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Comparative analysis of SEAR, ISCO, and S-ISCO for remediation of aged hydrocarbon-contaminated soils

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ABSTRACT

This study evaluates the effectiveness of Surfactant-Enhanced Aquifer Remediation (SEAR), In Situ Chemical Oxidation (ISCO), and Surfactant-Enhanced In Situ Chemical Oxidation (S-ISCO) for remediating aged fuel-contaminated soil. Experiments were conducted using real sandy loam soil contaminated with 5556 mg/kg of Total Petroleum Hydrocarbons (TPHs). The study employed two surfactants: anionic sodium dodecyl sulfate (SDS) and nonionic E-Mulse® 3 (E3), both at 5 g/L, and sodium persulfate (PS) 40 g/L activated with 13.5 g/L NaOH as the oxidant.

Column experiments were performed, simulating field conditions by injecting six pore volumes (PV 26-29 mL each) of treatment solutions over 480 h. SEAR tests achieved TPH removals of 12.3 % with SDS and 14.8 % with E3, highlighting effective desorption but necessitating more PVs or higher surfactant concentration and on-site treatment of extracted solutions. ISCO with alkaline PS removed 23 % of TPHs, indicating limited oxidant access to sorbed contaminants. S-ISCO showed superior performance, achieving TPH removals of 44.2 % with SDS and 39.3 % with E3, eliminating the need for contaminated effluent extraction and treatment on site. The use of SDS demonstrated lower non-productive oxidant consumption and slighter oxidation efficiency enhancement. These findings underscore S-ISCO potential for improving TPH degradation, optimizing resource use, and reducing operational complexities in field applications.

1. Introduction

The contamination of soil and groundwater by petroleum-based hydrocarbons, collectively known as Total Petroleum Hydrocarbons (TPHs), is a persistent environmental issue with far-reaching impacts on ecosystems and public health. Hydrocarbon spills, originating from industrial accidents, leaking underground storage tanks, or other sources, release complex mixtures of organic compounds into the subsurface [1–5]. These compounds present unique challenges for remediation due to their hydrophobic nature, low solubility in w1ater and strong affinity for soil particles [2].

Over time, hydrocarbons can diffuse into soil micropores and adhere to fine-grained particles, leading to aged contamination that is resistant to treatment [6,7]. This persistent binding limits the mobility and bioavailability of TPHs [8], making conventional methods like bioremediation or in situ chemical oxidation (ISCO) [9] less effective, needing bio-stimulation [10,11] or higher oxidant dosages [12] and prolonged times or multiple injections. This problem is even more critical in aged contamination, where hydrocarbons are tightly bound to soil particles, making desorption a significant bottleneck for bioremediation processes [13,14] and ISCO. In addition, the presence of natural soil organic matter and minerals also leads to non-productive consumption of the oxidant, reducing the overall efficiency of the process. This limitation underscores the need for strategies that enhance the interaction between oxidants and contaminants, particularly in aged, hydrophobic contaminant scenarios [12,15,16].

The use of surfactants in soil remediation has become increasingly widespread to address the hydrophobic nature of contaminants and facilitate their transition from soil to the aqueous phase. This approach enhances the desorption of contaminants from the soil matrix, making it an effective method for treating sites impacted by hydrocarbon contamination [17–20].

Soil washing (SW) is a conventional method that involves excavating contaminated soil and treating it with aqueous solutions or surfactants to remove pollutants [21,22]. Although effective for near-surface contamination [23,24], this method becomes impractical for deeper contamination, particularly in the saturated zone or groundwater table (phreatic zone). The logistical and economic challenges of excavating deep soil layers make in situ remediation methods more appealing and

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Nomenclature

Abbreviation

TPHs	Total Petroleum Hydrocarbons
ISCO	In Situ Chemical Oxidation
SW	Soil Washing
SEAR	Surfactant Enhanced Aquifer Remediation
NAPL	Non Aqueous Phase Liquid
DNAPL	Dense Non Aqueous Phase Liquid
CMC	Critical Micelle Concentration
S-ISCO	Surfactant Enhanced In Situ Chemical Oxidation
E3	E-Mulse® 3
SDS	Sodium Dodecyl Sulfate
PS	Sodium Persulfate
IC	Inorganic Carbon
TOC	Total Organic Carbon
MeOH	Methanol
PV	Pore Volume
SFT	Surface Tension
EPA	Environmental Protection Agency (from USA)
GC	Gas Chromatography
MSD	Mass Spec Detector
FID	Flame Ionization Detector
ID	Inner Diameter
NOD	PS Consumption
PAH	Polycyclic Aromatic Hydrocarbons

Symbols

L	Column length (cm)
W	Mass (g)
PV	Pore Volume (mL)
C	Aqueous concentration (surfactants in g/L, TPHs in mg/L))
Kd	Partition coefficient
q	Concentration adsorbed in soil (surfactants in g/kg, TPHs in mg/kg)
V_L	Volume of Liquid (L)
X	TPHs reduction in soil (%)
x	Pore volume number
NOD	PS consumption (g/kg)
N'_{PS}	PS consumption exclusively for TPHs oxidation (g/mg)
$r\text{-}_{PS}$	Average rate of oxidant consumption
t	Time (h)

Subscripts

S	Surfactant
0	Initial
PS	Sodium Persulfate
NaOH	Sodium Hydroxide
j	SDS, E3 or TPHs
SDS	Sodium Dodecyl Sulfate
E3	E-Mulse® 3
EQ	Equilibrium
TPHs	Total Petroleum Hydrocarbons
PV	Pore Volume
total	Total sum in all PVs
soil	Soil phase
removed	Removed
to	Theoretical value
soil	Soil phase
removed	Removed
teo	Theoretical value

necessary. Surfactant Enhanced Aquifer Remediation (SEAR) is attracting the attention of researchers and technicians to overcome this disadvantage [25,26].

SEAR is an advanced approach developed to address the challenges posed by the low solubility and limited bioavailability of hydrocarbons in contaminated sites [25–30]. This method involves injecting surfactant solutions into the subsurface to promote the desorption and mobilization of TPHs. SEAR operates through two primary mechanisms: mobilization and solubilization [26,31]. Mobilization focuses on the physical displacement of NAPLs, reducing the interfacial tension between NAPLs and water. The surfactant facilitates the movement of NAPL droplets trapped in soil pore spaces and enables their extraction. This process is particularly effective for recent spills where NAPLs exist as continuous phases; however, it carries the risk of promoting contaminant migration if not appropriately managed [32–36].

On the other hand, NAPL solubilization is essential for addressing aged contamination [37]. When surfactant concentrations exceed their critical micelle concentration (CMC), micelles form and encapsulate hydrophobic TPH molecules, enhancing their solubility and facilitating their transfer to the aqueous phase [35]. This fact is especially beneficial for residual hydrocarbons strongly adsorbed onto soil particles and difficult to mobilize as free-phase NAPLs. The choice of surfactants is influenced by the type of NAPL and the specific soil characteristics [28, 38–40].

The SEAR treatment presented two disadvantages: i) surfactants can adsorb onto soil particles, reducing their concentration within the aqueous phase. This loss of surfactant can diminish the overall effectiveness of pollutant solubilization. Therefore, minimizing surfactant adsorption and ensuring sufficient active concentration are crucial for the successful application of SEAR in field conditions [41–45], ii) SEAR transfers contaminants from the soil phase to an aqueous phase, which must then be extracted and treated on-site. This shift introduces challenges related to the selective removal of contaminants and the recovery of surfactants from the resulting aqueous solution [46–48]. The treatment process must ensure that contaminants are efficiently separated and eliminated without significant loss or degradation of the surfactant, which can be reused to minimize operational costs and environmental impact [48–50]. This goal often involves additional steps and procedures such as advanced filtration, adsorption techniques, or chemical treatments, each presenting technical and economic challenges [45].

SEAR coupled with ISCO (S-ISCO) has been recently proposed as an innovative approach to eliminate the need for post-treatment processes to handle the emulsions generated in SEAR [51–54]. In S-ISCO, surfactants and oxidants are injected simultaneously into the subsurface, eliminating the need for fluid extraction. Surfactants enhance contaminant availability in the aqueous phase by promoting desorption and solubilization, while chemical oxidants degrade these contaminants directly in situ. This integrated approach combines desorption and oxidation in a single step, reducing the logistical and economic challenges associated with post-extraction treatments, such as contaminant removal and surfactant recovery.

Despite their promise, there are significant gaps in the literature regarding applying SEAR and S-ISCO to real contaminated soils, especially those involving aged contamination [55]. Most existing studies have been conducted under controlled laboratory conditions using artificial contamination [15,56] or simplified soil matrices, which do not reflect the complexity and heterogeneity of real field sites. Most SEAR research relies on batch experiments with high liquid-to-soil ratios [17, 57–59] that maximize contact between surfactants and contaminants, often overestimating the efficacy of SEAR compared to real subsurface applications. These studies fail to replicate the limited contact times and flow dynamics of field conditions, leading to a gap in understanding how

SEAR behaves in real-world scenarios.

The research on S-ISCO is even more limited. While laboratory tests have demonstrated S-ISCO potential, they often do not account for the non-productive reactions between oxidants, surfactants, and soil components in complex field conditions. Moreover, spiked soils are often used [54]. The lack of studies involving column or pilot experiments, which better simulate the heterogeneity and flow regimes found in the subsurface, restricts the current knowledge of how S-ISCO performs at the field scale. Such experiments are crucial for evaluating the distribution of surfactants and oxidants, assessing oxidant consumption, and determining the kinetics of contaminant desorption and degradation.

This research aimed to assess the efficacy of SEAR, ISCO, and S-ISCO for remediating actual, aged fuel-contaminated soil. Two types of surfactants, sodium dodecyl sulfate (SDS) as an anionic surfactant and E-Mulse® 3 (E3) as a nonionic surfactant, were selected for their compatibility with the oxidation system and differing chemical properties. Emulse-3® was selected as a nonionic surfactant due to its lower unproductive oxidant consumption than others like Tween 80 [60], achieving similar LNAPL solubilizations. Surfactants such as Tween 80 or Span 80 are more oxidizable, leading to higher oxidant and surfactant use with lower contaminant conversion. The experiments evaluated oxidant consumption by soil, TPHs and surfactants, quantified surfactant loss through adsorption and degradation, and measured the overall effectiveness in TPH removal. Partition coefficients for TPHs and surfactants were calculated to better understand their distribution between soil and water phases, both with and without surfactants.

Column experiments were chosen to simulate more realistic field conditions than batch testing, which often fails to replicate the complexity of contaminant transport and interactions in the subsurface. By injecting pore volumes of treatment solutions and analyzing the composition of the eluate and remaining soil, this study aimed to draw comprehensive insights into the dynamics of contaminant removal and oxidant efficiency.

Sodium persulfate (PS), activated with an alkali, was chosen as the oxidant for this study due to its high oxidation potential and stability under the soil conditions tested. Unlike hydrogen peroxide, which can rapidly decompose in carbonate-rich soils, sodium persulfate offers sustained reactivity that can be tailored through pH manipulation and catalytic activation [16]. Alkaline-activated PS generates sulfate, superoxide, and hydroxyl radicals (which are potent oxidants capable of mineralizing complex hydrocarbons effectively [60].

This study evaluates SEAR, ISCO, and S-ISCO for the remediation of aged-fuel contaminated soil under field-representative conditions. Unlike previous research on artificially contaminated soils, this work employs real-aged contamination, which poses more significant challenges for remediation. It also provides the quantitative assessment of surfactant losses due to adsorption and non-productive reactions with the oxidant, a key factor in optimizing S-ISCO efficiency for field applications. Furthermore, a comparison between anionic and nonionic surfactants regarding TPH removal and non-productive persulfate consumption, both critical parameters for evaluating treatment efficiency, is considered. To our knowledge, this is an original systematic comparison of SEAR, ISCO, and S-ISCO that incorporates these crucial aspects using real contaminated soils. The comparative analysis of SEAR, ISCO, and S-ISCO methods provides valuable information for selecting the optimal remediation strategy for persistent hydrocarbon pollutants, emphasizing the balance between oxidant effectiveness, surfactant loss, and overall environmental impact.

2. Materials and methods

2.1. Soil

The soil was obtained from an area in Spain contaminated by a fuel spill. It is classified as sandy loam and was collected at a depth of 2.6 m below the surface. The soil was sieved, and the fraction between 0.25 and 1 mm was selected, representing 29 % of the total sieved soil. The following properties were determined: pH, TPH concentration, metal content, and inorganic carbon (IC). The main characteristics are presented in Table 1. The TOC of the soil (not shown) was comparable to the TPH levels, indicating that no other organic compounds were present in the soil at significant concentrations.

2.2. Reagents

The surfactants used in this study were sodium dodecyl sulfate (SDS) and E-Mulse® 3 (E3). The anionic surfactant SDS was chosen due to its common application in soil washing and SEAR applications [29,61–63] and industrial applications and household products, particularly detergent manufacturing [64]. The nonionic surfactant E3, commercialized by EthicalChem, had previously been used for soil TPHs removal [65]. Table SM-1 in the supplementary material details their formulas and chemical properties. Notably, the nonionic surfactant E3 exhibits a lower critical micelle concentration (CMC) than SDS (80 m/L and 1800 mg/L, respectively).

Sodium persulfate (PS) from Fisher Scientific, activated with sodium hydroxide (NaOH, Fisher Scientific), was the oxidizing agent due to its proven efficacy in eliminating organic contaminants in soil and aqueous environments.

Soil samples were prepared using sodium sulfate (Fisher Scientific) for drying. Hexane (Honeywell) and methanol (MeOH) were employed as extractants. Potassium iodide (Fisher Scientific), sodium hydrogen carbonate (Panreac), sodium thiosulfate pentahydrate (Sigma-Aldrich), and acetic acid (Sigma-Aldrich) were utilized for analyzing oxidant concentration in the aqueous phases. All aqueous solutions were prepared using Milli-Q water.

2.3. Experimental procedure

2.3.1. Partition experiments

Partition experiments were conducted in batch mode by mixing 10 g of soil with 30 mL of an aqueous phase containing surfactant concentrations of 9, 15, and 25 g/L for each of the two surfactants used (SDS and E3) in 40 mL Teflon tubes. The tubes were placed on a rotary shaker for 24 h to ensure equilibrium between the aqueous and soil phases was reached. After this period, the tubes were centrifuged, and the concentrations of surfactant and TPH in the aqueous phase were analyzed.

The selected concentrations were based on previous studies using these surfactants in polluted soils with DNAPL [66]. Experiments were performed in duplicate, with variations remaining below 8 %.

2.3.2. Removal of TPHs experiments

Three remediation treatments—SEAR, ISCO, and S-ISCO—were tested to remediate real soil contaminated with TPHs. The experiments were conducted using a column setup (Fig. 1) under the conditions

Table 1
Soil characterization.

Compound	C, mg/kg
Fe	34673.8
Mg	22334.4
Zn	12038.4
Ni	2423.5
Ca	133372.8
Cu	27118.1
V	110.9
Mn	1172.2
Al	13970.9
Na	4736.2
K	7033.0
IC	42000.0
TPHs	5556
pH	7.1

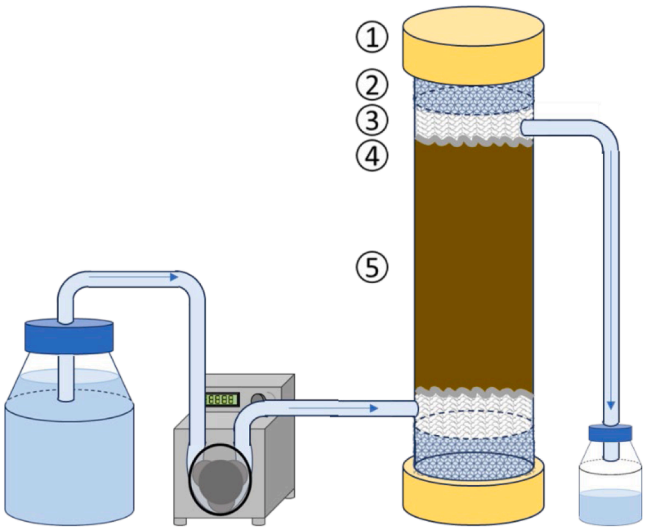

Fig. 1. Scheme of experimental column set up: 1) Silicone stopper; 2) Glass spheres; 3) fiberglass; 4) metallic mesh; 5) soil bed with PV summarized in Table 2.

summarized in Table 2. To ensure a consistent comparison of surfactant and oxidant efficiency across these treatments, this study employs a fixed concentration of both in the SEAR, ISCO, and S-ISCO processes.

Six glass columns were prepared, each with an internal diameter of 3 cm and a length of 6 cm (measured between the inlet and outlet ports). Each column was sealed at the bottom with a silicone stopper, filled with 0.25 mm glass spheres, and layered with fiberglass. Subsequently, a metallic mesh was added to support 55–60 g of densely packed contaminated soil with a pore volume (PV) of approximately 26 mL (the specific soil amount, length, and PV used in each experiment are detailed in Table 2). The columns had an additional metallic mesh, a fiberglass layer encasing the lateral outlet, more glass spheres, and a sealing cap. The aqueous phase was injected through the bottom port using a peristaltic pump (Spetec Perimax 12), while the feed solutions were stored in a glass bottle.

After assembling the columns, a pore volume (PV), as summarized for each run in Table 2, of Milli-Q water was injected to saturate the system and ensure complete soil wetting. The SEAR, S-ISCO, and ISCO treatments involved injecting six successive PVs of the aqueous phase containing the respective reagents into the column. Each injected PV remained in the column for 48–96 h before the subsequent injection. The injected fluid displaced an equivalent volume of liquid already present in the column, and the effluent was collected through the outlet port at the top. The effluent was analyzed to quantify TPHs, surfactant and oxidant concentrations, and pH. After the resting period following the sixth PV injection, the columns were rinsed with Milli-Q water to remove residual reactants. Finally, the columns were dismantled to analyze the remaining TPHs in the soil. A blank run was also carried out by injecting six MilliQ water PVs.

The column experiments were not duplicated for all runs due to sample and time constraints. Duplication was conducted only for runs with oxidant without surfactants (R4) and for those with oxidant and surfactants (R5 and R6) under conditions similar to those used in Table 4 (mass of polluted soil, pore volumes, and column runtime). The values obtained in duplicate for R4, R5, and R6 differ by less than 10 % .

In the first column (R1), Milli-Q water was injected as a blank experiment. The SEAR treatment was tested in columns R2 and R3 with 5 g/L of SDS and E3, respectively. In columns R4, R5 and R6, the ISCO and S-ISCO treatments were tested. In these experiments, two PVs of 13.5 g/L of NaOH solution were fed to the columns after the first Milli-Q injection. The second pore volume was kept in the column for 48 h to ensure the alkalinization of the soil bed. The ISCO treatment used 40 g/L of persulfate activated with 13.5 g/L NaOH. Columns R5 and R6 were treated with alkaline persulfate under the same conditions as R4 but with 5 g/L SDS in R5 and 5 g/L E3 in R6. The experimental conditions used in the PV injected are summarized in Table 2.

2.4. Analytical methods

Oxidant concentration in aqueous effluents was analyzed using iodometric titration. A solution of KI and $NaHCO_3$ (60 mL with 64 g/L and 3.2 g/L, respectively) was prepared, and 0.1 mL of the aqueous sample was added. After 15 min of magnetic stirring, the sample was titrated using 1.35 g/L sodium thiosulfate solution. The process used TIAMO® software (Metrohm), a specialized Pt redox probe, and a 905 Titrando module (Metrohm). The pH of the samples was measured using a Metrohm pH electrode.

The SDS concentration in the aqueous effluents was measured using the methylene blue method [67]. The E3 concentration was measured by the automated determination of the CMC by measuring the SFT at different dilutions with a Krüss Tensíio. Surface tension was measured using the wetting force of the sample on a platinum plate or rod. The surfactant concentration was established as the product of the E3 CMS (80 mg/L) and the dilution value.

Total organic carbon (TOC) and inorganic carbon (IC), both liquid and solid samples, were analyzed using a TOC-V CSH (Shimadzu) and the SSM-5000A module for solids, respectively. For IC, 35 % phosphoric acid was used.

TPHs in aqueous samples were analyzed by extraction with hexane, using a hexane-to-aqueous sample volume ratio between 0.2 and 4, depending on the surfactant concentration in the aqueous phase. NaCl was added to the aqueous phase before the extraction to enhance phase separation. TPHs in soil samples were extracted using a 50 % hexane/acetone mixture at 110 °C in an ETHOS ONE, following the EPA method 3546. Before the analysis, the organic extract phase was filtered with a nylon membrane (0.22 μm). These samples were analyzed using GC-MSD or GC-FID with an HP5-MSUI column (30 m length × 0.25 mm ID × 0.25 μm film thickness). Helium was the carrier gas at a 1 mL/min flow rate. The GC oven was operated with a programmed temperature gradient initially held at 60 °C for 6 min, then ramped at 7.35 °C/min up to 300 °C, where it was maintained for 13 min. The aliphatic and aromatic fractions in the extracted TPHs were measured by SPE using a standard procedure using Resprep EPH Fractionation SPE (Restek, cat. # 25999) cartridges. Hexane and methylene chloride were used as elution dissolvents for aliphatic aromatic fractions respectively.

Metal Content in Soil Samples was measured after acid digestion performed in ETHOS ONE (EPA 3051A) using nitric and hydrochloric

Table 2
Experimental conditions for runs carried out in the column setup. 6 PV injections. Soil bed density 1.56 g/cm³.

RUN	Treatment	L soil, cm	W soil,g	PV, mL	total time,h	Surfactant	C_{So}, g/L	C_{PSo} g/L	C_{NaOHo},g/L
R1	Blank	4.2	47	28	480	—	0	0	0.0
R2	SEAR	4.5	49	27	480	SDS	5	0	0.0
R3	SEAR	4.3	47	28	480	E3	5	0	0.0
R4	ISCO	3.9	42	29	480	—	0	40	13.5
R5	S-ISCO	5.0	55	26	456	SDS	5	40	13.5
R6	S-ISCO	5.1	56	26	456	E3	5	40	13.5

acids. The sample was heated to 175 °C and maintained for 5.5 min. The extract was diluted with methanol and analyzed for metals using microwave plasma atomic emission spectroscopy (Agilent, MP4100-AES).

3. Results

3.1. Surfactant and TPHs partitioning

Partition coefficients (Kd_j) for the surfactants and TPHs were calculated considering their distribution between soil and the aqueous phase. The concentrations of the species in the aqueous phase were measured after 24 h of batchwise contact. Eq. (1) was used to estimate the partition coefficients.

$$Kd_j = \frac{q_j}{C_j} \quad j = \{SDS,\ E3,\ TPHs\} \tag{1}$$

Let q_j and C_j be the concentration adsorbed onto the soil, in g/kg for SDS and E3 (mg/kg for TPHs) and the concentration in the aqueous phase, in g/L for SDS and E3 and in mg/L for TPHs, respectively.

The experimental results of the surfactants and TPHs concentrations in soil and aqueous phases and the corresponding Kd_j values are summarized in Table SM- 2. In addition, the latter values are represented in Fig. 2 for E3 and SDS and Fig. 3 for TPHS. These *Kd* values are in the range previously reported in the literature for anionic and nonionic surfactants [17].

As shown in Fig. 2, E3 (nonionic surfactant) had higher *Kd* values than SDS (anionic surfactant). The difference indicates that E3 was more likely to be absorbed onto the soil surface than SDS. This observation aligns with the reported in the literature that nonionic surfactants often demonstrate stronger adsorption due to reduced electrostatic repulsion and increased hydrophobic interactions with soil particles [24,66]. As a result, while SDS presents lower soil affinity, potentially minimizing loss through adsorption, E3 surfactant increased adsorption could affect its overall availability in the aqueous phase. The data in Fig. 2 were fitted to the Langmuir isotherm summarized in Eqs. (2) and (3) for SDS and E3, respectively.

$$Kd_{SDS}\left(\frac{L}{kg}\right) = \frac{0.367}{1 + 0.090 \cdot C_{SDS}\left(\frac{g}{L}\right)} \tag{2}$$

$$Kd_{E3}\left(\frac{L}{kg}\right) = \frac{0.790}{1 + 0.071 \cdot C_{E3}\left(\frac{g}{L}\right)} \tag{3}$$

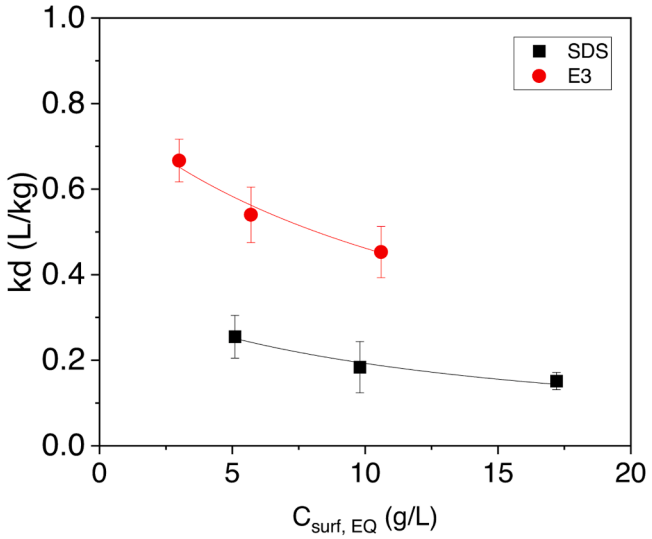

Fig. 2. Soil and aqueous phase partition coefficients of surfactants.

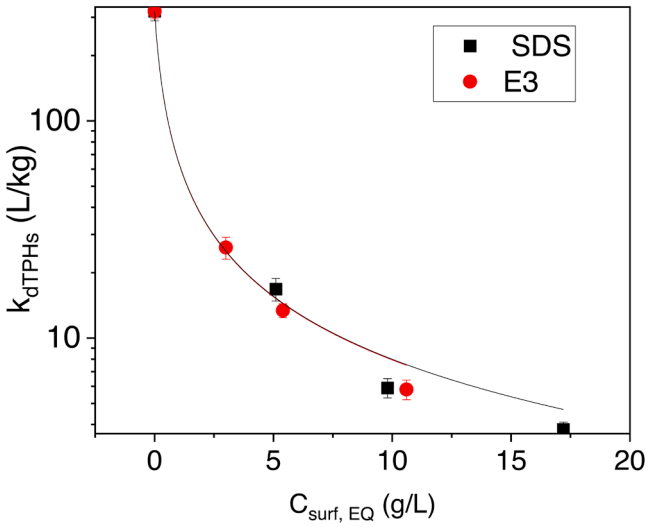

Fig. 3. Partition coefficient values of TPHs between the soil and aqueous phases.

An asymptotic Kd value in Fig. 2 indicates that soil adsorption follows a non-linear trend as the surfactant concentration increases. E3 reaches a maximum adsorption of approximately 11 g/kg of soil for aqueous-phase concentrations above 15 g/L. This behavior aligns with previous findings for the same surfactant in soils heavily contaminated with DNAPL from a long-term pollution event spanning over 20 years [52], where contaminants were found to reduce surfactant adsorption.

In the case of SDS, the asymptotic adsorption value is lower than that of E3, reaching approximately 7 g/kg of soil for concentrations exceeding 15 g/L.

Fig. 3 represents the partition coefficient of TPHs between soil and aqueous phases. As can be seen, the partition coefficients of TPHs are higher than those obtained for the surfactants. This experimental evidence indicates that surfactants demonstrate comparatively lower affinity for the soil, facilitating TPHs desorption into the aqueous phase. This affinity contrast suggests a favourable role for surfactants in enhancing TPHs desorption from soil, supporting their potential for remediation applications.

The desorption behaviour of TPHs in the presence of E3 and SDS showed similar *Kd* values for TPHs across both surfactants, indicating comparable effectiveness in solubilizing TPHs. Although SDS may present lower biodegradability than E3, its solubilizing capacity remains similar, suggesting both surfactants are viable for TPH desorption from soil. Thus, SDS lower adsorption could be advantageous regarding operational costs and environmental impact, although E3 higher biodegradability might still favor it in applications where environmental persistence is a concern. Values of K_{dTPH_s} obtained by Ritore et al. using four surfactants and different types of soil to remediate gasoline and diesel-contaminated soils (initial TPHs in soil = 8530 mg/kg) at batch conditions (V_L/W_{soil} = 8 L/kg) and surfactant concentration of 15 g/L have been calculated from their data and values obtained are shown in Table SM-3 [17]. As observed, the values obtained in this study fall within the range of those calculated from the data reported by Ritore et al.

The following relationship between the TPHs partition coefficient, K_{dTPHs}, and surfactant concentration in the aqueous phase at equilibrium conditions has been established for both surfactants:

$$K_{dTPHs}\left(\frac{L}{kg}\right) = \frac{320}{1 + 3.92 C_S\left(\frac{g}{L}\right)} \quad S = SDS,\ E3 \tag{4}$$

3.2. Column runs

3.2.1. Blank experiment

The soil in R1 was treated by injecting six pore volumes (PVs) of Milli-Q water. The average concentrations of the TPHs in the aqueous phases eluted from the column were around 17.6 mg/L, similar to those observed in batch tests without surfactant. The treatment efficiency X_{TPHs}(%) was calculated as the reduction of TPHs in soil with Eq. (5).

$$X_{TPHs}(\%) = \left(1 - \frac{q_{TPHs}}{q_{TPHs_0}}\right)\cdot 100 \quad (5)$$

Being the q_{TPHs} and q_{TPHs_0} the concentration of TPHs in the soil after and before the treatment, respectively in g/kg.

In R1, the concentration of TPHs in soil was 5496 mg/kg after the six PVs injection, obtaining a TPH removal efficiency of less than 1.5 % of the initial concentration. This limited effectiveness underscores the necessity for more advanced methods to improve TPH removal.

3.2.2. SEAR runs

SEAR treatments using SDS and E3 were applied in R2 and R3, respectively. The TPH and surfactant concentrations were measured in the aqueous phase eluted after each PV injection. The remaining TPHs in soil ($q_{TPHs}(x)$) and the cumulative surfactant adsorption ($q_S(x)$) after each PV can be calculated with the mass balance in Eqs. (6) and (7).

$$q_{TPHs}(x) = q_{TPHs_o} - \frac{\sum_1^x C_{TPHs}(x)\cdot PV(x)}{W_{soil}} \quad (6)$$

$$q_s(x) = \frac{\sum_1^x (C_{s_o} - C_s(x))\cdot PV(x)}{W_{soil}} \quad s = \{SDS,\ E3\} \quad (7)$$

where $PV(x)$ is the pore volume (L) being x the PV number from 1 to 6, and W_{soil} is the soil mass (kg) summarized in Table 2. $C_{TPHs}(x)$ in mg/L and $C_s(x)$ in g/L are the concentration of TPHs and surfactants eluted with each $PV(x)$, respectively. C_{s_o} correspond to the surfactant concentration in the solution injected.

The results are summarized in Table 3 and Fig. 4 for R2 and R3 experiments. Additionally, using these values, the partition coefficients of surfactants and TPHs in the aqueous and soil phases were calculated for each pore volume (PV) using Eq. (8), assuming equilibrium was reached in each injected-eluted PV.

$$Kd_j(x) = \frac{q_j(x)}{C_J(x)} \quad j = \{SDS,\ E3,\ TPHs\} \quad (8)$$

After eluting the final PV and disassembling the column, the remaining TPHs concentration in the soil, q_{TPHs}, was determined and compared to q_{TPHs}(6). The results for surfactant and TPH concentrations in each pore volume, the remaining concentration in the soil after column disassembly, and the TPH mass balance are also shown in Table 3.

As seen in Table 4, the surfactant concentration in the emulsion eluted from the column increased with the number of PVs injected in both R2 and R3, eventually reaching 5 g/L, the initial surfactant concentration injected. This finding indicates that the amount of surfactants adsorbed by the soil decreased with successive PV injections. The *Kd* values of SDS and E3 in each PV summarized in Table 3, matched the values predicted by Eqs. (2) and (3), confirming that equilibrium of surfactant adsorption was achieved in each injected and eluted PV during the SEAR runs.

After six pore volumes, results demonstrated a nearly 10-fold increase in eluted TPH concentrations with surfactant compared to pure water elution. The *Kd* values calculated from TPH concentrations in the soil and aqueous phases were consistent with those predicted by the equilibrium isotherm in Eq. (4), confirming that the partitioning equilibrium of TPHs between phases was achieved. Moreover, the calculated remaining TPH concentration in the soil after six PVs, using Eq. (6), closely matched the measured TPH concentration following column disassembly.

3.2.3. ISCO run

The ISCO test was performed in column R4. Six pore volumes (PVs) were injected, with a total residence time of 480 h for the aqueous phase containing the oxidant solution within the soil column. Experimental results obtained are shown in Table 4.

The TPH removal in R4, calculated with Eq. (5), was 23 %, lower than the yields reported in other studies. Lominchar et al. [68] achieved TPHs removal exceeding 50 % after 20 days of treatment using alkaline-activated persulfate in batch mode. This discrepancy can be attributed to the higher aqueous-to-soil ratio, the elapsed reaction time used by Lominchar et al., and the different nature of the contamination and soil [16].

The pH was above 12, and the average persulfate concentration in the pore volumes (PVs) eluted from the column was approximately 22 g/L. The oxidant demand in each PV $OD(X)$was evaluated by Eq. (9)) while the average oxidant consumption rate over each PV time ($\bar{r}_{PS}(x)$), was calculated with Eq. (10). The total oxidant demand (OD) was determined with Eq. (11). It was assumed that persulfate (PS) was exclusively consumed for TPH removal, and the mass of PS used per mass of TPH removed (N'_{PS}) was obtained with Eq. (12)). The values of these parameters, along with the remaining TPH concentration in the soil after extraction in R4, are summarized in Table 4.

Table 3
Experimental results obtained in SEAR experiments. q_{TPHs_o}=5561 mg/kg. $PV(x)$=28 mL, W_{soil}=48 g C_{s_o}=5 g/L.

RUN	Surfactant	PV	Time PV (h)	Cs g/L	qs g/kg	$C_{TPH}(x)$ (mg/L)	$q_{TPH}(x)$ mg/kg	Kd_s (L/kg)	Kd_{TPH} (L/kg)	pH
R2	SDS	1	72	3.9	0.6	221.4	5439.9	0.16	24.6	7.1
		2	96	4.3	1.0	319.8	5263.8	0.23	16.5	6.7
		3	72	4.7	1.2	236.4	5133.6	0.25	21.7	6.7
		4	96	4.9	1.2	256.1	4992.6	0.25	19.5	6.9
		5	72	5	1.2	264.9	4846.7	0.24	18.3	6.7
		6	72	5	1.2	201	4736.0	0.24	23.6	7.0
		$q_{TPH,\ soil}$, mg/kg extracted							4880.6	
		X_{TPHs}, %							12.25	
R3	E3	1	72	3	1.2	235	5421.6	0.39	23.1	7.1
		2	96	3.2	2.3	265	5263.4	0.71	19.9	6.7
		3	72	3.8	3	253	5112.4	0.78	20.2	6.7
		4	96	4.4	3.3	288	4940.5	0.75	17.2	6.8
		5	72	4.8	3.4	298	4762.6	0.72	16	6.8
		6	72	5	3.4	273	4599.7	0.69	16.8	7.0
		$q_{TPH,\ soil}$, mg/kg extracted							4735	
		X_{TPHs}, %							14.87	

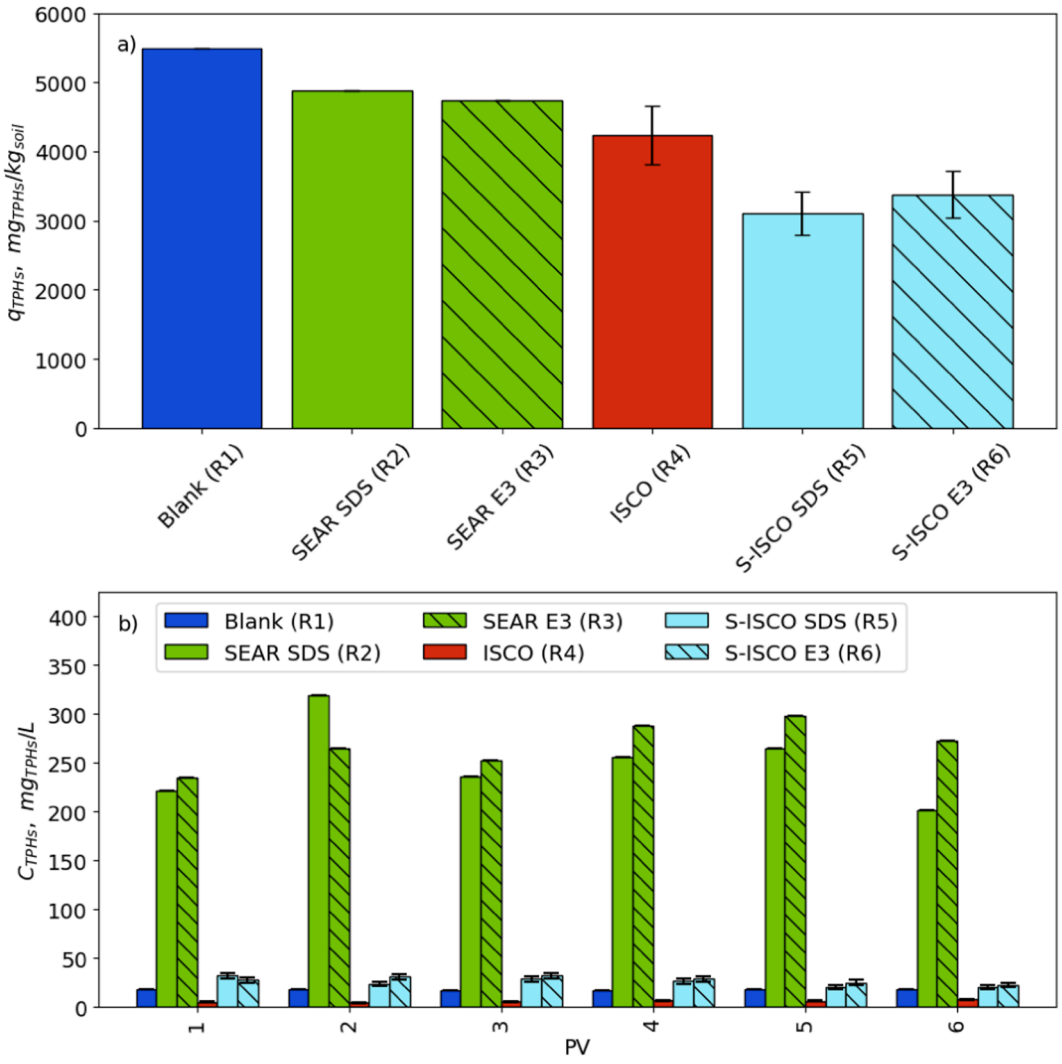

Fig. 4. Comparison of the treatments tested to reduce the TPHs in the soil a) remaining TPH concentration in the soil after 6 PVs injection b) TPH concentration in the aqueous phase eluted from the column after injection and resting time for each PV.

Table 4
Results in ISCO run. C_{PSo}=40 g/L, C_{NaOHo}=13.5 g/L, q_{TPHs_o}=5561 mg/kg. ***PV*** (***x***)=28 mL, W_{soil}=42 g.

RUN	PV	Time PV (h)	$C_{TPH}(x)$ (mg/L)	$C_{PS}(x)$, (g/L)	OD(x) (g_{PS}/kg_{soil})	$r_{PS}(x)$ ($g_{PS}/kg_{soil}.h$)	pH
R4	1	72	4.8	17.9	15.14	0.21	13.5
	2	96	4.2	17.2	15.61	0.163	13.5
	3	72	5.3	24.3	10.71	0.149	13.1
	4	96	6.7	19	14.36	0.15	13.4
	5	72	6.3	23	11.62	0.161	12.9
	6	72	7.5	24.3	10.71	0.149	12.6
	$q_{TPH,\ soil}$, mg/g extracted					4240	
	X_{TPHs}, %					23.8	
	OD_{TOTAL}, g_{PS}/kg_{soil}					78.2	
	$r_{PS}(6)$, g_{PS}/kg_{soil}					0.163	
	N'_{PS}, g_{PS}/mg_{TPHs}					0.059	

$$OD(x)\left(\frac{g}{kg}\right) = \frac{(C_{PSo} - C_{PS}(x))\cdot PV(x)}{W_{soil}} \quad (9)$$

$$\bar{r}_{PS}(x)\left(\frac{g_{PS}}{kg_{soil}.\ h}\right) = \frac{OD(x)}{\mathrm{t(x)}} \quad (10)$$

$$OD_{total}\left(\frac{g}{kg}\right) = \sum_{x=1}^{6} OD(x) \quad (11)$$

$$N'_{PS}\left(\frac{g_{PS}}{mg_{TPHs_{removed}}}\right) = \frac{OD_{total}}{\left(q_{TPHs_o} - q_{TPH_{soil}}\right)} \quad (12)$$

Where C_{PSo} and C_{PS} represent the oxidant concentrations injected and eluted at each x-th pore volume, respectively.

The observed OD for each PV at 72-96 hours ranged between 10–15 g of oxidant per kg of contaminated soil. The consumption of oxidant was higher than ODs reported for nonpolluted soils 1–5 g/L under similar

contact times [69–71]. The latter was explained for the presence of TPHs adsorbed in soil.

The rate $\bar{r}_{PS_x}$ was found to be slightly higher (0.21 g PS/kg soil·h) for the first PV but remained constant in subsequent PVs (0.15-0.16 g PS/kg soil·h), suggesting a correlation with TPH removal. The experimental values of N'_{PS} can be compared with the corresponding theoretical value for total mineralization of TPH calculated by Eq. (13), with an average TPHs formula of $C_{17}H_{34}$ (molar mass = 288 g/mol).

$$C_{17}H_{34} + 102\ OH\cdot \rightarrow 17CO_2 + 68\ H_2O \quad (13)$$

The reactions of persulfate (PS) generating radicals through alkaline activation are Eqs. (14) and (15) [72].

$$2S_2O_8^{2-} + 2H_2O \xrightarrow{OH^-} 3SO_4^{2-} + SO_4^{\cdot-} + O_2^{\cdot-} + 4H^+ \quad (14)$$

$$SO_4^{\cdot-} + OH^- \rightarrow SO_4^{2-} + OH^{\cdot} \quad (15)$$

The reactive oxidant species generated during the alkaline activation of persulfate include hydroxyl and superoxide radicals. As can be seen in Eqs. (14) and (15), 2 moles of PS forms 1 mole of $OH^{\cdot}$, so 204 mole of PS would be necessary to mineralize 1 mole of TPHs. Under this assumption $(N'_{PS})_{teo}$= 0.18 g of PS per mg of TPHs for complete mineralization. This value is likely overestimated since the potential role of other radicals, such as superoxide, $O_2^{\cdot-}$, in the oxidation of TPHs is not considered. For this reason, the theoretical PS requirement for TPHs mineralization (assuming as $C_{17}H_{34}$) could range between 0.18 and 0.09 g per mg of TPH mineralized. Additionally, TPHs may contain compounds such as PAHs, which have a lower H/C ratio than that assumed for alkanes, further reducing the stoichiometric oxidant demand. In the R4 column test, approximately 0.06 g of PS reacted per mg of TPH removed. Therefore, the complete mineralization of removed TPHs cannot be ensured.

3.2.4. S-ISCO runs

In the S-ISCO tests, 6 pore volumes (PVs) were introduced into columns R5 (with SDS surfactant) and R6 (with E3 surfactant). Each pore volume contained 40 g/L of PS (persulfate) and 5 g/L of the corresponding surfactant. The results are shown in Table 5, which presents the concentrations of TPHs, oxidants, and surfactants and the pH levels of each PV eluted from the respective columns. It also shows the residual concentration of TPHs in the soil after extraction and the percentage of TPHs removal. Using the results in Table 5 the parameters OD, $\bar{r}_{PS}(x)$ and N'_{PS} were calculated using Eqs. (10) to (13).

As shown in Table 5, the surfactant concentration in the eluted PVs was lower in the first PV than in subsequent PVs, regardless of the surfactant used. This observation can be attributed to higher surfactant adsorption during the first PV, which decreased to in subsequent PVs. A similar trend was observed during the SEAR tests conducted in R2 and R3. However, during the S-ISCO tests, the surfactant concentration at the column outlet after the first PVs reached an asymptotic value lower than the concentration fed into the column, even after injecting 6 PVs (contrary to the behavior observed in SEAR runs R2 and R3). This finding confirms that a reaction occurred between the oxidant and the surfactant during S-ISCO, with surfactant E3 exhibiting higher reactivity than SDS.

The PS concentration eluted with the first PV was lower than that found in run R4 (ISCO) in Table 4. However, the PS concentration increased in subsequent PVs, stabilizing at nearly constant values from the third PV onward. Notably, the eluted PS concentration was higher in the SDS test (R5) compared to the E3 test (R6). When SDS was used (R5), the total oxidant demand (OD) across six PVs was comparable to that observed in the R4 test without surfactant. In contrast, the non-oxidative demand (OD) measured in R6 with E3 surfactant was slightly higher than with SDS, confirming that E3 leads to greater non-productive PS consumption ([52]). This observation aligns with the higher SDS concentrations detected in the eluted PVs from column R5 compared to the E3 concentrations in column R6.

The lower non-productive PS consumption in SDS explains the higher surfactant concentration in the eluted PVs. Despite the similar solubilization capacity of E3 and SDS observed in partition experiments, the more selective oxidant utilization for TPH removal when SDS was employed explains the moderately higher TPH removal efficiency with SDS (44 %) compared to E3 (39 %). However, considering the experimental error in the duplicate runs R5 and R6 (less than 10 %), the differences in removal efficiencies may be smaller.

The obtained N'_{PS} values (0.032 and 0.043 $g_{PS}/mg_{TPHs_{removed}}$, for SDS and E3, respectively) are lower than expected for TPHs mineralization. This finding likely indicates that TPHs are not fully mineralized but become more biodegradable as oxygen is incorporated into their structures.

It is important to note that persulfate remained in the eluted PVs, indicating that longer residence times in the column could have resulted in higher TPH conversion rates. Over time, surfactant concentrations would also decrease due to oxidation processes. This gradual reduction of surfactants after injection would lower the concentration of

Table 5
Results in S-ISCO runs. CPSo = 40 g/L, CNaOHo = 13.5 g/L, qoTPHs = 5561 mg/kg. PV(x) = 26 mL, W_{soil} = 55 g. Csurfo = 5 g/L.

RUN	Surfac.	PV	Time PV (h)	C_S(x) (mg/L)	q_s (g/kg)	C_{TPH}(x) (mg/L)	C_{PS}(x) (mg/L)	OD(x) (g_{PS}/kg $_{soil}$)	r_{PS}(X) (g_{PS}/kg_{soil}.h)	pH
R5	SDS	1	72	1.1	1.8	32	3	17.5	0.243	11.5
		2	72	2.3	3.1	23.6	8.5	14.9	0.206	13
		3	48	2.8	4.1	29	17.3	10.7	0.223	13
		4	72	2.8	5.2	26.5	13.8	12.3	0.171	13
		5	96	3.2	6	20.1	16.1	11.2	0.117	12.8
		6	97	3.3	6.8	20.1	15.6	11.5	0.119	12.9
		$q_{TPH,\ soil}$, mg/kg extracted								3105
		X_{TPHs}, %								44.2
		OD_{TOTAL}, g_{PS}/kg_{soil}								78.1
		r_{PS}(6), g_{PS}/kg_{soil}h								0.171
		N'$_{PS}$, g_{PS}/mg_{TPHs}								0.032
R6	E3	1	72	1.6	1.6	28	1.2	17.9	0.248	10.5
		2	72	2	3	31	3	17	0.237	11
		3	48	2.5	4.1	32	10.9	13.4	0.28	11
		4	72	2.2	5.4	29	9.4	14.1	0.196	13
		5	96	2.4	6.6	25	6.6	15.4	0.16	12.7
		6	97	2.5	7.8	22	7.2	15.1	0.156	13.1
		$q_{TPH,\ soil}$, mg/kg extracted								3377
		X_{TPHs}, %								39.3
		OD_{TOTAL}, g_{PS}/kg_{soil}								93
		r_{PS}(6), g_{PS}/kg_{soil}h								0.204
		N'$_{PS}$, g_{PS}/mg_{TPHs}								0.043

solubilized TPHs, thereby reducing the potential risk to groundwater. The reduction of TPHs in the soil corresponds to a decrease in dissolved TPHs, driven by partition equilibrium. Additionally, both the anionic surfactant (SDS) and the nonionic surfactant (E3) used in the study are biodegradable over time, with E3 exhibiting a higher biodegradability than SDS.

No precipitation of SDS was observed under the experimental conditions used in S-ISCO, likely due to the surfactant concentrations used and the pH of persulfate activation. However, SDS stability in field conditions with more significant heterogeneity may require further investigation.

3.3. Treatment comparison

The comparison between the three treatments, SEAR, ISCO and S-ISCO, is accomplished by comparing the experimental results obtained for TPH concentration eluted after each PV and the remaining TPH concentration in the soil after the 6th PV. The results are shown in Tables 3, 4 and 5.

Fig. 4a shows the percentage of TPHs removed after injecting six pore volumes (PVs) across different tests outlined in Table 2, and the corresponding conversion of TPHs in soil, calculated by Eq. (5), is shown in Figure SM-1a. The control test (R1) exhibited minimal TPH removal (lower than 2 %), confirming that pump-and-treat methods alone are insufficient for significant contamination reduction. SEAR treatments (R2 and R3), using SDS and E3 surfactants, achieved moderate TPH removal (about 16 %), demonstrating the effectiveness of these methods and their limited capacity at low surfactant concentrations. While increasing the surfactant concentration in R2 and R3 could potentially enhance TPH removal, it may also lead to higher surfactant losses due to adsorption and complicating the on-site handling of the extracted contaminated effluent. In contrast, ISCO treatments showed a marked improvement in TPH removal (about 25 %) compared to SEAR, emphasizing the critical role of chemical oxidation in enhancing contaminant breakdown. The highest removal rates were observed with S-ISCO treatments (44 % and 39 % for R5 and R6, respectively), with SDS (R5) slightly outperforming E3 (R6). These results confirm that combining SEAR and ISCO is a more practical approach for TPH removal. As mentioned earlier, the differences in removal efficiencies between R5 and R6 may be less significant when accounting for experimental error.

Fig. 4b illustrates the TPH concentrations in the eluted PVs. In the ISCO experiment (R4), TPH concentrations in the eluted PVs were approximately 6 mg/L, lower than in control (R1). This fact suggests that the mass transfer of TPHs from soil to the aqueous phase may be the rate-limiting step rather than oxidation within the aqueous phase, as equilibrium concentrations were not reached despite the presence of the oxidant. Furthermore, ISCO treatment avoided the formation of a contaminated emulsion requiring management, though it involved significant oxidant consumption. In the S-ISCO runs, coupling surfactant and oxidant reduced the concentration of TPHs eluted by nearly tenfold compared to the PVs in SEAR experiments (R2 and R3). Therefore, TPHs were effectively degraded by the oxidant, producing a less contaminated emulsion than in SEAR. Unlike SEAR, where pollutants shift phases, S-ISCO facilitated actual contaminant removal, eliminating the need for extracting and treating contaminated emulsions. Based on partition equilibrium, the TPH concentrations in the eluted PVs from S-ISCO were lower than expected, suggesting that desorption from the soil remains the rate-limiting step. However, desorption and contaminant accessibility to the oxidant significantly improved compared to the ISCO test (R4), nearly doubling the TPH removal rate.

Figure SM-1b illustrates the surfactant losses due to adsorption or non-productive consumption during SEAR and S-ISCO tests. In SEAR (R2 and R3), SDS exhibited significantly lower surfactant loss than E3, indicating lower adsorption of the anionic surfactant. In S-ISCO (R5 and R6), both surfactants showed higher losses than in SEAR, with E3 showing the most significant loss, suggesting that under S-ISCO conditions, surfactants react with oxidants, leading to increased consumption. The higher loss of E3 aligns with SDS superior TPH removal due to its lower non-productive consumption. Although S-ISCO proved more effective for TPH removal, it involved greater surfactant consumption, especially with E3. However, unlike SEAR, S-ISCO avoided the formation of contaminated emulsions requiring treatment, simplifying the remediation process despite higher surfactant losses.

Figure SM-1c presents OD after 470 h (6 PVs) for different tests. ISCO and S-ISCO showed a higher OD than expected for clean soil, indicating significant oxidant consumption due to interactions with contaminants or surfactants. S-ISCO with SDS exhibited a similar OD level to ISCO, suggesting that adding SDS did not significantly increase non-productive oxidant consumption. In contrast, S-ISCO with E3 showed the highest OD, implying that E3 leads to greater non-productive oxidant use than SDS and ISCO. Overall, while both surfactants in S-ISCO resulted in slightly higher OD than ISCO alone, SDS demonstrated a more controlled and efficient use of the oxidant, whereas E3 led to increased consumption, slightly reducing the oxidant availability for effective contaminant degradation.

Figure SM1-d displays the mass (g) of oxidant (PS) reacted per mg of TPHs removed in ISCO and S-ISCO. ISCO exhibited the highest amount of PS reacted per mg of TPHs removed, indicating some inefficient oxidant use due to non-productive consumption, likely by soil components or side reactions unrelated to TPH degradation. S-ISCO with SDS demonstrated the lowest mass of PS reacted per mg of TPHs removed, showcasing more efficient oxidant use. This finding suggests that SDS helps direct the oxidant more effectively toward TPH removal, minimizing wasteful consumption. S-ISCO with E3 had an intermediate value—higher than S-ISCO with SDS but lower than ISCO—indicating that while E3 improves the process compared to ISCO, it is less efficient than SDS in optimizing oxidant use for TPH removal. Notably, the theoretical stoichiometric dose for complete TPH mineralization is estimated to be slightly below 0.09 g/mg, suggesting TPHs degraded are not fully mineralized.

The LNAPL adsorbed in the soil consisted of a mixture of non-aromatic and aromatic compounds (PAHs). Before treatment, aliphatic hydrocarbons comprised 70 % of the total TPHs, while PAHs accounted for 30 %. After the S-ISCO and ISCO treatments, the proportion of aliphatic compounds decreased to approximately 60 %, whereas PAHs increased to 40 %. These results indicate that oxidation demonstrated a slightly higher selectivity for linear hydrocarbons over aromatic ones.

Moreover, the distribution of hydrocarbon chain length before and after treatment was evaluated, as shown in Table SM-4. The results suggest that oxidation treatments are more effective at degrading shorter-chain hydrocarbons (C10-C16), while longer-chain hydrocarbons (C17-C35) tend to persist. Notably, the C22-C35 fraction increased in ISCO (R4) and S-ISCO with SDS (R5), likely due to reduced solubilization in these treatments, limiting its availability for oxidation.

4. Conclusions

The comprehensive evaluation of SEAR, ISCO, and S-ISCO techniques for remediating an actual, aged hydrocarbon-contaminated soil provided critical insights into the effectiveness and challenges associated with each method.

Using anionic (SDS) and nonionic (E3) surfactants, SEAR demonstrated moderate TPH removal by enhancing contaminant desorption. SDS exhibited lower adsorption than E3, reducing surfactant consumption and operational costs. However, SEAR generates a contaminated emulsion that requires proper management, increasing the overall cost of treatment.

Alkaline-activated sodium persulfate (PS) effectively oxidized TPHs in aged, contaminated soils during the ISCO process. However, the soil matrix limited TPH removal in this treatment by desorption constraints and non-productive oxidant consumption, resulting in a relatively high

NOD relative to the TPHs removed. This finding highlights the need for strategies to improve oxidant targeting and reduce wasteful reactions.

These limitations were addressed in the S-ISCO treatments, which coupled solubilization with oxidation without needing post-treatment. SDS proved slightly more effective than E3 in controlling oxidant consumption and achieving efficient TPH degradation. While SDS exhibited slighter higher effectiveness than E3, the surfactant selection should consider biodegradability concerns, though both SDS and E3 are expected to degrade within months.

In conclusion, this study demonstrated that S-ISCO is a promising, integrative approach for remediating aged hydrocarbon contamination in real soils. By leveraging the dual benefits of surfactant-enhanced desorption and in situ oxidation, S-ISCO provides a robust solution that enhances contaminant removal while simplifying on-site management and reducing environmental impact.

However, the successful field implementation of S-ISCO requires careful optimization of key operational parameters to enhance efficiency and minimize non-productive oxidant consumption. One critical aspect is the selection of surfactants and oxidants, ensuring compatibility to reduce losses due to side reactions while maintaining effective contaminant desorption. Additionally, injection strategies must account for soil heterogeneity, where pulsed injection techniques can improve reagent distribution and penetration into low-permeability zones. Another crucial factor is determining the optimal residence time, balancing oxidant consumption with TPH desorption kinetics to maximize contaminant removal while minimizing unnecessary oxidant depletion. These considerations provide valuable guidance for adapting S-ISCO to real contaminated sites, improving its applicability as a sustainable and efficient remediation approach.

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CRediT authorship contribution statement

Raúl García-Cervillla: Validation, Methodology, Investigation, Formal analysis. **David Lorenzo:** Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Arturo Romero:** Writing – original draft, Supervision, Funding acquisition, Conceptualization. **Aurora Santos:** Writing – original draft, Supervision, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ceja.2025.100733.

Data availability

No data was used for the research described in the article.

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