Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1141710

57 (2016) 23760–23769
October

Taylor & Francis
Taylor & Francis Group

Detoxification of synthetic and real groundwater contaminated with gasoline and diesel using Fenton, photo-Fenton, and biofilters

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Received 30 March 2015; Accepted 22 December 2015

ABSTRACT

The treatment of groundwater contaminated with gasoline and diesel with H_2O_2, $H_2O_2 + UV$, Fenton, and photo-Fenton was studied. Fenton reactions provided the best results with 1 mM of Fe^{2+} and 200 mM of H_2O_2. High contaminant removals were achieved, in particular those of COD (Fenton: 69%, photo-Fenton: 97%), Diesel Range Organics (99.9% both reactions), Gasoline Range Organics (99.9% both reactions), Total Petroleum Hydrocarbons (Fenton: 83.8%, photo-Fenton: 92.5%), Total Phenols (Fenton: 67.3%, photo-Fenton: 90.4%), and toxicity toward *Vibrio fischeri* (100%, both reactions). The experiments have been performed with synthetic and real samples. The economic cost of the proposed method (14 USD/m^3) is reduced by 60% with respect to that currently used in Ecuador.

Keywords: Toxicity; GRO; DRO; AOPs; Hydrocarbon polluted water

1. Introduction

Nowadays, hydrocarbons pollution is one of the main environmental concerns of modern societies because of their toxicity and the large amounts discharged. Among those hydrocarbons, fuel and diesel oils are more difficult to treat compared to gasoline due to their characteristics of lower volatility, biodegradability and mobility, and higher viscosity [1–3].

The presence of hydrocarbon pollutants in groundwater has caused many serious problems in communities where this natural resource is used for human consumption. In Ecuador, hydrocarbon spills from storage tanks and pipes used for distribution activities provoke the contamination of surface and groundwater water with a variety of toxic compounds, particularly from gasoline and diesel [4]. Fuels contain important amounts of benzene, toluene, ethyl benzene, and xylenes (BTEXs), which are among the most polluting and toxic compounds to living organisms. Currently, efficiency of conventional treatments such as physicochemical and biological processes is limited because of the high toxicity of the pollutants present in waters affected by oil spills [5]. The remaining toxic

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compounds after conventional treatments become a serious environmental problem when discharged into natural water bodies. Since surface and groundwater are sources of freshwater for agriculture and human consumption, it is important to control their quality.

In Nature, biodegradation is the main route of treatment of many xenobiotics although other abiotic processes such as hydrolysis or photolysis can play an important role. The fundamental problem is that many of the compounds present in industrial wastewater are recalcitrant and/or toxic [6]. Different conventional treatments such as biological membranes' [7] adsorption onto activated carbon [8], coagulation and flocculation [9], electrocoagulation [10], and catalytic vacuum distillation [11] have been applied to effluents contaminated with hydrocarbons. Quite often the efficiency of these treatments is high but not enough to completely remove recalcitrant pollutants and the toxic by-products generated, leading to increased economic costs [12–16].

In recent years, it has been shown that Advanced Oxidation Technologies (AOTs) such as Fenton and photo-Fenton (Fenton reactions) can achieve the degradation and detoxification of many organic pollutants [3]. Their high efficiency is provided by the on-site generation of the highly oxidizing hydroxyl radicals ($\cdot$OH) by the combination of H_2O_2 with Fe^{2+} ions, with and without UV–vis radiation (Eqs. (1) and (2)). $\cdot$OH radicals are able to oxidize many organic compounds in a non-selective way and with high reaction rates [5]. The basic Fenton reactions are the following:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^- \quad (1)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + {}^{\cdot}OH + H^+ \quad (2)$$

The production of $\cdot$OH radicals is responsible for the degradation and complete mineralization of organic compounds such as benzene, toluene, xylene, and phenols [17,18]. Fenton and photo-Fenton treatments can be considered as decentralized technologies since they can be applied *in situ*. In the last decade, Fenton reactions have achieved a relevant role in the treatment of hydrocarbons from diesel and gasoline mostly in soils [19–21] and to a lesser extent in groundwater [22]. Additionally, the existing literature on the application of Fenton reactions to the treatment of oily water spills from small facilities such as gas stations is still scarce [12].

Oily wastewaters generated in gas stations are mainly produced by cleaning operations and contain hydrocarbons, oils, detergents, and sediments. In Ecuador, these wastewaters are usually discharged into a three-stage oil trap designed to separate sludge from hydrocarbons and water. After this step, the oily wastewaters are mixed with domestic wastewater and poured into the general sewer system.

This paper aims to evaluate the effectiveness of Fenton reactions for the treatment of wastewaters contaminated with gasoline and diesel oils due to spills occurring in gas stations and petroleum facilities.

2. Materials and methods

2.1. Real and synthetic wastewater samples

A synthetic wastewater sample was prepared by mixing 400 ml of diesel oil and 400 ml of gasoline in 1,200 ml of distilled water and stirring for 2 h at 800–1,000 rpm. Then, the mixture was decanted for 1 h and a sample from the aqueous phase was taken and filtered through filter paper (0.45 μm). The characterization of the synthetic sample is shown in Table 3.

2.2. Experimental procedure

For Fenton reactions, high purity $FeSO_4{\cdot}7H_2O$ (Panreac, Spain) and 35% (w/v) H_2O_2 (Scharlau) were used. Aqueous solutions were prepared with Milli-Q water. All the experiments were performed at pH 3 and without aeration. When necessary, the initial pH was adjusted with H_2SO_4 (95–97%, Scharlau). At the end of the experiment, catalase from *Micrococcus lysodeikticus* (243,075 U/ml; Fluka) was used to remove the peroxide remaining from the Fenton reactions and to avoid interferences in the toxicity measurements.

The photo-Fenton and Fenton reactors used were 250 mL Pyrex cylinders. The UV lamp was a Solarium Philips HB175 UV set of lamps, comprising 4 × 15 W Philips CLEO fluorescent tubes (emission spectrum from 300 to 400 nm, maximum at 365 nm), which gave an irradiation level of 8.9 mW cm^{-2} at a distance of 10 cm as measured with a Graseby 5370 photometer.

The optimization of the H_2O_2 concentration was evaluated in the 50–200 mM range with 1 mM Fe^{2+}. Next, with the H_2O_2 optimal dosage the effect of Fe^{2+} concentrations was studied in the 0.01–2 mM range.

2.3. Analytical techniques

The reactions were monitored every 30 min for 4 h by analyzing total organic carbon (TOC) with a Shimadzu analyzer TOC-V CPH/CPN (procedure SM 5310B) and chemical oxygen demand (COD) by using the SM 5220 B [23]. The excess H_2O_2 concentration was determined by titration with $KMnO_4$ [24]. Toxicity was determined with the bioluminescence *Vibrio fischeri* method (European Standard NF EN ISO 11348-3) with an incubation period of 15 min for each sample after 1 and 4 h of reaction time. Before the analysis of toxicity and COD, it was necessary to eliminate the remaining H_2O_2 by adding 0.1 g/L solution of catalase (made from *M. lysodeikticus*, 1AU destroys 1 mM H_2O_2 at pH 7, 243.075 U/mL, Fluka). It was determined that 1.5 ml of this solution degraded 2.5 mM of H_2O_2. gasoline range organics (GRO) and diesel range organics (DRO) were also measured in samples treated with the optimal dosage after 4 h of reaction. These analyses were performed with a Gas Chromatograph (Gold, model GD-112A) equipped with a FID detector according to the method TNRCC-1005 [25]. The concentration of Total Petroleum Hydrocarbons (TPH) was also determined after the reaction, according to the EPA Method 418.1 [26] by using a Fourier transform Infrared Spectrophotometer (Shimadzu, model IRAffinity-1S).

The concentration of Polycyclic Aromatic Hydrocarbons was measured with a Gas chromatograph (Gold, model GD-112A) equipped with a FID detector according to the method SM6440 B [27].

3. Results and discussion

3.1. Characterization of the real samples

Oily wastewaters from gas stations contain a complex mixture of organic pollutants and hydrocarbons in the range C9–C20 with boiling points between 149 and 385°C. The effluent of the oil trap present in most gas stations contains dissolved and dispersed hydrocarbons such as BTEX, which are highly soluble, toxic, and provide high concentrations of organic matter in terms of COD.

The sample used in this study was collected from the oil trap effluent of a local gas station located in Guayaquil (Ecuador). Table 1 shows the results of the physicochemical characterization of the sample. As can be observed, it was toxic with 89% luminescence inhibition. TOC was 198.3 mg L^{-1} and TPH concentration was about 400 mg L^{-1}. More importantly, the concentration of HAPs was 6.19 mg L^{-1}, those of GRO and DRO were 55.8 and 443 mg L^{-1}, respectively. The presence of these pollutants highlights the importance of proper management of such effluents in order to avoid the contamination of water resources, particularly those devoted to human supply.

Ecuadorian legislation establishes the maximum concentration of TPH for discharge into natural water courses at 20 mg L^{-1}, that of COD in 250 mg L^{-1} and that of phenols at 0.2 mg L^{-1} [28]. As can be observed in Table 1, the concentrations of TPH, COD, and phenols of the sample were considerably higher (TPH: 420–463 mg L^{-1}, COD: 2,225 mg L^{-1}, phenols: 0.28 mg L^{-1}).

Table 1
Physicochemical characterization of the gas station effluent studied (real sample)

Parameter	Result	Units
TOC	198.30	mg/L
COD	2,225	mg/L
Phenols	0.28	mg/L
PAHs	6.19	mg/L
TPH	420–463	mg/L
DRO	443.00	mg/L
GRO	55.80	mg/L
SST	28	mg/L
Toxicity	89	% Inhibition
pH	5.56	pH
Electrical conductivity	560	µS/cm

Considering the high toxicity and environmental relevance of PAHs, the individual concentrations of the main PAHs were analyzed. The results are shown in Table 2.

According to the existing literature, the *V. fischeri* bioluminescence inhibition test is probably the fastest, most sensitive, cost-effective, and easy-to-operate method to measure toxicity [29]. Additionally, the method is regarded as a good ecotoxicological endpoint for the baseline toxicity caused by mixtures of chemicals such as petroleum hydrocarbons, with bioluminescence inhibition showing high correlations with the total PAHs level [30]. Fig. 1 shows the results

Table 2
Concentrations of the main PAHs of the real sample

PAHs	Concentration (µ L^{-1})
Naphthalene	<0.3
Acenaphtylene	287.4
Acenaphthene	<0.3
Fluorene	3,400
Phenanthrene	2,240
Anthracene	<0.5
Fluoranthene	<0.9
Pyrene	<0.8
Benzo(a)anthracene	221.8
Chrysene	<1.5
Benzo(b)fluoranthene	<0.7
Benzo(k)fluoranthene	<0.6
Benzo(a)pyrene	52.7
Benzo(g h i)perylene	<0.9

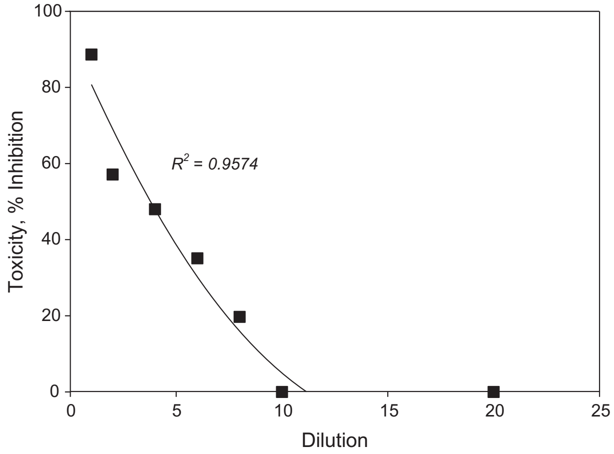

Fig. 1. Toxicity of the real sample at different dilutions.

of the bioluminescence test at different dilutions of the real sample. As can be observed, the initial inhibition value was above 80% showing the toxic character of the effluent. A 10-fold dilution would be necessary to remove toxicity completely. Although the bioluminescence inhibition is not particularly high, it has been shown that the application of AOTs can generate intermediates that are more toxic than the parental compound [31]. Consequently, the treatment time becomes longer and it should be determined by toxicity rather than organic matter analyses.

3.2. Optimization of photo-Fenton for the synthetic sample

The other techniques studied in this work (only H_2O_2, H_2O_2 + UV, and Fenton) are simpler but less efficient than photo-Fenton. In other words, if photo-Fenton were not efficient, neither would the other techniques be good. Consequently, it was decided to optimize photo-Fenton first and then to test the other techniques with the optimized conditions for the former.

Because of the presence of many different pollutants in a real oily wastewater sample, the optimization of photo-Fenton was also studied in a synthetic sample obtained by mixing and diluting diesel and gasoline in water (Section 2.1). This way, a simpler but representative matrix was used and the most relevant parameters from an environmental and toxicological viewpoint were measured: TPH, TOC, DRO, and GRO.

As indicated in Section 2.1, the synthetic sample was obtained by mixing and decanting gasoline, diesel oil, and water. Decantation was necessary because the efficiency of PAH removal by Fenton by the presence of suspended solids can be reduced by 26–70% [30]. The features of the synthetic sample are shown in Table 3.

Regarding the optimization of Fenton reagents (Fe^{2+} ions and H_2O_2), previous studies have shown that pollutant degradation was enhanced by increasing iron concentration [32]. Nonetheless, an excessive concentration of Fe^{2+} ions reduces UV radiation penetration into the solution by the precipitation of Fe^{3+} oxo-hydroxides (reaction 1) [33]. Additionally, Ecuadorian legislation establishes the limit for dissolved iron in effluents discharged to natural water courses at 0.9 mM [34]. According to the revised literature on the mineralization of organic compound, the tested concentrations ranged between 0.05 M and 2 mM [33].

Moreover, different studies have shown that within an optimal range, increased concentrations of the peroxide improved efficiency [32,35,36]. Thus, concentrations of H_2O_2 in the range between 50 and 400 mM were tested with a constant concentration of Fe^{2+} of 1 mM.

The total reaction time was 4 h and samples were taken every hour [30]. Fig. 2 shows the results obtained for TOC and toxicity removal with varying concentrations of H_2O_2 and 1 mM Fe^{2+}. Fig. 2(A) shows that mineralization increased progressively at increasing concentrations of the peroxide until 200 mM. At this point, a TOC reduction of 85% was achieved. However, above that peroxide concentration mineralization was reduced in time with an increment of the remaining peroxide. In this sense, it must be considered that excessive concentrations of H_2O_2 might act as a scavenger of the formed $^{\cdot}OH$ radicals to produce per-hydroxyl radicals ($^{\cdot}OOH$) which have much lower oxidation capabilities than $^{\cdot}OH$ radicals.

Note that reaction time was another important parameter in this study. This and other studies have revealed that Fenton reaction can achieve almost complete degradation and/or mineralization of parental pollutants in the first hour of reaction. Nevertheless,

Table 3
Characterization of the synthetic sample

Parameter	Result	Units
pH	7.7–8.0	–
TOC	115–150	mg/L
COD	1,725	mg/L
TPH	236	mg/L
Phenols	0.52	mg/L
DRO	119	mg/L
GRO	12.2	mg/L
Toxicity	100	%

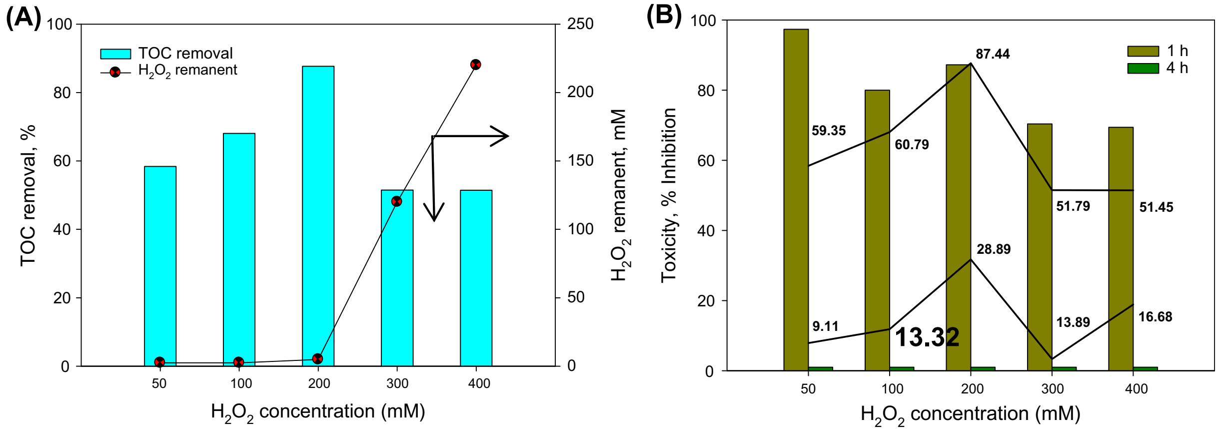

Fig. 2. (A) Removal of TOC after 4 h of reaction with photo-Fenton with 50, 100, 200, 300, and 400 mM of H_2O_2 and a constant concentration of 1 mM of Fe^{2+}; pH 3, T = 25˚C, and (B) Toxicity of the effluent after 1 and 4 h of treatment and TOC removal (%) after 1 h (bottom line) and 4 h (top line).

the degradation of the often more toxic intermediates takes longer. Hence, the reaction time was increased until 4 h. The obtained results are in agreement with this supposition as can be observed in Fig. 2(B). This was an indication of the high toxicity of the intermediates generated in the process as observed by other authors [31]. This is the case of phenol, a compound present in the sample that produces much more toxic intermediates such as catechol and hydroquinone [37].

It must be underlined that a TOC reduction of almost 90% was achieved with 200 mM of H_2O_2 while only 60% was attained with 50 mM. However, the sample was completely detoxified with both concentrations after 4 h.

The optimal concentration of Fe^{2+} ions was tested between 0.05 and 2 mM according to previous studies on the mineralization of waters contaminated with hydrocarbons [18]. The optimal H_2O_2 concentration was 200 mM.

Mineralization results after 4 h with photo-Fenton at different Fe^{2+} ions concentrations are shown in Fig. 3. As can be observed, the maximum TOC removal (above 85%) was achieved with 1 mM of Fe^{2+} but the sample was detoxified only with concentrations between 0.5 and 2 mM.

Fig. 3 shows that increasing concentrations of Fe^{2+} from 0.05 to 1 mM clearly improved TOC removal but a further increments up to 2 mM reduced removal.

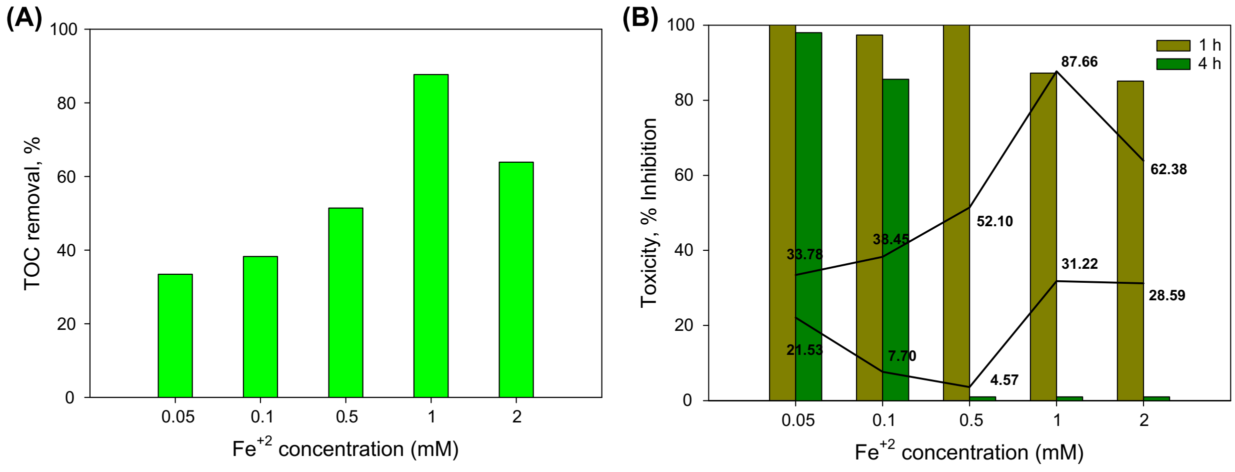

Fig. 3. (A) TOC removal after 4 h of reaction with photo-Fenton (λ = 254 nm) at different Fe^{2+} concentrations and 200 mM of H_2O_2; pH 3, T = 25˚C, and (B) toxicity of the effluent after 1 and 4 h of treatment and TOC removal (%) after 1 h (bottom line) and 4 h (top line).

Table 4
Pseudo-first-order mineralization rate constants for the different concentrations of Fe^{2+} and H_2O_2 for photo-Fenton

Fe^{2+} (200 mM H_2O_2)			H_2O_2 (1 mM Fe^{2+})		
(mM)	K_{TOC}(h^{-1})	R^2	(mM)	K_{TOC} (h^{-1})	R^2
0.01	0.0943	0.8432	50	0.2337	0.9645
0.1	0.125	0.9412	100	0.3022	0.9817
0.5	0.1863	0.9033	200	0.529	0.9813
1	0.4873	0.9337	300	0.2078	0.8858
2	0.2483	0.9653	400	0.1918	0.983

At iron concentrations above 1 mM, the solution color turned yellow-brownish most probably because of the precipitation of Fe^{3+} ions as oxo-hydroxydes. This reaction increased the sample turbidity and consequently radiation penetration. Thus, conversion of Fe^{3+} ions to the photoactive Fe^{2+} ions was hampered and consequently the radical production was also lower [38].

Furthermore, reaction rate constants for the different iron and peroxide concentrations were calculated assuming first-order kinetics (Table 4). The obtained results reveal that the best efficiencies were obtained with 1 mM of Fe^{2+} and 200 mM of H_2O_2 which provided mineralization rates of 0.4873 and 0.529 h^{-1}, respectively.

Another important variable considered in this work was the concentration of TPH for which the Ecuadorian legislation sets a limit of 20 mg L^{-1} [28]. Fig. 4 shows the removal of TPH for different concentrations of Fe^{2+} and H_2O_2. Note that only with 200–300 mM H_2O_2 and 0.5–1 mM Fe^{2+}, the concentration of TPH met the legal limit [28]. The optimal reagents concentrations for TPH removal coincided with those of best TOC removal. At this point, it must be considered that TPH is composed of a wide range of toxic, hardly biodegradable compounds such as hexane, benzene, toluene, xylenes, or naphthalene [39]. However, photo-Fenton achieved a TPH reduction of 84–98% with final concentrations as low as 5 mg L^{-1} with 300 mM of H_2O_2. This result can be explained by considering the higher concentration of $^{\bullet}OH$ radical produced. Nevertheless, such peroxide concentration was not high enough to achieve their mineralization. Similar results were obtained by Dehghani et al. [40] who achieved a TPH removal above 95% during the first hour of reaction.

Nevertheless, although the best TPH removal was achieved with 300 mM H_2O_2 and 1 mM Fe^{2+}, that of TOC was reduced at those reagent concentrations (Fig. 2 and Table 4) with a higher remaining concentration of the peroxide (Fig. 2). Consequently, considering the high economic cost of hydrogen peroxide, it can be concluded that the optimal doses are 1 mM of Fe^{2+} and 200 mM of H_2O_2.

3.3. Comparison with other advanced oxidation techniques in the treatment of the real sample

Once the reagents were optimized for photo-Fenton, the simpler techniques (only H_2O_2, H_2O_2 + UV, and Fenton) of the real sample were tested. In these experiments, the previously optimized concentrations of Fe^{2+} (1 mM) and H_2O_2 (200 mM) were employed. The best results were obtained with Fenton and photo-Fenton (Fig. 5), particularly the latter with 89% mineralization. In addition to this, the sample was detoxified and COD was reduced below the legal limit for both the Ecuadorian [28] (250 mg L^{-1}) and European Legislations (125 mg L^{-1}) [32]. Furthermore, the consumption of hydrogen peroxide was very low in comparison to those of

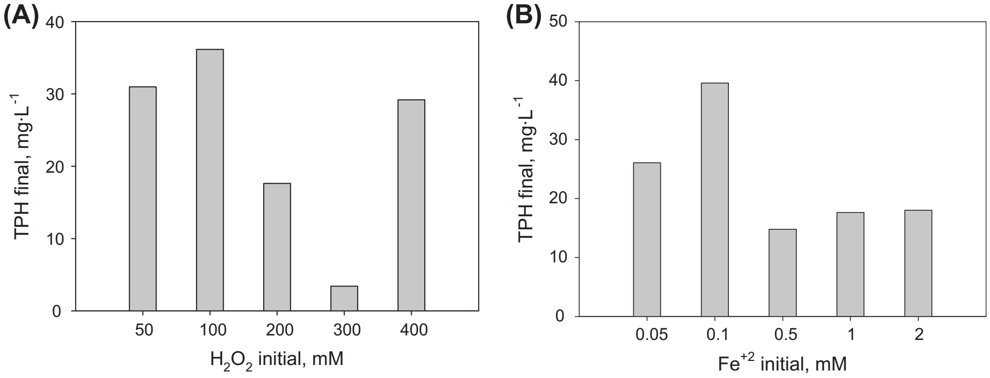

Fig. 4. Evolution of the concentration of THP according to the concentration of Fenton reagents: (A) [Fe^{2+}] = 1 mM; [H_2O_2] = variable and (B) [Fe^{2+}] = variable; [H_2O_2] = 200 mM.

Fenton and photo-Fenton, for which it was complete. The application of only H_2O_2 is limited by its low oxidation power to pollutants such as cianure, chloride, and certain organic compounds. In the present case, with more complex molecules in the sample degradation was inefficient and the peroxide did not react. On the other hand, the direct photolysis of H_2O_2 yields ·OH and small amounts of ·HOO radicals. However, this reaction is very slow and the production of hydroxyl radicals is not enough for the degradation of the organic pollutants present in the sample.

In the case of Fenton and photo-Fenton, Fe^{2+} ions accelerate the decomposition of H_2O_2 to provide a remarkably higher concentration of ·OH radicals which justifies the obtained results: high COD removal, complete detoxification, and almost total consumption of the peroxide.

Fenton and photo-Fenton have been equally effective at the removal of toxicity but not at TOC and peroxide consumption. To improve our knowledge on the applicability of these techniques in the removal of aromatic and aliphatic compounds in oily wastewaters, their efficiency at removing DRO and GRO and other parameters was analyzed. GRO includes C6–C10 range alkanes with a boiling point range of 60–170 EC, approximately. DRO includes C10–C28 alkanes with a boiling point range of approximately 170–430 EC [41]. The obtained results (Table 5) demonstrate the almost complete removal of DRO and GRO with both techniques. Nevertheless, there was a remaining TOC that may correspond to carboxylic acids. These compounds are recalcitrant to these techniques but are not toxic, nor do they exert any deleterious effect on living organisms at the concentrations generated as shown by toxicity measurements.

Although the removal of phenols was higher with Fenton for both samples, the Ecuadorian legal limit of 0.2 mg L^{-1} [28] was met.

Other authors have obtained efficiencies as high as 96.7% with Fenton in the removal of hydrocarbons in soil [33]. This result agrees with those of this work in water with Fenton and photo-Fenton. The latter was more efficient at the removal of TPH as it was able to meet the legal standard (20 mg L^{-1}) while Fenton was not.

3.4. Economic costs of treatment

Currently, the treatment of oily waters from gas stations in Ecuador consists of a phase separation. The non-aqueous phase is usually incinerated and the aqueous phase is discharged into the public sewerage. The economic cost of treatment is about 35 USD/m^3.

It is known that the AOTs are more expensive than other methods such as the biological ones and this has hampered their application. However, the biological methods cannot be applied with highly toxic and/or bio-recalcitrant effluents. Thus, it is important to have an idea of the economic cost of the implementation of the proposed alternative methods. Therefore, an estimation of the cost of the Fenton reagents and UV radiation is presented to ascertain the real applicability of Fenton and photo-Fenton. The cost of the application of UV radiation was determined by calculating the EE/O (Electrical Energy per order) parameter as provided by Eq. (3) [30,42]:

$$\mathrm{EE/O} = \frac{P \times t}{60 \times V \times \log\left(\frac{C_0}{C}\right)} \tag{3}$$

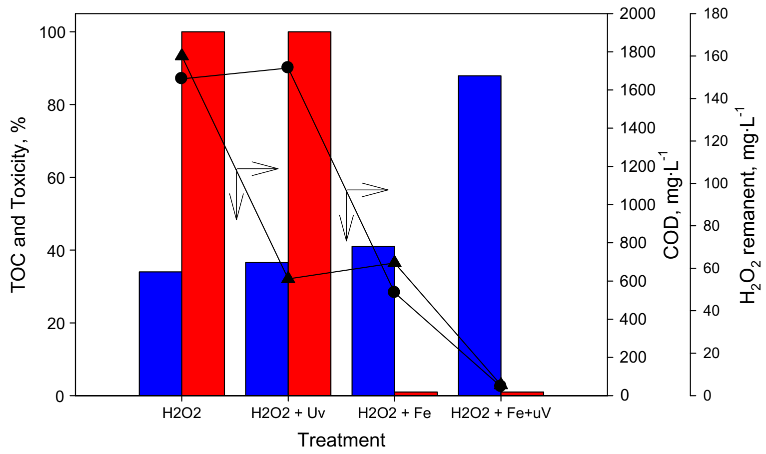

Fig. 5. TOC removal (%) 🟦, toxicity of the treated solution (%) 🟥, COD ●, and remanent H_2O_2 ▲ for the different treatments applied.

Table 5
Comparison of Fenton and photo-Fenton in the treatment of the real sample after 4 h of treatment with 1 mM of Fe^{2+} and 200 mM of H_2O_2

Parameter	Initial	Fenton	Photo-Fenton
GRO (mg/L)	55.8	0.835	0.021
DRO (mg/L)	443	1.91	0.837
COD (mg/L)	2,225	31	27
TPH (mg/L)	443	20.27	16.74
TOC (mg/L)	186.9	37.1	25.8
Phenols (mg/L)	0.28	0.11	0.01
Toxicity (%)	89	NT	NT

Note: NT: non toxic.

Table 6
Economic cost of the application of Fenton and photo-Fenton and the TOC removals achieved

	(mM)			
Process	H_2O_2	Fe^{2+}	TOC (%)	Cost (USD m^{-3})
Fenton	200	1	76	14.16
Photo-Fenton	200	1	89	16.28

where P is the lamp power, t is the radiation time, V is the sample volume, and C_0 and C are the initial and final organic matter concentrations, respectively.

For both techniques, a sample volume of 0.25 L was considered. In the case of photo-Fenton, the cost of using two different lamps was estimated: 4 UV lamps (16 W each and maximum emission at 254 nm) and 4 UV lamps (15 W each and maximum emission at 365 nm). Table 6 shows the results obtained.

Few studies determine the economic cost of the treatment of water contaminated with hydrocarbons with Fenton and/or photo Fenton. Other authors obtained notably higher prices, between 172 and 268 USD for the treatment of solids contaminated with hydrocarbons [32]. It must be noted that most estimative models are strongly influenced by the economic cost of reagents, the use of UV light, and the initial TOC, among other parameters [6,43]. The results obtained in this work show that Fenton and photo-Fenton are able to meet the Ecuadorian and European discharge limits and the complete detoxification of the samples. Additionally, the estimated economic cost for Fenton and photo-Fenton was calculated to be 14.2–16.3 USD/m^3, respectively, which is about half of the current cost.

4. Conclusions

The present work has shown that:

(1) Fenton and photo-Fenton are efficient techniques for the detoxification of gas station oily wastewater spills in Ecuador.
(2) The optimal doses of Fe^{2+} and H_2O_2 for photo-Fenton are 200 and 1 mM, respectively.
(3) Photo-Fenton was 34% more efficient at mineralization than Fenton.
(4) Fenton and photo-Fenton achieved removals of DRO, GRO, TPH, COD, and toxicity were above 95% with the optimized concentrations of Fe^{2+} ions and H_2O_2 and a reaction time of 4 h.
(5) The application of photo-Fenton or Fenton can help to meet Ecuadorian National and European legislations with a lower economic cost than the method currently used.

Acknowledgments

The authors acknowledge the support of Prometeo Project of the Ministry of Higher Education, Science, Technology and Innovation (SENESCYT) of the Republic of Ecuador.

References

[1] R.J. Watts, S.E. Dilly, Evaluation of iron catalysts for the Fenton-like remediation of diesel-contaminated soils, J. Hazard. Mater. 51 (1996) 209–224.
[2] J.R. Gallego, E. González-Rojas, A.I. Peláez, J. Sánchez, M.J. García-Martínez, J.E. Ortiz, T. Torres, J.F. Llamas, Natural attenuation and bioremediation of Prestige fuel oil along the Atlantic coast of Galicia (Spain), Org. Geochem. 37 (2006) 1869–1884.
[3] A. Goi, N. Kulik, M. Trapido, Combined chemical and biological treatment of oil contaminated soil, Chemosphere 63 (2006) 1754–1763.
[4] National Government of Ecuador, Environmental Ministry, Estudio para conocer los potenciales impactos ambientales y vulnerabilidad relacionada con las sustancias químicas y tratamiento de desechos peligrosos en el sector productivo del Ecuador (Study to determine the potential environmental impacts and vulnerability related to chemical substances and treatment of hazardous wastes in the productive sector of Ecuador), (2012).
[5] J.P. Salanitro, L.A. Diaz, M.P. Williams, H.L. Wisniewski, Isolation of a bacterial culture that degrades methyl t-butyl ether, Appl. Environ. Microb. 60 (1994) 2593–2596.
[6] I. Oller, S. Malato, J.A. Sánchez-Pérez, Combination of advanced oxidation processes and biological treatments for wastewater decontamination—A review, Sci. Total Environ. 409 (2011) 4141–4166.

[7] M.H. El-Naas, S. Al-Zuhair, A. Al-Lobaney, S. Makhlouf, Assessment of electrocoagulation for the treatment of petroleum refinery wastewater, J. Environ. Manage. 91 (2009) 180–185.

[8] L. Yan, H. Ma, B. Wang, Y. Wang, Y. Chen, Electrochemical treatment of petroleum refinery wastewater with three-dimensional multi-phase electrode, Desalination 276 (2011) 397–402.

[9] C.C. Teodosiu, M.D. Kennedy, H.A. van Straten, J.C. Schippers, Evaluation of secondary refinery effluent treatment using ultrafiltration membranes, Water Res. 33 (1999) 2172–2180.

[10] T. Misiti, U. Tezel, S.G. Pavlostathis, Fate and effect of naphthenic acids on oil refinery activated sludge wastewater treatment systems, Water Res. 47 (2013) 449–460.

[11] N.S. Mizzouri, M.G. Shaaban, Kinetic and hydrodynamic assessment of an aerobic purification system for petroleum refinery wastewater treatment in a continuous regime, Int. Biodeterior. Biodegrad. 83 (2013) 1–9.

[12] D.B. Hasan, A.R. Abdul Aziz, W.M.A.W. Daud, Oxidative mineralisation of petroleum refinery effluent using Fenton-like process, Chem. Eng. Res. Des. 90 (2012) 298–307.

[13] S.M. Ghoreishi, R. Haghighi, Chemical catalytic reaction and biological oxidation for treatment of non-biodegradable textile effluent, Chem. Eng. J. 95 (2003) 163–169.

[14] E. Forgacs, T. Cserháti, G. Oros, Removal of synthetic dyes from wastewaters: A review, Environ. Int. 30 (2004) 953–971.

[15] K. Singh, S. Arora, Removal of synthetic textile dye from wastewater: A critical review on present treatment technologies, Crit. Rev. Environ. Sci. Technol. 41 (2011) 807–878.

[16] S.R. Pouran, A.R. Abdul Aziz, W.M.A.W. Daud, Review on the main advances in photo-Fenton oxidation system for recalcitrant wastewaters, J. Ind. Eng. Chem. 21 (2015) 53–69.

[17] J.E. Moraes, F.H. Quina, C.A. Nascimento, D.N. Silva, O. Chiavone-Filho, Treatment of saline wastewater contaminated with hydrocarbons by the photo-Fenton process, Environ. Sci. Technol. 38 (2004) 1183.

[18] E. Aranda, E. Marco-Urrea, G. Caminal, M.E. Arias, I. García-Romera, F. Guillén, Advanced oxidation of benzene, toluene, ethylbenzene and xylene isomers (BTEX) by Trametes versicolor, J. Hazard. Mater. 181 (2010) 181–186.

[19] G.A. Silva-Castro, B. Rodelas, C. Perucha, J. Laguna, J. González-López, C. Calvo, Bioremediation of diesel-polluted soil using biostimulation as post-treatment after oxidation with Fenton-like reagents: Assays in a pilot plant, Sci. Total Environ. 445–446 (2013) 347–355.

[20] T. Tsai, J. Sah, C. Kao, Application of iron electrode corrosion enhanced electrokinetic-Fenton oxidation to remediate diesel contaminated soils: A laboratory feasibility study, J. Hydrol. 380 (2010) 4–13.

[21] T.T. Tsai, C.M. Kao, Treatment of petroleum-hydrocarbon contaminated soils using hydrogen peroxide oxidation catalyzed by waste basic oxygen furnace slag, J. Hazard. Mater. 170 (2009) 466–472.

[22] R. Baciocchi, L. D'Aprile, I. Innocenti, F. Massetti, I. Verginelli, Development of technical guidelines for the application of in-situ chemical oxidation to groundwater remediation, J. Cleaner Prod. 77 (2014) 47–55.

[23] E.R.L. Tiburtius, P. Peralta-Zamora, A. Emmel, Treatment of gasoline-contaminated waters by advanced oxidation processes, J. Hazard. Mater. 126 (2005) 86–90.

[24] N.V. Klassen, D. Marchington, H.C.E. McGowan, H_2O_2 determination by the I_3- method and by $KMnO_4$ titration, Anal. Chem. 66 (1994) 2921–2925.

[25] TNRCC, Total Petroleum Hydrocarbons, TNRCC Method 1005, 2001.

[26] United States Environmental Protection Agency (USEPA), Test Method for Evaluating Total Recoverable Petroleum Hydrocarbon, Method 418.1 (Spectrophotometric, Infrared), Government Printing Office, Washington, DC, USA, 1978.

[27] US EPA Federal Register, Rules and Regulations. Method 610 Polynuclear Aromatic Hydrocarbons, Environmental Protection Agency, 49, (1984), 209

[28] Ministerio del Ambiente del Ecuador, Norma de Calidad Ambiental y de Descarga de Efluentes al Recurso Agua (Norm of Environmental Quality and Effluent Discharge into Water Resource), Decreto N° 3516, Edición Especial N°2 del Registro Oficial, (2003).

[29] S. Parvez, C. Venkataraman, S. Mukherji, A review on advantages of implementing luminescence inhibition test (*Vibrio fischeri*) for acute toxicity prediction of chemicals, Environ. Int. 32 (2006) 265–268.

[30] S. Lee, H. Kang, J. Kwon, Toxicity cutoff of aromatic hydrocarbons for luminescence inhibition of *Vibrio fischeri*, Ecotoxicol. Environ. Saf. 94 (2013) 116–122.

[31] J.A.O. Méndez, J.A.H. Melián, J. Araña, J.M.D. Rodríguez, O.G. Díaz, J.P. Peña, Detoxification of waters contaminated with phenol, formaldehyde and phenol–formaldehyde mixtures using a combination of biological treatments and advanced oxidation techniques, Appl. Catal. B: Environ. 163 (2015) 63–73.

[32] F.J. Rivas, F.J. Beltrán, J. Frades, P. Buxeda, Oxidation of p-hydroxybenzoic acid by Fenton's reagent, Water Res. 35 (2001) 387–396.

[33] K. Nam, W. Rodriguez, J.J. Kukor, Enhanced degradation of polycyclic aromatic hydrocarbons by biodegradation combined with a modified Fenton reaction, Chemosphere 45 (2001) 11–20.

[34] Texto Unificado de la Legislación Ambiental (TULSMA) (2007).

[35] J.H. Baxendale, J.A. Wilson, The photolysis of hydrogen peroxide at high light intensities, Trans. Faraday Soc. 53 (1957) 344–356.

[36] S.H. Lin, C.C. Lo, Fenton process for treatment of desizing wastewater, Water Res. 31 (1997) 2050–2056.

[37] A. Akyol, O.T. Can, M. Bayramoglu, Treatment of hydroquinone by photochemical oxidation and electrocoagulation combined process, J. Water Process Eng. 8 (2015) 45–54.

[38] L.G. Devi, S.G. Kumar, K.M. Reddy, C. Munikrishnappa, Photo degradation of methyl orange an azo dye by advanced fenton process using zero valent metallic iron: Influence of various reaction parameters and its degradation mechanism, J. Hazard. Mater. 164 (2009) 459–467.

[39] ATDSR, Toxicological Profile for Total Petroleum Hydrocarbons, Agency for toxic substances and disease registry, Atlanta, GA, 1999. Available from: <www.atsdr.cdc.gov>

[40] M. Dehghani, M. Farzadkia, E. Shahsavani, M.R. Samaei, Optimizing photo-Fenton like process for the removal of diesel fuel from the aqueous phase, J. Environ. Health Sci. Eng. 12 (2014) 12–87.

[41] American Petroleum Institute, Health and Environmental Sciences Department, Interlaboratory Study of Three Methods for Analyzing Petroleum Hydrocarbons in Soils: Diesel-Range Organics (DRO), Gasoline-Range Organics (GRO), Petroleum Hydrocarbons (PHC), American Petroleum Institute, Washington, DC, 1994.

[42] N.N. Mahamuni, Y.G. Adewuyi, Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: A review with emphasis on cost estimation, Ultrason. Sonochem. 17 (2010) 990–1003.

[43] Y. Li, S. Sun, M. Ma, Y. Ouyang, W. Yan, Kinetic study and model of the photocatalytic degradation of rhodamine B (RhB) by TiO_2-coated activated carbon catalyst: Effects of initial RhB content, light intensity and TiO_2 content in the catalyst, Chem. Eng. J. 142 (2008) 147–155.