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Remediation of aged diesel contaminated soil by alkaline activated persulfate

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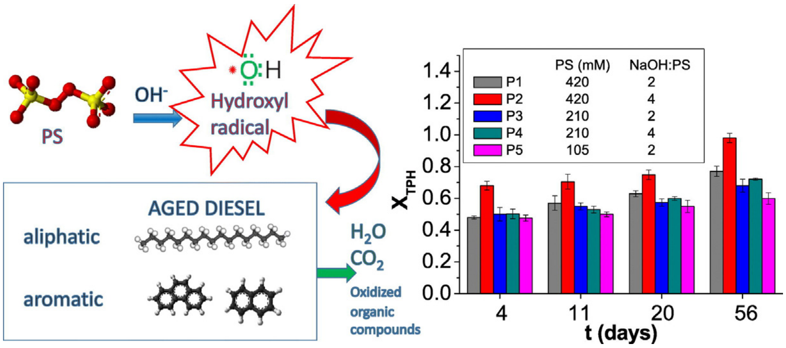
HIGHLIGHTS

- Aged diesel was effectively degraded in soil by alkali-activated persulfate (pH ≥ 12).
- A fast initial oxidation stage was noticed during the first 4 days.
- Total conversion of TPHs was found at 56 days at 420 mM of PS and NaOH:PS = 4 (molar).
- Aromatic fraction in aged diesel was more easily oxidized than aliphatic fraction.
- No aromatic byproducts were obtained as oxidation intermediates.

GRAPHICAL ABSTRACT



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ABSTRACT

The present work studies the efficiency of alkaline activated persulfate (PS) to remediate an aged diesel fuel contaminated soil from a train maintenance facility. The Total Petroleum Hydrocarbon (TPH) concentration in soil was approximately 5000 mg kg^{-1} with a ratio of aliphatic:aromatic compounds of 70:30. Aromatic compounds were mainly naphtalenes and phenanthrenes. The experiments were performed in batch mode where different initial concentrations of persulfate (105 mM, 210 mM and 420 mM) and activator:persulfate ratios (2 and 4) were evaluated, with NaOH used as activator. Runs were carried out during 56 days. Complete TPH conversion was obtained with the highest concentration of PS and activator, whereas in the other runs the elimination of fuel ranged between 60 and 77%. Besides, the abatement of napthalenes and phenantrenes was faster than aliphatic reduction (i. e. after 4 days of treatment, the conversions of the aromatic compounds were around 0.8 meanwhile the aliphatic abatements were 0.55) and no aromatic oxidation intermediates from naphtalenes or phenantrenes were detected. These results show that this technology is effective for the remediation of aged diesel in soil with alkaline pH.

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1. Introduction

Contamination of soils by petroleum hydrocarbons is a serious and common problem all over the world. The presence of these compounds in the environment could be related to different anthropogenic activities such as smelting, oily wastewater discharge and oil exploitation and transportation, and/or derived from accidental spills and leaks from storage tanks (Pinedo et al., 2013).

Among the different products included in the term petroleum hydrocarbons, diesel fuels have been extensively used as the power source of mining equipment and commercial transport such as ships, trucks or

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trains (Reşitoğlu et al., 2014) and therefore, the pollution of soils by this kind of hydrocarbons is very common.

Diesel fuel is a mixture of hydrocarbons, predominantly in the C10–C19 range, including aliphatic (approximately 64%), oleofinic (1–2%) and aromatic compounds (35%) (ATSDR, 1995). Special attention has to be paid to polycyclic aromatic hydrocarbons (PAH) often found in aged fuel (Kao et al., 2015). PAHs have mutagenic, tumorigenic and carcinogenic potential (Yap et al., 2011) and 16 of these compounds are included in the priority pollutant list of the US EPA (Keith, 2014) although some authors consider that this list is outdated, and propose the inclusion of new compounds (Andersson and Achten, 2015; Keith, 2014). Low volatility, high hydrophobicity and high sorption capacity are some of the properties that characterize these pollutants (Wu et al., 2016), especially in those compounds with long-chain or heavy molecular weight, hindering the use of technologies such as soil venting or soil vapor extraction (Khan et al., 2004; Rathfelder et al., 1995).

The application of In Situ Chemical Oxidation (ISCO) technologies has proved to be a good alternative for the remediation of these contaminated sites (Siegrist et al., 2011). Besides, if bioremediation is further employed, the application of ISCO as a pretreatment has demonstrated to decrease the pollutant concentration to levels more favorable for the microorganisms and to increase the bioavailability of the contaminants generating more biodegradables byproducts (Cuypers et al., 2000; Sutton et al., 2011). However, different parameters such as oxidant amount, nutrients or regeneration capacity of the microbial population after oxidant application should be taken into account for optimization (Cassidy et al., 2015; Chen et al., 2016; Richardson et al., 2011; Sutton et al., 2014; Tang et al., 2012).

Some of the possible oxidants that can be applied are Fenton's reagents (Pardo et al., 2014; Pignatello et al., 2006; Yap et al., 2011), ozonation (Goi et al., 2006; Rodriguez et al., 2017) or permanganate (Brown et al., 2003; Mahmoodlu et al., 2014). However, during the last decades, the use of activated persulfate has been increasing due to several advantages like easy handling, high aqueous solubility, high stability, relatively low cost, longer lifetime in the subsurface than hydrogen peroxide, and production of benign end products, which makes it very competitive against other oxidants (Sra et al., 2014).

As cited above, the high stability of persulfate in the subsurface make this oxidant especially suitable for injection into the soil: in situ application (Siegrist et al., 2011). However, the ex situ application of persulfate has been also described in literature for treatment of soils polluted with TPH (Oh and Shin, 2014), with PCBs (Gomes et al., 2013) or sediments contaminated with several pollutants (Yan et al., 2015).

The activation of persulfate can be achieved by different ways such as applying light, increasing the temperature (Eq. (1)) or adding a transition metal where Fe^{2+} is the most commonly used (Eq. (2)). When the persulfate anion is activated, sulfate radicals ($SO_4^{\cdot-}$), a non-selective oxidant with a high redox potential ($E^0 = 2.6$ V) are generated.

$$S_2O_8^{2-} \overset{hv\ or\ heat}{\rightarrow} 2SO_4^{\cdot-} \tag{1}$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\cdot-} \tag{2}$$

The use of heat activation in full scale remediation may be limited by the energy required and its associated cost (Matzek and Carter, 2016). In the case of iron activation, the pH must be kept at acidic conditions in order to avoid its precipitation (Liang et al., 2009), making its application not advisable in alkaline soils. Chelating agents could be added to keep iron in solution at near neutral pH. However, chelating agents may compete with the contaminants for the oxidant and its effectiveness may decrease (Pardo et al., 2015b).

Recently, alkaline activation of persulfate (pH > 10) has been gaining attention. The mechanism of alkaline activation is summarized in Eqs. (3) and (4) (Furman et al., 2010). Superoxide radicals ($O_2^{\cdot-}$, $E^0 = 0.33$ V), sulfate radicals and hydroxyl radicals ($OH^{\cdot}$, $E^0 = 2.7$ V) are produced. However, the prodution of hydroxyl radicals is predominant against sulfate radicals when pH values are higher than 12 (Liang and Su, 2009).

$$2S_2O_8^{2-} + 2H_2O \overset{OH^-}{\rightarrow} 3SO_4^{2-} + SO_4^{\cdot-} + O_2^{\cdot-} + 4H^+ \tag{3}$$

$$SO_4^{\cdot-} + OH^- \rightarrow SO_4^{2-} + OH^{\cdot} \tag{4}$$

Most studies employ sodium hydroxide (NaOH) as the activator (Huling et al., 2011; Liang et al., 2013; Liang and Lei, 2015; Watts, 2011) although other reagents like potassium hydroxide (KOH) and lime (calcium oxide - CaO) can also be applied (Cassidy et al., 2015; Liang and Guo, 2012; Waisner et al., 2008). Thus, the activation may be accomplished by adjusting the initial pH, maintaining an alkaline pH during the reaction time with some activator additions or applying a high enough molar ratio of activator to persulfate at the beginning of the experiment.

However, to our best knowledge, there are no studies with application of persulfate activated by alkali to remediate soils contaminated with diesel. Only few references applying persulfate activated by alkali to a soil spiked with fresh diesel are available (Liang and Guo, 2012). No references have been found in the literature using aged diesel with alkaline persulfate as oxidant. Nevertheless, the phenomenon of aging is a point to be taken into account in soil remediation because, as the contact time between pollutant and soil increases its (bio)availability decreases, (Hatzinger and Alexander, 1995; Semple et al., 2003) making the decontamination of the site more difficult.

Therefore, the aim of the present work is to assess the effectiveness of alkaline activated persulfate for the remediation of a soil contaminated with aged diesel spill taking into account different aspects such as initial concentration of oxidant and activator and the total petroleum hydrocarbons (TPH). Furthermore, while in the literature only TPH abatement is usually considered, the present work studies the evolution of 30 identified and quantified compounds of the aged diesel at different reaction conditions. These compounds have also been clasified in aliphatic and aromatic and the efficiency of the treatment for each group is discussed.

2. Material and methods

2.1. Reagents

Sodium persulfate (PS) ≥ 98% from Sigma-Aldrich was used as oxidant, while sodium hydroxide >98% from Riedel-de Haën was applied as activator. In terms of PS analysis, potassium iodide >99.5% (Fisher Chemical), sodium hydrogen carbonate 99.7% (Panreac), acetic acid >99% (Sigma-Aldrich) and sodium thiosulfate pentahydrate 99.5% (Sigma-Aldrich) were utilized. Sodium thiosulfate was also employed to quench PS. Ethylenediaminetetraacetic acid (EDTA) tetrasodium salt dihydrate ≥98% from Sigma-Aldrich was used as chelating agent for the extraction of the labile iron pool of the soil samples.

For the extraction of contaminants in soil, anhydrous sodium sulfate 99%, from Sigma-Aldrich, HPLC grade acetone 99.8% from Fisher Chemical and HPLC grade n-hexane 99% from Scharlab were used. The extraction of pollutants in the aqueous phase was also performed using n-hexane.

2.2. Characterization of soil sample

Soil samples were collected from a train maintenance facility located in Madrid (Spain). The site was contaminated with diesel fuel which had leaked over time from an underground storage tank. At the time of sampling, the tank had already been removed and the free non-aqueous phase liquid (LNAPL) had been pumped out, leaving behind a significant residual contamination. The local geology is complex, with frequent lateral changes of lithology which include tertiary detrital and evaporitic sediments, and Quaternary alluvial deposits. Underneath the southern section of the maintenance facility, where the soil core was

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