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Use of different kinds of persulfate activation with iron for the remediation of a PAH-contaminated soil

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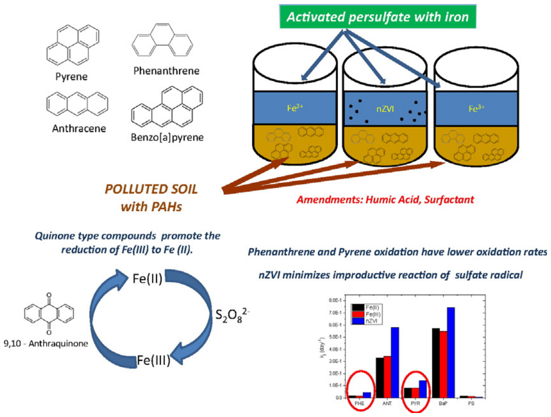
HIGHLIGHTS

- Soil polluted by PAHs was remediated by activated persulfate.
- Iron was added as Fe^{2+}, Fe^{3+} salt or nZVI without pH adjustment.
- Surfactant addition slightly improved PAHs removal efficiencies.
- Quinone type byproducts let Fe^{3+} be reduced to Fe^{2+} improving persulfate activation.
- The highest PAHs conversions were obtained by using nZVI.

GRAPHICAL ABSTRACT



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ABSTRACT

Contamination of soils by persistent pollutants is considered an important matter of increasing concern. In this work, activated persulfate (PS) was applied for the remediation of a soil contaminated with polycyclic aromatic hydrocarbons (PAHs), such as anthracene (ANT), phenanthrene (PHE), pyrene (PYR) and benzo[a]pyrene (BaP). PS activation was performed by different ways; where ferric, ferrous sulfate salts (1–5 $mmol \cdot L^{-1}$) and nanoparticles of zerovalent iron (nZVI) were used as activators. Moreover, in order to improve the oxidation rate of contaminants in the aqueous phase, the addition of sodium dodecyl sulfate (SDS), as anionic surfactant, was tested. On the other hand, it was also studied the role of humic acids (HA), as reducing agent or surfactant, on PAHs conversion. Removal efficiencies near 100% were achieved for ANT and BaP in all the runs carried out. Nevertheless, remarkable differences on removal efficiencies were observed for the different techniques applied in case of PHE and PYR. In this sense, the highest conversions of PHE (80%) and PYR (near 100%) were achieved when nZVI was used as activator. Similar results were obtained when activation was carried out either with Fe^{2+} or Fe^{3+}. This can be explained by the presence of quinone type compounds, as 9,10-anthraquinone (ATQ), that can promote the reduction of Fe^{3+} into Fe^{2+}, permitting PS radicals to be generated. On the other hand, the addition of HA

Abbreviations: PS, persulfate; PAHs, polycyclic aromatic hydrocarbons; ANT, anthracene; PHE, phenanthrene; PYR, pyrene; BaP, benzo[a]pyrene; nZVI, nanoparticles of zerovalent iron; SDS, sodium dodecyl sulfate; HA, humic acids; ATQ, 9,10-anthraquinone; SW, soil washing; ISCO, in situ chemical oxidation; NPC, non-productive consumption; BL, blank run; CMC, critical micelle concentration.

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did not produce an improvement of the process while surfactant addition slightly increases the PAHs removal. Furthermore, a kinetic model was developed, describing the behavior of persulfate consumption, and contaminants removal under first order kinetics.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are amongst the most widespread organic contaminants in soils, natural waters and wastewater (Puglisi et al., 2007). The release of this compounds into the environment can involve natural phenomenal (e.g. volcanic eruptions, forest fires) or anthropogenic activities (incomplete combustion of fuel, coal, wood, etc.). PAHs are a group of compounds that consist of two or more fused benzene rings (Rivas, 2006), thus, due to their hydrophobic nature and their low solubility in the aqueous phase, these species tend to be adsorbed on solid particulates, especially on the soil organic fractions (Tremblay et al., 2005). Knowing their potentially mutagenic or carcinogenic effects on human and animal health, and their tendency to accumulate in the environment (Tobiszewski and Namiesnik, 2012; Tsapakis and Stephanou, 2005), the removal of this kind of pollutants is considered a priority. In this sense, in order to restore soil and groundwater polluted with PAHs, a wide range of different kinds of treatments have been studied, such as natural attenuation, bioremediation, soil washing (SW) with surfactants and chemical oxidation. Despite natural attenuation is the less invasive technique to manage the remediation of contaminated soils, it is required a long-term monitoring of the soil as well as a deep understanding of the contaminants behavior (Hanser et al., 2015). Bioremediation is a readily available and relatively low cost (in relation to other treatment options) remediation technique for a wide number of organic contaminants, including PAHs (Juhasz et al., 2000; Kanaly and Harayama, 2000; Madueno et al., 2011). However, a general problem for the application of bioremediation on PAH-contaminated soils, lies in the usually rather slow degradation rate of these compounds (Coppotelli et al., 2008). The long time required for the application of bioremediation can be shortened if in situ chemical oxidation (ISCO) is firstly applied (Sakulthaew et al., 2014). ISCO has been increasingly regarded as a relevant alternative to conventional treatment technologies for remediation of groundwater and soils contaminated by recalcitrant organic contaminants (Watts and Teel, 2006), including PAHs (Rivas, 2006; Sirguey et al., 2008). The most commonly used oxidants include permanganate (MnO_4), Fenton's reagent (hydrogen peroxide and Fe^{2+}) (Ferrarese et al., 2008; Laurent et al., 2012; Pardo et al., 2014), ozone (Rivas et al., 2009), and sodium persulfate (PS) (Mora et al., 2014). These oxidants can effectively transform target contaminants in soil or water into harmless products, such as CO_2 and H_2O (Chen et al., 2009). Persulfate has drawn increasing attention as alternative oxidant in the abatement of organic contaminants in the last decade, in fact, persulfate has been recently used for the degradation of organic pollutants in wastewaters (Fang et al., 2013; Kusic et al., 2011; Rodriguez et al., 2012) and is an emerging oxidant for ISCO (Liang et al., 2008). It has several advantages (Tsitonaki et al., 2010) such as high aqueous solubility, high stability at room temperature, relatively low cost and benign end products. Since solubility of potassium persulfate in water is about one order of magnitude lower than that of sodium persulfate, this last is the most common and feasible oxidant form used in ISCO. Persulfate salts dissociate in water to persulfate anions that are strong and relatively stable oxidants (Usman et al., 2012) as shown in Eq. (1):

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}. \quad [1]$$

The use of PS as oxidant has kinetic limitations as it reacts much more slowly than other oxidants. However, when persulfate anion is activated, the sulfate radical ($SO_4^{\cdot -}$), a strong and non-selective oxidant ($E° = 2.6$ V), is produced. In this regard, this activation can be performed through different routes: thermal, photo activation (Eq. (2)) (Johnson et al., 2008) or activation by reduced metal ions, being Fe^{2+} the most commonly used (Eq. (3)) (Osgerby, 2006):

$$S_2O_8^{2-} \xrightarrow{\text{heat or } h\nu} 2SO_4^{\cdot -}, \quad [2]$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\cdot -}. \quad [3]$$

Given the difficulties involved in keeping high temperatures underground (50 °C e.g.), metal activation, in soil natural conditions, is preferred rather than thermal activation. However, in case of metal activation, a termination reaction can involve also undesired non-productive consumption of sulfate radical due to the scavenging of $SO_4^{\cdot -}$ by the activator, Fe^{2+} (Eq. (4))

$$SO_4^{\cdot -} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-}. \quad [4]$$

While reaction [4] takes place at high rate, adding an excess of Fe^{2+} would produce a loss of the oxidant. Therefore, the amount and delivery strategy for iron addition becomes a key point in the persulfate treatment (Vicente et al., 2011). In order to solve this disadvantage, the use of ZVI has been proposed in literature, as an alternative to the addition of Fe^{2+} given that ZVI allows a slow release of Fe^{2+} to the aqueous phase, minimizing the extension of reaction. Studies with PS + ZVI concern mainly water treatment (Deng et al., 2014; Liang and Guo, 2010; Liang and Lai, 2008; Oh et al., 2009) and to a lower extent soil treatment (Oh and Shin, 2014), where a ZVI powder was used as activator of persulfate for the treatment of a diesel-contaminated soil. To solve the suitability of the injection of ZVI in geological porous the use of ZVI in the form of nanoparticles has been studied (Al-Shamsi and Thomson, 2013).

$$Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + SO_4^{2-}. \quad [5]$$

As can be deduced from Eq. (3), Fe^{2+} is required to form sulfate radicals. However, as can be observed in Eq. (3), Fe^{2+} is oxidized to Fe^{3+}. Therefore, it would be required the reduction of Fe^{3+} to Fe^{2+} to let the sulfate radical generation continue. In some cases, this reduction can be produced by the organic pollutants in the media, which can be either original pollutants or organic oxidation intermediates which appear during reaction, like quinone type compounds (Rodriguez et al., 2014). On the other hand, the addition of some compounds, like humic acids, could enhance this reduction. In this regard, it has been reported the ability of humic substances to reduce Fe^{3+} to Fe^{2+} in the aqueous phase, thus improving the application of chemical oxidation techniques (Fukushima and Tatsumi, 1999; Voelker et al., 1997). Moreover, humic substances (HA), have been described as naturally occurring surfactants, begin to be recognized as a possible aid in soil bioremediation techniques (Conte et al., 2005; Conte et al., 2001). The bioavailability of PAH appeared to be increased by addition of exogenous humic substances to contaminated soils (Holman et al., 2002). An enhancement of the solubility of the pollutants in the aqueous phase could increase the oxidation rate of the hydrophobic compounds because the sulfate radical is produced in the aqueous phase. Surfactants are surface-active agents which lower the surface tension of a liquid and also decrease the interfacial tension between two immiscible liquids. Chemical surfactants increase the solubility of PAHs (Mesbaiah et al., 2014; Wang et al., 2013), and consequently facilitate their further oxidation in the aqueous phase. These surface active agents, either anionic or no-ionic, have been used

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widely for the remediation of PAHs-contaminated soils (Cheng and Wong, 2006; Peng et al., 2011; Saxe et al., 2000; Zhou and Zhu, 2005). Particularly, in this work, it has been selected the use of sodium dodecyl sulfate, an anionic surfactant, due to its biodegradability and low adsorption degree to the soil surface (Giannis et al., 2007). Application of surfactants in field can be carried out by two different ways, in series, injecting firstly the surfactant and treating subsequently the washed flow with chemical oxidation, or in parallel, where surfactant and oxidant are injected simultaneously in the contaminated soil (Wang et al., 2013). Therefore, the aim of this work is to study the remediation of a fresh spiked soil by 4 PAHs, anthracene (ANT), phenanthrene (PHE), pyrene (PYR) and benzo[a]pyrene (BaP), all included in the 16 PAHs priority list made by the EPA, by using persulfate activated with iron. Three types of iron addition have been considered: Fe^{2+}, Fe^{3+} and nZVI particles in order to analyze their importance on reactions in Eqs. (3)–(5). Besides, it was tested the addition of sodium dodecyl sulfate (SDS) as surfactant and HA. Analyses of contaminant and oxidant conversion and soil pH were studied along 40 days of treatment. In addition, a kinetic model was proposed for the description the behavior of the oxidant consumption and contaminants conversion. The presence and role of aromatic intermediates during reaction was also studied.

2. Material and methods

2.1. Reagents

Phenanthrene (PHE) ≥99.5% (sublimed grade), ref. 695114, from Aldrich (France), anthracene (ANT) 99% (ReagentPlus), ref. 141062, from Aldrich (France), Pyrene (PYR) 98%, ref. 185515, from Aldrich (France) and Benzo[a]pyrene (BaP) ≥96%, ref. B1760, from Sigma (France) were used for soil spiking and HPLC analysis. Sodium PS ≥98%, used as oxidant, was purchased from Sigma-Aldrich; ferric sulfate from Panreac 75% (anhydrous basis); ferrous sulfate heptahydrate ≥99%, from Fisher, and air-stable nZVI powder (NANOFER STAR) from Nanoiron s.r.o. were used, respectively, as activator species. For SW and coupled SW with activated persulfate it was used SDS ≥99%, from Sigma-Aldrich, as surfactant. As HA source it was used a HA sodium salt (45–70%), provided by Acros Organics. For persulfate determination, reagents required were sodium hydrogen carbonate 99.7% (Panreac), potassium iodide >99.5% (Fisher Chemical) and sodium thiosulfate pentahydrate 99.5% (Sigma-Aldrich). Sodium sulfate anhydrous 99%, from Fisher Chemical, Acetone 99.8% HPLC gradient grade from Fisher Chemical and n-hexane 99% HPLC grade from Scharlab were used for contaminant extraction from the soil samples. Dichloromethane ≥99.8% HPLC grade from Sigma-Aldrich for the analysis of intermediates. Phosphoric acid ≥85% from Sigma-Aldrich and acetonitrile HPLC gradient grade from Fisher Chemical were both used as mobile phase in HPLC for PAH analysis. For metal determination in aqueous solution in MP-AES analysis, nitric acid 69.5% was employed for the stabilization of iron ions.

2.2. Soil spiking

A sandy clay loam BT horizon ($pH = 7.22$; total organic carbon = 0.196%, free iron oxides = $7235\ mg \cdot kg^{-1}$) from the Autonomous Community of Madrid was used for spiking. Its characterization procedure and a detailed description of the properties are found elsewhere (Pardo et al., 2014; Vicente et al., 2012). Procedure of soil spiking was performed as followed in literature (Kulik et al., 2006; Mora et al., 2014), where an acetone solution with ANT, PHE, PYR and BaP was distributed and mixed manually onto the soil with a spatula. Contaminant concentrations obtained were $97 \pm 6\ mg \cdot kg^{-1}$ for ANT, $89 \pm 2\ mg \cdot kg^{-1}$ for PHE, $93 \pm 1\ mg \cdot kg^{-1}$ for PYR and $102 \pm 1\ mg \cdot kg^{-1}$ for BaP, respectively.

2.3. Set-up and procedure

All runs, in batch mode, were performed under isothermal stirring (Unitronic orbital shaker by Selecta) at 100 rpm and 20 °C, without pH adjustment, employing 50 mL PTFE centrifuge tubes with PTFE screw caps, placed horizontally. Each time point was represented by one PTFE tube, where 10 mL of aqueous solution (V_L) were added to 5 g of polluted soil (W_{soil}). This ratio was selected in order to simulate the removal of PAHs entrapped into soil pores or SOM present in the saturated or vadose zones and treatment can be applied both In Situ or Off Site after excavation. All remediation runs were carried out in duplicate. The non-productive consumption of oxidant (NPC) in this soil was studied in a previous work (Pardo et al., 2015) finding that about 20% of the oxidant was consumed after 83 days and 10% of initial PS was remaining after 20 days. Oxidation runs carried out are summarized in Table 1. A blank run (BL) without addition of oxidant in the aqueous phase and a SW run using an aqueous solution of SDS were carried out in order to determine the natural attenuation and the PAHs eluted by the surfactant in the period time studied (about 50 days).

Runs using PS as oxidant were carried out by using several types of iron (ferric, ferrous sulfate salts ($1–5\ mmol \cdot L^{-1}$) and nanoparticles of zerovalent iron (nZVI)). On the other hand, two runs consisted in the addition of either HA or surfactant, SDS was added at its critical micelle concentration (CMC), being $2.2\ g \cdot L^{-1}$ (20 °C) (Dahanayake et al., 1986; Watanabe et al., 2005), 24 h before PS addition. Humic Acids, HA, were added at a concentration of $2000\ mg \cdot kg^{-1}$. At the selected reaction time, two centrifuge tubes were sacrificed (differences lower than 15%). Afterwards, aqueous and soil phase were separated by centrifugation, analyzing pH, remaining oxidant, surfactant and metals in solution in the aqueous phase. In addition, PAHs and oxidation by-products were extracted as reported in previous works (Pardo et al., 2014), by following the EPA method 3540C, where Soxhlet extraction was used. For oxidation by-products identification, hexane and acetone were evaporated in a fume hood, after solvent extraction, at room temperature and reconstituted in 2 mL dichloromethane, analyzing afterwards in GC/MS.

2.4. Analytical method

The concentration of PS in solution was determined by iodometric titration with a solution of sodium thiosulfate, $Na_2S_2O_3$, 0.3 g/L, by using a combined-Pt ring electrode, specific for redox titrations, supplied by Metrohm, ref. 6.0451.100. pH was measured with a pH glass electrode also supplied by Metrohm. For the analysis of iron a microwave plasma-atomic emission spectrometer 4100 MP-AES (Agilent Technologies) with OneNeb nebulizer was used. The selected wavelength for iron determination was 259.94 nm. Oxidation byproducts were analyzed by GC/MS (HP 6890N MSD 5975B). For original PAHs determination, an HPLC (Agilent, mod. 1100) coupled with an Agilent 1290 Infinity Diode Array Detector was employed. The column used was a Poroshell 120 SB-C18 in 2.1 mm × 100 mm and 2.7 μm of particle size. Analysis was carried out under isocratic mode at a flow rate of $0.5\ mL \cdot min^{-1}$, selecting as mobile phase a mixture of 60% acetonitrile

Table 1
Experimental runs.

Run	Fe (type)	C Fe_0 $mmol \cdot L^{-1}$	C AH $mg \cdot L^{-1}$	C_{SDS} $g \cdot L^{-1}$
RPS1	II	1	0	0
RPS2	III	1	0	0
RPS3	nZVI	1	0	0
RPS4	II	1	0	2.2
RPS5	nZVI	1	0	2.2
RPS6	II	1	2000	0
RPS7	nZVI	5	0	0
BL	0	0	0	0
WS	0	0	0	2.2

$C_{PS0} = 50{,}000\ mg \cdot L^{-1}$, $C_{PAH} \approx 100\ mg \cdot kg^{-1}$ each, $T = 20$ °C, $W_{soil}/V_L = 0.5\ g \cdot cm^{-3}$.

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and 40% aqueous solution with phosphoric acid 75 mmol·L^{-1}, selected injection volume was 20 μL. Wavelength chosen were, 235 nm for PYR, 250 nm for PHE, and 295 nm for ANT and BaP. The presence of reaction intermediates was analyzed by GC/MS (HP 6890 N MSD 5975B). A HP-5 column (30 m × 0.32 mm i.d. × 0.25 μm) was used for the analysis. The chromatographic conditions were as follows: injector temperature: 280 °C; carrier gas (He) flow rate: 2 mL·min^{-1}; 8 μL of injected volume in splitless mode. The analysis was performed with an initial oven temperature: 45 °C, followed by a first ramp of 5 °C·min^{-1} to 150 °C and a second ramp of 8 °C·min^{-1} to 325 °C. The final run time was 62.88 min. The corresponding detection limits for PAHs were 0.27 mg·L^{-1} for PHE, 0.11 mg·L^{-1} for ANT, 0.37 mg·L^{-1} for PYR and 0.47 mg·L^{-1} for BaP.

3. Results and discussion

The effect of type and concentration of iron added (runs RPS1, RPS2, RPS3, RPS7), the influence of surfactant (runs RPS4 and RPS5) and HA addition (run RPS6 and RPS5), on PAHs conversion, oxidant consumption and pH evolution have been analyzed. PAH and oxidant conversions have been calculated according to Eq. (6).

$$X_j = \frac{C_0^j - C_t^j}{C_0^j}. \qquad [6]$$

Being X_j the conversion of contaminant or oxidant; C_0^j the initial concentration of a certain PAH or oxidant; C_t^j the concentration of PAH or oxidant at a time t.

Although PAHs were analyzed in both aqueous and solid phases (after extraction), the amount of these compounds in aqueous phase was negligible, in comparison with that remaining in the soil phase. Besides, the PAHs remaining in soil after 50 days of washing with distilled water or water with 2.2 g·L^{-1} of SDS was higher than 80% of their initial concentration. Moreover, negligible conversion of each of the PAHs was observed when PS (200 mmol·L^{-1}) was added alone.

3.1. Effect of type of iron added

As it was previously cited, iron was added as Fe^{2+}, Fe^{3+} or nZVI. Fig. 1 shows the results obtained when PS 200 mmol·L^{-1} and iron 1 mmol·L^{-1} were added to the polluted soil. PHE, ANT, PYR and BaP conversion are showed in Fig. 1a to d, respectively. PS consumption is plotted in Fig. 1e, while the non-productive consumption of the oxidant (without PAHs and iron addition) is also presented in Fig. 1e. As can be seen, PHE is the most recalcitrant PAH to persulfate oxidation, in the three runs showed in Fig. 1, followed by PYR. On the contrary, it was observed that ANT and BaP were quite readily oxidized. According to literature, this kind of trend is consistent with those works in which fresh spiked soils have been treated with chemical oxidation; on one hand, the way BaP, with the higher number of benzene rings (5), was the contaminant more easily degraded can be explained by, firstly, it may take more time to reach and bind with the soil organic matter than the rest of PAH (3 and 4 rings), thus its availability for the oxidant would be higher (Bogan and Trbovic, 2003). In addition, reactivity of PAHs towards oxidation, apart from absorption phenomena, reaction conditions, etc. generally increases with the number of aromatic rings, since less energy is needed to form the oxidation products (Forsey et al., 2010; Lemaire et al., 2013). Regarding ANT degradation, which is faster than PHE and PYR, it may be also explained by the lower energy that would be needed to form a highly stable oxidation product, as is 9,10-anthraquinone (ATQ) (Forsey et al., 2010). No differences were found regarding the source of iron added, as a ferrous or ferric salt, indicating that Fe^{3+} can be reduced by species in the reaction media. On the contrary, the addition of Fe as nZVI remarkably improved the abatement of both PHE and PYR while diminish slightly the PS consumption. This could be explained if nZVI produce a slow release of iron minimizing the radical scavenger in Eq. (4). In this sense, some works have reported this behavior, confirming that better results have been obtained with the use of nZVI against Fe^{2+} as persulfate activator, for the removal of a biodiesel-blend from a contaminated soil (Pardo et al., 2015), TCE (Al-Shamsi and Thomson, 2013) or 2,4-dichlorophenol (Li et al., 2015). As can be seen in Fig. 1e, PS consumption was about 60% after 50 days of reaction when Fe^{2+} or Fe^{3+} were added, while it remains at 40% for nZVI addition. In Fig. 1e it is also shown the non-productive consumption of PS for an unpolluted soil in absence of iron addition, being about 15% after 50 days. As the reaction progress, the acidification of the soil takes place, obtaining similar pH profiles for the three types of iron used, as can be seen in Fig. 1f.

3.2. Effect of the surfactant and HA addition

Effect of surfactant addition is shown in Fig. 2. PHE and PYR conversion are showed in Fig. 2a and b, respectively. PS consumption is showed in Fig. 2c and pH profile in Fig. 2d. A slight increase when using SDS was noticed for ANT and BaP conversion (not shown), this increase was difficult to quantify due to the high oxidation rate of both compounds with activated PS. As can be seen in Fig. 2a, the addition of SDS 24 h before PS an iron are supplied increases the PHE conversion. A lower effect of the surfactant is noticed on PYR conversion; probably due to PYR has a higher oxidation rate than PHE in absence of surfactant. Addition of SDS produces also a slight increase in the PS consumption (Fig. 2c), and has no effect on the pH evolution. This increase in PS consumption is probably due to the partial oxidation of the surfactant.

Effect of HA addition was analyzed by comparison of results obtained in runs RPS1 and RPS6. Effect on PHE and PYR conversion is showed in Fig. 3a. PS consumption obtained in both runs is plotted in Fig. 3b. As can be seen, no differences are obtained in presence of HA. Profiles of ANT, BaP and pH obtained in run RPS6 were also closed to those obtained in RPS1. In literature is reported the redox activity of some components presents in HA, such as quinone type compounds (Kappler et al., 2004; Tsang et al., 2009), which could help to improve the application of ISCO techniques by enhancing the reduction of Fe^{3+} to Fe^{2+} in the aqueous phase (Fukushima and Tatsumi, 1999; Voelker et al., 1997). Besides, HA can also act as surfactants, increasing the concentration of contaminants in the aqueous phase (Conte et al., 2005). In this case, the positive effect of HA was not observed. This can be explained because a lower amount of HA was used, moreover not all the compounds present in the HA have the ability of reducing iron, and also due to the fact that the oxidation intermediates of PAHs can reduce Fe^{3+} to Fe^{2+}. In fact, quinone type compounds, as ATQ, were detected as the main aromatic intermediate if PS was used. This explains the similar results obtained with Fe^{2+} and Fe^{3+} in runs RPS1 and RPS2. Besides, the presence of HA can also decrease the removal efficiency of contaminants, given that they can adsorb the contaminants decreasing their availability because of an increase in the number of hydrophobic sites (Bogan and Trbovic, 2003; Conte et al., 2001), besides, they can consume oxidant, increasing its non-productive consumption, as it was seen in the treatment of an ANT contaminated soil by using ozonation (Zhang et al., 2005).

3.3. Effect of iron concentration

Effect of concentration of initial iron added was studied by using 1 and 5 mmol·L^{-1} nZVI (runs RPS3 and RPS7). Effect on PHE and PYR conversion is showed in Fig. 4a. PS consumption obtained in both runs is plotted in Fig. 4b. Profiles of ANT, BaP and pH obtained in runs RPS3 and RPS7 were similar to those obtained in runs RPS3 and RPS7 (showed in Fig. 1). As can be seen in Fig. 4, the increase of nZVI concentration, at the range studied, produces a slight increase in the PHE conversion but an almost negligible effect on the PYR conversion. On the contrary, PS consumption is remarkable increased. According to Eq. (3), the higher the iron concentration, the higher the PS consumption,

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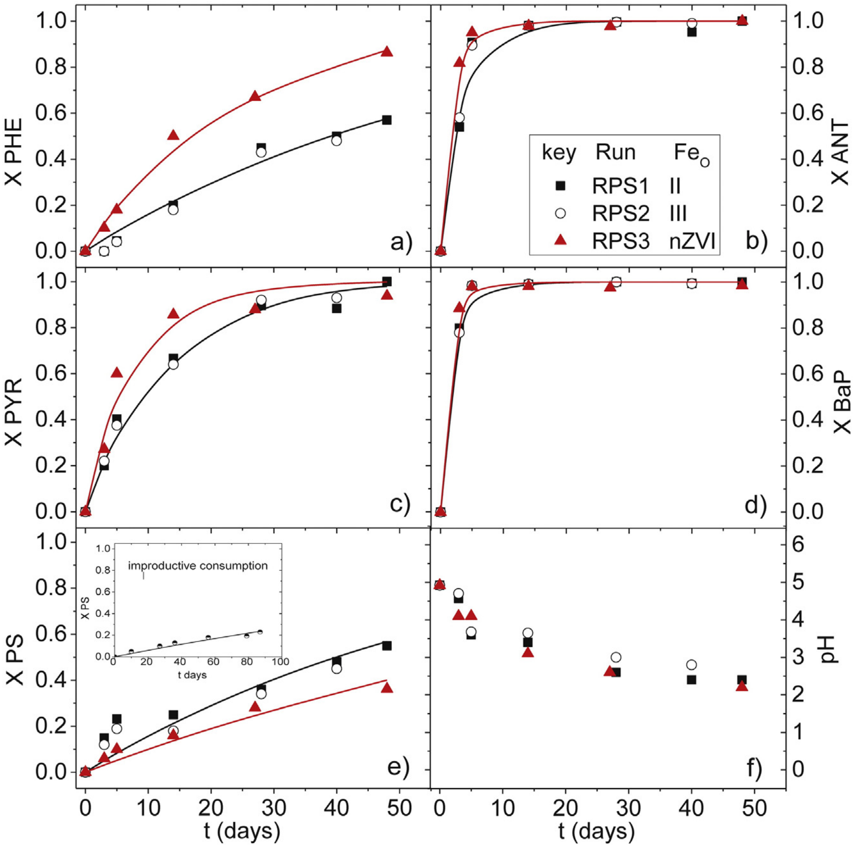

Fig. 1. Effect of type of iron initially added on a) PHE b) ANT, c) PYR, d) BaP, e) PS conversion and f) pH profile. $[Fe]_0 = 1\ mmol \cdot L^{-1}$ $[PS]_0 = 50{,}000\ mg \cdot L^{-1}$ $[PAH]_j \approx 100\ mg \cdot kg^{-1}$. Runs RPS1, RPS2 and RPS3 using Fe^{2+}, Fe^{3+} and nZVI, respectively. Symbols: experimental data. Lines: estimated values with Eq. (7) using parameters in Table 2.

then explaining the higher persulfate consumed at 5 $mmol \cdot L^{-1}$ nZVI. Small effect of nZVI concentration on PAH conversion (in the range studied) can be explained by the scavenging reaction between iron and sulfate radical given in Eq. (4). As the PS/Fe molar ratio increases, the removal efficiency of contaminants can increase; nevertheless, this improvement can be hindered due to scavenging reactions from an excess of Fe^{2+} which reacts with sulfate radicals, as has been reported in literature (Al-Shamsi and Thomson, 2013; Rodriguez et al., 2012; Vicente et al., 2011).

3.4. Kinetic model

As a significant amount of the initial PS remains in the media after oxidation of PAHs, the oxidation rate of each PAH has been described

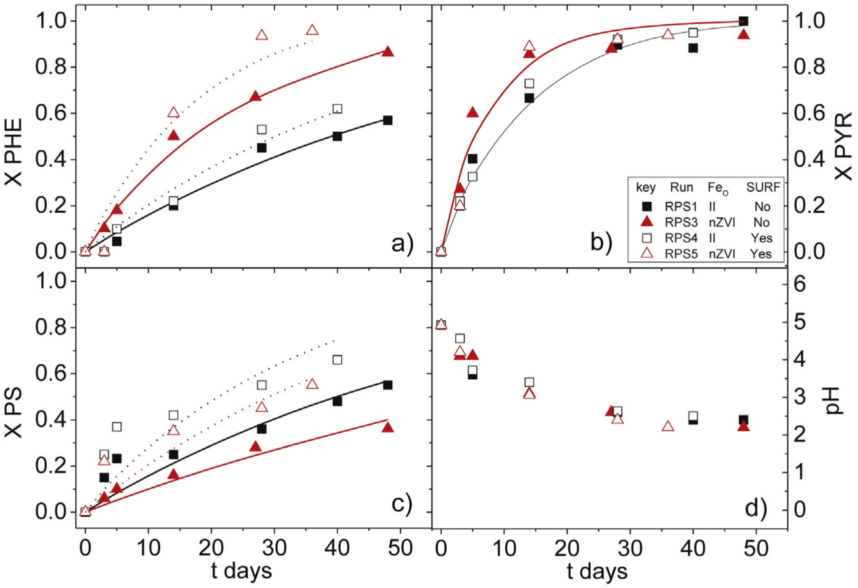

Fig. 2. Effect of surfactant addition on a) PHE b) PYR c) PS conversion and d) pH profile. $[Fe]_0 = 1\ mmol \cdot L^{-1}$ $[PS]_0 = 50{,}000\ mg \cdot L^{-1}$ $[PAH]_j \approx 100\ mg \cdot kg^{-1}$. Runs RPS1 and RPS3 without surfactant. Runs RPS4 and RPS5 with surfactant. Symbols: experimental data. Lines: estimated values with Eq. (7) using parameters in Table 2.

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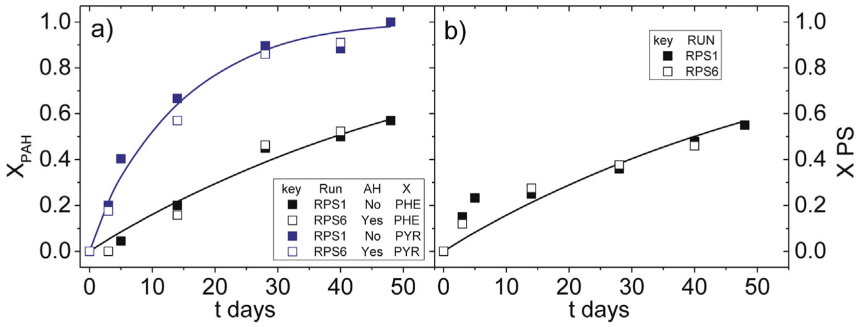

Fig. 3. Effect of HA addition on a) PHE and PYR b) PS conversion $[Fe]_0 = 1\ mmol \cdot L^{-1}$ $[PS]_0 = 50{,}000\ mg \cdot L^{-1}$ $[PAH]_j \approx 100\ mg \cdot kg^{-1}$. Run RPS1 without HA, run RPS6 with HA addition. Symbols: experimental data. Lines: estimated values with Eq. (7) using parameters in Table 2.

by using a first order reaction rate. Given that all runs have been carried out in batch way, the integrated expression for each PAH conversion results as follows:

$$X_{PAHj} = 1 - \exp(-k_j t). \tag{7}$$

The PS disappearance rate has been described by a first order reaction on PS concentration, with two contributions, a first one due to the non-productive consumption of PS for the unpolluted soil and a second contribution which considers the activation by iron at the experimental conditions used in each run, being the integrated equation as follows:

$$X_{PS} = 1 - \exp(-(k_{unp} + k_{PSFe})t). \tag{8}$$

The value of k_{unp} was obtained by fitting X_{PS} vs time, obtained with clean soil and no iron addition, getting a value of $k_{unp} = 0.0031\ day^{-1}$, which reproduce accurately the experimental data in Fig. 1e (symbols as experimental data, line as estimated value).

Kinetic constants in Table 2 were obtained by fitting each PAH conversion vs time and PS conversion vs. time to Eqs. (7) and (8), from each run. From the prediction of the PAH conversion values (plotted as lines in Figs. 1 to 4), calculated with the kinetic constants in Table 2, a good agreement between estimated an experimental values was obtained. As shown in Table 2, the higher kinetic constants for the degradation of all PAHs, corresponded to nZVI addition, while those calculated for the initial addition of Fe^{2+} or Fe^{3+} were lower. In this regards, it was noticed that this effect was more remarkable for PHE and PYR degradation, since these compounds are the more recalcitrant to chemical oxidation by using activated persulfate. In this sense, Forsey et al. (2010) found for permanganate oxidation of PAHs, that PYR constant of degradation was higher than that corresponding for PHE. On the other hand, Al-Shamsi and Thomson (2013) also determined the kinetic constants corresponding to TCE degradation by persulfate activated by Fe^{2+} and nZVI, finding out faster removal rates for the contaminant when nZVI was used rather than Fe^{2+}. Nevertheless, it is frequently observed, regarding treatments with nZVI-activated persulfate, a first stage where oxidant and contaminants are more quickly consumed, and a second lower one, due to passivation or deactivation of nZVI surfaces.

4. Conclusions

This study has provided valuable data in regard to the application of different kinds of persulfate activation for the remediation of a PAH contaminated soil with four different types of PAH, ANT and PHE (3-ringed) PAH, PYR (4-ringed) and BaP (5-ringed). For persulfate activation it was tested the effect of the type of iron species initially added (Fe^{3+} or Fe^{2+} sulfate salt and nZVI), concentration of nZVI and the addition of HA and surfactant. Evolution of species during reaction was carried out through the analysis of oxidant consumption, PAHs conversion and pH with time. It was observed that ANT and BaP were degraded near totally in all runs, while in case of PHE and PYR, different removal efficiencies were achieved depending on the technique used. In this sense, PHE and PYR removal efficiencies have been considered as crucial parameters in order to compare the effectiveness of each remediation technique applied. Thus, according to the type of iron initially added, best removal efficiencies, after 48 days, were achieved when nZVI was added, 86% for PHE and 99% for PYR, while for Fe^{2+} (57% PHE, 95% PYR) or Fe^{3+} (51% PHE, 93% PYR) were lower. The improvements found with nZVI, are due to the fact that it acts as a continuous release source of Fe^{2+}. Therefore sulfate radicals are produced in a more controlled way, thus minimizing the unproductive sulfate radical consumption noticed when same amount of iron was added as Fe^{2+}. The addition of Fe^{3+} leaded also to persulfate activation due to the appearance of quinone type organic compounds, as degradation products from their parent compounds, like ATQ, capable of reduce Fe^{3+} to Fe^{2+}, and consequently, activate persulfate. Regarding effect of surfactant addition, it was observed a slight improvement in the PAHs removal as a consequence of an increase in the mass transfer from the soil to the aqueous phase due to the solubilization. It is important to mention that, since it has been

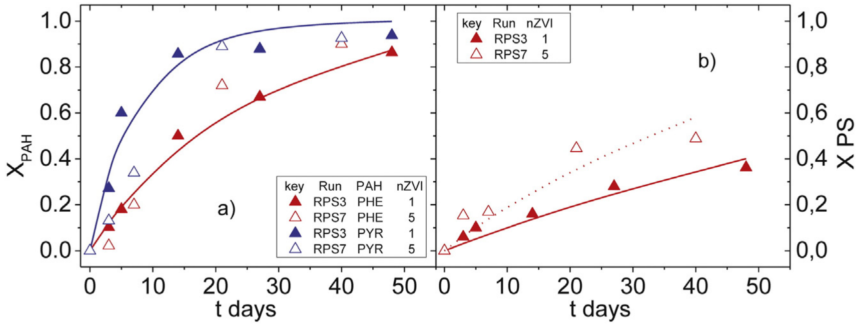

Fig. 4. Effect of nZVI concentration on a) PHE and PYR b) PS conversion $[PS]_0 = 50{,}000\ mg \cdot L^{-1}$ $[PAH]_j \approx 100\ mg \cdot kg^{-1}$. Symbols: experimental data. Lines: estimated values with Eq. (7) using parameters in Table 2.

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Table 2
Estimated kinetic constants for runs in Table 1. Kinetic model in Eqs. (6) and (7).

Run art	Fe (type)	C Fe_0 $mmol \cdot L^{-1}$	C AH $mg \cdot L^{-1}$	C_{SDS} $g \cdot L^{-1}$	k_{PHE} day^{-1}	k_{ANT} day^{-1}	k_{PYR} day^{-1}	k_{BaP} day^{-1}	k_{PSFe} day^{-1}
RPS1	II	1	0	0	$1.79 \cdot 10^{-2}$	$3.30 \cdot 10^{-1}$	$8.24 \cdot 10^{-2}$	$5.74 \cdot 10^{-1}$	$1.44 \cdot 10^{-2}$
RPS2	III	1	0	0	$1.69 \cdot 10^{-2}$	$3.41 \cdot 10^{-1}$	$8.15 \cdot 10^{-2}$	$5.48 \cdot 10^{-1}$	$1.25 \cdot 10^{-2}$
RPS3	nZVI	1	0	0	$4.33 \cdot 10^{-2}$	$5.79 \cdot 10^{-1}$	$1.43 \cdot 10^{-1}$	$7.45 \cdot 10^{-1}$	$7.58 \cdot 10^{-3}$
RPS4	II	1	0	2.2	$2.36 \cdot 10^{-2}$	$3.77 \cdot 10^{-1}$	$8.73 \cdot 10^{-2}$	$6.53 \cdot 10^{-1}$	$3.14 \cdot 10^{-2}$
RPS5	nZVI	1	0	2.2	$6.80 \cdot 10^{-2}$	$6.83 \cdot 10^{-1}$	$1.14 \cdot 10^{-1}$	$1.20 \cdot 10^{0}$	$2.11 \cdot 10^{-2}$
RPS6	II	1	2000	0	$1.85 \cdot 10^{-2}$	$2.75 \cdot 10^{-1}$	$6.38 \cdot 10^{-2}$	$5.74 \cdot 10^{-1}$	$1.42 \cdot 10^{-2}$
RPS7	nZVI	5	0	0	$4.95 \cdot 10^{-2}$	$1.73 \cdot 10^{-1}$	$7.37 \cdot 10^{-2}$	$5.12 \cdot 10^{-1}$	$1.87 \cdot 10^{-2}$

carried out the remediation of a fresh spiked soil, regardless the technique applied, all these PAHs conversions obtained can present some overestimation compared to those obtained when aged soils were treated. Nonetheless, the effect of using surfactant in case of aged soils could have been more remarkable. On the other hand, no significant improvement was noticed when HA were added. This can be due to the production of quinone type compounds as oxidation by-products from PAH, acting as Fe^{3+} reducers. The effect of reducing species present in the HA can be hidden by these quinone intermediates. In this sense, a higher concentration of HA could be tested in further research in order to verify this point. When iron was added at different concentrations, it was observed a more significant effect on persulfate consumption rather than the removal efficiency of the PAHs, the scavenging reactions between sulfate radicals and iron could have been hinderer the efficiency of the process. PAHs removal efficiencies were estimated accurately following a pseudo first order kinetics, on the other hand. PS consumption was also described by first order kinetics, but with two contributions, one related to the non-productive consumption and the other to the activation by iron. Therefore, this work has provided valuable data, in lab scale, with regard to the activation of persulfate, a useful tool of increasing implementation in field scale for the remediation of contaminated soils, outlining the benefits of adding nZVI as activator, which works as a continuous release source of iron, minimizing the sulfate radical scavenging by an excess of Fe^{2+}.

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