower than k_2. It therefore implies that the degradation of the intermediates was more rapid than the conversion of the phenol intermediate degradation products. Once k_3 on the transformation of intermediates into final substrate is slower than other reactions, it was concluded that complete oxidation of the organic pollutants CO_2 and H_2O is difficult to achieve since it appears that the formation of refractory intermediates as is the case with the short chain carboxylic acids (Luan *et al.*, 2012). Meanwhile, optimization of the treatment process was applied in a real effluent from a chemical plant containing phenol at a concentration of 312mg L^{-1} of phenol and 12000 mgC.L^{-1} of TOC, respectively. In **Figure 8**, the TOC are observed concentration curves in mgC·L^{-1} (C_{TOC}) and phenol (Cphenol) in mg.L^{-1}. In terms of percentage conversion, the TOC and phenol degradation occurred in 65% and 100%, respectively in 120 minutes of operation.

Figure 8: Comparison between calculated and observed values of reason TOC/TOC$_0$ kinetics.



Comparing the conversion result of the actual effluent TOC (65%) with the effluent produced in the laboratory (99.72%), a decline was observed.This can be attributed to the effluent having a high turbidity, inhibiting the passage of light and reducing the efficiency of the generation of hydroxyl radicals. It was shown that the photo-Fenton process achieved an effectiveness for treating high organic loads, which implements the biological processes, generally slow and loses efficiency by increasing the same. These results show that photo-Fenton process reactor annular HPLN mercury vapor lamp with 80W power efficiency showed 65% of the total mineralization of TOC degradation of phenol. Hence, it presents perspective use in treating real effluent industry sandpaper or a related field in the absence of solar radiation in rainy or nighttime.

5. Conclusion

The photo-Fenton technique ($Fe^{2+}/H_2O_2/UV$) applied attested to be effective for the degradation of phenol and a lower TOC conversion of the remaining reaction time. With the application of central composite design, there were optimized reaction conditions, obtaining the optimal point on the proportions of catalyst concentration (Fe^{2+}) = 14.15 mg·L^{-1}, H_2O_2=1663.40 mg·L-1 and the weather (126.18 minutes). Under these conditions, the conversion of TOC obtained was equal to 99.71% in 120 minutes of operation and 99.98% of phenol degradation. In testing conducted real effluent resulting from an abrasive industry, phenol concentration equals to 370 mgL^{-1} and 12000 mgL^{-1} · TOC using enhanced proportion to the concentrations of the variables involved and time 65% was obtained TOC conversion occurs almost complete degradation (99.80%) of the phenol. Hydrogen peroxide concentrations were added to the system consumed during the process, leaving little or no concentration thereof. The continuation of this research is relevant for the development of systems on an industrial scale. It is recommended to apply the used technique (photoFenton) as treatment of wastewater containing phenolics compounds.

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