

Article

Simultaneous Oxidation of Emerging Pollutants in Real Wastewater by the Advanced Fenton Oxidation Process

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Abstract: Since the conventional processes employed in most wastewater treatment plants (WWTPs) worldwide are not designed to entirely remove or oxidize emerging pollutants, which, due to their incidence and persistence, can cause damage to both the environment and human health, several options for their degradation and removal have emerged. Coupling the advanced Fenton oxidation process as a polishing or tertiary wastewater treatment alternative within conventional WWTP processes stands out among the treatment options. Therefore, the main objective of this research was to evaluate, at the laboratory level, the ability of the advanced Fenton oxidation process to oxidize triclosan, ibuprofen, DEET (*N, N*-diethyl-*meta*-toluamide), carbamazepine, caffeine, and acesulfame-K, which represent several groups of emerging pollutants in real wastewater from the second settling tank of a municipal WWTP. The compound used as a catalyst (Fe^{2+}) supplier in the advanced Fenton oxidation process was ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). The results obtained upon application showed that the advanced Fenton oxidation process could simultaneously oxidize and remove practically the total concentration of the above-mentioned emerging pollutants, except for DEET (85.21%), in conjunction with the chemical oxygen demand (COD), total suspended solids (TSS), and fecal coliforms (FC, pathogen group) in the effluent generated by the advanced Fenton oxidation process.

Keywords: wastewater; emerging pollutants; advanced Fenton oxidation process; simultaneous oxidation



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1. Introduction

The development of anthropogenic activities (agriculture, industry, and health, among others) has led to the production and use of chemicals called emerging pollutants or contaminants. Emerging pollutants are natural or synthetic organic chemicals, which are not commonly monitored in the environment but have the potential to cause harmful effects to both the environment and human health [1–3]. Emerging pollutants have been detected in surface water, groundwater, rivers, WWTPs, and drinking water [4]. Emerging pollutants can usually be classified into pharmaceuticals, personal care products, hygiene products, pesticides, hormones, food additives, flame-retardants, endocrine disruptors, lifestyle products, and others [4–8].

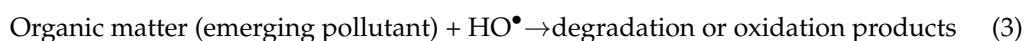
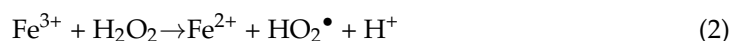
The emerging pollutants' main entry route into the general environment is through effluents generated by WWTPs using conventional biological treatments [6]. The conventional process most used worldwide for wastewater treatment by WWTPs is the activated sludge process, as far as secondary treatment is concerned [9]. Nonetheless, WWTPs usually consist of a pretreatment, which is designed to remove grease and large solids, a primary sedimentation tank, a secondary treatment, which is a biological process of

aerobic degradation (e.g., activated sludge) with a secondary settling tank, and a typical chlorination process, which is used to disinfect the effluent from the biological or secondary process [9]. However, the most used biological water treatment processes worldwide cannot remove emerging pollutants altogether [10,11], which leads to their release and constant input into the environment through treated wastewater effluents [4,6,12]. Moreover, Deblonde et al. [13], Gogoi et al. [14], and Tran et al. [15] have shown over the years that emerging pollutants are still present in the effluents of WWTPs using conventional biological processes.

Given such prospects, in recent years, there has been an increasing need to apply and add advanced tertiary treatments to conventional wastewater treatment plants (WWTP) for the emerging pollutants removal, since wastewater must be reintroduced into the environment in the most efficient way possible [6,16]. Researchers have reported that advanced oxidation processes (AOPs) are often a good option for use as tertiary or coupled processes in a conventional WWTP process for emerging pollutants removal because they generate hydroxyl radicals ($\text{HO}^\bullet$) [17] that, in sufficient quantities, can oxidize or mineralize emerging pollutants to CO_2 , H_2O , salts, and mineral acids [7,18]. It is essential to mention that the hydroxyl radicals generated by AOPs have high oxidative power, amounting to 2.8 eV [19,20].

Among the advanced oxidation processes, the advanced Fenton oxidation process stands out because it has been reported as an efficient method for removing organic matter [21], such as emerging pollutants, at low costs compared to other AOPs [9,22]. In addition, several studies have shown that the advanced Fenton oxidation process increases the biodegradability of the treated wastewater and the emerging pollutants oxidized by this process [7,23–25].

On the other hand, the advanced Fenton oxidation process has simple reaction mechanisms, in general, for generating hydroxyl radicals [26], as shown below (Equations (1)–(3)).



Furthermore, Equation (1) shows hydrogen peroxide participation as an oxidant and ferrous ion as a catalyst [27], generating hydroxyl radical ($\text{HO}^\bullet$) as the main product [28], which then interacts with organic matter and emerging pollutants (Equation (3)) to degrade or oxidize such emerging pollutants (organic matter of interest). Consequently, the main objective of this study was to evaluate the capability of the advanced Fenton oxidation process, at the laboratory scale, when this process is applied as a tertiary treatment or polishing process to treated wastewater from a traditional WWTP to simultaneously oxidize different emerging and conventional pollutants to reach the maximum permissible limits within the Mexican regulations (NOM-001-SEMARNAT-2021 [29]).

For this study, the emerging pollutants selected for simultaneous oxidation by the advanced Fenton oxidation process in the sampled real wastewater were DEET, caffeine, carbamazepine, acesulfame-K, ibuprofen, and triclosan.

DEET is an active compound used in many insect repellents [30,31]. It was selected because it has been established that humans exposed to this chemical can develop neurological problems, such as encephalopathy [30] and skin reactions [31]. Caffeine was selected for this study because a simulation of a conventional WWTP chlorination process showed that caffeine interacts with the added chlorine and tends to form a compound called 8-chlorocaffeine, which can cause mutagenic effects, according to the Ames test [32]. Carbamazepine was selected because studies have reported that it can cause environmental damage, especially to organisms living in freshwater, and it has been consistently found in effluents from municipal WWTPs [33]. Acesulfame-K (a sweetener commonly used in

beverages and food for human consumption) was selected because this compound contains a methyl group considered a toxic xenobiotic [11]. Ibuprofen was chosen because it is the third most prescribed drug worldwide and causes carcinogenic and endocrine-disrupting effects in microorganisms, algae, fish species, and humans [34]. Triclosan was also selected in this study, as it tends to cause problems such as dermatitis [35], endocrine disruption, and microbial resistance [5].

It should be noted that these emerging pollutants were also selected because they are representative of important groups of emerging pollutants such as pharmaceuticals (carbamazepine and ibuprofen), personal care and hygiene products (DEET and triclosan), and lifestyle compounds (caffeine and acesulfame-K). Additionally, to conclude this subsection, it should be emphasized that the selected emerging pollutants were determined in the real wastewater to be treated by the advanced Fenton oxidation process and were not added in spike form.

2. Results and Discussion

2.1. Physicochemical Characterization of the Influent (Real Wastewater) and Effluent Generated by the Advanced Fenton Oxidation Process

Table 1 shows the physicochemical characterization values of the influent subjected to the advanced Fenton oxidation process and the effluent generated by this process. The effluent generated by the advanced Fenton oxidation process decreased COD, TSS, and FC concentrations for the influent (real wastewater sampled from the secondary sedimentation tank of the WWTP).

Table 1. Results of the physicochemical characterization of the influent and effluent generated by the advanced Fenton oxidation process.

Determination	Influent (Sampled Real Wastewater)	Effluent Generated by the Advanced Fenton Oxidation Process	Percentage Removal (%)
pH	8.01	7.12 ± 0.07	ND
Temperature (°C)	25	25.35 ± 0.35	ND
Floating matter	Absence	Absence	ND
Settleable solids (mL/L)	Absence	Absence	ND
COD (mg/L)	54 ± 1.41	26.50 ± 7.78	50.93 ± 14.40
TSS (mg/L)	45 ± 21.21	17.50 ± 5.00	72 ± 7.54
Total phosphates (mg/L)	0.7	1.55 ± 1.63	ND
Total nitrogen (mg/L)	2.5	2.8	ND
FC (*MPN/100 mL)	111,200	<1	>99.9%
Iron total (mg/L)	*ND	4.41 ± 0.38	ND

*ND: Not determined; *MPN: Most probable number.

The influent went from average concentrations of COD = 54 mg/L, TSS = 45 mg/L, and FC = 111,200 MNP/100 mL to average concentrations of 26.5 mg/L, 17.5 mg/L, and <1 MNP/100 mL, respectively.

The 50.93% COD average removal (Table 1) indirectly indicates that there was also oxidation of the emerging pollutants of interest. López-Velázquez et al. [36] showed that, despite having an average COD removal of 37.33%, they could completely oxidize the emerging pollutants of interest for their research. Then, the reduction in COD also indicates the feasibility of the advanced Fenton oxidation process in removing this macro-pollutant from different types of wastewater, as several researchers have demonstrated in their studies over time [37–41].

In addition, the FC concentration reduction (>99.9%) in the effluent generated by the advanced Fenton oxidation process (Table 1) shows that the applied approach could act as a disinfection method, as indicated by Polo-López et al. [42].

Regarding the average removal of TSS (72%) (Table 1) generated by the advanced Fenton oxidation process, this is directly attributed to the precipitation of ferric ions since a large part of the suspended solids could adhere to such precipitates.

However, the average total iron concentration that remained in the effluent was 4.41 mg/L (Table 1). In terms of the total phosphate concentration, total nitrogen concentration, settleable solids concentration, and floating matter, there was no considerable change in these parameters after the advanced Fenton oxidation process.

Furthermore, according to the current regulations in Mexico (NOM-001-SEMARNAT-2021 [29]), the effluent provided by the advanced Fenton oxidation process at the laboratory level fulfills the quality required for wastewater discharges into receiving water bodies.

Additionally, as is displayed in Table 1, Equations (1), (5), and (6) were shown to be good choices for the hydrogen peroxide (H_2O_2 , oxidant) and ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, catalyst supplier) dosage, in terms of COD, total suspended solids (TSS), and fecal coliforms (FC) reduction in the real wastewater treated by the advanced Fenton oxidation process.

2.2. Simultaneous Oxidation of the Emerging Pollutants by the Advanced Fenton Oxidation Process

Figure 1 shows the concentrations of the emerging pollutants of interest in the real untreated wastewater and the water treated by the advanced Fenton oxidation process.

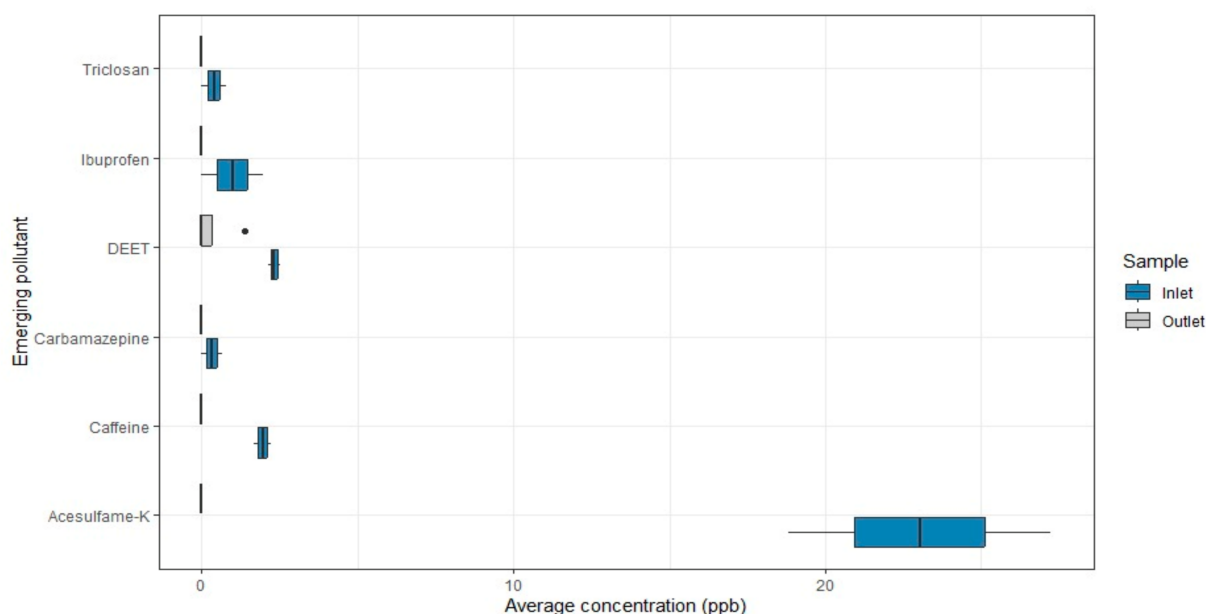


Figure 1. Emerging pollutants' concentration in untreated and treated real wastewater.

For the influent (real wastewater from the WWTP secondary settling tank), the initial concentrations determined for the emerging pollutants (Figure 1) of concern were as follows: triclosan (0.40 ± 0.56 ppb), ibuprofen (0.98 ± 1.39), DEET (2.32 ± 0.28 ppb), carbamazepine (0.33 ± 0.47 ppb), caffeine (1.96 ± 0.39 ppb), and acesulfame-K (23.03 ± 5.96 ppb) (Figure 1).

It should be noted that concentrations detected in the real wastewater from the second settling tank of the WWTP, subjected to the advanced Fenton oxidation process, are evidence that the conventional methods used in WWTPs cannot usually degrade all emerging pollutants [10,11,43].

However, it can be observed how the real wastewater treated by the advanced Fenton oxidation process brought most of the emerging pollutants of concern (Figure 1) to unquantifiable levels ($< \text{LOQ}$) in 1 h. This indicates that the advanced Fenton oxidation process did oxidize the emerging pollutants of concern despite having an average COD removal of 50.93%, which is like those previously reported by Lopez-Velazquez et al. [36], who,

despite having a COD removal of 37.33%, managed to oxidize the emerging pollutants of interest in their research. Consequently, based on the results obtained (Figure 1), it is feasible to use Equations (1), (5) and (6) in the advanced Fenton oxidation process to dose hydrogen peroxide (H_2O_2 , oxidant) and ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, catalyst supplier), using wastewater COD as the basis of calculation.

Additionally, it should be noted that the advanced Fenton oxidation process did not wholly oxidize DEET since 0.34 ± 0.69 ppb remained in the real treated wastewater (Figure 1).

On the other hand, the average oxidation percentage of most emerging pollutants of interest was almost 100%. For example, in the case of DEET, the average oxidation percentage was as high as $85.21\% \pm 20.92\%$. Therefore, the advanced Fenton oxidation process is an excellent option for simultaneously oxidizing and removing emerging pollutants of interest in real wastewater.

The simultaneous oxidation of emerging pollutants generated by the advanced Fenton oxidation process is attributed to the hydroxyl radicals ($\text{HO}^\bullet$) generated because these radicals are non-selective [6] and attack any contaminant indiscriminately.

Concerning research that has employed the advanced Fenton oxidation process and its variants, specifically for triclosan removal or oxidation, it has been observed that the studies carried out over time have had good removal percentages that vary from 90% to 99.5% [44–46]. However, unlike the present study, the studies mentioned above used synthetic triclosan solutions and not real wastewater as an influent of the advanced Fenton oxidation process.

Various research works using the advanced Fenton oxidation process to eliminate ibuprofen had removal percentages ranging between 60 and 84.68% [47,48], which are lower than those obtained in the present study. However, this could be attributed to the fact that different hydraulic retention times have been used in the research, and dosage calculations of the oxidant and the catalyst added to the wastewater have been different compared to those used in the present study.

Regarding carbamazepine and acesulfame-K, the present study shows higher oxidation yields in comparison to other works on acesulfame-K (50%) [49] and carbamazepine (53.73%) [50]. Nevertheless, for caffeine, the removal percentages are quite similar to those found in other works [36,51].

It should be highlighted that no research was found in the case of DEET. However, these results show that it can be removed by the advanced Fenton oxidation process (oxidation yield = 85.21%).

Moreover, all the investigations referenced in this subsection regarding removing the emerging pollutants of interest used different experimental conditions. They treated different water matrices than those used in this study. Therefore, the results obtained at the laboratory level show that the advanced Fenton oxidation process is a good option for the tertiary treatment of real wastewater with different emerging pollutants.

3. Materials and Methods

3.1. Real Wastewater Sampling

Real wastewater samples came from a WWTP in Durango, Mexico ($23^\circ 58' 30''$ N, $104^\circ 38' 10''$ W). Before disinfection, the sampling was conducted after the second settling tank (Figure 2). The WWTP has a conventional activated sludge process as a secondary treatment.

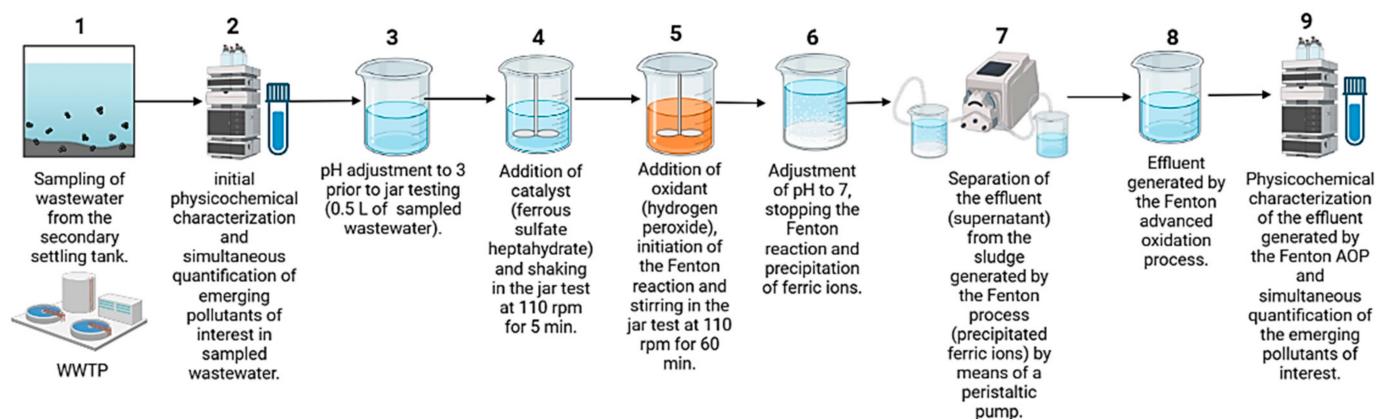


Figure 2. Experimental setup.

The samples were taken after the second settling tank because the AOPs are intended to be used as tertiary or polishing treatments to oxidize emerging pollutants. Then, the real wastewater sampled had already been subjected to the primary and secondary treatment (conventional biological activated sludge process).

Real wastewater sampling and preservation followed the standard Mexican NMX-AA-003-1980 [52].

3.2. Characterization of the Real Wastewater (Influent) and Effluent Generated by the Advanced Fenton Oxidation Process

The physicochemical characterization of the real wastewater sampled and treated by the advanced Fenton oxidation process was carried out based on the standards specified in Table 2. Due to the nature of the advanced Fenton oxidation process, the total iron was determined for the effluent generated.

Table 2. Methods and techniques used for the physicochemical characterization of real wastewater sampled and treated by the advanced Fenton oxidation process.

Determination	Method or Technique	Reference
pH	NMX-AA-008-SCFI-2011	[53]
Temperature	NMX-AA-007-SCFI-2013	[54]
Floating matter	NMX-AA-006-SCFI-2010	[55]
Settleable solids	NMX-AA-004-SCFI-2013	[56]
Chemical oxygen demand (COD)	HACH®	[57]
Total suspended solids (TSS)	NMX-AA-034-SCFI-2015	[58]
Total phosphates	HACH®	[57]
Total nitrogen	HACH®	[57]
Fecal coliforms (FC)	NMX-AA-042-SCFI-2015	[59]
Total iron	NMX-AA-051-SCFI-2016	[60]

3.3. Quantification of the Emerging Pollutants of Concern

The method and instrument used to quantify the emerging pollutants of interest were solid phase extraction and a liquid chromatography–mass spectrometer (Figure 2).

3.3.1. Solid Phase Extraction (SPE)

Waters Oasis HLB cartridges of 1 cubic centimeter were used for the solid phase extraction. The cartridges were initially activated with 1 mL of methanol and 0.3 mL of deionized water (the vacuum pump throughout the extraction process should have a vacuum of approximately 10 psi). All the reagents used were of chromatographic grade.

Then, 25 mL of real wastewater from the second settling tank of the WWTP untreated and treated by the advanced Fenton oxidation process was passed through the cartridges.

Given the pore size of the HLB cartridge, all the samples subjected to the extraction process were previously filtered with a Whatman grade 1 filter; then, disodium EDTA was added at a concentration of 500 mg/L, and the pH was adjusted to 2 with concentrated (98.08% m/m) sulfuric acid (H_2SO_4) before passing it through the extraction cartridge.

Subsequently, 0.5 mL of deionized water at pH 2 was passed through, and the cartridges were allowed to dry for 10 min with the vacuum pump on. As a final part of the extraction process, the compound of interest was eluted by passing 6 mL of methanol and 3 mL of acetone. Next, the extract was dried using nitrogen gas gently. Afterward, the dried extract was dissolved in 1 mL of formic acid (0.1% *v/v*) diluted in methanol.

3.3.2. Quantification of Emerging Contaminants of Interest

The liquid chromatograph used to quantify the emerging pollutants of interest was an Acquity UPLC[®], class I. The chromatographic system was coupled to a triple quadrupole mass spectrometer (XEVO-TQ-S micro (Waters)). The mobile phase composition is given in Table 3.

Table 3. Technical details of the operation of the liquid chromatograph–mass spectrometer.

Chromatograph			
Column	ACQUITY Premier CSH C18 1.7 μm, 2.1 × 150 mm		
Flow (mL/min)	0.4		
Sample temperature (°C)	7		
Column temperature (°C)	40		
Mobile phase A composition	water (Milli-Q) with 10 mM ammonium formate (chromatographic grade) plus 0.1% formic acid (chromatographic grade).		
Mobile phase B composition	Methanol–Acetonitrile (50% <i>v/v</i> –50% <i>v/v</i>)		
Injection volume (μL)	10		
Elution (min)	A (%)	B (%)	
0	2	98	
0.5	2	98	
14	90	10	
16	95	5	
16.5	2	98	
19	2	98	
Mass spectrometer			
Ionization source	Electrospray (ESI)		
Polarity	ES+ and ES–		
Source temperature (°C)	150		
Capillary voltage (kV)	3		
Cone gas flow (L/h)	50		
Desolvating temperature (°C)	500		
Desolvation gas flow (L/h)	100		
Coalition gas (argon)	0.15 mL/min		

The concentration of each emerging pollutant of interest was calculated based on Equation (4). The volume of the concentrate considered in Equation (4) refers to the volume of the sample used in the solid phase extraction, which is 25 mL

$$\text{Real concentration} = \frac{[\text{Concentrate read by the chromatograph}]}{\text{SPE concentrate volume}} \quad (4)$$

3.4. Experimental Setup (Advanced Fenton Oxidation Process)

The experimental setup is shown in Figure 2. The experiments were operated in batch mode. It should be noted that the experiments were carried out in duplicate, and the volume of real wastewater taken for each experiment was 0.5 L.

The pH was adjusted by adding concentrated sulfuric acid (H_2SO_4) at 98.08% m/m purity. On the other hand, the aqueous solution pH for the whole experiment was measured with a Thermo Electron Corporation ORION 3 STAR potentiometer. As a result, the initial pH in each trial was adjusted to 3, the pH value identified as the optimum level for carrying out the advanced Fenton oxidation process [61–63].

Now, ferrous sulfate heptahydrate ($\text{FeSO}_4 \bullet 7\text{H}_2\text{O}$, catalyst supplier (Fe^{2+})) of analytical grade (>99%) was the reagent used to obtain the ferrous ions (Fe^{2+}) since it is a reagent widely used in different investigations [64,65] where the homogeneous advanced Fenton oxidation process is applied. The hydrogen peroxide (H_2O_2 , oxidant) concentration was 30% v/v.

The hydrogen peroxide (H_2O_2) and ferrous sulfate heptahydrate ($\text{FeSO}_4 \bullet 7\text{H}_2\text{O}$) to be added to the real wastewater were calculated using Equation (1) [25,66,67], Equation (5) [6,68,69], and Equation (6), considering a $V = 0.5$ L as the sample base.

Equation (5) was used to determine the amount of hydrogen peroxide (H_2O_2) as a wastewater COD function. On the other hand, Equations (1) and (6) served as a reference to determine the ferrous ion (Fe^{2+}) amount to be added using ferrous sulfate heptahydrate ($\text{FeSO}_4 \bullet 7\text{H}_2\text{O}$) in relation to that calculated by Equation (5).

Since the advanced Fenton oxidation process is non-selective, wastewater COD is used as a basis of calculation to define the amounts of hydrogen peroxide (H_2O_2), ferrous ion (Fe^{2+}), and ferrous sulfate heptahydrate ($\text{FeSO}_4 \bullet 7\text{H}_2\text{O}$). On the contrary, if the amount of reagents is calculated based on the emerging pollutants of interest, they would be underestimated [6].

Equation (1) denotes the molar ratio necessary to initiate the Fenton reaction based on Equation (5).

In Equation (5), COD is the chemical oxygen demand concentration of the real wastewater to be treated in milligrams per liter. V is the volume of real wastewater to be treated in liters.

$$\text{Quantity (mg) } \text{H}_2\text{O}_2 = \frac{17}{8} \left[\text{COD, } \frac{\text{mg}}{\text{L}} \right] (V(\text{L})) \quad (5)$$

In Equation (6), $\text{nmol } \text{Fe}^{2+}$ are the moles of the ferrous ion calculated by Equation (1) in relation to Equation (5), and 278,010 is the molecular weight, in milligrams, of ferrous sulfate heptahydrate ($\text{FeSO}_4 \bullet 7\text{H}_2\text{O}$).

$$\text{Quantity (mg) } \text{FeSO}_4 \bullet 7\text{H}_2\text{O} = (278,010) (\text{nmol } \text{Fe}^{2+}) \quad (6)$$

As shown Figure 2, in step 5, the beaker is orange because when the Fenton reaction is initiated, in addition to hydroxyl radicals ($\text{HO}^\bullet$), ferric ions (Fe^{3+}) are also produced, which turn the color of the water orange.

The experiments were carried out through the jar test. The equipment used was Phipps & Bird (model PB-700), and all experiments were shaken at 110 rpm in the jar test (Figure 2). The hydraulic retention time used in the jar test was 1 h.

To raise the pH of the solution to 7, sodium hydroxide (NaOH) was added at $2 \text{ mol} \cdot \text{L}^{-1}$. This was carried out to remove the ferric ions (Fe^{3+}) generated in the advanced Fenton oxidation process from the effluent in the form of ferric hydroxides [67]. In the final part, the precipitation time was 5 min, and the effluent was obtained using a peristaltic pump (Figure 2).

3.5. Oxidation Percentage

The oxidation yield of each emerging pollutant was calculated using Equation (7).

$$\text{Oxidation}(\%) = \left(\frac{C_i - C_f}{C_i} \right) * 100 \quad (7)$$

C_i is the initial wastewater concentration of each emerging pollutant, and C_f is the final concentration of the emerging pollutant that resulted after subjecting the wastewater to the advanced Fenton oxidation process.

Note that the final concentrations of the emerging pollutants after the advanced Fenton oxidation process that were below the limit of quantification ($<LOQ$) were considered as $C_f = 0$ in Equation (7) for the percent oxidation calculations. Equation (7) was also used to calculate the removal yields of some physicochemical parameters obtained in the advanced Fenton oxidation process.

4. Conclusions

The increase and persistence of emerging pollutants in natural water bodies could be attributed to the treated wastewater discharge, where the conventional process was insufficient to remove these compounds before being returned to the environment. The results presented in this research show that the advanced Fenton oxidation process is a treatment alternative that can be coupled or integrated into the conventional treatment train, efficiently removing emerging pollutants, COD, TSS, and FC.

According to the results obtained at the laboratory level, the advanced Fenton oxidation process could oxidize different emerging pollutants simultaneously since the oxidation yields of the emerging pollutants present in samples of real wastewater were close to 100%, except for DEET, which had an average oxidation yield of 85.21%.

It should be highlighted that the advanced Fenton oxidation process could be used as a tertiary or polishing process coupled with a conventional WWTP since, as well as eliminating the emerging pollutants of interest, it also upgraded the quality of the treated water in terms of COD, TSS, and FC (pathogens).

Finally, based on the physicochemical characteristics established by the Mexican standard NOM-001-SEMARNAT-2021 [29], the advanced Fenton oxidation process provides an effluent with enough quality to be discharged into receiving water bodies owned by the nation or for use in garden irrigation systems, among other indirect benefits.

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