Remediation of PAH-contaminated sediments by chemical oxidation

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Abstract

The aim of this experimental investigation was to assess the feasibility of using chemical oxidation to degrade sorbed polycyclic aromatic hydrocarbons (PAHs) in case of old date sediment contamination. For this purpose several bench scale laboratory tests were performed, with the following liquid reactants: hydrogen peroxide, modified Fenton's reagent, activated sodium persulfate, potassium permanganate, as well as a combination of potassium permanganate and hydrogen peroxide, and a combination of activated sodium persulfate and hydrogen peroxide. The main target of the study was to find out what liquid oxidant was more effective in reducing the pollutant content and to assess the optimal reactant doses. The initial total PAH concentration in sediment samples was about 2800 mg/kg$_{SS}$ (light PAHs about 1600 mg/kg$_{SS}$, heavy PAHs about 1200 mg/kg$_{SS}$) and a 95% degradation was required to meet the remediation goals. Based on the results of this study, chemical oxidation proved to be an effective remediation technology, amenably applicable for the ex situ remediation of the sediments of concern. Different reactants resulted however in different removal efficiencies. The best remediation performances were achieved with the use of modified Fenton's reagent, hydrogen peroxide and potassium permanganate, with oxidant dosages about 100 mmols per 30 g sediment sample. In all these cases the residual heavy PAH concentration in the treated samples was below 100 mg/kg$_{SS}$. The optimal oxidant dosages determined in this study were quite high, as sorbed PAH mineralization requires very vigorous oxidation conditions, especially for soils and sediments with high organic matter content. The results indicated that the optimal oxidant dose must be carefully determined under site-specific conditions. In fact, if the oxidation conditions are not strong enough, the reactants cannot be able to attack the most recalcitrant compounds, while also too high oxidant doses can result in a decrease in the oxidation efficiency, thus failing in meeting the remediation goals.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic molecules composed of fused benzene rings, classified among hydrophobic organic compounds (HOCs). PAHs are released during the incomplete combustion of coal, petroleum products and wood. Natural sources include volcanic eruptions as well as forest and prairie fires; anthropogenic sources, which can be considered the major route of entry of PAHs into the environment, include combustion, gasification and liquefaction of fossil fuels, coke production, asphalt production, coal tar production, fuel processing, oil and diesel spills, waste incineration and motor vehicle emissions [1–4]. PAHs tend to persist in the environment and to occur in natural media such as soil, sediments, water and air, resulting in a widespread distribution; in particular, due to their hydrophobic nature and low water solubility, they can become rapidly associated with sediments [2,3,5].

Their presence in environmental matrices is of great concern due their high toxicity, carcinogenic effects and environmental persistence [1,2,6,7]. For this reason, they have been listed by the United States Environmental Protection Agency and by the European Community as priority environmental pollutants [1,2] and they have been subject of detailed research for more than 30 years [1,2,4,8].

Individual PAHs differ substantially in their physical and chemical properties. Overall, PAHs have low solubilities and low volatilities, while their lipophilicity is high, as measured by the octanol–water partition coefficient (K_{ow}). This parameter is the ratio of the concentration of a chemical in octanol and in water at equilibrium and at a specified temperature; it is often

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Table 1
Physico-chemical properties of the PAHs considered in this study [1,10]

PAH species	Chemical formula	Molecular weight	Partition coefficient $\log(K_{ow})$	Number of aromatic rings
Naphthalene	$C_{10}H_8$	128.2	3.28	2
Acenaphtylene	$C_{12}H_8$	152.2	4.07	2
Acenaphtene	$C_{12}H_{10}$	154.2	3.98	3
Fluorene	$C_{10}H_{10}$	166.2	4.18	3
Phenantrene	$C_{14}H_{10}$	178.2	4.45	3
Anthracene	$C_{14}H_{10}$	178.2	4.45	3
Fluoranthene	$C_{16}H_{10}$	202.3	4.90	4
Pyrene	$C_{16}H_{10}$	202.3	4.88	4
Chrysene	$C_{18}H_{12}$	228.3	5.16	4
Benzo(a)anthracene	$C_{18}H_{12}$	228.2	5.61	4
Benzo(b)fluoranthene	$C_{20}H_{12}$	252.3	6.04	5
Benzo(k)fluoranthene	$C_{20}H_{12}$	252.3	6.06	5
Benzo(a)pyrene	$C_{20}H_{12}$	252.3	6.06	5
Dibenzo(a,h)antracene	$C_{22}H_{14}$	278.4	6.84	6
Benzo(g,h,i)perylene	$C_{22}H_{12}$	276.3	6.50	6
Indeno(1,2,3-cd)pyrene	$C_{22}H_{12}$	276.3	6.58	6

used to indicate the fate of pollutants in the environment, as it represents the tendency of a chemical to remain sorbed onto organic matter (high K_{ow} values) or to dissolve in water (low K_{ow} values). As for PAH species, the lower molecular weight PAHs (light PAHs) are more volatile, water soluble and less lipophilic than the high molecular weight PAHs (heavy PAHs) [2]. These physico-chemical properties also determine the environmental behavior of different PAH species, as the transfer and turnover of low molecular weight PAHs will be more rapid than the heavy PAHs [1]. PAHs are regarded as persistent organic pollutants (POPs), and this persistence increases with ring number; it is also reported that the greater the number of benzene rings in the PAH molecule, the greater the resistance to degradation [2,9]. The main physico-chemical properties of the PAHs considered in this study are listed in Table 1.

Several remediation techniques have been applied for PAH removal form contaminated sites. Biodegradation of low-molecular weight PAHs by bacteria and microorganisms has been documented by various authors, but high-molecular weight PAHs (with five or six aromatic rings) have proven to be more recalcitrant to biological degradation [2,4,8,10–14]. It is believed that the limited mass transfer and bioavailability of PAH constrain the bioremediation of coal tar contaminated soils [12,15]. Sometimes environment friendly solvents are used to solubilize PAHs and to enhance the their contact with degrading bacteria [15–17]. Even so, a complete remediation of heavily contaminated soils is still difficult to achieve by biological methods. For this reason, the use of chemical techniques has gained much interest for PAH remediation, since these methods can offer a rapid and aggressive alternative that is not so sensitive to the type and concentration of contaminant as biological processes are [4]. Among physical and chemical remediation techniques, soil venting is usually ineffective in PAH remediation of PAH contaminated soils, because of PAH low volatility, while the use of solvents or surfactants is usually discouraged because of the high solvent concentrations that are generally required to achieve good results [12,13,18].

Chemical oxidation seems to be able to overcome these limitations and to be a promising technique for the remediation of environmental matrices contaminated by recalcitrant PAHs. The oxidants that are most commonly used for environmental purposes are ozone, hydrogen peroxide, permanganate and persulfate [19]. Advanced oxidation processes (AOPs) are chemical methods which use various combinations of reactants to enhance the formation of highly reactive radicals, which can mineralize even the most recalcitrant organic compounds; among AOPs, the Fenton's reagent, activated persulfate and perozone are the most common techniques.

Chemical oxidation can also be applied in combination with bioremediation. Several Authors have in fact reported that the oxidation can enhance the biodegradability of PAHs, the application of chemical pre-oxidation having found to overcome the PAH recalcitrance to biodegradation [8,20–23]. In certain conditions, the mineralization effect can be achieved by using a pressurized hot water flux (about 250–300 °C) as extracting or oxidant agent [24,25]. This technique, named supercritical water oxidation, has proved to be very effective in PAH remediation.

1.1. PAH chemical oxidation

Among different available oxidants, gaseous ozone is considered as an effective agent for the treatment of soils and sediments contaminated by PAHs, and it has been extensively applied for this purpose [4,8,13,19,20,26–28]. Among liquid oxidants, the experience is quite extended only as for the use of Fenton's reagent [19–21,29–32], while it is limited for other reactants, as permanganate and persulfate, as well as for AOPs, even if they are considered amenable techniques for PAH degradation [19].

Hydrogen peroxide (H_2O_2) is a liquid oxidant widely used in environmental applications, commonly at concentration ranging from 3 to 35% [19]. The dosage of hydrogen peroxide leads to the production of hydroxyl radicals $^\bullet OH$, which are very strong non-selective oxidizing agents (standard oxidation potential about 2.8 V), able to react both with alkanes and aromatic

compounds [19,20,29]. Hydrogen peroxide can be used alone, but it is considered not kinetically fast enough to degrade most of organic contaminants before its decomposition occurs [19]. In Fenton's reagent, hydrogen peroxide is dosed together with a solution of a transition metal (typically iron) to enhance the radical formation, as the catalyst addition dramatically increases the peroxide oxidative strength [19–22,29,31–36]. The typical Fenton's reaction is based on the hydrogen peroxide decomposition into hydroxyl radicals in the presence of ferrous iron, according to the reaction:
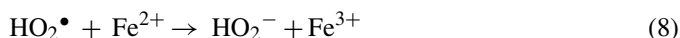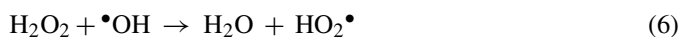
$$H_2O_2 + Fe^{2+} \rightarrow {}^\bullet OH + OH^- + Fe^{3+} \tag{1}$$
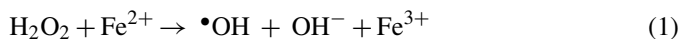
This catalytic reaction is propagated by the Fe(III) reduction, which leads to the Fe(II) regeneration:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + Fe\text{--}OOH \tag{2}$$

$$Fe^{2+} + Fe\text{--}OOH \rightarrow Fe^{2+} + H_2O \tag{3}$$
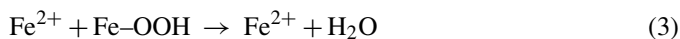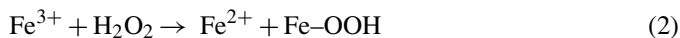
Since in environmental conditions iron is mainly found as Fe(III), low pH (optimal range about 3.5–5) or chelating agents (like citric acid, cyclodextrins, ethylene diamine tetra-acetic acid (EDTA), catechol) can be used to increase the availability of iron(II), so as to enhance the Fenton's reactions [19,22,37]. Once hydroxyl radicals have been created, the degradation can be due either to hydrogen abstraction (reaction (4)) or to hydroxyl addition (reaction (5)) [33]:

$$ROH + {}^\bullet OH \rightarrow {}^\bullet R + H_2O \tag{4}$$

$$R + {}^\bullet OH \rightarrow {}^\bullet ROH \tag{5}$$

In modified Fenton's system, the radical formation is enhanced by the addition of chemicals (e.g. chelating agents) and/or by high peroxide concentrations. When high oxidant concentrations are used, many complex reactions are involved in the Fenton's system, and numerous reacting species can be generated in addition to hydroxyl radical, including hydroperoxide radicals ($HO_2{}^\bullet$), superoxide anions ($O_2{}^{\bullet-}$) and hydroperoxide anions ($HO_2{}^-$) [19,29,30,34–36]:

$$H_2O_2 + {}^\bullet OH \rightarrow H_2O + HO_2{}^\bullet \tag{6}$$

$$HO_2{}^\bullet \rightarrow O_2{}^{\bullet-} + H^+ \tag{7}$$

$$HO_2{}^\bullet + Fe^{2+} \rightarrow HO_2{}^- + Fe^{3+} \tag{8}$$

These radicals are highly reactive and seem to be able to degrade even most recalcitrant compounds or contaminants in the sorbed form [19,29,33,24,25]. Therefore, vigorous oxidation condition can allow to increase the remediation efficiency, by attacking even the most refractory compounds. On the other hand, too high peroxide concentrations must be avoided, as they can enhance the oxidant self-consumption [33,34], leading to poorer oxidant efficiency.

In soils and sediments, the presence of natural occurring iron minerals can enable the Fenton reaction to proceed without any iron addition, if large amounts of hydrogen peroxide are dosed. Thus, the iron addition is not always required for the remediation of contaminated environmental solids, as the presence of natural iron can catalyze the formation of radicals and promote

Fenton-like reactions [20,29,30,32,33]. Sometimes, co-solvents or surfactants are used in combination with Fenton's reagent in order to improve the effectiveness of the process [20].

As the peroxide oxidation is exothermic, it can enhance desorption and dissolution of sorbed pollutants, making them more available for the oxidation treatment. On the other hand, the temperature increase can cause the contaminant to migrate or volatilize, diffusing them into the environment [19,20]; this must be taken into account when designing a remediation action.

Laboratory experiments have shown that spiked PAHs can be more easily oxidized than native pollutants, which are usually more sorbed onto solid matrices [32]. Moreover, recent studies have shown competition effects between PAHs, with slower oxidation of PAH mixtures as compared to single PAH solutions. For this reason, when treating a matrix with numerous pollutants, a larger amount of reagent must be used than the sum of the amounts required to treat the single compounds [32]. It has also been noticed that in case of low contamination levels, a large amount of oxidant is required in order to allow the oxidation of sorbed PAHs due to strong matrix–PAH interactions, which may reduce the cost-efficiency of the remediation process [32,37]. Therefore, the oxidation treatment seems to be more dedicated to highly contaminated environmental matrices, as the sources of contamination of industrial sites [26].

The main factors influencing the PAH removal efficiencies in bench scale laboratory experiments with modified Fenton's reagent (conducted in solid–liquid suspension form) seem to be the level and nature of the contamination (as contaminant concentration and contaminant availability, correlated to the date and level itself of contamination) and the solid matrix characteristics (as the organic matter content of the matrix) [32,22]. In particular, contaminant availability can highly influence the treatment efficiency, the less sorbed pollutants (i.e. the species that are less hydrophobic) being more available for oxidation, while the more hydrophobic and more sorbed molecules proved to be more resistant to oxidation [32,37]. The effects of sorption on contaminant degradability can be minimized with high oxidant dosages, which seem to be able to oxidize also contaminants in the sorbed form [31]. The contaminant availability also depends on the solid matrix characteristic, and in particular on the content of natural organic matter. Usually, the organic matter is considered as a scavenger of active oxidant species [20,28,31,32], as it tends to inhibit PAH mineralization by competing with pollutants for reactant consumption. Nevertheless, recent studies showed that for soils containing less than 5% organic matter, the pollutants were adsorbed in the micropores, being less available than for soils with higher organic matter content, where pollutants are mainly sorbed onto the organic matter [31]. The fact that in natural soils PAHs are commonly strongly sorbed and incorporated into organic matter is also thought to act as a sort of detoxification process, by reducing their bioavailability and their mass transfer, thus reducing their toxic effect towards natural microbial community [37,38].

Permanganate ($MnO_4{}^-$) is an oxidant agent with a standard oxidation potential about 1.7 V. It is reported to be effective in the remediation of many petroleum hydrocarbons and it has been widely applied for in situ and ex situ remediation actions in the

last years [19,39,40]. In an aqueous system the permanganate salts generate permanganate ions (MnO_4^-), which undergoes this decomposition reaction:

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_{2(s)} + 2H_2O \qquad (9)$$
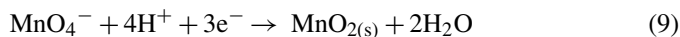
Both potassium permanganate ($KMnO_4$) and sodium permanganate ($NaMnO_4$) can be used for environmental applications, with similar results. Despite the relatively low standard oxidation potential, permanganate salts are considered strong oxidizing agents, able to break organic molecules containing carbon–carbon double bonds, aldehyde groups, or hydroxyl groups [19,40]. Permanganate oxidation mechanisms at contaminated sites are quite complex, as there are numerous reactions in which manganese can participate due to its multiple valence states and mineral forms [19,39].

So far, permanganate has received little attention as PAH oxidant, probably, because of its inability to attack the benzene ring. Nevertheless, bench scale studies have demonstrated that chemical oxidation of PAHs by permanganate can occur with different chemical reactivity for different PAH species, depending on the molecular structure (i.e. from the presence of aromatic rings and carbon–carbon double bonds) [40].

Persulfate is the most recent form of oxidant agent being used for environmental applications. Sodium persulfate ($Na_2S_2O_8$) is the most commonly used form of persulfate salt, as the low solubility of potassium persulfate ($K_2S_2O_8$) limits its application as remediation agent [19,39]. Persulfate salts dissociate in water to persulfate anions ($S_2O_8^-$), which, although strong oxidants (standard oxidation potential about 2.0 V), are kinetically slow in destroying most of organic contaminants. Like in the case of modified Fenton's regent, the addition of transition metal ions (as ferrous ion) could activate the persulfate anion ($S_2O_8^{2-}$) to produce a powerful oxidant known as the sulfate free radical ($SO_4^{\bullet-}$):

$$S_2O_8^{2-} + Fe^{2+} \rightarrow 2SO_4^{\bullet-} + Fe^{3+} \qquad (10)$$

Sulfate free radicals have a standard redox potential of 2.6 V and may be able to oxidize many organic pollutants [19,39,41,42]. The experience of application of persulfate for PAH remediation is currently very limited.

1.2. Experimental investigation scheme

This study was undergone to investigate the feasibility of using chemical oxidation to degrade sorbed PAHs in freshwater sediments, in case of old date contamination.

The contaminated sediments of concern were collected in a canal, located in the town of Trento (Italy), which for several decades had received industrial effluents polluted by organic and inorganic compounds, deriving from a coal tar production site. Several samples (total weight about 10 kg) of fine-grain silty sediments were collected from the first 30–40 cm layer at the bottom of the canal; these samples were then mixed together and mechanically stirred to produce a final, homogeneous sample.

At first, the sediments were characterized and analyzed for BTEX (i.e. aromatic hydrocarbons: benzene, toluene, ethylben-

zene, xylene), PAHs, pH and total organic matter, represented by the value of total organic carbon (TOC). Both organic pollutants and natural organic matter occurred in the sediment samples, which proved to be contaminated by PAHs, but not by BTEX, whose presence was detected just in traces. Both light and heavy PAHs were detected. The average PAHs concentration in sediment samples surpassed the Italian limit both for residential land use (10 mg/kg, as summation of heavy PAHs) and for industrial–commercial land use (100 mg/kg, as summation of heavy PAHs).

In order to investigate the effectiveness of chemical oxidation, several laboratory batch tests were carried on at bench scale. Some preliminary column tests showed that the permeability of the sediments of concern was very low. For this reason, an in situ chemical treatment could not be considered easily feasible, and the investigation was finalized to assess the feasibility of an ex situ treatment of chemical oxidation with liquid reactants.

Four liquid oxidants were used in laboratory tests: hydrogen peroxide (H_2O_2), modified Fenton's reagent (H_2O_2 catalysed by ferrous ions and catechol as chelating agent), potassium permanganate ($KMnO_4$) and activated persulfate ($Na_2S_2O_8$ catalysed by ferrous ions and catechol). Two combination of these chemicals were also tested: potassium permanganate in combination with hydrogen peroxide and activated sodium persulfate in combination with hydrogen peroxide.

2. Materials and methods

2.1. Chemical reactants

The reactants used for the tests were sodium persulfate ($Na_2S_2O_8$), potassium permanganate ($KMnO_4$), ferrous chloride ($FeCl_2$), catechol ($C_6H_6O_2$) and hydrogen peroxide (H_2O_2). All chemicals used for the tests were purchased from Sigma–Aldrich and were reagent grade. Deionized water was produced with a Milli-Q system from Millipore. For the production of modified Fenton's Reagent, hydrogen peroxide was dosed together with a solution of chelated iron ions (ferrous chloride was used to provide iron ions, while catechol was used as chelating agent). For the production of activated persulfate solution, $Na_2S_2O_8$ was dosed with the same solution of chelated ferrous ions.

2.2. Bench scale tests

For each bench test, a 30 g sample of sediments was transferred into a 500 mL glass reaction vessel. To avoid cross-contamination, before use all vessels were rinsed with HPLC grade acetone (>99.9%), and then rinsed several times with deionized milli-Q water. A solid matrix suspension (soil slurry) was prepared by adding deionized water to 30 g-sediment sample; the amount of water to be added was determined in order to have a final solution volume (including the oxidant volume to be added) of 100 mL. After stirring the suspension for a few minutes, so as to obtain an homogeneous slurry, the liquid oxidant was slowly added. A sudden addition of the entire reactant dose

was avoided because it would have resulted in very strong reaction, with foam formation and a sudden increase in the slurry temperature.

In the modified Fenton's regent tests, the hydrogen peroxide solution was added to the reaction vessel together with a 0.5 M solution of chelated ferrous ion, with a molar ratio catalyst:oxidant equal to 1:100 or 1:50. In both cases the ferrous salt and catechol were dosed at a molar ratio equal to 1:1. In order to produce an activated persulfate oxidant, the sodium persulfate solution was added to the reaction vessel together with a 0.5 M solution of chelated ferrous ion (the same solution used for modified Fenton's reagent), with a catalyst:oxidant molar ratio equal to 1:25.

The oxidation processes were conducted at room temperature and at soil natural pH. In fact, despite the Fenton's process optimal pH is very low, the organic pollutants mineralization is reported to occur also at neutral pH in presence of iron [29,33]. The sediment–oxidant slurries were stirred to obtain a complete mixing system and to allow a good contact between oxidant and soil matrix. During the first minutes of reaction, a magnetic stirring was used, and then the reaction vessels were periodically manually shaken.

The oxidation reactions are commonly quick and appear to be concluded within few hours or less, especially in case of modified Fenton's reagent [22]; however, in order to evaluate the total removal efficiency of different reactants, the reactions were not quenched and were allowed to continue till the complete consumption of all chemicals before being analyzed.

Prior to starting the experiments, some preliminary tests were conducted to verify that the amount of the oxidant solutions dosed did not cause excessive heating (especially in the case of modified Fenton's reagent) and to assess the compatibility of the volume of the dosed solution with sediment porosity and permeability. Based on the feedback from this pilot study, the experimental dosages were chosen.

All the tests performed and the dosages used are summarized in Table 2. For each reactant used (hydrogen peroxide, HP, modified Fenton's reagent, MF, potassium permanganate, PP, and activated sodium persulfate, AP), three dosages were considered, equal to 50, 100 and 200 mmols per sample, respectively. Two sets of experiments were performed with the use of modified Fenton's reagent. In the first set (characterized by the code MF100) hydrogen peroxide was dosed together with the solution of chelated iron ions with a molar ratio iron:peroxide equal to 1:100. In the second set of experiments (characterized by the code HP50) hydrogen peroxide was dosed together with the solution of chelated iron ions with a molar ratio iron:peroxide equal to 1:50. The test MF50.3, with a dosage of 200 mmols was not performed due to the excessive strength of the reactions experienced in tests MF100.3 and MF50.2, while test PP3 was not performed because of the large volume of permanganate solution required. Two experiments were performed with combinations of reactants: in tests PPHP, 50 mmols of potassium permanganate were dosed together with 50 mmols of hydrogen peroxide, while in tests APHP 50 mmols of activated persul-

fate were dosed in combination with 50 mmols of hydrogen peroxide.

2.3. Analytical methods

In order to achieve a good resolution both for light and for heavy PAH species, light PAH concentrations in sediments samples were determined with analysis by gas chromatography (GC) and heavy PAH concentrations were detected by high performance liquid chromatography (HPLC). The setups were tested before analyzing the samples; external standards were used for HPLC calibration, while internal standards were used for GC calibration. The extraction efficiencies were about 85% both for HPLC and for GC.

As for light PAH detection by GC, the pollutants were at first extracted by sonication and solvent addition (HPLC grade acetonitrile, >99.99%). A 2-μL sample of solvent was then injected into the gas-chromatograph and analyzed using a Varian 4000 GC/MS. The following temperature program was used: 80 °C for 1 min; isothermal from 80 to 260 °C at 10 °C/min; isothermal from 260 to 320 °C at 20 °C/min; 320 °C were maintained for 3 min (trap temperature 180 °C, manifold temperature 50 °C, transfer time temperature 250 °C).

As for heavy PAH detection, the samples were at first extracted by solvent addition (HPLC grade dichloromethane, >99.9%) and filtered on a 0.45-μm filter. The solvent was allowed to evaporate, and then an acetonitrile solution (70% HPLC grade acetonitrile and 30% water) was added to the sample. A 100-μL sample of the obtained solution was injected into the HPLC and analyzed. The HPLC included: auto-sampler Gilson ASPEC XL (solid base extraction), Dionex P680 HPLC Pump, Dionex STH 585 Column Oven, HPLC detector Dionex UVD 340U (diode array). A Supelco-SIL LC-PAH column (520 mm × 4.6 mm i.d., 5 μm particle size) was used for PAH detection. For the analysis, the acetonitrile concentration in the sample was maintained constant at 70% for 12 min, then it was increased with constant gradient up to 100% in 6.4 min; the 100% acetonitrile content was maintained for 1.6 min and then was decreased to 70% in 1 min. During the detection, the column temperature was maintained constant at 30 °C and the eluent flux was set at a constant rate of 1.5 mL/min.

To detect the contaminant content in the sediment samples, the solid and liquid phases were extracted together, so as to take into account all PAHs in the sample. Only in the experiments which aimed at determining the PAH distribution in sediments and pore water, the solid and liquid phases were separated by filtration and analyzed separately.

BTEX concentrations in the untreated sediment samples were determined trough purge & trap extraction followed by gas chromatographic analysis with VARIAN 4000GC/MS.

The TOC content was determined by IR analysis of thermal induced CO_2 with a TOC Analyzer Shimadzu TOC-V CSH, after heating the sample at 900 °C with a Shimadzu Solid Sample Module.

The pH was taken in a sediment/water suspension using a pH-meter HI 99121 by Hanna Instruments, with HI 1292D electrode for soil pH measurement.

Table 2
Bench scale oxidation tests: dosages and reactants

Oxidant	Test	Reactant	Oxidant dose (mmol/sample)	Concentration (M)	Solution volume (mL)	Deionized water volume (mL)
Hydrogen peroxide (H_2O_2)	HP1	H_2O_2	50	5	10	90
	HP2	H_2O_2	100	5	20	80
	HP3	H_2O_2	200	5	40	60
Modified Fenton's reagent (1:100)	MF100.1	H_2O_2	50	5	10	89
		Fe-chelated	0.5	0.5	1	
	MF100.2	H_2O_2	100	5	20	78
		Fe-chelated	1	0.5	2	
	MF100.3	H_2O_2	200	5	40	56
		Fe-chelated	2	0.5	4	
Modified Fenton's reagent (1:50)	MF50.1	H_2O_2	50	5	10	88
		Fe-chelated	1	0.5	2	
	MF50.2	H_2O_2	100	5	20	76
		Fe-chelated	2	0.5	4	
	MF50.3	H_2O_2	200	Test not perfomed[a]		
		Fe-chelated	4			
Activated sodium persulfate (1:25)	AP1	$Na_2S_2O_8$	50	2	25	71
		Fe-chelated	2	0.5	4	
	AP2	$Na_2S_2O_8$	100	2	50	42
		Fe-chelated	4	0.5	8	
	AP3	$Na_2S_2O_8$	200	2	100	0[b]
		Fe-chelated	8	0.5	16	
Potassium permanganate	PP1	$KMnO_4$	50	0.4	125	0[c]
	PP2	$KMnO_4$	100	1	100	0
	PP3	$KMnO_4$	200	Test not perfomed[d]		
Permanganate and hydrogen peroxide	PPHP	$KMnO_4$	25	0.4	62.5	27.5
Activated persulfate and hydrogen peroxide	APHP	$Na_2S_2O_8$	50	5	25	61
		Fe-chelated	2	0.5	4	
		H_2O_2	50	5	10	

[a] Test not performed because of too strong reactions.
[b] Total volume of resulting solution was 116 mL.
[c] Total volume of resulting solution was 125 mL.
[d] Test not performed because of too large required solution volume.

3. Results and discussion

The sediments samples of concern showed a concentration of total PAHs about 2816 mg/kg$_{SS}$ (light PAHs 1593 mg/kg$_{SS}$, heavy PAHs 1222 mg/kg$_{SS}$). The pH of the sediments was about 7.7.

The sediments also showed a significant metal content, with a total iron concentration about 30,621 mg/Kg$_{SS}$ and a manganese content about 614 mg/kg$_{SS}$. These metals were expected to influence the oxidation processes, especially those that involve the use of hydrogen peroxide, since the transition metals naturally occurring in the sediments can enhance the Fenton-like reactions and the production of hydroxyl radicals.

All the tests performed during the study and the dosages used are summarized in Table 2. The main results of the experimental investigation are presented in Table 3 and in Fig. 1, while Fig. 2 shows the residual concentrations of total PAHs achieved after chemical oxidation treatments. To assess the efficiency of the tested treatments, the removal percentages were calculated for single PAH species and of PAH summation; as well as for TOC,

which represents the total amount of the organic matter in the sample, both from natural and anthropogenic origin. The results were also correlated with PAH partition coefficient K_{ow} (Fig. 3).

As can be seen from the data shown, different reactants and different oxidant dosages resulted in different removal efficiencies. In the tests performed with hydrogen peroxide, the total PAH removal efficiency varied from about 52% (test HP1) to more than 90% (tests HP2 and HP3). The best PAH removal efficiencies were reached in tests HP2 and HP3, thus with a dosage of hydrogen peroxide of 100–200 mmols for a 30-g sediment sample. It could be concluded that dosages of hydrogen peroxide of this order of magnitude can ensure a good oxidation both of heavy and of light PAHs, with a total PAHs removal about 90–95%. The amount of residual TOC in the treated samples varied with the oxidant dose, the removal ranging from 18 (test HP1) to 31% for test HP3 and to 72% for test HP2. The low values of TOC removal can be considered due to the very high organic matter content in the sediments of concern.

The results achieved suggest that the removal efficiency increases with the oxidant dose if the dosage is low (as from test

Table 3
Contaminant concentrations in the sediments samples and removal efficiencies achieved

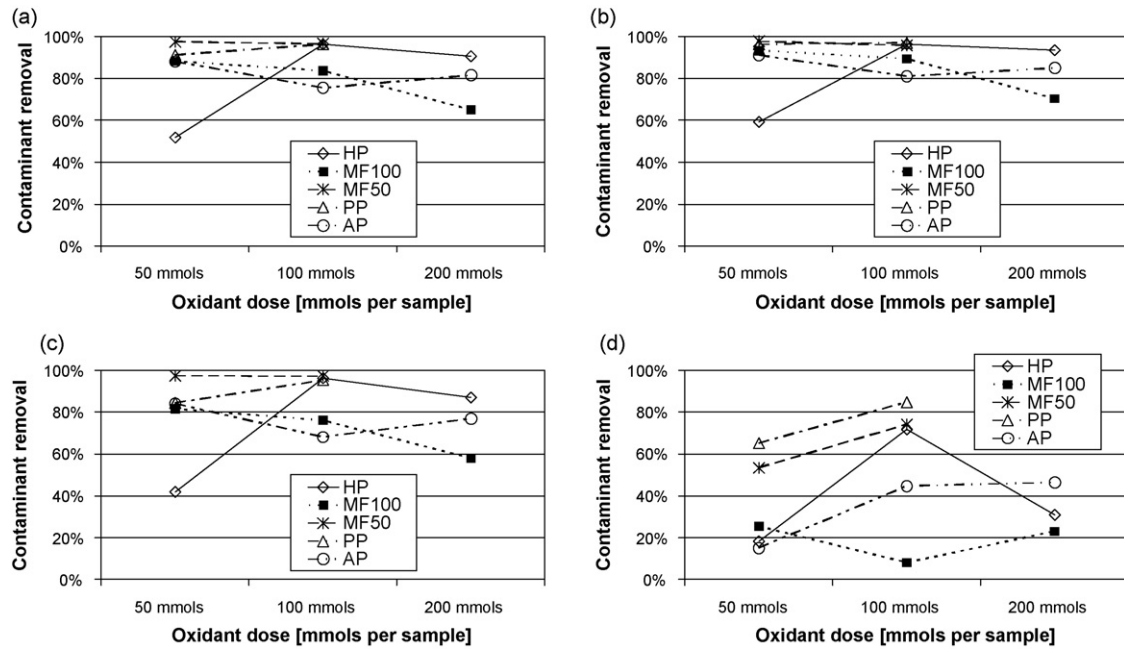| Contaminant concentration (mg/kg$_{SS}$)	Original untreated sample	Hydrogen peroxide			Modified Fenton's reagent—molar ratio 1:100			Modified Fenton's reagent—molar ratio 1:50		Potassium permanganate		Activated sodium persulfate			Permanganate + H$_2$O$_2$	Activated Per-sulfate + H$_2$O$_2$
		HP1	HP2	HP3	MF100.1	MF100.2	MF100.3	MF50.1	MF50.2	PP1	PP2	AP1	AP2	AP3	PPHP	APHP
1. Naphthalene	59.2	24.9	8.8	3.8	1.1	5.1	16.7	4.3	11.0	3.1	0.2	4.5	11.6	6.3	6.9	3.5
2. Acenaphtylene	5.6	0.8	0.2	2.5	0.3	2.7	0.7	0.2	0.1	2.4	0.0	2.6	2.8	0.4	2.8	2.5
3. Acenaphtene	211.4	93.1	10.1	10.1	11.8	18.4	72.0	9.4	8.9	6.8	0.4	15.5	40.6	32.8	33.1	11.2
4. Fluorene	119.1	50.4	4.8	7.5	6.3	12.3	38.9	5.0	4.9	5.7	0.5	10.6	24.3	18.0	20.8	7.9
5. Phenantrene	660.1	219.4	16.0	26.9	28.6	47.2	154.2	2.8	24.8	22.8	4.2	39.0	93.2	73.9	86.3	30.9
6. Anthracene	56.7	27.6	2.4	8.4	6.1	11.2	21.5	2.7	3.2	6.0	2.3	10.0	17.5	11.3	16.0	8.6
7. Fluoranthene	481.7	231.7	14.9	45.0	51.6	70.9	167.3	13.1	13.3	10.9	39.4	59.8	111.1	95.7	109.9	48.0
8. Pyrene	368.8	188.0	14.1	38.7	44.9	75.2	136.2	8.2	9.4	50.0	6.0	48.3	105.5	71.6	119.9	33.4
9. Chrysene	157.0	79.7	5.2	17.9	19.3	33.6	57.3	3.5	3.7	21.4	2.9	21.9	45.6	31.8	52.1	14.9
10. Benzo(a)anthracene	118.8	59.6	4.1	13.6	15.5	27.3	43.7	2.9	2.8	20.7	8.5	17.1	35.5	24.2	42.4	11.4
11. Benzo(b)fluoranthene	194.6	126.8	7.3	29.2	33.4	55.3	87.2	5.4	5.1	40.2	23.9	34.1	67.7	48.8	81.9	21.8
12. Benzo(k)fluoranthene	72.0	39.6	2.6	9.7	10.9	18.9	30.8	1.9	1.7	14.7	9.3	11.9	23.9	15.6	27.5	7.6
13. benzo(a)pyrene	142.7	89.8	5.1	19.7	24.2	36.8	62.9	3.8	3.5	8.1	0.7	24.2	44.6	32.6	53.9	14.2
14. Dibenzo(a,h)anthracene	17.4	9.9	0.5	1.9	2.4	3.6	7.6	0.3	0.3	2.5	0.3	9.0	4.9	4.6	6.8	1.5
15. Benzo(g,h,i)perylene	72.4	62.9	3.7	13.9	41.1	19.6	41.3	2.5	2.5	10.9	2.3	16.2	29.9	29.2	30.7	9.1
16. Indeno(1,2,3-cd)pyrene	79.0	55.0	5.0	12.8	33.4	21.2	45.4	3.1	3.9	20.8	3.3	9.3	31.2	23.3	29.9	9.5
Total Light PAHs (1-7)	1593.7	648.0	57.2	104.2	105.8	167.8	471.3	37.5	66.2	57.7	46.9	142.0	301.1	238.5	275.8	112.6
Total Heavy PAHs (8-16)	1222.7	711.3	47.7	157.4	225.1	291.5	512.4	31.6	32.9	189.3	57.2	192.0	388.8	281.7	445.1	123.4
Total PAHs	2816.4	1359.3	104.9	261.6	330.9	459.3	983.7	69.1	99.1	247.0	104.1	334.0	689.9	520.2	720.9	236.0
TOC	190.4	155.6	53.3	131.6	141.9	174.8	146.5	88.6	49.2	66.1	28.8	161.6	105.3	101.8	95.0	152.6
Contaminant removal [%]																
Total Light PAHs (1–7) (%)	–	59	96	93	93	89	70	98	96	96	97	91	81	85	83	93
Total Heavy PAHs (8-16) (%)	–	42	96	87	82	76	58	97	97	85	95	84	68	77	64	90
Total PAHs (%)	–	52	96	91	88	84	65	98	96	91	96	88	76	82	74	92
TOC (%)	–	18	72	31	25	8	23	53	74	65	85	15	45	47	50	20

Fig. 1. Results of the chemical oxidation tests: comparison of the removal efficiencies achieved with different reactants for total PAHs (a), light PAHs (b), heavy PAHs (c) and TOC (d) (HP = hydrogen peroxide; MF100 = modified Fenton's reagents, molar ratio catalyst:oxidant = 1:100; MF50 = modified Fenton's reagents, molar ratio catalyst:oxidant = 1:50; PP = potassium permanganate; AP = activated sodium persulfate).

HP1 to test HP2), while if the oxidant dose increases above a certain level, the removal efficiency may decrease. An additional test, performed with a lower hydrogen peroxide dose (25 mmols for a 30 g sample) confirmed this behavior, with a contaminant removal about 41% for total PAH (final concentration about 1666 mg/kg$_{SS}$), 51% for light PAHs (final concentration about 778 mg/kg$_{SS}$), 27% for heavy PAHs (final concentration about 888 mg/kg$_{SS}$). This fact was noticed also in the tests performed with modified Fenton's Reagent, as discussed as follows.

In both sets of experiments performed with modified Fenton's reagent (MF100 and MF50) the removal efficiency was dependent on the oxidants dosage. In MF100 tests, the PAH removal varied from 65 to 88%, while in MF50 tests the PAH removals were 96 and 98%, with very high removal efficiencies both for light PAHs and for heavy PAHs. Also in these cases, as in the previous ones, the removal efficiency for TOC was smaller than for PAHs, varying from 8 to 25% in tests MF100 and from 54 to 73% in tests MF50.
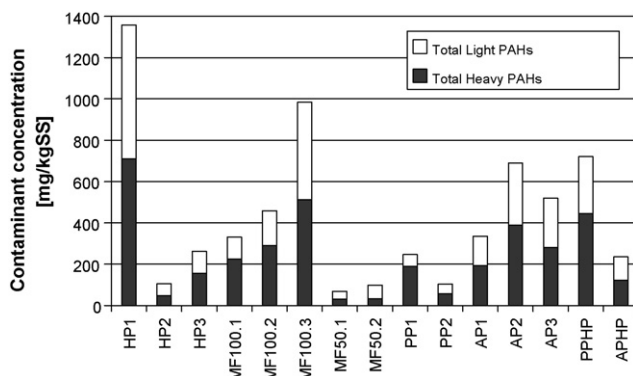

Fig. 2. Residual PAH contents in the sediment samples after chemical oxidation tests.

The tests MF100 showed the same behavior of PAH removal which was registered in the trials with hydrogen peroxide. In fact, in these tests the removal efficiency increases at lower oxidant dosages (as in tests MF100.1 and MF100.2), but it started to decrease at higher oxidant doses, as in test MF100.3. The removal efficiency decreased with oxidant dose can be clearly seen from Fig. 2, as for example from test HP2 to HP3, from MF100.1 to MF100.2 and MF100.3, and from test MF50.1 to MF50.2. This effect is thought to be due to the very strong and rapid reactions caused by the high reactant dosages, which may prevent a good contact between oxidant and pollutants (too strong and rapid reactions). However, this phenomenon must be further investigated and needs for further research.

On the whole, the results achieved with the use of modified Fenton's reagent can be considered very satisfying, the remediation efficiencies being very good in both tests MF100.1 and MF100.2, and even excellent, above 95%, in the tests MF50.1 and MF50.2. Hydrogen peroxide alone resulted in very good contaminant removal, but the application of hydrogen peroxide with supplementary ferrous ions (modified Fenton's tests) indicated a higher PAH removal, with increasing remediation efficiency for increasing iron:oxidant ratio. These results are consistent with other Authors, who experienced a strong dependency of Fenton's oxidation efficiency from catalyst dose [22,31].

A problem that is commonly encountered with Fenton's regents is the consumption of the hydroxyl radicals for undesired side reactions (oxidant scavengers), as for the mineralization of soil organic matter. Moreover, when high oxidant concentrations are used, a significant amount of radicals can be consumed by the dosed reactants themselves [33,34]. Usually, the remediation efficiency increases significantly with the oxidant dose till
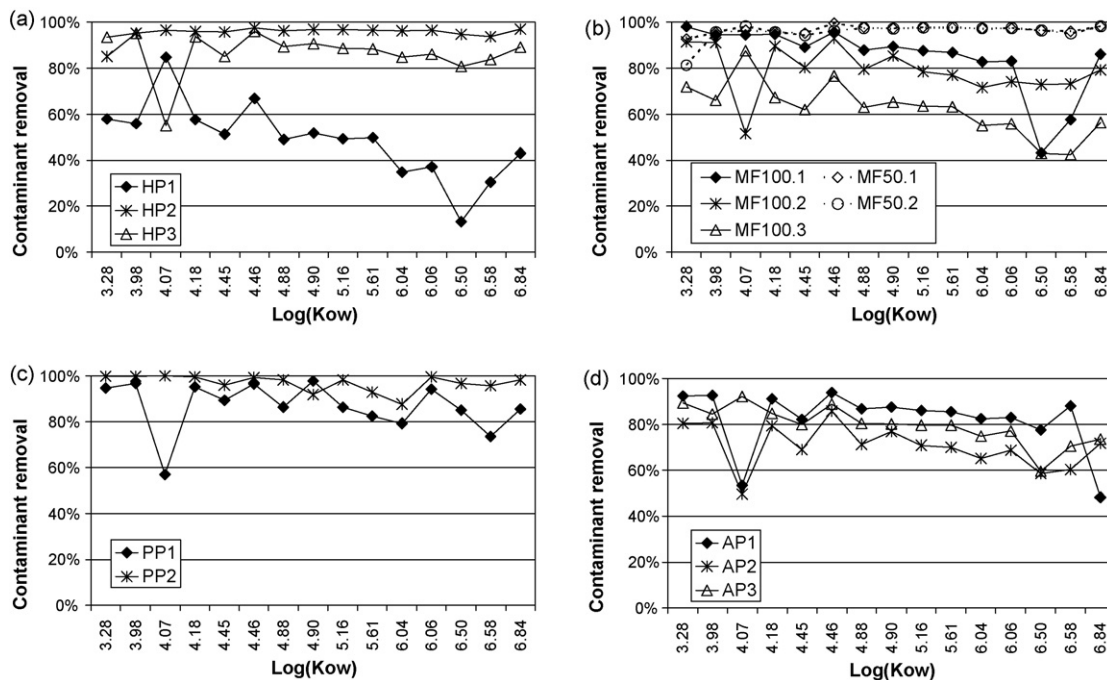
Fig. 3. Removal efficiencies achieved as a function of PAH octanol–water partition coefficient (K_{ow}) for chemical oxidation tests with hydrogen peroxide only (a), modified Fenton's reagent (b), potassium permanganate (c), activated sodium persulfate (d). Since benzo(a)pyrene and benzo(k)fluoranthene are characterized by the same value of K_{ow}, in the plots only the results for benzo(a)pyrene are presented.

a certain oxidant concentration, but does not increase appreciable afterwards [29]. Very high oxidant concentrations may even decrease system efficiency, likely because of an increase in the quenching reactions. This can explain the decrease of the remediation efficiency that was achieved in this study for increasing doses of hydrogen peroxide and of modified Fenton's reagent.

In conclusion, modified Fenton's reagent can be considered an effective chemical for the remediation of PAH contaminated sediments. For better results, a molar ratio iron:peroxide equal to 1:50 should be used rather than 1:100, while an oxidant dosage of 50–100 mmols of hydrogen peroxide for a 30-g sediment sample is recommended, and anyway the dose should not exceed 100 mmols per 30 g-sample, in order not to reduce the remediation efficiency because of too strong and rapid reactions.

At the end of the experimental investigation, one additional experiment was performed to assess the role of the chelating agent in the modified Fenton's treatment. During this trial, two tests were performed, one with modified Fenton's reagent and one with traditional Fenton's reagent, so as to compare their removal efficiencies. The original sample showed an initial total PAH content about 2383.8 mg/kg$_{SS}$ (light PAHs 688.0 mg/kg$_{SS}$, heavy PAHs 1695.8 mg/kg$_{SS}$). In the test with modified Fenton's reagent, 100 mmols of hydrogen peroxide were added to a 30-g sediment sample, together with 2 mmols of ferrous chloride (iron:catalyst molar ratio equal to 1:50) and 2 mmols of catechol. The total PAH content in the treated sample was about 472.5 mg/kg$_{SS}$ (−80%), with a light PAH concentration of 191.0 mg/kg$_{SS}$ (−72%), and a heavy PAH concentration of 281.5 mg/kg$_{SS}$ (−83%). In the test with traditional Fenton's reagent, 100 mmols of hydrogen peroxide were added to a 30 g sediment sample, together with 2 mmols of ferrous chloride

(iron:catalyst molar ratio equal to 1:50), without addition of the chelating agent. After the treatment, the total PAH content resulted in 867.2 mg/kg$_{SS}$ (−64%), with light PAH concentration of 134.2 mg/kg$_{SS}$ (−80%), and heavy PAH concentration of 733.0 mg/kg$_{SS}$ (−57%). Both tests were performed at sediment natural pH. According to the results achieved, traditional and modified Fenton's reagents had similar removal efficiencies as for light PAH mineralization, with little differences probably due to sample heterogeneity. However, the addition of catechol as chelating agents resulted in a significant increase in heavy PAH removal, which also led to a higher total PAH decrease. Therefore, catechol played an important role in the modified Fenton's process, as it helped to enhance the oxidation of the more lipophilic and more sorbed PAH species, also resulting in a higher remediation efficiency.

Other experiments were performed to evaluate the PAH solubilization during the experiments in the slurry form. For this purpose, a 30-g sediment sample was mixed with 100 mL of deionized water and stirred for about 1 h; then, the sample was filtered to separate the solid and the liquid phase, which were then analyzed separately. The PAH concentration in the solid was 1168.2 mg/kg$_{SS}$ (light PAHs 352.1 mg/kg$_{SS}$, heavy PAHs 816.1 mg/kg$_{SS}$). The total PAH content in the aqueous phase was 103 μg (light PAHs 76 μg, heavy PAHs 127 μg), with main contributions given by phenanthrene (46 μg), anthracene (11 μg) and fluoranthene (15 μg). The same experiment was repeated by using a solution of ferrous chloride and catechol (solution volume 100 mL and concentration 0.5 M) instead of water, to assess the solubilization before modified Fenton's tests. The PAH concentrations in the liquid phase were similar to the values measured for water solubilization, with a total PAH content

about 143 µg, entirely given by light PAHs (heavy PAHs content <1 µg). In this case the main contributions were due to acenaphtene (22 µg), fluorene (25 µg), phenanthrene (66 µg), anthracene (13 µg) and fluoranthene (17 µg). Overall, in both cases the PAH solubilization appeared to be very limited, as it interested less than the 1% of the PAH content in the sediments samples.

Both tests performed with potassium permanganate showed very good removal efficiencies, with removal percentages above 90% for total PAHs. Moreover, both tests showed very high remediation efficiencies not only of light PAHs, but also of heavy PAHs, while the TOC removal varied from 65 to 85%. The removal efficiencies increased slightly with the oxidant dosage.

While permanganate led to good results when it was used alone, when it was used in combination with hydrogen peroxide, the results were below the expectations, being lower than the ones obtained for permanganate only. In fact, while the dosage of 50 mmols of potassium permanganate lead to a 91% removal of total PAHs, the dosage of 50 mmols of permanganate and of 50 mmols of hydrogen peroxide resulted in only 74% PAH removal. This was probably due to the excessive strength of the reactions achieved, which proved to be very rapid and led to a strong foam formation. These results seem to confirm that when the reactions are too strong and rapid, the PAH removal may decrease, since the rapid oxidant consumption prevents the pollutants to come in contact with the reactants.

In the tests performed with activated sodium persulfate, the contaminant removal did not reach very high levels, the total PAH removal varying from 76 to 88%. When activate sodium persulfate was combined with hydrogen peroxide, better results were achieved, even with low oxidant dosages, the reactions being not too rapid or strong. In fact, the contaminants removal efficiencies achieved during test APHP (92% removal for total PAHs, 93% for light PAHs and 90% for heavy PAHs) can be considered fully satisfying.

It must be pointed out that in most of the tests performed the removal efficiency for light PAHs was found to be higher than for the heavy PAHs. This can be considered as a typical behavior of PAHs, whose lighter species are generally more available to reactants than heavy species, which are more hydrophobic and more sorbed onto sediments. This difference in the removal efficiency can be overcome by using vigorous oxidation conditions. For example, during hydrogen peroxide tests, the removal efficiencies of light and heavy PAHs were significantly different in the test with lower oxidant dosage (test HP1), but they became very similar or equal values in tests HP2 and HP3, i.e. for higher oxidant doses. This is thought to be due to the fact that higher oxidant doses can enhance the oxidation of pollutants, by increasing chemical reaction kinetics and the production of most reactive compounds, as superoxides and hydroperoxides, able to even with the most recalcitrant and sorbed pollutants. [19,29,34,35]. Moreover, the higher dosage of hydrogen peroxide could cause an increase in the slurry temperature, thus enhancing the desorption of PAHs, and consequently their release in the aqueous phase, making them more available for oxidation reactions.

This effect can be clearly seen from Fig. 3, which presents the contaminant removal as a function of the K_{ow} partition coefficient of different PAH species. As the K_{ow} coefficient represents the lipophilicity of a certain chemical, it indicates the tendency of that compound to be sorbed onto organic matter or to dissolve in water. The higher the K_{ow} coefficient is, the more the PAHs tend to be sorbed onto organic matter. Fig. 3 shows that when weak oxidation conditions were used, the contaminant removal was clearly decreasing for increasing K_{ow}, as for tests HP1, AP1, AP2 and AP3. On the opposite, when very vigorous oxidation conditions were created (as in tests HP2, HP3, MF50.1, MF50.2, PP1 and PP2), the contaminant removal was almost constant with K_{ow}, and the remediation efficiency is high also for the more lipophilic pollutants.

Other Authors [31] confirmed that contaminant availability can highly influence the treatment efficiency, the less sorbed pollutants (i.e. the species that are less hydrophobic) being more available for oxidation, while the more hydrophobic and more sorbed molecules proved to be more resistant to oxidation during chemical treatments than contaminants in solution. In addition, the effects of sorption on contaminant degradability were already reported to be minimized with high oxidant (H_2O_2) dosages [19,29,34,35].

A problem that may arise during the oxidation of a PAH contaminated soil is the risk of incomplete mineralization and the consequent production of degradation by-products. In this study, the identity of the oxidation reaction by-products has not been determined, but PAHs are known to create a certain number of degradation intermediates. These commonly include aldehydes, ketones, and quinones as main oxidation by-products (oxy-PAHs) [29,33,40,43,44]. The PAH derivatives are commonly found in low concentrations after chemical oxidation actions [33,45], but they are of concern because of the high toxicity of certain species. Most of them have polar functional groups, which are likely to enhance not only higher aqueous solubility, but also more availability for natural biodegradation than the parental compounds [23,40]. Despite the fact that many compounds are known as single PAH derivatives, a complete identification of all PAH by products has not been achieved yet, and further studies should be conducted to assess the extent of oxidation, and the formation of possible by-products.

On the whole, during this experimental investigation the best removal percentages were achieved with the use of: modified Fenton's reagent (tests MF50.1 and MF50.2, with a H_2O_2 dose of 50–100 mmols per 30-g sample of sediments), hydrogen peroxide (test HP2, 100 mmols of H_2O_2 per 30-g sample), or potassium permanganate (test PP2, 100 mmols of $KMnO_4$ per 30-g sample). In all these cases, the total PAH removal was above 95% and the residual PAH concentration in the treated samples did not exceed the Italian law limit for industrial and commercial land use (total heavy PAH content lower than 100 mg/kg$_{SS}$). On the opposite, the removal efficiencies of activate sodium persulfate were limited, and the total PAH removal did not exceed 88%.

The optimal oxidant dosages determined in this study are quite high (about 100 mmols of oxidant for a 30 g sediment sample), but these results were expected, as sorbed PAH mineralization is commonly reported to require very vigorous oxidation conditions (i.e. high oxidant concentrations) [23,29,46]. Moreover, it is known that a significant presence of natural organic

matter in a soil, as in the present case, can affect the results of the chemical oxidation, by reducing the treatment efficiency and increasing the optimal oxidant dose [20,22,31]. A further increase in the oxidant dose not only did not result in a higher contaminant removal, but led to a poorer remediation efficiency, probably because of a rapid oxidant consumption. This suggests that the optimal oxidant dose must be carefully determined under site-specific condition by bench scale screening tests. In fact, in the oxidation conditions are not strong enough, the reactants are not able to attack the most recalcitrant compounds, but also too high oxidant doses must be avoided, as they can determine a decrease in the oxidation efficiencies, thus failing in meeting the remediation goals.

4. Conclusions

The aim of this experimental investigation was to assess the applicability and to evaluate the effectiveness of chemical oxidation for the ex situ remediation of sediments contaminated with PAHs. For this purpose several laboratory tests were performed, with the following liquid reactants at different dosages: hydrogen peroxide, modified Fenton's reagent (catechol and ferrous chloride were used as catalyst agents, with molar ratio catalyst:oxidant equal to 1:100 and 1:50), activated sodium persulfate (catechol and ferrous chloride were used as catalyst agents, with molar ratio catalyst:oxidant equal to 1:25) and potassium permanganate, as well as a combination of potassium permanganate and hydrogen peroxide, and a combination of activated sodium persulfate and hydrogen peroxide.

Hydrogen peroxide resulted in good PAH removal efficiencies (above 90%), but only with high dosages (as 100–200 mmols per 30-g sediment sample), and on the whole the performances were worse than for modified Fenton's reagent, which gave excellent PAH removal efficiencies (above 95%) if used with a 1:50 molar ratio catalyst:oxidant. The use of potassium permanganate lead to very good results, with a total PAH removal above 90%; in contrast, the combined used of permanganate and hydrogen peroxide led to poorer removal efficiencies, with very strong, rapid and difficult to control reactions, characterized by a strong foam formation in the slurry. The PAH removal achieved with the use of activated persulfate was limited (below 90%), but the combined use of activated persulfate and hydrogen peroxide led to a better removal both of total PAHs, light PAHs and heavy PAHs.

On the whole, the best removal percentages were achieved with the use of modified Fenton's reagent (tests MF50.1 and MF50.2, with a H_2O_2 dose of 50–100 mmols per 30-g sample of sediments), hydrogen peroxide (test HP2, 100 mmols of H_2O_2 per 30-g sample), and potassium permanganate (test PP2, 100 mmols of $KMnO_4$ per 30 g-sample). In all these cases, the total PAH removal was above 95% and the residual heavy PAH concentration in the treated samples was below 100 mg/kg$_{SS}$.

The optimal oxidant dosages determined in this study are quite high (about 100 mmols of oxidant for a 30-g sediment sample), but this results was expected, as sorbed PAH mineralization requires very vigorous oxidation conditions, especially if the soil organic matter content is high. The results indicated

that the optimal oxidant dose must be carefully determined under site-specific conditions by bench scale screening tests. In fact, in the oxidation conditions are not strong enough, the reactants are not able to attack the most recalcitrant compounds, while also too high oxidant doses must be avoided, as they can determine a decrease in the oxidation efficiencies, thus failing in meeting the remediation goals.

Based on the results of this study, chemical oxidation proved to be an effective remediation technology for the contamination of concern, even if different oxidants and different reagent dosages showed different removal efficiencies. Further studies should be conducted to assess the extent of oxidation, and the nature and toxicity of the possible formation of by-products.

Besides the removal efficiencies obtained with laboratory tests, several factors must be taken into account when designing a real-scale application of this technology, including the cost and the availability of reactants, and the ability of the chosen method to reach target levels (i.e. residual contaminant concentration). Furthermore, for in situ application, it must be considered that the reactant delivery plays often the most important role, especially for the strongest oxidants, like modified Fenton's reagent, which can often reach only a small area around the injection point. As the oxidant delivery depends on the medium permeability, a good knowledge of site hydrogeology is required for an effective application of in situ chemical oxidation: this problem can be overcome by applying an ex situ, both on site or off site, technology.

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