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SURFACTANT-ENHANCED MOBILIZATION OF HYDROCARBONS FROM SOIL: COMPARISON BETWEEN ANIONIC AND NONIONIC SURFACTANTS IN TERMS OF REMEDIATION EFFICIENCY AND RESIDUAL PHYTOTOXICITY

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UNIVERSITÀ DEGLI STUDI DI PALERMO

ENGINEERING DEPARTMENT

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Dear Editor,
Please find attached our manuscript entitled "Surfactant-enhanced mobilization of hydrocarbons from soil: comparison between anionic and nonionic surfactants in terms of remediation efficiency and residual phytotoxicity" for possible publication in Process Safety and Environmental Protection.

As corresponding author, I would like to confirm that:
• The submitted manuscript is prepared according to GFA available in the Process Safety and Environmental Protection website.
All authors mutually agree for submitting this paper to Process Safety and Environmental Protection.
The manuscript is an original work of authors.
The manuscript has not been previously submitted to any journals, and will not be submitted elsewhere before a decision is made by Process Safety and Environmental Protection.

This study shows a new study on the feasibility of surfactants application for the remediation of soils contaminated by hydrocarbons, providing useful insight about the extraction efficiency as well as residual soil phytotoxicity.
We are confident that this article can be of particular interest to the readers of Process Safety and Environmental Protection.
Many thanks and I look forward to hearing from you.
Best regards
Federica De Marines

Should you need to contact me, please use the above address or the following references:

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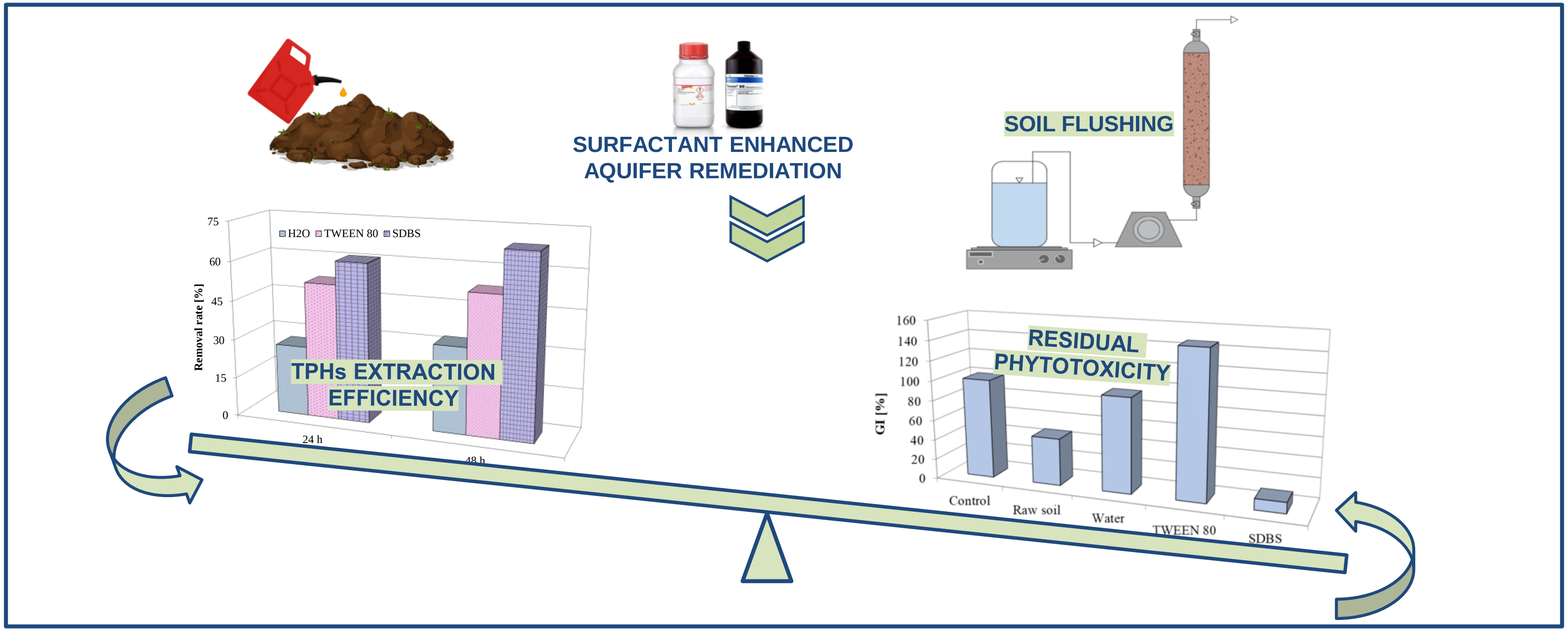
Graphical Abstract



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Abstract

The aim of the present study was to assess the effectiveness of two surfactants (*Polysorbate 80* – Tween 80 and *Sodium Dodecyl Benzensulphonate* – SDBS) for remediating hydrocarbon-contaminated soils. To study the effectiveness of these surfactants, an experimental laboratory-scale apparatus was set up which simulated a soil flushing intervention testing different concentrations of surfactant and washing flow rates. At the end of the experiments, the removal efficiency was evaluated and phytotoxicity tests were performed by means of a germination index (GI). Results showed that the use of both surfactants allows to reach high removal efficiency (~50% for Tween 80 and ~70% for SDBS) of hydrocarbons from soil and that both the surfactant concentration and the contact time between surfactant and contaminant affect the process performance. Results on the GI showed that the two surfactants have different effects on the phytotoxic characteristics of the soil after treatment. Indeed, while the soil treated with SDBS was found to be more phytotoxic, leading to a lowering of the GI (1.088%), the soil samples washed with Tween 80 were characterized by higher values (146.61%). These results might be of interest in the case of surfactant application in remediation interventions in soils intended for future agricultural activity.

Keywords: Soil flushing, Soil remediation, TPH, Surfactants, SEAR, phytotoxicity

1. Introduction

Soil and groundwater contamination caused by organic compounds is one of the most significant side effects of modern anthropic activities (Andrade and dos Santos, 2020). Among these concerns, soil pollution by fuel hydrocarbons is a major and pervasive environmental issue (Tsai et al., 2009; Ma et al., 2013; Silva-Castro et al., 2013; Yan et al., 2016), as they constitute the 50-60% of the primary pollutants affecting soils (Grifoni et al., 2020). Total Petroleum Hydrocarbons (TPH) is a broad category of fuel hydrocarbons primarily derived from crude oil and found in significant quantities in diesel fuels. When exposed to humans and animals, some of these compounds have the potential to cause cancer, central nervous system disorder and adverse effects on liver and lungs (ATSDR, 1999). Accidental spills of crude oil and its byproducts, wastes from petroleum refining, petroleum refining products and leaching of oil storage tanks are the primary sources of TPH in the environment (Haigh, 1996; Zhu et al., 2004; Iturbe et al., 2007). After fuel hydrocarbons are discharged into underground environments, they have the tendency of forming pools of free phase products, known as light non-aqueous-phase liquids (LNAPL), that get caught in the permeable soil medium or rest on top of the water table. Dealing with residual LNAPL presents a significant reclamation challenge, as it is practically immobile, non-dispersible, and therefore unreachable for microbial degradation (Fardin et al., 2021).

Several remediation technologies are available to remove fuel contamination from soils, such as electro-remediation (Page and Page, 2002), ozonation (Goi et al., 2006), solidification/stabilization (Knop et al., 2005), the application of Fenton's reagent (Xu et al., 2006), jet-fluidized bed (Arrar et al., 2007), bioventing and composting (Mao and Yue, 2010), biostimulation (Mariano et al., 2007), in situ bioremediation (Liu et al., 2008), soil washing and soil flushing (Zhou and Hua, 2004; Scullion, 2006). However, conventional water flushing methods have restricted efficacy on LNAPL due to the challenge of generating water flows capable of mobilizing or breaking up the LNAPL phase (Atteia et al., 2013).

Organic amendments (Hoang et al., 2021), solubilization (Kour et al., 2021), desorption (Rodríguez-Garrido et al., 2020), chelation (Sun et al., 2020) and complexation processes (Zhang and Zhou, 2019) can be employed to induce mobilization of contaminants in soil. This results in the relocation of pollutants from the soil-to-soil solution, thus enhancing their mobility and subsequent bioavailability (Fatin-Rouge, 2020; Palansooriya et al., 2020). Several studies investigated a number of amendments to mobilize pollutants from the solid phase and improve their mobility and accessibility for biological uptake (Kumar et al., 2022).

Research findings demonstrated that surfactant-enhanced aquifer remediation (SEAR) can significantly accelerate contaminant-mass removal for such systems (Zhong et al., 2016). Consequently, incorporating surfactants to enhance conventional remediation techniques, such as soil washing, soil flushing and biodegradation processes can be high effective for hydrophobic pollutants (Doong et al., 1998; Mulligan et al., 2001; Torres et al., 2003; López et al., 2004; Vreysen and Maes, 2005; Zhou and Zhu, 2007; Khalladi et al., 2009; Zhang and Zhu, 2010). Surfactants are widely used compounds for soil flushing and contaminants removal (Cheng et al., 2017), as they enhance LNAPL flushing efficiency by reducing the surface tension between LNAPL and groundwater and improving solubilization by promoting micelle formation (Mulligan et al., 2001). Surfactants can have either synthetic or natural origin, and they are categorized according to their ionic charge as anionic, cationic, non-ionic, or zwitterionic (Lamichhane et al., 2017; Moldes et al., 2021; Kumar et al., 2022). Among these categories, anionic and nonionic surfactants are the most used groups in soil remediation process (Karthick et al., 2019).

When the concentration of a surfactant in water surpasses its specific critical micelle concentration (CMC), the formation of micelles occurs (Majeed et al., 2020). These micelles possess characteristics similar to hydrocarbons, thereby facilitating the mobilization of contaminants from the water media (Fatin-Rouge, 2020; Kumar et al., 2022).

Surfactants possess several crucial properties, such as cost-effectiveness, low toxicity, biodegradability and low susceptibility to aggregate clay minerals (Franzetti et al., 2006; Ahn et al., 2008; Zhao et al., 2016; Sakhaei and Riazi, 2022) that make them suitable for soil remediation.

Nevertheless, surfactant application at polluted sites can be challenging. Indeed, if on the one hand they enhance pollutants' solubility, on the other they reduce the availability of the contaminants, and they can have negative effects on indigenous microbial communities (Kumar et al.,2021, 2022). The effectiveness of the surfactant treatment is influenced by several factors, including the surfactants concentration, their hydrophilic-lipophilic balance, the octanol-water partition coefficient (Kow) of the poluttants, soil pH, soil salinity, Dissolved Organic Matter (DOM), temperature, and co-solutes (Lamichhane et al., 2017).

Sodium Dodecyl Sulfate (SDS) and *Sodium Dodecylbenzene-Sulfonate* (SDBS) are two widely utilized anionic surfactants in subsurface remediation applications (Karthick et al., 2019; Sakhaei and Riazi, 2022). Nevertheless, the utilization of such compounds might negatively affect the soil features after treatment, especially in terms of soil phytotoxicity. This aspect could be of particular concern in soils destined to agronomic utilization after treatment.

A number of studies showed that nonionic surfactants are preferred over cationic and anionic surfactants for soil remediation (Qin et al., 2007; Wang and Keller, 2008; Luo et al., 2010; Cheng et al., 2017). Indeed, cationic surfactants can have adverse effects on the environment if not properly managed. Due to their positive charge, they can interact with negatively charged surfaces in soil and sediments, leading to potential sorption and accumulation in these matrices (Zhu et al., 2003; Cheng et al., 2017). Moreover, excessive or prolonged use of cationic surfactants may disrupt soil structure, reduce soil permeability, and impact important soil functions such as water retention and nutrient cycling. On the other side, anionic surfactants can precipitate with soil's cations; this interaction can lead to the formation of insoluble complexes, limiting the availability and extraction of contaminants and can also affect soil structure and aggregation, leading to changes in porosity, water retention and infiltration (Jafvert and Heath, 1991; Cheng et al., 2017). Besides, nonionic surfactants typically exhibit greater solubilization capacities and offer economic advantages (Alcántara et al., 2008; Cheng et al., 2017).

Among the nonionic surfactants, *polyoxyethylene-(20)-sorbitan monooleate* (Tween 80, $C_{64}H_{124}O_{26}$), has gathered particular interest. It possesses all the positive characteristics associated with nonionic surfactants and, in comparison to other nonionic surfactants, it is less expensive and exhibits low toxicity towards soil microorganisms (Fernando Bautista et al., 2009; Liu et al., 2010; Cheng et al., 2017).

In this context, the objective of the present study was to investigate the feasibility of surfactant application for the remediation of soils contaminated by hydrocarbons. In particular, an anionic (SDBS) and a non-ionic (TWEEN80) surfactant were tested, by simulating a soil flushing process carried out on an experimental laboratory scale apparatus. Hydrocarbon removal from soil at different surfactant concentrations and washing flow rates was assesses. Residual phytotoxicity of the washed soils was assessed by means of germination index (GI). The results from this study could provide useful insights about the application of surfactant hydrocarbon extraction from soil, assessing the role of operational parameters in the pollutants' extraction, also highlighting the effect of the investigated surfactants in terms of soil phytotoxicity after treatment.

2. Materials and methods

2.1 Description of the experimental campaign

During the experimental campaign, tests were conducted to simulate a soil flushing remediation on a sandy soil artificially contaminated by diesel fuel. In particular, the hydrocarbon removal efficiency was evaluated in the case of (i) washing with only water and (ii) washing with a solution of water and surfactant; two different types of surfactants were tested, an anionic (SDBS) and a non-ionic (Tween 80) surfactant. For each of these, the influence of the concentration of the solution and the washing flow rate on the removal efficiency was evaluated. Furthermore, at the end of each test, phytotoxic characteristics of the soil were determined by germination index (GI).

The experimental campaign was divided into 3 periods (P1, P2 and P3, respectively). During P1 soil flushing short-term tests were carried out with warm water only and represented the blank control. In particular, four tests were carried out at different flow rates: 2 ml/min, 4 ml/min, 6 ml/min and 8 ml/min. In the second period (P2) the influence of the two surfactants (SDBS and Tween 80) in the washing solution was evaluated in order to determine the optimal condition in terms of surfactant concentrations and flow rate for the remediation of the contaminated soil. For both surfactants, the behavior of four solutions at different concentrations was evaluated: 0.1%, 0.2%, 0.3% and 0.4%. In addition, tests at different flow rates (2 ml/min, 4 ml/min, 6 ml/min and 8 ml/min) were also carried out for all the solutions. During P3, basing on the best results obtained during the first and the second period, long-term flushing tests were carried out at laboratory scale columns. For short-term tests in P1 and P2 a volume of 1 liter was flushed, they had a duration varying from 2 to 8 hours depending on the flow rate and soil samples were taken at the end of each test; while, in P3 each test lasted 48 hours and soil samples were taken after 24 hours of washing and at the end of the test.

2.2 Soil characteristics

Soil sample consisted of quartz sand spiked with a known volume of commercial diesel fuel; in detail, 6% (w/w) of diesel was added to 5 kg of sand to obtain an initial TPH concentration close to 6000 mg/kg_{SS}. Before the start-up of the experimental activity, the sample was manually mixed for several days in order to allow the volatilization of the most volatile components. The choice of using a sandy soil derives from its physical-mechanical properties. The main advantageous property consisted in the dynamics of water into the soil and is due to the high incidence of macroporosity which positively affects the permeability: surface waters, in fact, rapidly infiltrate sandy soils, with positive effects in the prevention of surface stagnation and surface run-off water.

2.3 Surfactant characteristics

The tested surfactants (*Sodium Dodecyl Benzensulphonate* – SDBS and *Polyoxyethylene (20) sorbitan monooleate* – Tween 80) were purchased from *SigmaeAldrich* and were used for the batch flushing experiments.

SDBS is an anionic surfactant, with a molecular mass of 348.48 g/mol and a CMC of 0.612 mM (212.57 mg L^{-1}); while, Tween 80, a non-ionic surfactant, has a molecular mass of 1310 g/mol and a CMC of 0.012 mM (13.1 mg L^{-1}) at 25°C. Main characteristics of both surfactants are reported in Table 1. Tap water was used to prepare solutions containing different concentrations of SDBS and Tween 80.

Table 1. Main characteristics of SDBS and Tween 80

Chemical nomenclature	**CAS number**	**Chemical formula**	**Ionic Nature**	**Molecular mass [g/mol]**	**CMC [mM]**
Sodium Dodecyl Benzene-Sulfonate	25155-30-0	$C_{18}H_{29}NaO_3S$	anionic	348.48	0.612
Polysorbate 80	9005-65-6	$C_{64}H_{124}O_{26}$	non-ionic	1310	0.012

2.4 Experimental apparatus set-up

The experimental apparatus consisted of a Pyrex glass column (d = 2.1 cm, h = 13 cm), equipped at the bottom with a special conical-shaped piece with dimensions of 29/32 mm. For each test, about 80 g of contaminated soil was introduced inside the column. The flushing solution was stored in a storage tank and flushed through the column by means of a peristaltic pump. Figure 1 shows a panoramic view (a) and a schematic layout (b) of the experimental system.

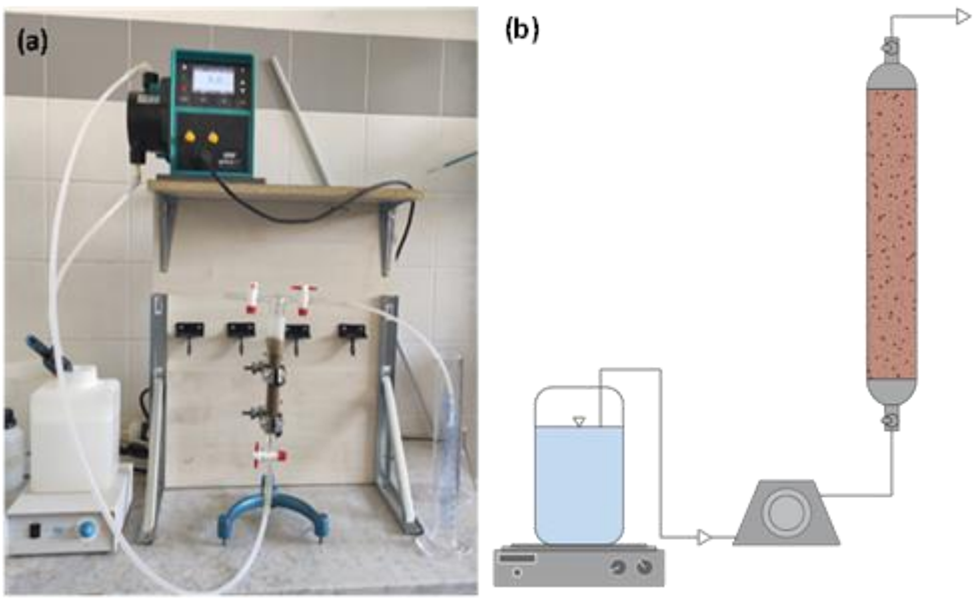

Figure 1. Panoramic view (a) and schematic layout (b) of the experimental apparatus

In each test washing solution was flushed through the contaminated soil sample in upward mode, alternatively with warm water and with a solution of water and surfactant at different concentrations. For each test, the flushing solution was maintained at a temperature of about 30°C and was continuously mixed through a magnetic stirrer. Before running each test, the column was flushed with water at a flow rate of 4 ml/min to remove the air contained in the pores; once the whole sample was saturated, the washing solution was started to be fed to the column.

2.5 Analytical methods

At the end of each flushing test, the soil sample was extracted and dried and subsequently subjected to (i) extraction for the measurement of TPH concentration in the solid phase and (ii) germination test for the evaluation of phytotoxicity.

For the extraction procedure, an aliquot equal to 10 g of the soil sample extracted from the column was taken. The measurement of TPH concentrations on the solid matrix was carried out by following "Procedura per l'analisi degli idrocarburi > C_{12} in suoli contaminati - Manuali e Linee Guida 75/11" proposed by (ISPRA, 2011), which refers to ISO 16703 (2004) and provides, downstream of a phase of extraction and purification on Florisil, analysis by GC-FID.

In detail, TPH concentration was determined by headspace gas-chromatographic analysis using a gas-chromatograph (*Agilent 6890N Network GC System*) equipped with a Flame Ionization Detector (FID) and the column *Agilent 7683 Series*; helium was employed as carrier gas, oven temperature was set at 170°C and injection temperature was 250°C.

The measurement of soil moisture was preliminary to that of TPH, and it was carried out according to the Italian official methodologies for soil analysis (Ministerial Decree 13/09/1999).

At the end of each test, therefore, once the initial $Ci_{,10-40}$ and final $Cf_{,C10-40}$ concentrations of TPH were known, the hydrocarbon removal efficiency was determined using the following formula [1]:

$$\eta = \frac{C_{i,C10-40} - C_{f,C10-40}}{C_{i,C10-40}} \cdot 100 \quad [\%] \qquad [1]$$

APAT method (APAT, 2004) was employed to conduct phytotoxicity tests, which involved seed germination and root elongation . *Lepidium sativum* seeds were used for germination and growth assays on sand aqueous solutions and placed in Petri dishes (90 mm diameter) with one sheet of filter paper as support (Avona et al., 2022).

A negative control, not containing substances that could inhibit germination and root elongation, and various dilutions with soil were prepared for each sample to be tested: in particular, sample-soil concentrations of 25%, 50% and 100% were used, for a total of 10 g of dry mass for each aliquot.

The Petri dishes were placed in a growth chamber at 27°C for 72 hours after being parafilm-sealed to assure closed-system models and. Following this time, the number of seeds germinated was counted and the radical length was measured. The Index of growth (IG) was calculated by multiplying the germinated seed number (G) and length of roots (L). The Germination Index (GI) results were used to calculate the effect, expressed as percentage (GI%), with respect to the control using the following equation [2]:

$$GI = \frac{G_S \cdot L_S}{G_C \cdot L_C} \cdot 100 \quad [\%] \qquad [2]$$

where S and C stands for the samples and the control, respectively.

3. Results and discussion

3.1 Performance of hydrocarbon extraction in the short-term tests

Figure 2 summarizes the TPH residual concentrations as well as removal rate obtained in the washing tests carried out with warm water in P1. The results reported in Figure 2 allow to appreciate the influence of the washing flow rate, and consequently of the contact time, on the extraction of TPH from soil. The contaminant solubilization is favored by the lower washing flow rates corresponding to high contact times. In detail, results showed a reduction in the removal efficiency as the washing flow rate increased, with a maximum removal efficiency of 25% for a flow rate of 2 mL min^{-1}, which decreased to 10% for a flow rate of 8 mL min^{-1}. In depth, a exhaustion trend was observed, as there was no appreciable increase in extraction from 6 to 8 mL min^{-1}; therefore a “limit” of treatment was probably reached for the conditions studied This result is in accordance with the study proposed by Yan et al. (2016) which indicated that water can mobilize and remove a portion of fuel hydrocarbons, also corroborating the results achieved in previous studies (Khalladi et al., 2009; Chien et al., 2011).

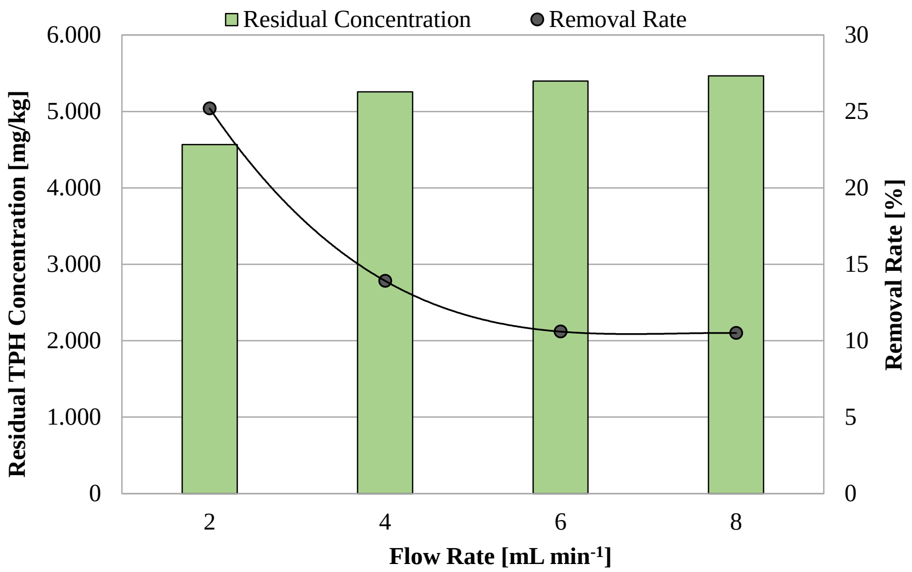

Figure 2. Residual concentration of TPH in soil samples and removal rate after water flushing

Referring to Period 2 and to the flushing tests carried out with Tween 80, Figure 2 shows that the removal rates were almost always higher compared to what observed with water, thus highlighting that the use of surfactant,

Tween 80 in this case, can provide an added value compared to what achievable in flushing tests with water; this result is in line with the hydrophobic nature of these contaminants.
In detail, the results showed that significant increase of hydrocarbon removal can be achieved by increasing both the surfactant concentration and the washing flow rate.

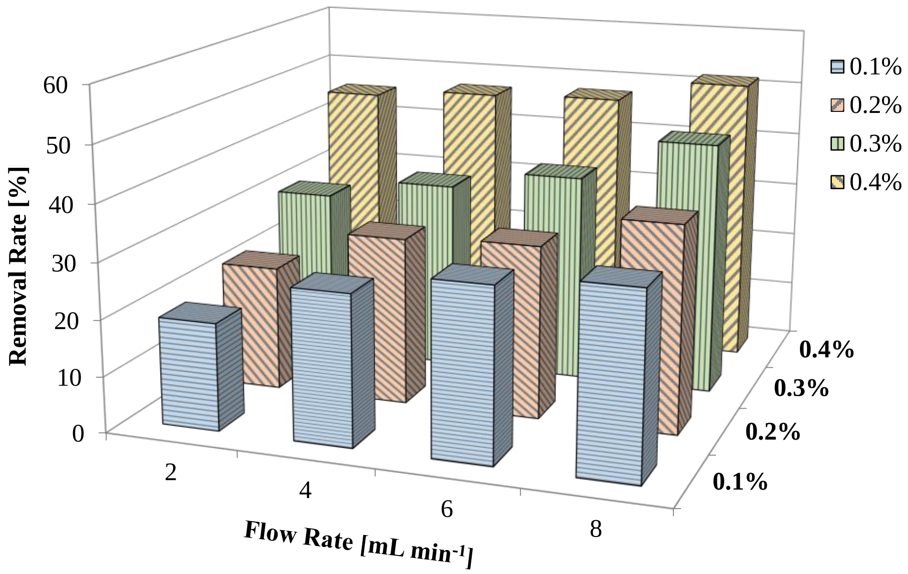

Figure 3. TPH removal rate depending on Tween 80 concentration and flow rate

This increasing trend could be related to: (i) an increase of pollutant solubility, due to the surfactant dosage at concentrations much higher than the CMC and (ii) an increase of the leaching effect of the contaminant, favored by the increase of the flow rate, corresponding to an increase of the upward fluid velocity, also enhanced by the presence of surfactant, contrarily to what observed in the tests with carried out with water. Indeed, the presence of surfactant in the flushed solution reduces the interfacial tension between the hydrophobic contaminant and water; this behavior being emphasized by surfactant concentration: in particular, the higher the surfactant concentration is above the CMC, the greater the number of micelles, thus increasing the solubility of the contaminant (Atteia et al., 2013).
Therefore, data reported in Figure 2 highlighted that the higher efficiency (51.7%) was obtained with a Tween 80 concentration of 0.4% at a flushing flow rate of 8 mL min^{-1}.
As an example, Figure 4 shows the chromatograms obtained from the GC analysis after the extraction and purification procedure for the raw contaminated soil (Figure 4a), contaminated soil washed with water only at a flow rate of 4 mL min^{-1} (Figure 4b) and contaminated soil washed with Tween 80 solution of 0.1%, 0.2%, 0.3% and 0.4% (Figure 4c-f) at a flow rate of 4 mL min^{-1}. From the observation of chromatograms, it can be seen that those related to the soil samples after washing with the surfactant solutions are more flattened (lowering of the peaks) and with the left side much more reduced, compared to those related to the raw contaminated soil and that washed with water only. In particular, in the chromatogram relating to the soil sample washed with Tween 80 at 0.4% (Figure 4f), the lack of the most soluble and volatile part (far left chromatogram) is evident, that is the compounds more effectively mobilized and removed after flushing.

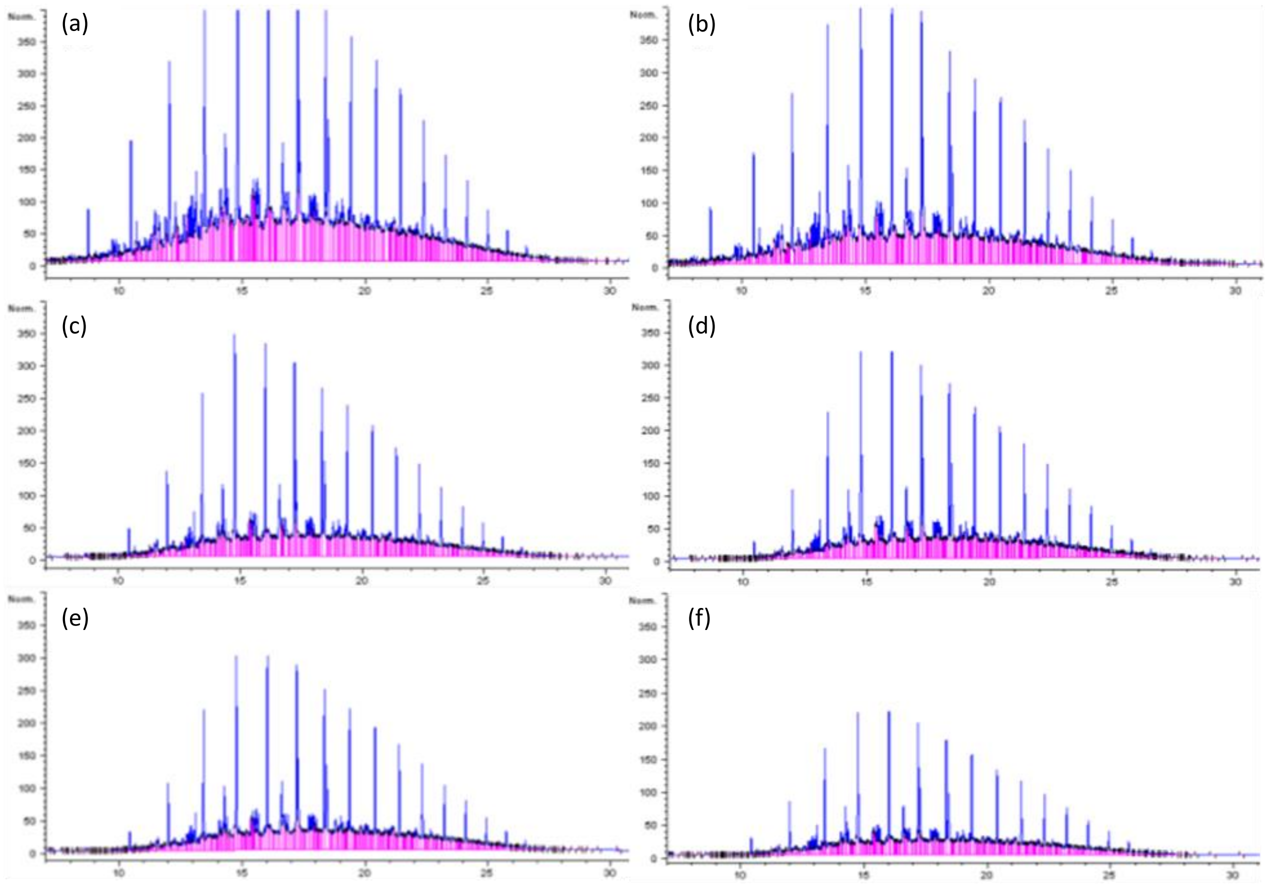

Figure 4. Chromatograms of raw contaminated soil (a), soil washed with only water (b), soil flushed with 0.1% (c), 0.2% (d), 0.3% (e) and 0.4% (f) of Tween 80 at a flow rate of 4 mL min^{-1}

In contrast, washing tests carried out with SDBS provided different results. In this case, in fact, the SDBS showed an opposite behavior, both in terms of flow rate and concentration, compared to Tween 80 in the hydrocarbon extraction efficiency.

Indeed, for the same concentration, as the flow rate increases, a significant decrease in extraction efficiency is observed in general (Figure 5); in this case, results would seem to suggest that there is no a predominant leaching effect as much as a contact time effect. In addition, referring to surfactant concentration, it appeared that, by increasing the surfactant concentration from 0.1% to 0.2%, for all four flow rates considered, the removal efficiency also increased significantly. By further increasing the surfactant concentration first to 0.3% and then to 0.4%, however, there was a slight decrease in the removal efficiency indicating, therefore, as in this study, exists a threshold beyond which the extraction performance is reduced. In detail, the highest efficiency was obtained for a SDBS concentration equal to 0.2% and with a washing flow rate of 2 mL min^{-1}; for these conditions, a removal of approximately 45% was achieved.

This result is in line with what has been reported in literature (Medjor et al., 2018), in which the presence of an optimal surfactant concentration threshold was observed, beyond which the removal performance was reduced; in particular, above the CMC the removal efficiency should increase but, in some cases (Zhao et al., 2014), it has been observed that exceeding the CMC can cause a reduction in the concentration of solubilized contaminant due to the excessive presence of micelles which might inhibit the solubilization potential.

Nevertheless, there is limited information available in the scientific literature which specifically addresses the reduction of hydrocarbon extraction efficiency due to an excessive dosage of surfactants and there is no enough evidence corroborating that an excessive dosage of SDBS could determine a decrease of extraction efficiency. This aspect deserves further investigations.

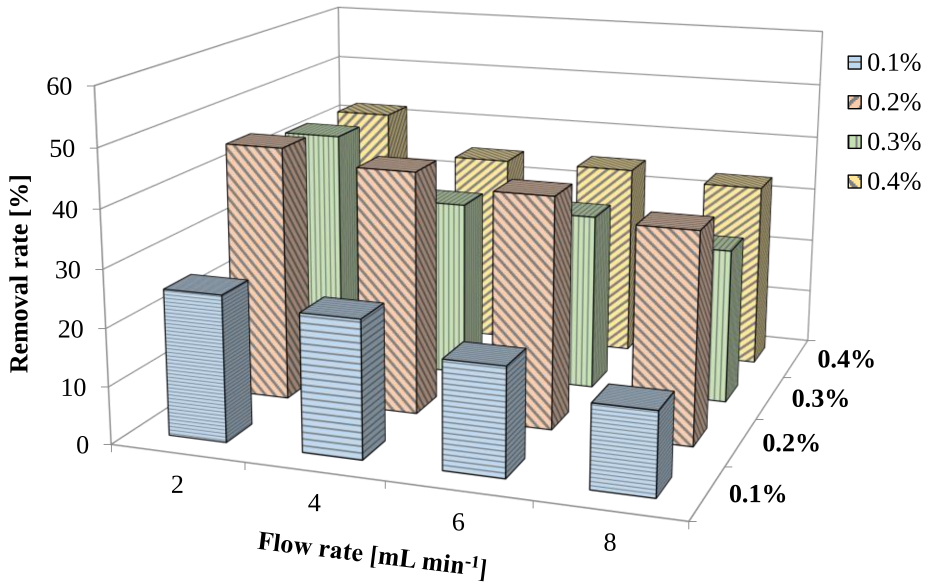

Figure 5. TPH removal rate depending on SDBS concentration and flow rate

As an example, Figure 6 shows the chromatograms obtained from the GC analysis after the extraction and purification procedure for the contaminated soil washed with SDBS solution of 0.1%, 0.2%, 0.3% and 0.4% at a flow rate of 2 mL min^{-1}.

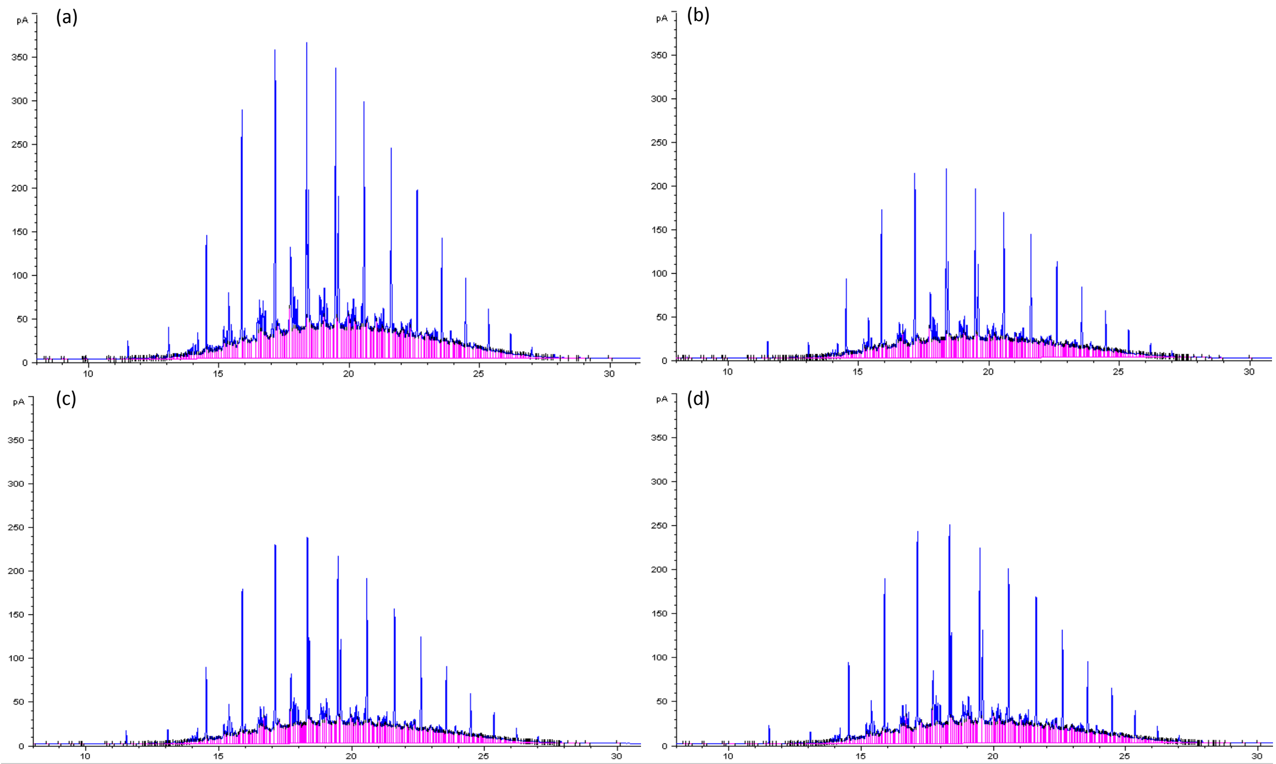

Figure 6. Chromatograms of soil flushed with 0.1% (a), 0.2% (b), 0.3% (c) and 0.4% (d) of SDBS at a flow rate of 2 mL min^{-1}

Even in this case, chromatograms related to the soil samples after washing with the surfactant solutions (Figure 6a-d) are more flattened (lowering of the peaks) and with the left side much more reduced, compared to those related to the raw contaminated soil (Figure 4a) and that washed with water only (Figure 4b).

3.2 Performance of hydrocarbon extraction in the long-term tests

On the basis of the results obtained in P1 and P2 periods, in P3 ”long-term” experiments (duration: 48 hours) were carried out on the same laboratory scale apparatus with the following operational conditions: (i) flushing tests with warm water at a flow rate of 2 mL min^{-1}, (ii) flushing tests with Tween80 at 0.4% and flow rate of 8 mL min^{-1} and (iii) flushing tests with SDBS at 0.2% and flow rate of 2 mL min^{-1}. The obtained results are shown in Figure 7, confirming in general what observed in the short-term tests.

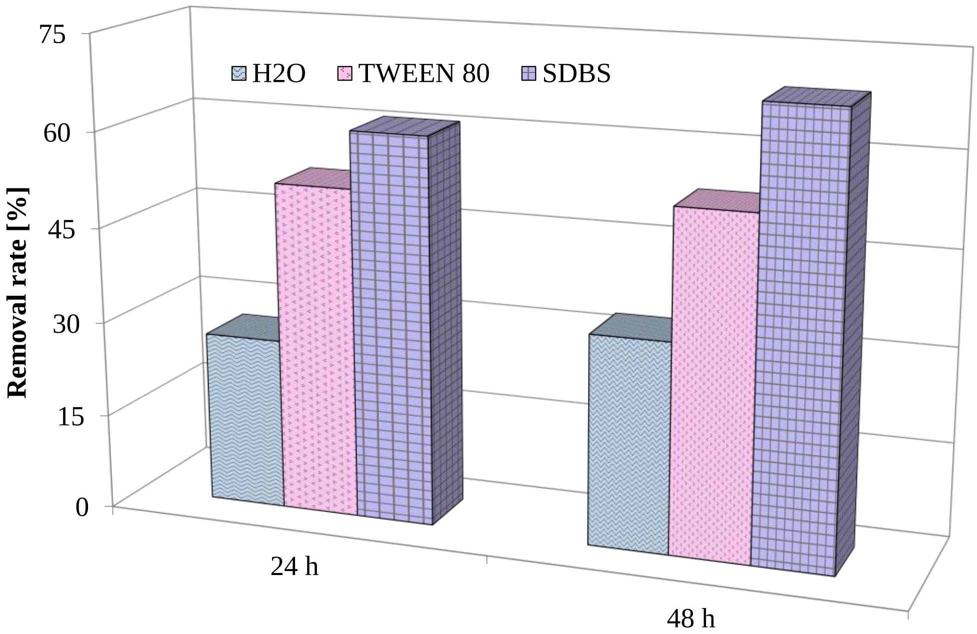

Figure 7. TPH removal rate after continuous flushing with water, Tween 80 and SDBS

As it can be seen from the graph reported in Figure 5, the washing test carried out with water provided an overall extraction efficiency of 32%, with a slight increase of the extraction efficiency over time, mainly related to the longer contact time between water and contaminant, thus confirming results reported by Gautam et al. (2020) and validating the ability of water to mobilize a non-negligible portion of the adsorbed hydrocarbons. Long term flushing with Tween 80 allowed to reach a removal efficiency of 53% after 48 hours; in this case the extraction efficiency remained almost constant between 24 and 48 hours, thus confirming that the contact time in this case is not relevant in the extraction mechanism and that surfactant concentration may play a decisive role. Referring to SDBS, the maximum removal was obtained at the end of the flushing test and was close to 70%, confirming that, when flushing the soil with a SDBS solution, a greater efficiency can be achieved by increasing the contact time between surfactant and contaminant.

3.3 Phytotoxicity features of the soil after washing

From the results obtained in the phytotoxicity tests by means of germination index, it emerged that the use of both water and surfactants had different effects on the phytotoxicity features of the soil after treatment. As an example, Figure 8 summarizes the GI data obtained in P3 period, assessed as the average values of the different dilutions.

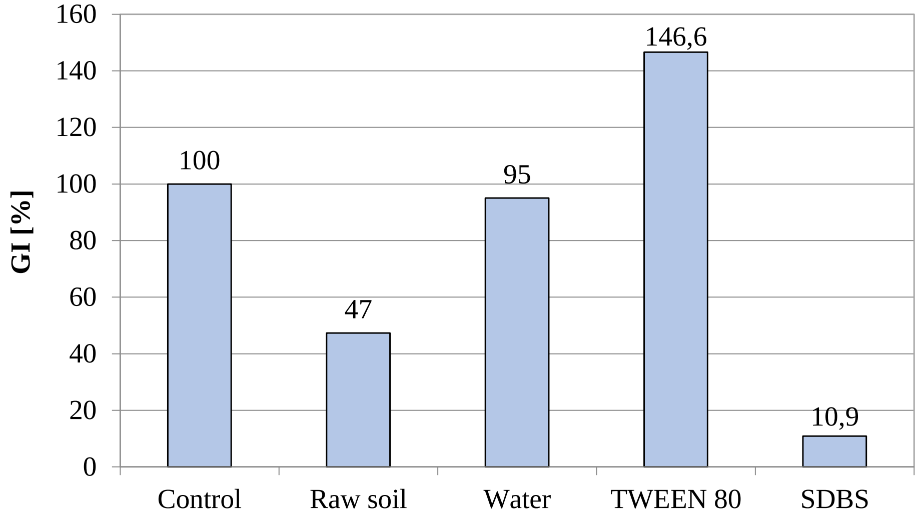

Figure 8. Average values of GI of soil samples after continuous flushing

The tests performed on the soil sample subjected to washing with water showed a germination index value similar compared to the blank control. On the contrary, for samples treated with SDBS, a much lower GI value (10.88%) of both the control and the raw soil was observed, also visible from a reduction in the growth of *Lepidium sativum* seeds (Figure 9). This result il likely related to the presence of SDBS; indeed, despite the concentration of hydrocarbons on the soil was significantly reduced after the flushing test, the residual SDBS caused a phytotoxic effect on the treated soil. This result is in line with the studies proposed by Chen et al. (2001) and Singh and John (2013), who identified SDBS as toxic and poorly biodegradable (20%). In contrast, the residual Tween 80 after treatment favored the growth of seeds (Figure 9). In this case, in fact, the GI was really high, and also significantly higher compared to the control (146.61%). This result could be due to the fact that Tween 80 holds carbon potentially bioavailable, which increases the root permeability, leading to a more efficient absorption of nutrients from soil (Cheng et al., 2017). Therefore, the use of Tween 80 for the treatment of soil flushing in soil destined to agricultural activity, would not compromise the characteristics of the soil in terms of phytotoxicity.

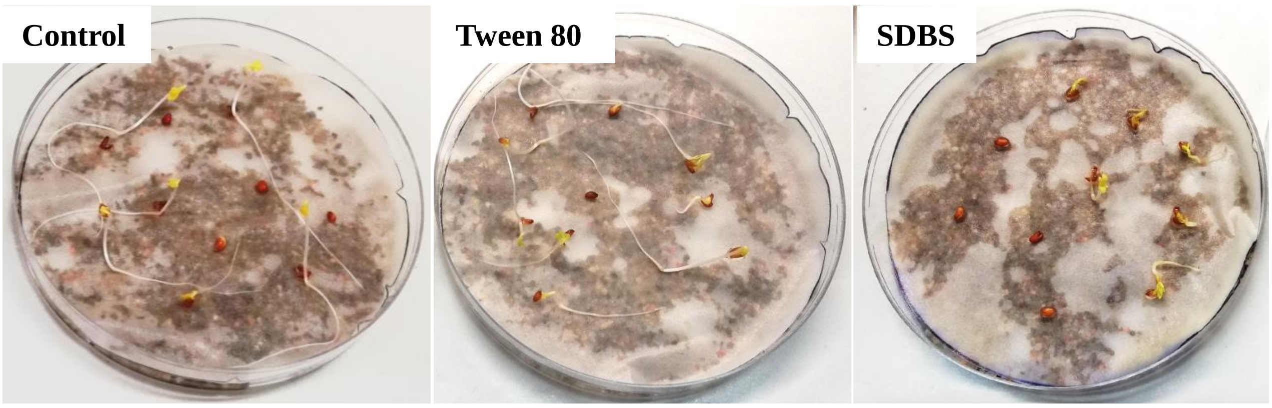

Figure 9. Comparison of growth of *Lepidium Sativum* seeds on control, soil treated with Tween 80 and SDBS

4. Conclusions

The use of both types of surfactants in the washing solution allowed to obtain significant extraction efficiency of hydrocarbons from the polluted soil, significantly higher compared to what achieved with flushing tests carried out with only water, thus confirming their important role in the remediation of hydrocarbon-contaminated soils. In addition, although the use of Tween 80 resulted in lower removal efficiencies than that of SDBS in long-term tests, the results in terms of residual phytotoxicity features of the soil after washing highlighted a strong difference among the surfactants. Indeed, the GI values showed that the soil samples washed with SDBS were characterized by a much higher phytotoxicity compared to that washed with Tween 80. These results could be of interest, since it would ensure better recoverability of treated soils for agronomic purposes.

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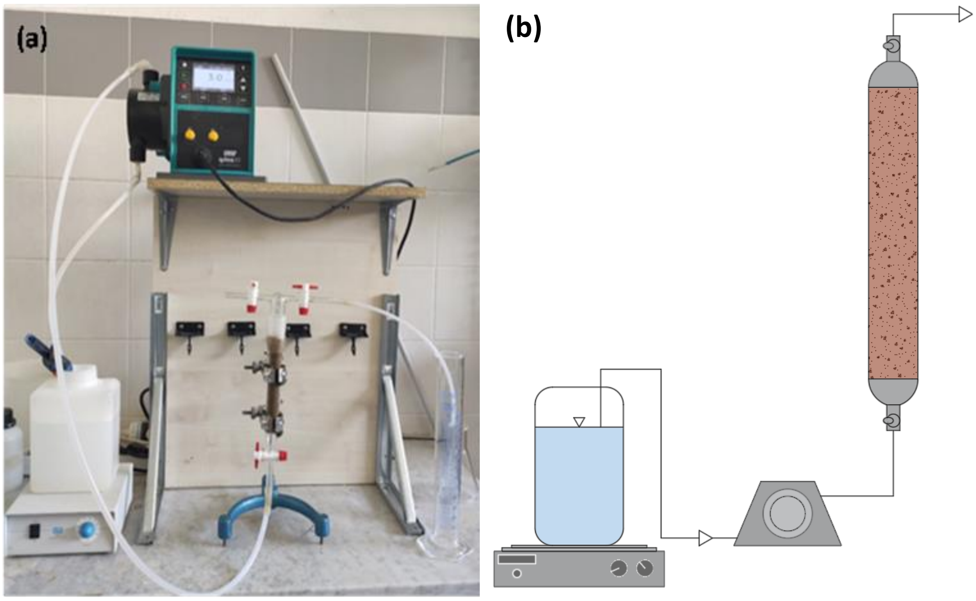

Figure 1. Panoramic view (a) and schematic layout (b) of the experimental apparatus

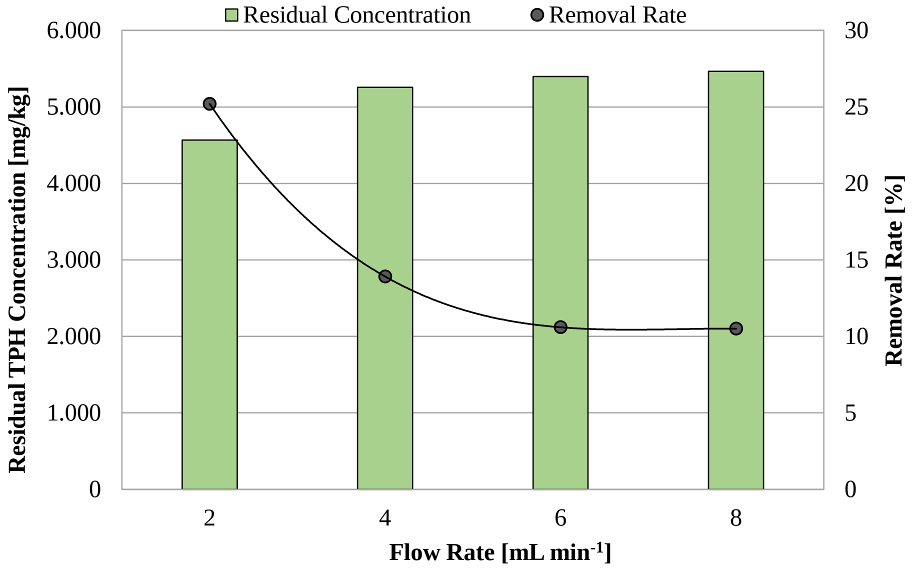

Figure 2. Residual concentration of TPH in soil samples and removal rate after water flushing

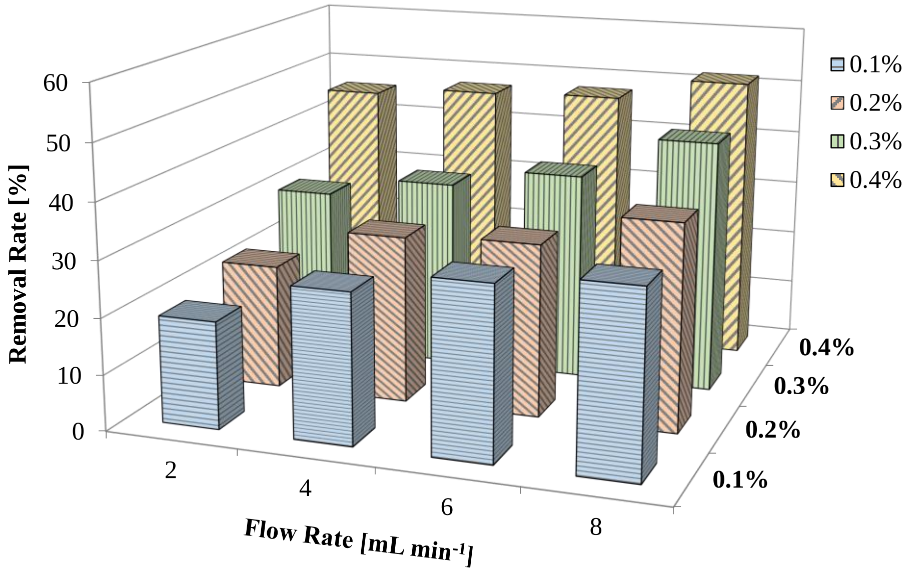

Figure 3. TPH removal rate depending on Tween 80 concentration and flow rate

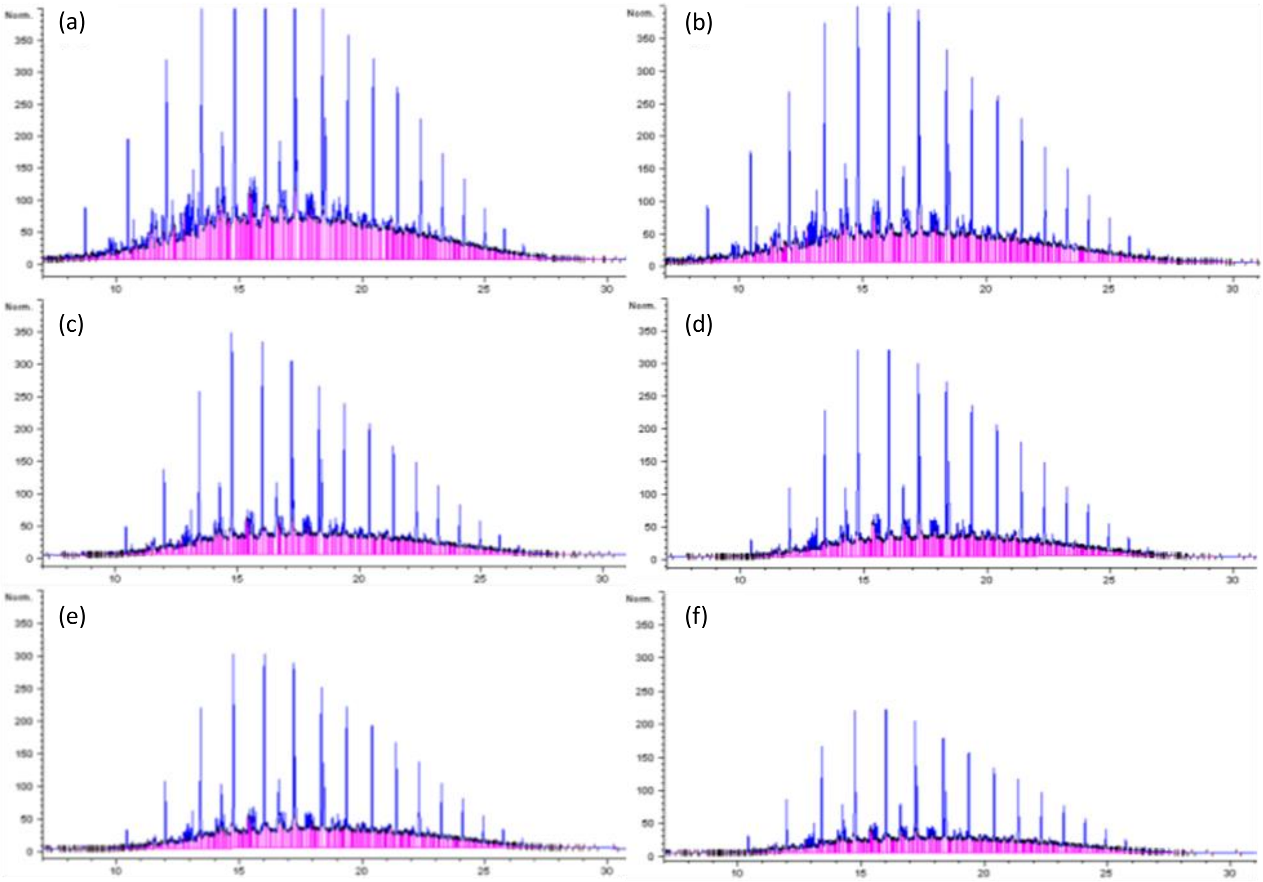

Figure 4. Chromatograms of raw contaminated soil (a), soil washed with only water (b), soil flushed with 0.1% (c), 0.2% (d), 0.3% (e) and 0.4% (f) of Tween 80 at a flow rate of 4 mL min^{-1}

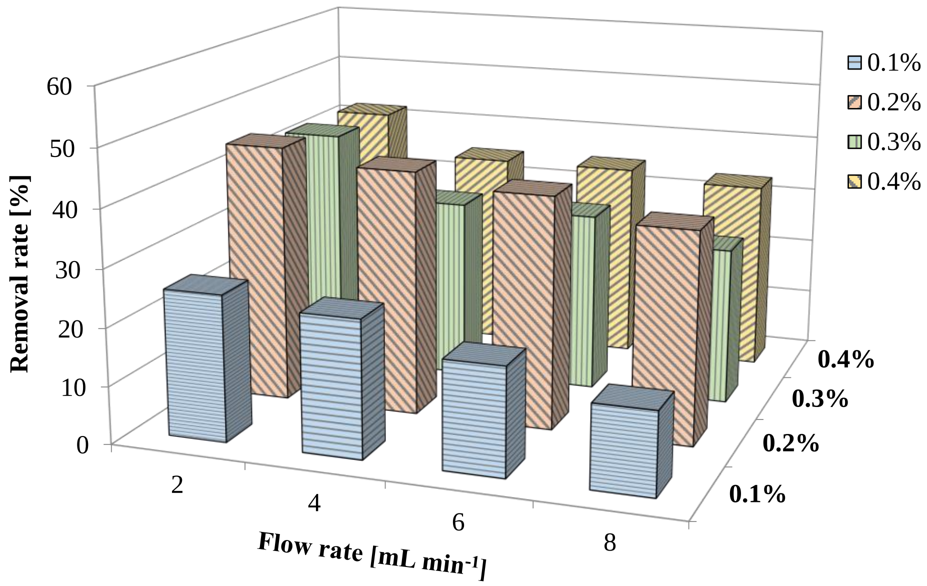

Figure 5. TPH removal rate depending on SDBS concentration and flow rate

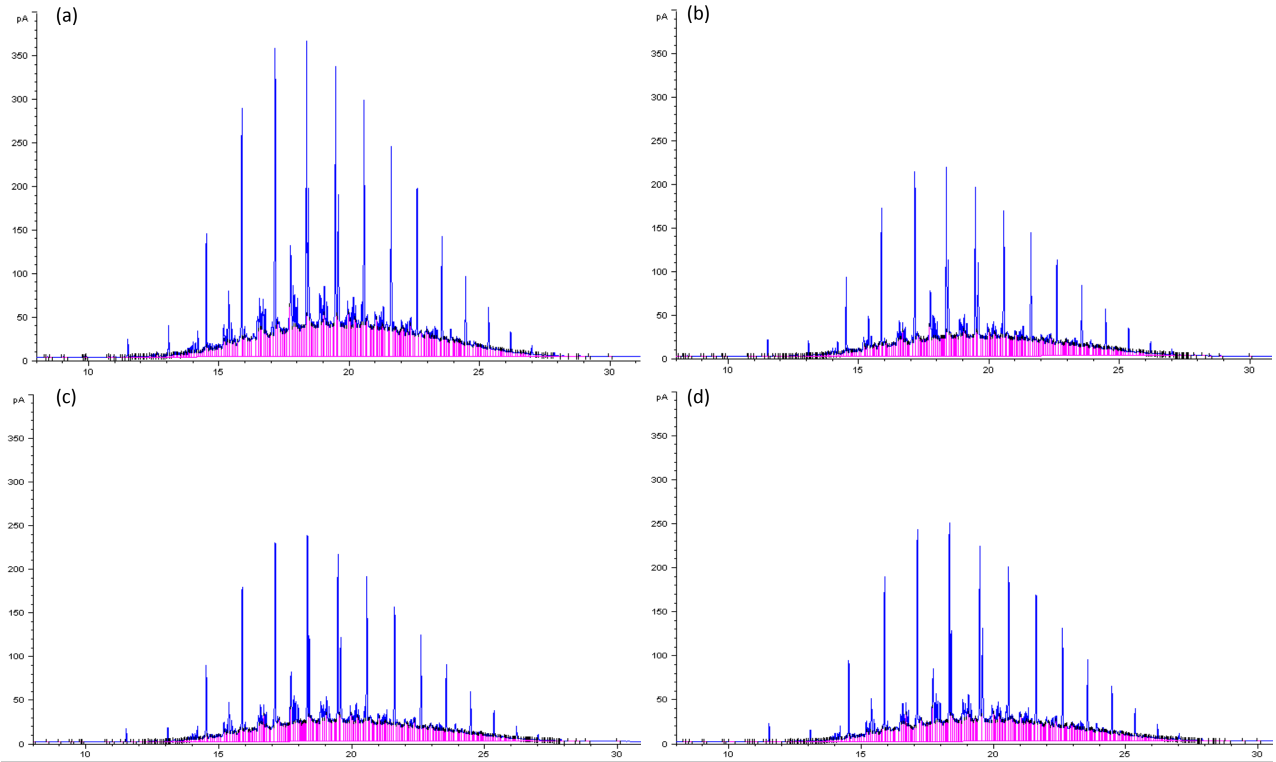

Figure 6. Chromatograms of soil flushed with 0.1% (a), 0.2% (b), 0.3% (c) and 0.4% (d) of SDBS at a flow rate of 2 mL min^{-1}

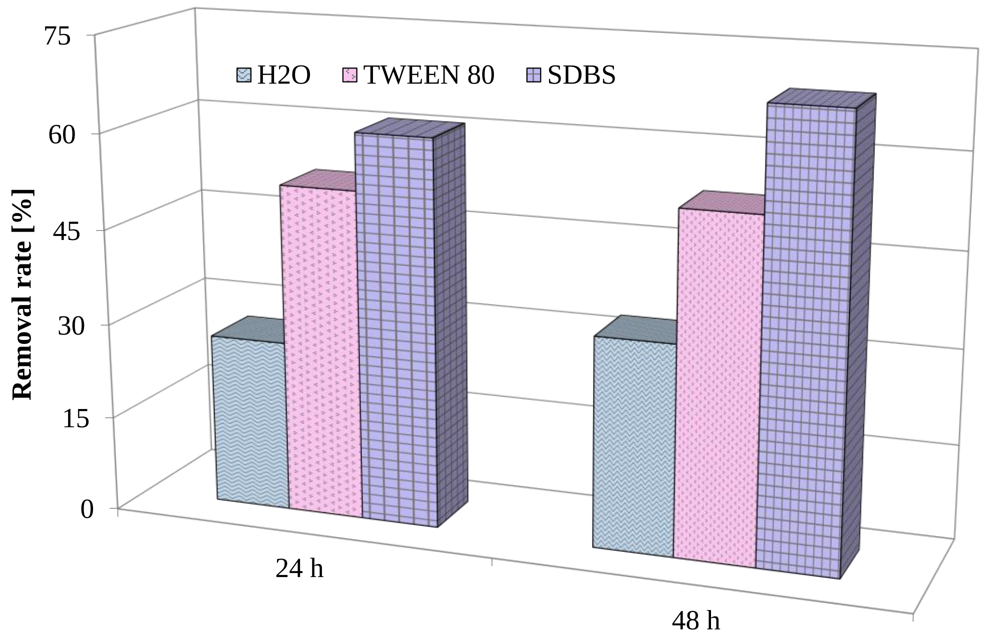

Figure 7. TPH removal rate after continuous flushing with water, Tween 80 and SDBS

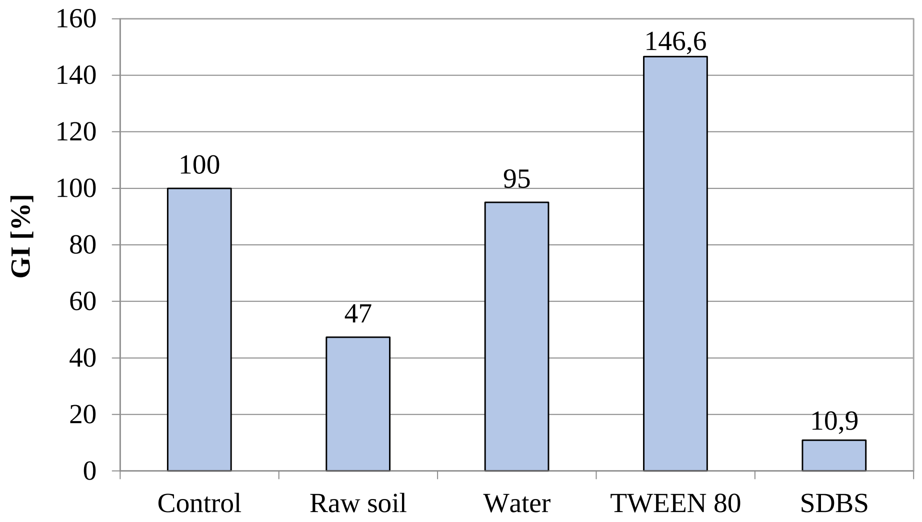

Figure 8. Average values of GI of soil samples after continuous flushing

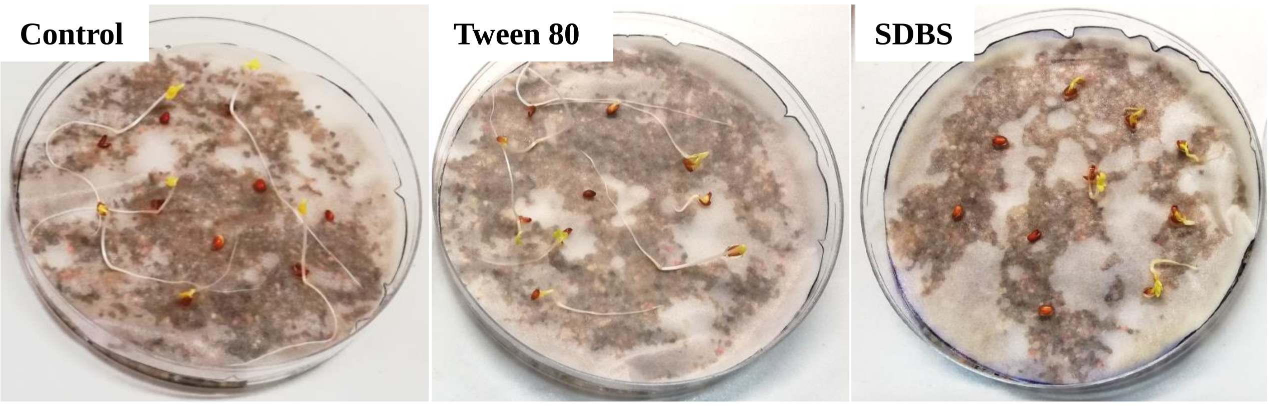

Figure 9. Comparison of growth of *Lepidium Sativum* seeds on control, soil treated with Tween 80 and SDBS

Table 1. Main characteristics of SDBS and Tween 80

Chemical nomenclature	CAS number	Chemical formula	Ionic Nature	Molecular mass [g/mol]	CMC [mM]
Sodium Dodecyl Benzene-Sulfonate	25155-30-0	$C_{18}H_{29}NaO_3S$	anionic	348.48	0.612
Polysorbate 80	9005-65-6	$C_{64}H_{124}O_{26}$	non-ionic	1310	0.012

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: