



Surfactant-enhanced mobilization of polycyclic aromatic hydrocarbons from an historically contaminated marine sediment: Study of surfactants' concentration effect and continuous test for sediment flushing simulation

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ABSTRACT

Contamination of marine sediments by polycyclic aromatic hydrocarbons (PAHs) poses a significant environmental threat, necessitating effective remediation strategies. This paper investigates the application of surfactants, both synthetic and natural, for the remediation of PAH-contaminated sediments, providing a systematic guideline for the preliminary selection of surfactants for flushing/washing operations, the optimal operative conditions, and the technical approach for PAH mobilization, especially in the context of a real aged contamination scenario. The study included a batch configuration test to evaluate the effect of surfactant concentration on PAH mobilization. Subsequently, a continuous configuration column experiment was performed to simulate a flushing operation of contaminated sediment. The study of process conditions highlighted that the increase in surfactant concentration led to a significant increase in PAH removal from the sediment, reaching almost 30 % efficiency using a 5 % wt surfactant solution. The column test showed great efficiency of the investigated surfactants in PAH mobilization through the flushing process of the contaminated matrix, resulting in 30 times greater efficiency than water within a much smaller pore volume range.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a class of organic compounds characterized by the structural arrangement of two or more aromatic rings condensed together. Among the several hundred known PAHs, 28 were identified as hazardous for humans by the United States Environmental Protection Agency (US EPA) in 2008, and only 16 are classified as priority pollutants due to their toxicity and adverse effects on human health [1–3].

Conventionally, PAHs are classified into light and heavy categories depending on whether the number of condensed aromatic rings is fewer

than or greater than 3, respectively [4,5]. Lighter PAHs exhibit lower persistence in the environment due to mechanisms like dilution, evaporation, and bacterial degradation. In contrast, heavy PAHs are characterized by poor water solubility and high hydrophobicity, leading to strong adsorption onto organic particles, making them much more recalcitrant and resistant to bacterial degradation [5,6].

Coastal areas, influenced by anthropogenic activities, serve as significant sources of pollution. PAHs can accumulate in sediments through strong adsorption, compromising water and sediment quality, and can bioaccumulate in marine organisms, ultimately reaching humans through the food chain [7–12].

Abbreviations: PAHs, Polycyclic aromatic hydrocarbons; US EPA, United States Environmental Protection Agency; ISB, *In-situ* bioremediation; ISC, *In-situ* capping; SER, Surfactant-enhanced remediation; NPS, National Priority Site; CMC, Critical micelle concentration; ASE, Accelerated solvent extractor; APGs, Alkyl-polyglycolides; SLs, Sophorolipids; RLs, Rhamnolipids; POECS, polyethoxylated co-surfactant; POEPCS, polyethoxylated-propoxylated co-surfactant; GC, Gas chromatography; MS, Mass spectrometer; PMMA, Polymethyl methacrylate; SIM, Selected Ion Monitoring; DCM, Dichloromethane; HRT, Hydraulic retention time; PV, Pores volume; VG, Geometrical volume; NIST, National Institute of Science and Technology.

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Remediation of PAH-contaminated marine sediments is a significant environmental challenge due to their recalcitrance and persistence [6]. Various techniques, both *ex-situ* and *in-situ*, have been studied and developed over the years [13]. *Ex-situ* technologies involve the excavation of polluted sediment and subsequent treatment at specific plants, although in most cases, the dredged sediment is sent to a landfill [14, 15]. However, *ex-situ* technologies can be expensive due to dredging operations and sediment transport, especially in offshore scenarios. *In-situ* technologies, such as *in-situ* bioremediation (ISB) and *in-situ* capping (ISC), are more cost-effective as they do not require sediment excavation from the seabed [16,17]. Bioremediation has been proven to be an environmentally friendly and cost-effective method for polluted soils and sediment remediation [14]. However, it can be affected by several limitations: low conversion rate, low efficiency when PAHs are less bioavailable (especially for aged contamination sources), and the possibility of generating more toxic intermediates which can inhibit the microbial population [9,18]. Capping technology is typically used for the isolation of contaminants and the drastic reduction of their mass flux to water above by installing a physical barrier [19], but pollutants are not treated and remain in the environment [9]. In most cases, it is possible to implement capping with reactive layers containing sorbent materials (activated carbon, biochar, zeolites) that allow a better immobilization of contaminants as well as the development of bacterial communities for biodegradation [20]. Other possible treatments of contaminated sediments reported in the scientific literature are thermal desorption and electrochemical processes, but despite offering high efficiencies are characterized by very high costs and high energy demands [17,21].

It is well known that *in-situ* processes are preferred over *ex-situ* processes, thanks to their lower costs, but in port areas sediment dredging is frequently required, for example to facilitate naval traffic. The dredged matrix can find several applications in various ways, including beach resurfacing, civil construction projects, and instances of land reclamation [22,23]. Considering the reuse of dredged sediment, if contaminated, its remediation with *ex-situ* approaches becomes necessary to ensure environmental and healthy safety standards.

In recent years, surfactant-enhanced remediation (SER) has emerged as a promising approach, leveraging the properties of surfactants to enhance the mobilization and subsequent removal of PAHs from sediments. Surfactants, or surface-active agents, possess amphiphilic structure (hydrophobic tail group directly linked with a hydrophilic head) that allow them to interact with both water and organic phases, facilitating the solubilization of hydrophobic PAHs and increasing their recovery [24,25]. The rationale behind employing surfactants lies in their ability to reduce the interfacial tension between sediment particles and pore water and at the same time to increase the apparent solubility of insoluble compounds, thereby promoting the desorption of PAHs from sediment matrices [26,27]. Thus, the presence of surfactants can enhance hydrophobic pollutants' mass transfer in the aqueous phase, offering several advantages over most common and most used technologies, including greater removal efficiency, which is reflected in shorter time of work, lower costs, and the possibility to treat aged sources, where pollutants are almost immobile under normal environmental conditions, while overcoming any possible rebound effect [28, 29].

Surfactants can be produced by chemical synthesis from both fossil and green raw materials or by microbial secondary metabolism [30,31]. Synthetic surfactants from fossil sources have notable environmental impacts, high levels of toxicity, and low biodegradability [31]. Consequently, new technologies are focusing on 100 % bio-based surfactants [32], such as sugar-based nonionic surfactants, both synthetic from renewable sources (e.g., biomass containing sugars and fatty acid esters) or produced by the secondary metabolism of microorganisms (e.g., biosurfactants) [33].

In this context, the present work deeply investigates a novel methodologic approach for the treatment of a PAHs-polluted marine

sediment using green non-ionic surfactants, both synthetic and natural, as extracting agents.

More in detail, a systematic process study was conducted through a sequence of lab-scale experiments to evaluate the effectiveness of surfactants in solubilizing PAHs from contaminated sediment. After a preliminary batch test conducted in a previous study [34] using a surfactant concentration of 5 times the critical micelle concentration (5x CMC), to evaluate the ability of the surfactants to solubilize PAHs in the aqueous phase, in this work additional batch tests were performed to explore the impact of surfactants concentration on PAHs mobilization. Then, by selecting the best surfactants in terms of mobilization efficiency and their optimal concentration, a continuous configuration column experiment was finally carried out to investigate PAHs mobilization under conditions representative of a real continuous flushing process, considering it as an alternative and innovative process configuration to the more traditional surfactant-enhanced sediment washing in batch configuration reactors. Overall, this work aims to provide valuable information on the feasibility and effectiveness of surfactant-based approaches to addressing PAHs contamination in marine environments. The results of this research have the potential to inform future remediation practices, offering an innovative solution to facilitate the efficient and sustainable removal of organic contaminants from contaminated sediments.

2. Materials and methods

2.1. Materials

2.1.1. Contaminated marine sediment

The marine sediment used for this study came from the National Priority Site (NPS) of Bagnoli-Coroglio (Naples) located in the Campania region, in the south of Italy, and is affected by a historical contamination by polycyclic aromatic hydrocarbons (PAHs) due to the activity of local steel industries that began operations in the early 20th century and were decommissioned in the early 1990s [35,36]. Therefore, it is an aged contamination source under sea level for more than 30 years in which the contaminants represent the most residual and more recalcitrant fraction, exhibiting markedly reduced mobility under standard environmental conditions [7,37]. Before starting any experimental activity, the sediment stock was well-dried. In this way, it was possible to work with a totally dry sediment without residual sea water which could provide significant content of dissolved ions. From the reference stock of the sediment, three different aliquots (100 mg each) were analyzed to determine the grade of contamination, extracting the interested analytes with n-hexane and acetone at 120°C and 1500 psi, using an Accelerated Solvent Extractor (ASE 200 Dionex), after the addition of surrogate standards, in accordance with EPA 3545a method [38]. Successively, a silica gel clean-up technique was utilized, using 3 g of silica, activated at 250°C for 1 night, and eluting, firstly, with 10 mL of n-hexane, and then with 20 mL of n-hexane:dichloromethane 2:1, as described in EPA 3630 procedure [39]. The analytical determination of PAHs was carried out as described in the analytical method section. Overall, 16 different PAHs were identified with a concentration range between 19.4 $\mu\text{g g}^{-1}$ and 695 $\mu\text{g g}^{-1}$, determining a concentration of 3.51 mg g^{-1} of total PAHs (\sum PAHs). All identified PAHs and their concentration in the sediment are shown in Table 1.

2.1.2. Surfactants

Seven different non-ionic, eco-friendly, biodegradable surfactants, both synthetic and biological, have been selected for investigation. All surfactants were supplied by Chimec S.p.A. from Pomezia (Rome) in the form of high-concentration stock aqueous solutions. Specifically, five synthetic alkylpolyglucosides (APGs) were used, designated in the manuscript as APG 1, APG 2, APG 2a, APG 2b, and APG 2c. APG 2a, 2b, and 2c refer to three formulations of APG 2, characterized by the presence of small amounts of additives: C6 branched alcohol, C10

Table 1

List of 16 identified PAHs in the sediment and their concentration.

Contaminant	Molecular Weight (g mol ⁻¹)	Aromatic Rings	Concentration (µg g ⁻¹)
Naphthalene	128.17	2	52.8
Acenaphthylene	152.20	2	19.4
Acenaphthene	154.21	3	43.7
Fluorene	166.22	3	51.4
Phenanthrene	178.23	3	238.7
Anthracene	178.23	3	70.4
Fluoranthene	202.26	4	695.0
Pyrene	202.26	4	427.9
Benzo(a)anthracene	228.29	4	282.2
Chrysene	228.29	4	145.6
Benzo(b+j)fluoranthene	252.32	5	332.6
Benzo(k)fluoranthene	252.32	5	92.6
Benzo(a)pyrene	252.32	5	636.3
Indeno(1,2,3-cd)pyrene	276.34	6	217.0
Dibenzo(a,h)anthracene	278.35	6	60.0
Benzo(g,h,i)perylene	276.34	6	142.1
∑ PAHs			3507.8
∑ LIGHT PAHs	< 200	< 4	476.4
∑ HEAVY PAHs	≥ 200	≥ 4	3031.4

polyethoxylated co-surfactant (POECS), and C10 polyethoxylated-propoxylated co-surfactant (POEPCS), respectively. All APGs surfactants used in the study were synthesized by the company using renewable raw materials, such as glucose from organic waste and fatty alcohol from vegetable oils [27,40], instead of fossil sources (typically used for synthetic surfactant production [31]) demonstrating their sustainability from both economic and environmental perspectives.

In addition, two biosurfactants were investigated: one rhamnolipid (named RL 2) and one sophorolipid (named SL), prepared in an alcoholic solution with 33 % glycerol and 33 % isopropyl alcohol.

Both RL 2 and SL were biosynthesized by microbial fermentation of an organic feedstock composed of vegetable oils and sugars. After biosynthesis, the biosurfactants were directly diluted with the glycerol-isopropyl alcohol mixture and were supplied by the producing company without any separation process for greater cost-effectiveness.

Looking at environmental implications, all investigated surfactants are recognized as readily biodegradable and non-toxic products for organisms and plants, as reported on the European Chemical Agency (ECHA) website [41–43].

These surfactants also exhibit low environmental persistence due to their non-ionic nature, which strongly reduces their adsorption on organic matter and prevents their precipitation by aggregation with counterions, unlike anionic and cationic surfactants. In addition, thanks to their non-ionic nature, all surfactants do not interact with dissolved ions (such as chloride), avoiding any interference that could cause an efficiency reduction in contaminants mobilization [44,45].

All surfactants have been characterized in previous works by several measurements of the liquid-air surface tension of surfactant solutions at different concentrations to experimentally determine the critical micellar concentrations (CMCs) [27,34]. The chemical structure, composition of all investigated surfactants and formulations, and their CMC values are detailed in Table 2.

2.2. Methods

2.2.1. Batch configuration experiment: surfactant concentration effect on PAHs mobilization

Several batch tests were performed to investigate the effect of surfactant concentration on the PAHs mobilization process. All batch tests were performed in duplicate at room temperature and pressure conditions (25 °C and 1 atm) in 42 mL borosilicate glass vials. Each reactor was loaded with 1 g of sediment and completely filled with 42 mL of surfactant solution. All reactors were mechanically stirred on a rotary plate for 48 hours and then centrifuged for 10 minutes at 3000 rpm to

allow the complete separation between the solid phase (washed sediment) and the liquid phase (surfactant solution containing mobilized PAHs). The supernatant was filtered with a 0.45 µm cellulose acetate syringe filter and then analyzed using a gas chromatograph equipped with a mass spectrometer detector (GC-MS) (Agilent 7890A-5975 C GC-MS).

For the experiments, three different surfactant concentrations were tested: 1 %, 3 %, and 5 % wt. In this way, for each condition, all solutions were prepared with the same surfactant concentration in order to quantitatively compare the PAHs mobilization performance.

2.2.2. Continuous configuration column experiment: flushing simulation of the sediment

The next phase of the study involved a continuous configuration column test to simulate a lab-scale flushing process on the contaminated sediment. Simultaneously, a thorough investigation into the surfactants' capacity to mobilize and enhance the solubility of PAHs was conducted.

Three column tests were performed, using three different flushing agents: i) distilled water as a control test; ii) the synthetic surfactant APG 2; and iii) the biosurfactant SL after a pre-treatment with distilled water. Both synthetic and natural surfactants were chosen based on batch test results, where they resulted as the most promise in PAHs mobilization. A surfactant concentration of 1 % wt was utilized. All continuous experiments lasted 14 days. The selection of these two surfactants allowed for a comparative assessment of the different performances and behaviors of synthetic and biological surfactants towards contaminants.

PMMA cylindrical 1D columns (H = 14 cm; Ø = 2.5 cm; volume = 68.7 cm³) were employed. Silica sand with a low adsorption capacity was used for the packing of 3 cm at the top and bottom of each column, while 8 cm of contaminated marine sediment from Bagnoli was packed in the middle. The columns were packed under mechanical stress to ensure a homogeneous liquid phase front and to prevent the formation of a preferential flow path of aqueous phase through the sediment. Before closing the columns, a non-woven fabric filter was applied at the top and bottom to avoid the obstruction of the tubes. Throughout the entire experiment, a peristaltic pump (Gilson Miniplus Evolution) was used to feed the column at a constant flow rate (Q) of 0.6 mL/min. At the exit, the tube was connected to a fraction collector (Gilson FC 204) to collect equal volumes of effluent every 16.5 minutes in different tubes. The effluent fractions were collected into 10 mL glass vials, hermetically closed with a Teflon butyl stopper (Wheaton, Millville, NJ), sealed with an aluminum cap, and then stored at -18 °C until analysis. For PAHs quantification, 1 mL of solution from each vial was analyzed by GC-MS. A schematic representation of the experimental setup is shown in Fig. 1. Details of the continuous systems are summarized in Table 3.

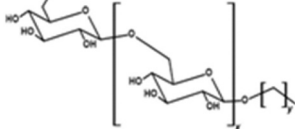
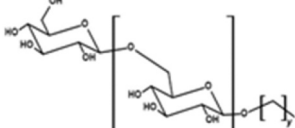
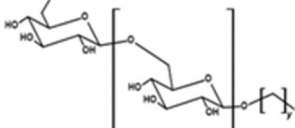
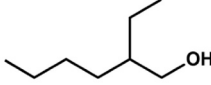
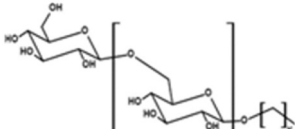
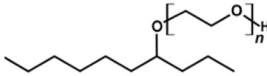
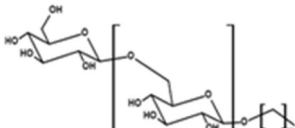
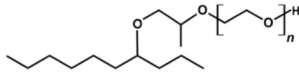
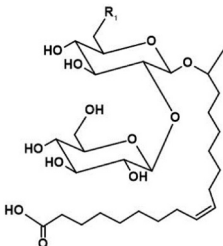
2.2.3. Analytical methods

For PAHs quantification in liquid samples (both from the solvent extraction of sediment characterization and mobilization tests), 1 mL of the solution was collected using a Gilson pipette and transferred into a vial (Supelco, Bellefonte, Pennsylvania) where 1 mL of dichloromethane (DCM) and the selected internal standards (a mix of deuterated PAHs: Naphthalene d-8, Acenaphthene d-10, Anthracene d-10, Pyrene d-10, Chrysene d-12, Perylene d12 – ULTRA Scientific J.T. Baker, Deventer, Holland) were also added. Before the analysis, each sample was centrifuged at 2500 rpm for 10 minutes for the separation of DCM and water.

The analytical determination of PAHs was carried out using an Agilent 7890A-5975 C GC-MS system equipped with a DB 5MS capillary column (30 m × 0.25 mm i.d. × 0.25 µm thickness film). The internal standard method was used to plot the calibration curve using the reference material NIST 2260a. The quantitation limit was 0.1 µg kg⁻¹ for each single compound. Helium (He) was used as the carrier gas at a flow rate of 0.5 mL min⁻¹, the injection temperature was set at 210 °C. The analysis was performed in Selected Ion Monitoring (SIM) mode with two temperature ramps. Specifically, an initial oven temperature of 60

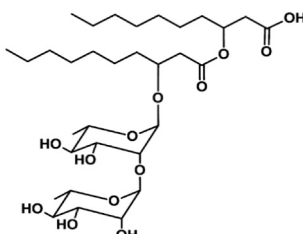
Table 2

Chemical structure, composition and CMC values of investigated surfactants and formulations. POECS: polyethoxylated co-surfactant; POEP: polyethoxylated – propoxylated co-surfactant. References: ^a Amanat et al [27]. ^b Moscatelli et al [34].

Name	Surfactant	Additive
APG 1 Alkylpolyglycoside CMC ^a = 0.06 % wt	 X = 1.7 (average) Y = 8 - 10	/
APG 2 Alkylpolyglycoside CMC ^a = 0.007 % wt	 X = 1.5 (average) Y = 8 - 14	/
APG 2a Alkylpolyglycoside CMC ⁶ = 0.065 % wt	 X = 1.5 (average) Y = 8 - 14	 C6 branched alcohol. C = 0.7 % wt
APG 2b Alkylpolyglycoside CMC ^b = 0.035 % wt	 X = 1.5 (average) Y = 8 - 14	 C10 POECS n = 3-9 C = 1.1 % wt
APG 2c Alkylpolyglycoside CMC ^b = 0.037 % wt	 X = 1.5 (average) Y = 8 - 14	 C10 POEPCS n = 5-14 C = 1.1 % wt
SL Sophorilipid CMC ^a = 0.0125 % wt		/

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Table 2 (continued)

Name	Surfactant	Additive
RL 2 Rhamnolipid CMC ^a = 0.0173 % wt		/

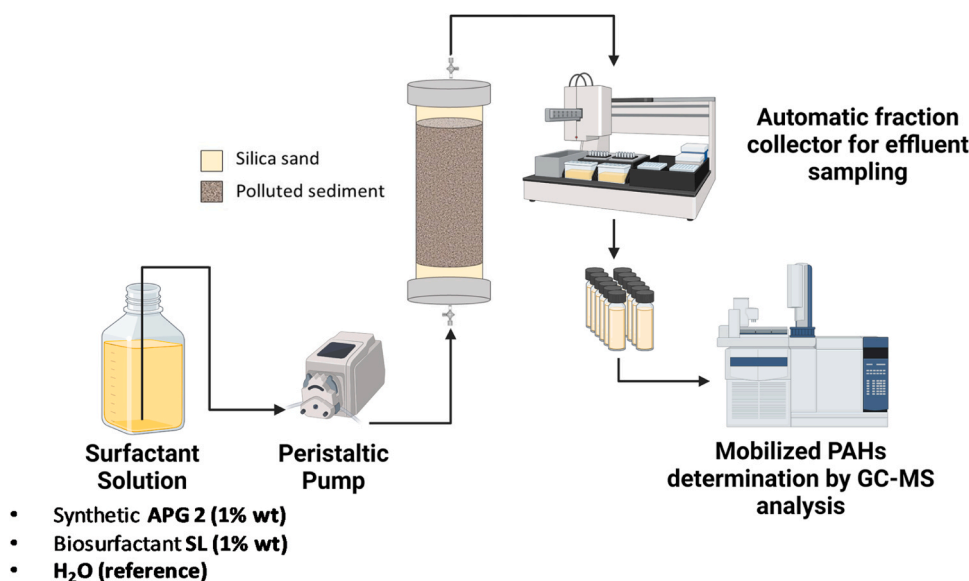


Fig. 1. Experimental set-up of continuous column tests.

Table 3

Characteristics of set-up columns.

Column	Flushing Agent	Sediment amount (g)	Duration of treatment
#1	H ₂ O	44	14 days
#2	APG 2 (1 % wt)	47.3	14 days
#3	H ₂ O + SL (1 % wt)	47.7	7 days (H ₂ O) + 7 days (SL)

°C is held for 1 minute. Then a first temperature ramp with a rate of 20 °C min⁻¹ is performed until 120 °C, held for 1 minute, and a second ramp is performed with a rate of 7 °C min⁻¹ up to 330 °C, held for 2 minutes, for a total run time of 37 minutes.

2.2.4. Tracer test

Before starting the column experiments, a tracer test for each column was carried out by feeding a 1 g L⁻¹ KCl solution with a constant flow rate $Q = 0.6 \text{ mL min}^{-1}$ (step signal) to calculate the fluid dynamic parameter of columns, such as the hydraulic retention time (HRT), the pores space's volume (V_p), and the porosity (ϵ). Since ion chloride (Cl⁻) does not interact with the stationary phase, its residence time is solely dependent on the fluid dynamics parameters of the column. The conductivity of the outlet of the reactor was continuously monitored by a HandyLab® 330 (SI-analytics, Weilheim, Germany) conductometer to monitor chloride concentration.

2.3. Calculation

For the tracer test, F-curves were built by plotting outlet Cl⁻ concentration normalized by inlet Cl⁻ concentration (C/C_0) as a function of time. The approach of the first derivate method was used for the flex point determination of the F-curve, representing the experimental hydraulic retention time (HRT). The pores space's volume (V_p) was calculated with Eq. 1 by multiplying the HRT and the flow rate (Q). Then, the ratio between V_p and the geometrical volume (V_G) gives the porosity (ϵ) of the fixed bed, as reported by Eq. 2.

$$V_p [\text{mL}] = \text{HRT} [\text{min}] \times Q [\text{mL/min}] \quad (1)$$

$$\epsilon (\%) = V_p [\text{mL}] / V_G [\text{mL}] \times 100 \quad (2)$$

Data of batch concentration test were processed in order to calculate the percentage of mobilized PAHs by the ratio between the total mass of PAHs in the aqueous phase after 48 hours of washing and the total mass of PAHs in the sediment before the test, as shown by Eq. 3.

$$\begin{aligned} \% \text{PAHs} &= (C_{\text{PAHs, aq}} \times V_{\text{aq}}) / (C_{\text{PAHs, s}} \times m_s) \times 100 \\ &= (m_{\text{PAHs, aq}} / m_{\text{PAHs, s}}) \times 100 \end{aligned} \quad (3)$$

Where, $C_{\text{PAHs, aq}}$ (mg mL⁻¹) and $C_{\text{PAHs, s}}$ (mg g⁻¹) are the concentrations of PAHs in the aqueous phase after the treatment and in the sediment at starting point (before the treatment), respectively; V_{aq} and m_s are the volume of surfactant solution used for the washing (42 mL) and the mass of sediment in each batch reactor (1 g), respectively. The terms $m_{\text{PAHs, aq}}$ and $m_{\text{PAHs, s}}$ indicate the masses (mg) of PAHs in aqueous phase after washing operation and in the sediment before the treatment,

respectively.

For continuous column test, PAHs concentration data were plotted against the pores volume (PV) (volume of the solution passing through the column normalized by the total pore volume (V_p) of the fixed bed to obtain the concentration profile of mobilized PAHs) [25].

Data processing of the column continuous test regarded the calculation of the total mass of mobilized PAHs and then the determination of a removal factor (in percentage) of each tested flushing agent, for a comparative assessment of the PAHs mobilization capacity. In the column tests, the PAHs concentration, the total mass of PAHs mobilized, and the percentage of mobilization have been calculated as follows:

- By the analysis in GC-MS, concentrations of PAHs (C_{PAHs}) ($mg L^{-1}$) in the effluent samples are determined. Concentration data were plotted against the pores volume of fed solution to obtain the profile of PAHs concentration.
- The total amount of PAHs mobilized (mg) is calculated by integrating the under-curve area, which represents the concentration of total PAHs in each fraction per volume unit, as the sum of the areas of the rectangular strips.
- The percentage of mobilization is calculated from the ratio between the extracted mass of PAHs in aqueous phase and the initial mass of total PAHs in the sediment.

3. Results and discussion

3.1. Batch configuration experiment: surfactant concentration effect on PAHs mobilization

Fig. 2 shows the trend of total PAHs (\sum PAHs) mobilization for all investigated surfactants at each tested concentration level. Qualitatively, the graph suggests that the ability of surfactants to mobilize PAHs increases almost linearly as the surfactant concentration rises above the CMC. This behavior is associated with the increased number of micelles in the solution, which enhances the pseudo-solubilization effect toward hydrophobic compounds, allowing for more efficient transfer into the aqueous phase [46].

At the lowest concentration (1 % wt), all surfactants showed a global PAHs removal efficiency ranging between 5 % and 14 %, except for the APG 2a formulation, which was the least promising with a total PAHs mobilization of 3.2 %. On the other hand, the SL biosurfactant and synthetic APG 2 gave the best results, with total PAHs mobilization of 14.4 % and 14 %, respectively. They were followed by APG 1 with a 13 % PAHs mobilization efficiency, then APG 2b and APG 2c with 10.4 % and 8.5 %, respectively. Lastly, RL 2 biosurfactant and APG 2a

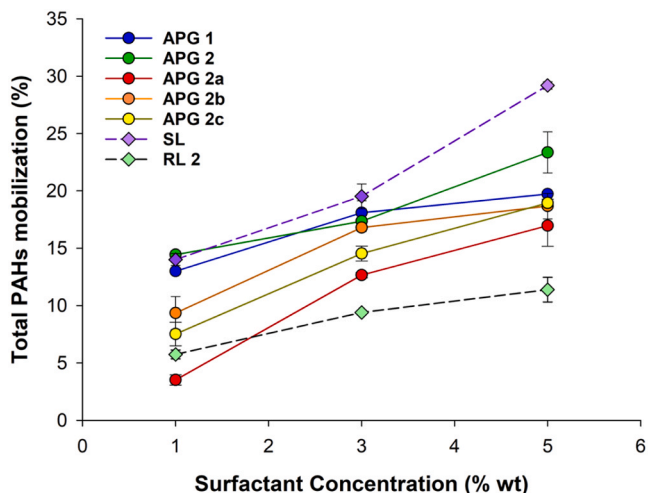


Fig. 2. PAHs mobilization (%) at different surfactant concentrations.

had mobilization efficiencies of 5.6 % and 3.2 %, respectively.

From the trends shown in Fig. 2, it is evident that the different surfactants responded differently to the concentration increase. Indeed, from 1 % wt to 3 % wt and 5 % wt, differences in the increase of PAHs mobilization ability were observed. For example, alkylpolyglycosidic formulations (APG 2a, APG 2b, and APG 2c) showed significantly higher performance enhancement than non-additivated APGs (APG 1 and APG 2). In particular, PAHs mobilization ability of the APG 2a formulation was four times higher, increasing from 3.5 % up to 12.6 % (a 295 % increase) when its concentration was raised to 3 % wt. With the subsequent concentration increase up to 5 % wt, the total PAHs mobilization further increased by about 34 % compared to the previous condition, reaching the value of 17 %.

For the APG 2b and APG 2c formulations, the improvement in PAHs mobilization ability was lower than for APG 2a. Specifically, with the concentration increase up to 3 % wt, total PAHs mobilization increased by 62 % (from 10.4 % to 16.8 %) and by 58 % (from 8.5 % to 13.5 %) for APG 2b and APG 2c, respectively. At a surfactant concentration of 5 % wt, PAHs mobilization for APG 2b and APG 2c reached 18.7 % and 19 %, respectively, with a corresponding increases of 11 % for APG 2b and 40 % for APG 2c. Considering the change in surfactant concentration from 1 % wt to 5 % wt, the global increases in PAHs mobilization were 430 %, 80 %, and 122 % for APG 2a, APG 2b, and APG 2c, respectively.

As previously mentioned, non-additivated APGs (APG 1 and APG 2) exhibited lower enhancement in PAHs mobilization ability than formulations at the same concentration. In the presence of APG 1, total PAHs mobilization increased by 39 % (from 12.9 % to 18 %) and by a further 9 % (from 18 % to 19.7 %) when the concentration was increased to 3 % wt and 5 % wt, respectively. For APG 2, total PAHs mobilization increased by 24 % (from 14 % to 17.4 %) and by 34 % (from 17.4 % to 23.4 %) as the surfactant concentration increased to 3 % wt and then to 5 % wt. Overall, with the increase in concentration from 1 % wt to 5 % wt, the mobilization of PAHs in the presence of APG 1 and APG 2 increased by 52 % and 66 %, respectively.

In the context of biosurfactants SL and RL 2, the response to increased surfactant concentration in the washing solution was less intense than for alkylpolyglycosidic formulations and slightly greater than for non-additivated alkylpolyglycosides. Specifically, SL experienced a performance increase of 35.2 % when its concentration was increased from 1 % wt (14.4 % mobilized total PAHs) to 3 % wt (19.5 % mobilized total PAHs). With the increase in concentration to 5 % wt, SL mobilizing capacity further increased by 41 %, reaching the value of 27.6 %. Thus, with the increase in surfactant concentration from 1 % wt to 5 % wt, the mobilization of total PAHs from the sediment almost doubled, with an overall increase of 102 %.

A similar behavior was observed with the rhamnolipid RL 2. In this case, PAHs mobilization increased by 64 % (from 5.7 % to 9.4 %) and by 21 % (from 9.4 % to 11.4 %) when surfactant concentration increased from 1 % wt to 3 % wt and from 3 % wt to 5 % wt, respectively.

Quantitatively, the biosurfactant SL and the synthetic APG 2, which have the lowest CMC values (see Table 2), provided the best performances in terms of PAHs mobilization for both minimum (1 % wt) and maximum (5 % wt) concentration conditions.

A very interesting aspect of this investigation is shown in Fig. 3, which illustrates the variation of the heavy PAHs fraction in the total mobilized PAHs in the aqueous phase. The bars diagram in the figure highlights that the heavy PAHs fraction becomes progressively greater as the surfactant concentration increases. Specifically, using 5 % wt surfactant solutions, the heavy PAHs fraction in the total mobilized PAHs reached values greater than 83 %. In this context, the best performances were obtained with both the sophorolipid SL and the alkylpolyglucoside APG 1, where the molar fraction of heavy PAHs was 88 % at a concentration of 5 % wt.

This behavior is particularly relevant because it demonstrates that increasing the concentration of surfactants not only enhances the total

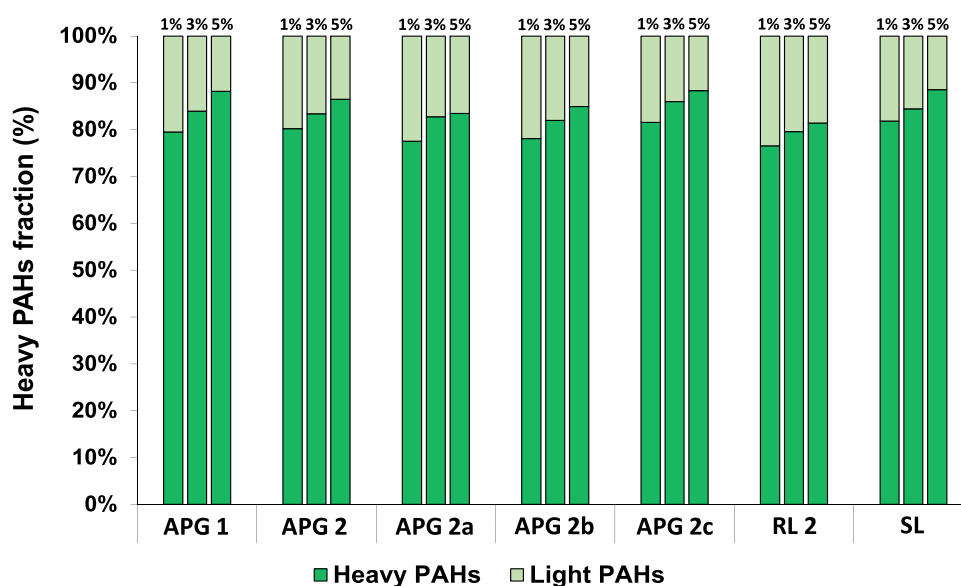


Fig. 3. Increase in heavy PAHs molar fraction in the total mobilized PAHs with the increase in surfactant concentration.

mobilization of PAHs but also increases the amount of the heavy fraction of PAHs, which includes the less soluble, less mobile, and most recalcitrant compounds.

3.2. Continuous configuration column experiment

3.2.1. Tracer tests

Step signal tracer tests were performed on all set-up columns for the experimental determination of fluid-dynamic parameters of the systems, such as hydraulic retention time (HRT), volume of the pores (V_p) and porosities (ϵ). These parameters are summarized in Table 4.

The difference of calculated parameters among the three columns is mainly due to the different packing of the sediment since the packing operations were made manually by mechanical percussions of reactors.

3.2.2. Flushing simulation of the sediment

Fig. 4 shows the concentration profile of total PAHs in the outlet for column #1, which was flushed with distilled water. For this system, total PAHs concentrations in the effluent were quite low, ranging from 45 to 225 $\mu\text{g L}^{-1}$, with an average value of $130 \pm 6 \mu\text{g L}^{-1}$. This low concentration is related to the low solubility of the pollutants, which represent the most residual and recalcitrant fraction over decades. A further characteristic aspect of H_2O flushing is that the mobilized total PAHs (grey circles) consisted almost exclusively of light PAHs (red circles), with only small traces of heavy PAHs (green circles).

By integrating the area under the flushing curve, it was possible to determine the total mobilized PAHs mass, which was equal to 1.6 mg of total PAHs. The related removal efficiency was 1.1 %.

For column #2, which was flushed with an APG 2 solution at 1 % wt (Fig. 5a), the first notable aspect is the immediate and rapid increase in PAHs concentration to a maximum value of 324.7 mg L^{-1} , that is four orders of magnitude greater than the PAHs concentration measured in column #1 (reported in the graph as blue squares). Additionally, the surfactant led to the mobilization of a significant fraction of heavy PAHs.

Table 4
Fluid-dynamics parameters of columns.

Column	Q (mL min^{-1})	HRT (min)	V_p (mL)	ϵ (%)
#1	0.57	90	51.3	74.7
#2	0.54	95	51.3	74.7
#3	0.60	85	51.0	74.2

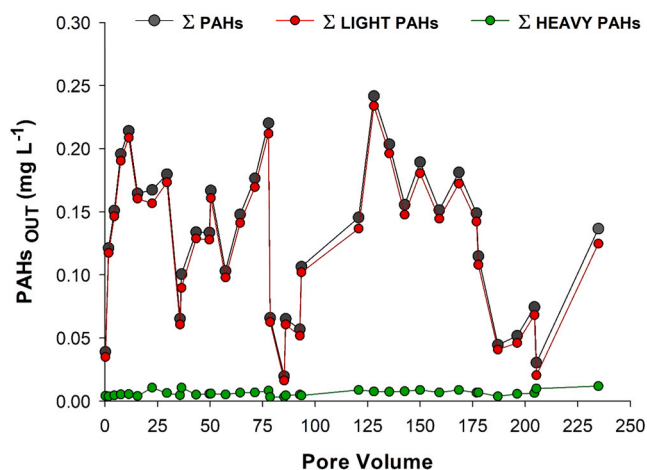


Fig. 4. Outlet PAHs concentration profiles for column #1 treated with distilled water.

These results confirm the ability of surfactants to enhance the solubilization and the mass transfer of pollutants, which were poorly mobile in the presence of water alone.

More specifically, Fig. 5b (with the x-axis scale zoomed in the range of 0–10 PV) shows that the PAHs mobilization process began within 1 pore volume of fed solution (indicated by the first PAHs concentration increase in the outlet) and reached the maximum after just 1.2 pore volumes, corresponding to about 60 mL of feeding. Considering a constant flow rate ($Q = 0.6 \text{ mL min}^{-1}$), the maximum PAHs mobilization was obtained in approximately 90 minutes of treatment. After reaching the maximum, the outlet concentration of PAHs decreased almost instantaneously, stabilizing at 1–2 mg L^{-1} after just 5.5 pore volumes. This stable concentration was maintained for the duration of the experiment (14 days, equivalent to 230 pore volumes of feeding).

From a quantitative perspective, by integrating the area under the curve, the mobilization of 46.3 mg of total PAHs was calculated, corresponding to a removal efficiency of 27.9 %.

Fig. 6a illustrates the outlet PAHs concentration profile after the complete flushing process conducted on column #3. This process was divided into three phases: i) pretreatment with distilled water for 7 days (125 pore volumes); ii) sediment flushing with SL biosurfactant for 7

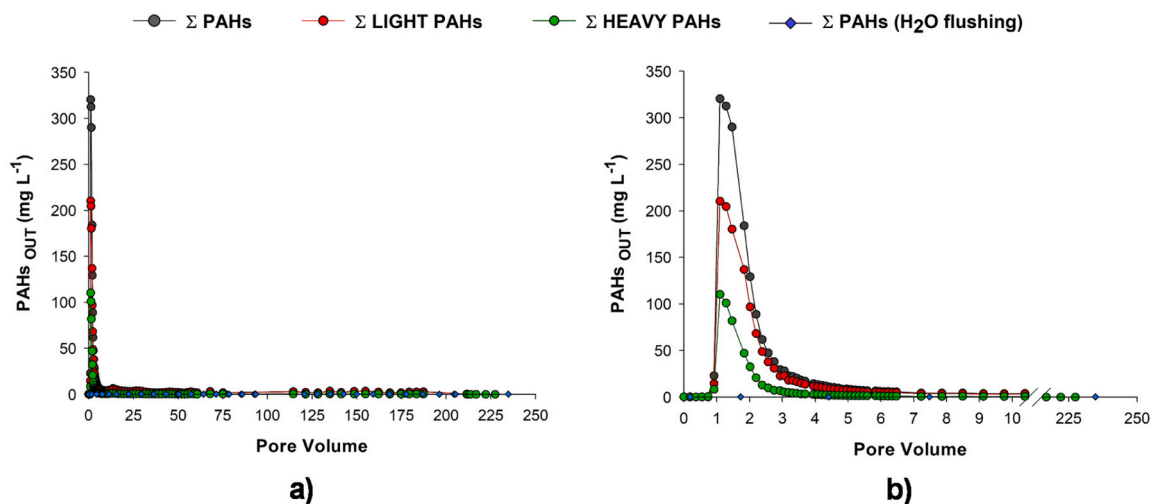


Fig. 5. Outlet PAHs concentration profile for column #2 treated with 1 % wt APG 2 solution. a) whole process; b) first 10 pores volumes.

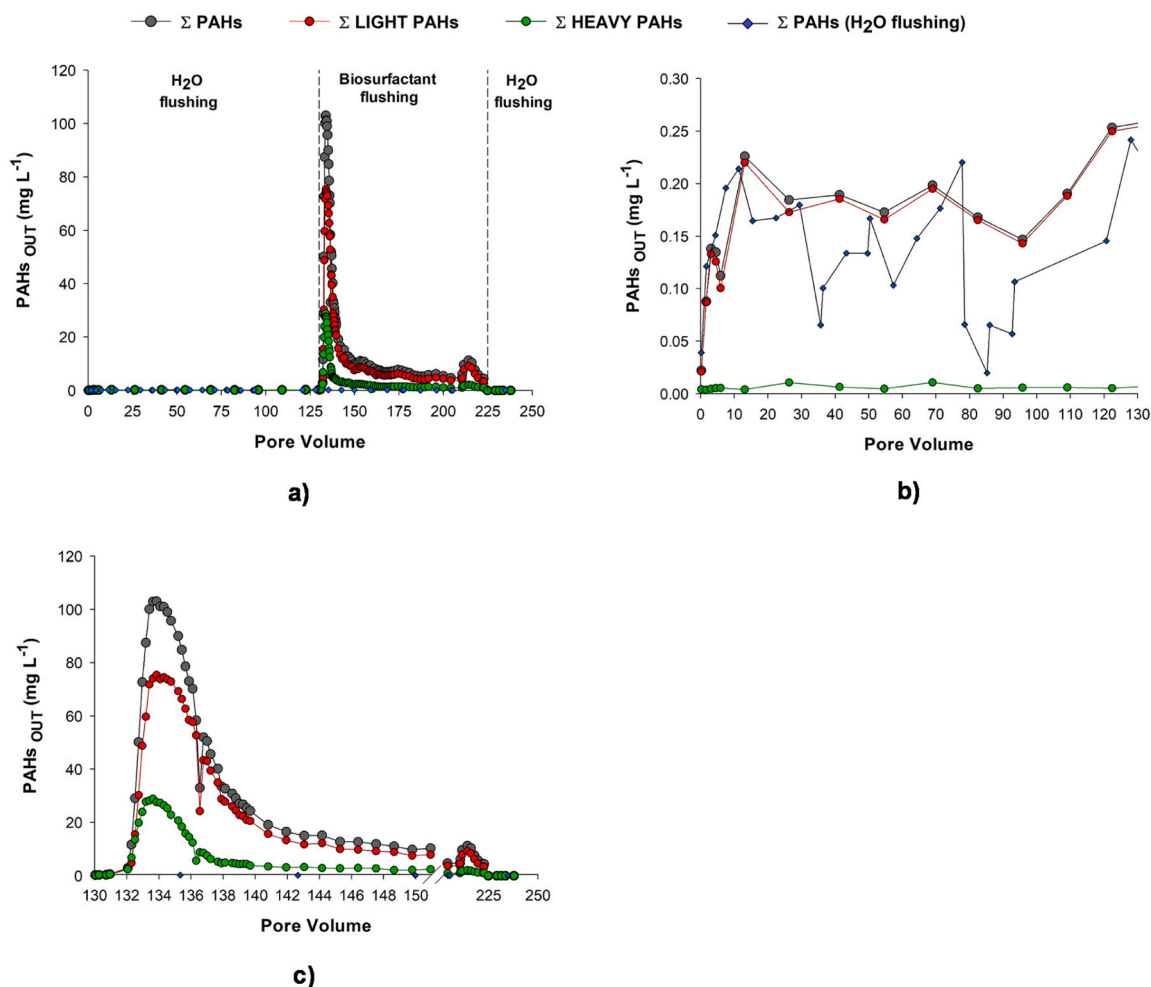


Fig. 6. Outlet PAHs profile concentration for column #3 treated with 1 % wt SL solution. a) whole process; b) pretreatment with distilled water (0–130 pore volume); c) SL flushing in the range 130–150 pore volumes.

days (125 pore volumes); and iii) a second treatment with distilled water for 2 days (approximately 20 pore volumes).

The water pretreatment phase was conducted to highlight the clear difference between H₂O and surfactants and to better underline the interfacial properties of surfactants that significantly enhance

contaminants' mobility. As seen in the first step, the PAHs concentration profile was relatively flat compared to the profile obtained in the second phase of the process (Fig. 6a). Fig. 6b shows that the PAHs concentration profile during the water pretreatment was consistent with the results obtained for column #1 (Fig. 4), where only the light fraction of PAHs

was present, with concentrations ranging between $45 \mu\text{g L}^{-1}$ and $225 \mu\text{g L}^{-1}$.

After 1 week of pretreatment, sediment flushing with SL biosurfactant was started. The effect of the surfactant is clearly visible, as indicated by the almost immediate formation of the characteristic PAHs concentration peak, due to the substantial increase in the apparent solubility of the contaminants. Due to the solubilising capacity of the biosurfactant, a significant fraction of heavy PAHs was found in the effluent samples, confirming the advantage that can be obtained from flushing with surfactant compared to treatment with H_2O (similar to a P&T operation).

Fig. 6c (with the x-axis scale zoomed into the range of 130–150 pore volumes) gives a more detailed examination of the system's behavior during the SL flushing process. PAHs mobilization began in 2 pore volumes and reached the maximum in 4 pore volumes, with a PAHs concentration peak of 104.6 mg L^{-1} . This indicates a notable enhancement in PAHs mobility compared to water, though less intense than APG 2. After reaching the maximum, the PAHs concentration exhibited a decreasing trend. The decrease in PAHs concentration was slower compared to the APG 2 flushing process, resulting in a smoother PAHs concentration profile. For this reason, with SL biosurfactant was obtained a smooth PAHs concentration profile, that reaches after about 10 pore volumes a long tailing in which the concentration of PAH decreases very slowly from 20 mg L^{-1} to 7 mg L^{-1} at the end of the treatment.

Despite the less intense PAHs solubilization compared to APG 2, the SL biosurfactant achieved a removal of 49.1 mg of total PAHs from the sediment, corresponding to an efficiency of 29.5% . This performance was slightly better than that of synthetic APG 2. Additionally, when the flow rate was reduced to 0.3 mL min^{-1} after 80 pore volumes of SL treatment, a new increase in PAHs concentration up to around 13 mg L^{-1} was observed. This increase can be attributed to the extended residence time of the surfactant solution in the system, which resulted in a longer surfactant-contaminant contact time and thus a local improvement in PAHs mobilization [47].

The bars diagram in Fig. 7 highlights the differences between the

flushing solutions used in the column experiments. The graph shows the removal efficiencies for each PAH using distilled water (grey bars), synthetic APG 2 (cyan bars), and SL biosurfactant (orange bars).

As noted previously, with distilled water only light PAHs were mobilized, with removal efficiencies lower than 12% . Only trace amounts of fluoranthene and pyrene ($< 0.2 \%$) were detected, which are the lightest among the heavy PAHs group. In contrast, the situation was markedly different with the surfactants. In his case, the mobilization efficiencies of light PAHs were significantly higher. For instance, phenanthrene removal reached 53% and 83% with APG 2 and SL, respectively (5 and 8 times higher than with water).

The most significant difference is observed in the mobilization of heavy PAHs, which are mobilized with efficiencies between 40% and 16% , unlike the H_2O treatment in which the heavy PAHs fraction is absent.

Table 5 summarizes the performances of each flushing agent used in continuous systems. For column #1 (H_2O treatment), after flushing 225 pore volumes, a total of 1.6 mg of PAHs were mobilized, corresponding to a global removal efficiency of 1.1% . Of the total mobilized mass, 97% (1.55 mg) were light PAHs and the remaining 3% (0.05 mg) were heavy PAHs, predominantly fluoranthene and pyrene.

In the case of column #2 (APG 2 flushing), a total of 46.3 mg PAHs were mobilized, resulting in 27.9% of removal efficiency. Similarly, for column #3 (SL biosurfactant flushing) 48.9 mg of total PAHs were mobilized with a removal efficiency of 29.2% , resulting slightly more efficient than APG 2. Notably, SL flushing was carried out for 7 days, compared to 14 days of APG 2 flushing. The data clearly show that surfactants significantly enhance the mobility and the mass transfer of PAHs, achieving up to 30 times greater efficiency than water with significantly smaller pore volume and operating time.

The data in the table also highlight the different behaviours of the two investigated surfactants towards the same contaminants. Although both surfactants achieved similar amounts of mobilized PAHs and removal efficiencies, APG 2 exhibited a higher concentration peak (three times higher than SL) and the complete mobilization of PHAs occurred

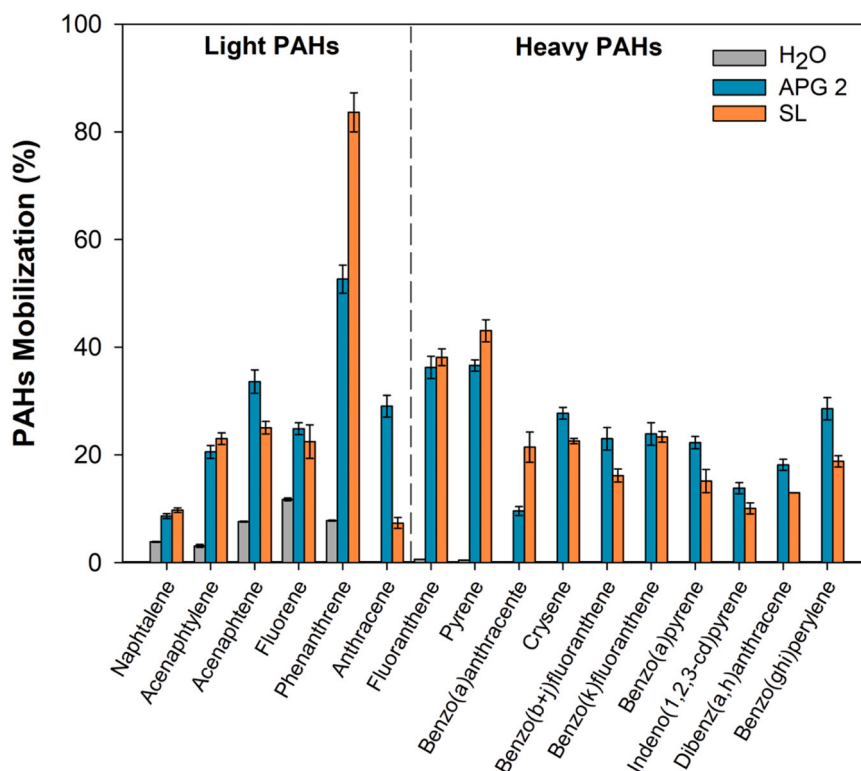


Fig. 7. Mobilization of each PAH by water (grey), APG 2 (cyan) and SL (orange).

Table 5

Summary of continuous test's data. Light and heavy PAHs fractions* are calculated with respect to the total PAHs mobilized mass; PV** is referred to the pore volume needed for the mobilization of 95 % of total mobilized amount; SL*** data are related to surfactant flushing phase with a total duration of 7 days (water pretreatment is not included).

CONTAMINATION			FLUSHING						
Column	Sediment amount (g)	Mass of PAHs (mg)	Flushing Agent	C _{OUT} max (mg L ⁻¹)	Mobilized mass of PAHs (mg)	Light PAHs fraction* (%)	Heavy PAHs fraction* (%)	PV**	Removal efficiency (%)
#1	44	133.2	H ₂ O	/	1.6	97	3	225	1.2
#2	47.3	165.9	APG 2	324.7	46.3	18	82	5.5	27.9
#3	47.7	167.3	SL ***	104.6	48.9	23	77	50	29.2

in just 5.5 pore volumes of fed solution after which the concentration of PAHs in the effluent stabilized around 1–2 mg L⁻¹ until the end of the process. In contrast, with SL biosurfactant the concentration peak reached the maximum value of 105 mg L⁻¹, and the total mobilization of PAHs occurred with more than 50 pores volumes of fed solution, considering the long tailing of outlet PAHs concentration ranging from 20 mg L⁻¹ to 7 mg L⁻¹. These observations agree with results already obtained by Barbati et. al [25] in their previous study about the application of APGs and RLs in Toluene and Perchloroethylene (PCE) mobilization, through a lab-scale soil flushing simulation in similar experimental conditions.

Considering these results, it is possible to conclude that synthetic APG 2 has a more intense and immediate mechanism of action on contamination, as mobilization occurred with the feeding of about 230 mL of solution in a process time of less than 6 hours. On the contrary, SL demonstrates a less intense but continuous and steady mechanism of action throughout the treatment duration.

Another notable difference concerns the molar fraction of light and heavy PAHs in the total mobilized PAHs. With APG 2 flushing, the light PAH fraction was 18 %, while the heavy PAH fraction was 82 %. In the presence of SL, there was a slight reduction in the mobilization capacity of heavy PAHs. Specifically, the fractions were 23 % for light PAHs and 77 % for heavy PAHs.

These calculated fractions align with the bars diagram shown in Fig. 7, which illustrates that APG 2 had a greater ability to mobilize most of the heavy PAHs compared to SL. On the contrary, SL biosurfactant proved more effective for mobilizing light PAHs, particularly phenanthrene, whose mobilization with SL reached 83 % (almost double compared to synthetic APG 2). For other light PAHs, APG 2 and SL exhibited similar mobilization abilities.

4. Conclusions

In the context of surfactant-assisted environmental remediation, this study investigated the impact of surfactants' concentration on PAHs mobilization mechanism through a series of batch tests. Then, the study was concluded with a direct evaluation of surfactant-enhanced mobilization of PAHs by performing continuous column experiments for a lab-scale sediment flushing simulation, that can be considered an innovative process configuration for contaminated sediment remediation.

With the batch configuration test, it has been observed that the mobilization of pollutants became more efficient as the surfactant concentration increased, reaching values of 23.4 % and 27.6 % with the long chain alkylpolyglycoside (APG 2) and sophorolipid (SL), respectively, both used at 5 % wt concentration. These two surfactants were found to be the most efficient also when used at the lowest concentration (1 % wt) giving about 14 % of total PAHs mobilization.

As a result, APG 2 and SL, both with concentrations equal to 1 % wt, were chosen for the continuous column test as flushing agents for mobilizing PAHs.

The results highlighted the significant mobilization of PAHs from marine sediments, with a removal efficiency equal to 27.9 % and 29.2 %

of total PAHs in the presence of APG 2 and SL, respectively. In both cases, the mobilization of PAHs resulted about 30 times greater than water, that allowed to reach 1.1 % of PAHs mobilization.

Moreover, two different ways of mobilizing PAHs were observed: with APG 2 a high and very thin concentration peak was immediately obtained (in just 1.1 pores volume) indicating a direct and intense mobilization of PAHs, that finished after 5 pore volumes. On the contrary, SL gave a larger PAHs concentration profile with a lower concentration peak originated after 4 pores volumes, which allowed to hypothesize a less intense but time-prolonged and constant mechanism of action on contamination.

In addition, this laboratory investigation demonstrates that switching from a batch configuration washing to a continuous flushing in tubular reactors is possible to increase PAHs removal efficiency. Particularly, using 1 % wt of surfactant concentration, PAHs removal was increased from 14 % to 27.9 % and 29.2 % in the presence of APG 2 and SL, respectively. Considering also the little pore volume range required for the achievement of those performances, these findings clearly underline the advantages of the continuous configuration process with respect of traditional batch configuration sediment washing.

Between these two surfactants tested in the continuous process, SL resulted the most promising as it led to the greater mobilization of total PAHs. It is also noteworthy that SL flushing lasted only 7 days and then PAHs mobilization could be much higher in a larger operative time (considering the long tail after the peak in Fig. 6C). Moreover, since SL is produced through the secondary metabolism of numerous yeast species [48], it is totally biodegradable and eco-compatible [42], representing the possible promising future of a sustainable surfactant-enhanced remediation process.

CRediT authorship contribution statement

Gabriele Moscatelli: Formal analysis, Data curation, Conceptualization. **Berardino Barbati:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Laura Lorini:** Writing – review & editing, Visualization, Validation, Supervision, Conceptualization. **Marco Petrangeli Papini:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Funding acquisition. **Laura Caiazzo:** Resources. **Marco Bellagamba:** Validation, Resources, 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.

Data availability

The data that has been used is confidential.

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References

- [1] S. Gan, E.V. Lau, H.K. Ng, Remediation of soils contaminated with polycyclic aromatic hydrocarbons (PAHs), *J. Hazard. Mater.* 172 (2009) 532–549, <https://doi.org/10.1016/J.JHAZMAT.2009.07.118>.
- [2] U.S. EPA, United States Environmental Protection Agency, Polycyclic Aromatic Hydrocarbons (PAHs), (2008). <http://www.epa.gov/osw/hazard/wastemin/priority.htm>.
- [3] B. Lukić, A. Panico, D. Huguenot, M. Fabbriano, E.D. van Hullebusch, G. Esposito, Evaluation of PAH removal efficiency in an artificial soil amended with different types of organic wastes Euro-Mediterranean, *J. Environ. Integr.* 1 (2016), <https://doi.org/10.1007/s41207-016-0001-x>.
- [4] C. Dai, Y. Han, Y. Duan, X. Lai, R. Fu, S. Liu, K.H. Leong, Y. Tu, L. Zhou, Review on the contamination and remediation of polycyclic aromatic hydrocarbons (PAHs) in coastal soil and sediments, *Environ. Res.* 205 (2022) 112423, <https://doi.org/10.1016/j.envres.2021.112423>.
- [5] S. Krzebietke, E. Mackiewicz-Walec, S. Sienkiewicz, D. Załuski, Effect of manure and mineral fertilisers on the content of light and heavy polycyclic aromatic hydrocarbons in soil, *Sci. Rep.* 10 (2020) 4573, <https://doi.org/10.1038/s41598-020-61574-2>.
- [6] S. Boitsov, H.K.B. Jensen, J. Klungsoy, Natural background and anthropogenic inputs of polycyclic aromatic hydrocarbons (PAH) in sediments of South-Western Barents Sea, *Mar. Environ. Res.* 68 (2009) 236–245, <https://doi.org/10.1016/J.MARENRES.2009.06.013>.
- [7] F. Molisso, M. Caccavale, M. Capodanno, C. Di Gregorio, M. Gilardi, A. Guarino, E. Oliveri, S. Tamburrino, M. Sacchi, Sedimentological analysis of marine deposits off the Bagnoli-coroglio site of national interest (SNI), Pozzuoli (Napoli) Bay, *Chem. Ecol.* 36 (2020) 565–578, <https://doi.org/10.1080/02757540.2020.1747447>.
- [8] J.A. McGrath, N. Joshua, A.S. Bess, T.F. Parkerton, Review of polycyclic aromatic hydrocarbons (PAHs) sediment quality guidelines for the protection of benthic life, *Integr. Environ. Assess. Manag.* 15 (2019) 505–518, <https://doi.org/10.1002/ieam.4142>.
- [9] M. Kumar, N.S. Bolan, S.A. Hoang, A.D. Sawarkar, T. Jasemizad, B. Gao, S. Keerthanan, L.P. Padhye, L. Singh, S. Kumar, M. Vithanage, Y. Li, M. Zhang, M. B. Kirkham, A. Vinu, J. Rinklebe, Remediation of soils and sediments polluted with polycyclic aromatic hydrocarbons: to immobilize, mobilize, or degrade? *J. Hazard. Mater.* 420 (2021) 126534, <https://doi.org/10.1016/j.jhazmat.2021.126534>.
- [10] B.M. Sahoo, B.V.V. Ravi Kumar, B.K. Banik, P. Borah, Polyaromatic hydrocarbons (PAHs): structures, synthesis and their biological profile, *Curr. Org. Synth.* 17 (2020) 625–640, <https://doi.org/10.2174/1570179417666200713182441>.
- [11] M. Honda, N. Suzuki, Toxicities of polycyclic aromatic hydrocarbons for aquatic animals, *Int. J. Environ. Res. Public Health* 17 (2020), <https://doi.org/10.3390/ijerph17041363>.
- [12] J.E. Balmer, H. Hung, Y. Yu, R.J. Letcher, D.C.G. Muir, Sources and environmental fate of pyrogenic polycyclic aromatic hydrocarbons (PAHs) in the Arctic, *Emerg. Contam.* 5 (2019) 128–142, <https://doi.org/10.1016/j.emcon.2019.04.002>.
- [13] Y. Zhang, C. Labianca, L. Chen, S. De Gisi, M. Notarnicola, B. Guo, J. Sun, S. Ding, L. Wang, Sustainable ex-situ remediation of contaminated sediment: a review, *Environ. Pollut.* 287 (2021) 117333, <https://doi.org/10.1016/j.envpol.2021.117333>.
- [14] F. Bianco, M. Race, S. Papiro, G. Esposito, A critical review of the remediation of PAH-polluted marine sediments: current knowledge and future perspectives, *Resour. Environ. Sustain.* 11 (2023) 100101, <https://doi.org/10.1016/j.resenv.2022.100101>.
- [15] M. Romero, A. Andrés, R. Alonso, J. Viguri, J.M. Rincón, Sintering behaviour of ceramic bodies from contaminated marine sediments, *Ceram. Int.* 34 (2008) 1917–1924, <https://doi.org/10.1016/j.ceramint.2007.07.002>.
- [16] C. Labianca, S. De Gisi, F. Todaro, M. Notarnicola, I. Bortone, A review of the in-situ capping amendments and modeling approaches for the remediation of contaminated marine sediments, *Sci. Total Environ.* 806 (2022) 151257, <https://doi.org/10.1016/j.scitotenv.2021.151257>.
- [17] F. Bianco, M. Race, S. Papiro, G. Esposito, A critical review of the remediation of PAH-polluted marine sediments: current knowledge and future perspectives, *Resour. Environ. Sustain.* 11 (2023) 100101, <https://doi.org/10.1016/j.resenv.2022.100101>.
- [18] S. Mallick, T.K. Dutta, Kinetics of phenanthrene degradation by *Staphylococcus* sp. strain PN/Y involving 2-hydroxy-1-naphthoic acid in a novel metabolic pathway, *Process Biochem.* 43 (2008) 1004–1008, <https://doi.org/10.1016/j.procbio.2008.04.022>.
- [19] D.J. Lampert, W.V. Sarchet, D.D. Reible, Assessing the effectiveness of thin-layer sand caps for contaminated sediment management through passive sampling, *Environ. Sci. Technol.* 45 (2011) 8437–8443, <https://doi.org/10.1021/es200406a>.
- [20] L. Silvani, P.R. Di Palma, C. Riccardi, E. Eek, S.E. Hale, P. Viotti, M. Petrangeli Papini, Use of biochar as alternative sorbent for the active capping of oil contaminated sediments, *J. Environ. Chem. Eng.* 5 (2017) 5241–5249, <https://doi.org/10.1016/j.jece.2017.10.004>.
- [21] Giorgia De Gioannis, Aldo Muntoni, Alessandra Poletti, Raffaella Pomi, Electrokinetic Treatment of Contaminated Marine Sediments, in: KRISHNA R. REDDY, CLAUDIO CAMESELLE (Eds.), *Electrochem. Remediat. Technol. Polluted Soils, Sediments Groundw.*, 2009: pp. 149–171. <https://doi.org/10.1002/9780470523650>.
- [22] N. Manap, N. Voulvoulis, Risk-based decision-making framework for the selection of sediment dredging option, *Sci. Total Environ.* 496 (2014) 607–623, <https://doi.org/10.1016/j.scitotenv.2014.07.009>.
- [23] P.L.A. Erftemeijer, B. Riegl, B.W. Hoeksema, P.A. Todd, Environmental impacts of dredging and other sediment disturbances on corals: a review, *Mar. Pollut. Bull.* 64 (2012) 1737–1765, <https://doi.org/10.1016/j.marpolbul.2012.05.008>.
- [24] B. Barbati, L. Lorini, M. Bellagamba, M.P. Papini, Characterization and application of sodium surfactin in mobilization of toluene and perchloroethylene by batch configuration, *Test., Chem. Eng. Trans.* 100 (2023) 547–552, <https://doi.org/10.3303/CET23100092>.
- [25] B. Barbati, L. Lorini, N. Amanat, M. Bellagamba, L. Galantini, M. Petrangeli, Enhanced solubilization of strongly adsorbed organic pollutants using synthetic and natural surfactants in soil flushing: column experiment simulation, *J. Environ. Chem. Eng.* 11 (2023) 110758, <https://doi.org/10.1016/j.jece.2023.110758>.
- [26] X. Mao, R. Jiang, W. Xiao, J. Yu, Use of surfactants for the remediation of contaminated soils: a review, *J. Hazard. Mater.* 285 (2015) 419–435, <https://doi.org/10.1016/j.jhazmat.2014.12.009>.
- [27] N. Amanat, B. Barbati, M.M. Rossi, M. Bellagamba, M. Buccolini, L. Galantini, M. P. Papini, Synthetic and natural surfactants for potential application in mobilization of organic contaminants: characterization and batch study, *Water* 14 (2022) 1182, <https://doi.org/https://doi.org/10.3390/w14081182>.
- [28] F. Zheng, B. Gao, Y. Sun, X. Shi, H. Xu, J. Wu, Y. Gao, Removal of tetrachloroethylene from homogeneous and heterogeneous porous media: combined effects of surfactant solubilization and oxidant degradation, *Chem. Eng. J.* 283 (2016) 595–603, <https://doi.org/10.1016/j.cej.2015.08.004>.
- [29] J.W. Liu, K.H. Wei, S.W. Xu, J. Cui, J. Ma, X.L. Xiao, B.D. Xi, X.S. He, Surfactant-enhanced remediation of oil-contaminated soil and groundwater: a review, *Sci. Total Environ.* 756 (2021) 144142, <https://doi.org/10.1016/j.scitotenv.2020.144142>.
- [30] C.F. Jesus, A.A.S. Alves, S.M. Fiuzza, D. Murtinho, F.E. Antunes, Mini-review: Synthetic methods for the production of cationic sugar-based surfactants, *J. Mol. Liq.* 342 (2021), <https://doi.org/10.1016/j.molliq.2021.117389>.
- [31] R. Jahan, A.M. Bodratti, M. Tsiannou, P. Alexandridis, Biosurfactants, natural alternatives to synthetic surfactants: physicochemical properties and applications, *Adv. Colloid Interface Sci.* 275 (2020), <https://doi.org/10.1016/j.cis.2019.102061>.
- [32] R. Kandasamy, M. Rajasekaran, S.K. Venkatesan, M. Uddin, New trends in the biomaterials of green surfactants: biobased surfactants and biosurfactants, *ACS Symp. Ser.* 1329 (2019) 243–260, <https://doi.org/10.1021/bk-2019-1329.ch011>.
- [33] T. Gaudin, H. Lu, G. Fayet, A. Berthaud-Drelich, P. Rotureau, G. Pourceau, A. Wadouchi, E. Van Hecke, A. Nesterenko, I. Pezron, Impact of the chemical structure on amphiphilic properties of sugar-based surfactants: a literature overview, *Adv. Colloid Interface Sci.* 270 (2019) 87–100, <https://doi.org/10.1016/j.cis.2019.06.003>.
- [34] G. Moscatelli, B. Barbati, L. Lorini, L. Caiazza, S. Chiavarini, M. Pezza, M. Bellagamba, M. Petrangeli, Preliminary study for Polycyclic aromatic Hydrocarbons mobilization from contaminated marine sediment using synthetic and natural surfactants, *Chem. Eng. Sci.* 298 (2024) 120317, <https://doi.org/10.1016/j.ces.2024.120317>.
- [35] G. Armiento, R. Caprioli, A. Cerbone, S. Chiavarini, C. Crovato, M. De Cassan, L. De Rosa, M.R. Montoreali, E. Nardi, L. Nardi, M. Pezza, M. Proposito, J. Rimauro, A. Salerno, A. Salluzzo, F. Spaziani, F. Zaza, Current status of coastal sediments contamination in the former industrial area of Bagnoli-Coroglio (Naples, Italy), *Chem. Ecol.* 36 (2020) 579–597, <https://doi.org/10.1080/02757540.2020.1747448>.
- [36] M. Tangherlini, C. Corinaldesi, E. Rastelli, L. Musco, G. Armiento, R. Danovaro, A. Dell'Anno, Chemical contamination can promote turnover diversity of benthic prokaryotic assemblages: the case study of the Bagnoli-Coroglio bay (southern Tyrrhenian Sea), *Mar. Environ. Res.* 160 (2020) 105040, <https://doi.org/10.1016/j.marenres.2020.105040>.
- [37] N. Ruocco, I. Bertocci, M. Munari, L. Musco, D. Caramiello, R. Danovaro, V. Zupo, M. Costantini, Morphological and molecular responses of the sea urchin *Paracentrotus lividus* to highly contaminated marine sediments: the case study of Bagnoli-Coroglio brownfield (Mediterranean Sea), *Mar. Environ. Res.* 154 (2020) 104865, <https://doi.org/10.1016/j.marenres.2019.104865>.
- [38] U.S. EPA, Method 3545A (SW-846): Pressurized Fluid Extraction (PFE), 2007.
- [39] U.S. EPA, SW-846 Test Method 3630C: Silica Gel Cleanup, 2008.
- [40] M.M.A. El-Sukkary, N.A. Syed, I. Aiad, W.I.M. El-Azab, Synthesis and characterization of some alkyl polyglycosides surfactants, *J. Surfactants Deterg.* 11 (2008) 129–137, <https://doi.org/10.1007/s11743-008-1063-9>.
- [41] ECHA, Alkyl-polyglycosides dossier, (n.d.). <https://echa.europa.eu/it/registration-dossier/-/registered-dossier/19013/11/?documentUID=2a97fc88-4e4f-4c56-b104-b0e6a4dc72df>.
- [42] ECHA, Sophorilipids dossier, (n.d.). <https://echa.europa.eu/it/registration-dossier/-/registered-dossier/12734/1/1>.
- [43] ECHA, Rhamnolipids dossier, (n.d.). <https://echa.europa.eu/it/registration-dossier/-/registered-dossier/20930/6/2/?documentUID=396f1e18-49f7-4496-b8d8-a66e396463fc>.
- [44] M. Cheng, G. Zeng, D. Huang, C. Yang, C. Lai, C. Zhang, Y. Liu, Advantages and challenges of Tween 80 surfactant-enhanced technologies for the remediation of

- soils contaminated with hydrophobic organic compounds, *Chem. Eng. J.* 314 (2017) 98–113, <https://doi.org/10.1016/j.cej.2016.12.135>.
- [45] A.A. Befkadu, Q. Chen, Surfactant-enhanced soil washing for removal of petroleum hydrocarbons from contaminated soils: a review, *Pedosphere* 28 (2018) 383–410, [https://doi.org/10.1016/S1002-0160\(18\)60027-X](https://doi.org/10.1016/S1002-0160(18)60027-X).
- [46] S. Li, Y. Pi, M. Bao, C. Zhang, D. Zhao, Y. Li, P. Sun, J. Lu, Effect of rhamnolipid biosurfactant on solubilization of polycyclic aromatic hydrocarbons, *Mar. Pollut. Bull.* 101 (2015) 219–225, <https://doi.org/10.1016/J.MARPOLBUL.2015.09.059>.
- [47] S.Y. Kudryashov, Y.I. Arutyunov, L.A. Onuchak, New methods for determining the volumetric flow rate in the column and the retention time of the unretained substance in gas chromatography, *Russ. J. Phys. Chem. A* 81 (2007) 102–107, <https://doi.org/10.1134/S0036024407010190>.
- [48] S. Jezierska, S. Claus, I. Van Bogaert, Yeast glycolipid biosurfactants, *FEBS Lett.* 592 (2018) 1312–1329, <https://doi.org/10.1002/1873-3468.12888>.