Preliminary study for Polycyclic aromatic Hydrocarbons mobilization from contaminated marine sediment using synthetic and natural surfactants

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ABSTRACT

The persistent presence of Polycyclic Aromatic Hydrocarbons (PAHs) in soils and sediments due to their chemical properties requires new methods to mobilize and make them more available for remediation purposes. In this work, the evaluation of the abilities of eight different non-ionic sugar-based and totally biodegradable surfactants, such as synthetic alkyl polyglycosides (APGs), biological sophorolipids (SLs) and biological rhamnolipids (RLs), was conducted in order to provide a preliminary guideline for the selection of the surfactant and the technical approach for PAHs extraction from the sediment. The reference sample was a marine sediment collected from Bagnoli (Naples, Italy) that was characterized to evaluate the level of PAHs contamination, which resulted equal to 3.51 g Kg^{-1} of total PAHs in the sediment. By using surfactants solutions with a surfactant concentration five times greater than critical micelle concentration (Cs = 5x CMC), a preliminary washing test in batch configuration was conducted, then followed by multiple consecutive washes (MCW) of the sediment to assess the solubilization of PAHs from the sediment by the action of selected surfactants. The results show an evident advantage given by the employment of each studied surfactant in mobilizing PAHs, compared to distilled water as benchmark. In detail, the synthetic alkyl polyglycosides APG2 led to a 3.4 % of total PAHs mobilization in the preliminary washing test with a maximum peak of 9.8 % for a single compound. The MCW test demonstrates that more consecutive washes can increase the amount of total PAHs removed, with a similar contribution from each wash, and that biosurfactants can be more attractive after several washes thanks to the increased capacity of PAHs mobilization. Interestingly, the high efficiency of surfactant to mobilize PAHs makes the soil washing a more attractive technology for removing PAHs from the marine sediments.

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are among the priority pollutants in soils and sediments due to their toxicity related to teratogenic, mutagenic, and carcinogenic effects on humans and other organisms (Brookes, 1977; Straif et al., 2005; Idowu et al., 2019). PAHs are a group of chemicals with multiple aromatic rings condensed to each other's that are produced by the incomplete burning of coal, oil, gas, wood, garbage, or other organic substances. They are formed during the thermal decomposition of organic molecules and their subsequent recombination. Incomplete combustion at high temperatures (500–800

°C) or subjection of organic material at low temperatures (100–300 °C) for long periods results in PAHs production (Herbes, 1977; Department of Health & Human Services, 1999; Balmer et al., 2019). As reported in the literature, based on the aromatic rings number in the structure, it is possible to divide PAHs into two groups: light PAHs, if they have up to 3 aromatic rings, or heavy PAHs, in the case they have more than 3 aromatic rings (Nikolaou et al., 2009; Krzebietke et al., 2020). There are more than 100 different PAHs, but only 28 of them are considered hazardous by the US Environmental Protection Agency (EPA) in 2008, and just 16 are considered EPA priority pollutants in terms of their toxicity (Gan et al., 2009). They are part of the Hydrophobic Organic

Compounds (HOC), indeed their main characteristics are high hydrophobicity and very low solubility in water (Pazos et al., 2010; Boulakradeche et al., 2015; Armiento et al., 2020). With an increase in molecular weight, their solubility in water decreases; on the other hand, melting and boiling point increase and vapor pressure decreases. Among the potential source of organic pollutants, such as polycyclic aromatic hydrocarbons, iron and steel industries have been identified (Armiento et al., 2020). Indeed, steel is mainly produced with a process that has different phases, including coke ovens and sinter plants, in which PAHs are produced (Amodio et al., 2014; 2014.).

The accumulation of PAHs in soils and sediments follows different paths: pyrogenic, petrogenic, and biological. While the biological pathway is marginal, the environmental accumulation of PAHs from pyrogenic and petrogenic sources is more widespread (Abdel-Shafy and Mansour, 2016). The pyrogenic pathway includes the release of PAHs in the air through the incomplete combustion of organic matter before their flow into the soil, water and sediments (Saha et al., 2009). Instead, the petrogenic sources release PAHs directly into the soils or sediments through accidental oil spills (Saha et al., 2009). PAHs released in the sea reach and accumulate in the sediments due to their low solubility in water (Boitsov et al., 2009; Botsou and Hatzianestis, 2012) becoming less mobile and bioavailable for mobilization. Especially in aged contamination scenarios, can be relevant low-rate speed contaminants migration phenomena (e.g., back-diffusion) from the sediments to the sea leading PAHs to spread in the water over the years (Tatti et al., 2018). Hence, developing appropriate remediation methods is required to mitigate the possible risk of PAHs on the environment and human health (Kariyawasam et al., 2022). In this regard, in recent years several innovative remediation technologies were studied and developed to increase the removal of hydrophobic pollutants, such as PAHs. Among these new technologies, increasing attention is given to soil washing or soil flushing processes enhanced with surfactants to improve pollutants extraction from aquifers, soils, and sediments (Kumar et al., 2021; Dai et al., 2022).

Surfactants are amphiphilic organic molecules, with a hydrophobic tail group and a hydrophilic head group (Alcántara et al., 2010), that give the affinity through organic phase and the solubility in water, respectively. Thanks to their characteristic molecular structure, surfactants are able to reduce the surface and interfacial tension between immiscible phases (water–air or water-organic phase) and, at the same time, the oil–soil attraction, favoring the mobility of organic phase (Xu et al., 2018; Amanat et al., 2022). Moreover, when surfactant concentration is equal to or higher than their critical micelle concentration (CMC), the monomers spontaneously aggregate into micelles, with the polar head groups exposed to the aqueous phase and the hydrophobic tail groups confined into the core (Amanat et al., 2022), providing a favorable environment for the dispersion of organic compounds (Malkapuram et al., 2021; Gaudin et al., 2016). Therefore, surfactants may increase the solubility of PAHs through micellar solubilization mechanism (Cheng et al.,2017;Estabragh et al.,2019;Ji et al.,2020;Prakash et al.,August, 2020). Among the different kinds of surfactants, non-ionic surfactants are the most used in remediation of soils/sediments due to their high solubilization capacity, biodegradability, and low dangerousness to both terrestrial and aquatic organisms. Since the hydrophilic group has no charge, non-ionic surfactants have negligible interactions with soil particles (Chen and Schechter,May, 2020;Dominguez et al.,2019). In addition, according with literature, non-ionic surfactants show the best performance in terms of PAHs removal from soils and sediments (Hahladakis et al., 2016; Niqui-Arroyo and Ortega-Calvo, 2010). Surfactants can be produced by chemical synthesis or microbial secondary metabolism, resulting in two different group: synthetic and natural surfactants (or biosurfactants), respectively (Jesus et al., 2021; Jahan et al., 2020). Nevertheless, synthetic surfactants could have a notable level of toxicity, low biodegradability and a great environmental impact since they are derived from fossil raw materials (Kandasamy et al., 2019; Barbati et al., 2023). For this reason, the new technologies

focus on 100 % bio-based surfactants (Kandasamy et al., 2019), such as sugar-based non-ionic surfactants, both synthetic from renewable sources (e.g., biomass containing sugars and fatty acid esters) (Gaudin et al., 2019) and produced by secondary metabolism of microorganisms (e.g., biosurfactant).

Considering the use of surfactants for environmental remediation purpose, the study presented in this paper was focused on the evaluation of the abilities of eight different non-ionic sugar-based surfactants, belonging to the families of synthetic alkyl polyglycosides (APGs), biological sophorolipids (SLs) and biological rhamnolipids (RLs), to solubilize and mobilize residual PAHs accumulated in marine sediments. This study can provide a preliminary guideline for the selection of the surfactant and the technical approach for PAHs extraction from the sediment.

In this context, after a chemical characterization of the sediment for determining the composition and the concentration of PAHs, a pollutants mobilization study was carried out through two series of batch configuration experiments. The first one was aimed to investigate the PAHs extraction ability of selected surfactants through 24-hour washing of the sediment, using a solution with a surfactant concentration five time higher than the CMC (5x CMC). On the other hand, the second batch experiment evaluated the effect of three consecutive washes of the sediment, in order to increase the mobilized amount of pollutants.

2. Materials and methods

2.1. Materials

2.1.1. Sampling and characterization of the sediment

Sediment samples were taken from Bagnoli (Naples, Italy). This site is heavily polluted by human and industrial activity, in particular from the important steel plant, "ILVA of Bagnoli", whose working activities started in 1910 and finished in 1990 (Armiento et al., 2020). All the gulf, where the industrial activity was located, had been characterized during the years, always showing the high contamination by Polycyclic Aromatic Hydrocarbons (PAHs) (Ruocco et al., 2020; Tangherlini et al., 2020; Molisso et al., 2020). Sediments from Bagnoli had been previously collected during ABBaCo Project, funded by the Italian Ministry for Education, University and Research (grant number C62F16000170001), started in 2017 (Musco 0000). The project foresaw to identify and test innovative actions aimed at environmental and ecological recovery of the Bagnoli-Coroglio area with a characterization of the site of marine sediments (Armiento et al., 2020). In this framework, more than 100 samples were characterized, but only the 28 most contaminated samples were combined and homogenized in a 1.350 Kg stock, that was taken as a reference sample (RS) in the present work. From RS, three different aliquots (100 mg each) were analyzed to determine the value of contamination, extracting the interested analytes with n-hexane and acetone according to EPA 3545a method (U.S. EPA. Method 3545A (SW-846): Pressurized Fluid Extraction (PFE)., 2007) at 120 °C and 1500 psi, using an Accelerated Solvent Extractor (ASE 200 Dionex), after the addition of surrogate standards. 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 (U.s. epa., 2008). The analytical determination of PAHs was carried out as described in the following analytical method section and the concentration of contaminants are reported in Table 1.

2.1.2. Synthetic and biological surfactants

In this research, eight different non-ionic sugar-based surfactants, both synthetic and natural, have been investigated. All surfactants were provided by Chimec S.p.A. Italian company. In particular, for the group of synthetic surfactants, five alkyl polyglycosides indicated as APG1, APG2, APG2a, APG2b and APG2c were used. Among these, the surfactants APG2a, 2b and 2c indicate three formulations of the same

Table 1
Concentration of each compound detected in the RS and their principal characteristic, such as molecular weight, partition coefficient octanol/water, water solubility. The last column is the carcinogenicity group to which they belong, as per US-EPA (where 1: carcinogenic to humans; 2A: probably carcinogenic to humans; 2B: possibly carcinogenic to humans; 3: non carcinogenic) (Mallah et al., 2022).

Contaminant	Concentration (μg/g)	Molecular weight (g mol^{-1})	Octanol-Water partition coefficient (log K_{ow})	Water solubility (mg L^{-1})	Carcinogenicity group
Naphthalene	52.8	128.17	3.29	31	2B
Acenaphthylene	19.4	152.2	4.07	16.1	3
Acenaphtene	43.7	154.21	3.98	3.8	3
Fluorene	51.4	166.22	4.18	1.9	3
Phenanthrene	238.7	178.23	4.45	1.1	3
Anthracene	70.4	178.23	4.45	0.045	3
Fluoranthene	695.0	202.26	4.9	0.26	3
Pyrene	427.9	202.26	4.88	0.132	3
Benzo(a)anthracene	282.2	228.29	5.61	0.011	2B
Chrysene	145.6	228.29	5.9	1.5×10^{-3}	2B
Benzo(b + j)fluoranthene	332.6	252.32	6.04	1.5×10^{-3}	2B
Benzo(k)fluoranthene	92.6	252.32	6.06	8×10^{-4}	2B
Benzo(a)pyrene	636.3	252.32	6.06	5×10^{-4}	1
Indeno(1,2,3-cd)pyrene	217.0	276.34	6.58	0.062	2B
Dibenzo(a,h)anthracene	60.0	278.35	6.84	5×10^{-4}	2A
Benzo(g,h,i)perylene	142.1	276.34	6.50	2.6×10^{-4}	3
$\sum$ PAHs	3507.8				

surfactant APG2 characterized by the presence of different additives, added to improve the ability of the main surfactant to mobilize organic compounds (Atteia et al., 2013). Specifically, the APG2a formulation is characterized by the presence of 0.7 % of a C6 branched alcohol, APG2b has in the composition the 1.1 % of a poly-ethoxylated co-surfactant and in APG2c there is the 1.1 % wt of a poly-ethoxylated pro-poxylated co-surfactant (with an oxopropyl linker between alkyl chain and poly-oxoethyl group). In parallel three biosurfactants, represented by one sophorolipid (SL) and two rhamnolipids (RL1 and RL2), were also investigated.

The chemical structure and the composition of all investigated surfactants are reported in detail in Table 2.

In our research group, APG1, APG2, SL, RL1 and RL2 have been deeply characterized by Amanat et al. (2022) (Amanat et al., 2022). Moreover, in this work, APG2a, APG2b, APC2c formulations have been characterized by determining their CMC through surface tension measurements (Du-Nouy ring method) (Amanat et al., 2022). Table 3 shows the CMC values of all investigated surfactants.

3. Methods

3.1. PAHs mobilization study

A preliminary batch test was performed to assess the solubilization of PAHs from the sediment by the action of the selected surfactants. A series of isothermal batch experiments with the sediment and the surfactant solution were carried out at room temperature (23 ± 2 °C) and atmospheric pressure (1 atm) in 42 mL batch reactors (VWR International borosilicate glass vials, Milan, Italy), using 1 g of sediment and 42 mL of surfactant solution (solid:liquid ratio = 1:42) to ensure the total absence of gaseous head space. A total surfactant concentration five times higher than the CMC (C_S = 5x CMC) was used, in order to ensure micelles formation for PAHs solubilization by using a low amount of surfactants. A reference test was also performed under the same condition using simple distilled water as extracting solution (without surfactant). The effective concentrations of different surfactants used in this test are reported in Table 4.

Each batch reactor containing the sediment and surfactant solution was hermetically closed with a polyethylene thread cap and then mechanically stirred on a rotatory plate (0.5 rad s^{-1}) for 48 h to ensure the achievement of the equilibrium condition for contaminant solubilization. Each test was performed in triplicate. Fig. 1 shows a schematic representation of the experimental set-up. After stirring, each vial was centrifuged for 10 min at 3500 rpm to achieve a complete solid–liquid

separation. Then, 5 mL of supernatant was sampled and filtered with syringe filter (0.45 mm) to remove residual solid particles. The resulting filtered samples were collected into 10 mL glass vials hermetically closed with Teflon butyl stopper (Wheaton, Millville, NJ), sealed with an aluminium cap, and finally stored at −18 °C until analysis with gas chromatograph coupled with mass spectrometer (GC–MS) for PAHs determination.

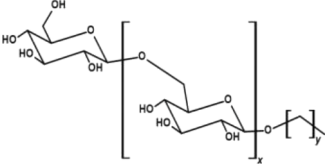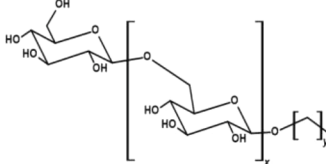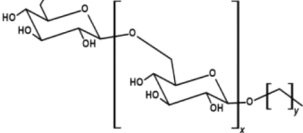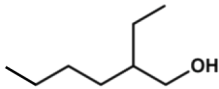### 3.2. Effect of multiple consecutive washes of the sediment
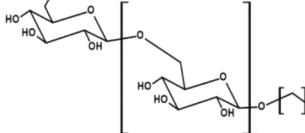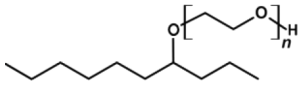
The second batch experiment involved a series of three consecutive washes of the sediment with the aim to increase the extraction of PAHs. The same operative conditions (temperature, surfactant concentration, solid: liquid ratio, contact time between sediment and surfactant solution) of previous batch test were used. After each washing step of the sediment, reactors containing sediment and surfactant solution were centrifuged (10 min, 3500 rpm) for sol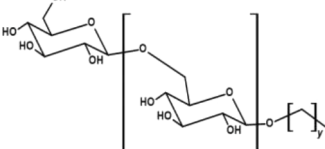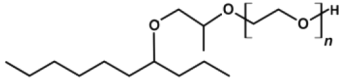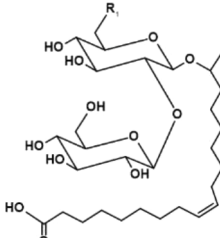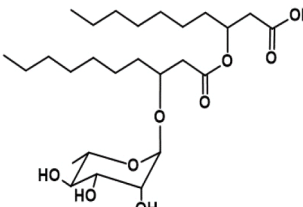id–liquid separation. Each test was performed in triplicate to evaluate the reproducibility. Treated sediments were dried at 50 °C for 24 h before starting the next wash with a new surfactant solution at the same surfactant concentration (C_S = 5x CMC).

3.3. Analytical methods

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, Acenaphtene 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 min for the separation of DCM and water.

The analytical determination of PAHs was carried out with Agilent 7890A-5975C 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 quantification 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 SIM mode with two temperature ramps: following the initial temperature of 60 °C hold for 1 min after the injection of the sample in the chromatographic column, the first ramp with a gradient of 20 °C min^{-1} for 3 min and a second ramp with a gradient of 7 °C min^{-1} were performed and holding the final temperature

Table 2
Chemical structure and composition of all surfactants and co-surfactant used in this work.

| Name	Surfactant	Additive	Name	Surfactant	Additive
APG 1 Alkylpolyglycoside	X = 1.7 (average) Y = 8-10 X = 1.7 (average) Y = 8–10	/	APG 2 Alkylpolyglycoside	X = 1.5 (average) Y = 8-14 X = 1.5 (average) Y = 8–14	/
APG 2a Alkylpolyglycoside	X = 1.5 (average) Y = 8-14 X = 1.5 (average) Y = 8–14	C6 branched alcohol. C = 0.7% wt C6 branched alcohol. C = 0.7 % wt	APG2b Alkylpolyglycoside	X = 1.5 (average) Y = 8-14 X = 1.5 (average) Y = 8–14	C10 Polyethoxylated co-surfactant n = 3-9 C = 1.1% wt C10 Polyethoxylated co-surfactant n = 3–9 C = 1.1 % wt
APG 2c Alkylpolyglycoside	X = 1.5 (average) Y = 8-14 X = 1.5 (average) Y = 8–14	C10 Polyethoxylated – propoxylated co-surfactant n = 5-14 C = 1.1% wt C10 Polyethoxylated – propoxylated co-surfactant n = 5–14 C = 1.1 % wt	SL Sophorilipid		/
RL2 Rhamnolipid					

Table 3

CMC values of used surfactants. [a]Amanat et al. 2022; [b] this study.

Material	APG1	APG2	APG2a	APG2b	APG2c	SL	RL1	RL2
CMC (%wt)	0.06[a]	0.007[a]	0.065[b]	0.035[b]	0.037[b]	0.0125[a]	0.0013[a]	0.0173[a]

Table 4

Effective surfactant concentration used in batch solubilization test.

Material	APG1	APG2	APG2a	APG2b	APG2c	SL	RL1	RL2
C_S = 5x CMC (%wt)	0.3	0.035	0.325	0.175	0.185	0.625	0.0065	0.0865
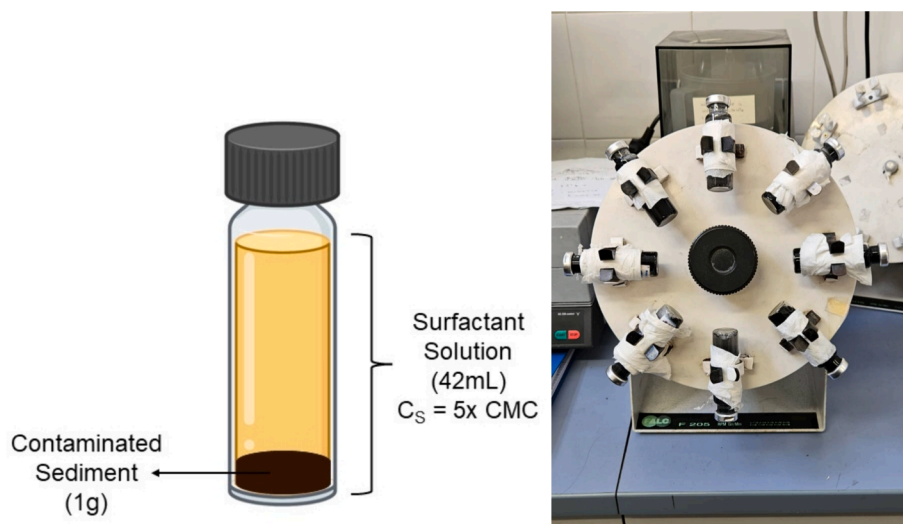
Fig. 1. Experimental set-up of batch reactors.

respectively for 1 min and 2 min at the end of the ramp.

4. Results and discussion

4.1. Pahs mobilization study

The isothermal batch experiments were carried out to simulate a soil washing test. PAHs concentration data were processed to calculate the percentage of total PAHs (Σ of all PAHs) mobilization, as described in Eq. (1).

$$\%PAHs_{TOT} = \frac{mgPAHs_{aq}}{mgPAHs_s} * 100 \qquad (1)$$

Where mg $PAHs_{aq}$ are the milligrams of mobilized PAHs in aqueous phase after 48 h of washing and $PAHs_s$ are the milligrams of PAHs in the sediment before the washing.

Mobilization results have been reported in the Fig. 2, where the mobilization of total PAHs in percentage is showed. As it is possible to observe from Fig. 2, all surfactants contribute to enhance the solubility of contaminants if compared to water which showed mobilization less than 0.1 % of the total PAHs amount present in the sediment before washing test. In fact, in the presence of synthetic surfactants, a general increase in the mobilization of total PAHs can be observed, reaching a maximum to 3.4 % of mobilization in the presence of APG2 followed by APG1 with a total PAHs mobilization of 3.0 %. On the contrary, the three formulations APG2a, APG2b and APG2c gave a total PAHs mobilization of 2.7 %, 2.2 % and 1.3 % respectively, indicating that the presence of the additives caused a worsening of the mobilising capacity of the original surfactant APG2. Moreover, among the synthetic surfactants, the main difference is between APG1 and APG2, where the length of the
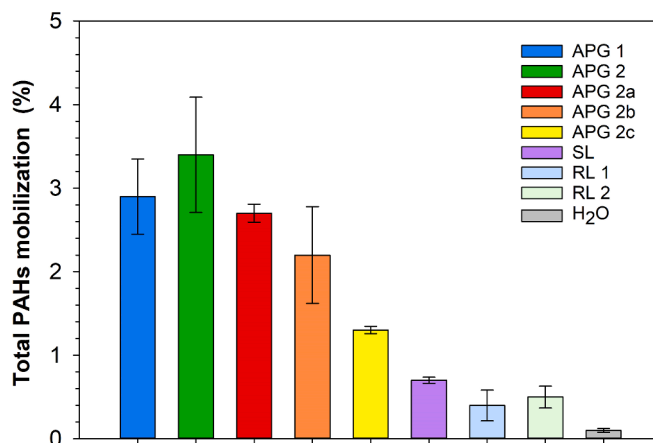
Fig. 2. Total PAHs mobilization related to the initial condition (total amount on the sediment before treatment).

alkyl tail is crucial because it affects the hydrophobic character of the molecule and consequently the interaction towards hydrophobic compounds, such as PAHs. In this regard, APG2, that has the longest tail (see Table 2), presented greater mobilization ability than APG1. From Fig. 2 is also evident that, globally, synthetic surfactants gave better performances than biosurfactants. Indeed, the sophorolipid (SL) with 0.8 % of total PAHs extraction resulted the most promising material among the biosurfactants, followed by the rhamnolipids RL2 and RL1 with a total PAHs mobilization of 0.5 % and 0.4 %, respectively. However, for all tests conducted with surfactants, the differences between the reference

test with only water is clear, confirming the great ability of surfactants to enhance the PAHs solubility in water.

Two graphs are reported in the Fig. 3a and b, which show the mobilization ability towards each contaminant in the sediment of synthetic and natural surfactants, respectively. The two graphs confirm that synthetic surfactants have an overall higher mobilization ability than biosurfactants, as already noted in Fig. 2.

Nevertheless, from the observation of these two graphs it is well remarked that the investigated surfactants didn't have the same interaction with all PAHs, resulting in different behaviors and different mobilization capacity for the different compounds in the sediment.

Taking into account synthetic surfactants (Fig. 3a), in the case of the APG2 surfactant and its formulation APG2b, the highest mobilization capacities have been observed towards light PAHs such as naphthalene, acenaphthene, fluorene, phenanthrene and fluoranthene. Among these, acenaphthene is the most effectively removed with mobilization values (with respect to the amount initially present in the sediment) of 8.5 % and 9.8 % in the presence of APG2 and APG2b, respectively. In the group of heavy PAHs, however, the performance of the formulation APG2b is drastically reduced as the size of the compound increases starting from 3.6 % of pyrene mobilization to 0.4 % of benzo(ghi)perylene mobilization. Regarding to APG2, the effect of the size of the PAH on the mobilization capacity of the surfactant is less intense, resulting in an overall greater mobilizing ability of APG2 than APG2b for heavy PAHs.

A further important aspect to consider concerns the behavior of the surfactant APG1 and the formulation APG2a. In fact, these surfactants appear to be poorly performing for the mobilization of light PAHs, achieving maximum performance with the mobilization of 6.5 % phenanthrene compared to the amount originally present in the sediment. In any case, for APG1 and APG2a, the mobilizations of light PAHs resulted 60–70 % lower than APG2 and APG2b. However, the scenario is quite different in the case of the mobilization of heavy PAHs in which APG1 and APG2a resulted certainly highly effective, especially for those PAHs with more than 4 condensed rings such as benzo(k)fluoranthene, indeno(1,23-cd)pyrene, dibenz(a,h)anthracene and benzo(ghi)perylene.

As already explained before, it is plausible that the greater mobilizing capacity of APG2 is due to its greater hydrophobic character than

APG1 thanks to the presence of a longer alkyl tail group. In the context of APG2 formulations, different effects on PAHs mobilization have been observed depending on the type of cosolvent/additive. For example, the formulation APG2a prepared with 2-ethylhexyl alcohol and the formulation APG2b containing a polyethoxylated co-surfactant (see Table 2) showed promising results for the mobilisation of heavy PAHs and light PAHs, respectively. These effects may probably be due to a synergic cosolubilization effect in the case of 2-ethylhexyl alcohol (APG2a) (Iglauer et al.,2011;Ji et al.,November, 2020;Mao et al.,2015) and an increase in hydrophobic character of micellar core in the case of polyethoxylated co-surfactant (APG2b) (Bodratti et al., 2019; Salager and louis, Marquez R, Bullon J, Forgiarini A., 2022). On the other hand, the formulation APG2c has been identified as the less promising synthetic surfactant for the mobilization of PAHs, probably because the presence of both propylene oxide linker group and large hydrophilic head group in the co-surfactant structure (see Table 2) may decrease the hydrophobicity character making the formulation less efficient in the solubilization and mobilization of hydrophobic compounds, such as PAHs (Bodratti et al., 2019; Salager and louis, Marquez R, Bullon J, Forgiarini A., 2022; Wang et al., 2019; Kittithammavong, 2021;(November 2020):631–648.).

In any case, the analysis of the experimental evidence on the different mobilization ability of synthetic surfactants towards the different PAHs shows that APG2 is the most efficient in the mobilization of total PAHs (as well highlighted in Fig. 2), although the bigger part is associated with the mobilization of light PAHs. On the other hand, APG1 and the formulation APG2a can be very interesting because, although they are characterised by a lower overall mobilization capacity of total PAHs than APG2, they resulted particularly able for mobilizing heavy PAHs, which are among the most recalcitrant and difficult compound to mobilize from a polluted soil or sediment.

In the context of biosurfactants, different behaviour of surfactants towards the different PAHs present in the sediment has been observed, too. From Fig. 3b, the mobilization of light PAHs is significantly higher than the mobilization of heavy PAHs for both sophorolipid SL and rhamnolipid RL1. The highest performances were recorded for acenaphthene with 4.7 % and 4.80 % mobilization in the presence of SL and RL1, respectively. In descending order, there are naphthalene with 4.0 %
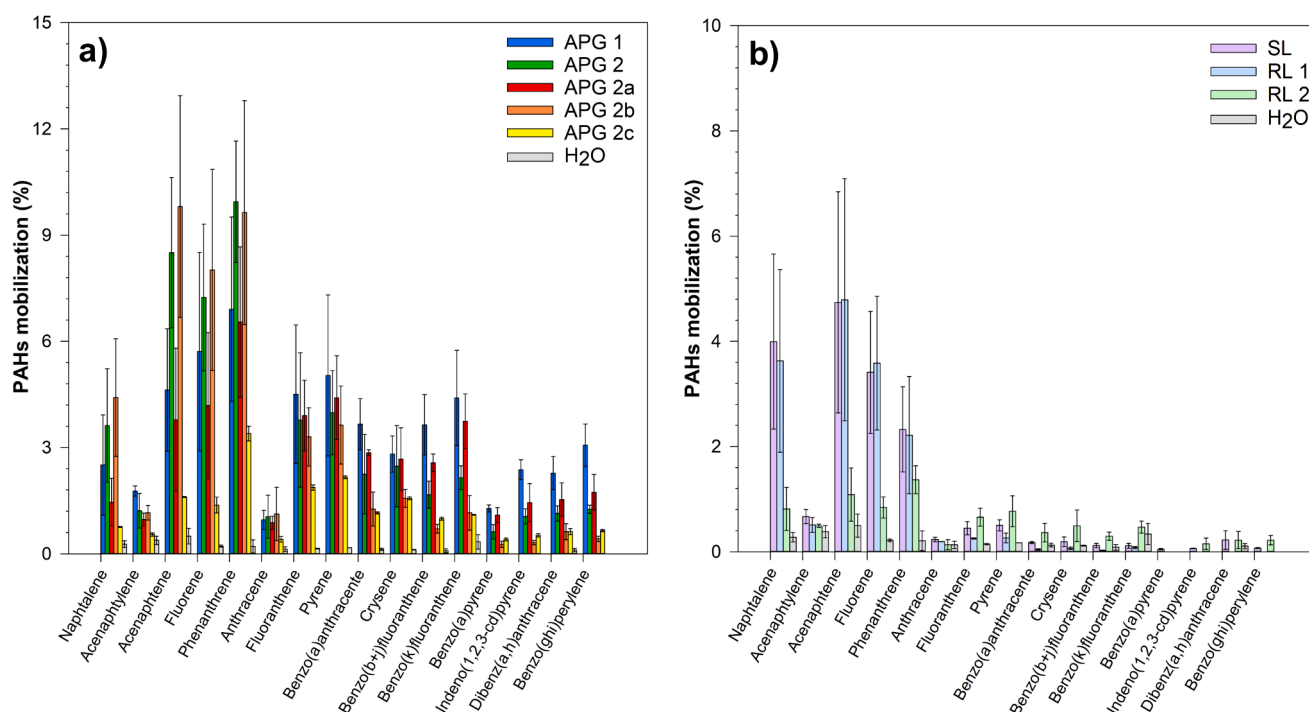

Fig. 3. PAHs mobilization by synthetic surfactants (a) and biosurfactants (b) compared with distilled water.

and 3.6 % of mobilization, respectively and finally the fluorene with 3.4 % of mobilization in presence of SL and 3.6 % in presence of RL1.

In contrast, rhamnolipid RL2 was more promising than other biosurfactants for the mobilization of heavy PAHs even though the recorded mobilization values were always less than 1 %. In fact, in the presence of RL2 the maximum mobilization was reached with pyrene, equal to 0.85 % of removal. From this value, the mobilization of heavy PAHs has progressively decreased as the molecular weight and number of condensed aromatic rings in the chemical structure of the compound increased. In any case, as it can be seen from the graphs in Fig. 2 and Fig. 3b, despite the low mobilization values, the contribution of biological surfactants is much higher than the mobilization provided by distilled water.

4.2. Effect of multiple consecutive washes

A multiple washing test was conducted at 5x CMC concentration of surfactants to evaluate if the maximum level of mobilization of heavy PAHs could be reached after one wash test, or if the total amount of PAHs mobilized could be increased with multiple washes of the sediment. This type of test is more interesting for heavy PAHs, due to their higher hydrophobicity and slower desorption rate than light PAHs. For this investigation, APG2c and RL1 were not tested as they resulted the less promising for the heavy PAHs mobilization in the preliminary study.

Fig. 4 shows the mobilization of heavy PAHs (not considered in terms of total heavy PAHs, but individually) by the effect of all investigated surfactants in each cycle of soil washing. In addition, it is important to note that the reported data refer to discrete mobilization values for each washing of the sediment. Thus, the overall PAHs mobilization after the third washing will be equal the algebraic sum of the mobilization values
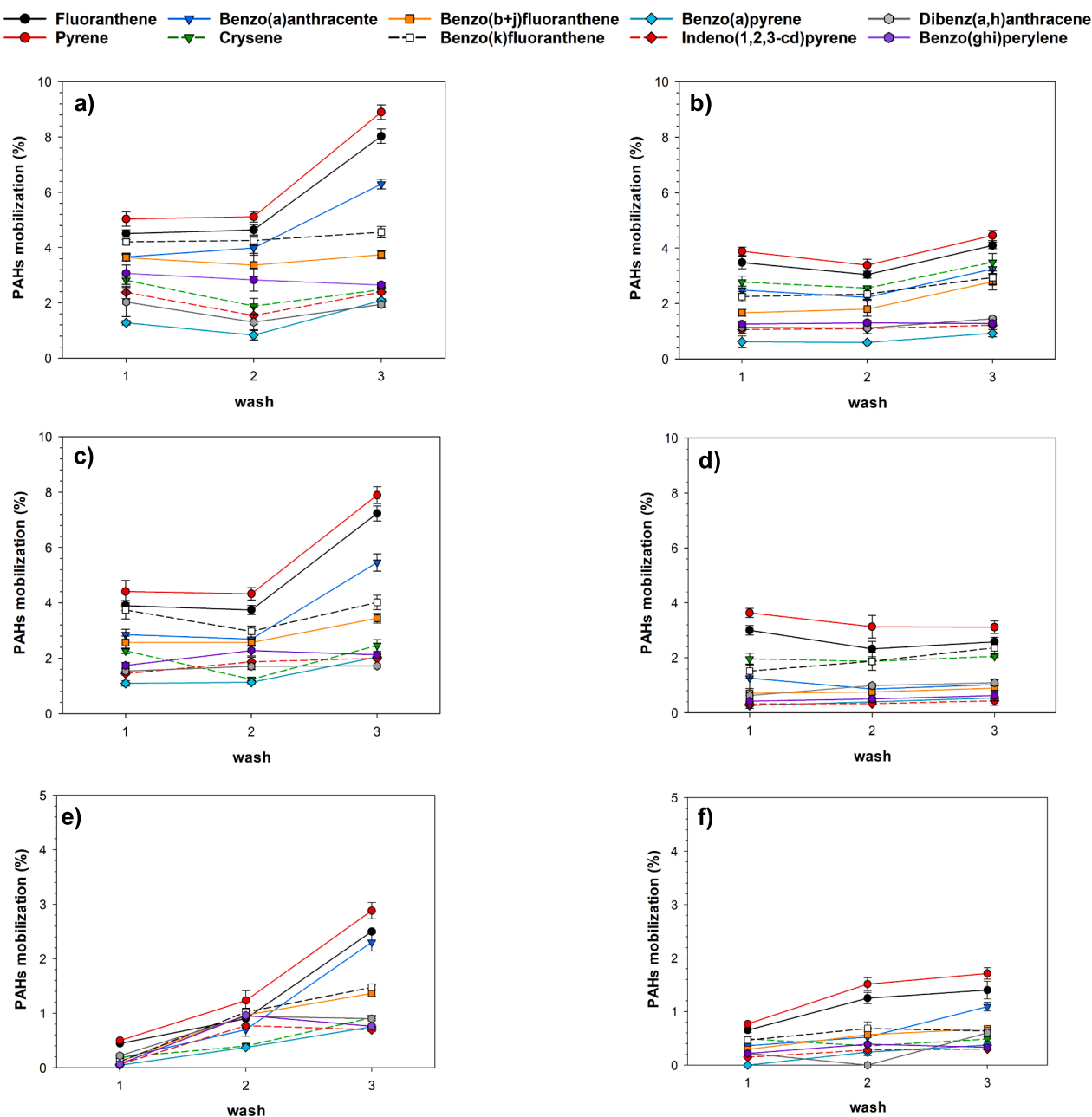

Fig. 4. PAHs mobilization in multiple washing test referred to the total amount of each contaminant in the sediment at initial condition in the presence of APG 1 (a), APG 2 (b), APG 2a (c), APG 2b (d), SL (e) and RL 2 (f).

obtained after each wash, as reported in Eq. (2).

$$PAHs_{cumul} = \sum_{i=1}^{3} PAHs_i = PAHs_1 + PAHs_2 + PAHs_3 \qquad (2)$$

Where $PAHs_{cumul}$ is the cumulative amount of mobilized PAHs at the end of the third wash, and $PAHs_i$ is the amount of mobilized PAHs related at each washing operation of the sediment.

As shown in Fig. 4a–d, the percentage of PAHs extracted in the first and second washes is almost stable for synthetic surfactants and increases after the third one, especially for fluoranthene, pyrene and benzo(a)anthracene. For the heavier PAHs (having more aromatic rings), from chrysene to benzo(ghi)perilene, mobilization values resulted lower and stable in all washings.

Among the synthetic surfactants, APG1 was the most promising to perform a treatment of the contaminated matrix by a series of consecutive washings. In fact, already in the first washing, APG1 has led to the highest mobilizations of heavy PAHs, compared to other synthetic surfactants investigated (as also highlighted in Fig. 3). Furthermore, APG1 was characterized by the highest increase in PAHs mobilization, reaching 8.0 %, 8.9 % and 6.3 % for fluoranthene, pyrene and benzo(a)anthracene, respectively. Considering fluoranthene, pyrene and benzo(a)anthracene, which resulted the most mobilized compounds among heavy PAHs, the cumulative mobilized amount in the presence of APG1 reached 17.3 %, 19.2 % and 13.2 %, respectively. In the case of APG2, the cumulative mobilization was 11.4 % for fluoranthene, 12.6 % for pyrene and 9.1 % for benzo(a)anthracene (about 35 % lower than APG1).

The performances of APG2a formulation were comparable to those obtained with APG1, resulting in a cumulative mobilization of fluoranthene, pyrene and benzo(a)anthracene equal to 14.9 %, 16.6 % and 11.1 %, respectively. APG2b was the less promising among the synthetic surfactants since the cumulative mobilization of fluoranthene, pyrene and benzo(a)anthracene was significantly lower (7.9 %, 9.8 % and 3.1 %, respectively).

On the other hand, for the biosurfactants group, the results shown in Fig. 4e for SL and 4f for RL2 emphasize that the first wash led to a very low percentage of extraction of heavy PAHs as already obtained in preliminary first mobilization test (previously reported). However, much more interesting is the results of the second and third wash. Indeed, the contaminant extraction increased with the number of washes: starting from a mobilization lower than 1 % in the first wash, the mobilization in the third wash doubled or even tripled, and in some cases increased by five times in comparison with the first one.

In this context, SL sophorilipid has been demonstrated to be the most interesting biosurfactant since its performances increased more than 500 %, from 0.45 % to 2.5 % for fluoranthene, from 0.5 % to 2.6 % for pyrene and from 0.2 % to 2.3 % for benzo(a)anthracene. A similar behavior was recorded for RL2, but with a smaller increase in PAHs mobilization than SL.

Fig. 5 shows the total mobilization of PAHs (as a sum of all 16 PAHs, considering both light and heavy ones, mobilized from solid to aqueous phase) after each washing operation, in terms of cumulative values (Eq. (2)). The improvement of the performance has been extremely relevant for APG1, which allowed to obtain a mobilization of total PAHs four times higher (12.5 %) after the third wash. Similar but lower performance was obtained for APG2 and APG2a, with a total PAHs mobilization equal to 11.1 % and 10.7 %, respectively. In the presence of APG2, the mobilization was about half of those reached with other synthetic surfactants. From this point of view, considering that after three consecutive sediment washes PAH mobilization is almost quadrupled (especially for synthetic surfactants), it is quite evident the great advantage of sediment treatment with multiple consecutive washes 2.

5. Conclusions

To the authors' best knowledge, this paper shows for the first time the results of a preliminary batch test and then a multiple washing test, conducted for evaluating the different capacity of eight selected nonionic biodegradable surfactants in mobilizing highly contaminated sediments by PAHs for further remediation purposes. Overall, the investigated surfactants, i.e., five synthetic surfactants (APG1, APG2, APG2a, APG2b and APG2c) and three biosurfactants (SL, RL1, and RL2), significantly improved the potential mobilization of all 16 considered PAHs. The results from the preliminary batch test highlighted that APG2
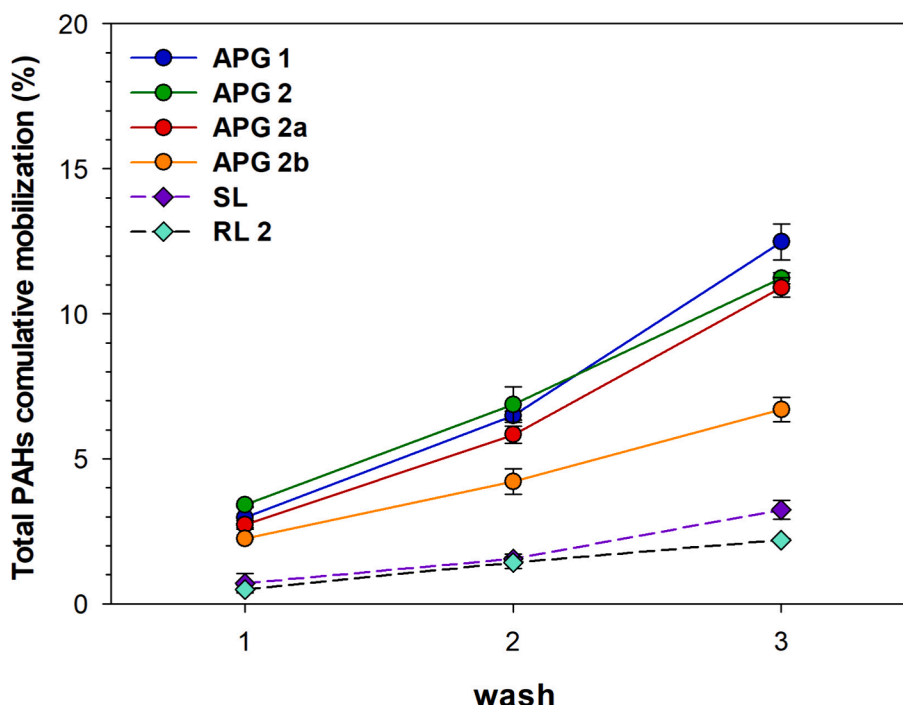

Fig. 5. Total PAHs cumulative mobilization in multiple washing test.

was the best synthetic surfactant (3.4 % of mobilization) and SL was the best biosurfactant (0.7 % of mobilization). On the contrary, in their respective classes, APG2c and RL1 were the less effective. In detail, APG2 and APG2b showed the best performance for light PAHs, whereas APG1 was optimal for the heavy PAHs mobilization.

Indeed, the multiple washing test confirmed the excellent APG1 performances towards heavy PAHs. Moreover, for the second experimentation, the results suggest that for both synthetic and natural surfactants, the multiple treatment of the sediment with consecutive washes ensured a gradual increase in the extraction of pollutants, improving the efficiency of a soil washing process. Considering the increase of mobilization performances, investigated biosurfactants gave the most interesting results since their efficiency rose to 500 %. However, despite the greatest increase in PAHs extraction, the investigated biosurfactants can be considered quite unpromising, due to the low cumulative mobilization of total PAHs. For this reason, synthetic APGs, especially APG1, can be considered highly promising, having contributed to a much higher mobilization of PAHs than other investigated surfactants.

In conclusion, as main results: (I) synthetic surfactants have an immediate response in terms of mobilized PAHs, contrary to natural surfactants that require, at least, one more wash with a new solution to increase PAHs removal; (II) natural surfactants could reach their optimal result increasing the number of washing treatments, thus becoming a real alternative to synthetic surfactants; (III) the amount of each extracted contaminant decreases in according with their number of aromatic rings.

CRediT authorship contribution statement

Gabriele Moscatelli: Writing – original draft, Investigation, Formal analysis, Data curation. **Berardino Barbati:** Writing – original draft, Investigation, Formal analysis, Data curation. **Laura Lorini:** Writing – original draft, Validation, Supervision, Conceptualization. **Laura Caiazzo:** Writing – original draft, Validation, Supervision, Conceptualization. **Salvatore Chiavarini:** Validation, Supervision. **Massimo Pezza:** Validation, Supervision. **Marco Bellagamba:** Supervision, Investigation, Conceptualization. **Marco Petrangeli Papini:** Visualization, Resources, Project administration, Methodology, 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

Data will be made available on request.

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