

A simple methodology to evaluate influence of H₂O₂ and Fe²⁺ concentrations on the mineralization and biodegradability of organic compounds in water and soil contaminated with crude petroleum

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Abstract

Simple measurements of H₂O₂ concentration or CO₂ evolution were used to evaluate the effectiveness of the use of Fenton's reagent to mineralize organic compounds in water and soil contaminated by crude petroleum. This methodology is suitable for application in small treatment and remediation facilities. Reagent concentrations of H₂O₂ and Fe²⁺ were found to influence the reaction time and temperature, as well as the degree of mineralization and biodegradability of the sample contaminants. Some H₂O₂/Fe²⁺ combinations (H₂O₂ greater than 10% and Fe²⁺ greater than 50 mM) resulted in a strong exothermic reaction, which causes peroxide degradation and violent gas liberation. Up to 75% TOC removal efficiency was attained in water and 70% in soil when high H₂O₂ (20%) and low Fe²⁺ (1 mM) concentrations were used. Besides increasing the degree of mineralization, the Fenton's reaction enhances the biodegradability of petroleum compounds (BOD₅/COD ratios) by a factor of up to 3.8 for contaminated samples of both water and soil. Our experiments showed that low reagent concentrations (1% H₂O₂ and 1 mM Fe²⁺) were sufficient to start the degradation process, which could be continued using microorganisms. This leads to a decrease in reagent costs in the treatment of petroleum-contaminated water and soil samples. The simple measurements of H₂O₂ concentration or CO₂ evolution were effective to evaluate the Fenton's reaction efficiency.

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1. Introduction

Surface water and groundwater pollution problems need to be controlled through effective and feasible intervention steps like minimization of wastewater generation, treatment and optimal reuse of nutrients, and enhancement of the self-purification capacity of receiving water bodies [1]. However, in some cases these types of pollution management are not effective, for example, in oil-contaminated waters, which may result from accidental spillages, deliberate dumping, leaching of older landfills or leakages from underground storage tanks. Conventional technologies, based on 'pump and treat', have been used for petroleum decontamination of water bodies, but some pollutants

are difficult to treat and/or are very dangerous, requiring a rapid and efficient treatment, such as employing the Fenton's reaction. In this reaction, the combination of hydrogen peroxide (H₂O₂) and the catalyst ferrous iron (Fe²⁺) produces the free hydroxyl radical •OH, which is an extremely powerful oxidizer of organic compounds [2]. Treatments using Fenton's reagent for the degradation of hydrocarbons in water bodies and wastewaters show a high efficiency when experimental conditions are optimized [3]. However, technical requirements for optimization or monitoring of the Fenton's reaction efficiency are complex and costly (e.g., GC-MS), which inhibits its common usage. Even with optimization of the reaction efficiency this treatment technique implies significant costs, which can be an important limitation in the choice of treatment. For this reason, Fenton's reaction may be recommended as a pre-treatment process to enhance later microbial transformation, lowering the operational costs. Experiments with different substrates have shown that a partial chemical oxi-

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duction of toxic wastewater may increase its biodegradability, generally through the cleavage of large organic compounds into smaller ones [4–6].

In this regard, the objective of this study was to investigate the feasibility of simple monitoring methodologies, such as spectrophotometric measurement of H_2O_2 concentrations and titrimetric quantification of CO_2 evolution to evaluate the effectiveness of Fenton's reagent in the mineralization (or change in biodegradability) of organic compounds in water contaminated by crude petroleum. Simple methodologies to ensure efficient optimization of the Fenton's reaction are important to small wastewater treatment facilities. Also, the proposed methodology was used to assess matrix oxidation effect using a soil contaminated with crude petroleum.

2. Material and methods

2.1. Water and soil contamination

To avoid adsorption interference due to the suspended solids, the original contaminated water was passed through a separatory funnel and then filtered (FG membrane, $0.45\ \mu\text{m}$). Recuperated crude petroleum was used to prepare experimental samples by oil dissolution in deionized water obtained from a Millipore Milli-Q system. In all treatments, regardless of reagent quantities, the petroleum concentration in the reaction volume was $2\ \text{g L}^{-1}$. Prior to contamination, soil samples were characterized in terms of pH (4.0), texture (clay loam), organic matter (3.1%), crystalline iron ($26,646\ \text{mg kg}^{-1}$), N_{total} (0.16%), field capacity (27.2%), and C:N ratio (1:1) according to published methodologies [7]. Dry soil was sieved ($0.3\ \text{mm}$) and contaminated at a proportion of 20 g of crude petroleum to 100 g of soil. After soil homogenization, 2 g of this soil was dissolved to 200 mL of reaction volume. Soil and water experiments were carried out using the same procedures.

2.2. Experimental conditions

The experiments were carried out in a 400 mL closed reactor, thermostated ($25\ ^\circ\text{C}$) and covered to avoid light (Fig. 1). The reaction mixture inside the reactor was magnetically stirred. The reactor cap had three ducts: N_2 carrier gas inlet; oxidized air ($\text{CO}_2 + \text{N}_2$) outlet; and hydrogen peroxide inlet. The sequential experimental steps were: addition of contaminated water (200 mL) or soil (2 g in 200 mL of Milli-Q water); pH adjust-

ment (3 ± 0.1) with 0.1 M HCl or NaOH solution; addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; closing of the reactor and purging with N_2 ; addition of different volumes of 30% H_2O_2 and capture of evolved gas in an external vessel (N_2 as carrier gas). From time to time this scavenger vessel was changed for a new vessel with fresh CO_2 -absorbent solution (100 mL of 0.05 M KOH). Attention was paid to avoid CO_2 losses during the experiments. All chemicals used were at least of reagent grade. All petroleum oxidations were made in duplicate and thus, results are expressed as the mean of two measurements. The variation in the results of experiment duplication for the same oxidation treatment was less than 20%.

2.3. Analytical methodology

Organic compounds in the crude petroleum were analyzed using a Varian GC 3400 equipped with a DB-WAX column ($60\ \text{m} \times 0.25\ \text{mm i.d.}$, $0.25\ \mu\text{m}$ film thickness) according to the EPA protocols [8], using carbon disulphide as the extractor solvent. The injector temperature was $280\ ^\circ\text{C}$ (splitless). Chromatographic conditions include an initial oven temperature of $50\ ^\circ\text{C}$, a 2.50 min isotherm, a program rate of $7\ ^\circ\text{C}/\text{min}$, and a final oven temperature of $240\ ^\circ\text{C}$ with an isotherm of 8 min. The carrier gas was N_2 , with a column flow of $1\ \text{mL min}^{-1}$ and detection was based on flame ionization. Total organic carbon (TOC) analysis was carried out by combustion method with a Shimadzu Total Organic Carbon Analyzer, model TOC-5000A, using a standard calibration curve [9]. The TOC of the contaminated soil samples was the sum of the petroleum found in solution and in the solid phase. Determination of chemical and biological oxygen demand (COD and BOD) was carried out according to a standard method [9]. In the BOD tests, a small amount of filtered activated sludge from a municipal wastewater treatment plant was used as the bacterial seed. Hydrogen peroxide concentrations were monitored by TiSO_4 spectrophotometry for below 1%, and by iodometric titration for greater than 1% [9], as follows: 30 mL of Milli-Q water and 20 mL of 1 M sulphuric acid were added to a 100 mL flask. Permanganate solution was added dropwise and the flask was shaken continuously until a slightly pink coloration was obtained, which persisted for 30 s. The CO_2 evolved from each experiment was captured in a closed external vessel containing an aqueous potassium hydroxide (KOH) solution (0.05 M, 100 mL). BaCl_2 was added to the used KOH scavenger solution, followed by titrimetric determination with HCl solution (0.05 M).

3. Results and discussion

3.1. Crude petroleum constituents

Table 1 shows the chemical constituents of the original crude petroleum found in original contaminated water where solubilization and volatilization process of some petroleum constituents must have occurred before recuperation with the separatory funnel.

Crude petroleum is a complex mixture containing many different chemical species with different physico-chemical prop-

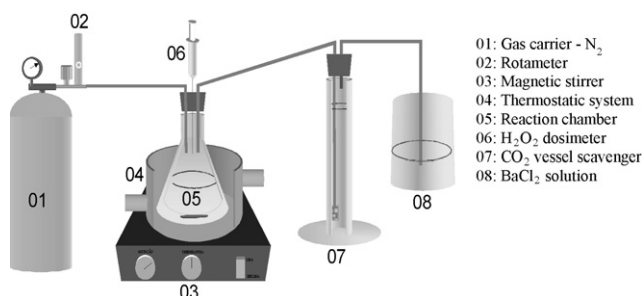


Fig. 1. Experimental setup used to carry out Fenton's reactions.

Table 1
Fractional composition of original crude petroleum

Class	Concentration (mg g ⁻¹)
Total organic carbon	827.0
Total hydrocarbons	924.3
Gasoline	163.4
Kerosene	33.5
Diesel	313.3
Benzene	4.6
Toluene	8.4
Ethylbenzene	2.3
Xylenes	14.1

erties, solubility being the most important parameter concerning its ecotoxicity or threat to public health [10,11].

3.2. Reliability of CO₂ evolution from organic mineralization process

A single methodological validation was carried out to assess the CO₂ evolution accuracy and precision from the potassium biphthalate oxidized by Fenton's reaction. Oxidation tests (in triplicates) were carried out with the following reagent concentrations (% H₂O₂–mM Fe²⁺: 1–1; 1–10; 5–1; 5–10), in the apparatus shown in Fig. 1, under the same experimental conditions used to treat the water and soil contaminated by crude petroleum. Table 2 shows data on the CO₂ evolved and H₂O₂ consumed in the biphthalate oxidation (500 mg).

Data from Table 2 show that the quantification of CO₂ evolved from biphthalate mineralization is sensitive to the concentration of both reagents, hydrogen peroxide and ferrous ion. Regression coefficients derived from the data of Table 2 showed that there was a good correlation between biphthalate oxidation and reagent concentrations. Thus, a more detailed reliability study of biphthalate mineralization was carried out and the results of this single methodological validation (accuracy, precision and coefficient of variation) based on CO₂ evolution are shown in Table 3.

Oxidation of 500–50 mg of biphthalate (theoric CO₂ of 861.7 and 86.17 mg, respectively) show an accuracy variation of 104.8–81.1%, with a good precision (CV below 5.13%). For the concentrations of 30 and 10 mg of biphthalate (theoric CO₂

of 51.7 and 17.2 mg, respectively), the accuracy was poor (62.5 and 8.7%), as was the precision (22.8 and 48.1%).

3.3. Fenton's reaction and temperature

Fenton's reaction is exothermic and is more effective when carried out between 10 and 20 °C [12]. Of the 12 reagent combinations tested, results for 5 reactions were discarded due to the high temperature reached during the reactions. The control reaction did not show significant temperature variation, but in some experiments, reagent combinations resulted in strong exothermic reactions and the thermostatic system used was insufficient to maintain the required temperature (25 ± 2 °C). Temperatures higher than 60 °C cause peroxide decomposition and, for this reason, these reaction results were discarded. Thus, due to the violent nature of some reagent combinations (H₂O₂ greater than 10% and Fe²⁺ greater than 50 mM), reactions with these combinations must be carried out with extreme prudence.

3.4. Influence of initial H₂O₂ concentration on the reaction time

Besides the reagent concentrations selected for each experiment, another important factor to be considered is the reaction time. With H₂O₂ concentration determination during the reaction, it was assumed that the reaction was completed when no H₂O₂ was detected. Table 4 shows the H₂O₂ concentration during the contaminated water treatment, while Table 5 is related to the soil sample treatment.

From Tables 4 and 5, it is clear that the H₂O₂ degradation kinetics is dependent on the Fe²⁺ concentration. According to Walling [13], the oxidation of organic compounds in the Fenton's reaction is likely to occur in several steps: (i) generation of •OH radicals and their oxidative reaction with organic compounds; (ii) direct action of H₂O₂ toward the pollutant; (iii) •OH scavenging due to Fe²⁺ ions and H₂O₂; (iv) reaction of Fe³⁺ with H₂O₂ leading to regeneration of Fe²⁺ ions and formation of hydroperoxyl radicals (HO₂•); and (v) reduction of Fe³⁺ to Fe²⁺ by HO₂•.

When organic compounds are absent and the Fe²⁺/H₂O₂ ratio is ≥ 2, the reaction of •OH occurs mainly with Fe²⁺ and the rate of this reaction is ten times faster than the reaction between •OH

Table 2
Quantification of CO₂ evolved and H₂O₂ in solution in the Fenton oxidation of 500 mg potassium biphthalate

Time (min)	mg CO ₂ evolved/% H ₂ O ₂ in the solution			
	1% H ₂ O ₂ /1 mM Fe ²⁺	1% H ₂ O ₂ /10 mM Fe ²⁺	5% H ₂ O ₂ /1 mM Fe ²⁺	5% H ₂ O ₂ /10 mM Fe ²⁺
0	0/1.0	0/1.0	0/5.0	0/5.0
10	48.9/0.80	218.5/0.60	122.5/4.7	429.8/2.4
20	63.3/0.70	451/0.35	339.1/4.5	844.1/1.8
30	150.4/0.65	640.6/0.22	496.3/4.1	861.8/0.8
40	279/0.60	860.1/0.18	710.7/3.8	859.9/0
50	381.1/0.58	861.1/0.12	860.5/3.4	860.1/0
60	450.7/0.55	860/0.09	859.7/3.1	861.4/0
R ²	0.9145	0.9688	0.9513	0.8075

Table 3
Accuracy, precision and coefficient of variation ($n=3$) obtained in the Fenton oxidation of different amounts of potassium biphthalate measured by CO_2 evolved

Reference mass of biphthalate (mg)	Measured mass of biphthalate (mg)	Mean	% Accuracy	Standard deviation (precision)	Coefficient of variation (%)
500	516.4	506.0	103.3	8.38	1.65
	508.5		101.7		
	493.1		98.62		
400	381.0	382.0	95.25	4.18	1.09
	376.7		94.17		
	388.4		97.10		
300	284.3	294.8	94.76	11.97	4.06
	314.4		104.8		
	285.9		95.30		
200	163.2	178.1	81.60	9.15	5.13
	184.5		92.25		
	186.6		93.30		
100	89.70	87.05	89.70	3.63	4.17
	81.14		81.14		
	90.32		90.32		
50	49.11	45.94	98.22	2.08	4.53
	43.29		86.56		
	45.41		90.82		
30	18.77	14.13	62.56	3.22	22.79
	13.98		46.60		
	9.65		32.16		
10	2.47	2.58	24.70	1.24	48.06
	4.39		43.90		
	0.87		8.70		

and H_2O_2 [14]. Thus, the presence of organic compounds only affects the behavior of Fe^{2+} , and not H_2O_2 , since the organic pollutant competes with Fe^{2+} for hydroxyl radicals [14]. The final reaction time was therefore based on the point where hydrogen

peroxide was no longer detected in the specific reaction. In this sense, when carrying out the Fenton's reaction, H_2O_2 concentration must be measured in order to determine the time reaction, which is dependent on $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio and sample composition.

Table 4
Variation in H_2O_2 concentration (%) during Fenton treatment of petroleum-contaminated water samples

Time (h)	H_2O_2 (%) ^a						
	1% $\text{H}_2\text{O}_2/1$ mM Fe^{2+}	1% $\text{H}_2\text{O}_2/10$ mM Fe^{2+}	1% $\text{H}_2\text{O}_2/50$ mM Fe^{2+}	1% $\text{H}_2\text{O}_2/100$ mM Fe^{2+}	10% $\text{H}_2\text{O}_2/1$ mM Fe^{2+}	10% $\text{H}_2\text{O}_2/10$ mM Fe^{2+}	20% $\text{H}_2\text{O}_2/10$ mM Fe^{2+}
0	1	1	1	1	10	10	20
1	0.95	0.3	0.6	0.2	9.8	9.2	19.8
2	0.6	0.2	0.35	0	9.6	8.4	19.7
3	0.55	0.15	0	–	9.4	6.6	19.5
4	0.4	0	–	–	9	5.4	19.1
5	0.25	–	–	–	8.6	4.9	18.5
6	0.15	–	–	–	8.1	4	17.7
12	0	–	–	–	7.7	3.2	17.4
24	–	–	–	–	4.9	2.5	16.8
36	–	–	–	–	3.1	0	15.5
48	–	–	–	–	1.6	–	8.4
60	–	–	–	–	0.5	–	4.9
72	–	–	–	–	0	–	3
84	–	–	–	–	–	–	2.6
96	–	–	–	–	–	–	2
108	–	–	–	–	–	–	0.5
120	–	–	–	–	–	–	0

Results are the mean of two experiments.

^a Assuming that the reaction was complete when no H_2O_2 was detected.

Table 5
Variation in H₂O₂ concentration (%) during Fenton treatment of petroleum-contaminated soil samples

Time (h)	H ₂ O ₂ (%) ^a							
	1% H ₂ O ₂ /1 mM Fe ²⁺	1% H ₂ O ₂ /10 mM Fe ²⁺	1% H ₂ O ₂ /50 mM Fe ²⁺	1% H ₂ O ₂ /100 mM Fe ²⁺	10% H ₂ O ₂ /1 mM Fe ²⁺	10% H ₂ O ₂ /10 mM Fe ²⁺	20% H ₂ O ₂ /10 mM Fe ²⁺	
0	1	1	1	1	10	10	20	
1	0.83	0.65	0.35	0.24	9.7	9.5	19.9	
2	0.75	0.47	0.21	0.14	9.5	8.9	19.8	
3	0.47	0.31	0.17	0.04	9.1	7.5	19.5	
4	0.38	0.17	0.07	0	8.5	6.7	19.4	
5	0.25	0	0		8	5.8	19.1	
6	0.18				7.8	4.5	18.4	
12				6.5	3.1	17.2		
24	–	–	–	–	5.1	1.9	15.4	
36	–	–	–	–	3.7	1.1	12.3	
48	–	–	–	–	2.8	0	10.7	
60	–	–	–	–	1.4	–	8.4	
72	–	–	–	–	0.9	–	6.1	
84	–	–	–	0	–	3.1	–	
96	–	–	–	–	–	1.9	–	
108	–	–	–	–	–	–	0.7	
120	–	–	–	–	–	–	0	

Results are the mean of two experiments.

^a Assuming that the reaction was complete when no H₂O₂ was detected.

3.5. CO₂ evolved from Fenton's reaction

For each oxidation experiment, degradation of organic compounds was related with the amount of CO₂ evolved from the oxidation. This CO₂ evolution allowed us to calculate the rate of TOC removal. Table 6 shows the CO₂ evolved from the oxidation of contaminated water and Table 7 shows the results related to the soil sample treatment. It must be remembered that quantification of CO₂ evolved could result in an underestimation of the oxidation process, since this methodology only quantifies total oxidation, i.e., mineralization.

In the oxidation of petroleum-contaminated water and soil samples, parallel quantification of CO₂ and H₂O₂ parameters showed opposite trends for the time course variations for mass of CO₂ evolved and H₂O₂ concentrations at each treatment time. In the control experiments, no CO₂ evolution was observed using our analytical methodology when oxidation was performed without iron ions and without hydrogen peroxide, or with hydrogen peroxide in absence of iron ions.

Many reported studies have proposed values for the [Fe²⁺]/[H₂O₂] ratio to optimize the Fenton oxidation efficiency, but according to our results, this ratio is case-specific and must be

Table 6
Quantification of CO₂ evolved (mg) during Fenton oxidation of petroleum-contaminated water samples

Time (h)	CO ₂ evolved (mg)							
	1% H ₂ O ₂ /1 mM Fe ²⁺	1% H ₂ O ₂ /10 mM Fe ²⁺	1% H ₂ O ₂ /50 mM Fe ²⁺	1% H ₂ O ₂ /100 mM Fe ²⁺	10% H ₂ O ₂ /1 mM Fe ²⁺	10% H ₂ O ₂ /10 mM Fe ²⁺	20% H ₂ O ₂ /10 mM Fe ²⁺	
0	0	0	0	0	0	0	0	
1	25.6	44.7	55.3	59.3	–	–	–	
2	60.5	98.3	98.9	76.7	–	–	–	
3	75.5	102.9	108.9	76.7	38.8	90.4	28.9	
4	124.1	102.9	109	–	–	–	–	
5	163.8	–	–	–	–	–	–	
6	193.8	–	–	–	74.5	320	80.7	
12	193.4	–	–	–	200.1	336.5	250.4	
24	–	–	–	–	240.5	–	348.8	
36	–	–	–	–	310.4	–	378.1	
48	–	–	–	–	313.6	–	440	
60	–	–	–	–	–	–	455.3	
72	–	–	–	–	–	–	470.5	
84	–	–	–	–	–	–	475.8	
96	–	–	–	–	–	–	478.3	
108	–	–	–	–	–	–	–	
120	–	–	–	–	–	–	–	

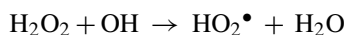
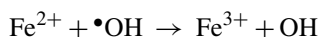
Results showed are mean of two measures.

Table 7
Quantification of CO₂ evolved (mg) during Fenton oxidation of petroleum-contaminated soil samples

Time (h)	CO ₂ evolved (mg)						
	1% H ₂ O ₂ /1 mM Fe ²⁺	1% H ₂ O ₂ /10 mM Fe ²⁺	1% H ₂ O ₂ /50 mM Fe ²⁺	1% H ₂ O ₂ /100 mM Fe ²⁺	10% H ₂ O ₂ /1 mM Fe ²⁺	10% H ₂ O ₂ /10 mM Fe ²⁺	20% H ₂ O ₂ /10 mM Fe ²⁺
0	0	0	0	0	0	0	0
1	18.5	14.9	28.4	51.4	–	–	–
2	50.4	35.4	70.4	60.7	–	–	–
3	109.2	87.63	101.8	60.6	45.3	85.5	86
4	130	87.63	101.6	–	–	–	–
5	149.3	–	–	–	–	–	–
6	181.95	–	–	–	193.4	254.7	177.4
12	181.95	–	–	–	193.4	301.9	177.4
24	–	–	–	–	200.8	302.4	253.8
36	–	–	–	–	235.1	–	273.3
48	–	–	–	–	284.5	–	309.5
60	–	–	–	–	284.5	–	340
72	–	–	–	–	–	–	388.6
84	–	–	–	–	–	–	445.1
96	–	–	–	–	–	–	450.9
108	–	–	–	–	–	–	454
120	–	–	–	–	–	–	453.9

Results showed are mean of two measures.

experimentally determined, which explains why many authors have reported different optimum ratios for the Fenton's reagent [15–17]. Furthermore, it is well established that excessive quantities of Fe²⁺ or H₂O₂ can decrease the reaction efficiency, since these chemical species can react with hydroxyl radicals, according to the reactions shown below [18]:



An interesting optimization study of Fenton's reaction has been carried out using the central composite design (CCD) technique to evaluate the effect of Fenton's peroxidation on the removal of organic pollutants from olive oil mill wastewater (OMW) [19]. These authors concluded that optimum conditions for this wastewater treatment were obtained with a H₂O₂-to-Fe(II) ratio of 8.33, at a pH and OMW concentration of 4 and 70%, respectively. Although this methodology is very useful, we must consider that small wastewater treatment plants are operated without specialists, and in this regard, a single, rapid and cost-effective optimization of Fenton's reaction could be made if CO₂ evolution is used to calculate oxidation rate.

3.6. Influence of initial H₂O₂ and Fe²⁺ concentrations on mineralization process

The effects of the initial concentration of Fenton reagents (H₂O₂ and Fe²⁺) on the mineralization of the contaminated water and soil constituents were as follows: higher Fe²⁺ concentrations stimulated H₂O₂ decomposition, while higher H₂O₂ concentrations resulted in greater mineralization. When [Fe²⁺]₀ was constant (1 mM) and [H₂O₂]₀ varied (1, 10 and 20%), the results obtained showed that the mineralization process was related to the initial H₂O₂ concentration (Fig. 2). The H₂O₂ concen-

trations used in this study did not appear to accelerate H₂O₂ auto-degradation, since mineralization increased when higher H₂O₂ concentration was used.

The reagent cost is a very important factor in selecting a recalcitrant waste treatment technology. The results in Fig. 2 show that an increase in the [Fe²⁺]₀ from 1 to 100 mM decreases the mineralization by 19% for both water and soil samples, when 1% H₂O₂ is used, and is practically the same when a 10% H₂O₂ concentration is used. On the other hand, an increase in the initial H₂O₂ concentration from 1 to 10% increases petroleum mineralization in water (15%) and soil (20%) when the same ferrous ion concentrations are used (1 mM). When 1 mM of Fe²⁺ is used as the catalyst, an increase in H₂O₂ concentration from 10 to 20% increases mineralization in water (28%) and soil samples (26%). From Fig. 2, it is clear that mineralization of the soil samples was lower to that of the water samples, which could be attributed to the soil petroleum adsorption [20]. The high mineralization observed when high hydrogen peroxide concentrations were used indicated that oxidation of adsorbed

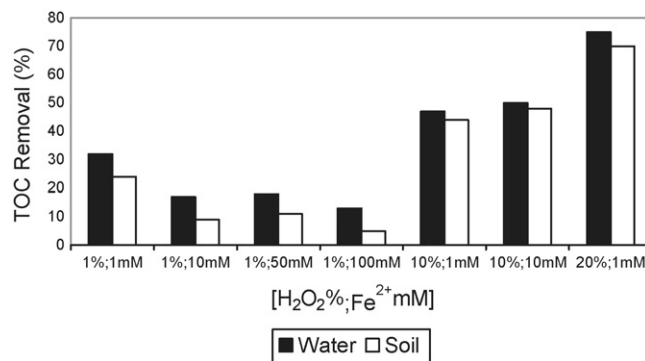


Fig. 2. Percent mineralization of crude petroleum in contaminated water and soil treated by Fenton's reagent under different reagent concentrations [H₂O₂% ; Fe²⁺ mM]. Data are the mean of two experiments.

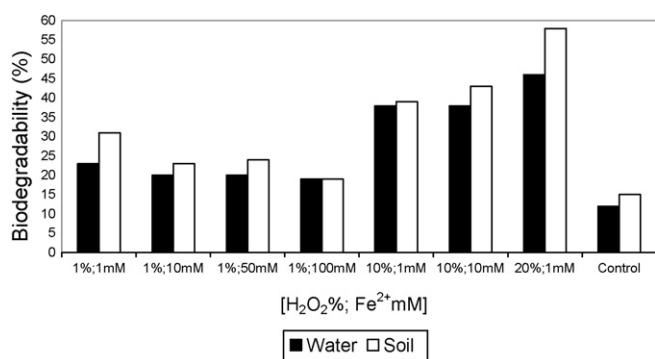


Fig. 3. Biodegradability (%) for petroleum-contaminated water and soil samples after treatment using Fenton's reaction with different reagent ratios [H₂O₂%; Fe²⁺mM]. Data are the mean of two experiments.

petroleum occurred, at least in part, as previously observed by others authors [20–22].

If we consider that cost is a priority in treating contaminated samples, the biodegradability of treated samples must be considered, which could avoid unnecessary use of reagents, since the use of microbial degradation can lead to high TOC mineralization.

3.7. Effect of oxidation on the biodegradability of contaminated samples

At the end of the oxidation reactions, the samples were analyzed for COD and BOD₅ in order to establish changes in biodegradability. The results obtained for water and soil samples are shown in Fig. 3.

Ratios of BOD₅/COD higher than 0.4 (or biodegradability of 40%) indicate a high biodegradability of the sample, while values lower than 0.4 indicate low degradability [23]. In this respect, a more careful consideration should be made when the water or soil contaminants are not oxidized or are only partially oxidized in the COD assay, which could lead to false BOD/COD ratio results [24]. In general, Fig. 3 shows an increase in the biodegradability for the reactions in relation to the control, for contaminated samples of both water and soil. Thus, after the Fenton's reaction, almost all samples became more biodegradable. The control sample (without Fenton oxidation) showed a low biodegradability for water (12%) and soil (15%), that is, these samples have a low degradability, which could be attributed to the toxicity and/or low solubility of compounds present in this sample [25]. In fact, several studies have shown that dissolved compounds can be more easily biodegraded [26–28]. The increase in sample biodegradability observed in Fig. 3 could be associated with the Fenton's reagent concentrations: while lower H₂O₂ concentrations (1%) slightly increased the biodegradability, higher H₂O₂ concentrations (10 and 20%) strongly increased the biodegradability of contaminated water and soil samples. Therefore, higher Fenton's reagent concentrations increased both biodegradability and mineralization of the contaminated samples. Since the Fenton's reagent represents a significant cost, partial oxidation is of interest because microorganisms can be used in a post-treatment process for the complete mineralization

of contaminants in a water matrix. In this regard, the potential for the use of Fenton's reagent (H₂O₂ + Fe²⁺) in an oxidation pre-treatment process to enhance the microbial transformation of two model polycyclic aromatic hydrocarbons, anthracene and benzo[*a*]pyrene, in an aqueous system has previously been evaluated. The authors concluded that the removal of substrates by a combined Fenton's-biotreatment was two to four times higher than with Fenton's treatment or biotreatment alone [29]. Therefore, the use of chemical oxidation followed by microbiological degradation may provide more economical and effective process conditions than oxidation or biodegradation alone.

4. Conclusions

Spectrophotometric measurements of H₂O₂ concentration and titrimetric quantification of CO₂ evolution were used to evaluate the efficiency of Fenton's oxidation, leading to a more feasible, rapid and low cost monitoring of this treatment technique. With this simple methodology, it was shown that Fenton's oxidation of water and soil contaminated with crude petroleum could be an efficient pre-treatment option, with a decrease in TOC of 75% for water and 70% for soil samples when high H₂O₂ (20%) and low Fe²⁺ (1 mM) concentrations were used. Nevertheless, high percentages of TOC removal were only attained when very large amounts of hydrogen peroxide were used (10 and 20%). Since this represents a drawback in terms of cost, after an initial oxidation using a low H₂O₂ concentration, a microbiological treatment could be applied. In this regard, the BOD₅/COD ratios obtained in our experiments showed that low reagent concentrations (1% H₂O₂ and 1 mM Fe²⁺) were sufficient to start the degradation process, which could be continued using microorganisms. Thus, besides increases the mineralization, the Fenton's reaction enhances the biodegradability of petroleum compounds by a factor of up to 3.8 for contaminated samples of both water and soil. This leads to a decrease in reagent costs for the treatment, which is desirable when large volumes of contaminated samples must be treated in a short space of time. In the case of biorecalcitrant hydrocarbons, an increase in the biodegradability resulting from Fenton pre-oxidation is highly desirable. Also, an economic and feasible methodology to control the Fenton's reaction efficiency will be of great interest to small treatment facilities. Additional studies should be carried out with different contaminants/matrixes to assess the reliability of the proposed methodology for the Fenton's reaction optimization.

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