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Engenharia Química

Sourwater treatment by fenton process and its effect on phytotoxicity with *Lactuca sativa*

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Abstract:

In this work, degradation of stripped sourwater by Fenton´s oxidation process was investigated by a central composite design and response surface methodology. The effects of initial concentrations of H_2O_2 and Fe^{2+} on the total phenols degradation was studied in a batch reactor. The optimum total phenols degradation was 92% achieved within an H_2O_2 concentration of 4.4 g L^{-1} and iron concentration of 162 mg L^{-1}. The mathematical kinetic model adequately represented the experimental results. The results indicated that the Fenton oxidation rate (1/m) and removal efficiency (1/b) were more dependent on iron concentration than H_2O_2 concentration. After the Fenton process, the sourwater presented a seed germination rate (*L. sativa*) above 80%, indicating reduced phytotoxicity of the treated effluent. It was also observed that the H_2O_2 concentration significantly affected the inhibition concentration (IC_{50}).

Keywords: petroleum effluent, advanced oxidative process, total phenols, bioassays, experimental design.

Introduction

Petroleum refinery uses a huge amount of water in its processes, consequently, a significant volume of wastewater is generated and depends on several factors such as the type and setting of its process and the characteristics of the processed oil (Yavuz, Koparal, & Ö#ütveren, 2010; El-Naas, Alhaija, & Al-Zuhair, 2014) . In general, the chemical composition of petroleum refinery effluent presents several inorganic substances, emulsified oil, phenols, sulfides, ammonia and cyanides (Yan, Ma, Wang, Mao, & Chen, 2010) . Due to the toxicity and the harmful effects on human health and environment, it is necessary to develop efficient and economically feasible methods to remove these pollutants from petroleum refinery effluents and

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to monitor its toxicity. In this context, bioassay tests can be used as a complementary response for treated wastewater to determine its toxicity.

Due to the global concern about water scarcity, new methods for reusing water in petroleum refineries are required. According to Coelho, Castro, Dezotti, and Santanna (2006), a stream of sourwater can be segregated and treated for possible reuse. This wastewater is generated from the condensation of the steam that is used in the distillation, catalytic cracking, and other applications. The sourwater production in refineries is comprised of about 0.2 $m3ton^{-1}$ and 0.5 $m3ton^{-1}$ of crude oil processed (Coelho et al., 2006) . This effluent is the stream which contains hydrocarbons, which in turn contain hydrogen sulphide (H_2S) and ammonia (NH_3). These compounds are absorbed into the water at levels that typically require stripper treatment (International Petroleum Industry Environmental Conservation Association [Ipieca], 2010) . However, the stripped sourwater still contains phenols and cyanide.

Conventional treatments of refinery wastewater are based on primary and biological treatments in the integrated activated sludge treatment unit. However, these methods are not suitable to remove non-biodegradable and high-concentration organic substances. Thus, advanced techniques for removing these substances from petroleum refinery wastewater must be developed (Sun, Zhang, & Quan, 2008) . According to Hasan, Aziz, and Daud (2012) , an advanced oxidation process (AOP) has been proposed to treat petroleum refinery effluents (PRE), including photocatalytic degradation, ozonation, and photo-degradation. There are several studies on pre-treatment, but studies on sourwater treatment are still scarce. Some patents have been proposed, dealing with oxidation by Fenton process (Solvay Interox Inc., 2001) and membrane process (Hydrometric, 2002) . Coelho et al. (2006) studied sourwater treatment using several AOPs and concluded that Fenton and photo-Fenton processes show the best performance in removing dissolved organic carbon (DOC) from sourwater (55 and 83%, respectively).

The Fenton process entails hydrogen peroxide catalysis by the ferrous ion to produce hydroxyl radical ($HO^{\bullet}$) and involves numerous reactions (Wu, Zhou, Qin, Zheng, & Ye, 2010; Brink, Sheridan, & Harding, 2017). Its efficiency depends on several variables: pH, temperature, H_2O_2 and Fe^{2+} concentrations.

Bioassays provide a biological response (germination, root elongation, and others) and these data complement the chemical data (total phenols concentration, COD, TOC, and others) to assess *in vivo* toxicity of the treated effluent. The plant-based bioassays have advantages of low-cost test and easy handle and measure (Sobrero & Ronco, 2004; Garcia et al., 2009) . *Lactuca sativa* is widely used for germination, and the growth inhibition of the root is used as evaluation endpoints of phytotoxic effects (International Organization for Standardization [ISO], 1995; United States Environmental Protection Agency [EPA], 1996; Organização para a Cooperação e Desenvolvimento Econômico [OECD], 2003) .

The aim of this work was to investigate the kinetics of sourwater degradation by Fenton process. A 2^2 factorial design of experiments was proposed to study the initial concentration of hydrogen peroxide and Fe^{2+} and maximize the degradation of stripped sourwater total phenols. A mathematical kinetic model was also derived to predict the reaction kinetics. Based on the lettuce seeds (*Lactuca sativa*), the toxicity of non-treated and treated effluent was estimated.

Material and methods

Experimental

A sample of stripped sourwater was obtained from Getúlio Vargas Refinery (Petrobrás) located in Araucaria, Paraná State, Brazil. The sample was collected, stored under refrigeration (4 °C) and used without any pre-treatment at room temperature (22 ± 2°C). The hydrogen peroxide (30%, v v^{-1}), H_2SO_4 and NaOH were

purchased from Merck. The Na_2CO_3 and phenol were acquired from Vetec, the Folin-Ciocalteau reagent from Sigma-Aldrich, and the $FeSO_4.7H_2O$ from Dinâmica.

Experimental arrangement

Chemical oxidation was performed in a batch reactor (600 mL capacity) containing 500 mL of stripped sourwater. The reactor operated under constant stirring, accomplished by a magnetic bar. The reaction temperature was maintained at 22 ± 1°C. Reagents employed in the oxidation process were $FeSO_4.7H_2O$ and H_2O_2. The pH of the reaction mixture was adjusted to the desired value 3.0 ± 0.1 using solution of H_2SO_4. The catalyst (iron sulfate) was introduced after the pH adjustment to avoid iron precipitation. Time zero of the run was set as the moment when the hydrogen peroxide solution was added. The Fenton reaction was stopped by adding a solution of NaOH to reach the pH of above 7.0. A pH-meter from Thermo Scientific was used for measuring the solution pH.

Analytical techniques

Total phenols concentration was determined by using *Folin-Ciocalteau* reagent according to the protocol described by Scalbert, Monties, and Janin (1989) , and it was expressed as mg L^{-1} of phenol (C_6H_5OH). The percentage of total phenols degradation was obtained using Equation 1:

$$TP(\%) = \frac{C_{TP,o} - C_{TP}}{C_{TP,o}} x100 \quad (1)$$

(1)

where:
$C_{TP,0}$ and C_{TP} are the initial and time t of total phenols concentration, respectively.

Factorial design

The independent factors (variables) considered in this work were H_2O_2 (Pe) and Fe^{2+} (Fe) concentrations in g L^{-1} and mg L^{-1}, respectively, whereas percentage total phenols degradation (y_1) was considered as the response (dependent factor). Room temperature of 22 ± 2°C and initial pH of 3 ± 0.1 were kept constant to avoid the influence of additional factors. Table 1 shows the independent variable and Central Composite Design (CCD) levels used in this work. The ranges of selected parameters were determined based on Coelho et al. (2006). The [H_2O_2] varied from 1.6 to 4.4 g L^{-1} and [Fe^{2+}] from 59 to 162 mg L^{-1}.

Based on the CCD principle, the design consisted of 2^k factorial points plus 2*k axial points and 3 center points, where k is the number of variables (in this case, k = 2). Thus, 11 experiments were conducted: four (2^2) factorial points, four (2*2) axial points, and 3 central points to estimate the experimental error; three replications were used. CCD in RSM (response surface methodology) was used to illustrate the output nature of the response surface in the designed experiment and to explain the optimization level of the two independent variables.

Kinetic models for total phenols degradation

The kinetics of process can be quite complex due to a significant number of steps performed simultaneously during the process (Behnajady, Modirshahla, & Ghanbary, 2007) . Three kinetic models, the pseudo first-order, the pseudo second-order and the mathematical kinetic model, were used on the experimental data points obtained from total phenols degradation.

The rate of total phenols (TP) degradation regarding first-order rate can be described by the Equation 2.

$$\frac{C_{TP}}{C_{TP,0}} = exp^{-k_1 t} \quad (2)$$

where:

$C_{TP,0}$ and C_{TP} are the total phenols concentration (mg L^{-1}) in the initial and time t, respectively, k_1 is the apparent first order rate constant ($min.^{-1}$), and t is the reaction time (min.).

The rate of total phenols (r_{TP}) described by second-order reaction kinetics is given by Equation 3 (Guedes, Madeira, Boaventura, & Costa, 2003; Sun et al., 2009) :

$$\frac{1}{C_{TP,0}} - \frac{1}{C_{TP}} = -k_2 . t \quad (3)$$

where:

k_2 is the s order kinetic parameter (L $mg^{-1}min.^{-1}$).

A mathematical kinetic model to simulate the reaction kinetics were derived by Chan and Chu (2003) and Behnajady et al. (2007) and are presented in the Equation 4.

$$\frac{C_{TP}}{C_{TP,0}} = 1 - \frac{t}{m + bt} \quad (4)$$

where:

m and *b* are constants relating the reaction kinetics and oxidation capacity. The terms *m* and *b* (Equation 5) can be determined by taking the derivation of Equation 4.

$$\frac{\frac{dC_{TP}}{C_{TP,0}}}{dt} = \frac{-m}{(m + bt)^2} \quad (5)$$

where:

t is very short or approaching zero, Equation 5 can be written according to Equation 6.

$$\frac{\frac{dC_{TP}}{dC_{TP,0}}}{dt} = \frac{-1}{m} \quad (6)$$

(6)

The corresponding physical meanings of m and b parameters were investigated by examining two extreme cases. The higher $1/m$ value, the faster initial degradation rate of total phenols. When t is long and approaches to infinity, the $1/b$ value indicates the maximum total phenols degradation fraction, which is equal to the maximum oxidation capacity of the Fenton process at the end of the reaction, according Equation 7.

$$\frac{1}{b} = 1 - \frac{C_{TP,t\to\infty}}{C_{TP,0}} \quad (7)$$

(7)

TABLE 1.
Factor levels for central composite design (CCD) in the Fenton process.

Factors	Parameters	Coded level				
		-1.41	-1	0	+1	+1.41
Pe	$[H_2O_2]$ (g L^{-1})	1.6	2	3	4	4.4
Fe	$[Fe^{2+}]$ (mg L^{-1})	59	74	111	147	162

The parameters of kinetic models for total phenols degradation at different Fenton´s reagent concentration were calculated by applying non-linear regression to ($C_{TP}/C_{TP,0}$) versus t for the first-order model and mathematical model and linear regression analysis to ($1/_{CTP}$) – ($1/_{CTP,0}$) versus t for the second-order model.

Toxicity test with Lactuca sativa L.

The lettuce seeds (*Lactuca sativa L.*) were used to assess the non-treated and treated stripped sourwater toxicological response. The lettuce seeds were used as toxicity level bioindicators due to their fast response to concentrated and diluted by-product solutions. Bioassays in lettuce seed were conducted for germination index, the length of the radicle and length of hypocotyl structure, following the methodology proposed by Sobrero and Ronco (2004) . Five dilutions were tested (6, 12, 25, 50 and 100%) of non-treated and treated stripped sourwater solutions. The test was carried out in 90 mm diameter Petri dishes lined filter paper with 10 seeds each, containing 2 mL of sample dilution or control water. The plates were covered and placed in a plastic bag to prevent moisture loss and incubated for 120 hours at 22 ± 2ºC. Each assay was done in triplicate. The lettuce seeds containing mineral water was used as negative control (United States Environmental Protection Agency [EPA], 1989; Sobrero & Ronco, 2004) . The absolute germination (AG) and germination index (GI) for bioassays, were calculated according to Equation 8 and 9.

$$AG(\%) = \frac{N_{germ}}{N_{seed}} x100 \quad (8)$$

(8)

$$GI(\%) = \frac{N_{germ}}{N_{cont}} \frac{RL_{germ}}{RL_{cont}} x100 \quad (9)$$

(9)

where:

N_{germ} is the average number of germinated seeds to indicate that the dilution was being performed with treated stripped sourwater; N_{seed} is the total number of seeds, and Ncont is the average number of germinated control seeds in mineral water. RL_{germ} is the average root length of germinated seed in the diluted treated stripped sourwater, and RL_{cont} is the average root length of germinated seed in control. The half inhibition growth concentration (IC_{50}) was calculated by germination index (GI) using Probit method in Statistica® 7.0. Means values of IC_{50} were compared among the treatments by analysis of variance (ANOVA) and the Tukey test at the significance level ($p < 0.05$).

Results and discussion

Table 2 presents the characteristics of the sourwater employed in the oxidation experiments and data found in the literature.

The characteristics of stripped sourwater show the recalcitrant nature of the organic compounds (263 mg L^{-1} total phenols) and an advanced oxidation process, such as Fenton´s reagent, seems to be a suitable option to treat this effluent.

The performance and optimization of Fenton treatment were investigated applying a CCD full factorial design with two factors: hydrogen peroxide concentration [H_2O_2] and iron concentration [Fe]. Table 3 shows the results of the Fenton experiments as the average of percentual of total phenols degradation after 15 min. of reaction (experimental response).

Based on the experimental results, an empirical equation on Fenton process of stripped sourwater was written in a coded term for the percentage of total phenols degradation (Equation 10). All model terms were analyzed by a t-test, and the term found to be insignificant ($p > 0.05$) was excluded from the model. The initial iron concentration was the most significant factor in the Fenton process of sourwater that decomposes H_2O_2 to generate $^{\bullet}OH$ followed by hydrogen peroxide concentration (Pe). The square interaction (Pe*Pe and Fe*Fe) and interaction terms (Pe*Fe) were not statistically significant ($p > 0.05$) upon total phenols degradation of stripped sourwater by Fenton oxidation. All linear terms showed positive effects.

$$TP(\%) = (82.79 \pm 0.26) + (2.07 \pm 0.31)\, Pe + (3.60 \pm 0.31)\, Fe \qquad (10) \qquad (10)$$

The ANOVA analysis indicated that F-values of 91.54 implies that the proposed model was significant for total phenols and the 'lack of fit' p-value for total phenols was not significant ($p = 0.204$). The R^2 for empirical equation was 0.87 indicating the reliability to estimate total phenols.

The mathematical model (Equation 10) was used to generate 2D and 3D plots (Figure 1) demonstrating the interaction between initial iron and hydrogen peroxide concentration.

Figure 1 shows an increase of TP degradation with increasing iron concentration. The fact that higher degradation of total phenols was achieved at high Fe^{2+} dosages was attributed to the higher production of $^{\bullet}OH$ in Fenton´s reaction.

The H_2O_2 plays a very important role as a source of $^{\bullet}OH$ generation in Fenton´s reaction. The response surface of total phenols removal gradually increased with increasing H_2O_2 concentration from 1.6 to 4.4 g L^{-1}. This can be explained due to a large amount of H_2O_2. Consequently, the additional production of hydroxyl radicals can occur.

The adequacy of the proposed model for TP oxidation of stripped sourwater by Fenton process was evaluated at the optimum operating conditions. According to the model, the optimum conditions were: hydrogen peroxide concentration of 4.4 g L^{-1} and iron concentration of 162 mg L^{-1}, prediction 90.7%

of TP degradation. Under these optimal conditions, new experiments were conducted in triplicate and a TP degradation 89.9% was achieved, which is in agreement with the oxidation predicted by the model. Furthermore, for the entire range of the tested factors, the experimental results are very close to the predicted values obtained from the model.

The high amounts of reagents necessary to obtain removal of total phenols can be explained by the nature of the effluent which contains predominantly recalcitrant compounds. Besides that, it decreases the process efficiency due to intermediates compounds, which can trap hydroxyl radical to react with the hydroxyl radical producing less reactive radicals. In relation to the concentration of iron, if the amount of Fe^{2+} is high, the $^{\bullet}OH$ radicals are trapped by Fe^{2+} ions in excess. Furthermore, the high concentrations of iron are not desirable for two practical reasons: the cost of the reagent and the need of iron sludge treatment (Bautista, Mohedano, Gilarranz, Casas, & Rodriguez, 2007; Garcia-Segura, Bellotindos, Huang, Brillas, & Lu, 2016) . Regarding H_2O_2 high concentration, this may be due to recombination of hydroxyl radicals and also hydroxyl radicals' reaction with H_2O_2, contributing to the $HO^{\bullet}$ scavenging capacity.

Therefore, this model of sourwater degradation by Fenton process is applicable for H_2O_2 concentration between 1.6-4.4 g L^{-1} and iron concentration between 59-162 mg L^{-1}. Consequently, the amount of catalyst (Fe^{2+}) has greater effect on the TP degradation than the amount of H_2O_2. Other studies have also demonstrated that the impact of catalyst (Fe^{2+}) dosage has a more pronounced effect on contaminant removal in the Fenton process (Tony & Bedri, 2014; Brink et al., 2017) .

Kinetic models

The kinetic parameters and corresponding determination coefficient (R^2) obtained by kinetics models for the degradation of total phenols of stripped sourwater are presented in Table 4.

The determination coefficient (R^2) above 0.99 found by the mathematical kinetic model suggests that this model is better suited to describe the experimental data during the Fenton oxidation.

Figure 2 shows total phenols decay curves of stripped sourwater for different Fenton conditions for the three kinetic models.

TABLE 2.
Stripped sourwater average characteristics.

Parameters	In this study	(Coelho et al., 2006)	(Ipieca, 2010)
BOD_5 (mg O_2 L^{-1})	225	570	
COD (mg O_2 L^{-1})	900	850 – 1020	600 – 1200
Ammoniacal nitrogen (mg NH_3-N L^{-1})	21	5.1 – 21.1	
Sulfide (mg S^{2-} L^{-1})	15	15 – 23	< 10
Total suspended solids (mg L^{-1})	< 10		< 10
Total solids (mg L^{-1})	140		
pH	7.9	8.0 – 8.2	
Conductivity (µS cm^{-1})	230		
Turbidity (NTU)	3.8		
DOC (mg C L^{-1})	288	297 – 440	
Total phenols (mg L^{-1})	263	98 – 128	> 200

TABLE 3.
Design matrix and levels based on the central composite design with results and predicted values of total phenols degradation of sourwater by Fenton process.

Run	Actual		Coded		TP (%)	
	$[H_2O_2]$ g L^{-1}	[Fe] mg L^{-1}	Pe	Fe	Observed	Predicted
F (-, -)	2	74	-1	-1	76.5	77.1
F (+, -)	4	74	1	-1	79.4	81.3
F (-, +)	2	147	-1	1	83.8	84.3
F (+, +)	4	147	1	1	86.2	88.5
F (0, 0) 1	3	111	0	0	83.6	82.8
F (0, 0) 2	3	111	0	0	85.3	82.8
F (0, 0) 3	3	111	0	0	84.0	82.8
F (-1.41, 0)	1.6	111	-1.41	0	79.2	79.9
F (+1.41, 0)	4.4	111	1.41	0	87.2	85.7
F (0, -1.41)	3	59	0	-1.41	77.6	77.7
F (0, +1.41)	3	162	0	1.41	88.0	87.9

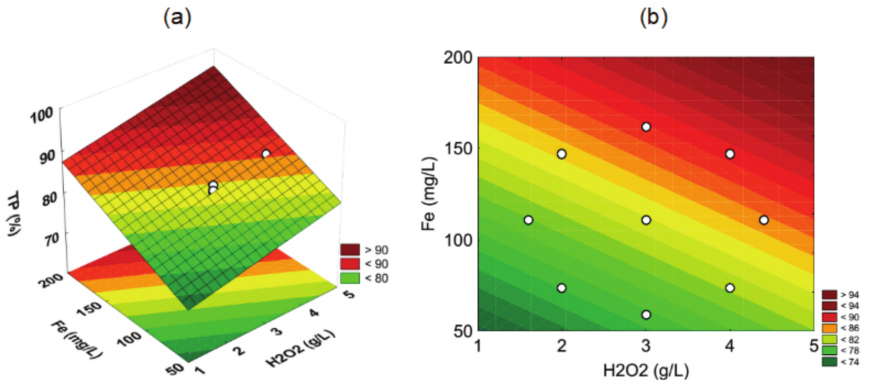

FIGURE 1.
Response surface (a) and contour plots (b) for total phenols (TP) degradation versus iron concentration and hydrogen peroxide concentration used in the Fenton process.

TABLE 4.
The parameters of kinetic models and correlation coefficient (R^2) for the degradation of total phenols of stripped sourwater at different reaction conditions.

Run	Actual		Coded		First-order		Second-order		Mathematical model		
	$[H_2O_2]$ (gL^{-1})	$[Fe^{2+}]$ (mg L^{-1})	Pe	Fe	k_1 ($min.^{-1}$)	R^2	$k_2 \times 10^3$ (L mg^{-1} $min.^{-1}$)	R^2	m (min.)	b	R^2
F (-, -)	2	74	-1	-1	0.130	0.708	0.236	0.848	1.903	1.152	0.996
F (+, -)	4	74	1	-1	0.148	0.780	0.290	0.871	1.839	1.123	0.998
F (-, +)	2	147	-1	1	0.212	0.833	0.321	0.795	1.063	1.109	0.999
F (+, +)	4	147	1	1	0.227	0.904	0.440	0.781	1.203	1.071	0.999
F (0, 0) 1	3	111	0	0	0.205	0.838	0.334	0.821	1.168	1.105	0.999
F (0, 0) 2	3	111	0	0	0.226	0.871	0.376	0.804	1.073	1.091	0.999
F (0, 0) 3	3	111	0	0	0.203	0.849	0.343	0.814	1.223	1.100	0.999
F (-1.41, 0)	1.6	111	- α	0	0.150	0.735	0.237	0.808	1.583	1.145	0.998
F (+1.41, 0)	4.4	111	α	0	0.243	0.901	0.463	0.841	1.050	1.075	0.999
F (0, -1.41)	3	59	0	-α	0.131	0.732	0.240	0.839	2.001	1.143	0.998
F (0, +1.41)	3	162	0	α	0.269	0.909	0.514	0.856	0.872	1.074	0.999

According to Figure 2, the total phenols decomposition was performed in two stages: through a rapid first-stage (up to 10 min.) followed by a slow second-stage (from 10 min to end). During the first 10 min. of reaction, rapid pollutant degradation is attributed to high HO● concentrations, as a result of greater amounts of Fe^{2+} catalyst in a solution that reacts with H_2O_2. At the second stage, Fe^{3+} ions were combined

with H_2O_2 to produce weaker oxidant radicals compared to $HO^{\bullet}$, in addition to their slower rate of production (Luna, Silva, Nogueira, Kummrow, & Umbuzeiro, 2014) .

The parameters obtained by the mathematical kinetic model 1/m (initial TP degradation - Equation 11) and 1/b (maximum TP degradation - Equation 12) was also correlated with operational parameters (H_2O_2 and Fe concentrations) regarding coded factors.

$$\frac{1}{m} = 0.789 + 0.203Fe \quad (11) \quad (11)$$

$$\frac{1}{b} = 0.903 + 0.017Pe + 0.020Fe \quad (12) \quad (12)$$

The ANOVA analysis shows that the linear terms of iron concentration (Fe) affect the initial rate TP degradation (1/m) and maximum TP degradation (1/b). The hydrogen peroxide concentration (Pe) also influence the maximum TP degradation (1/b).

Toxicity assay

For bioassays, the experiments were conducted only in the factorial conditions of experimental design and added a central point, resulting in five experiments. Means values of IC_{50} were compared for each treatment by analysis of variance (ANOVA) and the Tukey test at the significance level ($p < 0.05$) (Table 5).

The absolute germination (AG) and the germination index (GI) were strongly inhibited by the presence of soluble toxic compounds in non-treated sourwater.

Regarding treated stripped sourwater by Fenton process, the absolute germination (AG) obtained was greater than 80%. This fact may be related to the low concentration of toxic compounds, which were insufficient to affect the germination process.

From IC_{50} values, the ANOVA analysis was applied with Tukey test ($p < 0.05$) to evaluate the difference among the Fenton treatments. It was shown that H_2O_2 concentration was the factor that affected the most the inhibition concentration (IC_{50}). For treated sourwater, the experiments using a lower concentration of H_2O_2 presented higher IC_{50}. Accordingly, treatments using the highest initial concentration of H2O2 resulted in lower inhibition growth concentration (IC_{50}). In these cases, treated sourwater showed greater degradation of total phenols, but probably the generation of oxidation intermediates inhibited the root growth and presented lower values of GI and IC_{50}.

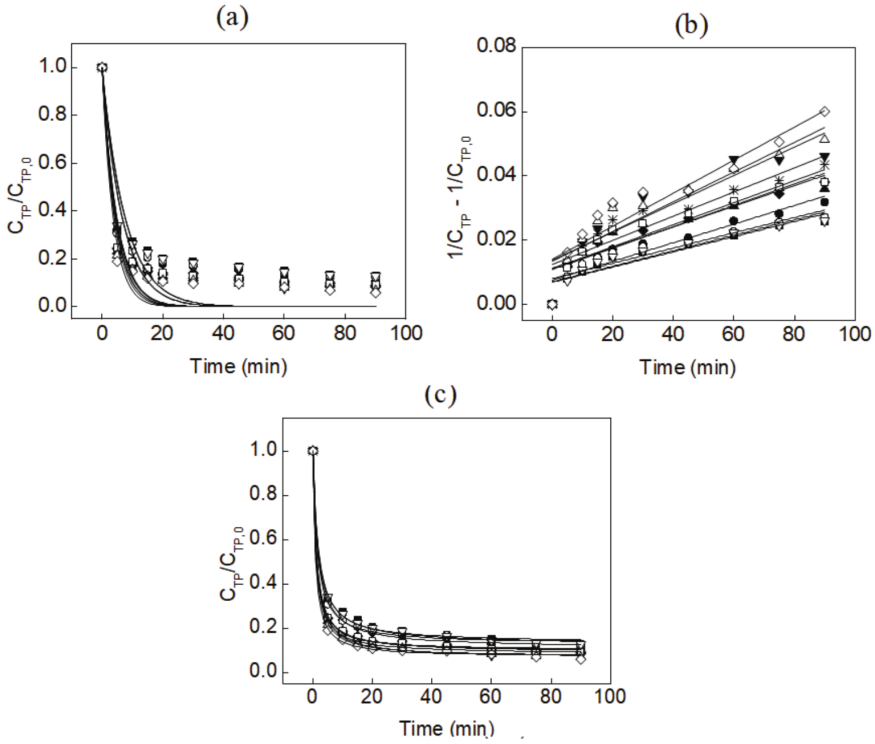

FIGURE 2.
Total phenols decay curves of stripped sourwater for different Fenton conditions(▪) F (-, -); (●) F (+, -); (▲) F (+, -); (▼) F (+, +); # F (0, 0) 1; (*) F (0, 0) 2; (□) F (0, 0) 3; (○) F (-1.41, 0); (Δ) F (+1.41, 0); F (0, -1.41); (◊) F (0, +1.41); (-) Model; (a) Pseudo-first order model; (b) Pseudo-second order model; (c) Mathematical kinetic model.

TABLE 5.
Percentage of the absolute germination and the germination index average value for lettuce seed bioassays, at different dilutions (6, 12, 25, 50 and 100%) and estimated half inhibition growth concentration (IC50) of non-treated and treated stripped sourwater solutions.

Process	% Treated stripped sourwater solution										IC_{50} (%)	Confidence interval (95%)
	6		12		25		50		100			
	AG	GI	AG	GI	AG	GI	AG	GI	AG	GI		
EF	93	76	90	65	23	10	10	2	0	0	22[a]	(2-41)
F (-, -)	100	73	97	112	93	78	97	68	87	37	80[cd]	(75-84)
F (-, +)	90	95	100	102	93	107	97	68	90	55	99[d]	(85-114)
F (+, -)	97	98	93	89	97	54	87	13	83	6	42[ab]	(36-48)
F (+, +)	90	61	90	76	90	43	93	40	87	10	32[a]	(30-34)
F (0, 0)	90	106	93	112	93	78	100	73	80	20	66[bc]	(54-77)

AG – Absolute germination; GI – Germination index; EF- untreated sourwater. Data are expressed as the mean of IC_{50} and were analyzed by one-way analysis of variance (ANOVA). Mean values followed by the same letter within a column are not significantly different by Tukey test at the 5% level among samples for each treatment.

Conclusion

The CCD full factorial design combined with response surface methodology was applied to the treatment of sourwater by Fenton process. The iron concentration was the factor that affected the most the total phenol degradation of the process. The optimal reaction conditions were H_2O_2 concentration 4.4 g L^{-1} and iron concentration 162 mg L^{-1}.

The mathematical model based on the studies of Chan and Chu (2003) and Behnajady et al. (2007) was suitable for describing the kinetic total phenols degradation of sourwater by Fenton process.

In general, treated sourwater by Fenton process revealed an improvement in the effluent quality, due to the results presented germination rate above 80% with *Lactuca sativa*.

The overall results of this study indicate that the application of Fenton′ reagents is a feasible treatment due to its easy handling, allowing to achieve a satisfactory degradation of total phenols. The use of RSM and kinetic models allow predicting the results of TP degradation of Fenton reagents. The use of a simple tool such as the toxicity test using L. sativa allows the assessment of the quality and effectiveness of the effluent treatment system.

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References

Bautista, P., Mohedano, A. F., Gilarranz, M. A., Casas, J. A., & Rodriguez, J. J. (2007). Application of Fenton oxidation to cosmetic wastewaters treatment. Journal of Hazardous Materials, 143(1-2), 128-134. doi: 10.1016/j.jhazmat.2006.09.004

Behnajady, M. A., Modirshahla, N., & Ghanbary, F. (2007). A kinetic model for the decolorization of C.I. Acid Yellow 23 by Fenton process. Journal of Hazardous Materials, 148(1-2), 98-102. doi: 10.1016/j.jhazmat.2007.02.003

Brink, A., Sheridan, C. M., & Harding, K. G. (2017). The Fenton oxidation of biologically treated paper and pulp mill effluents: a performance and kinetic study. Process Safety and Environmental Protection, 107, 206-215. doi: 10.1016/j.psep.2017.02.011

Chan, K. H., & Chu, W. (2003). Modeling the reaction kinetics of Fenton's process on the removal of atrazine. Chemosphere, 51(4), 305-311. doi: 10.1016/S0045-6535(02)00812-3

Coelho, A., Castro, A. V., Dezotti, M., & Santanna, G. L. (2006). Treatment of petroleum refinery sourwater by advanced oxidation processes. Journal of Hazardous Materials, 137(1), 178-184. doi: 10.1016/j.jhazmat.2006.01.051

El-Naas, M. H., Alhaija, M. A., & Al-Zuhair, S. (2014). Evaluation of a three-step process for the treatment of petroleum refinery wastewater. Journal of Environmental Chemical Engineering, 2(1), 56-62. doi: 10.1016/j.jece.2013.11.024

Garcia-Segura, S., Bellotindos, L. M., Huang, Y. H., Brillas, E., & Lu, M. C. (2016). Fluidized-bed Fenton process as alternative wastewater treatment technology - A review. Journal of the Taiwan Institute of Chemical Engineers, 67, 211-225. doi: 10.1016/j.jtice.2016.07.021

Garcia, J. C., Simionato, J. I., Almeida, V. C., Palácio, S. M., Rossi, F. L., Schneider, M. V., & Souza, N. E. (2009). Evolutive follow-up of the photocatalytic degradation of real textile effluents in TiO2 and TiO2/H2O2 systems and their toxic effects on Lactuca sativa seedlings. Journal of the Brazilian Chemical Society, 20(9), 1589-1597. doi: 10.1590/S0103-50532009000900005

Guedes, A. M. F. M., Madeira, L. M. P., Boaventura, R. A. R., & Costa, C. A. V. (2003). Fenton oxidation of cork cooking wastewater - Overall kinetic analysis. Water Research, 37(13), 3061-3069. doi: 10.1016/S0043-1354(03)00178-7

Hasan, D. B., Aziz, A. R. A., & Daud, W. M. A. W. (2012). Oxidative mineralization of petroleum refinery effluent using Fenton-like process. Chemical Engineering Research and Design, 90(2), 298-307. doi: 10.1016/j.cherd.2011.06.010

Hydrometric. (2002). Treatment of sour water at a petroleum refinery, US Patent 5,925,255. Hydrometric.

International Organization for Standardization [ISO]. (1995). Soil quality - determination of the effects of pollutants on soil flora. Part 2: Effects of chemicals on the emergence of higher plants. Genève, CH: ISO.

International Petroleum Industry Environmental Conservation Association [IPIECA]. (2010). Petroleum refining water / wastewater use and management. London, GB: Ipieca.

Luna, L. A. V., Silva, T. H. G., Nogueira, R. F. P., Kummrow, F., & Umbuzeiro, G. A. (2014). Aquatic toxicity of dyes before and after photo-Fenton treatment. Journal of Hazardous Materials, 276, 332-338. doi: 10.1016/j.jhazmat.2014.05.047

Organização para a Cooperação e Desenvolvimento Econômico [OECD]. (2003). OECD Guideline for the testing of chemicals proposal for a new guideline. Terrestrial Plant Test: 208 seedling emergence and seedling growth test. Retrieved from https://www.oecd-ilibrary.org/docserver/9789264070066-en.pdf?expires=1557957504&id=id&accname=guest&checksum=D8F3CA3AE83379F4CB37413FF41D4331

Scalbert, A., Monties, B., & Janin, G. (1989). Tannins in wood: comparison of different estimation methods. Journal of Agricultural and Food Chemistry, 37(5), 1324-1329. doi: 10.1021/jf00089a026

Sobrero, M., & Ronco, A. (2004). Ensayo de toxicidad aguda con semillas de lechuga (Lactuca sativa L.). In G. Castillo (Ed.), Ensayos toxicologicos y métodos de evaluacion de calidad de aguas (p. 55-68). Ottawa, CA: IMTA.

Solvay Interox Inc. (2001). Hydrogen peroxide. Controlling reduced sulfur compounds, US patent 5,621,097. Solvay Interox Inc.

Sun, S. P., Li, C. J., Sun, J. H., Shi, S. H., Fan, M. H., & Zhou, Q. (2009). Decolorization of an azo dye Orange G in aqueous solution by Fenton oxidation process: effect of system parameters and kinetic study. Journal of Hazardous Materials, 161(2-3), 1052-1057. doi: 10.1016/j.jhazmat.2008.04.080

Sun, Y., Zhang, Y., & Quan, X. (2008). Treatment of petroleum refinery wastewater by microwave-assisted catalytic wet air oxidation under low temperature and low pressure. Separation and Purification Technology, 62(3), 565-570. doi: 10.1016/j.seppur.2008.02.027

Tony, M. A., & Bedri, Z. (2014). Experimental design of photo-fenton reactions for the treatment of car wash wastewater effluents by response surface methodological analysis. Advances in Environmental Chemistry, 2014, 1-8. doi: 10.1155/2014/958134

United States Environmental Protection Agency [EPA]. (1989). Lettuce seed germination (Lactuca sativa). In EPA (Org.), Protocol for short term toxicity screening of hazardous waste sites. environmental research laboratory (p. 84-94). Corvallis, OR: EPA.

United States Environmental Protection Agency [EPA]. (1996). Ecological effects test guidelines (OPPTS 850.4200): Seed germination/root elongation toxicity test. Corvallis, OR: EPA.

Wu, Y., Zhou, S., Qin, F., Zheng, K., & Ye, X. (2010). Modeling the oxidation kinetics of Fenton's process on the degradation of humic acid. Journal of Hazardous Materials, 179(1-3), 533-539. doi: 10.1016/j.jhazmat.2010.03.036

Yan, L., Ma, H., Wang, B., Mao, W., & Chen, Y. (2010). Advanced purification of petroleum refinery wastewater by catalytic vacuum distillation. Journal of Hazardous Materials, 178(1-3), 1120-1124. doi: 10.1016/j.jhazmat.2010.01.104

Yavuz, Y., Koparal, A. S., & Ö#ütveren, Ü. B. (2010). Treatment of petroleum refinery wastewater by electrochemical methods. Desalination, 258(1-3), 201-205. doi: 10.1016/j.desal.2010.03.013