



Strategies for oxidation of PAHs in aged contaminated soil by batch reactors

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) are neutral, nonpolar and hydrophobic molecules that tend to sorb onto soil organic matter. Chemical oxidation is a good choice to avoid the limitations of bioremediation.

To evaluate the efficiency of different types of oxidation (permanganate, hydrogen peroxide, and persulfate) and activation (heat, alkaline, and iron), batch reactors were prepared. The soil was contaminated with phenanthrene and pyrene (1200 ± 200 and 2800 ± 100 mg per kg of dry soil, respectively) and aged for fifteen months. Treatments were prepared with 10 g of contaminated dry soil and 20 ml of water and incubated at room temperature for 7 days. Analyses of phenanthrene and pyrene concentrations, soil pH and electric conductivity were performed. Counts of heterotrophic cultivable bacteria on R2A medium and PAH-degraders were carried out after 7 days of treatment. The persulfate treatment at room temperature, without the addition of activators, achieved better results than treatments with the same doses of permanganate or hydrogen peroxide. All the strategies to improve persulfate treatments yielded higher degradation of pyrene than the biological control, as expected from the structural description of this compound by Clar's model. The thermal activation of persulfate (65°C for 6 h) led to the degradation of more than 90% of both PAHs after 7 days of treatment.

1. Introduction

Industrial activities have left behind large areas contaminated with persistent organic pollutants, especially polycyclic aromatic hydrocarbons (PAHs) (Barnier et al., 2014). These pollutants represent a threat to human health because of their recognized carcinogenic and mutagenic effects. Up to now, approximately 130 PAHs have been identified, but only 16 PAHs have been listed by the US Environmental Protection Agency (US EPA) as priority contaminants due to their prevalence (Lemaire et al., 2013a). These neutral, nonpolar and hydrophobic molecules are slightly volatile, slightly soluble in water, and tend to sorb onto soil organic matter (SOM). In the case of high contamination levels, thermal desorption is commonly used to treat soil after excavation (Ranc et al., 2016), while less contaminated soils are generally left to naturally attenuate or are treated by monitored biological treatments (Lu et al., 2011). PAH bioremediation usually needs more time than other technologies (Singh et al., 2009) and can be incomplete because of the low availability and recalcitrance of PAHs (Posada-Baquero and Ortega-Calvo, 2011). Chemical oxidation can be used to degrade PAHs and not merely transfer them to another compartment. However, the remediation of PAH-contaminated soil using chemical oxidation technology remains a big challenge (Lemaire et al.,

2013a) because the efficiency of the chemical oxidation of PAHs in soils depends on the soil characteristics (such as organic matter and oxide contents, specific surface area, etc.) and PAH properties (such as molecular weight, water solubility, amount of aromatic rings, etc.) (Gan et al., 2009).

Permanganate has been widely used to break down organic and inorganic compounds. The main advantage of this oxidant is that it persists in soils and groundwater. It is also relatively cheap and easy and safe to use compared to hydrogen peroxide. However, its natural oxidant demand is generally high, leading to high permanganate consumption, which is a drawback. The oxidation of organic compounds by permanganate ions produces manganese dioxide (MnO_2) as well as CO_2 or organic intermediates. The excess of MnO_2 could reduce soil permeability, an obviously undesirable side effect that may affect soil quality (Siegrist et al., 2002; Sirguy et al., 2008).

Chemical oxidation by Fenton reagents is a well-developed technology for the remediation of soils and water contaminated with organic compounds. In particular, they were applied to remediate soils contaminated with pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and total petroleum hydrocarbons (TPHs) (Cheng et al., 2016a). A Fenton reaction is based on the generation of reactive hydroxyl radicals ($\text{HO}\cdot$) (Usman et al., 2016).

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The strong standard oxidation potential [$E^\circ(\text{HO}\cdot/\text{H}_2\text{O}) = +2.8 \text{ V}$] and nonselective reactivity of $\text{HO}\cdot$ are primarily responsible for the high efficiency in removing recalcitrant organic compounds (Bokare and Choi, 2014). The production of $\text{HO}\cdot$ by Fenton reagents occurs with the addition of H_2O_2 to Fe^{2+} salts. Studies have demonstrated that Fenton/Fenton-like reactions cannot only be catalysed by free iron ions (Fe^{3+} and Fe^{2+}) but also by endogenous (Lemaire et al., 2013a) or synthesized iron oxides (FeO , Fe_2O_3 and Fe_3O_4) (Cheng et al., 2016b). Therefore, it is not always necessary to add external iron to produce $\text{HO}\cdot$.

Persulfate (PS) has been investigated because it can be activated by heat (Mora et al., 2009), transition metals (Anipsitakis and Dionysiou, 2004), bases (Furman et al., 2010), and ultraviolet light (Lin and Lee, 2015) to form the highly reactive sulfate radicals. These radicals are an alternative method for the degradation of organic contaminants due to the high removal efficiency of pollutants that cannot be eliminated by traditional treatments (Ranc et al., 2016). They have a high oxidation potential ($E^\circ(\text{SO}_4^{\cdot-}/\text{SO}_4^{2-}) = +2.60 \text{ V}$) and are nonselective (Matzek and Carter, 2016). Activated persulfate has widespread applications for remediation because formed radicals react with organic chemicals to cause either partial or complete mineralization. In situ remediation with activated persulfate oxidation may be preferred over hydrogen peroxide-based processes because the persulfate anion is more stable and may be transported further into the subsurface before being activated for contaminant degradation (Waldemer et al., 2007; Yan et al., 2013). For in situ applications, Fe(II) and Fe(III) are the most commonly used activators due to their natural abundance in porous media and benign nature (Tsitonaki et al., 2010). In a previous work, we found that soil natural conditions were sufficient to decompose PS without the addition of activators and that the persistence of PS was approximately 7 days (Mora et al., 2014).

The choice of an oxidant for a given remediation situation is governed by several factors, as reported by some authors (Anipsitakis and Dionysiou, 2004; Lemaire et al., 2013a; Pardo et al., 2015). The soil composition (SOM nature and content), texture and porosity strongly affect PAH availability (Lemaire et al., 2013a). Another important factor is pH, since a low pH is preferred for Fenton reactions (Pardo et al., 2015) and the metal activation of persulfate (Anipsitakis and Dionysiou, 2004) because of the behaviour of soluble iron species.

Remediation of some recalcitrant xenobiotic chemicals may require a combination of chemical, physical and biological steps to increase the efficacy of contaminant destruction (Singh et al., 2009). Frequently in aged contaminated soil remediation, a low PAH removal rate is attained with chemical oxidation. Then, in order to efficiently combine chemical oxidation with bioremediation posttreatment, it is necessary to control the impact of the oxidation on the soil properties such as pH and salinity (Haapea and Tuhkanen, 2006; Sutton et al., 2011; Valderrama et al., 2009). Moreover, the addition of high doses of the oxidant affects the viability of later biodegradation.

In some cases, treatment effectiveness increases with the oxidant dosage (Ferrarese et al., 2008; Huang et al., 2005; Ravikumar and Gurol, 1994). However, when the mechanism of the chemical reaction involves radicals, the reaction may be stopped by radical scavenging, and so a high oxidant dose can cause negative effects (Lemaire et al., 2013a). For these reasons, a bench scale study is required for each remediation situation in order to choose the best operational conditions and predict the expected PAH degradation rate.

The aim of this contribution is to investigate the efficiency of low doses of potassium permanganate, hydrogen peroxide, Fenton reactions, persulfate and activated persulfate to degrade phenanthrene and pyrene (as model PAHs) in batch systems with artificially spiked and aged soil.

2. Materials and methods

2.1. Chemicals

Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, $\geq 99.0\%$, Merck), sodium hydroxide (NaOH , $\geq 97.0\%$, Cicarelli), ethyl acetate ($\text{C}_4\text{H}_8\text{O}_2$, $\geq 99.5\%$, Cicarelli), anhydrous sodium sulfate (Na_2SO_4 , $\geq 97.0\%$, Carlo Erba), iron sulfate heptahydrate ($\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, $\geq 97.0\%$, Mallinckrodt), hydrogen peroxide (H_2O_2 , 30% w/v (100 vol.), Biopack), phenanthrene ($\text{C}_{14}\text{H}_{10}$, $\geq 99.5\%$, Carlo Erba) and pyrene ($\text{C}_{16}\text{H}_{10}$, $\geq 98.0\%$, Sigma) were used. Potassium permanganate (KMnO_4 , $\geq 99.0\%$), monobasic potassium phosphate (KH_2PO_4 , $\geq 99.4\%$) potassium phosphate (K_2HPO_4 , $\geq 98.0\%$), disodium ethylenediaminetetraacetic acid ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8\cdot 2\text{H}_2\text{O}$, $\geq 99.0\%$) were provided by Anedra.

2.2. Soil

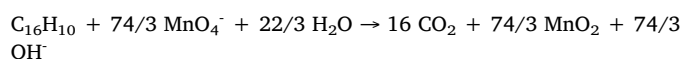
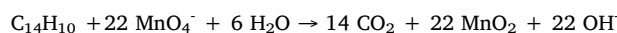
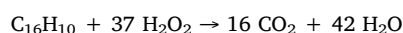
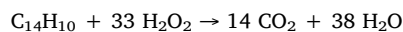
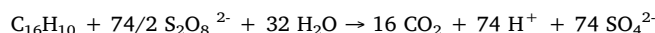
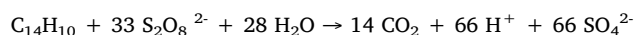
The soil selected for the study was an uncontaminated soil from an area near La Plata City, Argentina ($34^\circ 50' \text{ S}$, $58^\circ 10' \text{ W}$). It was analysed in the Laboratory of Soil Science at the University of La Plata and showed the following physicochemical properties: a pH of 6.6, 4.67% organic carbon (Walkley-Black method), 8.05% SOM, 3.89 mg/kg total nitrogen (wet digestion, and evaluation by Micro-Kjeldahl method), 4.0 mg/kg available phosphorus (Bray Kurtz No. 1 method), electrical conductivity of $3.3 \pm 0.3 \text{ dS m}^{-1}$ (on the saturated paste extract) and $109.9 \pm 0.9 \text{ mg}$ of Fe per kg of dry soil (extracted with EDTA and determined according to EPA method 7950).

The soil was contaminated with 2000 mg of phenanthrene and 3000 mg of pyrene per kg of dry soil (kg_{DS}) and aged at 4° C for 15 months. The concentrations of both PAHs were determined before each set of experiments. The PAHs were delivered in an acetone solution and mixed manually into the soil with a spatula, as reported (Mora et al., 2014).

2.3. Oxidant doses

For the field application of ISCO (in situ chemical oxidation), one major issue is the determination of the optimal doses of the reagents in the oxidizing solution. The oxidant/pollutant dose is the molar or mass amount of oxidant needed to degrade a known amount of pollutants (Ranc et al., 2016).

The calculation of the oxidant doses was based on the stoichiometric balances for each PAH/oxidant couple, and we considered the reaction leading to CO_2 and H_2O (Lemaire et al., 2013b).



2.4. Treatments

Batch reactors consisting of 10 g dry soil (g_{DS}) and 20 ml of aqueous phase (which contains the oxidant, the activator or distilled water) were placed in a glass container with continuous stirring. All the treatments were carried out in triplicate trays and incubated at $24 \pm 2^\circ \text{ C}$ (regional climate conditions) for 7 days. For the experiments of thermal activation of PS, the reactors were held at $65 \pm 2^\circ \text{ C}$ for the first 6 h and then were incubated at $24 \pm 2^\circ \text{ C}$ for 7 days.

Table 1
Details of the systems with different oxidative treatments.

System	Condition
BioD	Control without oxidant addition
PM/24 °C	(110 ± 1)gKMnO ₄ /kg _{DS}
HP/24 °C	(129.5 ± 0.5)mlH ₂ O ₂ /kg _{DS}
HP/Fe/EDTA	(129.5 ± 0.5)mlH ₂ O ₂ + (14.6 ± 0.1)gFeSO ₄ ·7H ₂ O + (16.2 ± 0.1)gEDTA /kg _{DS}
PS/24 °C	(267 ± 3)gPS/kg _{DS}
PS/Fe/EDTA	(267 ± 3)gPS + (14.6 ± 0.1)gFeSO ₄ ·7H ₂ O + (16.2 ± 0.1)gEDTA /kg _{DS}
PS/buffer	(267 ± 3)gPS/kg _{DS} with the addition of buffer KH ₂ PO ₄ /K ₂ HPO ₄ (pH ≈ 7)
PS/NaOH	(267 ± 3)gPS/kg _{DS} with the addition of NaOH solution until pH 10
PS/65 °C	(267 ± 3)gPS/kg _{DS} , at (65 ± 2) °C for the first 6 h

The first set of experiments (details are listed in Table 1) was done with initial concentrations of approximately 1200 ± 200 mg of phenanthrene and 2800 ± 100 mg of pyrene per kg of dry soil (kg_{DS}) and with approximately 1.5 doses of the corresponding oxidant. A batch reactor without the oxidant addition was used for biological degradation measurement (BioD).

A second set of experiments with different initial concentrations of phenanthrene and pyrene were performed: System A had 2140 ± 20 mg kg_{DS}⁻¹ of phenanthrene and 190 ± 20 mg kg_{DS}⁻¹ of pyrene (ratio [phenanthrene]₀/[pyrene]₀ = 11.3), while system B had 550 ± 50 mg/kg_{DS} of phenanthrene and 2040 ± 50 mg/kg_{DS} of pyrene (ratio [phenanthrene]₀/[pyrene]₀ = 0.3). In this set of experiments, the selected treatment was PS activated by heating at 65 °C for 6 h. Because of the chosen initial concentrations, in both cases, the dose of PS was 2.5 ± 0.1. For each condition (with the same amount of contaminant), a control system without the oxidant and heating at 65 °C for 6 h was run.

The pH and electrical conductivity (1:2) values were determined from the supernatant with a glass electrode (Phoenix Electrode Company).

For the analysis of iron content in the aqueous phase, 10 g dry soil (g_{DS}) and 20 ml of sodium persulfate solution (267 g_{PS}/kg_{DS}) were placed in a glass container with continuous stirring for 6 h at 24 ± 2 °C or 65 ± 2 °C to compare the effect of temperature on iron solubilization. The mixture was centrifuged at 300 rpm for 10 min. The aqueous phase was removed and filtered (nylon filter 0.45 µm pore size). This solution was fed into an atomic absorption spectrophotometer (Shimadzu AA 6650).

For the determination of phenanthrene and pyrene concentrations, each system was lyophilized (L-3 by REFICOR) and later homogenized with a mortar. Three sequential (exhaustive) extractions were performed with a subsample of 5 g of lyophilized soil with 20 ml, 20 ml and 10 ml of ethyl acetate. For each step, phenanthrene and pyrene were extracted using the ultrasonic bath (Testlab Ultrasonic TB10TA, 40 kHz, 400 W) for 60 min, as described elsewhere (Luque-García and Luque de Castro, 2003; Song et al., 2007). The mixture was centrifuged at 3000 rpm for 10 min (Presvac model DCS-16 RV), and the solution was filtered (nylon filter 0.45 µm pore size). Then, 20 µl of ethyl acetate extract was injected into a Hewlett–Packard HPLC model 1050 (Ti series) chromatograph with multiwavelength detection, with a C18 Restek Pinnacle II column (particle size 5 µm, 2.1 mm, id 250 mm) using 15 mM phosphoric acid in nanopure water solution and methanol (20:80 v/v) as the eluent at 0.5 ml/min constant flux. Retention times of phenanthrene and pyrene were determined with standard solutions (100 mg of each PAH per 1000 ml), and quantifications were done with adequate calibration curves (5 points ranged from 100 to 8 mg per 1000 ml, with a linear correlation coefficient R² > 0.99).

2.5. Microbiological analysis

To determine total cultivable heterotrophic bacteria and PAH-degraders, samples were taken from the aqueous phase. The total

cultivable heterotrophic bacteria were quantified in duplicates by successive 1/10 dilutions. These suspensions were spread on R2A medium plates (Reasoner and Geldreich, 1985) and after 7 days of incubation at 24 ± 2 °C, the colonies were counted. The PAH degraders were quantified in sterile polypropylene microplates. The wells contained a liquid mineral medium and a PAH mix in pentane as the substrate (Festa et al., 2016). The pentane was evaporated, and the wells were inoculated with an aliquot of serial dilutions of the sample and incubated at 24 ± 2 °C for 21 days. The most probable number (MPN) method was used to enumerate PAH degraders. The microbial enumeration was carried out in triplicate.

2.6. Statistics

All experiments in this study were performed in triplicate. The mean and standard deviations of triplicate independent experiments were calculated. The mean values were compared by a parametric two-way ANOVA test. All statistical analyses were performed using Microsoft Excel 2010.

3. Results and discussion

The efficiency of phenanthrene and pyrene removal by different treatments was evaluated after 7 days of incubation. Table 2 shows the impact of oxidative treatments on pH, electrical conductivity (EC), and cultivable heterotrophic and PAH-degrading bacteria counts.

Despite having used no drastic conditions, all treatments caused a negative impact on the soil characteristics studied, with the exception of HP/24 °C. The increase in EC values was a direct consequence of the addition of salts (KMnO₄ or Na₂S₂O₈), which increase the number of ions in the aqueous phase. The addition of KMnO₄ increased the pH, as reported by others authors (Bendouz et al., 2017). The PS/24 °C treatment produced a dramatic decrease in pH values, independently of the activation strategy used, because the PS aqueous solutions were acidic.

Table 2
Impact of oxidative treatments on pH, electrical conductivity (EC), and cultivable heterotrophic and PAH-degrading bacteria counts after 7 days. The BioD control was included for comparative purposes.

System	pH	EC(1:2)	Cultivable heterotrophic bacteria (log CFU/g _{DS})	PAH-degrading bacteria (log MPN/g _{DS})
BioD	6.8 ± 0.2	0.3 ± 0.2	10.4 ± 0.6	7.7 ± 0.4
PM/24 °C	9.6 ± 0.2	5.8 ± 0.2	3.98 ± 0.02	4.06 ± 0.03
HP/24 °C	6.8 ± 0.2	0.3 ± 0.2	11.2 ± 0.7	5.0 ± 0.9
HP/Fe/EDTA	5.2 ± 0.2	3.9 ± 0.2	≤ 7.80	4.06 ± 0.01
PS/24 °C	1.5 ± 0.2	≥ 10	4.6 ± 0.4	4.06 ± 0.01
PS/Fe/EDTA	1.3 ± 0.2	≥ 10	4.0 ± 0.1	4.4 ± 0.1
PS/buffer	2.2 ± 0.2	≥ 10	4.05 ± 0.05	4.06 ± 0.02
PS/NaOH	2.4 ± 0.2	≥ 10	5.5 ± 0.3	5.06 ± 0.03
PS/65 °C	1.5 ± 0.2	≥ 10	4.94 ± 0.03	5.1 ± 0.06

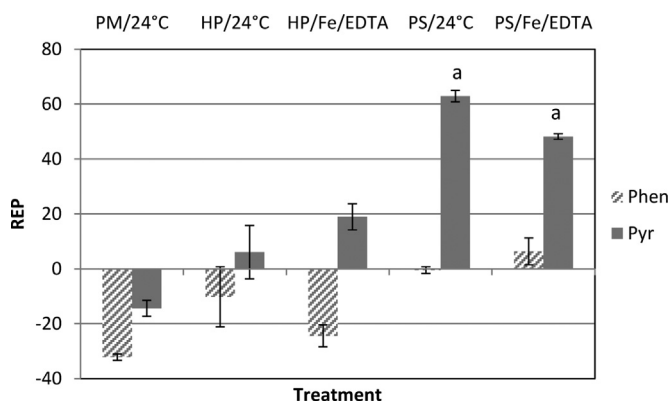


Fig. 1. Relative elimination percentages (REP) for PM/24 °C, HP/1 24 °C, HP/Fe/EDTA, PS/24 °C, PS/Fe/EDTA compared with BioD, for each PAH. Values followed by an “a” are significantly different from BioD at the 5% level (two-way ANOVA, Tukey’s test).

Decreases ranging from 2.8 to 6 pH units were observed under laboratory conditions using aqueous (Huang et al., 2005; Liang et al., 2004) and soil slurry experiments (Tsitonaki et al., 2008). Even at low doses, all oxidants caused a significant decrease in the cultivable PAH-degrading bacterial populations and a negative impact on cultivable heterotrophic bacterial populations. It is well known that the use of combined chemical and biological treatments increases the degradation of PAHs (Huang et al., 2017) Therefore, our results are relevant to consider in post-oxidation biological treatments.

The BioD system, a control that measures biological and physical PAH removal, reached $35 \pm 10\%$ and $17 \pm 10\%$ elimination for phenanthrene and pyrene, respectively. Low molecular weight PAHs, such as phenanthrene, are usually readily degraded by bacteria and fungi in soil and under laboratory conditions. However, high molecular weight PAHs (four or more rings) are more persistent due to their hydrophobicity and low bioavailability (Morelli et al., 2013).

Fig. 1 shows the relative elimination percentages (REP) for PM/24 °C, HP/24 °C, HP/Fe/EDTA, PS/24 °C, and PS/Fe/EDTA for each PAH compared with BioD. Different reactants and different activation strategies resulted in different removal efficiencies. Under the conditions of this study (low dose of oxidants), only the PS treatments reached a percentage of elimination significantly higher than that of BioD ($p < 0.05$), as shown in Fig. 1. The treatment with KMnO_4 showed elimination percentages lower than those achieved by BioD, while the treatments with H_2O_2 did not show significant differences from BioD.

The low efficiency of the treatment with permanganate seems contrary to the reported performance for this oxidant. Yen and coworkers reported 60% diesel degradation (initial concentration: 5000 mg/kg_{DS}) after 40 days (Yen et al., 2011). However, this treatment involved the use of 300 g/kg_{DS} of permanganate, i.e., 3 times more oxidant than PM/24 °C. A similar observation could be made for the batch experiments with aged contaminated soil reported by Lemaire and coworkers. They reached 75% degradation (initial concentration: 1300 mg/kg_{DS} PAH), after 4 days with the application of 7.5, 15 and 30 doses of permanganate (Lemaire et al., 2013a). In another study, Silva and coworkers found a high degradation rate for phenanthrene and pyrene (between 80–90% and 50–70%, respectively, from an initial concentration of approximately 700 mg/kg_{DS}) after 3 days with less than 2 doses (De Souza e Silva et al., 2009), an amount of oxidant similar to the one used in our assays. The main difference between their experiments and ours was the SOM content (1% and 8%, respectively). The low efficiency observed with PM/24 °C could be assigned to the well-known reactivity of PM with SOM (De Souza e Silva et al., 2009).

The HP/24 °C system did not show better degradation than BioD, possibly due to the pH value (6.8) that diminishes the availability of soluble iron from soil. Most of the ferrous ions will be Fe^{2+} below pH 3, but at a higher pH, ferrous salts are quite insoluble in water and will

tend to precipitate (Pignatello et al., 2006). Minerals from soil can act as catalysts by yielding free radicals via surface reactions. However, mineral surfaces can also act as nonproductive oxidant sinks, where hydrogen peroxide is decomposed without producing any reactive intermediates (Petri et al., 2011). To increase the efficiency of the H_2O_2 treatment, the addition of Fe(II) with EDTA (HP/Fe/EDTA system) was tested (Fig. 1). No significant improvement was observed. This behaviour indicates that the presence of available iron species was not the limiting parameter. As Petri and coworkers reported (Petri et al., 2011), the presence of SOM can enhance or limit the reaction kinetics involved in catalysed hydrogen peroxide treatment processes depending on the characteristics of each SOM. Our study seems to indicate that ubiquitous SOM reduces the efficiency of HP treatments.

Despite the low PS amount used and the absence of activators, in the PS/24 °C treatment, the phenanthrene REP was similar to that of BioD, while pyrene degradation was highly enhanced. As previously reported, natural soil conditions were sufficient to decompose PS without the addition of activators (Mora et al., 2014). It is noteworthy that a low pH value (1.5) could be responsible for the availability of soluble iron from soil, enhancing the activation of PS. For the PS/Fe/EDTA system, where Fe(II) was added, the phenanthrene and pyrene REPs were not better than for PS/24 °C. Hence, the degradation of phenanthrene was not limited by the amount of iron available.

Although it is commonly reported that the oxidation of sorbed PAH on soil requires high oxidant concentrations, especially when the SOM content is high (Ferrarese et al., 2008; Kulik et al., 2006), our results showed that a low amount of PS (1.5 doses) was able to remove PAHs. The PS/24 °C and PS/Fe/EDTA treatments had the same phenanthrene REP ($p < 0.05$) as BioD, while for pyrene, they presented better results, despite the negative impact on cultivable heterotrophic and PAH-degrading bacterial populations observed after PS addition. Then, in order to improve the global degradation, different PS activation strategies were assayed. The results of these treatments (PS/24 °C, PS/Fe/EDTA, PS/buffer, PS/NaOH, PS/65 °C) are shown in Fig. 2.

The addition of PS yields an acid pH (see Table 2), and low pH values may result in significant environmental perturbation that would limit the survival and activity of the soil microorganisms and thus the biodegradation process (Mora et al., 2014). The system with the addition of phosphate buffer was proposed to maintain a neutral pH throughout all experiments, supporting biological activity. In the PS/buffer, however, the buffer capacity was broken by the amount of PS added, and the pH value after 7 days was 2.2 (see Table 2). Initially, the pH value could sustain biological activity, but it was not the optimum to maintain available Fe(II). After 7 days, the decrease in pH led to the inhibition of cultivable populations and simultaneously supported the presence of soluble iron. The PS/buffer treatment had high values of REP for both phenanthrene and pyrene. Moreover, the REP for

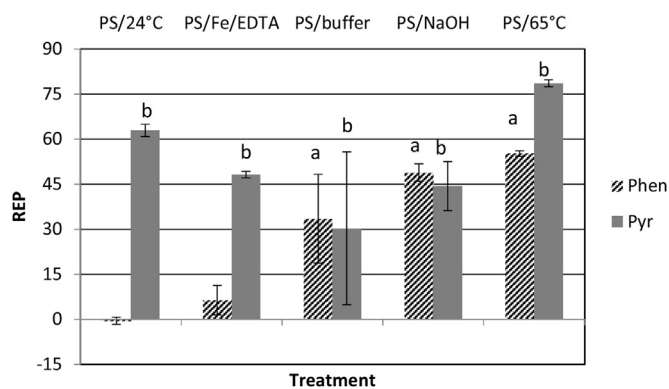


Fig. 2. Relative elimination percentages (REP) for PS/24 °C, PS/Fe/EDTA, PS/buffer, PS/NaOH, PS/65 °C compared with BioD, for each PAH. Values followed by an “a” are significantly different from BioD for phenanthrene and “b” for pyrene at the 5% level (two-way ANOVA, Tukey’s test).

phenanthrene was higher than for PS/24 °C, while for pyrene, it was not significantly different.

In the PS/NaOH treatment, phenanthrene and pyrene REPs were significantly higher than in the BioD system by approximately 45%. To study the possible contribution of a biological process in this system, the number of cultivable heterotrophic bacteria and the pH were determined daily and compared with the BioD system. Regardless of the initial alkaline pH ($\text{pH}_0 = 10$), a rapid decline was observed, and after 6 h, a pH value of 2.5 was reached. This behaviour was already reported by Waisner and coworkers (Waisner et al., 2008). Although this decrease correlated with the results of cultivable heterotrophic bacteria counts, these values were significantly higher ($p < 0.05$) than for the other PS treatments (except PS/65 °C, exposed to a higher temperature).

It has been reported that the application of low PS doses could enhance the biological process through the oxidation of organic matter, increasing the nutrient and PAH availability (Bosio et al., 2008; David Gara et al., 2008; Mora et al., 2014; Sirguyev et al., 2008). Therefore, our results suggest that in PS/NaOH, phenanthrene removal could be attributed, at least partially, to biodegradation processes.

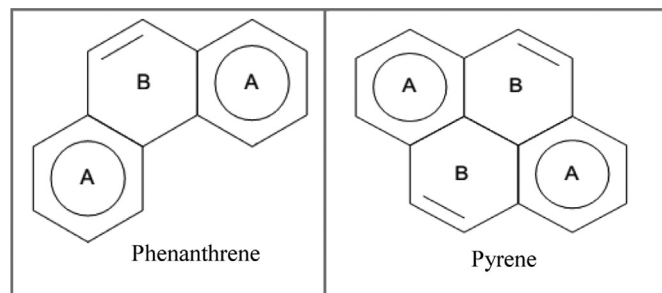
In the PS/65 °C treatment, the REPs of both phenanthrene and pyrene were significantly higher ($p < 0.05$) than in BioD. Moreover, the degradation of phenanthrene and pyrene reached $91 \pm 5\%$ and $96 \pm 1\%$ respectively, indicating that the thermal activation of PS was very effective. Despite the temperature, the cultivable heterotrophic counts had no significant differences with the PS/24 °C treatment, but PAH-degrading bacteria counts were significantly higher than in the PS/24 °C treatment.

The pH was 1.5 (see Table 2), allowing PS activation via soluble iron species. The concentration of Fe(II) was measured in the aqueous phase of the two treatments with the same amount of PS, one after 6 h at room temperature (pH 1.3) and the other after 6 h of heating at 65 °C (pH 1.2). The concentrations were $8 \pm 2 \text{ mg/kg}_{\text{DS}}$ and $1634 \pm 75 \text{ mg/kg}_{\text{DS}}$, respectively. The high efficiency in the degradation of both PAHs could be related to the simultaneous thermal and metal activation of PS at 65 °C.

It is noteworthy that the efficiency of all PS treatments was higher than that of BioD. Pyrene degradation improved in all of them, while phenanthrene degradation seemed to correlate with the PAH-degrading bacteria counts.

The chemical oxidation of phenanthrene and pyrene is related to their structures. The concept of aromaticity is important in physical organic chemistry for the rationalization of the structure, stability and reactivity of many molecules. One of the most successful has been Clar's model of the extra stability of $6n$ π -electron benzenoid species. This model has been validated by the calculation of the electronic (PDI), geometric (HOMA) and magnetic (NICS) aromaticity criteria at the same level of theory (Portella et al., 2005).

Clar's structure (see Scheme 1 for phenanthrene and pyrene) of a given PAH is the resonance structure that has the maximum number of isolated and localized aromatic π -sextets (A), with a minimum number of localized double bonds (B). In general, aromatic π -sextet rings are



Scheme 1. Clar's structure for phenanthrene and pyrene. A: localized aromatic π -sextets; B: localized double bonds.

considered to be the most aromatic centers in the PAH, and the other rings are less aromatic and are chemically more reactive (Solà, 2013).

Both PAHs studied have two localized aromatic π -sextets (indicated as circles with "A" in Scheme 1), but while pyrene has two fewer aromatic and more reactive rings, phenanthrene has just one.

The activation of PS generates stronger oxidant sulfate radical anions, $\text{SO}_4^{\cdot-}$. These radicals are responsible for the effectiveness of the persulfate anion in oxidative treatments (Osgerby, 2006). The reaction of $\text{SO}_4^{\cdot-}$ with aromatic compounds is an electrophilic reaction (Fang et al., 2013). Therefore, pyrene is easier to degrade than phenanthrene because it has two "more reactive rings". This analysis could explain the preference for pyrene degradation in all PS treatments.

Similar results were reported by Shih and coworkers (Shih et al., 2016). They suggest that the properties that reflected the reactivity of PAHs with oxidants, such as ionization potential, electron affinity and the homo-lumo gap, better explained the treatability of individual PAHs than did hydrophobicity-involved factors, including Kow, Koc and Sw (octanol/water, octanol/carbon partition coefficients and solubility, respectively), which were responsible for the sequestering of PAH into sediments.

To study the influence of the presence of one PAH on the chemical removal of the other, two systems (systems A and B) with different initial phenanthrene to pyrene concentration ratios (1.3 for A and 0.3 for B) were performed. The amount of PS was kept constant for these experiments to consider the same effect on pH and EC. Moreover, the initial concentrations of phenanthrene and pyrene were chosen to maintain the same oxidant demand (2.5 doses of PS).

The REPs of phenanthrene and pyrene for systems A and B after 6 h of heating (at 65 °C) are listed in Table 3. In both cases, the treatments were better than the corresponding controls, which measured the physical PAH removal without PS addition (sublimation or thermal decomposition, for instance). The biological contribution could be neglected because the treatments were performed for 6 h. Then, the degradation of phenanthrene and pyrene observed in systems A and B was due to the PS addition.

No significant ($p < 0.05$) differences in the REP of each compound between A and B were found, although the initial concentrations were very different. Because the REP was calculated by normalizing with the initial value, these results indicated that the degraded amounts of phenanthrene and pyrene were proportional to their initial concentrations and independent of the presence of the other. Moreover, in both systems, pyrene degradation was higher than that of phenanthrene, indicating that chemical oxidation (based on Clar's structures) was the dominant process. It is noteworthy that the efficiency of this treatment was independent of the initial concentration or of the presence of the other PAH.

4. Conclusions

The efficiency of different oxidants (potassium permanganate, hydrogen peroxide and persulfate) to degrade phenanthrene and pyrene in batch systems with artificially aged contaminated soil was evaluated. With the same dose of oxidant (1.5 doses) at 24 °C, and without external activators, the PS treatment gave the best results (36% of degradation for phenanthrene and 80% for pyrene) due to its lower affinity to natural soil organic matter than the other oxidants tested.

Different PS activation strategies (PS/24 °C, PS/Fe/EDTA, PS/buffer, PS/NaOH, PS/65 °C) were also assayed. All the PS treatments improved pyrene degradation, according to chemical oxidation related to the structures described by Clar, while no inhibition of phenanthrene biodegradation was observed.

The highest degradation was achieved by PS/65 °C, at 91% and 96% for phenanthrene and pyrene, respectively.

Experiments with PS at 65 °C, with different relative amounts of phenanthrene and pyrene, showed that the percentage of degradation of both contaminants was proportional to the initial value and

Table 3

Initial concentrations and relative elimination percentages (REP) of phenanthrene and pyrene for the treatment with (267 ± 3) g_{PS}/kg_{DS} at 65 °C for 6 h.

System	[phen] ₀	[pyr] ₀	[phen] ₀ / [pyr] ₀	phen REP	pyr REP
A	2140 ± 20 mg/kg _{DS}	190 ± 20 mg/kg _{DS}	11.3	71 ± 4	96 ± 3
B	550 ± 50 mg/kg _{DS}	2040 ± 50 mg/kg _{DS}	0.3	73 ± 5	97 ± 2

independent of the presence of the other PAH.

The combination of a low dose of PS addition and biodegradation was shown to be a promising strategy for the treatment of soils polluted with low and high molecular weight PAHs.

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