

(wileyonlinelibrary.com) DOI 10.1002/jctb.5485

# Remediation of soil contaminated by PAHs and TPH using alkaline activated persulfate enhanced by surfactant addition at flow conditions

Miguel A Lominchar,\*  David Lorenzo, Arturo Romero and Aurora Santos



## Abstract

**BACKGROUND:** Remediation of a soil polluted with fuel oil #2 and polycyclic aromatic hydrocarbons (PAHs) has been carried out by alkaline activated persulfate (PS). The effect of surfactant addition on the abatement of TPH and PAHs was studied. Accordingly, four runs were performed at flow conditions using: only water, only surfactant (15 g L<sup>-1</sup> of Verusol-3), activated persulfate (210 mmol L<sup>-1</sup> PS and 840 mmol L<sup>-1</sup> NaOH) and surfactant (15 g L<sup>-1</sup> Verusol) with activated persulfate (210 mmol L<sup>-1</sup> PS and 840 mmol L<sup>-1</sup> NaOH).

**RESULTS:** Washing with water was found to achieve negligible desorption of the pollutants. Washing with surfactant or a combination of surfactant and oxidant completely removed the contaminants from soil, however only the addition of oxidant yielded an aqueous effluent without pollutants. When adding activated persulfate alone (without surfactant), about 30% residual contamination remained in the soil.

**CONCLUSION:** Results suggest that the combined application of surfactant and alkali persulfate produces a significant improvement in the elimination of organic compounds such as fuel oil #2 and PAHs.

© 2017 Society of Chemical Industry

Supporting information may be found in the online version of this article.

**Keywords:** PAHs; chemical oxidation; environmental remediation; kinetics

## INTRODUCTION

Soil and groundwater contamination by organic compounds resulting from human activities has become a major problem.<sup>1</sup> Among these organic pollutants, those derived from the accidental release of petroleum hydrocarbon from storage tanks are a widespread cause of soil and groundwater pollution.<sup>2</sup> These contaminants generally have low solubility and persist as a separate liquid phase, termed non-aqueous phase liquids (or NAPLs). When NAPL is less dense than water, as is the case in many petroleum products, they are known as light non-aqueous phase liquids (LNAPLs), being found above the water table.<sup>3–5</sup> Contamination derived from gasoline spills mainly consists of BTEX compounds, while heavier and less soluble compounds in the aqueous phase are found in fuel oil spills, compounds generally known as total petroleum hydrocarbon (TPH),<sup>6</sup> which contain a mixture of carbon chain length C14–C40.<sup>7</sup>

Apart from the petroleum spills, polycyclic aromatic hydrocarbons (PAHs), which consist of two or more fused benzene rings, a number of them being catalogued as potential carcinogens by various international agencies,<sup>8</sup> are also widely found in contaminated soils.<sup>9</sup>

Organic mixtures in fuel and PAHs show low volatilities and solubilities in water. Their high hydrophobicity often produces

a remarkable interaction with the soil matrix. Several mechanisms can be responsible for the sorption of these organic mixtures to soil, including van der Waals forces, hydrogen bonding, dipole–dipole interactions, ion exchange, and covalent bonding mechanisms. Their contribution depends on the nature of the organic contaminant and the soil granulometry and composition.<sup>10</sup> This sorption complicates their removal from soil by methods such as soil venting or soil vapor extraction, commonly used in remediation of gasoline spills.<sup>11</sup> Besides, remediation technologies such as *in situ* chemical oxidation (ISCO)<sup>12,13</sup> is not sufficiently effective to achieve the decontamination of soil polluted with hydrophobic compounds (TPHs or PAHs). As oxidation takes place in the aqueous phase, the low concentration of these compounds in this phase implies that unaffordable times would be required to eliminate the residual contamination from the soil. The oxidant–pollutant contact could be limited due to

\* Correspondence to: M<sup>A</sup> Lominchar, Dpto. Ingeniería Química, Facultad CC, Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain. E-mail: mlomin01@ucm.es; miguel.lomin@gmail.com

Dpto. Ingeniería Química, Facultad CC, Químicas, Universidad Complutense de Madrid, Madrid, Spain

the hydrophobic behavior of these contaminants and their strong adsorption in the soil matrix<sup>14</sup>.

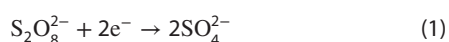
Among remediation technologies that could be applied,<sup>15</sup> surfactant enhanced aquifer remediation (SEAR)<sup>16</sup> is suitable for TPH and PAH-polluted soil. Surfactants modify the properties of the surfaces of soil particles enhancing the removal of pollutants to the surfactant solution.<sup>17–20</sup> Surfactant effectivity is affected by the sorption mechanism of the pollutants into the soil matrix. If soil contains SOM such as organic polymeric matter the effectivity of the extractability is lower. By contrast, if pollutants are sorbed onto water wet organic or inorganic surfaces or into the microporous structure of the soil, the sorbate is more easily extracted by means of an adequate solvent.<sup>9</sup>

However, surfactants only transfer the pollutant from the soil to the aqueous phase and further treatment of this polluted aqueous solution is required.<sup>21–23</sup> An emergent technology to avoid the further on-site treatment of the washing solution is the simultaneous injection of surfactants and oxidants, known as S-ISCO,<sup>24</sup> with the purpose of increasing the rate of contaminant desorption from the soil to the aqueous phase and therefore, improving the availability of the organic compounds to aqueous reagents. With regard to this approach, only few patents<sup>12,24</sup> and research works<sup>13,25</sup> can be found in the literature. Also, these research papers are based on a batch study, whereas an in-depth understanding of the behavior of surfactants would ideally require a column method as a better alternative to mimic *in situ* conditions.

When surfactants and oxidants are applied simultaneously, the unproductive consumption of the oxidant by the surfactant should be studied and minimized, this aspect being scarcely reported in the literature. Furthermore, it should be ensured that the surfactant yields pollutant transport to the aqueous phase at a rate that allows oxidation of the pollutants in the aqueous phase but not their mobilization to this phase. The surfactant should be a biodegradable substance, to avoid additional pollution of the soil and groundwater caused by the addition of this chemical.<sup>26</sup> For better biodegradability, nonionic surfactants have usually been selected in SEAR.<sup>27</sup>

The most commonly used oxidants in ISCO are permanganate, ozone and Fenton's reagent.<sup>28–30</sup> However, the application of sodium persulfate (PS) as an alternative to these oxidants has increased over the last decades.<sup>29,31–37</sup> Some properties, such as ease of handling, high aqueous solubility, high stability, relatively low cost, longer lifetime in the subsurface than hydrogen peroxide, and production of benign end products, characterize this compound, providing it with a competitive advantage over other oxidants.<sup>38</sup>

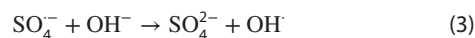
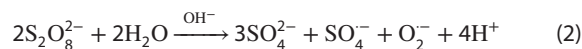
Chemistry of persulfate as oxidant in ISCO has been widely studied.<sup>39</sup> In aqueous solution, persulfate salts dissociate to persulfate anions as shown in Equation (1):



Subsequently, when persulfate anion is activated, sulfate radical ( $\text{SO}_4^{\cdot-}$ ), a non-selective oxidant with a high redox potential ( $E^0 = 2.6 \text{ V}$ ) is produced. This activation can be achieved by adding a transition metal, by light or heat activation, adding hydrogen peroxide or by alkaline activation ( $\text{pH} > 10$ ). Iron activation has the drawback that pH must be maintained in the acid region to avoid iron precipitation,<sup>40</sup> whereas the cost of thermally activated persulfate at field scale can be unaffordable. Alkaline activation has gained attention recently<sup>41</sup> but only few works have studied

remediation of soils contaminated with TPHs or PAHs by using this technology.<sup>13,14,35,42</sup>

In the case of alkaline activation, hydroxyl radicals ( $\text{OH}^{\cdot}$ ,  $E^0 = 2.7 \text{ V}$ ) are generated following Equations (2) and (3), being the predominant chemical species against sulfate radicals when pH values are higher than 12.<sup>43</sup>



Both sulfate and hydroxyl radicals are high reactive species than can oxidize a variety of organic compounds.<sup>31,44</sup> However, different reaction mechanisms are involved. It is usually accepted that sulfate radicals produce an organic radical cation by electron removal from the organic molecule while the hydroxyl radicals add to C=C bonds or abstract hydrogen from the C–H bond.<sup>31</sup>

Therefore, the aim of this work is to study the effect of surfactant addition to an oxidant solution in the remediation of a soil polluted with a commercial home heating oil and 4- ring PAHs. To this end, four columns of contaminated soil were built and worked on under saturated conditions. Results obtained using only oxidant (persulfate activated by alkali) were compared with those obtained with flushing water, surfactant and an oxidant/surfactant mixture. Nonionic surfactant formulations, Tween 80/Span 80 (from Sigma Aldrich) and Verusol-3 (from EthicalChem) have been tested to evaluate the non-productive consumption of the oxidant in aqueous phase. These surfactants have been proved to be biodegradable and their oxidation byproducts are harmless according to previous studies in the literature.<sup>27,45–47</sup> Aqueous effluent and column soil were analyzed during and after column runs, respectively. The fingerprint of the fuel was obtained before and after treatment. Not only TPH abatement but elimination of individual compounds present in the fuel and PAHs were analyzed and quantified. Persulfate and pH were monitored over 25 days in the aqueous effluent. A transport-reactive model was proposed and the parameters calculated.

## MATERIALS AND METHODS

### Reagents

The chemicals used are summarized in Table SI-1, which is enclosed as Supporting information of this work, in this table the acronym and commercial brand are provided.

A commercial home heating oil (HHO) was used as pollutant. All reagents were analytical grade. Phenanthrene (PHE), anthracene (ANT), pyrene (PYR), and benzo[a]pyrene (BaP), were used for soil spiking and in HPLC standards analysis. Besides, 9,10-anthraquinone (ATQ) was used for calibration and quantification. Sodium persulfate (PS) was used as oxidant, while sodium hydroxide was used as activator. Tween 80 (TW), Span 80 (SP) and Verusol-3 were used as surfactants. Potassium iodide, sodium hydrogen carbonate, acetic acid and sodium thiosulfate pentahydrate were utilized for PS analysis. Sodium thiosulfate was employed to quench PS. Sodium sulfate anhydrous, acetone, n-hexane, were used for the extraction of contaminants in soil. HPLC grade acetonitrile and sulfuric acid were used as mobile phase in HPLC for PAH analysis. All solutions were prepared with ultrapure laboratory grade water (Milli-Q) obtained from a deionizing system.

## Soil spiking

The soil selected for this study was a sandy clay loam Bt horizon from the Autonomous Community of Madrid. Property values such as  $\text{pH} = 7.22$ , total organic carbon = 0.196% and labile iron =  $7235 \text{ mg kg}^{-1}$ ,  $\text{dp} < 2 \text{ mm}$  and hydraulic conductivity =  $14.1 \text{ cm day}^{-1}$ , were characterized in previous work.<sup>48,49</sup> The spiking procedure was developed according to the literature.<sup>40,50,51</sup> An acetone solution containing heating oil, ANT, PHE, PYR and BaP was applied to the soil and mixed manually with a spatula simultaneously. Once the spiking was completed, the contaminated soil was aged for three months at room temperature in the absence of light and for the following six months at  $10^\circ\text{C}$ . After this ageing, TPH and PAH concentration was measured in the spiked soil, with results: HHO  $4820 \text{ mg kg}^{-1}$  soil, PHE  $101 \text{ mg kg}^{-1}$  soil, ANT  $31 \text{ mg kg}^{-1}$  soil, ATQ  $92 \text{ mg kg}^{-1}$  soil, PYR  $106 \text{ mg kg}^{-1}$  soil, BaP  $26 \text{ mg kg}^{-1}$  soil. It is noted that natural degradation of anthracene to 9,10-anthraquinone was obtained during the aging period. This had also been observed in previous work with the same soil.<sup>49</sup>

## Experimental design

### *Oxidant demand and stability of surfactant in aqueous solution*

Stability of the surfactant in aqueous solution containing PS ( $210 \text{ mmol L}^{-1}$ ) or NaOH ( $840 \text{ mmol L}^{-1}$ ) or both reagents was studied. Non-productive oxidant consumption by the surfactant was also analyzed. All experimental runs are summarized in Table SI-2, which is provided as Supporting information of this work, and were performed using the batch method in 20 mL glass bottles. As noted, two solutions of nonionic and readily biodegradable surfactants were chosen for the study: a mixture of Tween 80–Span 80 (35:65 w.w) and Verusol-3. Three different concentrations of each formulation were evaluated (15, 30 and  $50 \text{ g L}^{-1}$ ).

For comparison with results obtained elsewhere<sup>49</sup> using persulfate activated by iron the initial persulfate concentration was fixed at  $210 \text{ mmol L}^{-1}$ . The initial molar ratio NaOH:PS was set at 4 to ensure a higher production of hydroxyl radicals and maintenance of pH above 12.<sup>52</sup> In addition, a blank run without surfactant addition was carried out in order to determinate the decomposition of activated persulfate. Magnetic stirrer (StarFishTM) at 100 rpm was used and the operational temperature was  $20^\circ\text{C}$ . All experiments were performed in triplicate.

Oxidant/pollutant ratios were selected according to previous studies in the literature with alkaline persulfate in diesel and PAHs abatement.<sup>35,42</sup> Molar ratio of activator/oxidant in the literature range from 2 to 6.<sup>41</sup> A value of 4 has been chosen here to ensure that pH remains at about 12 in spite of the acidic oxidation byproducts of pollutant oxidation.

The surfactant concentration used was chosen in the range usually applied in SEAR,<sup>27,53</sup> this being slightly higher than that commonly applied for S-ISCO.<sup>13</sup>

At several reaction times, samples were drawn from each experiment and concentration of PS and interfacial tension (IFT) were measured in duplicate. Total organic carbon (TOC) was also determined at the beginning and at the end of reaction time. The corresponding results are shown as average values with a relative standard deviation (RSD) lower than 10%.

### *Nonproductive oxidant demand by soil*

In order to establish the consumption of activated persulfate by the soil (without pollutant), 10 g of a clean soil sample was placed in contact with 20 mL of alkaline persulfate solution ( $210 \text{ mmol L}^{-1}$  PS,  $840 \text{ mmol L}^{-1}$  NaOH) using 50 mL PTFE centrifuge tubes

with PTFE screw caps as batch reactors. These tubes were stirred isothermally ( $20^\circ\text{C}$ ) in an orbital shaker (Unitronic Orbital by Selecta) at 100 rpm for 864 h. The study was performed in triplicate. At several times the remaining PS was measured in duplicate. The consumption of only persulfate in contact with this soil was studied in a previous work.<sup>33</sup>

### *Remediation at flow conditions*

Runs at flow conditions were performed in glass columns 12 cm in length and 3 cm internal diameter. Each column was filled and compacted with approximately 45 g of soil to a length of 5.5 cm. Packed glass beads were placed to a length of 3.25 cm below and above the soil bed to avoid channeling.

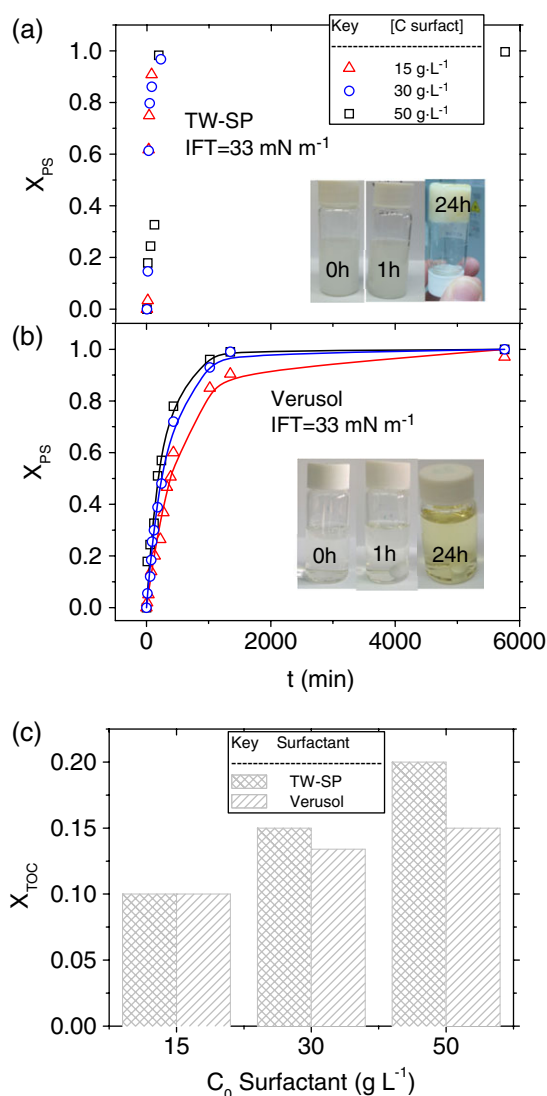
The set up conditions were similar to those established in a previous work with the same soil,<sup>49</sup> these being as follows: bulk density of the dried porous soil bed was  $1.445 \pm 0.012 \text{ g cm}^{-3}$ , inlet flow was for 25 days from bottom to top by a peristaltic pump at  $43.2 \pm 1.5 \text{ cm}^3 \text{ day}^{-1}$ , corresponding to an interstitial velocity of  $13.9 \text{ cm day}^{-1}$  in the column, which is close to the flow velocity of groundwater in saturation conditions ( $14.1 \text{ cm day}^{-1}$ ). Column porosity was about 0.43. Therefore, the residence time of the liquid flow in the soil section ( $t_{\text{RS}}$ ) was about 9.2 h (0.4 days), in the glass section ( $t_{\text{RG}}$ ) about 11 h (0.45 days) and in the whole column ( $t_{\text{RC}}$ ) about 20.2 h (0.85 days).

Before each run, dry columns were filled, from bottom to top, with Milli-Q water in order to reach saturation conditions. The four remediation runs carried out at flow conditions over 25 days are summarized in Table SI-3, which is provided as Supporting information of this work. Briefly, four runs were carried out: in run C-B pure water without oxidant or surfactant addition was fed into the column, in run C-S an aqueous solution  $15 \text{ g L}^{-1}$  of Verusol-3 was fed into the column, in run C-ISCO an aqueous solution  $210 \text{ mmol L}^{-1}$  in PS and  $840 \text{ mmol L}^{-1}$  in NaOH was fed into the column, and in run C-SICO and aqueous solution containing surfactant ( $15 \text{ g L}^{-1}$ ), oxidant ( $210 \text{ mmol L}^{-1}$ ) and activator ( $840 \text{ mmol L}^{-1}$ ) was fed into the column.

During the treatment period (25 days, 600 h), samples from effluent were taken periodically at column outlet and IFT, pH and remaining PS concentration were measured. The aqueous effluents from the columns were continuously collected in 150 to 250 mL volumes. The TPH and PAH concentration in the collected aqueous volumes was determined by liquid–liquid extraction with hexane and subsequent analysis in GC/MS as explained in the analysis section. PAHs in the aqueous effluent were also determined by HPLC by the procedure described below. The analyses of the effluents were developed in duplicate (RSD < 10%).

After 25 days of treatment, soil was removed from the glass column and divided into 3 fractions along the length of the column, with a similar weight of wet soil. After that, 2 g of wet soil from each section was dried at  $105^\circ\text{C}$  for 2 h to determine the water content. Subsequently, 7 mL of  $400 \text{ mmol L}^{-1}$  sodium thiosulfate pentahydrate was added to the remaining wet soil of each section and mixed to quench the generation of sulfate and hydroxyl radicals. After that, the samples were stored at  $4^\circ\text{C}$  until the solvent extraction step.

Extraction of HHO and PAH content in the fractions of quenched soil was carried out by EPA method 3546. To do this, the quenched soil was dried with anhydrous sodium sulfate and milled in a ceramic mortar; 25 mL of a mixture of hexane:acetone 1:1 was then added to 10 g of dry soil and the resulting mixture was introduced in a microwave extraction device (Milestone Ethos One) applying a temperature program with an initial ramp of 15 min from room



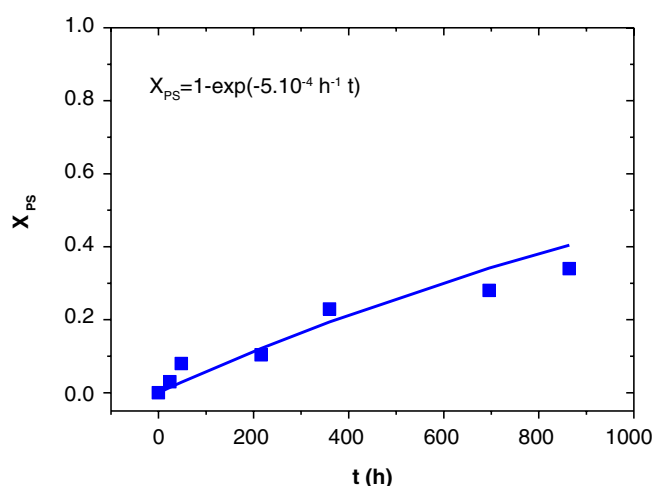
**Figure 1.** Study of unproductive consumption of persulfate by surfactants. Conversion of persulfate ( $X_{PS}$ ) obtained in: (a) runs S-13, S-14 and S-15 (mixture Tween–Span) and (b) runs S-16, S-17 and S-18 (Verusol-3). Points: Experimental data. Lines: Predicted values with Equation (4). (c) TOC conversion ( $X_{TOC}$ ) obtained using TW-SP or Verusol-3 at 24 h.

temperature to 110 °C, followed by a sustained temperature of 110 °C for 15 min, under a maximum power of 1000 W. About 15 mL of organic phase after extraction were recovered from supernatant, filtered with a 0.45  $\mu$ m filter and concentrated to 3 mL in a Syncore® Polyvap system (Buchi).

### Analysis

The concentration of PS in solution was measured by iodometric titration with a solution of sodium thiosulfate,<sup>54,55</sup> of known concentration, by using a potentiometric titration analyzer supplied by Metrohm (905-Titrando). pH was measured with a pH glass electrode also supplied by Metrohm. The total organic carbon was measured using a Shimadzu TOC-V CSH analyzer by oxidative combustion at 680 °C, using an infrared detector.

For identification and quantification of main HHO and PAH compounds from the soil extracts and column effluent, a GC/MS (HP 6890 N MSD 5975B) equipped with HP-5 column (30 m  $\times$  0.32 mm



**Figure 2.** Non-productive consumption of PS by soil ( $[PS]_0 = 210 \text{ mmol L}^{-1}$ ,  $[NaOH]_0 = 840 \text{ mmol L}^{-1}$ ,  $T = 20 \text{ }^\circ\text{C}$ ). Symbols: experimental values. Lines: predicted values with Equation (6).  $W/V_L = 0.5 \text{ g mL}^{-1}$ .

i.d.  $\times 0.25 \mu\text{m}$ ) was used. The diesel concentration was determined by the sum of the total peak area (EPA method 8015B).<sup>56</sup> The chromatographic conditions used were as follows: injector temperature: 280 °C; carrier gas (He) flow rate: 1 mL  $\text{min}^{-1}$ ; 3  $\mu\text{L}$  of injected volume in splitless mode. The analysis was performed with an initial oven temperature of 45 °C for 5 min, followed by a first ramp of 8 °C  $\text{min}^{-1}$  to 260 °C, sustained for 35 min, and a second ramp of 12 °C  $\text{min}^{-1}$  to 325 °C, sustained for 5 min. The final run time was 76.21 min. Mass Hunter Quantitative Analysis (Agilent Technologies) was used to quantify the singular compounds in the HHO and PAHs. This Software calculates the area of a compound by searching in a retention time window characteristic ions (qualifiers) and their relative response.

PAHs in the aqueous phases were also measured by HPLC (Agilent, mod. 1100) coupled with an Agilent 1290 Infinity Diode Array Detector. The column used was a Poroshell 120 SB-C18 in 2.1 mm  $\times$  100 mm and 2.7  $\mu\text{m}$  of particle size. Analysis was carried out under isocratic mode at a flow rate of 0.5 mL  $\text{min}^{-1}$ , selecting as mobile phase a mixture of 60% acetonitrile and 40% acid water; selected injection volume was 20  $\mu\text{L}$ . Wavelengths chosen were: 235 nm for PYR, 250 nm for PHE, ANT and ATQ, and 295 nm for BaP. Detection Limit was less than 50 ppbs. The interfacial tension was measured using a Krüss tensiometer.

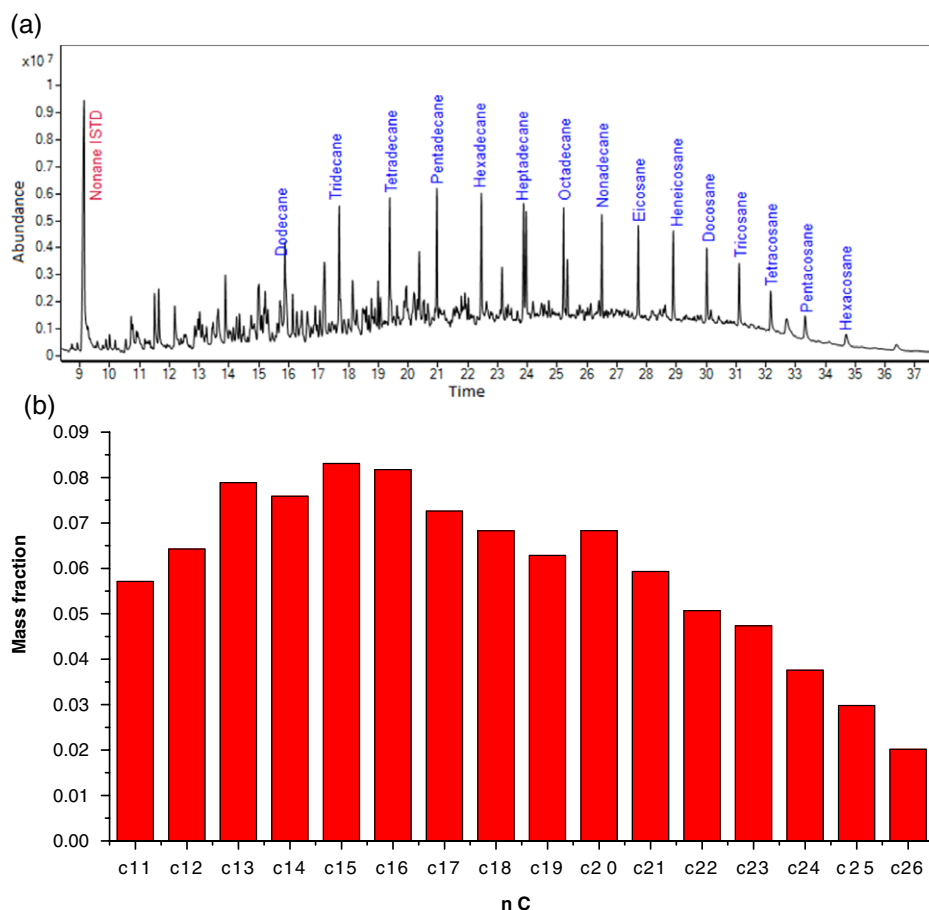
## RESULTS AND DISCUSSION

### Surfactant stability vs oxidant

Before applying a treatment to the soil, compatibility between the oxidant and the surfactant needed to be analyzed in order to establish which combination produces the lowest unproductive oxidant consumption and also does not affect the surfactant properties.

First, the effect of the activator (NaOH) on the surfactant stability was studied in runs S-1 to S-6 (Table SI-2, Supporting information). It was noted that the presence of NaOH, in the absence of oxidant did not affect the physicochemical properties, concentration and IFT of Verusol-3 solution. However, the addition of 840 mmol  $\text{L}^{-1}$  of NaOH to the Tween–Span mixture produced a remarkable increase of sample viscosity independently of the concentration of surfactant.





**Figure 3.** Fingerprint of the HHO used to spike the soil. (a) Elution GC/MS chromatogram. (b) Mass fraction.

Second, the possible activation of persulfate by the surfactant was evaluated in runs S-7 to S-12 (Table SI-2). In these runs (absence of alkali) pH was acidic due to PS addition. Persulfate consumption below 0.15 was detected in all these experiments after 144 h of reaction. Therefore, a significant activation of PS at acidic pH by either surfactant could be discarded. A similar result was obtained for other nonionic surfactants in the study developed by Elloy *et al.*<sup>57</sup>

Finally, the interaction of the surfactant and alkali activated PS was tested in runs S-13 to S-18 (Table SI-2). The results obtained are shown in Fig. 1. As can be seen, at the oxidant and alkali concentrations tested both surfactant formulations used (Tween–Span mixture and Verusol-3) reacted with the activated PS. However, the persulfate consumption using Verusol-3 was much lower than that obtained using the Tween–Span mixture. Thus, the PS conversions in runs with Verusol were lower than 0.25 at 80 min, meanwhile the elimination of oxidant in the Tween–Span mixture was about 0.9 at the same time for all runs. Comparing the persulfate conversions obtained with and without alkali addition, the effect of the alkali on PS activation is clear.

A remarkable increase of viscosity (Fig. 1) was observed in the mixture Tween–Span as noted before in the experiments where only NaOH was added (S1 to S3 in Table SI-2). By contrast, the addition of oxidant to the sample containing Verusol-3 and alkali had no effect on this property (as shown in Fig. 1). IFT was also measured over time in these runs up to 96 h, obtaining a constant value between 33 and 35 mN m<sup>-1</sup>, as indicated in Fig. 1.

Surfactant mineralization achieved after total PS consumption was quite low (TOC conversion between 0.1 and 0.2) in all runs. Therefore, the low mineralization and the constant IFT value obtained even when the initial surfactant was oxidized, indicates that the oxidation intermediates of both surfactant formulations (Tween–Span and Verusol-3) also have surfactant properties.

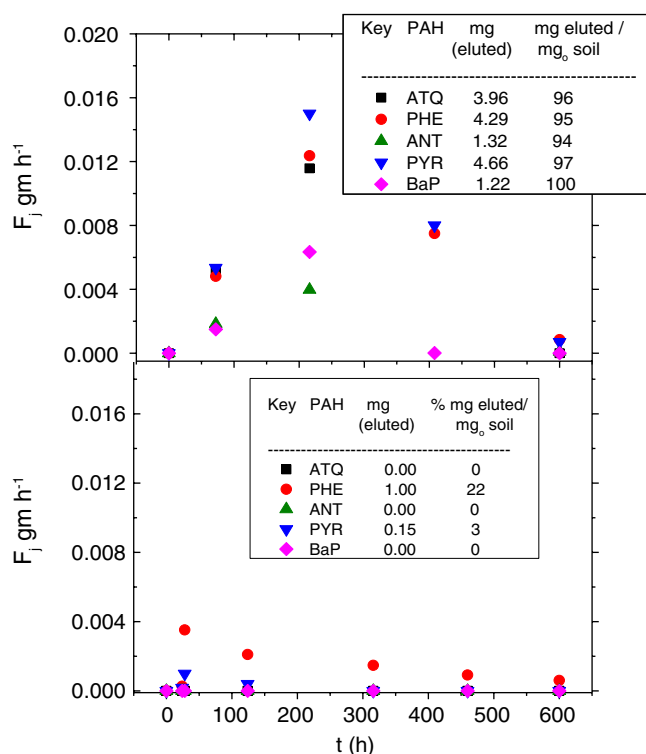
Data obtained in the oxidation runs of Verusol-3 (S-16, S-17, S-18) in Table SI-2 have been fitted to a first-order rate equation (Equation (4))

$$\ln(1 - X_{ps}) = -k_{ds}t \quad (4)$$

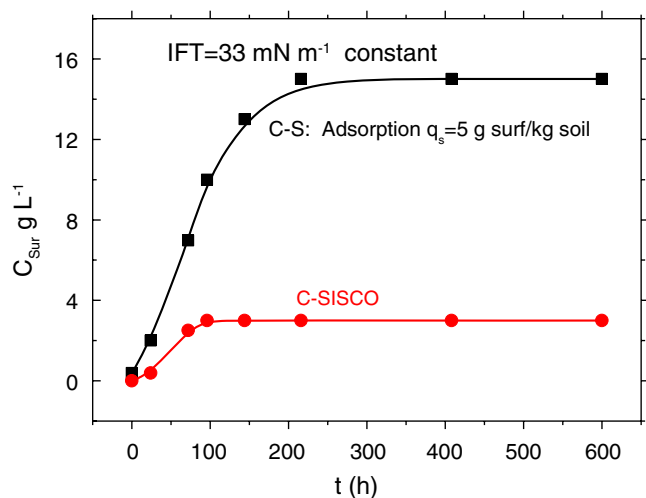
wherein  $X_{ps}$  is the persulfate conversion and  $k_{ds}$  the kinetic constant of persulfate consumption using Verusol-3 as surfactant.

Values obtained for kinetic constant of  $k_{ds}$  were 0.0018, 0.0029 and 0.0036 min<sup>-1</sup> when 15, 30 and 50 g L<sup>-1</sup> of Verusol-3 were used respectively. In Fig. 1(b), persulfate conversions predicted by Equation (4) with these kinetic constants are shown as lines. A good agreement is noticed between predicted and experimental values (correlation coefficient  $r^2$  was >0.97).

Therefore, and considering the higher stability of Verusol-3 in contact with activated persulfate compared with Tween–Span mixture, the former was selected to carry out the remediation runs in column operation. In order to minimize oxidant consumption, the surfactant concentration chosen was 15 g L<sup>-1</sup>, since, in addition, the surface tension remains constant at both concentrations studied.



**Figure 4.** Mass flow of PAHs ( $\text{mg h}^{-1}$ ) in the column effluent and fraction of eluted PAHs of the initial PAHs in soil after 25 days. (a) C-S run, (b) C-SISCO run. Conditions in Table SI-3 (SI).

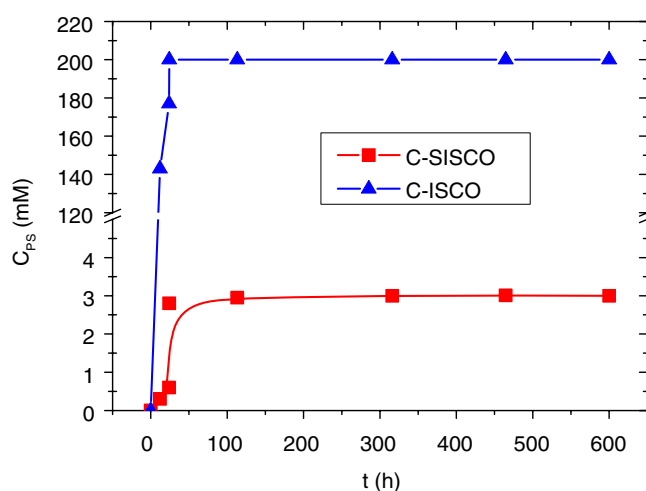


**Figure 5.** Concentration of Verusol-3 in the column effluent in run C-S and C-SISCO. [Verusol-3]<sub>0</sub> fed to the column  $15 \text{ g L}^{-1}$ . IFT of the effluent  $33 \text{ mN m}^{-1}$  (constant over 25 days).

### Soil oxidant demand

The consumption of persulfate when clean soil is in contact with the aqueous solution containing the PS and the alkali is shown in Fig. 2. The mass balance of PS in the soil–aqueous media, considering a first-order reaction for the non-productive PS consumption can be expressed according to Equation (5)

$$-\frac{dn_{\text{PS}}}{Wdt} = k_{\text{dn}} C_{\text{PS}} \cdot - \frac{dn_{\text{PS}}}{V_L dt} = - \frac{dC_{\text{PS}}}{dt} = k_{\text{dn}} \left( \frac{W}{V_L} \right) C_{\text{PS}} = k'_{\text{dn}} C_{\text{PS}} \quad (5)$$



**Figure 6.** Concentration of persulfate in the column effluent in run C-SISCO and C-ISCO. Operating conditions in Table SI-3.

wherein  $k_{\text{dn}}$  is the kinetic constant of non-productive PS consumption by the soil, related to the mass of soil ( $\text{cm}^3 \text{ h}^{-1} \text{ g}^{-1}$ ) and  $k'_{\text{dn}}$  the kinetic constant related to the liquid volume ( $\text{h}^{-1}$ ),  $W$  the mass of soil (g),  $V_L$  the volume of the aqueous solution ( $\text{cm}^3$ ),  $n_{\text{PS}}$  and  $C_{\text{PS}}$  the mmol and  $\text{mmol L}^{-1}$  of PS, respectively. Integrated mass balance for PS in the batch system yields Equation (6)

$$\ln(1 - X_{\text{PS}}) = -k'_{\text{dn}} t \quad (6)$$

Experimental PS conversion with clean soil was fitted to Equation (6) and the kinetic constant  $k'_{\text{dn}}$  obtained was  $5 \times 10^{-4} \text{ h}^{-1}$  ( $k_{\text{dn}} = 10^{-3} \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$ ). Predicted values with Equation (6) are represented as a line in Fig. 2. The value of  $k'_{\text{dn}}$  at the same  $W/V_L$  ratio used here but without the addition of alkali was estimated in previous work at  $5.16 \times 10^{-5} \text{ h}^{-1}$ .<sup>49</sup>

### Diesel fingerprint and calibrated compounds in HHO

A chromatogram of fuel oil #2 in n-hexane obtained by GC/MS is shown in Fig. 3(a), where main alkanes identified by Mass Hunter quantitative software are indicated. Peaks were deconvoluted and scored to the main ions, and qualifiers were higher than 95% in all the identified peaks. The fingerprint derived from this chromatogram is given in Fig. 3(b).

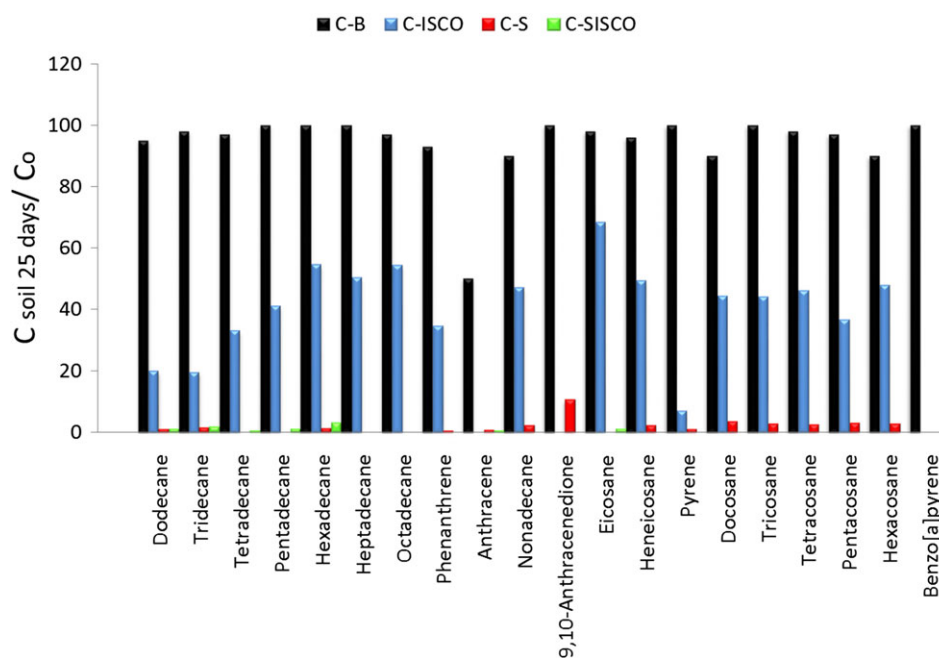
### Soil remediation

Results of the flow rate of each PAH (as  $\text{mg h}^{-1}$ ) in the column effluent for runs C-S and C-SISCO are shown in Fig. 4(a) and 4(b), respectively. The eluted PAH in these runs during the operating range was calculated as the integrated mass flow of each PAH (Equation (7))

$$\text{mg}_j \text{ eluted} = \int_0^{600 \text{ h}} F_j \left( \frac{\text{mg}}{\text{h}} \right) dt \quad (7)$$

Taking into account the initial concentration of each PAH in the soil (given in the section 'Soil spiking'), and the soil weight placed in the column (45 g), the fraction of the total PAH eluted in the effluent related to the initial PAH in the soil was calculated, and its value is also indicated in the caption of Fig. 4(a) and 4(b).

In Fig. 4(a), it can be seen that most of the initial PAHs in the soil were extracted in run C-S after 600 h of treatment. The profiles of



**Figure 7.** Aliphatic C<sub>n</sub> compounds and PAHs remaining in soil after 25 days of treatment (as fraction of the initial concentration in soil) in runs C-B, C-ISCO, C-S and C-SISCO. Operating conditions in Table SI-3.

the mass flow for each PAH were similar, indicating non-selective extraction of the PAHs by the surfactant. On the other hand, as can be seen in Fig. 4(b), the mass flow of PAHs eluted in the C-SISCO run was much lower than that obtained in the C-S run. Amounts of eluted ATQ, ANT and BaP were almost negligible in C-SISCO and only some PYR and PHE were found in the effluent. Calculated amounts of eluted PHE and PYR were about 22% and 3%, respectively, related to the initial content of these PAHs in soil.

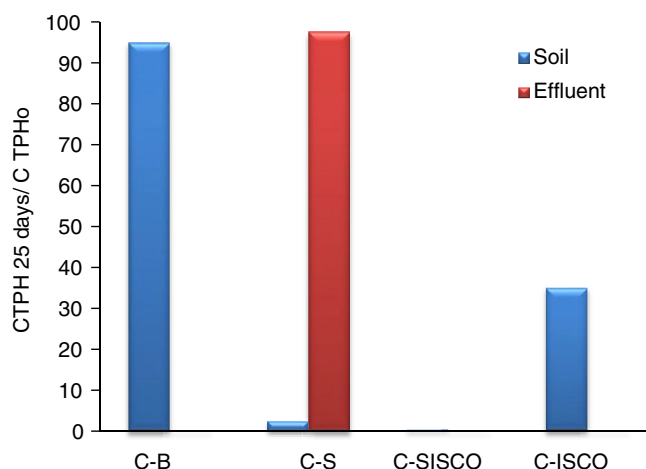
In runs C-B and C-ISCO, none of the PAHs tested were found in the aqueous fraction collected after extraction with hexane. This means that no mobilization took place by washing with water, or in the case of C-ISCO, the pollutants were oxidizing as they were being desorbed. TPHs were also measured in the volumes collected from the aqueous column effluent: no TPHs were found in the aqueous volumes collected in runs C-B, C-ISCO and C-SISCO.

Surfactant concentration in the column effluent was also measured in runs C-S and C-SISCO, and their results are given in Fig. 5. As can be seen, an adsorption breakthrough curve for the surfactant is obtained in the C-S run, the adsorption of the surfactant being  $5 \text{ g kg}^{-1}$  soil when equilibrium is reached.

The surfactant concentration in the effluent of run C-SISCO is about  $3 \text{ g L}^{-1}$  ( $t > 48 \text{ h}$ ). As the concentration of the surfactant at the column inlet is about  $15 \text{ g L}^{-1}$ , the difference between outlet and inlet concentration of the initial surfactant can be attributed to the oxidation of this compound. However, the IFT was kept at  $33 \text{ mN m}^{-1}$  throughout the treatment and the TOC of the effluent was similar to the inlet TOC.

The PS concentration in the column effluent was measured in runs C-SISCO and C-ISCO and results are shown in Fig. 6. As can be seen, higher consumption of PS took place in the C-SISCO run. This can be explained by persulfate consumption by the surfactant and the greater availability of pollutants to be oxidized. The pH of the effluent was about neutral in C-B and C-S and around 12 in C-ISCO and C-SISCO during the whole treatment time.

Finally, after 25 days treatment, the soil was removed from the column, divided into three sections and remaining TPHs, aliphatic



**Figure 8.** TPHs remaining in soil and effluent after 25 days of treatment (as fraction of the initial concentration in soil) in runs C-B, C-ISCO, C-S and C-SISCO.

compounds and PAHs were measured. Due to the small amount of soil used in the column (5.5 cm), and the low residence time in the soil column (related to the treatment time), similar values of TPHs, aliphatic compounds and PAHs were obtained in the three sections (relative differences lower than 10%). Therefore, an average value was obtained. Remaining aliphatic compounds and PAHs measured in the soil removed from the column in C-B, C-S, C-SISCO and C-ISCO runs at 25 days are shown in Fig. 7. TPH conversions are given in Fig. 8.

As can be seen in Figs 7 and 8, washing with water did not remove the pollutants, indicating strong adsorption of these NPAL by the soil. On the other hand, PAHs, aliphatic compounds and TPHs were almost entirely removed in C-S and C-SISCO runs. However in C-S, these pollutants were transferred to the aqueous effluent while in C-SISCO they were oxidized.

With regard to results obtained in the C-ISCO run, it was found that after 25 days of treatment, a significant amount of pollutants was still present in the soil (35% of TPH and about 40% of phenanthrene). C-ISCO run results can be compared with those obtained in previous work using the same soil employed here yet spiked with approximately 100 mg kg<sup>-1</sup> of PHE, PYR, ANT and BaP.<sup>49</sup> The same flow rate, PS inlet concentration (210 mmol L<sup>-1</sup>) and treatment time (25 days) used here were employed, but, in that case, iron was used as activator (like Fe(III) or nZVI). Best results were obtained with nZVI as activator (6 mg Fe cm<sup>-3</sup> column) with 70% PHE conversion and only 20% ATQ removal. While the refractory behavior of this compound has been previously reported in the literature using permanganate<sup>58</sup> or persulfate activated by iron,<sup>40</sup> it follows that alkaline activation of PS used here yields better results in the abatement of ATQ. On the other hand, similar results in conversion of TPHs were obtained in alkaline PS activation compared with those obtained in iron activated PS.<sup>14,40</sup> These works pointed out that the TPH was not completely removed due to several factors, some of the most important being the adsorption into organic matter and soil micropores.

## CONCLUSIONS

The surfactant Verusol-3 was more stable in the aqueous solution in contact with the oxidant (persulfate at pH 12) than the Tween 80–Span 80 mixture. Low mineralization of Verusol-3 was achieved (<10%) and its oxidation intermediates with surfactant properties kept a constant IFT value of about 33 mN m<sup>-1</sup>.

Based on the results obtained at flow conditions, it was found that in the absence of surfactant in the oxidation treatment, 30% of the TPHs remained in the soil after 25 days, which can be explained by the strong adsorption of the pollutants by the soil, probably the soil micropore, producing a residual contamination which is difficult to eliminate without surfactant addition. Compared with iron activated persulfate, alkaline activation of PS seems to be similarly effective for TPH abatement but offers enhanced oxidation of refractory PAHs such as 9,10-anthraquinone.

For the case in which Verusol-3 was fed into the column, total removal of TPH and PAHs from the soil was achieved by taking them to the aqueous phase. Furthermore, when alkali activated persulfate is added to the surfactant solution inlet, the oxidation of TPHs and PAHs solubilized in the aqueous phase takes place and no organic pollutants are transferred to the effluent. Oxidation without mobilization of pollutants is a key aspect for S-ISCO application. The process could be optimized by adjusting the surfactant dosage fed into the column, to thus lower the oxidant consumption due to the side reaction of surfactant oxidation.

Results obtained from runs at flow conditions are expected to be more representative of an *in situ* remediation procedure than the results obtained in batch operation.

## ACKNOWLEDGEMENTS

The authors acknowledge financial support from the Regional Government of Madrid and MINECO provided through the projects CARESOIL (S2013- MAE-2739), CTM2013-43794-R, and CTM2016-77151-C2-1-R.

## Supporting Information

Supporting information may be found in the online version of this article.

## REFERENCES

- van Liedekerke M, Prokop G, Rabl-Berger S, Kibblewhite M and Louwagie G, *Progress in the Management of Contaminated Sites in Europe* (2014).
- Ivshina IB, Kuyukina MS, Krivoruchko AV, Elkin AA, Makarov SO, Cunningham CJ *et al.*, Oil spill problems and sustainable response strategies through new technologies. *Environ Sci Process Impacts* **17**:1201–1219 (2015).
- Sulaymon AH and Gzar HA, Experimental investigation and numerical modeling of light nonaqueous phase liquid dissolution and transport in a saturated zone of the soil. *J Hazard Mater* **186**:1601–1614 (2011).
- Soga K, Page JW and Illangasekare TH, A review of NAPL source zone remediation efficiency and the mass flux approach. *J Hazard Mater* **110**:13–27 (2004).
- Schaefer CE, White EB, Lavorgna GM and Annable MD, Dense nonaqueous-phase liquid architecture in fractured bedrock: implications for treatment and plume longevity. *Environ Sci Technol* **50**:207–213 (2016).
- Newell CJ, Acree SD, Ross RR and Huling SG, *Ground water issue: light nonaqueous phase liquids*. Groundwater Services, Inc., Houston, TX (United States) (1995).
- Christensen JH and Tomasi G, Practical aspects of chemometrics for oil spill fingerprinting. *J Chromatogr A* **1169**:1–22 (2007).
- Wise SA, Sander LC and Schantz MM, Analytical methods for determination of polycyclic aromatic hydrocarbons (PAHs) - a historical perspective on the 16 US EPA priority pollutant PAHs. *Polycycl Aromat Comp* **35**:187–247 (2015).
- Rivas FJ, Polycyclic aromatic hydrocarbons sorbed on soils: a short review of chemical oxidation based treatments. *J Hazard Mater* **138**:234–251 (2006).
- Chu W, Choy WK and Hunt JR, Effects of nonaqueous phase liquids on the washing of soil in the presence of nonionic surfactants. *Water Res* **39**:340–348 (2005).
- Nadim F, Hoag GE, Liu S, Carley RJ and Zack P, Detection and remediation of soil and aquifer systems contaminated with petroleum products: an overview. *J Petrol Sci Eng* **26**:169–178 (2000).
- Hoag GE and Collins J, Soil remediation method and composition. United States Patent US7976241 (2011).
- Wang WH, Hoag GE, Collins JB and Naidu R, Evaluation of surfactant-enhanced *in situ* chemical oxidation (S-ISCO) in contaminated soil. *Water Air Soil Pollut* **224**:1–9 (2013).
- Wu H, Sun LN, Wang H and Wang XX, Persulfate oxidation for the remediation of petroleum hydrocarbon-contaminated soils. *Polish J Environ Stud* **25**:851–857 (2016).
- Caliman FA, Robu BM, Smaranda C, Pavel VL and Gavrilescu M, Soil and groundwater cleanup: benefits and limits of emerging technologies. *Clean Technol Environ* **13**:241–268 (2011).
- Mulligan C, Yong R and Gibbs B, Surfactant-enhanced remediation of contaminated soil: a review. *Eng Geol* **60**:371–380 (2001).
- Couto HJ, Massarani G, Biscaia EC Jr and Sant'Anna GL Jr, Remediation of sandy soils using surfactant solutions and foams. *J Hazard Mater* **164**:1325–1334 (2009).
- Lee M, Kang H and Do W, Application of nonionic surfactant-enhanced *in situ* flushing to a diesel contaminated site. *Water Res* **39**:139–146 (2005).
- Khalladi R, Benhabiles O, Bentahar F and Moulai-Mostefa N, Surfactant remediation of diesel fuel polluted soil. *J Hazard Mater* **164**:1179–1184 (2009).
- Chong ZY, Liao XY, Yan XL, Sun L, Zhao D and Liang T, Enhanced desorption of PAHs from manufactured gas plant soils using different types of surfactants. *Pedosphere* **24**:209–219 (2014).
- Rosas JM, Santos A and Romero A, Soil-washing effluent treatment by selective adsorption of toxic organic contaminants on activated carbon. *Water Air Soil Pollut* **224**:1506 (2013).
- Rosas JM, Vicente F, Santos A and Romero A, Soil remediation using soil washing followed by Fenton oxidation. *Chem Eng J* **220**:125–132 (2013).
- Trellu C, Oturan N, Pechaud Y, van Hullebusch ED, Esposito G and Oturan MA, Anodic oxidation of surfactants and organic compounds entrapped in micelles – selective degradation mechanisms and soil washing solution reuse. *Water Res* **118**:1–11 (2017).
- Dugan PJ, Siegrist RL and Crimi ML, Method and Compositions for Treatment of Subsurface Contaminants. United State Patent US7553105-B1 (2009).



- 25 Dugan PJ, Siegrist RL and Crimi ML, Coupling surfactants/cosolvents with oxidants for enhanced DNAPL removal: a review. *Remediation J* **20**:27–49 (2010).
- 26 Scott MJ and Jones MN, The biodegradation of surfactants in the environment. *BBA - Biomembranes* **1508**:235–251 (2000).
- 27 Cheng M, Zeng G, Huang D, Yang C, Lai C, Zhang C *et al.*, Advantages and challenges of Tween 80 surfactant-enhanced technologies for the remediation of soils contaminated with hydrophobic organic compounds. *Chem Eng J* **314**:98–113 (2017).
- 28 Albergaria JT and Nouws HP, *Soil Remediation: Applications and New Technologies*. CRC Press, London (2016).
- 29 Baciocchi R, Principles, developments and design criteria of *in situ* chemical oxidation. *Water Air Soil Pollut* **224**:1–11 (2013).
- 30 Baciocchi R, D'Aprile L, Innocenti I, Massetti F and Verginelli J, Development of technical guidelines for the application of *in situ* chemical oxidation to groundwater remediation. *J Clean Prod* **77**:47–55 (2014).
- 31 Tsitonaki A, Petri B, Crimi M, Mosbaek H, Siegrist RL and Bjerg PL, *In situ* chemical oxidation of contaminated soil and groundwater using persulfate: a review. *Crit Rev Env Sci Technol* **40**:55–91 (2010).
- 32 Krembs FJ, Siegrist RL, Crimi ML, Furrer RF and Petri BG, ISCO for groundwater remediation: analysis of field applications and performance. *Ground Water Monit R* **30**:42–53 (2010).
- 33 Pardo F, Rosas JM, Santos A and Romero A, Remediation of a biodiesel blend-contaminated soil with activated persulfate by different sources of iron. *Water Air Soil Pollut* **226**:1–12 (2015).
- 34 Do SH, Kwon YJ and Kong SH, Effect of metal oxides on the reactivity of persulfate/Fe(II) in the remediation of diesel-contaminated soil and sand. *J Hazard Mater* **182**:933–936 (2010).
- 35 Liang CJ and Guo YY, Remediation of diesel-contaminated soils using persulfate under alkaline condition. *Water Air Soil Pollut* **223**:4605–4614 (2012).
- 36 Oh SY and Shin DS, Treatment of diesel-contaminated soil by Fenton and persulfate oxidation with zero-valent iron. *Soil Sediment Contam* **23**:180–193 (2014).
- 37 Yen CH, Chen KF, Kao CM, Liang SH and Chen TY, Application of persulfate to remediate petroleum hydrocarbon-contaminated soil: feasibility and comparison with common oxidants. *J Hazard Mater* **186**:2097–2102 (2011).
- 38 Sra KS, Thomson NR and Barker JF, Stability of activated persulfate in the presence of aquifer solids. *Soil Sediment Contam* **23**:820–837 (2014).
- 39 Devi P, Das U and Dalai AK, *In situ* chemical oxidation: principle and applications of peroxide and persulfate treatments in wastewater systems. *Sci Total Environ* **571**:643–657 (2016).
- 40 San Roman I, Galdames A, Alonso ML, Bartolome L, Vilas JL and Alonso RM, Effect of coating on the environmental applications of zero valent iron nanoparticles: the lindane case. *Sci Total Environ* **565**:795–803 (2016).
- 41 Furman OS, Teel AL and Watts RJ, Mechanism of base activation of persulfate. *Environ Sci Technol* **44**:6423–6428 (2010).
- 42 Zhao D, Liao X, Yan X, Huling SG, Chai T and Tao H, Effect and mechanism of persulfate activated by different methods for PAHs removal in soil. *J Hazard Mater* **254–255**:228–235 (2013).
- 43 Furman OS, Teel AL, Ahmad M, Merker MC and Watts RJ, Effect of basicity on persulfate reactivity. *J Environ Eng* **137**:241–247 (2011).
- 44 Wacławek S, Lutze HV, Grübel K, Padil VV, Černík M and Dionysiou DD, Chemistry of persulfates in water and wastewater treatment: a review. *Chem Eng J* **330**:44–62 (2017).
- 45 Hoag GE, Innovative green treatment of former manufactured gas plant dense non-aqueous phase liquids using surfactant-enhanced *in situ* chemical oxidation (S-ISCOTM) (2009).
- 46 Dahal G, Holcomb J and Socci D, Surfactant Oxidant Co. Application for soil and groundwater remediation. *Remed J* **26**:101–108 (2016).
- 47 Ye S, Huang L, Li YO, Ding M, Hu Y and Ding D, Investigation on bioremediation of oil-polluted wetland at Liaodong Bay in northeast China. *Appl Microbiol Biotechnol* **71**:543–548 (2006).
- 48 Pardo F, Rosas JM, Santos A and Romero A, Remediation of a biodiesel blend-contaminated soil by using a modified Fenton process. *Environ Sci Pollut Res Int* **21**:12198–12207 (2014).
- 49 Pardo F, Santos A and Romero A, Fate of iron and polycyclic aromatic hydrocarbons during the remediation of a contaminated soil using iron-activated persulfate: a column study. *Sci Total Environ* **566–567**:480–488 (2016).
- 50 Kulik N, Goi A, Trapido M and Tuhkanen T, Degradation of polycyclic aromatic hydrocarbons by combined chemical pre-oxidation and bioremediation in creosote contaminated soil. *J Environ Manage* **78**:382–391 (2006).
- 51 Mora VC, Madueno L, Peluffo M, Rosso JA, Del Panno MT and Morelli IS, Remediation of phenanthrene-contaminated soil by simultaneous persulfate chemical oxidation and biodegradation processes. *Environ Sci Pollut Res Int* **21**:7548–7556 (2014).
- 52 Watts RJ, Enhanced reactant-contaminant contact through the use of persulfate *in situ* chemical oxidation. *Strategic Environmental Research and Development Program* (2011).
- 53 Collins J and Hoag G, Surfactant enhanced *in situ* chemical oxidation (s-isco tm) treatment of non-aqueous phase liquids. White Paper, VeruTEK Technologies, Inc. www.verutek.com (2008).
- 54 Kolthoff IM and Stenger VA, *Volumetric Analysis*. Interscience Publishers, Inc., New York, NY (1947).
- 55 Lingane JJ, *Volumetric analysis, Volume III. Titration methods: oxidation-reduction reactions*. *J Am Chem Soc* **80**:2599–2600 (1958).
- 56 Hydrocarbons ETP, as Gasoline and Diesel SW-846 Method 8015B. Revision (1996).
- 57 Elloy FC, Teel AL and Watts RJ, Activation of persulfate by surfactants under acidic and basic conditions. *Ground Water Monit R* **34**:51–59 (2014).
- 58 Forsey SP, Thomson NR and Barker JF, Oxidation kinetics of polycyclic aromatic hydrocarbons by permanganate. *Chemosphere* **79**:628–636 (2010).