

Optimization of the application of the Fenton chemistry for the remediation of a contaminated soil with polycyclic aromatic hydrocarbons

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Abstract

BACKGROUND: A contaminated soil with 100 mg kg⁻¹ each of the following pollutants: anthracene (ANT), phenanthrene (PHE), pyrene (PYR) and benzo(a)pyrene (BaP) was treated by three different kinds of Fenton's reaction without pH adjustment, Fenton-like reaction (hydrogen peroxide (H₂O₂) with a ferric iron salt (Fe(III)), Fenton catalyzed with nanoparticles of zerovalent iron (nZVI), and Fenton-like reaction coupled simultaneously with soil washing, using sodium dodecyl sulfate (SDS) as surfactant.

The influence of initial iron concentration (1–5 mmol L⁻¹), oxidant dosage (88–1765 mmol L⁻¹), type of iron initially added (Fe(III) or nZVI) and effect of surfactant addition were tested.

RESULTS: Almost total conversion of ANT and BaP was achieved for the majority of the experiments, having obtained the best results for the Fenton like reaction with initial Fe(III) concentration of 5 mmol L⁻¹, where a total abatement for all contaminants was obtained in less than 10 days. Besides, the coupling of Fenton reagent and soil washing enhanced the removal of the PAHs studied. 9–10 anthraquinone (ATQ) was detected as the main aromatic intermediate.

CONCLUSIONS: The results put forward in this work reveal the suitability of new effective alternatives to conventional Fenton Reagent for the removal of PAH in soils.

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Keywords: : PAHs; Fenton's Reagent; zerovalent iron nanoparticles; surfactant

INTRODUCTION

The presence of polycyclic aromatic hydrocarbons (PAHs) in soils may be due to natural phenomena (e.g. forest fires) or, to a greater extent, anthropogenic activities (incomplete combustion of wood, fuel, coal, etc.). As a consequence, PAHs are usually found at important concentrations, in hazardous waste sites such as manufactured gas plants, coal coking plants, etc.^{1,2} Despite their low solubility in water, the presence of PAHs in subsoil is frequent; as they can interact with soil organic matter (SOM) they can also reach the water table in the form of non-aqueous phase liquids (NAPLs), such as creosote, coal tar or diesel fuel.^{3,4}

Due to their toxicity and carcinogenic potential, the need for controlling the pathways from the sources of contamination to human exposure (e.g. inhalation, skin contact or ingestion of soil particles) has become of increasing concern.^{5,6} This increasing concern has resulted in the development of a large number of technologies for the removal of this kind of pollutant in the last two decades, such as solvent extraction, which includes soil washing with surfactants, organic solvents, cyclodextrins, subcritical and supercritical fluids; anaerobic or aerobic bioremediation; phytoremediation; photocatalytic and electrokinetic remediation; chemical oxidation using Fenton's reagent, ozone, persulfate, permanganate,

etc.; integrated treatments such as biological–chemical, physical–chemical or physical–chemical–biological.^{7,8}

Among chemical oxidation processes, also called advanced oxidation processes (AOPs), special attention has been paid to the use of Fenton's reagent, which consists in the release of hydroxyl radicals, with high oxidation potential ($E^\circ = 2.73$ V), from the catalytic decomposition of H₂O₂ by Fe(II) or Fe(III), having the ability to oxidize a wide range of organic pollutants. However, implementation of this technique has to deal with important factors which affect critically the efficiency of the process. First, with respect to the oxidant, hydroxyl radical's lifetime is short and there is also a non-productive consumption of H₂O₂, due to its interaction with SOM and iron, manganese oxyhydroxides

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or other transition metals in solution;^{9,10} regarding catalyst, iron cation precipitates at circumneutral pH, resulting in important problems of loss of catalyst;^{11,12} and finally, regarding the organic nature of the contaminant, its low solubility in water hinders the mass transfer between phases. In order to solve these aforementioned drawbacks, the oxidant doses onto the soil must be added at higher quantities to ensure a total degradation of the contaminants,^{13,14} pH of the reaction must be kept at acidic conditions, or a chelating agent can be added in order to keep iron in solution at near neutral pH,^{8,15,16} and a surfactant can be added simultaneously to the oxidant in order to increase contaminant solubility in the aqueous phase.^{17,18}

As reported elsewhere,¹⁵ the chelating agent (CA) competes with the contaminant for the oxidant, and consequently, the oxidant concentration available for the pollutant decreases. Moreover, if pollutants are more recalcitrant to oxidation than the chelating agent, the contaminant removal efficiencies can diminish owing to the CA.

The catalyst added in Fenton's reagent has usually been an iron salt (Fe(II) or Fe(III)), but in recent years, zerovalent iron (ZVI) has been also tested, mainly in aqueous phase.^{19,20} In the case of Fenton's reagent applied to remediation of contaminated soils, nanoparticles of zerovalent iron (nZVI) could be injected into the subsurface as a continuous source of iron. The use of nZVI in soil remediation has been described in the literature as a method of chemical reduction for some contaminants,²¹ but little attention has been paid to the use of nZVI as a source of iron in soil remediation by Fenton's reagent.

Besides, until this moment, the coupling of soil washing and chemical oxidation in soil remediation, also called surfactant enhanced chemical oxidation (SCO), has been scarcely studied in soil remediation.^{17,18} However, it could be a potential combined method for the abatement of pollutants with high hydrophobicity (as PAHs) while the surfactant promotes the solubilization of these compounds to the aqueous phase and the oxidation reaction takes place in this same phase.

Therefore, the aim of this work is to study the remediation of a contaminated soil by 4 PAH, (PHE), (ANT), (PYR) and (BaP), all included in the 16 PAHs priority list of the EPA, by using Fenton's reagent under different conditions, catalyzed by Fe(III), nZVI and using a surfactant coupled to the Fenton's reagent. Oxidant, total iron in solution, contaminant conversion and pH were followed during the reaction, and the effects of oxidant concentration, iron concentration, source of iron and surfactant addition were studied. Besides, aromatic intermediates were identified and quantified in order to evaluate the effectiveness of each technique, not only in terms of removal efficiency of the contaminants.

EXPERIMENTAL

Reagents

PHE $\geq 96\%$ (HPLC grade) from Sigma, ANT 99% from Aldrich, PYR 98% from Aldrich and BaP $\geq 96\%$ from Aldrich were used as contaminants and for the preparation of calibration levels for their analysis by HPLC. For the remediation runs, H₂O₂ $\geq 35\%$ (RT) from Sigma-Aldrich was used as oxidant; ferric sulfate from Panreac 75% (anhydrous basis) and air-stable nZVI powder (NANO FER STAR) from Nanoiron s.r.o. were used, respectively, as catalyst species. For soil washing and coupled soil washing with Fenton reagent, SDS $\geq 99\%$, from Sigma-Aldrich, was used as surfactant. For H₂O₂ determination, sulfuric acid $>95\%$, from Fisher Chemical, and potassium permanganate 99.5%, from Panreac, were both used. Sodium

Table 1. Concentration of each contaminant in the spiked soil

	Number of rings	Concentration (mg kg ⁻¹)
ANT	3	97 ± 6
PHE	3	89 ± 2
PYR	4	93 ± 1
BaP	5	102 ± 1

sulfate anhydrous 99%, from Fisher Chemical, acetone 99.8% HPLC gradient grade from Fisher Chemical and n-hexane 99% HPLC grade from Scharlab were used for extraction of the contaminant in the soil samples. Dichloromethane $\geq 99.8\%$ HPLC grade from Sigma-Aldrich was used for the analysis of intermediates. Phosphoric acid $\geq 85\%$ from Sigma-Aldrich and Acetonitrile HPLC gradient grade from Fisher Chemical were both used as mobile phase in HPLC for PAH analysis. For metal determination in aqueous solution in MP-AES analysis, nitric acid 69.5% was employed as iron ions stabilizer.

Soil spiking

The soil used for the remediation runs consists of a sandy clay loam BT horizon from the Autonomous Community of Madrid; the characterization procedure and a detailed description of the properties are given elsewhere.^{22,23} Soil spiking was carried out as detailed in the literature,^{24,25} where an acetone solution with approximately 60 mg of each ANT, PHE, PYR and BaP was distributed and mixed manually onto 600 g of clean soil with a spatula. Table 1 shows the concentrations achieved for each recovered PAH in soil, after soxhlet extraction.

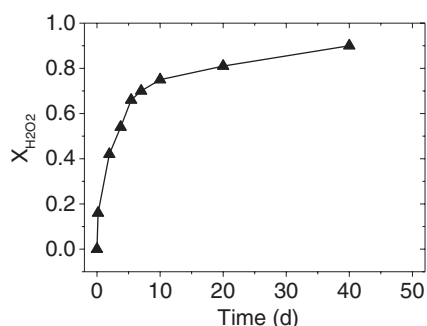
Set-up and procedure

All experiments were carried out without pH adjustment in batch mode using 50 mL PTFE centrifuge tubes with PTFE screw caps. An orbital shaker (Unitronic Orbital by Selecta), under isothermal stirring (100 rpm, 20 °C) was used and tubes were placed horizontally in the shaker. Each reaction tube represents one time point, in which 10 mL of aqueous solution (V_L) were added to 5 g of polluted soil (W_{soil}). Two tubes for each time were used in order to get duplicated values. As can be seen in Table 2, five different types of runs were conducted: non-productive consumption of oxidant (NPC) to study the interaction of the non-polluted soil with the oxidant; a blank run (BL) without addition of oxidant in the aqueous phase; a soil washing (SW) run using an aqueous solution of SDS 7.6 mmol L⁻¹; runs using Fenton's Reagent without surfactant (FR runs), or with surfactant (SCO runs). With regard to the experiments which involved surfactant addition (SW or SCO), SDS was added at its critical micelle concentration (CMC), 7.6 mmol L⁻¹ (20 °C).^{26,27} Initial iron concentration [Fe]₀, type of iron (ferric sulfate or nZVI) and initial oxidant concentration [H₂O₂]₀ were the variables modified in the FR runs. In SCO runs the influence of adding the surfactant previously or simultaneously to the oxidant was also analyzed.

In runs where H₂O₂ was added, a control tube was used only for determination of the remaining oxidant every 24–48 h throughout the reaction time. Afterwards, having achieved specified oxidant conversions (about 25, 50, 75 and 100%), two centrifuge tubes with the same reaction time, were sacrificed (measurements were obtained by duplicate and differences were lower than 15%). After centrifugation for 10 min at 10 000 rpm, two differentiated

Table 2. List of experiments performed $V_L = 10$ mL, $V_L/W_S = 2$ mL g⁻¹, $T = 20$ °C

	Run	Fe type	[Fe] ₀ mmol L ⁻¹	[H ₂ O ₂] ₀ mmol L ⁻¹	Polluted soil	[SDS] ₀ mmol L ⁻¹
NPC	1	-	-	882	No	-
BL	2	-	-	-	Yes	-
SW	3	-	-	-	-	7.6
FR	4	III	1	882	-	-
FR	5	III	5	882	-	-
FR	6	-	-	882	-	-
FR	7	nZVI	1	882	-	-
FR	8	nVZI	5	882	-	-
FR	9	III	1	1765	-	-
SCO	10	III	1	882	-	7.6
SCO	11	III	1 (24 h)	882 (24 h)	-	7.6

**Figure 1.** Non-productive consumption of H₂O₂ at 20 °C, $V_L/W_{\text{soil}} = 2$ mL g⁻¹, $[H_2O_2]_0 = 882$ mmol L⁻¹.

phases were obtained. 50 µL of the aqueous phase were taken for quantification of the remaining H₂O₂, 500 µL of aqueous phase were filtered (≤ 45 µm) for the analysis of iron in solution, and a glass pH electrode was inserted in the aqueous phase for pH measurement. Subsequently, the aqueous phase was extracted with 10 mL n-hexane, and after filtration (≤ 45 µm) of the organic extract, 1 mL was taken for PAH analysis by HPLC.

Remaining PAHs in the soil phase were extracted by Soxhlet extraction, following the method described by the EPA (method 3540 C). About 5 g of soil were extracted using a mixture of n-hexane–acetone (50:50 v:v), as reported in previous work.¹⁵ PAHs were identified in the organic phase after extraction using HPLC. For the identification of possible reaction intermediates, about 20 mL of the organic phase, after extraction, were evaporated at room temperature in a fume hood and reconstituted in 2 mL dichloromethane by GC/MS.

Analytical method

H₂O₂ concentration was measured by potentiometric titration with potassium permanganate 0.005 mol L⁻¹ under acidic conditions (sulfuric acid 10%). For the analysis of iron, 20 mL of ultrapure water, previously acidified with HNO₃, with final concentration of 1% v/v in acid, were added to 500 µL of the filtrated aqueous phase from the slurry. This solution was fed into a microwave plasma-atomic emission spectrometer 4100 MP-AES (Agilent Technologies) with a peristaltic pump operating at 8 rpm. The selected wavelength for iron determination was 259.94 nm and a OneNeb nebulizer was used.

The presence of reaction intermediates was analyzed by GC/MS (HP 6890 N MSD 5975B). A HP-5 column (30 m × 0.32 mmol L⁻¹

i.d. × 0.25 µm) was used for the analysis. The chromatographic conditions were as listed: injector temperature 280 °C; carrier gas (He) flow rate 2 mL min⁻¹ and 8 µL of injected volume in splitless mode. The analysis was performed with an initial oven temperature 45 °C, followed by a first ramp of 5 °C min⁻¹ to 150 °C and a second ramp of 8 °C min⁻¹ to 325 °C. The final run time was 62.88 min.

For original PAH determination, an HPLC (Agilent, mod. 1100) coupled with an Agilent 1290 Infinity Diode Array Detector was employed. The column used was a Poroshell 120 SB-C18 in 2.1 mm × 100 mm and 2.7 µm particle size. Analysis was carried out in isocratic mode at a flow rate of 0.5 mL min⁻¹, selecting as mobile phase a mixture of 60% acetonitrile and 40% aqueous solution with phosphoric acid 75 mmol L⁻¹; the volume injected was 20 µL. The wavelengths chosen for each PAH were 235 nm for PYR, 250 nm for PHE, and 295 nm for ANT and BaP. The corresponding detection limits for PAHs were 0.27 mg L⁻¹ for PHE, 0.11 mg L⁻¹ for ANT, 0.37 mg L⁻¹ for PYR and 0.47 mg L⁻¹ for BaP.

RESULTS AND DISCUSSION

Non-productive consumption of hydrogen peroxide

First, the non-productive consumption of oxidant in soil was studied by following its conversion – Equation (1) – over 20 days of reaction (H₂O₂ 882 mmol L⁻¹). Oxidant conversion has been calculated as:

$$X_{H_2O_2} = \frac{C_0^{H_2O_2} - C_t^{H_2O_2}}{C_0^{H_2O_2}} \quad (1)$$

where C_0 is the initial concentration of H₂O₂ and C_t is the concentration at a given time. The evolution of oxidant (H₂O₂ 882 mmol L⁻¹) with time in run 1 (NPC), within 40 days, is shown in Fig. 1. As can be seen in Fig. 1, the oxidant is decomposed unproductively by reacting with the soil organic matter, and catalytically by the soil metal oxides, such as Fe or Mn, which may interact with H₂O₂, leading to the Fenton-like reaction.²⁸ Therefore, an oxidant amount higher than that, calculated by stoichiometry for the pollutant amount in soil, should be added.¹⁴ Fastest consumption of the oxidant is noticed in the first 10 days before it was slowed down. This decrease may occur due to a first faster stage of soil organic matter and reduced species oxidation and a second catalytic stage, in which the oxidant is still interacting with metal oxides from soil.^{10,29} As can be seen, about 80% of the initial oxidant was consumed in the 20 days.

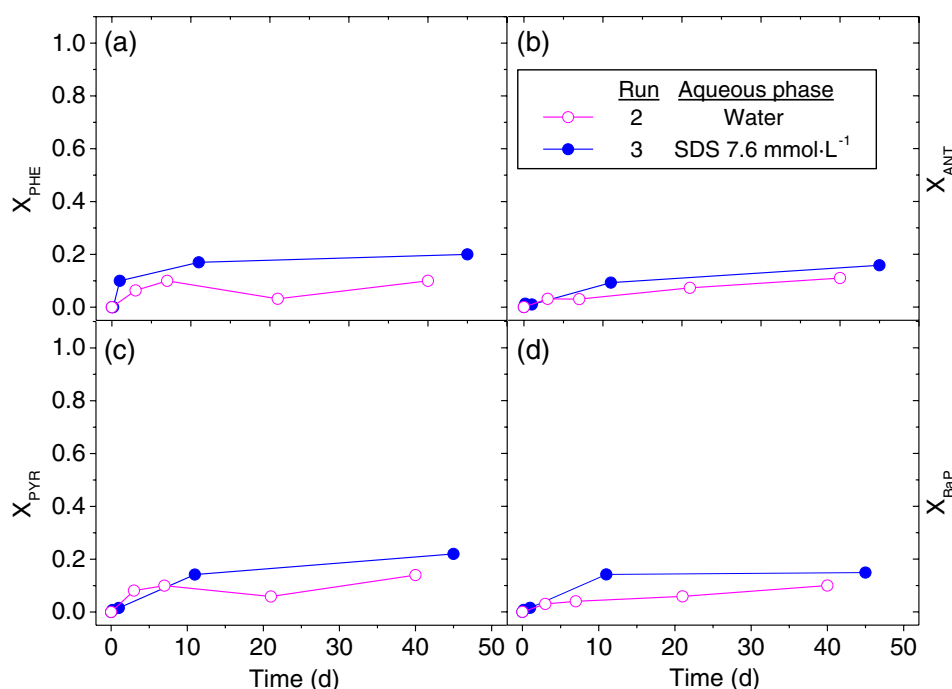


Figure 2. Preliminary runs (blank and soil washing). Evolution of the conversion of PHE, ANT, PYR and BaP in soil. Runs at 20 °C, $V_L/W_{soil} = 2 \text{ mL g}^{-1}$.

Soil washing and blank experiments

Before the remediation experiments, two runs were performed by adding, on one side, ultra-pure water (BL, run 2), and on the other, a surfactant solution of SDS 7.6 mmol L^{-1} on the contaminated soil (SW, run 3). Concentration of each pollutant was monitored with time in order to evaluate the possibility of biodegradation^{25,30} and the effectiveness of soil washing alone. The contaminant conversion – Equation (2) – has been calculated for each PAH:

$$X_{PAH} = \frac{C_0^{PAHj} - C_t^{PAHj}}{C_0^{PAHj}} \quad (2)$$

with C_0^{PAHj} the initial concentration of the j PAH ($j = \text{PHE, ANT, PYR, BaP}$) in soil and C_t^{PAHj} the concentration of the PAH in soil at time t . In SW and BL runs, given that leaking to the aqueous phase was negligible for BL run (<1%) and a little bit higher for the SW run (~5%), PAH conversion corresponds to the PAH degraded by natural attenuation during this period. Evolution of the conversion of each PAH in BL and SW runs is shown in Fig. 2. The PAH conversion showed a similar trend for all PAHs. As can be seen in Fig. 2, after 45 days, a plateau at about 15–20% conversion was achieved for all contaminants, both in control and soil washing runs. Moreover, a slightly higher PAH conversion was observed for SW run, which could be explained by the fact that surfactants improve biological degradation of organic contaminants given their ability to improve their solubility through micelle formation and also their mobility due to the decrease of interfacial tension.^{31,32}

Taking into account the low organic matter content in the soil treated (0.3%), its ability to develop some kind of biodegradation, without additional stimulation is very limited due to the lack of nutrients for microorganisms.^{33,34}

Influence of iron concentration

For the study of the influence of iron concentration on the application of Fenton's Reagent, ferric sulphate was added, without pH

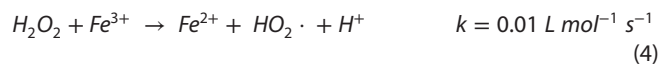
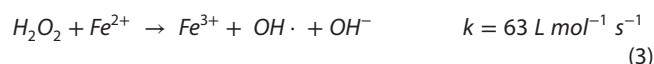
adjustment, at two different concentrations, Fe(III) 1 mmol L^{-1} and Fe(III) 5 mmol L^{-1} , both compared with a run in which no iron was added (FR, runs 4, 5 and 6).

Figure 3 shows the evolution of oxidant conversion (3(a)), pH (3(b)), and iron in solution (3(c)), as well as the corresponding conversions of each PAH, PHE (3(d)), ANT (3(e)), PYR (3(f)) and BaP (3(g)).

When aqueous and soil phase were separated and extracted, as well as in the blank and soil washing runs, no significant concentrations of PAHs were detected from the organic extract of the aqueous phase (<1% with respect to the soil organic extract) in any of the runs using Fenton's Reagent.

From Fig. 3(a) to 3(c), a faster consumption of oxidant was observed for the run where initial concentration of Fe(III) was 5 mmol L^{-1} . Given that ferric sulfate is an acidic salt, the addition of ferric sulfate resulted in a decrease of the pH of the media. Besides, as can be seen in Fig. 3(c), a significant amount of the iron initially added precipitated in a short time. Moreover, the results obtained without external addition of iron are similar to those obtained by adding initially 1 mmol L^{-1} Fe(III). This can be explained by taking into account that iron can be extracted from that naturally occurring in soil, in fact, concentration of iron in solution after adding 1 mmol L^{-1} of Fe(III) and iron extracted from soil are quite similar, with the Fenton-like reaction taking place where hydrogen peroxide is catalyzed by the metals present in soil.^{28,35}

Knowing that the maximum rate of hydroxyl radical in the catalytic cycle – Equations (3) and (4) – is at about $\text{pH} = 3$,^{12,36,37} the faster consumption of H_2O_2 when 5 mmol L^{-1} of Fe(III) is added can be attributed to a higher iron concentration in solution and lower pH of the reaction media.



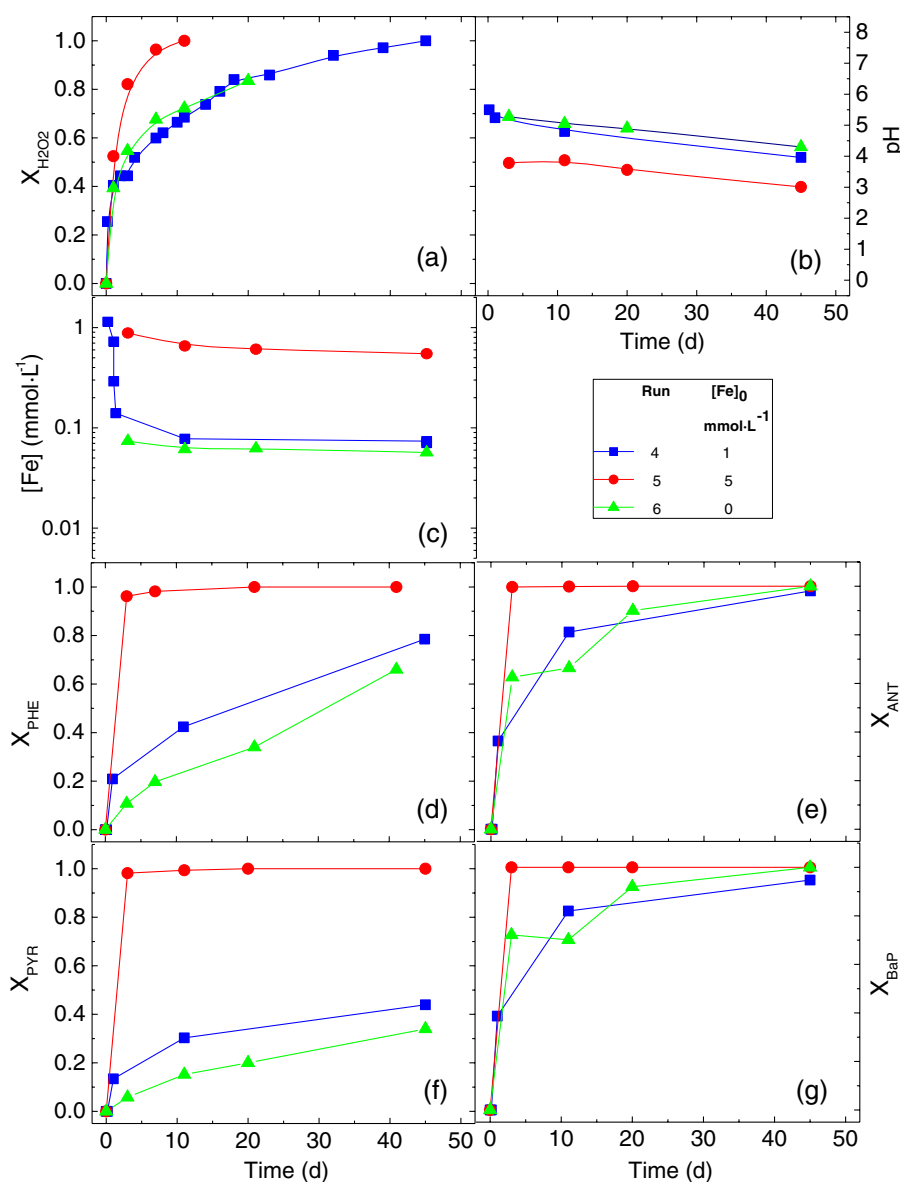


Figure 3. Influence of initial Fe(III) concentration. Evolution of H₂O₂ conversion (a), pH (b), iron in solution (c), PAHs conversion, PHE (d), ANT (e), PYR (f), and BaP (g), at 20 °C, $V_L/W_{\text{soil}} = 2 \text{ mL g}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 882 \text{ mmol L}^{-1}$.

With respect to the PAH removal efficiencies (Fig. 3(d) to 3(g)), the best results were observed when Fe(III) 5 mmol L⁻¹ was added. Similar results were observed in cases where Fe(III) initial concentration was 1 mmol L⁻¹ or when no iron was added, as aforementioned, the close values of iron in solution found, the reaction occurred at almost identical conditions in both runs. In the case of adding Fe(III) 5 mmol L⁻¹, the higher the Fe concentration in solution (about 1 mmol L⁻¹) the higher the amount of hydroxyl radicals released into the media – Equations (3) and (4) – yielding higher conversion of each of the PAHs, achieving almost total abatement of the pollutants in less than 5 days. However, for runs 5 and 6, where iron remaining in solution is as low as 0.1 mmol L⁻¹, significant removal efficiencies were also achieved, almost 100% for ANT and BaP, near 80% for PHE and 40% for PYR.

Influence of the type of iron added (ferric sulfate or nZVI)

To study the influence of different sources of iron on the effectiveness of the Fenton reaction, iron was added as a ferric salt (FR, runs

4 and 5) or as nZVI (FR, runs 7 and 8). Runs 4 and 7 had an initial iron concentration in the aqueous phase of 1 mmol L⁻¹, while in runs 5 and 8 initial iron concentration was 5 mmol L⁻¹.

Figure 4 shows the evolution of the H₂O₂ conversion (4a), pH (4b) and iron concentration in solution (4c) with time. As can be seen in Fig. 4(a) to 4(c), no significant differences in oxidant consumption and pH were noticed with reaction time in runs 4 and 7 ([Fe]₀ = 1 mmol L⁻¹). Besides, no differences were found between adding nZVI at 1 mmol L⁻¹ (run 7) or 5 mmol L⁻¹ (run 8). These similar values obtained in runs 4, 7 and 8 can be explained by the low and almost constant iron in solution observed in these runs. Regarding total iron concentration in solution in Fig. 4(c), a sharp decrease is seen at the beginning in run 4, while in runs 7 and 8 concentration remains constant over time. The fast initial drop of iron noticed after the addition of the iron salt can be explained by both the iron solubility with pH and the iron–soil interaction that enhances iron precipitation or adsorption onto the soil,³⁸ on the other hand, in runs 7 and 8, iron was added in the form of metallic

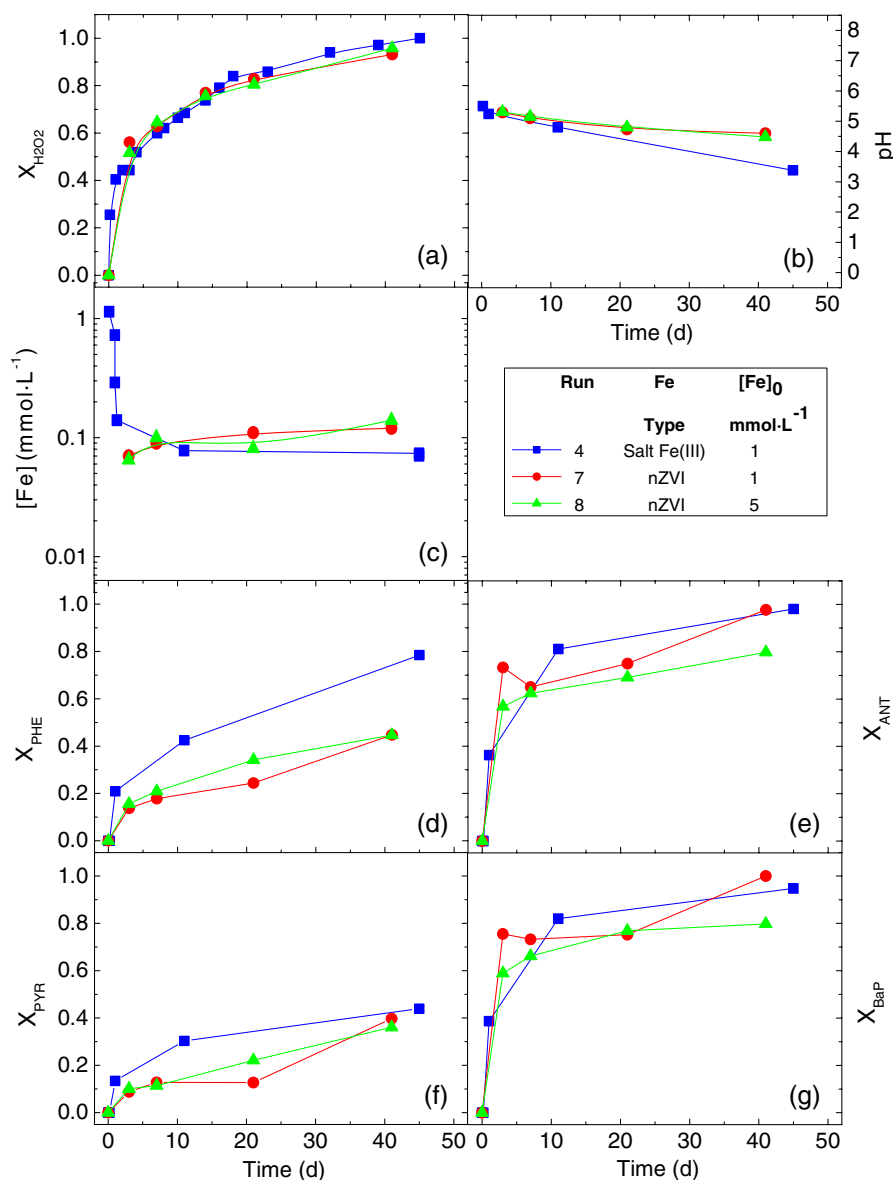


Figure 4. Influence of iron valence initially added. Evolution of H_2O_2 conversion (a), pH (b), iron in solution (c), PAHs conversion, PHE (d), ANT (e), PYR (f), and BaP (g), at 20 °C, $V_L/W_{soil} = 2 \text{ mL g}^{-1}$, $[H_2O_2]_0 = 882 \text{ mmol L}^{-1}$.

nZVI and the iron measured was iron in solution, which was also affected by iron solubility with pH and interaction between nZVI and soil.

On the other hand, results in Fig. 4(d) to 4(g) show the removal efficiency of the PAHs. As can be seen, similar results were obtained in runs 4, 7 and 8, as expected from the iron in solution found in Fig. 4(c). As reported in the literature, H_2O_2 catalyzed by nZVI has been successfully employed for the removal of several pollutants, in which better results were obtained when pH was adjusted to 3.^{39,40} The negligible improvement noticed in this work by using nZVI could be attributed to the higher pH here used, which limits the iron solubility. However, the nZVI could be an efficient method for the injection of iron into the subsurface, as it can be distributed and act as a continuous source of iron.

Influence of H_2O_2 concentration

Two experiments were carried out in order to analyze the influence of H_2O_2 concentration. For this purpose, initial H_2O_2

concentrations were fixed at 882 mmol L^{-1} or 1765 mmol L^{-1} in runs 4 and 9, respectively. In the case of the addition of H_2O_2 882 mmol L^{-1} , the oxidant/contaminant molar ratio was 15 times higher than stoichiometric (for the sum of PAHs), while for H_2O_2 1765 mmol L^{-1} this concentration was near 30 times higher. The Fe(III) concentration initially added was 1 mmol L^{-1} in both cases.

Figure 5 shows the evolution of H_2O_2 consumption (a), pH (b) and total iron (c) concentration with time. Slightly faster oxidant conversion is observed at lower H_2O_2 concentration. On the other hand, pH and Fe in solution have very similar profiles during the reaction. The first stage of H_2O_2 consumption corresponds to the SOM and reduced species in the soil, while the second is a catalytic stage due to the metal oxides in the soil, therefore it is expected that the higher the H_2O_2 amount in the media, the slower its conversion in the first stage, when the rest of the variables remain fixed.¹⁴

According to Fig. 5(d) to Fig. 5(g), where conversions of each PAH are shown, an improvement in the removal rate of PYR and BaP

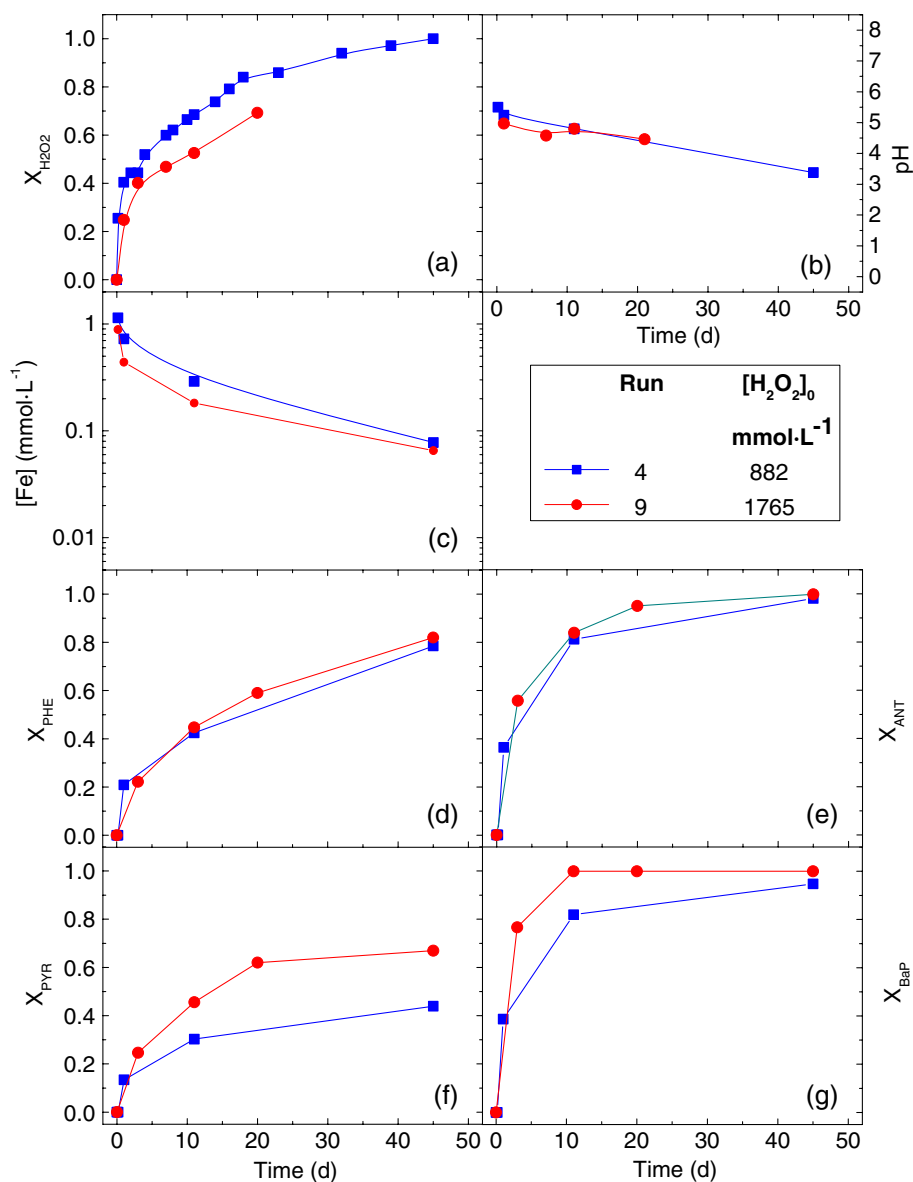


Figure 5. Influence of H_2O_2 concentration. Evolution of H_2O_2 conversion (a), pH (b), iron in solution (c), PAHs conversion, PHE (d), ANT (e), PYR (f), and BaP (g), at $20^\circ C$, $V_L/W_{soil} = 2 mL g^{-1}$, $[Fe]_0 = 1 mmol L^{-1}$ added as Fe(III) salt.

was seen while no significant differences were observed for ANT and PHE removal rates. As can be seen, although concentration was increased two-fold, PAHs removal efficiency was increased to a smaller extent, explained by the scavenging effects on hydroxyl radicals due to an excess of H_2O_2 .

Application of soil washing and chemical oxidation simultaneously

In order to analyze the possibility of enhancement in the remediation effectiveness, by simultaneous application of a surfactant (SDS) and Fenton's Reagent, results obtained in runs 4, 10 and 11 were compared. Iron was initially added as a ferric salt at a $1 mmol L^{-1}$ Fe (III) concentration and initial H_2O_2 concentration was fixed at $882 mmol L^{-1}$. In run 10, SDS was added simultaneously with the oxidant while in run 11 oxidant and iron were added 24 h after surfactant addition. In run 4 no SDS was added.

Figure 6 shows the evolution of H_2O_2 consumption (a), pH (b) and total iron (c) in solution during the reaction. According to graphs 6(a), 6(b) and 6(c), no remarkable differences in the results for H_2O_2 consumption and Fe in solution (runs 4, 10 and 11), were noticed; in fact, profiles of H_2O_2 conversion and Fe evolution both follow an almost identical trend. In the case of pH, a higher pH was observed for the experiment where SDS was added 24 h prior to the addition of oxidant and iron.

According to Fig. 6(d) to (f), where the conversion of every PAH is shown, PHE (d), ANT (e), PYR (f) and BaP (g), the addition of SDS (runs 10 and 11) resulted in faster abatement of all the PAHs studied. Total conversion was obtained for ANT and BaP while conversions obtained for PHE and PYR were close to 80%, once all oxidant was totally consumed.

Comparing runs 10 and 11, where the difference was in the procedure for adding SDS into the media, it was observed that, although similar removal efficiencies of contaminant were achieved at the final reaction time, in the case of run

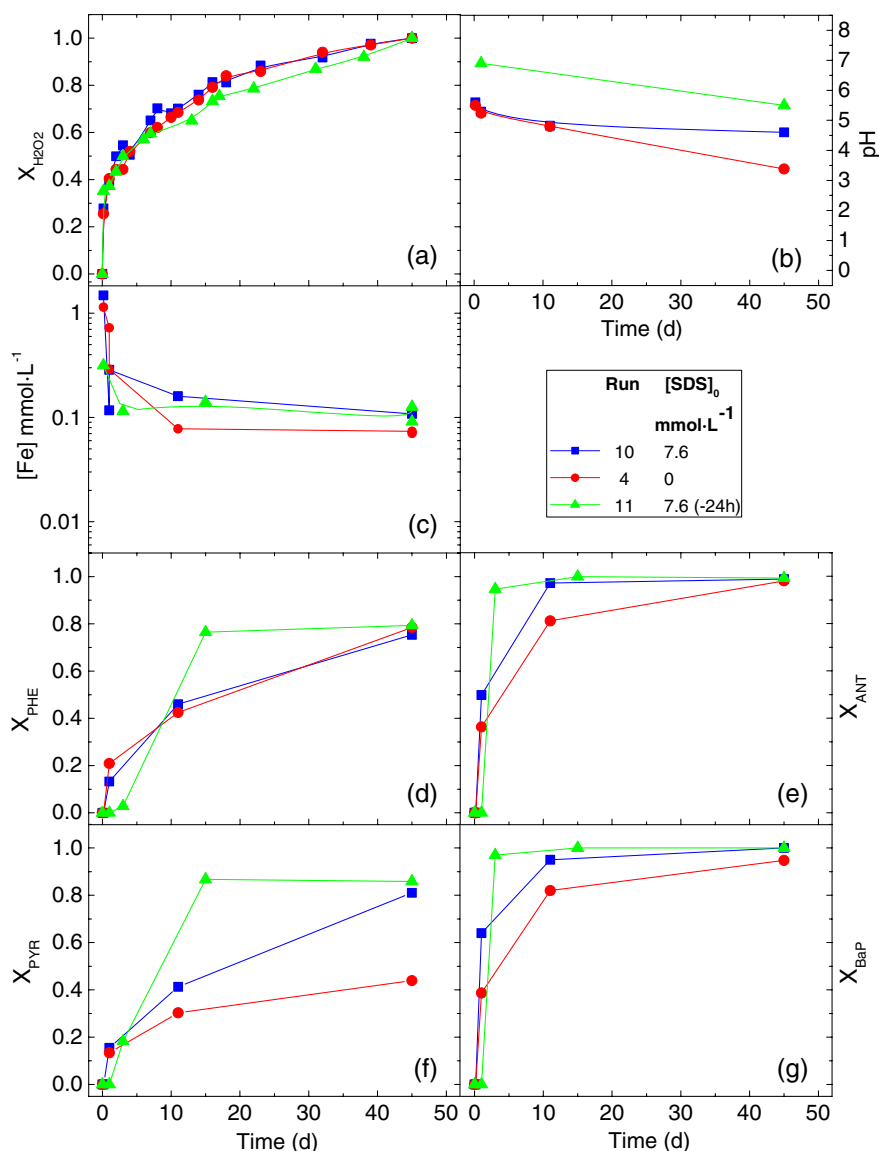


Figure 6. Influence of addition of a surfactant (SDS) to the Fenton's Reagent. Evolution of H_2O_2 conversion (a), pH (b), iron in solution (c), PAHs conversion, PHE (d), ANT (e), PYR (f), and BaP (g), at $20\text{ }^\circ\text{C}$, $V_L/W_{\text{soil}} = 2\text{ mL} \cdot \text{g}^{-1}$, $[\text{Fe}]_0 = 1\text{ mmol L}^{-1}$ as Fe(III) salt, $[\text{H}_2\text{O}_2]_0 = 882\text{ mmol L}^{-1}$.

11, those pollutant conversions were achieved sooner. This comparison confirms the fact that the addition of a surfactant improves the solubilization of contaminants, therefore they can be oxidized faster in the aqueous phase, where the reaction takes place.^{17,18}

Transformation products

Under the experimental conditions used, the main aromatic product detected in the oxidation runs was 9–10 anthraquinone (ATQ), confirmed by both HPLC and GC-MS analysis. This transformation product, as reported in the literature, was also found in PAHs oxidation in soil^{41,42} and the aqueous phase.⁴³ Besides, it is supposed that the presence of this byproduct in soil can be temporary, given that it could be biodegraded more easily and quickly than the parent PAH.^{41,42} Figure 7 shows the evolution of ATQ with time for all experiments carried out. It is necessary to point out that ATQ appeared in all runs except that in which Fe(III) 5 mmol L^{-1} was added (run 5), which was the run where total removal of all PAHs

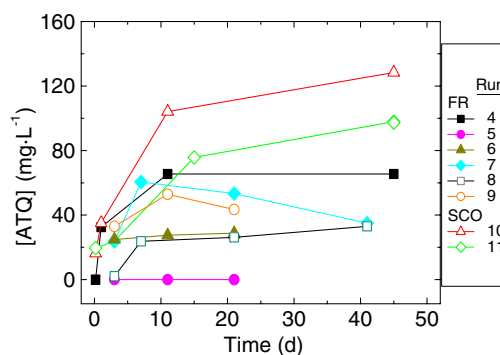


Figure 7. Evolution of ATQ concentration with time in all oxidation reactions (runs 4 to 11).

was achieved. The fact of not having detected ATQ in run 5 means that it was fully degraded as well as the rest of the PAHs, given the strong conditions generated by adding 5 mmol L^{-1} Fe(III).

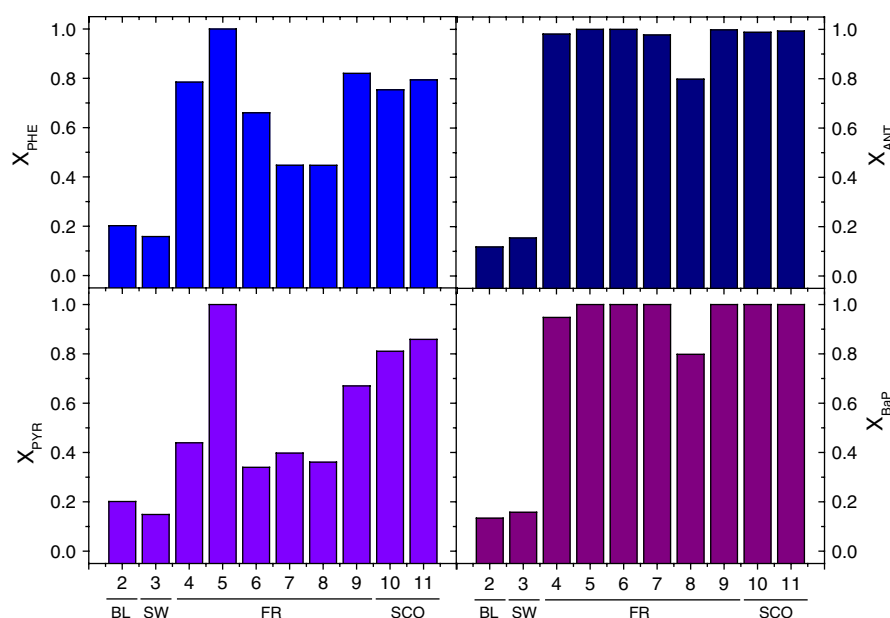


Figure 8. Efficiencies of removal of PHE, ANT, PYR and BaP for all experiments carried out ($t = 48$ days).

Summary of all experiments

Figure 8 shows the corresponding removal efficiencies of each PAH for all experiments at their final reaction time. According to the criteria described in the set-up and procedure section, four groups were established (BL, SW, FR and SCO). In this sense, it is noticed that for both ANT and BaP, almost all techniques applied achieved near total conversions, with lowest conversion of about 80% for run 8 (Fenton reagent with nZVI 5 mmol L^{-1}). On the other hand, lower conversions were reached for PHE and PYR, except for run 5, in which all PAHs were almost completely removed.

CONCLUSIONS

The remediation of a contaminated soil by four different types of PAHs (ANT, PHE, PYR and BaP) by applying Fenton's reagent under different conditions has been investigated. H_2O_2 catalyzed by Fe(III) and nZVI, and also coupled with soil washing with SDS. During reactions the conversion of oxidant, contaminant, concentration of iron in solution and pH were measured.

Natural attenuation and soil washing during the treatment time (48 days) removed less than 20% of the PAHs in soil. In contrast, in the treatments where Fenton reagent was applied, higher removal efficiencies for all PAH were observed. According to the results obtained, PYR and PHE were the PAHs which offered highest resistance to the treatments.

It was found that higher concentrations of iron in solution produced higher PAH and aromatic intermediates removal. pH is a critical factor during treatments with Fenton reagent: with higher acidity higher iron concentration in solution can be obtained. With 1 mmol L^{-1} of iron in solution a time of 5 days was enough to completely eliminate the PAHs and the aromatic intermediates. On the other hand, iron in solution as low as 0.1 mmol L^{-1} was able to catalyze hydrogen peroxide decomposition producing hydroxyl radicals resulting in almost total removal of PAHs in less than 48 days, the controlling step being the hydrogen peroxide lifetime. This iron in solution was obtained by adding an iron salt or nZVI particles. Besides, iron can be extracted from that naturally present in the soil at the pH used. In spite of the addition of nZVI not

increasing the PAHs conversion due to the low solubility of iron at the pH used, nZVI can act as a continuous source of iron release.

Addition of the surfactant 24 h prior to the oxidation treatment enhanced PAHs conversion, even if pH was increasing to the neutral range when surfactant was added. This can be attributed to the enhancement in PAHs solubilization and therefore, the increase in oxidation rate in the aqueous phase.

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