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Remediation of a diesel contaminated soil by means of anionic and non-ionic surfactants: Effect on soil phosphorus availability and *Vicia Faba* L. growth

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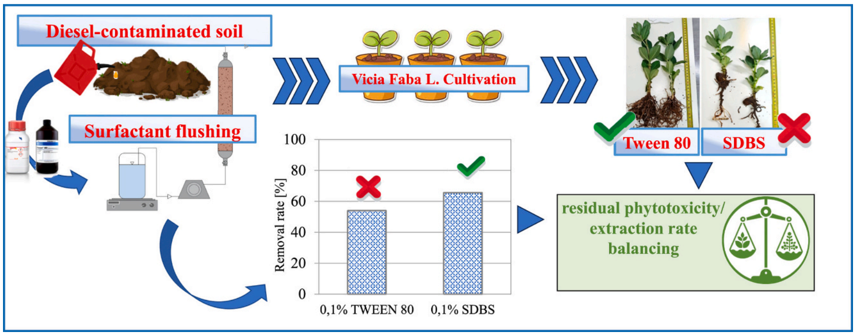
HIGHLIGHTS

- Surfactants increased the extraction efficiency of TPHs from soil up to 65 %.
- Tween 80 enhances TPHs removal while not hindering the growth of *Vicia Faba*.
- Residual SDBS in soil after flushing promoted inhibitory effect on plants growth.
- Plants cultivated in soil treated with SDBS showed the lowest amount of P adsorbed.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, the effectiveness of two surfactants (Polysorbate 80 – Tween 80 and Sodium Dodecyl Benzensulphonate – SDBS) was investigated for the remediation of a hydrocarbon-contaminated soil. Moreover, it was elucidated the impact of surfactants on soil phosphorus (P) availability and phytotoxic effect on the growth of *Vicia Faba L.* An experimental laboratory-scale apparatus (bench and pilot scale) was set up for the simulation of a soil flushing intervention. Different surfactant concentrations and flushing flow rates were investigated. Hydrocarbon extraction efficiency was evaluated after treatment and phytotoxicity tests were performed by means of germination index (GI). The treated soil with the pilot scale apparatus was then used for *Vicia Faba* (faba beans) cultivation in pots. The growth of *Vicia Faba* plants was monitored and, at the end of the growth period, the plants were uprooted and subjected to biometric and chemical analyses. Results highlighted that the use of surfactants significantly increased the efficiency of hydrocarbons extraction compared to flushing test with water (19.6 %, 53.9 %, and 65.6 % for water, 0.1 % by weight of Tween 80 and SDBS, respectively, at pilot scale). Referring to *Vicia Faba L.*, the plants grown in the blank control and in the soil treated with Tween 80 reached the same average height thus suggesting that this surfactant does not inhibit plant growth. In contrast, the lowest plant growth occurred in the soils treated with SDBS; this suggests a negative impact on plant growth.

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Due to the reduced plant growth, total P uptake was the lowest in plants grown in SDBS-treated soils, although such soils experienced a 20 % increase of soil available P. This increase could be ascribed to P supplied by the surfactant or high P availability as a consequence of soil pH decrease.

1. Introduction

The contamination of soil and groundwater by organic pollutants, with a particular concern to hydrocarbons, has become a worldwide issue in recent years due to the increased use of petroleum products (Babaei and Copty, 2019; Huo et al., 2020). Beside, all human production activities, including fossil fuel combustion and the production of coke and asphalt, result in the generation of Polycyclic Aromatic Hydrocarbons (PAHs) (Ailijiang et al., 2022). Due to their toxicity, abundance of species and slow degradation in soil, hydrocarbons may damage human health and the surrounding environment (Mao et al., 2015). Specifically, once in the soil or water, PAHs can bind strongly to organic matter, making them difficult to remove. They are persistent compounds and can have toxic, mutagenic, and carcinogenic effects. Moreover, with reference to petroleum products, they usually have high oil/water distribution coefficient and low solubility in water; therefore, they are prone to be adsorbed into soil matrix, with a possible formation of non-aqueous phase liquid in aquifers (Rogers and Logan, 2000). Such non-aqueous phase trapped in pore space can slowly solubilize into groundwater, leading to a long-term persistent source of aquifer contamination (Zhong et al., 2016). Due to the high risk for human health and ecological security, soils contaminated by hydrocarbons need to be reclaimed. The success of remediation relies on developing a dynamic conceptual site model, assessing and selecting potential treatment technologies. Nevertheless, due to the high sorption on soil matrix and the consequent slow desorption, the remediation process represents a big challenge (Cheng et al., 2017). The heterogeneous nature of soil and its composition contribute to entangle an effective remediation, since the particle size distribution (sand, silt, clay) and organic matter content in the soil influence TPHs behaviour. For instance, a clay soil rich in organic matter, being hydrophobic and having a large surface area, reduces the bioavailability of hydrocarbons for microbial degradation and makes contaminants less accessible for treatment methods. Moreover, since TPHs contain a mixture of many substances, each type of hydrocarbon has unique properties (e.g. volatility, solubility, and degradability) that affect how it behaves in the environment.

In recent years, several techniques have been proposed for the remediation of soils contaminated by hydrocarbons, including physical (Jeong and Lee, 2013; Gautam et al., 2020; Ren et al., 2020), chemical (Choong et al., 2021; Ritoré et al., 2023) and biological (Palanisamy et al., 2014; Guirado et al., 2023; Zhang et al., 2023) techniques. One of the most promising remediation technologies is represented by the use of surfactants in soil washing or soil flushing applications, even at full scale (Karthick et al., 2019; Huang et al., 2021; Liu et al., 2021; Kumar et al., 2022). What makes surfactants suitable for soil remediation is their cost-effectiveness, low toxicity, biodegradability and low susceptibility to aggregate clay minerals (Zhao et al., 2016; Sakhaei and Riazi, 2022). Surfactants are constituted by hydrophilic heads and hydrophobic tails. The hydrophobic groups bond with the organic compound while the hydrophilic group with the polar solvent, thus promoting its extraction from soil. Therefore, when surfactant-enhanced soil washing is performed, the organic pollutant can be desorbed from the soil surface and moved away. Surfactants can have either synthetic or natural origin and, depending on their hydrophilic head, they are classified as anionic, cationic, non-ionic or zwitterionic (Kumar et al., 2021). Among these categories, anionic and non-ionic surfactants are the most used in soil remediation (Karthick et al., 2019). The solubilization of organic compounds in soil/water systems begins when the surfactant reaches a specific concentration, namely critical micelle concentration (CMC), at which ellipsoidal or spheroidal micelles will form (Bolan et al., 2023). Besides the surfactant concentration, the effectiveness of the treatment depends also on surfactant hydrophilic-lipophilic balance, the octanol-water partition coefficient (K_{ow}) of the pollutants, soil pH and salinity, dissolved organic matter (DOM), temperature, and co-solutes (Lamichhane et al., 2017).

Fardin et al. (2021) coupled electrokinetic (EK) with anionic (SDS) or non-ionic (Tween 80) surfactants at different concentrations for the remediation of a kerosene-contaminated soil. They found that the use of this combined technology allowed for achieving up to 67 % removal of kerosene. Baigadilov et al. (2024) applied surfactant foam injection for remediation of diesel-contaminated soil, investigating Cocamidopropyl Hydroxysultane’s (CAHS) role as a co-surfactant in enhancing foam stability against antifoaming diesel oil; Baigadilov and co-workers found an increase of over 10 % of diesel mobilization. Ayele et al. (2020) applied surfactant-enhanced soil washing for the remediation of diesel-contaminated soils by using response surface methodology, reaching a 79.5 % removal of diesel. Nevertheless, the application of surfactants in polluted sites can be challenging, due to the potential environmental and health implications. Indeed, despite some biodegrade, they might be harmful to the environment, aquatic organisms and humans because of their bioaccumulation and persistence (Villarreal-Reyes et al., 2022). Therefore, if on one hand they enhance pollutants’ solubility, on the other hand they might produce negative effects on indigenous microbial communities (Kumar et al., 2021). Moreover, surfactants can induce secondary pollution in soil due to the residual surfactant in soil after treatment (Zhong et al., 2016). The latter side effect should be avoided, especially when agronomic use of the treated soil is expected or when surfactant remediation should be coupled to phytoremediation (Sun et al., 2013). Previous studies highlighted that the addition of Tween 80 is not phytotoxic rather, in some cases, plants grown even higher compared with soil not treated with Tween 80 (Cheng et al., 2017; Di Trapani et al., 2023). In contrast, despite the anionic surfactants *Sodium Dodecyl Sulfate (SDS)* and *Sodium Dodecylbenzene-Sulfonate (SDBS)* have been successfully used in subsurface remediation applications (Karthick et al., 2019; Sakhaei and Riazi, 2022), they might negatively impact soil features after treatment promoting secondary pollution, or adversely impacting the plants health by enhancing inhibitory effects on the living organisms in subsurface system also entailing phytotoxicity (Huo et al., 2020; Bolan et al., 2023).

Based on the above considerations, the aim of this study was to investigate the feasibility of surfactants application for the remediation of a real sandy soil, artificially contaminated with diesel-fuel. The role of surfactant concentration and flushing flow rate was assessed in terms of hydrocarbon solubilization effectiveness. Two different surfactants were tested, one anionic (SDBS) and one non-ionic (Tween 80), by simulating a soil flushing process carried out on a laboratory scale apparatus. The above surfactants were chosen due to their cost-effectiveness and numerous applications in previous literature experiences. Furthermore, another reason for this choice was related to provide a comparison with the results achieved in a previous study by authors (Di Trapani et al., 2023). Hydrocarbon removal from soil at different surfactant concentrations and flushing flow rates was assessed. Moreover, the suitability of treated soil for crop cultivation was elucidated by determining the germination index (GI) on *Lepidium sativum* seeds and by using remediated soil for *Vicia Faba L.* (faba bean) cultivation. The novelty of the present study is the elucidation of the relationship between surfactant concentration, flushing flow rate and flushing duration in the hydrocarbon extraction from a contaminated soil, providing useful operational insights in view of full-scale applications. This investigation will provide novel insights towards phytotoxic implications of surfactants

Table 1
Main features of the soil after contamination.

Parameter	Units	Value
Total petroleum hydrocarbons (TPH)	mg kg_{SS}^{-1}	1585
Clay	%	2.2
Silt	%	6.2
Sand	%	91.6
Permeability coefficient k	m s^{-1}	10^{-4}
Porosity n	–	0.325
Effective porosity n_e	–	0.173
pH	–	7.7
Electrical conductivity (EC)	μS cm^{-1}	202
Total organic carbon (TOC)	g kg^{-1}	8.1
Dissolved organic matter (DOM)	g kg^{-1}	0.15
Total nitrogen (TN)	g kg^{-1}	0.7
Available P	mg P kg^{-1}	8.6
Cation exchange capacity (CEC)	cmol kg^{-1}	14.1

after treatment on plant growth. Moreover, the findings of the present study will provide a valuable contribution in the case of coupled application of surfactant-phytoremediation techniques for the remediation of hydrocarbon-contaminated soils. Finally, the results of this study could be of interest to ensure better recoverability of treated soil in case of agronomic reuse.

2. Materials and methods

2.1. Description of the experimental campaign

The experimental campaign was divided into 2 periods (namely P1 and P2), lasting 2 months each. During P1, an experimental apparatus was set up to simulate a soil flushing process by alternatively flushing water or a surfactant solution at different flow rates and concentrations. Two different surfactants were tested: one anionic (SDBS) and one non-ionic (Tween 80) surfactant. In more detail, a preliminary set of bench-scale tests was carried out to assess the best operational conditions. For each test, three replicates were performed. Based on the results of these preliminary tests, a process scale-up was realized, and soil flushing experiments were carried out on a pilot-scale experimental apparatus. After each test, the soil's phytotoxic properties were determined by calculating the germination index (GI) on *Lepidium sativum* (garden cress) seeds.

In period P2, the soil samples treated with the pilot-scale system as well as raw polluted soil samples were used for *Vicia Faba* (faba beans) cultivation in pots. The growth of *Vicia Faba* plants was monitored and at the end of the growth period, the plants were uprooted and subjected to biometric and chemical analyses.

2.2. Soil characteristics

The soil used during the experimental campaign was collected in an olive orchard in the province of Palermo (Sicily, Italy). The soil was spiked with a known volume of commercial diesel fuel; in detail, 1 % (*w/w*) of diesel was added to 7.5 kg of soil to obtain an initial TPH concentration of 1600 mg kg_{SS}^{-1}. The aim was to obtain a TPH concentration that indicated potential soil contamination, slightly higher than the contamination threshold concentrations for commercial and industrial sites (750 mg kg_{SS}^{-1}) listed in column B, Table 1, part IV, Annex 5, Legislative Decree n. 152/06. After contamination and before the start of the experimental tests, the sample was manually mixed for 15 days to allow the volatilization of the volatile fractions. Specifically, the spiked soil was mixed by using spatulas; hand mixing was performed continuously during the addition of the spiking solution (Hartzell et al., 2018) and for 15 min after spiking and on all subsequent days, to accomplish the homogenization. Table 1 shows the main features of the soil used and the initial level of contamination.

Table 2
Best operating conditions observed in bench-scale tests and conditions applied in pilot-scale tests.

Flushing solution	Bench-scale tests		Pilot-scale tests	
	Flow rate	Volume flushed	Flow rate	Volume flushed
Water	8 mL min^{-1}	1 L	40 mL min^{-1}	6.2 L
0.1 % Tween 80	8 mL min^{-1}	1 L	30 mL min^{-1}	5.5 L
0.1 % SDBS	6 mL min^{-1}	1 L	30 mL min^{-1}	5.5 L

2.3. Surfactant characteristics

The used surfactants (*Sodium Dodecyl Benzensulphonate* – SDBS and *Polyoxyethylene (20) sorbitan monooleate* – Tween 80) were purchased from *Sigma Aldrich* (Milan, Italy). Surfactant solutions were prepared using tap water. The main properties of both surfactants are provided in Table S1. The selection of the above surfactants relies on the fact that the main aim was to compare the extraction efficiency of one anionic and one non-ionic surfactant, also highlighting the residual phytotoxicity of the soil after flushing; since SDBS and Tween 80 are common surfactants investigated in remediation applications (Paria, 2008; Bolan et al., 2023) authors decided to select them for the experimental campaign; moreover, these surfactants were already applied in a previous study by authors (Di Trapani et al., 2023) and the results of the present study could be somehow compared to what achieved in the previous experience. Furthermore, the above surfactants generally differ in their environmental behaviour. Particularly, SDBS is of environmental concern due to its potential toxicity and persistence; on the contrary, Tween 80 is considered more environmentally friendly, mainly due to its higher biodegradability (Zhang et al., 2024).

2.4. Description of the experimental apparatus for the flushing tests during P1

Bench-scale apparatus. The experimental apparatus consisted of a Pyrex glass column (d = 2.1 cm, h = 13 cm), with a special conical-shaped piece of 29/32 mm at the bottom. For each test, the column was filled with approximately 80 g of diesel-contaminated soil, with an estimated pore volume (PV) value of 8.8 mL. One liter of solution (water, SDBS or Tween 80) was flushed through the column in upward mode by means of a peristaltic pump. Surfactant solutions were stored in a storage tank, maintained at a temperature of about 30 °C and continuously mixed through a magnetic stirrer. Bench-scale flushing tests were carried out with water and surfactant solutions at washing flow rate of 6 and 8 mL min^{-1}. Moreover, two different concentrations were used for both surfactants, respectively, 0.05 % and 0.1 % by weight. In terms of CMC, these concentrations correspond approximately to 32 × CMC and 64xCMC for Tween 80 and to 2.5 × CMC and 5 × CMC for SDBS, respectively. The choice of such high concentrations relies on the fact that because of adsorption in a complex system like soil, micelles form well above the CMC. Furthermore, concentrations and flow rates were chosen based on those used in previous studies (Lai et al., 2009; Zacarias-Salinas et al., 2013; Liu et al., 2022; Di Trapani et al., 2023).

Depending on the best results obtained in the bench-scale tests, a system scale-up was made, and soil flushing experiments were carried out on a pilot-scale experimental apparatus. The best operational conditions are reported in Table 2.

Pilot-scale apparatus. The experimental apparatus consisted of a Pyrex glass column (d = 4.2 cm, h = 70 cm). For each test, the column was fed with 1.3 kg of contaminated soil, with an estimated PV value of 191.5 mL. The reference parameter used for the scale up of the system was the effective upward velocity through the column. Using this

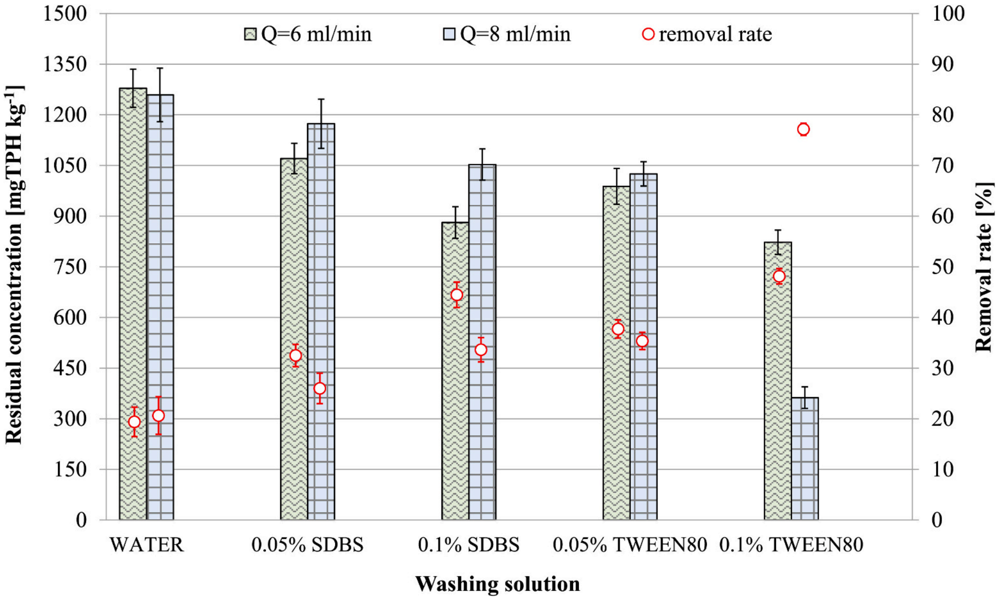

Fig. 1. Residual concentration of TPHs in soil samples and removal rate after bench-scale water flushing.

parameter and knowing the dimensions of the pilot-scale column, it was possible to determine the washing flow rates and the volumes of extracting solutions to be flushed through the pilot-scale system.

For the washing tests with water and Tween 80, the optimal flow rate was 40 mL min^{-1}; concerning SDBS, the optimal flow rate was 30 mL min^{-1}. However, due to technical issues in the tests carried out at 40 mL min^{-1} with Tween 80, it was decided to decrease the flow rate at 30 mL min^{-1}. The above issues could be related to the decrease of soil hydraulic conductivity, caused by the presence of Tween 80 (Abu-Zreig et al., 2003; Tumeo, 2007). This reduction in the hydraulic conductivity, indeed, resulted in soil cracking, thus hindering the correct execution of the test. Therefore, for the scale-up to field applications, a comprehensive study on the interactions between flow dynamics, soil heterogeneity and surfactant features is pivotal. For both bench-scale and pilot-scale configurations, before starting each test, with the aim to remove the air trapped into the pores, a volume of water almost equal to 6.50 PV was fed into the column. Once soil saturation was reached, the solution flushing started. Each test was performed in duplicate. Fig. S1 shows a panoramic view of the bench-scale (Fig. S1a) and pilot-scale (Fig. S1b) apparatus and a schematic layout (Fig. S1c) of the experimental system.

2.5. Testing soil for crop cultivation (P2)

All soil samples (not contaminated, raw contaminated not treated and treated contaminated soil at pilot scale with water, SDBS, and Tween 80) were air-dried for approximately one week. Then, soil samples were mixed with 15 % by volume of perlite and amended with 5 % by weight of mature compost as organic fertilizer. Subsequently, the soil was used to fill polyethylene pots (h = 12 cm, d = 10 cm) where two seeds of faba bean per pot were sown (Fig. S2). Fava (*Vicia faba* L.) plants were selected for the experimental trial because they are a typical crop cultivated in semi-arid environments, such as Sicily in the same period during which the experiment was carried out (12 December – 13 February). Fava beans are also easy to grow in greenhouses and pots, and it responds well to changes in soil available P. The experiment was carried out in triplicate. After Fava beans were sown, pots were moved to a greenhouse. Pot irrigation was carried out at regular intervals of 3–4 days by adding an amount of tap water to maintain the soil at 50 % of its water holding capacity thus avoiding leaching. At the end of the growing period, plants were carefully extracted from the pots to avoid any damage to the roots. Subsequently, steams and roots were divided and oven-dried at 40 °C until a constant weight (ca. after 72 h), and separately weighed. Dried roots and leaves were ground and kept in a plastic bottle at 4 °C before further analysis. Also soil samples were collected to be analysed.

2.6. Analytical methods

Hydrocarbons residual concentration. The measurement of residual hydrocarbon concentration was performed on: (i) soil samples subjected to the flushing treatment, (ii) soil samples after *Vicia Faba* plant removal, and (iii) plant roots to assess hydrocarbons absorption by the root system. The determination of the residual concentration of TPHs was carried out by following "Procedure for the analysis of hydrocarbons C>12 in contaminated soils - Manuals and Guidelines 75/11" proposed by ISPRA (2011), which refers to ISO 16703 (2004) and involves a first phase of solid-phase extraction, followed by purification on Florisil, and GC-FID analysis. Specifically, TPHs concentration was determined by headspace gas chromatographic analysis using a gas chromatograph (Agilent 6890 N Network GC System) equipped with a flame ionization detector (FID) and an Agilent 7683 Series column. Helium was used as the carrier gas; the oven temperature was set at 170 °C and the injection temperature was 250 °C.

Residual soil phytotoxicity. Potential phytotoxicity of soil samples (raw contaminated as well as after flushing) was detected using the germination index (GI) following tests on *Lepidium sativum* (Garden cress) seeds according to APAT (2004) procedure, which refers to USEPA (1988) protocol. The aim was to highlight the role of hydrocarbons/surfactants on soil phytotoxicity. The seeds were placed in Petri dishes (90 mm in diameter) with a filter paper sheet as support (Avona et al., 2022). In some details, a blank control (negative control) was prepared, which was a matrix not containing substances that could inhibit germination and root elongation (clean soil in this case), while for each test three dilutions of the sample with clean soil were prepared. Specifically, sample-sand percentages (*w*/w) of 25 %, 50 %, and 100 % were used, corresponding to a total amount of 10 g of dry mass for each test. In addition, the GI of *Lepidium sativum* was also evaluated on contaminated and untreated soil samples (positive control). The Petri dishes were incubated in a growth chamber at 27 °C for 72 h after being parafilm-sealed to ensure closed-system models. At the end of incubation period, the number of germinated seeds was counted, and root length was measured. The Germination Index (GI) was calculated by multiplying the number of germinated seeds (G) and the root length (L). GI results were used to calculate the effect, expressed as percentage (GI %), with respect to the control using the following Eq. (1):

$$GI = \frac{G_S \cdot L_S}{G_C \cdot L_C} \cdot 100\ [\%] \tag{1}$$

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

Soil chemical analysis. Soil reaction and electrical conductivity (EC) were determined in water extract (1:2.5 *w/v*) by a pH meter (FiveEasy, Mettler Toledo Spa, Milan, Italy) and a conductometer (HI5321, Hanna Instruments Italia srl, Padua, Italy), respectively.

Considering the key role of P in nitrogen fixation by legumes, root development, nutrient uptake, and growth of legume crops (Mitran et al., 2018), soil available P was measured using the colorimetric Olsen method (Olsen et al., 1954) with sodium bicarbonate extraction at pH 8.5. The concentration of P in the extract was determined by colorimetry using the spectrophotometer Shimadzu UVmini-1240 (Shimadzu Italia srl, Milan, Italy).

Plant biometric properties and chemical analysis. The biometric properties of plants, such as shoot height, leaf length and width, and number of leaves were monitored every 4 days during the 2 months of cultivation.

Moreover, for each plant, fresh and dry weight of both roots and shoots were determined. Dry weight was determined after drying the samples in an oven at 50 °C for one week. Starting from the knowledge of the dry weight, the shoot-to-root weight ratio (S/R ratio) was calculated.

Total P on steams samples was determined, on mineralized plant samples, by acid (HNO_3 and 30 % H_2O_2) and the wet digestion procedure (Jones Jr. and Case, 1990) and by the Spectroquant® Phosphate test using a spectrophotometer (UVmini-1240, Shimadzu Italia srl, Milan Italy) after the formation of an orange-yellow complex.

3. Results and discussion

3.1. Performance of hydrocarbon extraction in the bench-scale and pilot-scale tests

Fig. 1 summarizes the TPH residual concentrations in soil as well as removal rate obtained in the bench-scale flushing tests. Removal efficiencies obtained with water flushing were moderate. Indeed, the maximum removal efficiency was close to 20 % and achieved with a flow rate of 8 mL min^{-1}. Such result agrees with previous findings and suggest that water can mobilize hydrocarbons only in a limited amount (Yan et al., 2016); lower removal efficiencies were observed in a previous study carried out by authors (Di Trapani et al., 2023), with removal rates close to 10 % for flushing rates of 6 and 8 mL min^{-1}, respectively. The slight lower removal rates observed in the previous study could be related to the different soil contamination level; indeed, in the study by Di Trapani et al. (2023) it was around 6000 mg$_{TPH}$ kg$_{SS}^{-1}$, in the present study it was close to 1600 mg$_{TPH}$ kg$_{SS}^{-1}$, thus justifying the higher removal rates achieved with the same surfactant concentrations. Moreover, the different textures of soil in the two studies (pure quartz sand in the study by Di Trapani et al. (2023) and a real sandy soil with 8.4 % in weight of clay and silt in the present study) could have affected the results in a certain amount. Nevertheless, as general result, both studies confirmed that water alone can mobilize only a small portion of adsorbed compounds. In contrast, the use of surfactants enabled to increase significantly the TPH extraction from the soil; in fact, the removal efficiency of TPH by surfactants were significantly higher than that with water. Specifically, the flushing tests with SDBS at a concentration of 0.05 % showed average efficiencies close to 30 %. When the SDBS concentration was increased to 0.1 %, an increase of extraction efficiency (up to about 40 %) was observed. It is worth noting that for both SDBS concentrations, the highest efficiency occurred with the lowest flushing rate (6 mL min^{-1}), thus suggesting that in this case the contact time between polluted soil and surfactant solution plays a major role than the leaching effect due to the increased flow rate. Moreover, the observed results likely suggest a threshold flow rate efficacy that could be of interest for full scale applications. This result confirms the general behaviour observed in the previous study by authors (Di Trapani et al., 2023), where a similar performance was found for SDBS, but with lower removal rates for the same operational conditions, highlighting that the initial contamination as well as soil features can affect the process performance. For the flushing tests carried out with Tween 80, the observed extraction efficiencies were significantly higher compared to that of SDBS, likely related to the lower CMC of Tween 80, as better outlined below. Indeed, by increasing the Tween 80 concentration from 0.05 % to 0.1 % the extraction efficiency increased for both flow rates, by 30 % as average. Furthermore, it was noticed that for the Tween 80 concentration of 0.1 %, the highest removal efficiency (77 %) was obtained at the highest flow rate (8 mL min^{-1}). This result suggested that the removal efficiency of Tween 80 might be increased by increasing both the

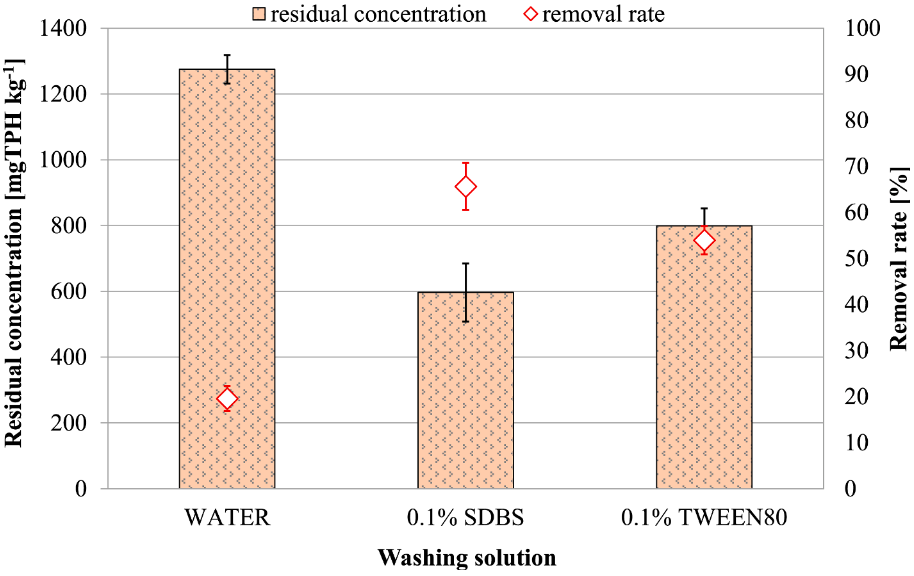

Fig. 2. Residual concentration of TPHs in soil samples and removal rate after pilot-scale water flushing.

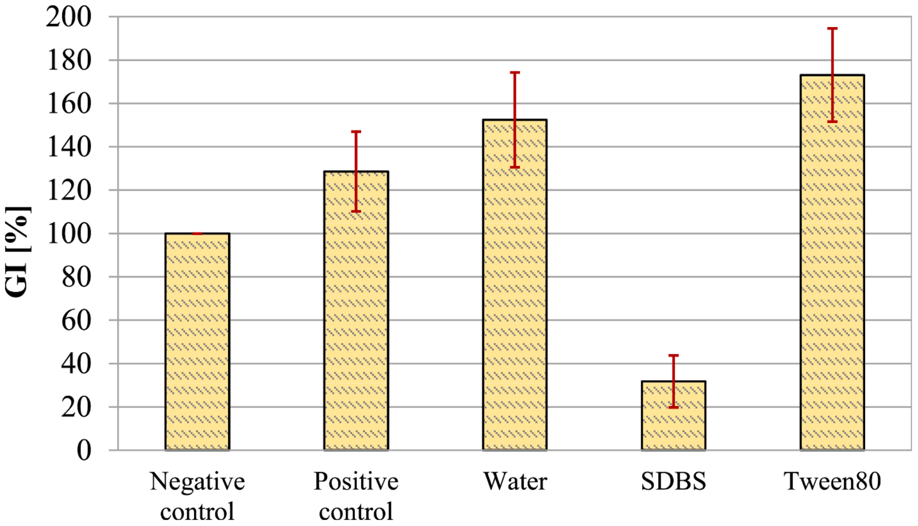

Fig. 3. Average GI values of soil samples after pilot-scale water flushing.

surfactant concentration and the flushing flow rate. Similar results were reported by Guo et al. (2009), who found that relatively high Tween 80 concentrations had positive effect on the organic pollutant desorption from soil. According to what above discussed for SDBS, the removal rates achieved for Tween 80 confirmed in general the trend observed in the previous study by authors (Di Trapani et al., 2023); nevertheless, referring to the same operational conditions (surfactant concentration of 0.1 % and flow rates equal to 6 and 8 mL min^{-1}), the removal efficiencies observed in the present study were quite higher, in agreement with what observed for water and SDBS, thus highlighting the role of raw contamination level on the extraction efficiency. The different behaviour between SDBS and Tween 80 agrees with what reported by Deshpande et al. (1999), who observed that a SDBS concentration 10 times higher than Tween 80 was required to obtain the same rate of pollutant removal. This is because the CMC of Tween 80 (15.72 mg L^{-1}) is much lower than that of SDBS (418.20 mg L^{-1}) and this would result in a higher desorption of hydrocarbons for Tween 80 at the same concentration. Indeed, non-ionic surfactants, as Tween 80, are easier to micellize due to the non-polar hydrophobic groups that can quickly aggregate while hydrophilic chains may easily separate in the aqueous phase. In contrast, a significantly higher concentration is required to anionic surfactants to overcome the electrostatic repulsion between ionic heads to form micelles (Ji et al., 2021). On the other hand, it was highlighted that soil adsorption of surfactants is not a major factor impacting the effectiveness organic pollutants removal since the adsorbed amount is usually relatively small (Ji et al., 2021).

However, it is worth noting that the effectiveness of surfactants in TPH removal strongly depends on the soil properties (e.g. type, particle size, organic matter content) (Huo et al., 2020). As an example, several studies reported that Tween 80 performed well independently of the soil type (Li et al., 2016; Wang et al., 2017), on the contrary, it performed worse in soil with a high content of organic matter (Chen et al., 2017; Rongsayamanont et al., 2020). Differently, literature reported that high sand content is beneficial to anionic surfactants (such as SDBS), while high silt and clay content is the opposite (Li et al., 2016; Urum and Pekdemir, 2004). These aspects deserve to be addressed in future investigations.

Based on the results obtained with the bench-scale flushing tests, pilot-scale tests were carried out by imposing the following operational conditions: flushing tests with water at a flow rate of 40 mL min^{-1} and flushing tests with 0.1 % Tween 80 or 0.1 % SDBS at a flow rate of 30 mL min^{-1}. Results of the pilot-scale flushing test are reported in Fig. 2.

Results obtained with the pilot-scale flushing tests confirmed that surfactants solution are more effective than water in extracting TPH. Precisely, the average removal rates were 19.6 %, 53.9 %, and 65.6 % respectively for water, Tween 80 and SDBS. However, contrarily to what observed in the bench-scale flushing tests, the extraction efficiency was higher for SDBS compared to Tween 80. The decrease of Tween 80 extraction efficiency could be due to the technical issues outlined above that hampered the regular development of the test. As a result, the lower flushing flow rate may have negatively impacted the final extraction rate. Nonetheless, this result supports previous findings (Di Trapani et al., 2023) where it emerged that for Tween 80, the leaching effect due to the higher flow rate play a key role in TPHs removal, prevailing on the contact time between the contaminant and the surfactant.

3.2. Soil phytotoxicity after flushing

Table S2 summarizes the GI values obtained for the 25 %, 50 %, and 100 % dilutions, respectively, on soil samples subjected to flushing with water as well as with SDBS and Tween 80 solutions, related to the bench-scale tests. Flushing with water or with the two surfactants had significantly different effects on the potential phytotoxicity of soil. Indeed, higher GI were observed in soil flushed with water and Tween 80 compared to the negative control (GI = 100 %). Conversely, soil flushed with SDBS showed lower GI values as well as low growth of *Lepidium Sativum* seeds. Such results are consistent with studies carried out by Zheng et al. (2007), Ni et al. (2014) and Di Trapani et al. (2023), which demonstrated that Tween 80 does not exhibit any inhibitory effect on plant growth in aqueous solutions: indeed, referring to its molecular structure and the consequent interactions with soil particles, it is worth noting that Tween 80 olds carbon potentially bioavailable, which increases the root permeability, leading to a more efficient absorption of nutrients from soil (Cheng et al., 2017). Also, the toxicity and inhibitory effect of SDBS are supported by studies conducted by Garon et al. (2002) and Singh and John (2013), who identified SDBS as toxic and poorly biodegradable (20 %).

Results obtained from the germination tests conducted on soil samples after the pilot-scale experiments (Fig. 3) confirmed those obtained from the bench-scale tests, underlining the negative impact exerted by SDBS on soil residual phytotoxicity compared to Tween 80, and confirming the hypothesis of higher toxicity of SDBS. Among the most important features of surfactants that might affect the environment are its toxicity and biodegradability. A surfactant can be considered biodegradable when its chemical structure can be broken down completely by microbial communities to accomplish their metabolic activities. Nevertheless, most of the chemical surfactants used in soil remediation, including SDBS, are not biodegradable and can promote a

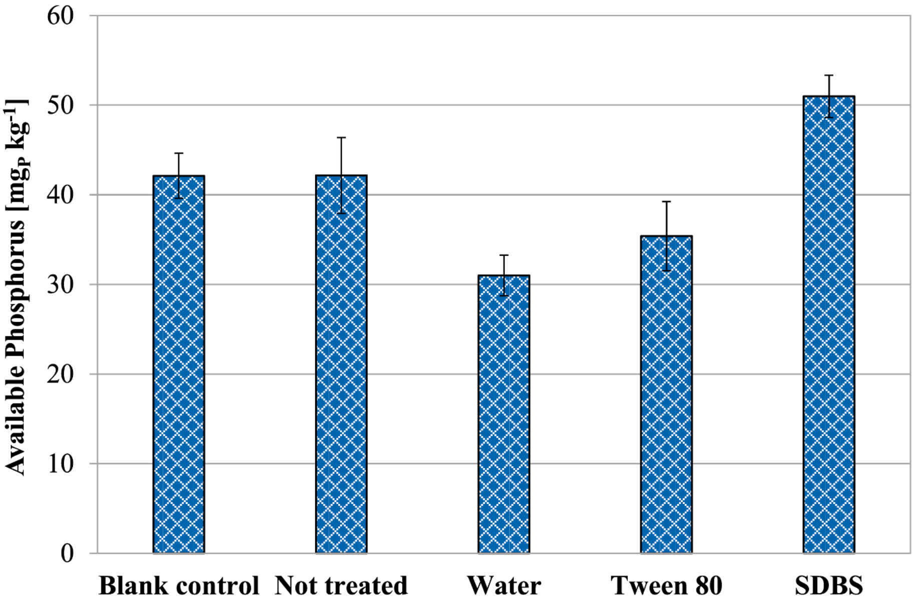

Fig. 4. Available phosphorus in soil after plant removal.

toxic impact on the soil environment, mainly due to their ability to absorb on the surface of the soil grains, leading to toxic accumulation (Karthick et al., 2019). Anionic surfactants, including SDBS, are generally more toxic than non-ionic ones, like Tween 80. In particular, the highest GI value (173 %) was achieved for soil samples treated with Tween 80, while the lowest GI (31.7 %) was observed in the test carried out with soil treated with SDBS, thus confirming its toxic effect on seeds germination. The phytotoxic effect exerted by SDBS was more significant compared to that caused by hydrocarbons, which, in contrast, showed less or no negative influence on seeds germination and this could impact the biological and physicochemical properties of soil in the long-term, negatively impacting the environment, human and soil health (Bolan et al., 2023). Indeed, for the positive control, GI (128.6 %) was higher than the negative control. This result is supported by Smith et al. (2006), who demonstrated that the presence of hydrocarbons in the soil does not negatively affect plant growth but rather promotes their accumulation in the root system. To confirm this statement, the TPH concentration was also evaluated on the fava plant roots after eradication, as better outlined in a section below.

3.3. Soil chemical properties after flushing and faba bean cultivation

Soil chemical properties are depicted in Table S3. Soil reaction (pH) after flushing and cultivation of faba bean did not show significant differences among treatments although in the TPH-contaminated soils it showed lowest values. In addition, TPH contamination increased soil EC. In particular, the EC of SDBS-treated soil showed the highest value. Such behaviour can be ascribed to the increased concentration of ions in the soil solution such as sodium and sulfate ions. The increase of soil salinity is a negative drawback, since it may cause osmotic stress to plant roots. Furthermore, it may negatively affect soil particles aggregation and, hence, permeability, hydraulic conductivity and microbial community (Machado and Serralheiro, 2017).

However, it is important to note the electrical conductivity was always lower than 2 dS m^{-1}, a threshold values above which some crops may be injured (Brady and Weil, 2008).

Contamination with TPH did not affect the amount of available phosphorus (P), showing the same value as the control soil (Fig. 4). Conversely, treatment with water and Tween 80 reduced the available P content. On the other hand, the SDBS-treated soil showed an available P increase of about 20 % compared to the control. The decrease of available P in Tween 80 and water-treated soils can be ascribed to the effect of the treatment (i.e. soil flushing) that leached soil available P, or to a greater P uptake by plants. Considering that P uptake did not show significant differences among treatments, the lower available P in Tween 80 and water treatments compared to the control can be ascribed to soil P leaching.

On the other hand, the increase of available P in SDBS-treated soil is probably due to the supply of P through the surfactant which holds 5.1 mg P g^{-1} (Table S1). However, an increase of available P already held by soil following the treatment with SDBS cannot be excluded. Indeed, following TPH and SDBS treatment, soil pH decreased from 7.6 to 7.0, thus increasing the solubility and availability of P. Penn and Camberato (2019) reported that the highest amount of available P usually occurs at soil pH between 6.5 and 7. Furthermore, the sulfate group of SDBS may substitute the phosphate group on soil colloids thus further increasing the availability of soil P. Such an increase, if on the one hand could promote plant growth, on the other hand might contribute to eutrophication of surface waters.

Table 3
Final average stem heights, number and average sizes of leaf (in brackets the standard deviation).

Sample	Final stem height [cm]	Number of leaves [−]	Leaf length [cm]	Leaf width [cm]
Blank control	17.7 (±2.6)	7 (±2.0)	6 (±0.2)	4 (±0.2)
Not treated	16.0 (±1.8)	7 (±1.5)	5 (±0.2)	3 (±0.4)
Water	15.7 (±1.7)	7 (±2.5)	4.5 (±0.3)	3.5 (±0.2)
Tween 80	17.6 (±2.7)	7 (±1.5)	6 (±0.3)	5 (±0.3)
SDBS	10.4 (±3.2)	6 (±1.4)	3 (±0.3)	2.5 (±0.4)

3.4. Biometric and chemical characteristics of faba bean plants grown in reclaimed soil

Fava plants started to sprout after 15 days from sowing and the first measurements were taken after an additional 10 days.

Fava grew well in all soil samples (Fig. S3). Specifically, plants grown in the blank control and in the soil treated with Tween 80 reached the same average height thus suggesting that this surfactant does not inhibit plant growth. On the contrary, the lowest plant growth occurred in the soil treated with SDBS thust suggesting its negative impact on plant

Fig. 5. Comparison of roots and plants growth: blank control (a), not treated (b), water (c), Tween 80 (d) and SDBS (e).

growth. This result is in accordance with findings reported by Garon et al. (2002), who showed that the presence of the anionic surfactant inhibited the growth of fungal strains, negatively impacting the nutrients cycles thus resulting in reduced plant growth. Instead, in the not treated soil and in the one treated with only water, a modest growth was observed, indicating that the presence of hydrocarbons does not negatively influence plant development. Table 3 reports the final average stem heights and the average leaf sizes.

Fig. 5 provides a comparison of plant growth and roots development after their eradication.

From Fig. 5, it can be observed that all plants exhibited comparable stem growth and root development (Fig. 5a–d), excepting those grown in the soil treated with SDBS (Fig. 5e). This difference was also corroborated by the weights of the plants (Table S4). In fact, the plants grown in the soils treated with SDBS exhibited the lowest weight values compared to those cultivated in the blank control and in the other treatments. In addition, the analysis of stem/root ratio showed no significant differences from the control, except for plants grown in soils

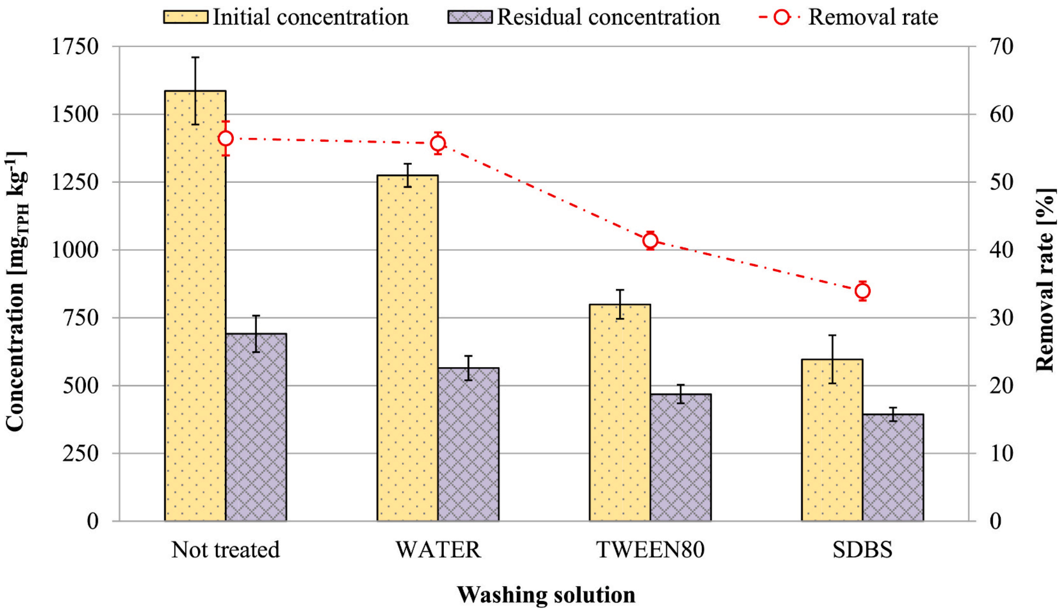

Fig. 6. Residual concentration and removal rate of TPHs in soil after plants removal.

treated with water and SDBS, where the highest stem/root ratios were recorded. These results suggest that the two treatments caused the root system to develop less than the stem. These results confirm that the residue of TPHs and presence of SDBS in the soil may have had a toxic or growth-inhibiting effect on *Vicia Faba* plants.

The total amount of P in the Fava steams is shown in Fig. S4. Although the SDBS-treated soils had higher values of available P compared to the other treatments, the total amount of P in the steams of plants grown in SDBS treated soil was lower than that of plants cultivated in the other soils, both treated or not treated. Considering that the concentration of P in plants did not differ among treatments, such result can be ascribed to the reduced growth of plants cultivated in SDBS treated soil and explain the highest amount of available P in soil treated with SDBS.

3.5. Residual TPH concentration in soil after fava plant removal and TPH mass balance

Fig. 6 shows the residual concentration and TPH removal efficiency in soil where *Vicia Faba* was grown. At the end of the cultivation period, hydrocarbon concentrations decreased compared to those immediately before planting, suggesting their adsorption by faba bean. The highest removal efficiency (>55 %) was observed in the soil not subject to the flushing process (not treated); this result could be probably due to the highest availability of hydrocarbons for plant uptake also coupled to the potential toxic effect of surfactant, especially referring to SDBS. Conversely, in soil treated with water or surfactants the removal efficiency was lower. In soil flushed with Tween 80 and SDBS the removal efficiency was 41 % and 34 %, respectively. These results suggest an absorption of hydrocarbons by the root system of *Vicia Faba*, confirming the findings of Nageswara Rao et al. (2007), who demonstrated the absorption of aliphatic hydrocarbons present in the soil by the root system of *Vicia Faba*.

Fig. S5 shows the balance of hydrocarbons referring to the whole experimental period, thus comprising periods P1 and P2. It can be observed that *Vicia Faba* led to a removal of approximately 50 % of the TPH present in the contaminated soil not subjected to any flushing treatment, while in the soil flushed with water, the TPH adsorption by the plant roots was close to 34 %. In the other cases, the dual effect between surfactant flushing and absorption by *Vicia Faba* allowed to achieve removal rates close to 70 % (as average), thus significantly mitigating soil contamination. The lowest rate of adsorption by *Vicia Faba* was achieved in the soil samples flushed with SDBS, thus confirming the GI results. In general, from the achieved results it was highlighted a higher hydrocarbon adsorption in the soils without residual surfactant concentrations. This result is not in line with previous experimental evidence, referring to Tween 80 coupled with phytoremediation, which highlighted a beneficial role exerted using surfactant in pollutant adsorption by vegetal species (Cheng et al., 2017). It is worth nothing that in the present study the flushing with surfactant and *Vicia Faba* growth occurred separately; a possible reason could be that in the flushing tests the surfactant enhanced the extraction of hydrocarbon classes more affine with root adsorption. However, this aspect deserves further experimental research, such as studies on surfactant-hydrocarbon interactions in the presence of plants, to be fully eviscerated.

4. Conclusions

In the present study batch- and pilot-scale tests with SDBS and Tween 80 were carried out to assess the extent of hydrocarbon removal from a soil contaminated with diesel-fuel. Tested surfactants were more effective than water in removing hydrocarbons from soil. In fact, plant roots cultivated in soil contaminated with hydrocarbons and then treated with surfactants showed the lowest content of hydrocarbons. However, the two surfactants behaved differently in removing hydrocarbons depending on the flushing rate. Tween 80 was more effective at the highest flushing rate, while SDBS at the lowest thus suggesting that the latter needs a high contact time to be effective. Basing on this, future activities should explore the role of soil features on the extraction performance. Potential phytotoxic effect of soil contaminated with hydrocarbons and subsequently treated with water or surfactants was assessed by the germination test and by growing *Vicia Faba* plants. Moreover, hydrocarbon adsorption by plant roots was assessed. The germination index values highlighted that soil samples treated with SDBS had higher phytotoxicity compared to those treated with Tween 80 (31.7 % vs 173 %, respectively). Such results were also confirmed by the response of *Vicia Faba L.* that showed the lowest heights and weights when cultivated in soil treated with SDBS, thus suggesting an inhibitory effect of SDBS on plant growth. Due to reduced development, the total P uptake was the lowest in plants grown in SDBS-treated soils, although there was a 20 % increase in soil available P. This increase is probably due to the surfactant which contains 5 mg P g^{-1} and decreased soil pH. From practical perspectives, the findings of the present study might provide useful indications in terms of surfactant choice and operational conditions in case of treatment scale-up, with special concern on agronomic reuse of soil after treatment, since the prolonged or excessive use of surfactants may exert adverse effects being detrimental to biodiversity and soil enzymatic activities. Nevertheless, field applications require a thorough site characterization, to properly design and operate the treatment, with the aim of finding the trade-off between economic and environmental aspects. Additional research should also highlight the economic issues related to the flushing time and volume of flushing solution, assessing the measurement of cumulative pore volume and removal rate, also exploring different typology of surfactants, as biosurfactants, that are characterized by low toxicity. Moreover, in view of practical applications, future research should focus on quality and safety of agricultural products as well as soil microbial community.

CRediT authorship contribution statement

Federica De Marines: Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Gaetano Di Bella:** Writing – original draft, Supervision, Data curation, Conceptualization. **Vito Armando Laudicina:** Writing – original draft, Supervision, Methodology, Data curation. **Sara Paliaga:** Writing – original draft, Methodology, Formal analysis. **Daniele Di Trapani:** Writing – original draft, Supervision, Methodology, 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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.177999.

Data availability

Data will be made available on request.

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