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Article

Endogenous Iron as a Photo-Fenton Reaction Catalyst for the Degradation of Pah's in Soils

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Hidrocarbonetos policíclicos aromáticos (HPA) estão presentes no óleo diesel, sendo considerados perigosos devido à sua toxicidade. Neste estudo relatamos a degradação de 16 HPA em dois solos diferentes (S1 e S2) contaminados artificialmente com óleo diesel, usando processos foto-Fenton e pseudo-foto-Fenton. Planejamentos fatoriais foram usados para obter condições de tratamento mais eficientes e econômicas. Para a reação foto-Fenton, as condições mais favoráveis resultaram 94,6% e 95,6% de degradação dos HPA para os solos S1 e S2, respectivamente. O processo pseudo-foto-Fenton também apresentou um nível satisfatório de degradação, obtido em condições econômicas, com ferro endógeno, baixa concentração de peróxido, curto tempo de exposição à radiação e sem ajuste do pH do solo. Os resultados demonstram a eficiência do processo pseudo-foto-Fenton para tratar áreas contaminadas por HPA.

Polycyclic aromatic hydrocarbon (PAH) components of diesel fuel are considered hazardous, due to their toxicity. We report the degradation of 16 PAHs using photo-Fenton and photo-Fenton-like processes in two different soil samples (S1 and S2) artificially contaminated with diesel oil. Experimental factorial designs were used to determine the most effective treatment conditions, with a view to achieving economical feasibility. For photo-Fenton reactions, the best degradation conditions resulted in an overall PAH concentration reduction of 94.6% and 95.6% for soils S1 and S2, respectively. The photo-Fenton-like processes also led to satisfactory degradation levels, obtained with only endogenous iron, low hydrogen peroxide concentration, short exposure time and no soil pH adjustment. These results demonstrate the viability of photo-Fenton-like processes to treat PAH contaminated areas.

Keywords: soil, remediation, petroleum fuel, photo-Fenton, photo-Fenton-like

Introduction

Environmental problems faced by petroleum industries demand sophisticated solutions, especially those related to the remediation of contaminated areas. Contamination occurs as a result of leakage, spills and accidents during the exploration, refinement, transportation and storage of petroleum and its by-products, such as diesel, fuel or lubricant oils, natural gas, liquefied petroleum gas, naphtha, paraffin, coal tar, gasoline and kerosene. Among the pollutants contained in these oily materials, polycyclic aromatic hydrocarbons (PAHs) require special attention, because they are hydrophobic, recalcitrant to degradation and some are known to be mutagenic and carcinogenic. Human exposure to PAHs can therefore lead to serious health problems. Moreover, because of their hydrophobicity, PAHs tend to remain strongly adsorbed in organic materials for long periods, turning contaminated soil areas into sources of these hazardous compounds to the environment.[1-3]

Many remediation techniques are available for use in contaminated soils, including soil vapour extraction, bioventing, solvent extraction, phytoremediation, and on site or ex-site bioremediation.[4] Some of these processes, however, involve extended treatment periods and high costs, which often make them economically unfeasible. Advanced

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*e-mail: leaq_val@yahoo.com.br; vlins@ufpe.br oxidation processes (AOPs) have been studied as a possible, more economical, and alternative to degrade recalcitrant organic compounds in soils.[5-11] AOPs are destructive processes in which the contaminant can be totally mineralized by chemical reactions. They include Fenton's reagent processes,[6-7,11-12] oxidation by potassium persulphate[13] or potassium permanganate,[14] and heterogeneous photocatalysis using titanium dioxide.[15-16] Using solar radiation to mediate the degradation of organic compounds has proved useful in the remediation of several kinds of contaminated matrixes. For example, Sanchez-Prado *et al.*[7] studied the degradation of triclosan in water by sunlight, and Higarashi[18] demonstrated the efficiency of solar radiation in the degradation of diuron in Brazilian soil samples by in situ heterogeneous photocatalysis. Some studies coupling AOPs with solar radiation have shown that the two processes present a synergy that makes remediation more economical and efficient. Nogueira *et al.*[19] successfully used Fenton's reagent with sunlight to degrade chlorinated organic compounds in water.

Applying Fenton's reagent to the remediation of contaminated soils requires special care with variables such as soil pH, carbonate concentration, presence of organic matter and amount of available iron, which acts as a catalyst for hydrogen peroxide decomposition in Fenton's reagent.[9,20] The combination of solar radiation and endogenous iron (in a photo-Fenton-like process) can form the basis for a remediation process possibly more attractive than conventional treatments. The use of factorial designs allows more efficient and economical remediation conditions to be found with a relatively small number of experiments, as compared to traditional one-variable-at-a-time experimentation.[21]

The aim of the present study was to search for advantageous experimental settings to remediate two types of soil from Pernambuco State (Northeastern Brazil) artificially contaminated with diesel oil, using the photo-Fenton process and exploring the possibility of using only endogenous iron. Sunlight, which is abundant in Northeastern Brazil, was employed as the radiation source.

Experimental

Chemicals

Commercial diesel oil was used to contaminate the soil samples. The photo-Fenton reactions were performed using diluted 50% hydrogen peroxide (Degussa-Hüls) and iron (II) sulfate (Merck). All solvents were purchased from Mallinckrodt (Germany) and were suitable for organic trace analysis. All the others reagents were purchased from Merck (Germany) with > 95% purity.

Soil samples

Two soil samples, S1 and S2, were collected from different regions in the Metropolitan Area of Recife, the capital of the State of Pernambuco (Brazil). Before contamination, some physical and chemical properties of the soils were determined. Their values are shown in Table 1. Iron extraction from the samples was performed using the sodium citrate-bicarbonate-dithionite method,[22] followed by determination using ICP-OES (Spectroflam-Spectro Ciros CCD).

Table 1. Physical and chemical characteristics of the two samples of virgin and contaminated soils

Properties	S1	S2
pH	6.0	5.1
Carbon / (g kg^{-1})	4.1	7.8
Organic matter / (g kg^{-1})	7.1	13.4
Nitrogen / (g kg^{-1})	0.3	0.5
C/N ratio	13.7	15.6
Sand (%)	78.0	89.5
Silt (%)	12.0	4.0
Clay (%)	10.0	6.5
Textural classification	Loam sandy	Sandy
Easily extractable Fe / (g kg^{-1})	9.1	0.6
Contaminated soil		
Carbon / (g kg^{-1})	23.6	31.6
Organic matter / (g kg^{-1})	40.7	54.5

Soil contamination

About 4 kg of each soil sample (S1 and S2) were air-dried at room temperature for two days and sieved to 2 mm. Contamination was carried out by adding 300 mL of commercial diesel per kilogram of soil. This ratio was selected to simulate an actual contamination case reaching the intervention levels specified by Dutch guidelines.[23] The contaminated soils were homogenized, stored in glass recipients and kept at 4 °C until the remediation experiments. Table 1 also shows some properties of the contaminated samples.

Statistical designs and degradation tests

Four factors were selected to assess their influence on PAH degradation: soil pH, reaction time under sunlight exposure, iron concentration and hydrogen peroxide concentration. A 2^{4-1} fractional factorial design, augmented with duplicate runs at the central point, was performed for the S1 and S2 soils. The higher and lower levels chosen for each factor were based on previous studies by Kong *et al.*,[6] Watts *et al.*[7] and Higarashi[18] and also aiming at feasible conditions to be later scaled up for industrial production. Table 2 shows the real and coded values of all factor levels. PAH degradation experiments were performed using combinations of these levels, as discussed in results and discussion section. Considering that solar light penetrates only few centimeters of the soil surface, we used a reactor 6 cm in diameter and 10 cm high, in which a 5 g soil sample was placed, with 10 mL of deionised water added to improve the contact between peroxide and soil. The reagents were added to this slurry to reach the levels given in Table 2. All the experiments were conducted under sunlight exposure, from 9 a.m. to 5 p.m. After exposure, the samples were filtered and analysed for PAHs, following the procedure described below. Blank experiments were also carried out with 5 g soil samples and 10 mL H_2O, without addition of H_2O_2 or Fe (II).

Table 2. Levels of the two factorial designs. (1) 2^{4-1} fractional factorial design using photo-Fenton reagent; (2) Full 2^2 design using a photo-Fenton-like process

Factor	Level		
	-1	0	+1
	2^{4-1} design		
1 - t (h)	4	6	8
2 - H_2O_2 (mmol)	34.0	51.0	68.0
3 - Fe (mmol)	Endogenous	0.17	0.34
4 - pH	No adjustment	5-6	3-4
	2^2 design		
1 - H_2O_2 (mmol)	17.0	25.5	34.0
2 - t (h)	4	6	8

After the results of the fractional design had been analyzed, a full 2^2 factorial design was run, using hydrogen peroxide concentrations in a lower range but maintaining the same exposure time levels to sunlight. The new peroxide levels are also shown in Table 2. In this design, only endogenous iron was used, without any pH adjustment, in an attempt to obtain a more economical route for *in-situ* degradation. The experimental details are the same of the first design.

PAH extraction from soils, cleanup and chromatographic analysis

Approximately 5 g of each contaminated soil sample was Soxhlet-extracted with 150 mL of a 1:1 (v:v) acetone:hexane solution for 16 h. The extract was concentrated in a rotary evaporator to approximately 2 mL. After the addition of 2 mL isooctane, the volume was concentrated to about 1 mL in the rotary evaporator. The cleanup step was performed in a chromatographic column containing approximately 3 g calcinated sodium sulfate, 5 g activated silica, 3 g basic silica, and 3 g sodium sulfate from base to top. The extract was eluted with 60 mL of an 8% dichloromethane solution in hexane. The eluted solution was concentrated in a rotary evaporator to 2 mL and the solvent was exchanged for isooctane. The final extracted volume was adjusted to 1 mL with a gentle flow of pure nitrogen.

Chromatographic analysis of the PAHs was performed on a GC-MS equipment (Shimadzu, model QP-5050 A) based on the EPA 8270 method. The capillary column used was a DB-5MS (J&W Scientific): 30 m x 0.25 mm ID x 0.25 µm film thickness. To achieve better separation, a few adjustments in the temperature gradient were performed. The GC gradient oven temperature varied from 80 °C (1 min) to 120 °C at 20 °C min^{-1} and from 120 °C to 285 °C (10 min) at 2.8 °C min^{-1}. Both the injector and the interface temperatures were set at 280 °C. The carrier gas was helium, at a constant flow of 0.7 mL min^{-1}. A 1 µL aliquot of the final extract was injected in the splitless mode. Data acquisition was performed in the SIM mode. Each PAH was individually quantified using a six-point (50-1500 µg L^{-1}) calibration curve obtained after the appropriate dilution of a certified stock solution (AccuStandard, Z-014G-PAK). The correlation coefficients of each individual PAH analytical curve were above 0.99.

Results and Discussion

The PAH compositions of the contaminated soils are shown in Table 3. Compounds with two or three aromatic rings are predominant, which is consistent with the results published by Liang *et al.*[24] for pure diesel oil. Naphthalene, phenanthrene and fluorene are the main contaminants, with concentrations of 52.1 and 26.2, 28.9 and 30.5, 12.5 and 10.2 mg kg^{-1} dry weight (dw) for samples S1 and S2, respectively. These three PAHs are responsible for 82.7% and 78.9% of the total PAHs content in the contaminated soils. The individual concentrations of the other compounds are all below 4.8 mg kg^{-1} dw.

The degradation of toxic organic compounds by Fenton's process mediated by light has attracted attention because of its higher efficiency in comparison with processes without illumination. Using sunlight instead of artificial radiation increases the degradation rate of the contaminants[25,26] and reduces the operational costs of the treatment.[16,19,27] For each type of soil, ten different degradation experiments based on the 2^{4-1} fractional factorial design were carried out, with a duplicate run at the central point. The degradation values obtained in these experiments are given in Table 4, which also shows the factor level combinations used for

Table 3. Concentrations of 16 PAHs in S1 and S2 soil samples after contamination with diesel oil

PAH (mg kg^{-1} dry weight)	S1	S2
Naphthalene	52.1	26.2
Acenaphthene	1.6	2.4
Acenaphthelene	4.7	3.5
Fluorene	12.5	10.2
Phenanthrene	28.9	30.5
Anthracene	1.4	1.7
Fluoranthene	0.9	0.33
Pyrene	4.8	3.1
Benzo[a]anthracene	0.9	0.32
Chrysene	1.9	3.13
Benzo[k]fluoranthene	0.8	0.24
Benzo[b]fluoranthene	0.8	2.2
Benzo[a]pyrene	0.5	0.32
Indeno[123-cd]pyrene	0.8	0.28
Dibenzo[ah]anthracene	<LQ[1]	0.22
Benzo[ghi]perylene	0.5	0.13
∑PAHs	113.1	84.8

[1] LQ – Limit of Quantification (0.01 mg kg^{-1} dry weight).

each experimental run. Overall the degradation results are good, ranging from 80.3% (run 1) to 94.6% (run 4) for soil S1 and from 63.2% (again run 1) to 95.6% (run 7) for soil S2. The worst results for both soils occurred in run 1, when all factors were maintained at their lower levels: 34 mmol hydrogen peroxide, 4 h exposure time, using endogenous iron and no pH adjustment. The most effective degradation conditions (run 4 for soil S1 and run 7 for soil S2) have in common a high peroxide level (68 mmol) and the absence of pH adjustment. However, run 4, which uses only endogenous iron and led to the most favourable result for soil S1, yields the second best degradation value for soil S2, practically indistinguishable from the value observed in run 7. This indicates that it may be possible to obtain acceptable degradation levels for both kinds of soil without adding iron or adjusting the pH of the sample.

Since this first design is a half-fraction, it is not possible to calculate pure factor effect values but only contrasts between the responses, which in this case are sums of two effects chosen to minimally confound the main – and presumably most important – effects with factor interactions.[21] The calculated values are called contrasts because despite being calculated as linear combination of

Table 4. Residual PAH concentrations and degradation efficiencies obtained with the photo-Fenton reactions based on the 2^{4-1} factorial design. Runs 9 and 10 are duplicates*

Soil	Run	Factor				∑PAHs	Degradation
		1	2	3	4	(mg kg^{-1} dw)	(%)
S1	1	-1	-1	-1	-1	22.3	80.3
	2	1	-1	-1	1	18.3	83.8
	3	-1	1	-1	1	14.1	87.5
	4	1	1	-1	-1	6.1	94.6
	5	-1	-1	1	1	13.3	88.2
	6	1	-1	1	-1	7.2	93.6
	7	-1	1	1	-1	13.0	88.5
	8	1	1	1	1	9.1	92.0
	9; 10	0	0	0	0	11.3; 12.0	90.0; 89.4
S2	1	-1	-1	-1	-1	31.2	63.2
	2	1	-1	-1	1	12.2	85.6
	3	-1	1	-1	1	14.7	82.7
	4	1	1	-1	-1	5.7	93.3
	5	-1	-1	1	1	5.7	93.3
	6	1	-1	1	-1	14.4	83.0
	7	-1	1	1	-1	3.7	95.6
	8	1	1	1	1	7.7	90.9
	9; 10	0	0	0	0	10.1; 9.4	88.1; 88.9

* Coding as in Table 2.

all responses, with equal numbers of positive and negative coefficients, they are not true effects, but rather sum of them, two at a time. These results in a confounding pattern, from which the true effect values could only be extracted if the other half-fraction were also carried out, restoring the full factorial design. The statistical significance of the calculated contrast values can be determined from the replications performed on the central points of each design. The contrast values and their confounding patterns (that is, the sums of the actual effects each contrast represents) are displayed in Table 5, where significant values appear in boldface. The contrasts associated with the first three factors are all negative for both soils. For soil S1 they are also statistically significant (at the 95% confidence level). For soil S2, the results are similar, except that the contrast corresponding to the 1 + 234 pattern is not significant. However, this occurs by a very small margin. The calculated value, –3.83 mg kg^{-1} dw, is significant at the 94% level. These results suggest that raising the levels of factors 1 (exposure time), 2 (hydrogen peroxide) and 3 (adding iron) tend to lower the residual PAH concentrations in both soils. The contrast associated with pH adjustment appears to be of secondary importance. There are also two significant interaction contrasts, one for each soil, but it is difficult to extract their physicochemical meaning, because they are sums of two actual second-order interaction effects.

Table 5. Contrasts calculated from ΣPAH residual values after the photo-Fenton process. Numerical statistically significant values at the 95% confidence level are shown in boldface

Contrast	Confounding Pattern	S1	S2
1	1 + 234	-5.50	-3.83
2	2 + 134	-4.70	-7.92
3	3 + 124	-4.55	-8.07
4	4 + 123	1.55	-3.68
12	12 + 34	-0.45	1.32
13	13 + 24	0.50	10.17
14	14 + 23	5.50	3.58

The content of endogenous iron in the soils is an important variable for Fenton and Fenton-like processes. As shown in Table 1, soil S1 has 9.1 g kg^{-1} dry weight iron, while soil S2 has only 0.6 g kg^{-1} dry weight. Some experiments were performed to find out if these amounts of iron were sufficient to promote the photo-Fenton reaction without an iron supplement. The degradation results in Table 4 show that adding iron (runs 5 to 8) is more important for soil S2 than for soil S1. This effect could be anticipated, since soil S2 has 15 times less endogenous iron than soil S1. The importance of endogenous iron for the degradation of organic compounds was demonstrated by Kong *et al.*,[6] Watts *et al.*,[7] Flotron *et al.*[9] and Kulik *et al.*,[28] Tyre *et al.*[29] observed a high degradation of pentachlorophenol and dieldrin without the addition of exogenous iron for a soil containing 4.4 g kg^{-1} of mineral iron.

A visual comparison of all degradation results can be seen in Figure 1, where the dashed lines indicate the intervention limits set by the Dutch guidelines for total PAHs in soils. For both types of soil, these limits have not been crossed in any of the experiments. Figure 1 also shows that the best overall conditions for the photo-Fenton reaction are those of run number 4 in Table 4, which is characterized by high levels of factors 1 and 2, *i.e.* 8 h reaction time and 68 mmol hydrogen peroxide. PAHs degradation in this run was 94.6% and 93.3% for soils S1 and S2, respectively.

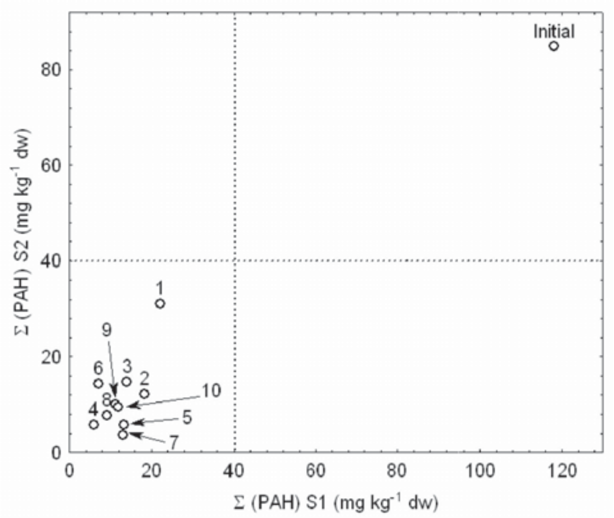

Figure 1. Comparison of the initial and final ΣPAH values after the photo-Fenton reactions for both soils. Dashed lines correspond to the limits set by Dutch guidelines. Numbers identify the factorial design runs according to Table 4.

The recalcitrance of aromatic compounds is well documented.[27,28] Table 6 shows the concentrations of 4 PAHs with different numbers of aromatic rings (naphthalene, phenanthrene, benzo[a]anthracene and benzo[a]pyrene) after the photo-Fenton reactions, for each factorial design run. In general, the larger the number of aromatic rings in the compound the smaller the reaction's degradation efficiency. Average naphthalene degradation was 99.4% for both soils, but only 74.8% for phenanthrene. Since the initial concentrations of the heavier PAHs were quite small, great variation in their degradation efficiency is not surprising. For benzo[a]anthracene and benzo[a]pyrene, percent degradation was even lower, but this is probably only an indication, since the initial concentrations of these compounds in the contaminated soils are already very low.

Table 6. Concentrations of some PAHs with different number of aromatic rings after each run of the 2^{4-1} design. Units are mg kg^{-1} dry weight

Soil	Run	Naphthalene	Phenanthrene	Benzo[a]anthracene	Benzo[a]pyrene
S1	raw	52.1	28.9	0.9	0.5
	1	0.31	13.6	0.30	0.2
	2	0.24	4.7	0.54	<LQ
	3	0.19	8.6	0.41	<LQ
	4	0.17	3.7	<LQ	<LQ
	5	0.37	7.8	0.27	<LQ
	6	0.13	4.8	<LQ	<LQ
	7	0.60	8.8	0.26	0.15
	8	0.50	3.5	0.70	0.40
	9	0.14	8.6	0.50	0.18
	10	0.13	8.7	0.53	0.20
S2	raw	26.2	30.5	0.32	0.32
	1	0.34	21.7	0.30	0.27
	2	0.13	9.5	0.30	0.19
	3	0.16	10.6	0.28	0.19
	4	0.14	4.0	<LQ	0.16
	5	0.13	7.7	0.27	0.18
	6	0.13	1.9	0.31	0.16
	7	0.13	4.8	0.30	0.18
	8	0.13	6.2	0.30	0.18
	9	0.14	5.3	0.31	0.19
	10	0.18	4.7	0.29	0.15

The use of endogenous iron to promote Fenton's reaction is an economic alternative for the remediation of contaminated sites. Considering this and the PAH degradation results presented above, a new factorial design was carried out, in which the only factors were reaction time and hydrogen peroxide concentration. The exposure time levels were the same as in the first design, but the peroxide concentration range was significantly lowered, to search for more economical settings (see Table 2). Natural pH and iron concentration of the soils were used in these experiments. Using natural pH is always preferable, since pH adjustment may cause environmental problems to the soil ecosystem.[29] Residual PAH concentrations and percent degradation values observed in this design are shown in Table 7. For both soils, the best degradation results were achieved with a reaction time of 4 h and a hydrogen peroxide concentration of 17 mmol. Although soil S2 has less endogenous iron, its degradation was better than that of soil S1. It is worth mentioning that this soil is more acidic and contains less organic matter than soil S1. Due to the relatively high variance of the replicate runs on the respective central points in the second design, no statistically significant effect could be detected at the 95% of confidence level.

Table 7. PAH concentrations and degradation efficiencies obtained with the photo-Fenton-like reactions based on the 2^2 factorial design. Factors 1 and 2 are peroxide concentration and exposure time, respectively. Real level values are given in Table 2

Soil	Run	Factor		ΣPAH	Degradation
		1	2	(mg kg^{-1} dry weight)	(%)
S1	1	-1	-1	50.4	57.3
	2	1	-1	27.5	76.7
	3	-1	1	36.0	69.5
	4	1	1	33.9	63.0
	5; 6	0	0	42.4; 35.7	64.1; 70.0
S2	1	-1	-1	19.1	77.5
	2	1	-1	18.7	77.9
	3	-1	1	20.7	75.6
	4	1	1	25.4	70.0
	5; 6	0	0	29.1; 16.4	65.7; 80.6

The degradation results obtained for both soils in this second design can be visualized in Figure 2. Again, the dashed lines indicate the Dutch guideline limits for PAH. For soil S2, the experiments showed higher degradation yields, all the residual PAHs concentrations being below the Dutch intervention limit. For soil S1, two runs (1 and 5) did not comply with the Dutch guidelines. Despite these two results, a photo-Fenton-like process appears to be a viable alternative for the remediation of sites contaminated by diesel oil. In the present study, it should be recalled that the degradation experiments were performed in laboratory contaminated soils, simulating a recent contamination. In an older contamination, since there is a strong interaction of the PAHs with the organic

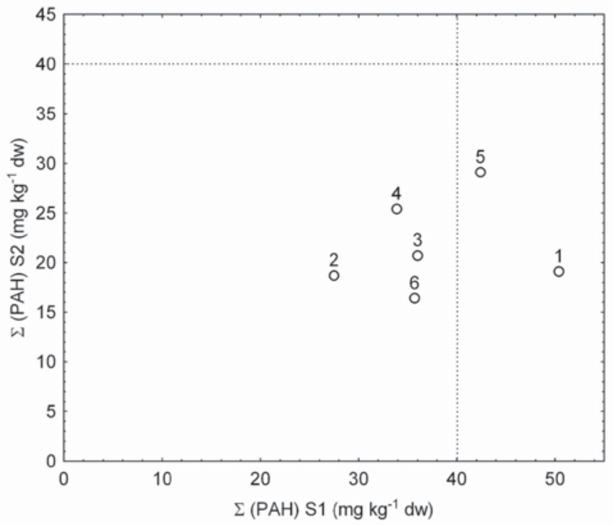

Figure 2. Comparison of the initial and final ΣPAH values after the photo-Fenton-like reactions for both soils. Dashed lines correspond to the limits set by Dutch guidelines. Numbers identify the factorial design runs according to Table 7.

matter present in the soil,[31,32] the degradation process may be less effective or demand larger reagent amounts to yield the same results.

Degradation of PAHs in soil using Fenton's, photo-Fenton or photo-Fenton-like reactions is not a recent issue. Nam *et al.*[33] studied the possibility of combining the biodegradation process with Fenton's reaction to degrade PAHs in soil, reaching 77% of degradation within 24 h. Goi and Trapido[34] assessed the efficiency of PAH degradation in soil using ozonation and Fenton's reaction combined with biodegradation, resulting in 60% PAH degradation within 24 h. Flotron *et al.*[9] studied PAH degradation by Fenton's process in three different solid matrices, reaching 85% degradation in agricultural soil within 24 h. Watts *et al.*[7] used a Fenton-like process to degrade benzo[a]pyrene in two different soil samples: one with silt characteristics and another with sandy characteristics. In a 24 h period, the degradation was 85% in the silty soil and reached 59% in the sandy soil. A comparison of these results with those of this work is presented in Table 8.

In the present study, the treatment was finished in 4 h and sunlight was employed as the radiation source to promote a photo-Fenton-like reaction. Degradation efficiency also depends on hydrogen peroxide and iron concentrations, and, in the case of soil, whether there is sufficient endogenous iron to catalyze a photo-Fenton-like reaction. The degradation efficiency was similar in all the tests, despite the different initial PAH concentrations and iron content in the soils. Using factorial designs to estimate the effects of the process variables, it was possible to achieve more economical conditions, considering the 4 h radiation time and the possibility of using the mineral iron contained in the soil, thereby allowing the use of a photo-Fenton-like reaction in both types of soil. The amount of endogenous iron in soil S1 was higher than that of soil S2 but, as both types of soil had more sandy characteristics, even the smaller amount of iron was found to be readily available to react with peroxide, thus facilitating the formation of hydroxyl radicals. Blank experiments showed no PAH desorption and very low PAH loss by evaporation (< 1% total concentration).

Conclusions

The need for effective remediation processes for contaminated sites is growing and AOPs emerge as one of the most promising alternatives for this purpose. Among all AOPs, photo-Fenton-like processes appear to be the least expensive alternative for soils with high endogenous iron concentrations. This work demonstrates the efficiency of photo-Fenton and photo-Fenton-like processes in the degradation of PAHs in two sandy soils from Brazil. Photo-Fenton conditions studied showed high degradation percentages, reaching values of 95%. In some cases, photo-Fenton-like reactions promoted a reduction of more than 70% in the concentration of PAHs. The use of sunlight as a radiation source proved to be viable even with short exposure periods, such those used in this study. The combination of endogenous iron, no pH adjustment, sunlight radiation and low hydrogen peroxide concentration makes the photo-Fenton-like process an economical alternative for the remediation of PAHs in contaminated soils.

Table 8. Comparison with other remediation treatments for PAHs in soil

Initial PAH concentration/ (mg kg^{-1} dry weight)	pH	Organic carbon (%)	Available iron / (g kg^{-1} dry weight)	Treatment	Reaction time / (h)	PAH degradation (%)	Reference
600	5.9	2.94	n.a.[1]	Fenton	24	77.0	Nam *et al.*[32]
0.22	7.1	1.7	94	Fenton	24	87.2	Flotron *et al.*[9]
32.46	6.7	0.47	0.27	Fenton	24	60	Goi and Trapido[33]
25.22	7.2	0.11	0.04	Fenton-like	24	70	Watts *et al.*[7]
113.1	6.0	0.41	9.1	Photo-Fenton-like	4	76.7	This work
84.8	5.1	0.78	0.6	Photo-Fenton-like	4	75.6	This work

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