



## Oxidation by Fenton's reagent combined with biological treatment applied to a creosote-contaminated soil

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### ABSTRACT

In this study, we investigated the feasibility of using Fenton oxidation to remove sorbed polycyclic aromatic hydrocarbons (PAHs) in aged soil samples with creosote oil from a wood preserving site. The optimal dosage of reagents was determined by a statistical method, the central composite rotatable experimental design. The maximum PAH removal was 80% with a molar ratio of oxidant/catalyst equal to 90:1. In general low molecular weight PAHs (3 rings) were degraded more efficiently than higher molecular weight PAHs (4 and 5 rings). The hydrogen peroxide decomposition kinetic was studied in the presence of  $\text{KH}_2\text{PO}_4$  as stabilizer. The kinetic data were fitted to a simple model, the pseudo-first-order which describes the hydrogen peroxide decomposition. The PAH kinetic degradation was also studied, and demonstrated that non-stabilized hydrogen peroxide was consumed in less than 30 min, whilst PAH removal continued for up to 24 h. In a second part of the work, a combined chemical and biological treatment of the soil was carried out and shown to be dependent on the pre-oxidation step. Different reagent doses ( $\text{H}_2\text{O}_2$ :Fe) were used (10, 20, 40, 60:1) in the pre-treatment step. An excess of hydrogen peroxide resulted in a poor biological removal, thus the optimal molar ratio of  $\text{H}_2\text{O}_2$ :Fe for the combined process was 20:1. The combined treatment resulted in a maximum total PAH removal of 75% with a 30% increase in removal due to the biodegradation step. The sample with highest PAH removal in the pre-oxidation step led to no further increase in removal by biological treatment. This suggests that the more aggressive chemical pre-oxidation does not favour biological treatment. The physico-chemical properties of the pollutants were an important factor in the PAH removal as they influenced chemical, biological and combined treatments.

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### 1. Introduction

Abandoned gasworks, asphalt factories and wood impregnation facilities contribute to coal tar and creosote oil contamination in industrialized countries. Creosote oil is manufactured by distilling coal tar and may consist of up to 200 compounds [1]. Contaminated soils typically consist of 85% polycyclic aromatic hydrocarbons (PAH), 1–10% phenols, 5–13% heterocyclic aromatics containing nitrogen, sulphur or oxygen, and 1–3% monoaromatic compounds. PAHs are a group of compounds that consist of two or more benzene rings and are classified as hydrophobic organic compounds. PAHs tend to persist in the environment and to occur in natural

media such as soil, sediments, water and air. They are widely distributed due to their hydrophobic nature and low water solubility [2,3]. In fact, PAHs are considered the most widely distributed class of potent human carcinogens. In aquatic systems, the toxicity of PAHs increases as molecular weight increases. Therefore, they have been listed by the United States Environmental Protection Agency (USEPA) and by the Environmental European Agency (EGA) as priority environmental pollutants [2–5].

Thermal desorption after excavation is the most widely used treatment technology for highly contaminated soils. For lower contamination levels, biological treatment has proved feasible, but its applicability may be limited because of low PAH bioavailability due to the sequestration [6,7]. Chemical techniques are promising alternatives that may be highly efficient in a relatively short time. They can also be combined with bioremediation to design complete soil treatment processes [8–11].

In situ chemical oxidation (ISCO) is an emerging technology and a relatively simple process. It involves the use of a strong oxidant, with or without a catalyst, to oxidize organic contaminants. Exam-

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ples of potential contaminants that are amenable to treatment by ISCO include BTEX, PCE, TCE, MTBE and PAHs [12]. Chemical oxidation technologies are predominantly used to address contaminants in a source area's saturated zone and capillary fringe. Cost concerns may preclude the use of chemical oxidation technologies to treat large and dilute petroleum contaminant plumes [13].

Like most remediation technologies, in situ chemical oxidation has its limitations, which generally fall into two categories: (i) reactivity with contaminants of concern and (ii) the mass transfer of contaminants from the sorbed phase and dense non-aqueous phase liquids (DNAPLs) to the medium in which the reactive species exists, which is usually water. These contaminants are problematic as almost all reactants used in soil and groundwater remediation (e.g. bacteria, hydroxyl radicals and reductants) exist in the aqueous phase. Therefore, sorbed contaminants must desorb or dissolve into the aqueous phase before transformation can occur [14]. As the contaminants are degraded in the aqueous phase, the concentration gradient between the sorbed phase and the aqueous phase increases, which drives the subsequent desorption or dissolution. This treatment process, which is referred to as desorption or dissolution-limit requires a long time for site cleanup. However, the Fenton reaction can potentially treat sorbed contaminants and DNAPLs at a faster rate than the desorption and dissolution processes [15].

The Fenton reaction is often used to treat wastewater from different types of industries [16,17]. It can also be applied to the remediation of contaminated sediments, sludges and soils [8,14,18,19]. Furthermore, Fenton oxidation is a process that can be used in combination with bioremediation techniques, either as a pre-treatment for the oxidation of contaminants to more degradable compounds or as a post-treatment for residual contaminants [8,20].

The Fenton reaction is based on hydrogen peroxide decomposition in the presence of ferrous iron to produce hydroxyl radicals, which are the main oxidizing species:



Hydroxyl radicals are strong, relatively unspecific oxidants that react with most organic contaminants, including PAHs, at rates close to their theoretical limit, which is controlled by the diffusion rate in water [21,22]. Treatment with the Fenton reaction is conducted in an acid medium (pH 2–3) to prevent iron salt precipitation [8]. The Fenton reaction process has some limitations such as excessive  $\text{H}_2\text{O}_2$  decomposition via non-productive reactions; pH change (e.g. acidification), which is problematic in well-buffered aquifers; radical scavenging; problematic delivery of  $\text{H}_2\text{O}_2$ ,  $\text{Fe}(\text{II})$ , acid, and stabilizers due to reactive transport; and health and safety issues regarding the release of volatiles and strong oxidant solutions [3,12,13].

Biodegradation studies suggest that PAHs sorbed onto or partitioned into a solid phase are not readily degraded by microorganisms, so hydrocarbons must be released from the solid phase to the aqueous phase in which they are available [23,24]. As a result of low mass-transfer rates in the soil matrix, this release often limits the effectiveness of bioremediation.

The combination of chemical oxidation and biodegradation has a great advantage over either of the two treatments alone in the remediation of organic contaminants [1,2,25]. It was established that pre-oxidation of PAH and by Fenton/Fenton like reactions leads to oxidation products that are more soluble in water and also with better availability to microorganism [1,8,9].

Previous studies have shown that the efficiency of the chemical treatment was dependent on the soil characteristics and on the PAH physico-chemical properties of PAHs [25,26]. In addition several specific conditions are required to efficiently apply each method. The extent of PAH removal by the Fenton-like-treatment depended

on the applied  $\text{H}_2\text{O}_2$ /soil weight ratio and the addition of a catalyst to a creosote spiked soil [1]. Partial removal of PAHs from iron-rich creosote oil-contaminated soil was achieved by a modified Fenton reaction without iron addition or pH adjustment, and subsequent incubation [27].

Use of chemical treatment in conjunction with biodegradation to remove organic pollutants in creosote contaminated soil has not been widely studied, especially for aged soils with a history of contamination, laboratory experiments have shown that spiked PAHs can be more easily oxidized than native pollutants, which are usually sorbed onto solid matrices over years or decades and make their desorption and subsequent chemical or biological treatment difficult.

The present study was thus conducted to evaluate the efficiency of the chemical oxidation treatment and the combination of chemical oxidation and biodegradation in the remediation of sandy aged soil contaminated with creosote oil. The optimal reagent doses were determined in the chemical process and a kinetic study was performed in order to evaluate the impact of chemical pre-treatment on PAH biodegradation.

## 2. Materials and methods

### 2.1. Contaminated soil

Sandy creosote oil contaminated soil samples from a wood preserving site were used. The contamination origin is 30–40 years ago. The polluted soil contained high amounts of PAH compounds. Creosote oil was also found as a free phase on top of the bedrock and as a dense non-aqueous phase in liquid blobs in the overlying soil. At the sampling site, the bedrock is at a depth of 5 m. Soil core samples were taken from a depth of 3–5 m. The soil was sieved to a particle size of <2 mm before the experiments were performed. The total PAH concentration in the soil was  $1203 \text{ mg kg}^{-1}$ . Eleven different PAH compounds were detected. The total iron concentration in the soil was  $4 \text{ g kg}^{-1}$ . The percentage of organic matter was 1.5 wt%. The humidity of the soil was 7.7%.

The concentrations of the 11 PAHs detected in the untreated soil are shown in Table 1. The concentrations of the PAHs in the soil exceed the screening threshold values established in Spain to regulate the potentially unacceptable risk of contamination,

**Table 1**

The concentrations and standard deviations of PAHs in the contaminated soil ( $\text{mg PAH kg}^{-1}$  dry soil) and general levels of reference for PAHs ( $\text{mg kg}^{-1}$  dry weight) based on the soil use, defined in the Spanish Royal Decree 9/2005 [28].

PAHs concentration in the soil sample and generic levels of reference defined by the Spanish Royal Decree 9/2005				
PAH	$\text{mg kg}^{-1} \pm \text{S.D.}$ dry soil	Industrial use	Urbane use	Others
Naphthalene	nd	10	8	1
Acenaphthylene	nd			
Acenaphthene	$165 \pm 12$	100	60	6
Fluorene	$124 \pm 4$	100	50	5
Phenanthrene	$258 \pm 16$			
Anthracene	$68 \pm 4$	100	100	45
Fluoranthene	$228 \pm 18$	100	80	8
Pyrene	$153 \pm 10$	100	60	6
Benzo(a)Anthracene	$41 \pm 4$	20	2	0.2
Chrysene	$58 \pm 4$	100	100	20
Benzo(b)Fluoranthene	$44 \pm 5$	20	2	0.2
Benzo(k)Fluoranthene	$25 \pm 3$	100	20	2
Benzo(a)Pyrene	$40 \pm 5$	2	0.2	0.02
Dibenzo(a,h)Anthracene	nd	3	0.3	0.03
Benzo(g,h,i)Perylene	nd			
Indeno(1,2,3-cd)Pyrene	nd	30	3	0.3
Total	$1203 \pm 70$			

nd = not detected.

for instance the limits values for benzo(a)pyrene are 2 mg kg<sup>-1</sup> (industrial soil use) and 0.2 mg kg<sup>-1</sup> (urban soil use) [28].

## 2.2. Batch experiments of PAH oxidation by the Fenton reaction

Borosilicate vials with PTFE septum closures were used as laboratory scale batch reactors. The reactors were charged with 4 g of soil and 20 cm<sup>3</sup> of an aqueous solution containing H<sub>2</sub>O<sub>2</sub> and iron(II) sulphate at different concentrations. The pH was adjusted to 3 with a few drops of sulphuric acid 0.5 M and the reactor was maintained with vigorous magnetic stirring. The stabilized hydrogen peroxide solution was prepared by mixing 40 cm<sup>3</sup> of hydrogen peroxide solution with 1.8 g of monobasic potassium phosphate KH<sub>2</sub>PO<sub>4</sub>. The chemical reaction was commonly strong and exothermic, specially when hydrogen peroxide was present in excess, for that reason reaction time was limited to half an hour and then was interrupted by adding 10 wt% of aqueous solution of Na<sub>2</sub>SO<sub>3</sub>. The molar ratio of H<sub>2</sub>O<sub>2</sub>:Fe ranged from 10:1 to 234:1.

## 2.3. Biological treatment

The biological treatment was carried out in an aerobic bench scale sequencing batch reactor (SBR) of 510 cm<sup>3</sup> equipped with an air diffuser. The OxiTop<sup>®</sup> measuring system (WTW, Weilheim, Germany) provided a special stirring platform Model IS-12 with software-controlled speed regulation (180–450 min<sup>-1</sup>), the method provides a direct measurement of the oxygen consumed by microorganisms in a closed vessel in which the inbuilt datalogger records and calculates BOD readings in every 4 h. The activated sludge used came from a municipal Tampere (Finland) wastewater treatment plant. The mineral medium prepared contained a suitable proportion of nutrients (2.5 g L<sup>-1</sup> MgSO<sub>4</sub>; 27.5 g L<sup>-1</sup> CaCl<sub>2</sub>; 0.25 g L<sup>-1</sup> FeCl<sub>3</sub>) and a phosphate buffer solution (KH<sub>2</sub>PO<sub>4</sub>, K<sub>2</sub>HPO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub>·7H<sub>2</sub>O) at pH 4. 15 g of soil was used in each experiment. Tests were conducted in a dark room at stable temperature (21 ± 1 °C) and test solutions were never in contact with daylight. An automatic BOD controller, the OxyTop<sup>®</sup> OC 100, was used to monitor BOD evolution.

A soil sample was mixed with 1 L of aerated deionized water, in which 5 ml of municipal wastewater had been previously added to ensure that the sample contained sufficient microorganisms. A few drops of the nitrification inhibitor solution NTH 600 (5 g L<sup>-1</sup> N-allylthiourea) were also added to the sample. A blank sample was prepared to evaluate the oxygen consumption of the wastewater. After the treatment, solid samples were separated from the liquid phase through a 0.20 μm PTFE filter and analysed for PAHs by GC/MS.

The pre-chemical treatment in a combination tests was performed as described in Section 2.2, non-stabilized hydrogen peroxide was used and four molar ratios of H<sub>2</sub>O<sub>2</sub>:Fe (10, 20, 40, 60:1). Thus, each soil sample treated by the chemical oxidation process contained a different amount of PAH at the start of the biological treatment.

## 2.4. Experimental design

Previous studies [27] have shown that PAH removal can be achieved by a modified Fenton reaction without no pH adjustment, which results in 50% of PAHs being removed by the chemical treatment. Other authors have reported [7] the effect of five variables and have found that maximum removal was obtained at the highest level of all the parameters, including hydrogen peroxide and iron concentration, acidity, reaction time and exposure to UV light. In this work, experiments were conducted to optimize two of the parameters (hydrogen peroxide and iron concentration) and pH,

was fixed as 3 in order to increase the production of hydroxyl radicals. A central composite rotatable experimental design [29] was used to define the optimal H<sub>2</sub>O<sub>2</sub> and Fe(II) concentration. Using this statistical method, the parameter  $\alpha$  was defined as equal to 2<sup>N<sup>0.25</sup></sup>. Like *N*, the number of variable parameters was equal to 2 (hydrogen peroxide and Fe concentration) thus  $\alpha = 1.4142$ . The experimental data were used to develop regression equations to quantitatively describe the system using a least squares analysis. Three sets of experiments were performed, each with 13 trials and replicates for all trials except for the central points. The regression equation was obtained by computing the design matrix to obtain the equation coefficients, thus, the regression equation was defined as:

$$\text{PAH removal \%} : C_0 + C_1[\text{Fe(II)}] + C_2[\text{H}_2\text{O}_2] + C_{11}[\text{Fe(II)}]^2 + C_{22}[\text{H}_2\text{O}_2]^2 + C_{12}[\text{Fe(II)}][\text{H}_2\text{O}_2] \quad (2)$$

## 2.5. Instrumental analyses

Solid and liquid phases were separated by centrifugation at 644 × *g* for 3 min. The concentration of H<sub>2</sub>O<sub>2</sub> was analysed from the liquid samples. After phase separation solid samples were extracted with 70 cm<sup>3</sup> of dichloromethane in a Soxhlet apparatus for 16 h. The samples were then dried with anhydrous sodium sulphate prior to extraction. The volume of the extract was recorded after extraction. The extracts were filtered with a 0.2 μm PTFE filter and diluted with dichloromethane prior to analysis. The concentration of PAHs was quantified by analysing the extracts with a Hewlett-Packard HP 6890 gas chromatograph, equipped with an HP 5972A mass-selective detector in selected ion monitoring (SIM) mode. The GC was installed with a Supelco Equity-5 capillary column. The temperature of the GC oven was kept at 80 °C during the injection and increased to 320 °C during the analysis, injector and detector temperatures were 250 and 280 °C respectively.

Kinetic evolution experiments were carried out as mentioned in Section 2.1. The evolution of hydrogen peroxide concentration was determined by iodometric titration of liquid samples collected from the chemical oxidation experiments at different time intervals. Hydrogen peroxide in the sample reacted with excess potassium iodide in the presence of an ammonium molybdate catalyst to produce triiodide ions, which were subsequently titrated with a standard thiosulphate solution [30]. The amount of organic matter in the soil was determined by the Walkley–Black method [31].

## 3. Results and discussion

### 3.1. Chemical oxidation treatment

In order to define the optimal values of both hydrogen peroxide and Fe(II) concentrations for the oxidation of PAHs from the polluted soil, a series of experiments was designed following the central rotatable composite design with an  $\alpha$  value equal to 1.4142 [29].

Three series of experiments were performed to find out the optimal dose of reagents in the Fenton reaction. The maximum and minimum ratios of H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> used in each experimental series were as presented in Table 2. These values started in a 10:1 H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> ratio, which Kulik and co-workers [1,32] reported as the optimum ratio of reactants. Other authors reported that PAHs may be oxidized from a sorbed state under strong oxidizing conditions [2,3,25,33], thus the maximum ratio of reagents was 284:1. The PAH maximum degradation obtained in the three series of experiments is shown in Table 2.

Previously published studies have demonstrated that an extremely high H<sub>2</sub>O<sub>2</sub> concentration is required to oxidize strongly sorbed organic compounds [2,25,33–35]. Fig. 1 shows the oxidation

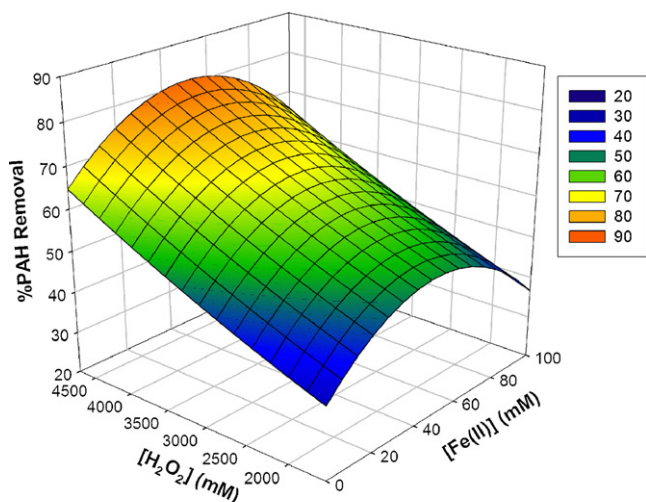
**Table 2**Reagents doses H<sub>2</sub>O<sub>2</sub>:Fe and the maximum PAH removal % by the Fenton treatment for three series of experiments.

	Contaminated soil (%)	First series	Second series	Third series
[Fe(II)] (mM)		60–180	0–100	47–142
[H <sub>2</sub> O <sub>2</sub> ] (mM)		1574–4721	1574–4721	2970–8862
Maximum and minimum		55:1	284:1	130:1
Ratio H <sub>2</sub> O <sub>2</sub> : Fe(II)		10:1	Without iron	30:1
Optimum ratio H <sub>2</sub> O <sub>2</sub> : Fe(II)		25:1	90:1	60:1
PAH				
Total 3 rings PAH	51	84	100	96
Total 4 rings PAH	40	47	72	66
Total 5 rings PAH	9	4	8	7
Total PAH		63	76	73

response surface, as a function of the H<sub>2</sub>O<sub>2</sub> and Fe(II) concentrations. The maximum efficiency ( $\approx 80\%$ ) was obtained with a H<sub>2</sub>O<sub>2</sub>:Fe(II) ratio of 90:1. The oxidation efficiency varied between 50 and 80% (the maximum PAH removal for each set of experiments is reported in Table 2), except for one value of 36% removal in the second series, which was performed with no iron addition. Thus, some part of the iron present in the soil acted as a catalyst in the H<sub>2</sub>O<sub>2</sub> degradation [2,7,8], however, this lower value suggests that H<sub>2</sub>O<sub>2</sub> needs to be catalysed by additional Fe(II) as was also reported in the literature [1,2,8,25].

A higher percentage of oxidation was obtained with less Fe(II). An excess of Fe(II) in the solution may cause unproductive consumption of hydroxyl radicals. Simultaneously, an excess of H<sub>2</sub>O<sub>2</sub> may result in unproductive consumption of hydroxyl radicals and in ineffective oxidation [2,10,22], as can be observed in Fig. 1.

The efficiency of the chemical oxidation of PAHs in soils depends on a complex interplay of factors, including the properties of the specific PAH pollutants and the soil characteristics. The values reported in Table 2 indicate that 2-ring PAHs are more easily removed than 4- and 5-ring PAHs. This could be related to the fact that strong sorption of the hydrophobic contaminants into the microporous structure of particulates may impede the fast penetration of the oxidizing agents, which leads to slow diffusion process [3]. Additionally, soils with less than 5% of organic matter tend to sorb PAH into their microporous structure (if it exists), thus impeding the appropriate contact between contaminants and reagents [25,26].



$$\text{PAH removal \%} = 65.4 + 0.1[\text{Fe(II)}] + 9.4[\text{H}_2\text{O}_2] - 7.0[\text{Fe(II)}]^2 + 0.6[\text{H}_2\text{O}_2]^2 + 0.2[\text{Fe(II)}][\text{H}_2\text{O}_2]$$

**Fig. 1.** Response surface of PAH removal by the Fenton reaction as function of H<sub>2</sub>O<sub>2</sub> and Fe(II) concentrations and the regression equation obtained by the central composite rotatable experimental design. The result shows that the model accuracy was above 90%.

Jonsson et al. [25] studied the effect of PAH properties and soil characteristics on chemical oxidation efficiency. Ten soils were studied, each with a different source of contamination (former gas works, wood impregnation sites and a working coke plant), type of soil matrix (sandy till, fine and coarse sand), and aging time (50–100 years). The results showed that smaller PAHs with relatively low water solubility and PAHs with particularly high reactivity were most susceptible to chemical oxidation. Meanwhile, the organic matter and specific surface area were the soil properties that had the greatest negative impact on the degradation of the lower molecular weight (LMW) PAHs. The age of contamination and pH were more negatively correlated with to the degradation of large PAHs with five or six fused rings. Table 3 shows the results obtained by Jonsson et al. [25] for the wood preservation sites, in order to compare them with the results obtained in this study. Jonsson et al. [25] reported lower amounts of degradation, especially for the large PAHs (4 and 5 rings), which did not degrade in some cases. The reaction conditions and some soil properties were also compared. The chemical reaction took place under strong oxidation conditions (higher excess of hydrogen peroxide). In both cases, the pH was adjusted to 3. With regard to the soil properties, the organic matter content and pH values of the sample reported as coarse sand wood preservation were relatively similar to the sample used in this study.

Table 3 shows the results reported by Ferrarase et al. [2] of a modified Fenton process to remove PAH from the coal tar site sediment. The reaction conditions and the soil properties are also reported. The degradation efficiency was higher (above 95%), with a 1:50 molar ratio catalyst/oxidant. Unfortunately there was no data on the age of contamination and the content of organic matter, two parameters of great importance in the chemical oxidation of soil.

Other authors' results are summarized in Table 3 [1,27]. However, laboratory experiments have shown that spiked PAHs can be more easily oxidized than native pollutants, which are usually sorbed onto solid matrices over years or decades, which make their desorption and subsequent chemical or biological treatment difficult [11]. Thus, their values cannot easily be compared to those obtained in this work. In general, good results were obtained in this study compared to other studies with similar soil properties and age of contamination.

### 3.2. Chemical oxidation using stabilized H<sub>2</sub>O<sub>2</sub>

Previous results have demonstrated that one of the drawbacks of an in situ Fenton-like treatment is the instability of hydrogen peroxide, due to interaction with inorganic compounds, such as iron and manganese oxyhydroxides catalysts, or organic compounds, such as catalase or peroxidase enzymes, which are widespread in surface soils [36]. This instability may dramatically reduce the concentration of hydrogen peroxide unless a proper stabilizer compound is used together with hydrogen peroxide [37]. Phosphates and silicates are recognized as effective stabilizers against the decomposition of hydrogen peroxide [22].

**Table 3**  
Comparison of the values reported in literature for soil contaminated (PAHs) treatment by Fenton reaction and those obtained in this study.

Reference	Soil type; age of contamination (years)	Reagent doses ( $\text{H}_2\text{O}_2$ :Fe); [ $\text{H}_2\text{O}_2$ M]; pH	PAH removal %
[25]	Sandy till wood preservation (PAH); 50–100 Sandy till wood preservation (PAH); 50–100 Fine sand wood preservation (PAH); 50–100 Coarse Sand wood preservation (PAH); 50–100	(1000:1); [1.7]; 3	25 27 30 42
[2]	Sediments from coal tar site (PAH); n.a.	(50:1); [5]; natural pH	98
[1]	Dry soil sand spiked with creosote (PAH); spiked Dry soil peat skipped with creosote (PAH); spiked	(10:1); [0.2]; natural pH (10:1); [0.8]; natural pH	88 70
[27]	Creosote oil contaminated soil (PAH); n.a.	Without iron addition; [0.4]; natural pH	50
This study	Creosote oil contaminated sand (PAH); 30–40	(90:1); [4.7]; 3	76

na = not available data.

The stabilizer compound used in this study was potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ). Fig. 2a shows the decomposition of stabilized and non-stabilized  $\text{H}_2\text{O}_2$  as a function of time. The presence of the stabilizer is clearly reduces the decomposition rate of  $\text{H}_2\text{O}_2$ . The increase in stability may be related to the inactivation of the primary catalysts, either by precipitation reactions or by conversion to relatively inactive complexes [22].

The hydrogen peroxide decomposition was studied using reagents dose ( $\text{H}_2\text{O}_2$ :Fe) equal to 60:1. The pH was adjusted to 3, this condition was used instead of the optimal (90:1) in order to avoid an excess of hydrogen peroxide and subsequent strong exothermic reaction. The determination of the residual  $\text{H}_2\text{O}_2$  concentration in the liquid phase was performed at the same reaction time intervals that were used in the oxidation experiments.

The residual concentration of  $\text{H}_2\text{O}_2$  over time was analysed to determine the decomposition rate. After evaluating the simple order 0, 1 and 2 kinetic rate models; a first-order rate was selected to characterize the decomposition rate of hydrogen peroxide for both cases in the absence and with the presence of stabilizer, according

to the integrated rate expression [38],

$$\ln \frac{[\text{H}_2\text{O}_2]}{[\text{H}_2\text{O}_2]_0} = -kt \quad (3)$$

where  $[\text{H}_2\text{O}_2]_0$  and  $[\text{H}_2\text{O}_2]$  denote the initial and time-dependent hydrogen peroxide concentration in  $\text{mol L}^{-1}$ ; and  $t$ , time in  $h$ , and  $k$  is the first-order rate constant in  $h^{-1}$ . The rate constant ( $k$ ) is in fact a pseudo-first-order kinetic constant, because it is influenced by the reagent concentration, the pH and the phosphate concentration. The  $k$  values were obtained by linear regression analysis of the measured data.

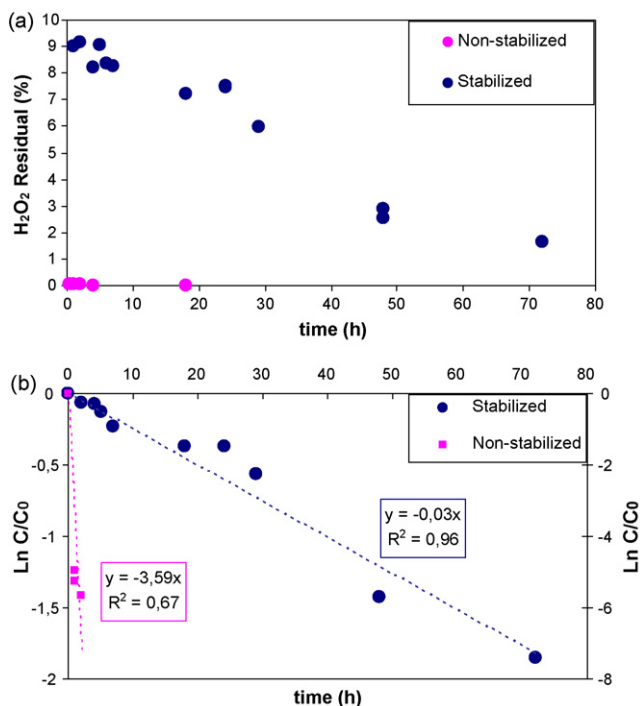
Given the short residence time of the hydrogen peroxide in the reaction, the use of stabilized hydrogen peroxide through the addition of potassium dihydrogen phosphate was considered in order to compare the kinetic behaviour of the two oxidizing solutions.

The pseudo-first-order reaction could be used to describe the decomposition of hydrogen peroxide with an  $R^2$  of 0.96 for the stabilized solution. Fig. 2b shows the comparison of the experimental data for the pseudo-first-order model for both  $\text{H}_2\text{O}_2$  solutions. Some authors have reported that the Fenton reaction frequently fast and appears to be concluded in a few hours [2,39]. The fast consumption of hydrogen peroxide was described by Kanel et al. [40], who explained that more than 80% of the consumption of  $\text{H}_2\text{O}_2$  took place within 30 min. From Fig. 2a, It is evident that the consumption of non-stabilized  $\text{H}_2\text{O}_2$  was faster and the values of residual  $\text{H}_2\text{O}_2$  concentration were lower than 1% of the initial concentration. Thus, in Fig. 2b, the values of data fitted for non-stabilized  $\text{H}_2\text{O}_2$  are concentrated in a small area of the graph and have the poorest correlation. In the case of stabilized  $\text{H}_2\text{O}_2$ , experimental data are well described by the pseudo-first-order rate. The stabilized solution reported a kinetic constant of  $\text{H}_2\text{O}_2$  decomposition of  $5 \times 10^{-4} \text{ min}^{-1}$ , which can be compared with the values reported by Baciocchi et al. [37] for two different soils ( $2 \times 10^{-3}$  and  $3 \times 10^{-3} \text{ min}^{-1}$ ). These values were obtained at pH 6.5 and in the absence of Fe(II). These conditions differ to those used in this study, especially for the pH, which is an important parameter in the  $\text{H}_2\text{O}_2$  decomposition, as demonstrated by Watts et al. [35] who reported slow  $\text{H}_2\text{O}_2$  decomposition ( $2 \times 10^{-5} \text{ min}^{-1}$ ) at low pH and with the presence of phosphate as a stabilizer.

### 3.3. PAH kinetic oxidation by the Fenton reaction

Experiments were carried out with several soil samples and the same reagent doses as those used in Section 3.3. The initial concentration of hydrogen peroxide stabilized and non-stabilized solutions was kept constant for all soil samples at different reaction times. Once the reaction had stopped, the residual amount of PAH in the soil was determined, as mentioned in Section 2.5.

Fig. 3 shows the evolution of PAH oxidation over time by both stabilized and non-stabilized  $\text{H}_2\text{O}_2$ . The non-stabilized  $\text{H}_2\text{O}_2$  achieved maximum degradation efficiency (80%) after 24 h of



**Fig. 2.** (a) Evolution of residual hydrogen peroxide as a function of time for non-stabilized and stabilized  $\text{H}_2\text{O}_2$  solutions. (b) Kinetic of the hydrogen peroxide decomposition data fitted to the pseudo-first-order equation for the stabilized and non-stabilized  $\text{H}_2\text{O}_2$  solutions.

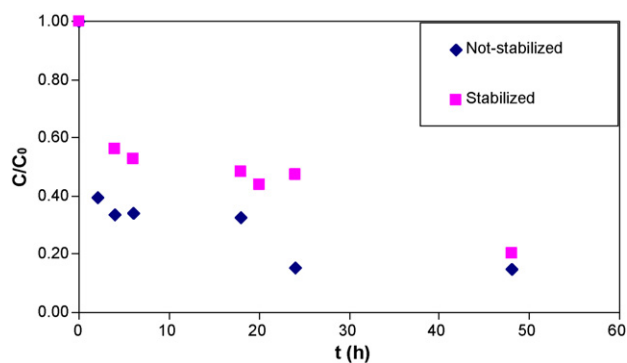


Fig. 3. Evolution of the total PAH (sum of the 11 PAH concentrations) removal by treatment with stabilized and non-stabilized H<sub>2</sub>O<sub>2</sub> solutions.

treatment. At the same time stabilized H<sub>2</sub>O<sub>2</sub> achieved 50% of degradation, but after 48 h of treatment the degradation efficiency of stabilized H<sub>2</sub>O<sub>2</sub> was approximately equal to the efficiency obtained with non-stabilized H<sub>2</sub>O<sub>2</sub>.

These results were unexpected considering the decomposition of H<sub>2</sub>O<sub>2</sub>. For non-stabilized H<sub>2</sub>O<sub>2</sub>, the hydrogen peroxide decomposed in less than 30 min, but the removal of PAHs continued up to 24 h. This behaviour could be related to the fact that reductive transformation in Fenton oxidation systems may play an important role in degradation of organic pollutants [12,14]. Watts et al. [15] describes how vigorous Fenton reaction using high concentration of H<sub>2</sub>O<sub>2</sub> generates non-hydroxyl radical species, such as perhydroxyl radical (HO<sub>2</sub><sup>•</sup>), superoxide radical anion (O<sub>2</sub><sup>•-</sup>), and hydroperoxide anion (HO<sub>2</sub><sup>-</sup>). Perhydroxyl radical is a relatively weak oxidant; superoxide is a weak reductant and nucleophile in aqueous systems, and hydroperoxide anion is a strong nucleophile. Other authors have reported the co-existence of other active molecules like high valence iron cations [3,35]. Reductive transformations, when combined with oxidation, yield greater potential for overall contaminant transformation [12].

Unfortunately the lifetime of the non-hydroxyl radical species were unknown and out of the scope of this study. Then, it is necessary to carry out a more detailed study of Fenton kinetic mechanism to take into account the particular features of the soil presence (desorption, surface reactions, diffusion, etc.) and the other active oxidising species.

However, in order to compare the results, a kinetic study was carried out using a simple model. Thus, the Fenton oxidation of PAHs can be represented by the following *m*th reaction order kinetics:

$$\frac{dC}{dt} = -kC^m \quad (4)$$

where *C* represents the PAH concentration in mg g<sup>-1</sup>, *m* the order of reaction and *k* the reaction rate constant. The integration of Eq. (4) for *m* = 1 and 2 provides the following equations:

$$\ln\left(\frac{C}{C_0}\right) = -k_1 t \quad (5)$$

$$\frac{1}{C} = k_2 t + \frac{1}{C_0} \quad (6)$$

where *C*<sub>0</sub> is the initial PAH concentration. According to the previous equations, a plot of ln(*C*/*C*<sub>0</sub>) against *t* and 1/*C* against *t* will yield a straight line with slope *k*<sub>1</sub> and *k*<sub>2</sub>.

In both cases *k*<sub>1</sub> and *k*<sub>2</sub> have to be considered pseudo-first and pseudo-second-order kinetic constants, because the reagents concentrations, pH and phosphate concentration were fixed and the results depended on these variables.

The experimental values shown in Fig. 3 were fitted to Eqs. (5) and (6); the correlation coefficient obtained for the total PAH concentration in soil was over 0.7 for the stabilized and non-stabilized H<sub>2</sub>O<sub>2</sub> samples. However, these values represent the general behaviour of a group of pollutants. To obtain more detailed information about the kinetic oxidation of each PAH in the soil sample, experimental concentration data of each PAH were fitted to Eqs. (5) and (6). Table 4 presents the kinetic constants (*k*<sub>1</sub> and *k*<sub>2</sub>) and correlation coefficients obtained for PAH consisting of three to five rings. The kinetic constant values reported were in the same order of magnitude for both types of hydrogen peroxide solutions and the correlation coefficients were generally higher than 0.8 for 3 rings PAHs, while for the 4 and 5 rings the correlation decreased to values around 0.3.

The basic trend for the oxidation of PAHs by non-stabilized and stabilized hydrogen peroxide is a clear dependence of the kinetic behaviour on the physical properties of the PAH molecules. A higher oxidation percentage and kinetic constants in the same order of magnitude were reported for the low molecular weight PAHs (3 rings), while for the high molecular weight PAHs (4 and 5 rings) the oxidation efficiencies were lower. This could be related to the fact that the high molecular weights of PAHs favour strong sorption to the soil matrix, in such cases less hydrophobic molecules are available for the oxidation process [26,41].

The values reported in the literature are in the same order of magnitude as those obtained in this study. Lee et al. [42] described the Fenton oxidation process by pseudo-first-order kinetics for PAH contaminated soil remediation. Values reported for benzo(a)pyrene and benzo(k)fluoranthene were 1.2 × 10<sup>-2</sup> and 4.3 × 10<sup>-2</sup> h<sup>-1</sup> respectively. In this study, the two PAHs reported 1.4 × 10<sup>-2</sup> and 3.8 × 10<sup>-2</sup> h<sup>-1</sup> for non-stabilized and 2.7 × 10<sup>-2</sup> and 2.3 × 10<sup>-2</sup> h<sup>-1</sup> for stabilized H<sub>2</sub>O<sub>2</sub> respectively. Kanet et al. [40] also reported a pseudo-first-order of PAH removal from sand by hydrogen peroxide decomposition in the presence of goethite. The kinetic constant reported by these authors was 1.2 × 10<sup>-2</sup> h<sup>-1</sup> for phenanthrene. In this work, 4.2 × 10<sup>-2</sup> for non-stabilized and 5.7 × 10<sup>-2</sup> h<sup>-1</sup> for stabilized H<sub>2</sub>O<sub>2</sub>, respectively were obtained for the same PAH.

### 3.4. Integrated chemical and biological treatment

The biodegradability test of PAHs in the soil was carried out by studying the biological oxygen demand (BOD) evolution. For this purpose, soil samples were pre-treated by chemical oxidation and then treated biologically. The total degradation rate of each sample was determined after each step and for the overall treatment process. Each soil sample was chemically pre-treated at different reagents doses in order to obtain different soil degradation efficiencies of PAHs in the first step and thus different starting points for

Table 4

Kinetic constant (pseudo-first and second) and correlation coefficient *R*<sup>2</sup> obtained for PAH oxidation by Fenton treatment using stabilized and non-stabilized H<sub>2</sub>O<sub>2</sub> solutions.

PAH	H <sub>2</sub> O <sub>2</sub> non-stabilized				H <sub>2</sub> O <sub>2</sub> stabilized			
	<i>k</i> <sub>1</sub> (h <sup>-1</sup> )	<i>R</i> <sup>2</sup>	<i>k</i> <sub>2</sub> (g mg <sup>-1</sup> h <sup>-1</sup> )	<i>R</i> <sup>2</sup>	<i>k</i> <sub>1</sub> (h <sup>-1</sup> )	<i>R</i> <sup>2</sup>	<i>k</i> <sub>2</sub> (g mg <sup>-1</sup> h <sup>-1</sup> )	<i>R</i> <sup>2</sup>
3 rings	3.9 × 10 <sup>-2</sup>	0.75	2.3 × 10 <sup>-3</sup>	0.85	2.6 × 10 <sup>-2</sup>	0.89	3.1 × 10 <sup>-4</sup>	0.95
4 rings	2.0 × 10 <sup>-2</sup>	0.75	1.2 × 10 <sup>-4</sup>	0.71	1.6 × 10 <sup>-2</sup>	0.58	5.9 × 10 <sup>-5</sup>	0.63
5 rings	6.2 × 10 <sup>-3</sup>	0.29	2.0 × 10 <sup>-4</sup>	0.25	7.7 × 10 <sup>-3</sup>	0.27	2.9 × 10 <sup>-4</sup>	0.39
Total PAH	1.9 × 10 <sup>-2</sup>	0.77	8.8 × 10 <sup>-5</sup>	0.75	1.8 × 10 <sup>-2</sup>	0.73	5.3 × 10 <sup>-5</sup>	0.79

**Table 5**  
Degradation of PAHs between three and five rings by chemical (pre-treatment) and biological treatment.

Sample/[H <sub>2</sub> O <sub>2</sub> :Fe]	Degradation (%) by chemical treatment				Degradation (%) by biological treatment				Overall removal (%)
	3 rings	4 rings	5 rings	Treatment removal	3 rings	4 rings	5 rings	Treatment removal	
0/untreated	–	–	–	–	89	23	15	45	45
1/[10:1]	66	28	10	42	26	20	17	20	62
2/[20:1]	66	31	9	43	30	35	28	32	75
3/[40:1]	82	51	15	61	7	10	16	9	70
4/[60:1]	86	70	35	71	–	–	–	0	71

the biological step. Table 5 presents the degradation rates obtained by each treatment (chemical and biological).

The starting conditions for the biological step are determined by an increasing trend in the degradation efficiency of the chemical treatment. Fig. 4a shows the percentage of degradation obtained by chemical treatment. A rise in the amount of hydrogen peroxide increased the PAH removal from 40% in sample 1 (10:1 H<sub>2</sub>O<sub>2</sub>:Fe) to more than 70% in sample 4 (60:1 H<sub>2</sub>O<sub>2</sub>:Fe). It was observed that 3 ring PAHs were almost removed in this step (86%). In contrast 4 and 5 ring PAHs the maximum degradation was reported as expected in sample 4 with 70 and 35%, respectively.

The same behaviour was observed for the biological treatment as can see it in Table 5. The untreated sample reported an overall removal of 45%. The results of this study indicate that 3-ring PAHs removal was above 90%, while PAHs with 4 and more rings were removed less efficiently (20%). It indicates that PAH biodegradation is influenced by the hydrophobic character of the pollutants. PAHs tend to bind to organic matter of soil, which limits their availability to microorganisms. As a result, the extent of biodegradation tends to decrease. Thus, there is a strong interdependence between a decrease in concentration and the number or fused rings [1,8].

Previous studies showed that biodegradation of low molecular weight PAHs (2 and 3 rings) occurred much more rapidly and extensively than that of high molecular weight PAHs (4 or more rings) [8,43]. Kulik et al. [1] reported 80% and 30% rates of removal for 3 and 4 rings, respectively for untreated soil sample after 4 weeks, in a study in which PAHs removal from creosote contaminated sand was treated in a combined process.

The application of combined chemical pre-oxidation and biodegradation to remediate creosote contaminated soil demon-

strates a clear dependence on the reagent dosages. Fig. 4b shows the percentage of degradation obtained by subsequent chemical and biological treatment.

The increase in removal by the biodegradation step was notable in samples 1 and 2 (20 and 32%, respectively) as can see it in Table 5. Thus, the maximum total PAH degradation efficiency obtained in a chemically pre-oxidized sample was 75% (sample 2). This can be explained by the fact that the microorganisms were not prepared to remove the sorbed PAHs in the solid matrix, thus limiting the bioavailability of hydrophobic organic contaminants.

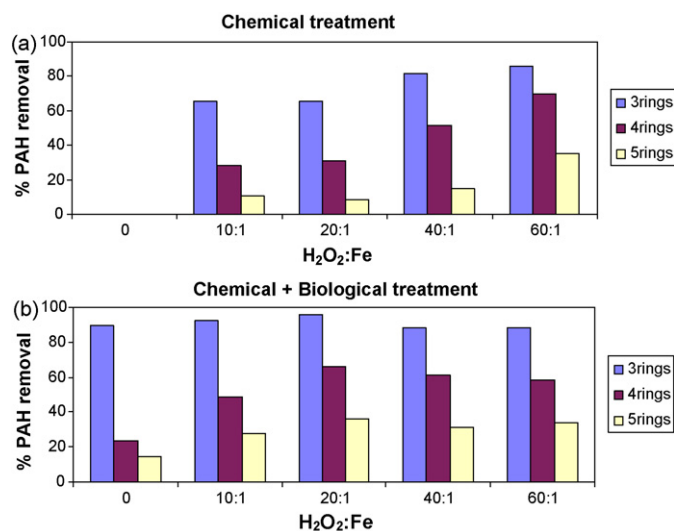
The lower biological removal in samples 3 and 4 can be explained by the inhibition of biodegradation caused by residual hydrogen peroxide that may remain in the soil after the application of high doses of hydrogen peroxide [1,32]. Sample 3 reported (in Table 5) poor increase in degradation of 9% (40:1 H<sub>2</sub>O<sub>2</sub>:Fe) and there was no increase in sample 4 (60:1 H<sub>2</sub>O<sub>2</sub>:Fe), which indicates that more aggressive chemical pre-treatment conditions do not favour biological treatment. Further, it is possible that the chemical oxidation degrades the same portion of the PAHs as the biological treatment, limiting the possibility of using biodegradation after strong chemical oxidation. The remaining PAHs content in the soil sample was basically conformed by 4 and 5 ring PAHs and low amounts of 3 ring PAHs (less than 10%), thus confirming that the hydrophobic character is an important parameter in combined chemical and biological treatment of PAHs in soils.

Other studies reported similar values to those obtained in this work, e.g. Kulik et al. [1] reported a 20% increase in PAH degradation of 20% after 8 weeks of biological treatment after Fenton-like pre-oxidation treatment in the remediation of creosote contaminated sand. Palmroth et al. [27] reported a biological removal of 22–30% and a combined chemical and biological removal of 43–50% of PAH in an iron-rich creosote oil-contaminated soil using modified Fenton reaction with no iron supplementation or pH adjustment.

The BOD of the chemically treated soil was higher in sample 1, with relatively low chemical treatment efficiency. The BOD decrease in samples with more efficient chemical treatment. This denotes that it is possible to obtain more effective degradation with a biological step when the previous chemical treatment is not very aggressive. The increase in the BOD in the sample previously treated by chemical oxidation is related to the fact that Fenton reaction increased the toxicity of soil [27]. Further, the potential of the Fenton reaction to desorb contaminants from the soil and oxidize reduced contaminants such as PAHs can bring PAHs into solution and make them available to biodegradation [35].

#### 4. Conclusions

This study reported a maximum PAH degradation of 80% by Fenton treatment with a reagent ratio of 90:1 H<sub>2</sub>O<sub>2</sub>:Fe. Additional iron was needed to improve PAH removal and an excess of hydrogen peroxide did not lead to an increase in the degradation rate. The efficiency of the chemical oxidation of PAHs depends on the physico-chemical properties of specific PAHs and on the soil characteristics. Smaller PAHs (3 rings) were more susceptible to chemical



**Fig. 4.** PAH removal in creosote oil contaminated soil by (a) Fenton reaction using different reagents doses and (b) subsequent biological treatment.

oxidation than the high molecular weight PAHs (4 and 5 rings), which were not effectively removed.

Decomposition of stabilized hydrogen peroxide can be described by a simple model, the pseudo-first kinetic order. The PAH degradation kinetics showed that the consumption of non-stabilized  $H_2O_2$  (less than 30 min) led to 60% of PAH removal. PAH degradation kinetic data were fitted to the pseudo-first and pseudo-second orders, but there was only an acceptable correlation for 3 ring PAHs, which indicates a dependence of the kinetic behaviour on the physical properties of the PAHs.

The PAHs removal by a combination of chemical pre-oxidation and biodegradation demonstrated to be dependent on the pre-oxidation step. In this study, the optimal reagent ratio was 20:1  $H_2O_2$ :Fe. An increase in hydrogen peroxide in the pre-oxidation step, followed by poor biological removal, indicated that an excess of  $H_2O_2$  inhibits the biodegradation step.

Biological treatment in the untreated soil sample resulted in a 45% removal rate of PAH, with removals of 90 and 20% for the 3-ring and more than 4-ring PAHs, respectively. In the pre-oxidized soil sample, the biodegradation step increased PAH removal by 30%, thus, the maximum total PAH degradation efficiency obtained in a chemically pre-oxidized sample was 75%.

In this study, the maximum efficiency was obtained with similar degradation rate by the Fenton reaction treatment and the integrated chemical and biological treatment. However, the use of moderate reagents doses, which minimize the environmental impact and costs, favours the combined chemical and biological treatment as an effective remediation technology for PAHs in creosote oil contaminated aged soil.

Further studies should be conducted to determine the nature and toxicity of the possible formation of by-products, the contaminant sequestration process of the soil related to the chemical treat-ability and to the soil organic matter; finally a more detailed kinetic study of the Fenton reaction mechanism is required to the define oxidant, reductants and nucleophiles effect on the organic pollutants degradation.

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