



Fate of iron and polycyclic aromatic hydrocarbons during the remediation of a contaminated soil using iron-activated persulfate: A column study

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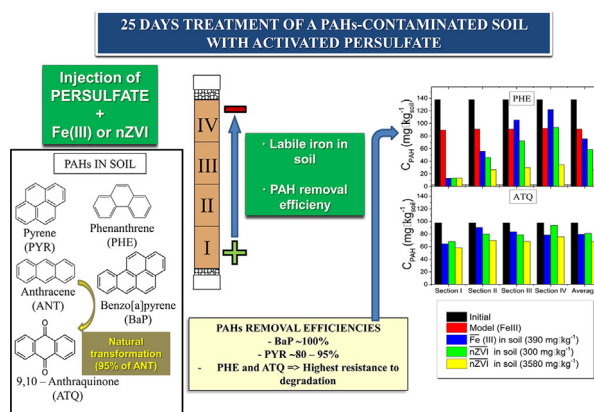
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HIGHLIGHTS

- A PAH-contaminated soil was treated under flow conditions with activated persulfate.
- Fe(III) and nZVI were used for persulfate activation, being nZVI more efficient.
- PAH conversions were higher in the nearer sections of the injection point.
- Transport of iron across the column length was related to removal efficiency.
- The oxidation byproduct, anthraquinone, was more resistant than the rest of PAH.

GRAPHICAL ABSTRACT



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ABSTRACT

Remediation of contaminated soils under flow-through conditions is an issue of great interest since it provides a better approach to real case applications than batch experiments. In this work, a column filled with soil, artificially spiked and aged for three months with Phenanthrene (PHE), Anthracene (ANT), Pyrene (PYR) and Benzo(a)pyrene (BaP), was treated for 25 days with persulfate (PS) activated by Fe^{3+} and nanoparticles of zerovalent iron (nZVI). Effects of type of iron fed into the column (Fe^{3+} or nZVI) and nZVI concentration were studied. PS inlet concentration was 0.2 mmol cm^{-3} and residence time in the column was close to 1.72 days. Iron, PS and polycyclic aromatic hydrocarbons (PAHs) concentration, as well as pH, were monitored during treatment. Concentration profiles of iron and PAHs were observed along the column, with higher iron concentrations and higher PAHs removal efficiencies in the closest sections to the column entrance. BaP and ANT were completely depleted regardless the conditions used, but PHE and PYR showed higher resistance to oxidation, achieving near a 90% removal in the closest sections to the injection source in all runs, but decreasing significantly with column length. Besides, natural degradation of ANT resulted in the formation 9,10-anthraquinone (ATQ), an oxy-

Abbreviations: PHE, phenanthrene; ANT, anthracene; PYR, pyrene; BaP, benzo(a)pyrene; PS, persulfate; nZVI, nanoparticles of zerovalent iron; PAH, polycyclic aromatic hydrocarbons; ATQ, anthraquinone; oxy-PAHs, oxidized species from PAHs; ISCO, in situ chemical oxidation; $q_{\text{Fe col}}$, average amount of iron retained in the column (mg cm^{-3}); V_{col} , column volume (cm^3); Q , inlet flow rate ($\text{cm}^3 \text{ day}^{-1}$); C_{Fe0} , initial concentration of iron in the inlet flow (mg cm^{-3}); C_{Fe} , concentration of iron measured at the exit of the column (mg cm^{-3}); t_{ini} , time in which iron was added initially (days); t_{delay} , time corresponding to the residence time in the column (days); N_{PS} , mmol of persulfate consumed ($\text{mmol kg}^{-1} \text{ day}^{-1}$); C_{PS0} , initial concentration of persulfate in the inlet flow (mmol cm^{-3}); C_{PS} , concentration of persulfate measured at the exit of the column (mmol cm^{-3}); $-I_p$, ionization potential; HOMO, highest occupied molecular orbital; C_{PAH} , concentration of PAH in soil ($\text{mg}_{\text{PAH}} \text{ kg}_{\text{soil}}^{-1}$).

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Fe³⁺
nZVI

PAH which showed higher resistance than PHE and PYR. Although higher PAHs removal efficiencies were achieved when nZVI was used as activator, only a moderate improvement was noticed when the highest concentration of nZVI was used as a consequence of radical scavenging by an excess of Fe²⁺. Finally, a kinetic model based on runs performed in batch, from a previous work, was able to predict the experimental average concentrations of PAHs in the column when Fe³⁺ was used as activator.

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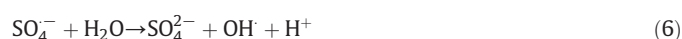
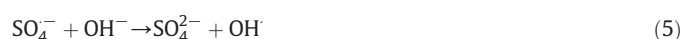
1. Introduction

For decades, Polycyclic Aromatic Hydrocarbons (PAHs) have appeared and accumulated in soils and groundwater, becoming one of the most widespread contaminants in the world (Peluffo et al., 2015; Puglisi et al., 2007). Soil and groundwater contamination by PAHs is a consequence of the development and growth of several industrial activities, such as those related to manufacture gas plants, wood impregnation, coke manufacturing, hydrocarbon production and metal processing, (Brown et al., 2003; Sims and Overcash, 1983), as well as diverse natural phenomena (volcano eruptions, forest fires). PAHs are organic species composed of two or more aromatic fused benzene rings, possessing very low solubility in water (lipophilicity), low volatility and high solid-water partition coefficient which makes them interact easily with soil organic matter, decreasing their availability to microorganisms or to degrading agents, thus tending to accumulate in soils (Hamdi et al., 2006). Given that PAHs have been proven to possess carcinogenic and mutagenic potential (e.g. benzo(a)pyrene), most of them are included in the 16 priority pollutants list made by the EPA. Furthermore, not only the original PAHs present in soil, but their corresponding oxidized species, mainly the quinone species, known as oxy-PAHs, represent a serious risk. In fact, Oxy-PAHs are more soluble in water and possess higher mobility in the aqueous phase than their corresponding parent PAH. Therefore, given their similar toxicity and harmful effects to human health as well as their higher stability to degradation than the parental PAH, oxy-PAHs may be even more dangerous than PAHs (Lundstedt et al., 2007; Rodgers-Vieira et al., 2015). Regarding PAHs removal from contaminated soils or groundwater, there is a wide variety of different techniques that can be applied, such as natural attenuation (Biache et al., 2011; Hanser et al., 2015), biostimulation (Hwang and Cutright, 2002; Liebig and Cutright, 1999), bioaugmentation (Juhász et al., 2000; Madueno et al., 2011; Rockne et al., 1998) or even the application of bio barriers (Ferreira et al., 2013; Thiruverikatachari et al., 2008). Unfortunately, these techniques require long-term control and application and it is rather frequent that contaminants remain strongly bonded to the soil organic matter, resulting in bioavailability limitations that decrease the effectiveness of their application, hindering to reach the cleanup goals (Antizar-Ladislao et al., 2005; Mahmoudi et al., 2013). In this sense, the application of In Situ Chemical Oxidation (ISCO) techniques has shown good results for the removal of several organic contaminants, as in the case of PAHs, by applying permanganate oxidation (Brown et al., 2003; Rauscher et al., 2012), Fenton's Reagent (Flotron et al., 2005; Jonsson et al., 2006; Pardo et al., 2015a; Venny et al., 2012), ozonation (Jonsson et al., 2006; Luster-Teasley et al., 2009; Rivas et al., 2009) and activated persulfate (PS) (Killian et al., 2007; Liang and Guo, 2010; Zhao et al., 2013). Particularly, in the last ten years, the application of activated PS has been of increasing relevance, as it has several advantages, such as the high oxidation potential of the sulfate radicals ($E = 2.60$ V), its higher stability in soil at room temperature than hydrogen peroxide or ozone, its high solubility and the fact that it is a cost-effective technique which makes it an attractive alternative to traditional ISCO methods, such as Fenton's reagent, permanganate or ozonation (Tsitonaki et al., 2010). On its own, PS ion ($E = 2.05$ V) has a lower oxidation potential than sulfate radicals, thus being less effective to degrade recalcitrant compounds. In aqueous solution, PS salts dissociate into PS anions, which act as electrophilic specie,

generating sulfate anions (Eqs. (1) and (2)):



To enhance the effectiveness of PS, some activators can be used for the production of sulfate radicals, therefore activation can be achieved via Fe²⁺ (Eq. (3)) by adding ferrous salts or zerovalent iron (Eq. (4)) (Chen et al., 2015; Killian et al., 2007; Peluffo et al., 2015), by heat or light activation, by peroxide activation (Zhao et al., 2013), or more recently by alkaline activation (Deng et al., 2014; Liang and Guo, 2012; Liang and Lei, 2015). In addition, during PS activation, sulfate radicals and hydroxyl radicals ($E = 2.70$ V) may coexist, as shown in Eqs. (5) and (6) (Al-Shamsi and Thomson, 2013b). Activation pathways from Fe³⁺ may occur if Fe³⁺ is reduced to Fe²⁺, being this step promoted by the presence of certain species, which can act as electron transfer species, like quinone type compounds (Chen and Pignatello, 1997; Rodriguez et al., 2014), which can be found as oxidation intermediates during the treatment, or as certain components present in the humic acids in soil (Fukushima and Tatsumi, 1999; Kappler et al., 2004).



On the other hand, an important drawback that should be taken into account is the fact that Fe²⁺ can act as radical scavenger of the sulfate radicals, producing a non-productive consumption of the oxidant (Eq. (7)) (Liang et al., 2004; Romero et al., 2010; Vicente et al., 2011):



To minimize reaction in Eq. (7), a slow release of Fe²⁺ to the media has been proposed (Vicente et al., 2011), which can be also achieved by using zerovalent iron (ZVI) (Rodriguez et al., 2014). Indeed, it has been reported higher removal efficiencies of pollutants when activation was due to ZVI, either in the form of granular, micro or nanoparticles, than Fe²⁺ (Oh and Shin, 2014; Pardo et al., 2015b; Rodriguez et al., 2014). Despite the benefits of ZVI, the difficulties derived from the injection of granular particles or powder, which make its application unsuitable, have led to the development of nanoparticles of zerovalent iron or nanoscale particles of zerovalent iron (nZVI). In this regard, injection of nZVI in the subsurface would solve the problems related to the injection of higher size particles (Al-Shamsi and Thomson, 2013b). Given the reactivity due to its reducing potential, it has been reported the effectiveness of nZVI as reducing agent for certain pollutants, like chlorinated hydrocarbons (Kober et al., 2014; Kocur et al., 2014), as well as an efficient PS activator for the degradation of aliphatic hydrocarbons (e.g. Diesel) or PAH (Pardo et al., 2015b; Peluffo et al., 2015). In accordance to literature, the vast majority of the studies that have assessed the use of activated PS for the remediation of hydrocarbon contaminated

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