



**Treatment of wastewater from the petrochemical industry by chemical Fenton process**  
**Tratamiento de agua residual procedente de la industria petroquímica con el proceso Fenton químico**

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**Abstract**

Advanced oxidation processes aid in the degradation of contaminating organic matter, as they can form easily degradable compounds by biologic processes or break organic matter down to its minerals. In this study, it was tested the chemical Fenton process of chemical oxidation for organic matter degradation of petrochemical wastewater with chemical oxygen demand higher than 20 g/L, batch laboratory experiments and continuous pilot plant tests. In batch testing, it was used the statistical factorial experiments design, confirmed by verification tests utilizing various concentrations in water and subsequently in continuous flow in a pilot plant by oxidation under the Chemical Fenton process. Variables' effects on contaminant degradation in water follow an order: pH > relation  $Fe^{2+}/H_2O_2$  > time >  $[H_2O_2]$ . The chemical Fenton process removes more than 50% of contaminants chemical oxygen demand in batch laboratory testing and more than 70% in continuous pilot plant testing. Easily oxidized organic matter consumes  $H_2O_2$  at the beginning of the process, whereas organic matter that was more difficult to degrade was oxidized with a hydroxyl radical (OH•).

*Keywords:* Wastewater, petrochemical industry, chemical Fenton process, pilot test.

**Resumen**

Los procesos de oxidación avanzada son de ayuda para la degradación de la materia orgánica contaminante, porque puede formar compuestos fácilmente degradables por procesos biológicos o definitivamente degradar la materia orgánica hasta su mineralización. En este trabajo se probó el proceso Fenton de oxidación química para la degradación de la materia orgánica de un agua residual procedente de la industria petroquímica con más de 20 g/L de Demanda Química de Oxígeno. Se realizaron pruebas de lote en laboratorio y pruebas en continuo en planta piloto. En las pruebas de lote se usó un diseño de experimentos estadístico factorial, el cual se corroboró con pruebas de verificación empleando aguas con diferentes concentraciones y posteriormente en un flujo continuo en una planta piloto de oxidación con proceso Fenton químico. El efecto de las variables sobre la degradación de los contaminantes en el agua va de acuerdo al siguiente orden: pH > relación  $Fe^{2+}/H_2O_2$  > time >  $[H_2O_2]$ . El proceso Fenton químico puede remover más del 50 por ciento de la Demanda Química de Oxígeno en las pruebas de lote y más del 70% en las pruebas continuas. La materia orgánica fácilmente oxidable consume el  $H_2O_2$  en el inicio, mientras que la materia orgánica más difícil de degradar fue oxidada con el radical hidroxilo (OH•).

*Palabras clave:* Aguas residuales, industria petroquímica, proceso Fenton químico, planta piloto.

**1 Introduction**

Waste generation by companies dedicated to petroleum refining and transformation is high; therefore, alternative options should be sought to

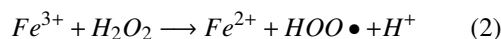
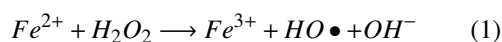
treat this waste (Awaleh *et al.*, 2014; Diya'uddeen *et al.*, 2011; Hu *et al.*, 2013; Hernández-Martínez *et al.*, 2018; López *et al.*, 1999). Generated waste includes wastewater transporting abundant organic loads when leaving processes, which indicates a high concentration of petroleum products or byproducts (Yu *et al.*, 2017).

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Companies generating process wastewater or contaminated water treat them by biological processes, which sometimes are insufficient due to the high organic load present in the water. Alternative or complementary processes exist for treatment of this type of water (Diya *et al.*, 2011; Yu *et al.*, 2017; Zhong *et al.*, 2003), including advanced oxidation processes producing a hydroxyl radical (HO•) (Cheng *et al.*, 2016; Oliveros *et al.*, 1997), with oxidation potential only exceeded by fluorine. The hydroxyl radical can degrade large amounts of organic compounds. Systems capable of generating hydroxyl radicals include Fenton processes (chemical, electro, and photo) (Arslan-Alaton *et al.*, 2014; Araña *et al.*, 2001; Bing *et al.*, 2015; Babuponnusami and Muthukumar, 2014; Chang *et al.*, 2004; Anotai *et al.*, 2006; Guivarch *et al.*, 2003; Khoufi *et al.*, 2004; Peralta-Hernandez *et al.*, 2005; Saltmiras and Lemley, 2000; Umar *et al.*, 2010), UV-H<sub>2</sub>O<sub>2</sub> (Castillo *et al.*, 1999; Molkenthin *et al.*, 2013; Peralta-Hernandez *et al.*, 2008), O<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> (Gulyas *et al.*, 1994), photocatalysis, and radiocatalysis with titanium oxides as catalysts (Jiménez-Becerril *et al.*, 2013), among others (Dimoglo *et al.*, 2004; Hesse *et al.*, 1999; Merayo *et al.*, 2013; Oller *et al.*, 2011). In Mexico, specifically in Coatzacoalcos-Minatitlán-Cosoleacaque, an industrial zone in Veracruz, many petrochemical companies are clustered (Gonzalez-Mille *et al.*, 2010; Rodríguez-Dozal *et al.*, 2012; SEMARNAT 2008), including PEMEX petrochemical complexes. Those companies wastewater treatment systems can no longer purify their organic loads; therefore, it is necessary to explore other appropriate processes to work online with current processes or replace existing ones to discharge treated waters to rivers or lagoons. An alternate process to treat petrochemical waters is the Fenton chemical process, in which ferrous ions are oxidized into ferric ions by the hydrogen peroxide effect (Equation 1), forming a hydroxyl radical and hydroxide ion. Ferric ions are subsequently reduced to ferrous ions by another hydrogen peroxide molecule forming the superoxide radical and a proton (Equation 2). The proton and hydroxide ions are combined to form water molecules, and free radicals react with contaminant substances to oxidize them (GilPavas *et al.*, 2012; Panizza, and Cerisola, 2001; Peralta-Hernandez *et al.*, 2006).



From Equations 1 and 2, it can be determined that concentrations of free hydroxyl radicals are directly influenced by ferrous ions, hydrogen peroxide, and [OH<sup>-</sup>] (Park *et al.* 1999). In this study, it was tested the Chemical Fenton process of chemical oxidation for organic matter degradation of Petrochemical wastewater with COD higher than 20 g/L, batch laboratory experiments and continuous pilot plant tests

## 2 Materials and methods

The present work included the following three procedures:

### 2.1 Tests developed under statistical experiment design (Series I)

Experiment's Samples were analyzed by COD and toxicity. The COD was measured according to the procedure indicated in the HACH water analysis manual (HACH, 2000), using a HACH DR 4000 spectrometer. Testing was done in 1-L beakers agitated in stainless-steel flat propellers in a Phipps & Bird agitator model PB-700. Values obtained were normalized to initial value as the percentage of total removal after the experiment. Batch testing was performed.

Toxicity was determined with Deltatox high-sensitivity equipment using the bacteria lyophilisate (*Vibrio fischeri*), which is a standardized method to measure toxicity used in tasks in which it plays an important role (Steliga *et al.*, 2015).

The ferrous sulfate used during testing was analytical-grade FeSO<sub>4</sub>·7H<sub>2</sub>O (J. T. Baker ACS). The hydrogen peroxide solution utilized was 30% analytical degree (HACH). Analytical-grade H<sub>2</sub>SO<sub>4</sub> was used to adjust the pH. Wastewater samples were taken from a petrochemical company whose specialty is tensoactive and surfactant manufacturing. Its characterization was carried out by Intertek Testing Services according to the following standards: Conductivity NMX-AA-093-SCFI-2000, pH NMX-AA-008-SCFI-2000, COD NMX-AA-030-SCFI-2001, BOD NMX-AA-028-SCFI-2001 (Table 1).

Table 1. Characterization of wastewater from a petrochemical company.

Parameter	Conductivity ( $\mu\text{S cm}^{-1}$ )	pH (mg/L)	COD (mg/L)	BOD (%)	Toxicity
Waste water	590.2	5.17	31,650	11,414	97.33

Table 2. Variables and levels used in the experimental design.

Level \ Parameter	pH	[H <sub>2</sub> O <sub>2</sub> ] (g/L)	Ratio Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub>	Time (h)
L1	3	4.5	0.27	1
L2	4	13.6	0.33	3

Variables and levels in the chemical Fenton process considered in the experimental design are indicated in Table 2 (Oliveros *et al.*, 1997; Panizza and Cerisola, 2001), showing that two levels and four variables are utilized. [H<sub>2</sub>O<sub>2</sub>] values are respect to high COD concentration.

The expression Experiments = Levels<sup>parameters</sup> reveals, 2<sup>4</sup>=16 experiments to be developed by applying the Stat-graphics program, which is an assistance program in statistical-experiment design and data analysis (San Pedro-Cedillo *et al.*, 2015; Lira-Pérez *et al.*, 2019). Analysis of variance (ANOVA) is a decision-making tool for detecting variations in process parameters. It is a statistical technique used to determine the optimal level of factors for the verification of the optimal design parameters through confirmation experiments. ANOVA is one of the most common statistical methods applied to analysis results

to determine each parameter’s contribution ratio and rank (Hernández-Martínez *et al.*, 2018). In general, the ANOVA technique has been used to find the significant effect level of influencing parameters in response. The resulting experimental matrix is shown in Table 3.

## 2.2 Verification testing with degradation reaction variables on various COD wastewater concentrations (Series 2)

The wastewater used here came from the same company as the wastewater used in the Series 1 experiments. The experiment procedure and materials utilized were the same as those utilized in the Series 1 experiments. Series 1 testing results provided experimental conditions with the highest COD removal percentage, and wastewater testing was developed with various initials, as shown in Table 4.

Table 3. Experimental conditions matrix.

Experiment number	pH	[H <sub>2</sub> O <sub>2</sub> ] (g/l)	Ratio Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub>	Time (h)
1	3	4.49	0.27	1
2	4	4.49	0.27	1
3	3	13.65	0.27	1
4	4	13.65	0.27	1
5	3	4.49	0.33	1
6	4	4.49	0.33	1
7	3	13.65	0.33	1
8	4	13.65	0.33	1
9	3	4.49	0.27	3
10	4	4.49	0.27	3
11	3	13.65	0.27	3
12	4	13.65	0.27	3
13	3	4.49	0.33	3
14	4	4.49	0.33	3
15	3	13.65	0.33	3
16	4	13.65	0.33	3

Table 4. Initial conditions and COD removal for the verification tests of series 2. (pH = 3, [H<sub>2</sub>O<sub>2</sub>] = 13.6 g/L, Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> = 0.27).

Experiment number	17	18	19	20	21	22	23	24
Time (h)	1	3	1	3	1	3	1	3
Initial COD (mg/L)	29850	29850	31900	31900	35450	35450	13400	13400
COD removal (%)	57.8	64.7	40	49.5	49.6	54.9	56.3	66.4

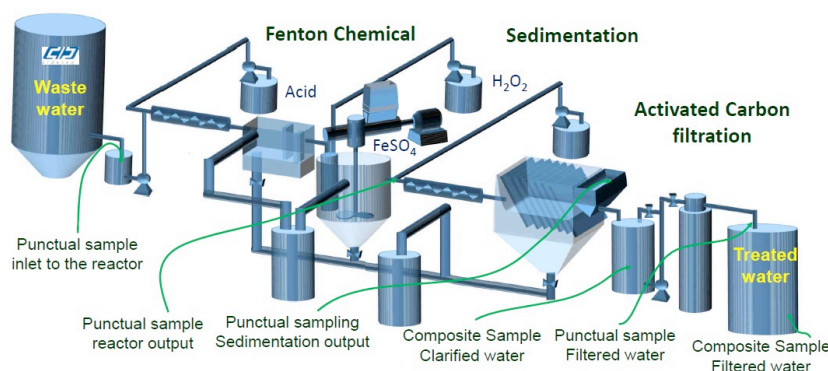


Fig. 1. Fenton Chemical pilot plant process schematic diagram.

### 2.3 Pilot testing developed with the wastewater sample (Series 3)

With the conditions obtained in Series 1 and 2, pilot-level testing was developed. The pilot plant used for Fenton chemical oxidation had a capacity of 0.7 L/min of wastewater with non-biodegradable organic compounds. Pilot plant process: Wastewater was stored in a 2 m<sup>3</sup> tank and afterwards it was fed to the continuous process using a PVC pipe with a peristaltic pump (Fig. 1). Later it was conducted to a static mixer and sulfuric acid was added to adjust pH= 3.0. The wastewater was submitted to a coalescing plate separator, where the fat and oil were separated, before to be conducted to the Fenton oxidation reactor. In this reactor, wastewater was mixed with H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub>. H<sub>2</sub>O<sub>2</sub> solution was fed with a dosing pump and the FeSO<sub>4</sub> powder through a screw feeder. The reaction time was 3 h. The produced foams were separated by overflow into the fat and oil collecting tank. The oxidized wastewater that leaves the Fenton oxidation reactor leads to a second static mixer where the effluent was neutralized at pH=6 with NaOH solution. The separation of the total suspended solids was done in a Lamellar Plate settler, where the clear water was separated and stored in a clear water

tank. Clear water was filtered in an activated carbon filtration system and finally discharged into the treated water tank. Fig. 1 shows the scheme used in the pilot plant, indicating sampling points.

The iron sulphate used in the pilot testing was FeSO<sub>4</sub>·7H<sub>2</sub>O technical degree added in solid form with a worm screw dispenser designed to insert the required dose continuously. The hydrogen peroxide solution used was 30% technical degree. The water was obtained from the same company as in series 1 and 2; however, this sample was obtained at a later date. The COD concentration in the water was 23,725 mg/L. Samples of process were taken and they were analyzed by COD and toxicity.

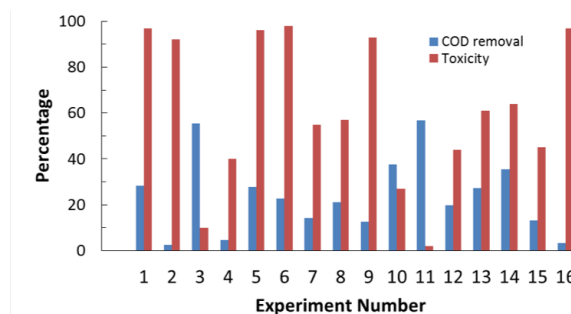


Fig. 2. COD removal and toxicity percentage for the experiments of series 1.

### 3 Results and discussion

#### 3.1 Results of the tests of the factorial statistical experimental design (Series 1)

Degradation resulting in the function of response variables is shown in Fig. 2, revealing that the maximum COD removal obtained was 56.6% and toxicity was reduced at 2%.

For the purpose of result analysis, they were grouped together according to variables. The variable pH-Time-% of COD removal (Fig. 3) on the graph indicates that when pH = 4, at longer times, the compound's degradation reaction in the sample was facilitated by the chemical Fenton process effect; however, when pH = 3, the removal percentage decreased with longer reaction times. Fig. 3 shows that the removal percentage was lower when pH = 4.

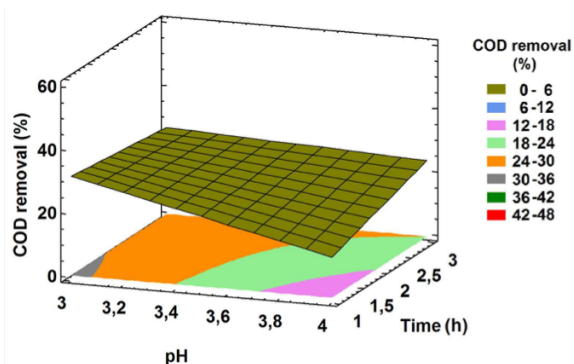


Fig. 3. The pH value and time effect over COD removal percentage of series 1.

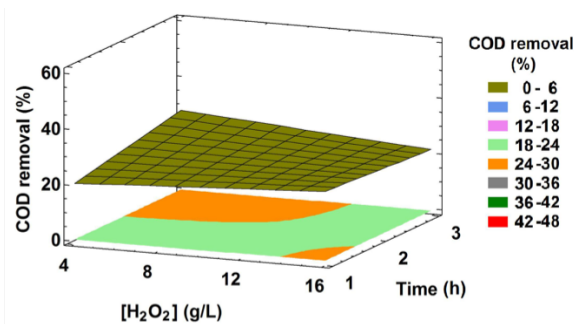


Fig. 4. [H<sub>2</sub>O<sub>2</sub>] value and time effect over COD removal percentage of series 1.

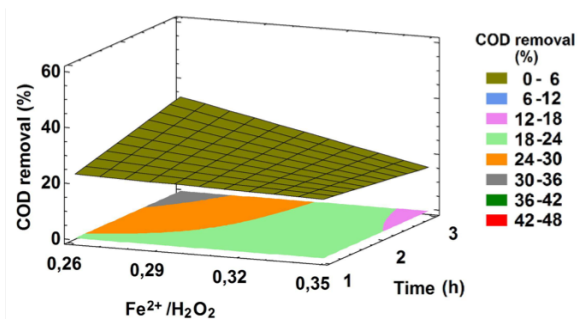


Fig. 5. Fe<sup>2+</sup>/ H<sub>2</sub>O<sub>2</sub> rate and time effect over COD removal percentage of series 1.

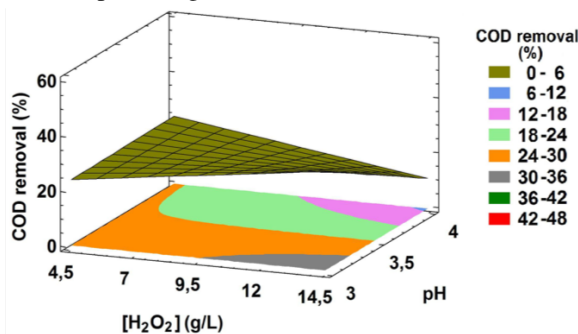


Fig. 6. [H<sub>2</sub>O<sub>2</sub>] value and pH effect over COD removal percentage of series 1.

Fig. 4 shows that [H<sub>2</sub>O<sub>2</sub>]-time rate has little influence on COD removal: the removal percentage increases slightly, which means that with increasing [H<sub>2</sub>O<sub>2</sub>] and shorter retention times, a slight increase occurs within an interval from 18% to 20% removal, but when reaction times are approximately 3 h, the removal percentage decreases, and the [H<sub>2</sub>O<sub>2</sub>] level increases.

On the other hand, at low [H<sub>2</sub>O<sub>2</sub>] levels, the removal percentage is affected to a greater extent than at high [H<sub>2</sub>O<sub>2</sub>] levels, as the reaction speed is higher with high [H<sub>2</sub>O<sub>2</sub>] levels with almost no time effect; therefore, more time is necessary with lower [H<sub>2</sub>O<sub>2</sub>] levels for a total reaction to occur.

During the Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> rate increase at 1-h reaction times, this event causes the COD removal percentage to remain almost constant (Fig. 5); however, when the time is 3 h, the removal percentage decreases as the Fe<sup>2+</sup>/ H<sub>2</sub>O<sub>2</sub> rate increase. Under Fe<sup>2+</sup>/ H<sub>2</sub>O<sub>2</sub> rates of 0.26, as well as comparing 1 and 3 h, the removal percentage increases from 20% to 30% approximately. Also, the Fe<sup>2+</sup>/ H<sub>2</sub>O<sub>2</sub> rate is equal to the 0.32 removal percentage and suffers slight variations in the 10% to 20% range, indicating that [H<sub>2</sub>O<sub>2</sub>] addition has a higher effect over removal percentage, thus requiring more time to allow reaction completion.



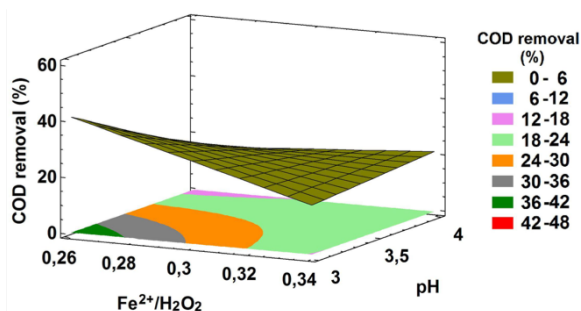


Fig. 7. [H<sub>2</sub>O<sub>2</sub>] value and time effect over COD removal percentage of series 1.

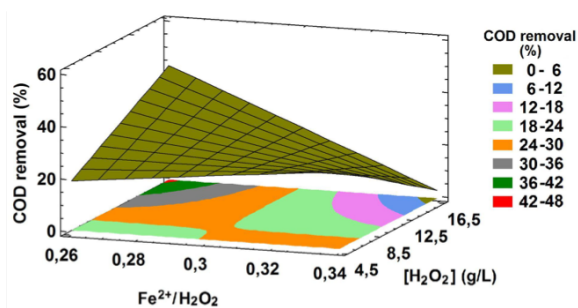
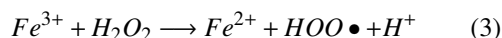


Fig. 8. Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> rate and [H<sub>2</sub>O<sub>2</sub>] value over COD removal percentage of series 1.

By relating [H<sub>2</sub>O<sub>2</sub>] to pH, it can be observed that at pH = 3, the COD removal increases with [H<sub>2</sub>O<sub>2</sub>] (Fig. 6) and at pH = 4, the removal percentage is reduced from 22% to 10%. When the [H<sub>2</sub>O<sub>2</sub>] value is maintained at 5 gr/L and the pH value varies from 3 to 4, a slight increase in removal percentage occurs. When the [H<sub>2</sub>O<sub>2</sub>] value is 13, the removal percentage is reduced from 35% to 10%; this situation indicates that [H<sub>2</sub>O<sub>2</sub>] positively impacts the reaction as the pH value decreases; therefore, at low pH values and high [H<sub>2</sub>O<sub>2</sub>] concentrations, higher organic matter removal percentages occur. It means that H<sub>2</sub>O<sub>2</sub> in excess react with the organic matter easily degradable before the HO• production. High [H<sup>+</sup>] promote the Equation 1 by OH<sup>-</sup> neutralization. In any case, the expectation is that high acidity concentrations will inhibit organic matter degradation reaction due to Equation 2, as the production of high H<sup>+</sup> ions concentrations will cause the Equation 2 trends to occur slowly or to stop occurring.



The H<sub>2</sub>O<sub>2</sub> concentration plays an important role in water contaminants removal, as its concentration increase affects more than the Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> rate increase

when working at low rates (Fig. 8); however, when the Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> rate is high, there is no substantial effect by the H<sub>2</sub>O<sub>2</sub> rate increase. Under the Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> rate and H<sub>2</sub>O<sub>2</sub> concentration conditions, the best COD removal efficiencies are obtained (from 32 to 42%, at Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> = 0.27 and [H<sub>2</sub>O<sub>2</sub>] higher than 11 g/L). The high COD concentration in waste water is 31.650 g/L while [H<sub>2</sub>O<sub>2</sub>] is 13.6 g/L, it means that there are organic matter available and the COD removal may be improved by H<sub>2</sub>O<sub>2</sub> addition.

The best conditions during previous tests, and the results obtained showed that variables most affecting the process follow the order, pH > Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> > time > [H<sub>2</sub>O<sub>2</sub>], which is in agreement with the ANOVA analysis and Pareto diagram. This may be due to the high content of organic matter degradable by oxidation, which, when contacted with acid and hydrogen peroxide, reacts instantaneously by avoiding the pair Fe<sup>2+</sup>-H<sub>2</sub>O<sub>2</sub> to work in a normal way so as to produce the hydroxyl ion (OH•). However, after a while, the relational effect of Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> becomes important due to the depletion of organic matter easily degradable by oxidation. It is observed that part of the organic matter reacts by reducing the pH; thus, due to the addition of sulfuric acid, the reduction reaction becomes more predominant than the oxidation reaction. Due to the reactivity of the system, the use of prolonged reaction times only helps when there is an excessive amount of reagents that allow reaction with the products of the initial reactions or that allow the products to come into contact with the organic matter degradable by the oxidation that is still present. The ANOVA analysis and Pareto diagram indicate that the combined effects follow the next order:

$$Fe^{2+}/H_2O_2/[H_2O_2] > [H_2O_2]/pH > Fe^{2+}/[H_2O_2]/pH > pH/time > Fe^{2+}/H_2O_2/time > [H_2O_2]/time$$

### 3.2 Verification testing over degradation reaction at different COD concentrations in water (Series 2)

Table 4 shows the replicated test results, with the best conditions obtained in previous tests, showing that the COD removal percentage for samples varied between 40% and 66.4%. However, for the compound samples (Experiments 23 and 24), the same removal percentage was maintained between 56.3% for 1 and 66.4% for 3 reaction hours, and this situation has certain similarity with previous results (i. e. 56.6%)

### 3.3 Pilot-level testing performed over wastewater sample (Series 3).

The pilot plant operation was carried on under the following condition: pH 3,  $[H_2O_2]$  13.65,  $Fe^{2+}/H_2O_2$  0.27 and time 3 h.

COD degradation values reached a steady state for Test through the treatment train in the pilot plant, as shown in Fig. 9. The identification samples mentioned above correspond to Fig. 1, showing each sampling points where they were taken. The results indicate that, following the pilot plant diagram, a COD removal percentage of 84.4 can be obtained; likewise, at the chemical Fenton reactor exit, between 55% and 63% of COD removal is obtained, and these values coincide with those obtained during experimental testing through laboratory tests. The increase in COD removal using all the treatment plant processes is due to the combination of the oxidation process and the adsorption process, in which the organic matter undergoes a primary degradation; subsequently, the residual organic matter is adsorbed on activated carbon (San Pedro-Cedillo et al., 2015).

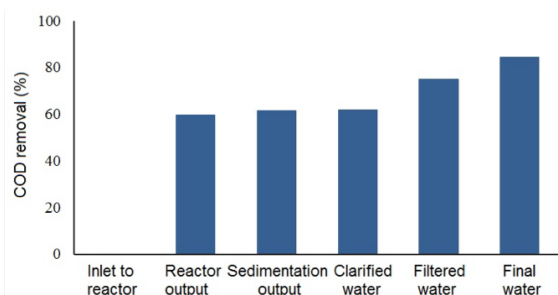


Fig. 9. COD removal percentage with respect to the sampling points in the pilot plant with Fenton chemical process, Series 3.

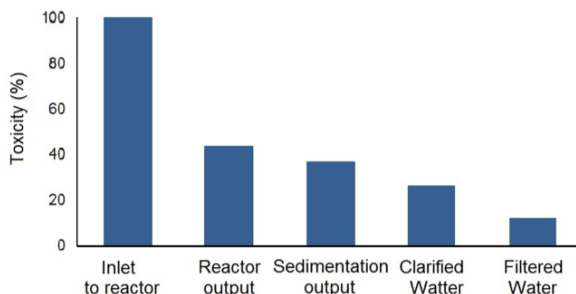


Fig. 10. Toxicity values with respect to the sampling points in the pilot plant with Fenton chemical process, Series 3.

Fig. 10 shows the toxicity values for a chemical industry-treated effluent over each sampling point in the chemical Fenton advanced oxidation pilot plant in a steady state. Toxicity values, that determine toxicity, show that the chemical Fenton pilot plant has a decreased toxicity value according to the 100% original sample value, reaching values between 6% and 25% toxicity for a sample treated after the filtration process and between 27% and 31% toxicity for a sample treated before the clarified water tank. The toxicity measurements are an indirect indication that treated wastewater has changed its characteristics due to higher biodegradability. The results of the tests performed under a statistical design system, series 1 (i.e., tests with water with different COD values and the Fenton pilot plant tests) maintained consistency because COD removal percentages of around 56% were obtained when the chemical Fenton system was utilized. In the results of the tests performed at the pilot plant, COD removal of ~80% was obtained due to the complementary operations carried out in its design.

The above indicates that the studied system presents an alternative for petrochemical wastewater treatment; however, it should be taken as a complementary process as the contaminants present are not completely eliminated.

## Conclusions

In the performed tests, it was showed that the variables effects over water pollutants to reduce COD has the following order:  $pH > Fe^{2+}/H_2O_2 > time > [H_2O_2]$ ; also, the combined variables have the following order:  $Fe^{2+}/H_2O_2/[H_2O_2] > [H_2O_2]/pH > Fe^{2+}/[H_2O_2]/pH > pH/time > Fe^{2+}/H_2O_2/time > [H_2O_2]/time$ . The chemical Fenton process proved the ability to reduce petrochemical wastewaters' COD by more than 50% in batch testing; however, continuous testing proved the ability to remove more than 70% COD in the pilot plant due to the use of a more complete process (oxidation-adsorption).

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