



Combining biodegradable surfactants and potassium inorganic salts for efficiently removing polycyclic aromatic hydrocarbons from aqueous effluents

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ABSTRACT

The use of aqueous solutions of non-ionic surfactants like Tergitol 15-S7 and Tergitol 15-S9 is proposed for the first time to ex-situ remediation of Phenanthrene, Pyrene and Benzo[a]anthracene polluted soils, thus generating aqueous Polycyclic Aromatic Hydrocarbons (PAH)-polluted effluents. The effectiveness of several potassium based-inorganic salts (K_3PO_4 , K_2HPO_4 , K_2SO_4 , $K_2S_2O_3$ and K_2CO_3) to act as PAHs extractants was evaluated. The immiscibility region of the aqueous solutions was determined at room temperature, correlated by three empirical equations and compared with other non-ionic surfactants belonging to Tween and Triton families. The segregation capacity of the salts was analyzed in the light of their water-structuring degree and molar Gibbs free energy of hydration ($\Delta_{hyd}G$). Tie-line determination was the tool used to determine the more viable PAHs removal strategy. Thus, the efficiency of combining K_3PO_4 to salt out Tergitol 15-S9 aqueous solutions polluted with the selected PAHs was investigated. The extraction percentage of the pollutants was 75% of Benzo[a]anthracene, 72% of Phenanthrene and 60.5% of Pyrene. The process was simulated at real scale through SuperPro Designer v.8.5 for the treatment of 156,000 tons/year of PAH-polluted soil.

1. Introduction

The most well-known feature of the Polycyclic Aromatic Hydrocarbons (PAHs) for the global population is the evidence that they cause cancer risks in animals and humans [1]. The main problem of these contaminants is their increasing ubiquity. More specifically, their presence is associated to natural sources like coal deposits, volcanic activity or a byproduct derived of anthropogenic activities as incomplete combustion of fossil fuels [2,3]. In this scenario, PAHs have been classified as persistent organic contaminants by the USEPA (US Environmental Protection Agency, 2008) [4] and this categorization can be derived from their chemical composition. Polycyclic Aromatic Hydrocarbons are defined as hydrocarbons with two or more fused benzene rings. Moreover, they include C—C bonds which provide them some special characteristics, such as high boiling point and vapor pressure [5]. These properties are decisively affected by the molecular weight and consequently the efficiency of the removal treatments may be reduced [6]. In this sense, they are divided into two groups related to the aromatic ring

number: i) Low Molecular Weight (LMW) with 2 or 3 rings considered less toxic and ii) High Molecular Weight (HMW) with more than 4 and more carcinogenic. Taking into account the different combinations, hundreds of PAHs exist but only 16 of them are named as priority pollutants by the USEPA and their removal is a topic in the limelight. One of the key physical characteristics of these contaminants is their low solubility but, even in this case, PAH concentration in water is significant throughout the world independently of their geographical situation [7]. These values range from 0.03 ng/L in Japan Sea to 16.59 mg/L in South Africa [8,9]. The previous references to the toxicity, carcinogenic, persistent and mutagenic properties have urged to different organizations to set the water quality guidelines for PAHs to preserve drinking, fresh and marine water, e.g. European Parliament and the Council of the European Union in 2013 limited the anthracene content in fresh water to 0.1 $\mu\text{g/L}$.

The United Nations Sustainable Development Goals address the challenges associated with water pollution [10]. Several initiatives have emerged with this objective, for example adsorption using various

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efficient and cost effective materials as well as bioremediation or electrochemical process among others [11–14]. Although these actions could be considered successful, more efficient, ecofriendly affordable, and sustainable strategies to achieve the abovementioned goals by 2030 are necessary. Although PAHs removal from solid matrices is not new, the reported methodologies are in their vast majority based on the use of hazardous and volatile organic solvents or mechanical treatments. The removal of PAHs from soils and sediments have been traditionally tackled by washing with surfactants because the hydrophobic group absorbs them, favouring the migration of aromatic compounds to the organic phase and then easing the separation of the contaminant from the solid. The extended use of these compounds has resulted attractive due to their lower toxicity and higher biodegradability than that recorded for other conventional organic solvents [15]. Among the broad range of synthetic surfactants, non-ionic and anionic surfactants have been the most widely used in contaminant soil washing. More specifically, their use to remove PAHs from solid matrices is the most popular option for ex-situ remediation of contaminated areas [16]. This remediation treatment has suffered from great volumes of wastewater with aromatic pollutants that should be economic, sustainable and effectively treated. As a result, the scientific community is prompted to search for an efficient process to remove them from aqueous media.

During the last decades, processes using extracting agents have shown promising results to remove different compounds from aqueous media. Particularly, Aqueous Two-Phase Systems (ATPS) could be considered a competitive strategy to effective, less expensive and environmentally friendly PAHs removal. In this option, the existence of aqueous solutions containing soluble aromatic compounds derived from a contaminated solid matrix washing pre-treatment with surfactants. Since ATPS have been demonstrated to be a versatile tool to extract from biocompounds [17], organic pollutants [18] and heavy metals [19,20] to emerging contaminants [21], we have hypothesized its suitability to be used in this context. In this particular case, the presence of surfactants is an opportunity to disengage two immiscible phases (one of them rich in PAHs) after addition of an adequate agent. A deep revision of the literature indicates that inorganic salts have traditionally affected water structure. Thus, taking into account our previous experience, Hofmeister series was the basis for a judicious selection and five potassium based inorganic salts have been proposed with this aim: K_3PO_4 , K_2HPO_4 , K_2SO_4 , $K_2S_2O_3$ and K_2CO_3 [22,23].

In order to maintain a sustainable approach, the selection of a more suitable surfactant that meets biodegradability standards is mandatory. Thereby, two polyalkoxylated nonionic surfactants, Tergitol 15-S7 and Tergitol 15-S9 have been selected to remove three model PAHs, namely phenanthrene (PHE), pyrene (PYR) and benzo[a]anthracene (BZA). The rationale behind this choice is founded on the lack of an aromatic ring in these compounds. This feature guarantees its degradation capacity and avoids the interference in PAHs analysis. Moreover, their low cloud-point temperature, density and CMC are advantages that ensure their appropriateness [24,25]. In this work, we have investigated the extraction capacity of K_3PO_4 , K_2HPO_4 , K_2SO_4 , $K_2S_2O_3$ and K_2CO_3 in aqueous solutions of Tergitol 15-S7 and Tergitol 15-S9 polluted with PHE, PYR and BZA at room temperature. To our knowledge, this is the first time that this combination is proposed in open literature. First of all, the experimental solubility curves have been determined and the experimental data have been correlated by three empirical equations. The efficiency of the proposed potassium inorganic salts was discussed in the light of their degree of lyotropy and quantitatively analyzed with the molar Gibbs free energy of hydration ($\Delta_{hyd}G$). From this analysis, the experimental tie-lines were determined using K_3PO_4 and K_2HPO_4 as extractant agents to Tergitol 15-S9 aqueous mixtures at room temperature. The more adequate platform to remove the selected aromatic pollutants was established by analyzing the tie-line length and slope. Finally, the extraction percentage of the abovementioned PAHs from Tergitol 15-S9 aqueous solutions adding K_3PO_4 as extractant was carried out at room temperature. The present proposal aims to be applied in a

commercial remediation activity for the removal of common PAHs from the industrial activity. Albeit no information about scale up criteria and cost of manufacturing is available for this process, PAHs extraction has been studied in this study at laboratory scale. Afterwards, the viability of the treatment at real scale was studied through the commercial simulation tool, SuperPro Designer v8.5.

2. Experimental section

2.1. Chemicals

PAHs (Phenanthrene, pyrene and benzo[a]anthracene) and surfactants (Tergitol 15-S7 and Tergitol 15-S9) were acquired from Sigma-Aldrich and their relevant properties are presented in Table 1. The purity and supplier of the inorganic salts are K_3PO_4 (97%, Alfa-Aesar), $K_2HPO_4 \cdot 3H_2O$ (99%, Merck), K_2CO_3 (99%, Scharlau), $K_2S_2O_3$ (95%, Sigma-Aldrich) and K_2SO_3 (90%, Sigma-Aldrich) and they were used as received.

2.2. Aqueous two-phase system determination

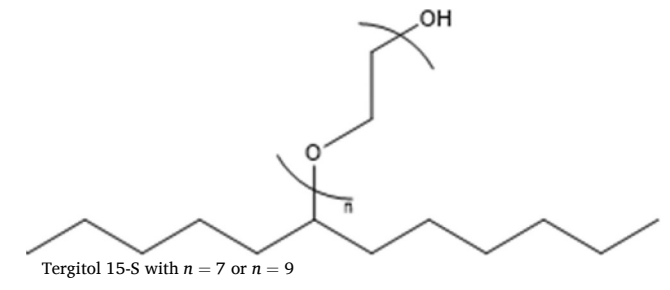
The solubility curves were characterized by means of the cloud point titration method [26] at room temperature. In brief, a binary mixture with known composition of non-ionic surfactant-based aqueous solution was prepared in a glass tube. A known amount of inorganic salt was added under constant agitation until turbidity was detected. At this concentration the two-phase region is defined and the ternary composition was determined by the mass quantification with a Sartorius Cubis MSA balance ($\pm 10^{-4}$ g). This procedure was repeated until the immiscibility region was completely defined at room temperature.

2.3. Tie-line determination

The tie-lines (TLs) were carried following previous relevant literature [23]: an aqueous solution of Tergitol 15-S7 or Tergitol 15-S9 and potassium-based salt (K_3PO_4 or $K_2HPO_4 \cdot 3H_2O$ or K_2CO_3 or $K_2S_2O_3$ or K_2SO_3) at a composition falling into the immiscibility region (c.f. Table 6) was prepared. The mixture was vigorously stirred at room temperature and left to settle for 24 h to ensure a complete separation of the layers. The estimated uncertainty in the determination of surfactant and salt phase mass compositions is less than $2 \cdot 10^{-4}$. The top and bottom concentration of the TL were determined by solving four equations: two of them consider the relationship between the upper phase and the overall system mass composition by means of the lever arm rule and the others are based on Merchuk equation [27]. From these experimental data, significant tie-line information like the tie-line lengths (TLL) and slopes (S), were determined as follows:

Table 1
Main properties of surfactants.

Compound	HLB*	CMC (mg/L)**
Tergitol 15-S7	12.1	38
Tergitol 15-S9	13.3	52



HLB: hydrophilic and lipophilic balance; CMC: critical micelle concentration.

$$TLL = \left[(w_1^I - w_1^{II})^2 + (w_2^I - w_2^{II})^2 \right]^{0.5}, \tag{1}$$

$$S = \frac{w_1^I - w_1^{II}}{w_2^I - w_2^{II}}, \tag{2}$$

being w_1 and w_2 the mass fraction percentages of surfactant and potassium inorganic salt, respectively. Tergitol-rich phase and salt rich-phase are represented by the superscripts I and II, respectively.

2.4. PAHs extraction and analysis

50 μ L of each of the contaminants (PHE, PYR and BZA) was added to a ternary mixture containing 15% salt, 15% surfactant and 70% water. The mixture was shaken and left to settle for 24 h at room temperature. PAHs quantification in the aqueous solution was analyzed by reversed-phase high performance liquid chromatography (HPLC) with a reversed phase C18 column (250 \times 4.6 mm, 5 μ m particle size, Phenomenex Luna) [12]. The HPLC device was an Agilent 1100 equipped with a quaternary pump and photodiode array UV/Vis detector (252.4 nm). An aliquot (20 μ L of the sample) was injected and then eluted from the column at flow rate of 1.5 mL min⁻¹, firstly, a mixture containing 50% water and 50% acetonitrile was included, and after 36 min was changed to pure acetonitrile at 298.15 K. The extraction capacity (E) has been calculated as follow:

$$\text{Extraction (\%)} = \left(\frac{m_i^I}{m_i} \right) \cdot 100 \tag{3}$$

being m_i^I the PAHs content in the Tergitol-rich phase and m_i the total PAHs content. The residence times for PHE, PYR and BZA are 16.9, 20.2

and 22.9 min.

3. Results and discussion

The viability of the present proposal to remove PHE, PYR and BZA from aqueous solutions of Tergitol 15-S was evaluated from two points of view: i) the non-ionic surfactant selected as detergent and ii) the inorganic salt employed for PAHs. After this initial screening to identify the most promising configuration, the extraction yield of the PAHs was carried out at room temperature.

Aqueous solutions of surfactant (Tergitol 15-S7 or Tergitol 15-S9) were prepared and inorganic potassium salts (K₃PO₄ or K₂HPO₄·3H₂O or K₂CO₃ or K₂S₂O₃ or K₂SO₃) were added to identify the best extractant of the selected PAHs (PHE, PYR and BZA) at room temperature. The solubility data for the ternary mixtures were determined by the cloud point method and they are listed in Tables 2 and 3. These experimental data were correlated by means of Merchuk equation and two empirical models, described as follows:

$$w_1 = A \cdot \exp(Bw_2^{0.5} - Cw_2^3), \tag{4}$$

$$w_1 = \exp(A + Bw_2^{0.5} + Cw_2 + Dw_2^2), \tag{5}$$

$$w_1 = A \cdot \exp(Bw_2^D - Cw_2^E), \tag{6}$$

where w_1 is the mass fraction percentage of Tergitol 15-S7 or Tergitol 15-S9, w_2 is the mass fraction percentage of inorganic salt, and (A , B , C , D and E) are the fitting parameters obtained after minimization of the root mean square deviation (σ):

Table 2
Experimental binodal data for: Tergitol 15-S7 (1) + inorganic salt (2) + H₂O at 298.15 K.

K ₃ PO ₄		K ₂ HPO ₄ ·3H ₂ O		K ₂ S ₂ O ₃		K ₂ SO ₃		K ₂ CO ₃	
100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁
0.96	57.94	0.42	56.27	1.06	55.73	1.37	54.10	0.65	52.90
1.38	52.06	1.64	51.69	1.83	53.21	2.79	48.36	1.34	50.63
2.58	43.46	2.13	49.71	2.78	50.60	3.89	43.83	1.82	49.02
3.15	37.79	2.22	47.21	4.43	46.13	4.92	39.44	2.55	47.16
3.57	34.33	2.87	45.53	4.53	43.96	5.20	35.70	3.24	44.92
4.08	32.34	3.30	39.13	5.64	40.35	5.30	32.02	3.74	43.30
4.12	31.59	3.63	35.90	6.05	38.64	5.66	23.81	4.04	39.81
4.19	30.02	4.99	27.42	7.30	32.57	5.84	19.57	4.10	35.48
4.23	27.88	5.00	23.45	8.00	25.40	6.21	15.08	4.32	30.43
4.53	24.71	5.01	20.96	8.06	24.15	6.25	12.78	4.47	26.16
4.57	22.21	5.10	18.85	8.20	20.65	6.30	8.80	4.70	21.22
4.62	19.96	5.18	11.15	8.39	16.89	6.30	7.84	4.77	16.49
4.68	22.14	5.13	11.62	8.43	15.24	13.55	0.49	4.79	13.96
4.82	18.28	5.26	18.35	8.60	11.04	9.76	0.50	4.85	11.66
5.35	15.93	5.39	16.51	35.30	0.20	8.09	0.50	4.87	8.91
5.55	14.14	5.55	6.49	33.30	0.21	7.51	3.34	4.87	6.91
5.59	12.57	2.72	46.31	28.52	0.25			47.93	0.23
5.54	9.58	3.80	36.79	24.29	0.27			42.54	0.29
5.85	6.91	4.34	32.66	18.25	0.28			37.68	0.33
6.52	2.33	5.59	7.34	15.79	0.29			33.56	0.35
48.11	0.22	5.05	27.05	9.98	0.30			28.42	0.38
43.04	0.24	5.01	12.96	9.58	6.06			24.25	0.40
37.98	0.26	5.10	14.22					19.14	0.44
32.61	0.27	5.12	12.34					14.60	0.47
28.50	0.28	5.50	8.12					8.77	0.50
23.35	0.29	6.52	2.35					5.22	2.64
18.58	0.29	37.27	0.21					15.15	0.37
13.75	0.30	22.47	0.45						
8.82	0.30	33.45	0.31						
14.95	0.35	30.27	0.34						
		25.15	0.42						
		17.28	0.48						
		13.87	0.51						
		9.77	0.52						
		7.34	0.51						

Table 3

Experimental binodal data for: Tergitol 15-S9 (1) + inorganic salt (2) + H₂O at 298.15 K.

K ₃ PO ₄		K ₂ HPO ₄ ·3H ₂ O		K ₂ S ₂ O ₃		K ₂ SO ₃		K ₂ CO ₃	
100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁
1.28	57.91	7.45	13.55	2.01	61.55	0.79	56.90	2.24	51.09
1.72	55.11	7.69	11.37	2.41	60.32	2.13	46.92	3.08	44.03
1.86	52.77	1.07	60.63	3.34	55.38	3.85	38.22	3.70	39.27
2.11	51.23	5.92	25.52	3.53	54.46	4.83	32.61	4.05	35.71
2.86	45.83	6.35	22.53	4.83	48.79	5.55	28.08	4.39	34.06
3.42	41.77	7.01	18.99	6.87	37.26	5.73	26.55	4.83	30.86
3.92	38.81	1.52	56.75	7.21	35.83	6.49	22.56	5.15	28.14
4.03	38.70	1.72	54.99	8.39	30.78	7.65	17.54	5.42	26.05
4.67	34.43	3.48	41.38	9.24	26.07	8.54	13.22	5.54	25.17
5.13	32.21	0.82	63.38	10.72	20.66	8.97	11.19	5.77	23.35
5.95	27.66	1.61	56.14	11.13	18.61	9.35	7.73	5.94	20.49
6.23	26.39	2.67	49.14	11.50	16.56	13.88	0.34	5.91	20.10
6.76	23.03	3.32	42.68	11.75	15.35	11.09	0.33	6.16	18.01
7.17	20.65	4.08	38.89	11.75	15.35	0.79	56.90	6.29	16.55
7.20	20.07	4.41	36.40	12.15	12.99			6.54	15.14
7.44	18.65	5.09	30.77	12.44	11.53			6.66	14.04
8.28	14.31	5.49	28.18	13.58	6.00			6.85	12.57
8.55	12.82	33.11	0.22	37.03	0.33			7.10	11.54
8.81	10.81	30.06	0.24	32.07	0.34			7.22	10.12
9.31	8.46	26.20	0.27	26.91	0.38			7.35	9.01
46.70	0.24	23.16	0.30	22.88	0.41			7.52	7.70
42.71	0.27	19.94	0.33	19.69	0.42			49.09	0.19
38.85	0.29	17.03	0.35	16.16	0.45			43.23	0.21
32.30	0.32	14.91	0.38					37.65	0.24
28.22	0.35	10.51	0.41					31.48	0.25
24.12	0.39	9.79	4.36					28.46	0.27
18.71	0.42							22.56	0.29
15.00	0.42							18.52	0.31
15.06	0.29							15.54	0.32
11.35	2.35							9.79	0.34
								15.08	0.35
								8.54	3.65

$$\sigma = \left(\frac{\sum_i^{n_{DAT}} (z_{exp} - z_{adjust})^2}{n_{DAT}} \right)^{1/2} \tag{7}$$

where z_{exp} , and z_{adjust} , are the experimental and theoretical data, respectively, and n_{DAT} are the number of experimental data. The obtained fitted constants (*A*, *B*, *C*, *D* and *E*) were obtained by minimizing the above deviation equation and these values are included in [Tables 4 and 5](#). An analysis of the root mean square deviations, obtained after applied the three empirical equations to correlate the immiscibility regions, indicates that modified-Merchuk equation is the most adequate one to describe the immiscible region, no matter the surfactant or potassium salt present in the aqueous solution.

3.1. Immiscible region: effect of surfactant

Once the experimental binodal data are obtained it is necessary to determine the surfactant ability to perform solubility curves closer to the origin. In our case, Tergitol 15-S7 and Tergitol 15-S9 exhibit a similar trend and then the decision should be grounded in other factors. In this way, the hydrophobic nature of a surfactant quantified by the empirical number hydrophilic-lipophilic balance (HLB) has been used. In this study, Tergitol 15-S7 possesses an HLB of 12.1 while the value for Tergitol 15-S9 reaches 13.3. The slight difference is translated into similar immiscibility regions where less amount of extractant is required to salt out the surfactant based aqueous solutions.

As expected, the HLB data is a valuable tool for a first approach in an extraction strategy involving aqueous solutions. This premise has been confirmed with previous results for systems composed of other surfactants [23,28]. In these papers, the experimental studies were carried out in the presence of Tween 20, Tween 80, Triton X-100 and Triton X-102 (HLB = 16.7, 15.0, 13.4, and 14.4, respectively) and the mentioned

Table 4

Fitting parameters and standard deviation of the ternary system: Tergitol 15-S7 (1) + potassium salts (2) + H₂O (3).

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	σ
Tergitol 15-S7 (1) + K ₃ PO ₄ (2) + H ₂ O (3)						
Eq. (1)	63.248	-0.1200	0.0079			1.687
Eq. (2)	7.0240	-5.4494	2.6928	-0.2168		1.429
Eq. (3)	107.79	-0.6378	0.0003	0.3484	4.8175	1.369
Tergitol 15-S7 (1) + K ₂ HPO ₄ ·3H ₂ O (2) + H ₂ O (3)						
Eq. (1)	53.638	0.0214	0.0089			3.668
Eq. (2)	5.2002	-2.8829	1.7533	-0.1843		3.576
Eq. (3)	50.99	0.0147	0.0020	0.2158	3.8773	3.540
Tergitol 15-S7 (1) + K ₂ S ₂ O ₃ (2) + H ₂ O (3)						
Eq. (1)	50.805	0.0496	0.0020			2.951
Eq. (2)	5.9944	-3.2770	1.4331	-0.0805		2.803
Eq. (3)	51.356	0.0001	0.0001	0.3213	4.5981	2.507
Tergitol 15-S7 (1) + K ₂ SO ₃ (2) + H ₂ O (3)						
Eq. (1)	31.713	0.4190	0.0074			3.865
Eq. (2)	13.760	-16.290	7.3699	-0.4235		2.304
Eq. (3)	51.441	0.0001	0.0001	0.3484	5.8664	2.333
Tergitol 15-S7 (1) + K ₂ CO ₃ (2) + H ₂ O (3)						
Eq. (1)	31.195	0.4830	0.0151			4.596
Eq. (2)	8.0650	-8.9975	5.2021	-0.4588		3.554
Eq. (3)	49.671	0.0001	0.0001	0.3484	7.2021	2.301

potassium salts. It is possible to conclude that higher immiscibility is related to lower HLB. The possible explanation could be supported by the different hydrogen bonding capacity of the surfactants. Thus, while Tween compounds have a great number of ethoxylate groups that highly interact with water, Triton ones include a structural aromatic ring that

Table 5

Fitting parameters and standard deviation of the ternary system: Tergitol 15-S9 (1) + potassium salts (2) + H₂O (3).

	A	B	C	D	E	σ
Tergitol 15-S9 (1) + K ₃ PO ₄ (2) + H ₂ O (3)						
Eq. (1)	86.820	-0.3548	0.0014			0.519
Eq. (2)	5.2471	-1.6286	0.5767	-0.0394		0.566
Eq. (3)	123.95	-0.6823	0.0003	0.3519	3.6658	0.383
Tergitol 15-S9 (1) + K ₂ HPO ₄ ·3H ₂ O (2) + H ₂ O (3)						
Eq. (1)	83.834	-0.3110	0.0022			0.799
Eq. (2)	4.8658	-1.1691	0.4656	-0.0448		0.914
Eq. (3)	13.137	1.5467	0.0041	-0.1287	2.7970	0.838
Tergitol 15-S9 (1) + K ₂ S ₂ O ₃ (2) + H ₂ O (3)						
Eq. (1)	56.802	0.0001	0.0009			2.449
Eq. (2)	5.1137	-1.1537	0.3668	-0.0202		1.042
Eq. (3)	88.180	-0.2270	0.0001	0.5929	3.5785	0.828
Tergitol 15-S9 (1) + K ₂ SO ₃ (2) + H ₂ O (3)						
Eq. (1)	73.516	-0.2920	0.0015			1.082
Eq. (2)	4.7190	-1.1195	0.4315	-0.0365		1.137
Eq. (3)	88.170	-0.4759	0.0005	0.3877	3.5219	0.983
Tergitol 15-S9 (1) + K ₂ CO ₃ (2) + H ₂ O (3)						
Eq. (1)	67.278	-0.1693	0.0038			0.687
Eq. (2)	9.2851	-7.3706	2.8802	-0.1531		0.488
Eq. (3)	89.011	-0.3594	0.0005	0.5396	3.9501	0.535

diminish their water affinity. On the other hand, Tergitol 15-S family presents a long alkyl chain that hinders the formation of hydrogen bonds with water molecules, which increases the hydrophobicity. Finally, Tergitol 15-S9 was selected as the most viable candidate to wash PAHS contaminated soils because its higher values of CMC (52 mM) compared to Tergitol 15-S7 (38 mM). This fact is based on the necessity to minimize foam formation in the pollutant removal stage where vigorous agitation is mandatory, which would be reflected in a high process time required for phase segregation.

3.2. Immiscibility region: effect of the inorganic salts

An initial screening of several potassium inorganic salts (K₃PO₄, K₂HPO₄·3H₂O, K₂CO₃, K₂S₂O₃, K₂SO₃) was made in order to establish the most reliable extractant. A previous literature revision reveals that no solubility data were carried out dealing with the above Tergitol 15-S detergents and the selected salts. In our case, five inorganic salts were dissolved in surfactant-based aqueous solutions and a competition for the water molecules was established. The inorganic ions build a stronger interaction than the surfactant and consequently a Tergitol rich phase is separated from the solution. Historically, the Hofmeister series was employed to order the segregation capacity of inorganic salts but a more plausible explanation could be based on the Gibbs free energy of hydration of the ions [29]. So, a comparison of the binodal data aiming to determine the influence of the salt in the ATPS formation is graphically presented in Figs. 1 and 2. In these figures, the order in the biphasic region promotion is: K₃PO₄ > K₂HPO₄·3H₂O > K₂CO₃ > K₂SO₃ > K₂S₂O₃ no matter the surfactant employed. These results follow the Hofmeister series and corroborate those ones previously obtained by our research group [23,28]. Thus, the anion with the strongest extractant effect is PO₄³⁻ and the lowest is S₂O₃²⁻.

The possible explanation that could be considered is that the trivalent anion favours the attraction with the dipole of the water molecules and this stronger interaction is decisive in terms of salting out potential [30]. Another interesting factor is the analysis of the basic strength of the inorganic salts and then the basicity of the mixture when the divalent salts are added. Different authors [30–32] have observed that the presence of hydroxide anion in the solution could be a key parameter to

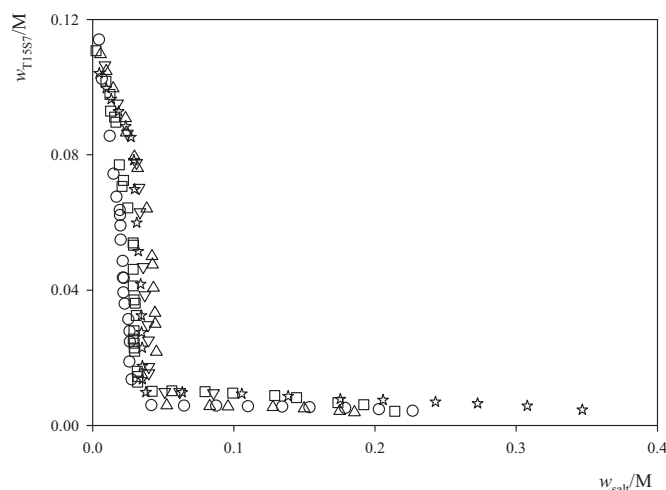


Fig. 1. Solubility curves in molar fraction of the ternary mixture: Tergitol 15-S7 (1) + inorganic salt (2) + H₂O (3) at room temperature. K₃PO₄ (○), K₂HPO₄·3H₂O (□), K₂CO₃ (☆), K₂SO₃ (▽), K₂S₂O₃ (△).

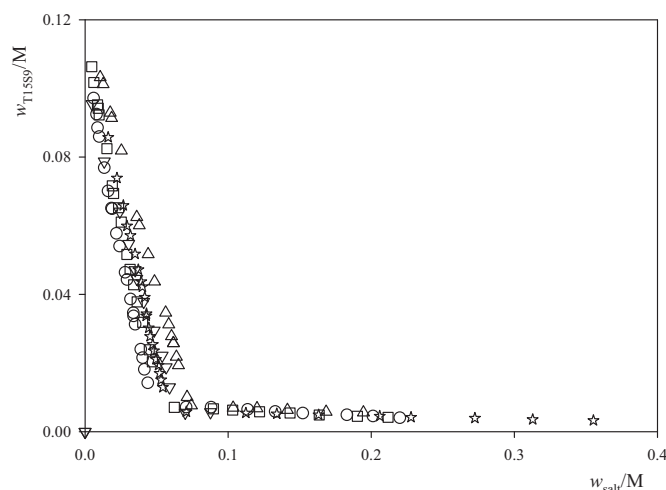


Fig. 2. Solubility curves in molar fraction of the ternary mixture: Tergitol 15-S9 (1) + inorganic salt (2) + H₂O (3) at room temperature. K₃PO₄ (○), K₂HPO₄·3H₂O (□), K₂CO₃ (☆), K₂SO₃ (▽), K₂S₂O₃ (△).

explain the lower extraction capacity of the divalent inorganic salts. In this case, the acidic anions diminish the hydroxide concentration and this fact could reduce the interactions with the surfactant and, consequently, the phosphate anion has a higher ability than its homologue hydrogenphosphate to form ATPS.

Finally, the extraction capacity of the salts can be quantitatively analyzed on the basis of the Gibbs energy of hydration ($\Delta_{\text{hyd}}G$). Thus, the data reported by Marcus [29] confirm the obtained trend: PO₄³⁻ (−2765 kJ·mol^{−1}) > CO₃²⁻ (−1315 kJ·mol^{−1}) > SO₃²⁻ (−1295 kJ·mol^{−1}), which is in agreement with our results. These values indicate that negative values of $\Delta_{\text{hyd}}G$ promote the formation of water-ion complexes that contributes to phase disengagement.

3.3. PAHS removal from effluents

The use of water-based mixtures at room temperature is a more sustainable and biocompatible approach. At this moment, immiscibility regions of both surfactants have been thoroughly characterized (Figs. 1 and 2). The analysis of the immiscibility regions of the ternary mixtures confirms that Tergitol 15-S9 aqueous solutions are the best option to

efficiently remove the model PAHs (PHE, PYR and BZA). In this scenario, it is necessary to determine the most appropriate potassium salt able to remove the abovementioned pollutants. This judicious selection is based on the previous results of their salting out potential. The experimental tie-line determination is the selected tool to assess in the phases distribution of the pollutants. In Table 6, the selected feed composition and the heavy and light phases have been listed for K_3PO_4 and $K_2HPO_4 \cdot 3H_2O$ at room temperature.

An analysis of the tie-line lengths (*TLL*) and slopes (*S*) values indicates that K_3PO_4 is the salt enabling longer tie-line and shorter slope. It is necessary to check whether this information is effective to increase PAHs efficient removal. In this particular case, the higher salt concentration in the ternary mixture, the more purity in the Tergitol 15-S9-rich phase. This fact could be the rationale behind the strong interactions of this trivalent potassium salt with water molecules, favouring the segregation of the surfactant. In view of these results, it is possible to state the real relationship between immiscibility region and *TL*, considering that only the experimental results are the viable tool to determine this extraction capacity. Currently, there are no theoretical approaches to efficiently predict how the compounds under study will partition in the newly designed separation platform. Previous research works [33,34] confirm that PAHs partition is highly influenced by water content since it decisively influences the volume of the surfactant-rich phase where the PAHs are solubilized. This trend is confirmed when analyzing the water content in Tergitol-rich phase (Table 6).

The last issue dealing with this research work is to determine the extraction capacity of K_3PO_4 in a Tergitol 15-S9 aqueous solution polluted with PHE, PYR, BZA at room temperature, taking into account that PAHs are preferentially dissolved in the surfactant-rich phase.

The extraction percentages obtained for each of the studied cases are shown in Fig. 3, showing the following extraction percentage: 75% of BZA, 72% of PHE and 60.5% of PYR. It is essential to note that the concentrations of pollutants from which the solutions were based is 3600 ppm for PHE and 2500 ppm for PYR and BZA and after the addition of K_3PO_4 it is possible to concentrate in the organic phase contaminants up to a concentration of 31.1 ppm for PHE, 22.3 ppm for BZA and 17.3 ppm for PYR. Thus, the proposed surfactant tends to form micelles above the CMC, creating an ecofriendly environment for solvation of these hydrophobic pollutants. As the selected surfactants do not ionize in aqueous solutions, their main mechanism of action is chemically based on the formation of intermolecular hydrogen bonds, which eases micelle formation due to the agglomeration of the hydrophobic moiety, thus lowering the CMC regarding ionic surfactants. This is the reason why this kind of surfactants outperforms for the remediation of PAH-polluted soils, as already demonstrated [35]. In this particular case, the promising results could be attributed to the greater affinity to the Tergitol 15-S9 phase for the PAHs with high hydrophobicity, so it could be the criteria for choosing a segregation platform for scaling-up. This pretreatment is planned as the first stage for a combined PAHs treatment in high charge pollutant effluents. Actually, previous research work of our group [21] have demonstrated the robustness of this kind of ATPS to salt out recalcitrant pollutants like antibiotics even in complex effluents like artificial urine or swine husbandry waste water streams, which also

Table 6

Experimental tie-lines (*TL*), tie-line length (*TLL*) and slope (*S*) of the ternary mixture: Tergitol 15-S9 (1) + potassium salts (2) + H_2O (3) at 298.15 K.

Surfactant-rich phase		Salt-rich phase		Feed composition		<i>TLL</i>	<i>S</i>
$100w_1^I$	$100w_2^I$	$100w_1^{II}$	$100w_2^{II}$	$100w_1$	$100w_2$		
K_3PO_4							
52.20	1.97	0.01	20.59	16.08	14.85	55.41	-2.803
$K_2HPO_4 \cdot 3H_2O$							
51.04	2.28	0.01	15.29	15.10	11.44	52.66	-3.922

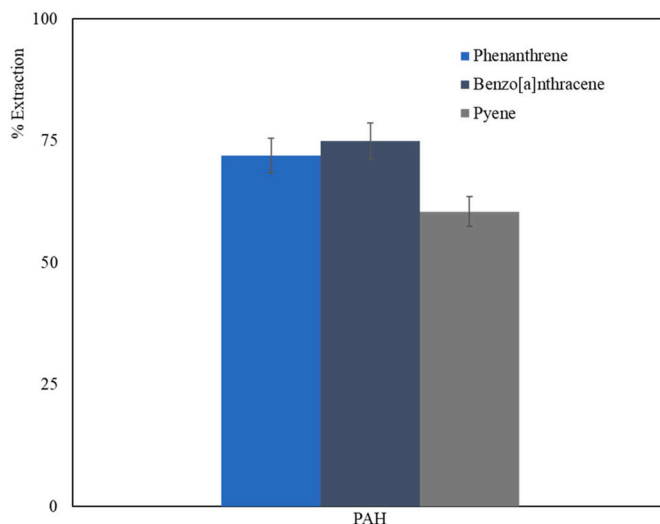


Fig. 3. Extraction percentage of PAHs from Tergitol 15-S9 aqueous solutions adding K_3PO_4 as extractant at room temperature.

proves promising potential of the present strategy.

3.4. Simulation of the process

The final stage of this work was focused on including the proposed Tergitol 15-S9-based ATPS in a washing procedure of BZA-polluted soil. Based on the data proposed in previous research works [36], a process for washing 151,000 tons of soil polluted with about 15 tons of BZA. The proposed flowsheet diagram presented in Fig. 4 is the basis for the process simulation developed by means of the software SuperPro Designer v.8.5. This tool is one of the preferred options to investigate the viability of scaling-up this kind of environmental processes, and it allows optimizing raw materials consumption and process time in a simple and efficient manner. In this sense, this tool is appropriate to comprehensively visualize the scheduling and execution of this remediation process without expending time in costly laboratory experiments.

Therefore, the simulation of this process was carried and the process was optimized to attain a plant able to treat the abovementioned amount of polluted soil (151,000 tons containing 15,000 Kg BZA p.a. (1%)). The mass flow compositions per batch can be visualized in Table 7, observing that 3 tanks for storing aqueous surfactant solution ($80 m^3$) one silo for storing BZA-polluted soil ($30,000 m^3$) three washing belts (treating 11,200 Kg polluted soil/h) and a mixer ($45 m^3$)-settler extractor ($455 m^3$) allow the treatment of 67 tons of soil/batch, leading to 2261 batches per year, which involves the treatment of about 152,000 tons of BZA-polluted soil. The operation in the mixer-settler extractor was carried out at the tie-line compositions demonstrated to be suitable at laboratory scale. In summary, the present simulation data demonstrates the suitability of the proposed ATPS-based strategy to be included in current soil-washing remediation processes for concentrating PAH pollutants present in aqueous solutions, which is indispensable prior to approach the economic evaluation of the whole remediation process.

4. Conclusions

In this study, novel ATPS containing potassium inorganic salts (K_3PO_4 , $K_2HPO_4 \cdot 3H_2O$, K_2CO_3 , K_2SO_3 , $K_2S_2O_3$) and Tergitol 15S surfactants at room temperature were characterized by determining both the solubility data and tie-lines. Once the experimental values were correlated with well-known empirical models, the extraction of three model PAHs was approached with the most efficient segregation agent (K_3PO_4) and Tergitol 15S9, obtaining very high remediation levels for all of them (75% of BZA, 72% of PHE and 60.5% of PYR). Finally, the

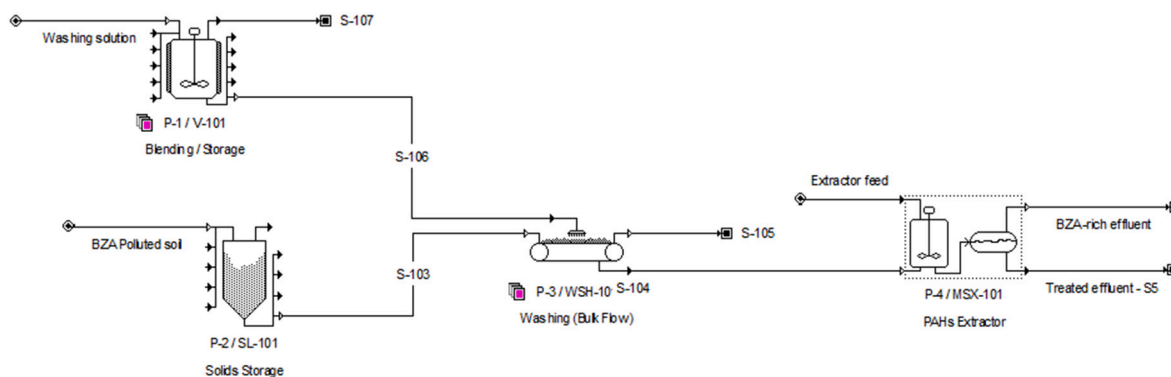


Fig. 4. Flowsheet diagram of the washing procedure of BZA-polluted soil with Tergitol 15-S9-based

Table 7

Composition of the main streams in a sequential treatment of a BZA-polluted soil (67,000 Kg/batch).

Components	Washing solution Kg/batch	S-104 Kg/ batch	Extractor feed Kg/batch	Treated effluent Kg/batch
BZA	0	4.33	0	2.3
Tergitol 15-S9	10,000	10,000	36,478	2276
Water	200,000	200,000	0	159,486
K ₃ PO ₄	0	0	43,478	41,639

ATPS-based strategy was simulated in a plant for remediating about 152,000 tons of BZA-polluted soil p.a., using the robust software tool SuperPro Designer v8.5. It allowed concluding the necessity of one silo (30,000 m³), three washing belts (11,200 Kg soil/h), three tanks for surfactant storage (80 m³) and a mixer (45 m³)-settler extractor (455 m³) for treating the target amount of the polluted soil.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jwpe.2022.102796>.

Declaration of competing interest

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

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References

- Z. Huang, Y. Liu, H. Dai, D. Gui, B.X. Hu, J. Zhang, Spatial distribution and source apportionment of polycyclic aromatic hydrocarbons in typical oasis soil of North-Western China and the bacterial community response, *Environ. Res.* 204 (2022), 112401.
- A. Masih, A. Taneja, Polycyclic aromatic hydrocarbons (PAHs) concentrations and related carcinogenic potencies in soil at a semi-arid region of India, *Chemosphere* 65 (2006) 449–456.
- J. Wang, Z. Tian, Y. Huo, M. Yang, X. Zheng, Y. Zhang, Monitoring of 943 organic micropollutants in wastewater from municipal wastewater treatment plants with secondary and advanced treatment processes, *J. Environ. Sci.* 67 (2018) 309–317.
- US EPA (Environmental Protection Agency), Polycyclic Aromatic Hydrocarbons (PAHs) - EPA Fact Sheet, in: National Center for Environmental Assessment, Office of Research and Development, Washington (DC), 2008.
- M.S. Hedayati, L.Y. Li, Removal of polycyclic aromatic hydrocarbons from aqueous media using modified clinoptilolite, *J. Environ. Manag.* 273 (2020), 111113.
- A.A. Akinpelu, M.E. Ali, M.R. Johan, R. Saidur, M.A. Qurban, T.A. Saleh, Polycyclic aromatic hydrocarbons extraction and removal from wastewater by carbon nanotubes: a review of the current technologies, challenges and prospects, *Process Saf. Environ. Protect.* 122 (2019) 68–82.
- G.K. Gaurav, T. Mehmood, M. Kumar, L. Cheng, K. Sathishkumar, A. Kumar, D. Yadav, Review on polycyclic aromatic hydrocarbons (PAHs) migration from wastewater, *J. Contam. Hydrol.* 236 (2021), 103715.
- K. Hayakawa, F. Makino, M. Yasuma, S. Yoshida, Y. Chondo, A. Toriba, Y. Koudryashova, Polycyclic aromatic hydrocarbons in surface water of the southeastern Japan Sea, *Chem. Pharm. Bull.* 64 (2016) 625–631.
- J.N. Edokpayi, J.O. Odiyo, E.O. Popoola, A.M.T. Msagati, Determination and distribution of polycyclic aromatic hydrocarbons in rivers, sediments and wastewater effluents in Vhembe District, South Africa, *Int. J. Environ. Res. Public Health* 13 (2016) 387–398.
- United Nations Information Centre, The sustainable development goals report. <https://unstats.un.org/sdgs/files/report/2017/the-sustainable-development-goals-report2017.pdf>, 2017. (Accessed 21 February 2022).
- F. Li, J. Chen, X. Hu, F. He, E. Bean, D.C.W. Tsang, Y.S. Ok, B. Gao, Applications of carbonaceous adsorbents in the remediation of polycyclic aromatic hydrocarbon-contaminated sediments: a review, *J. Clean. Prod.* 255 (2020), 120263.
- M.S. Álvarez, F. Moscoso, A. Rodríguez, M.A. Sanromán, F.J. Deive, Hybrid sequential treatment of aromatic hydrocarbon-polluted effluents using non-ionic surfactants as solubilizers and extractants, *Bioresour. Technol.* 162 (2014) 259–265.
- C. Trellu, E. Mousset, Y. Pechaud, D. Huguenot, E.D. van Hullebusch, G. Esposito, M.A. Oturan, Removal of hydrophobic organic pollutants from soil washing/flushing solutions: a critical review, *J. Hazard. Mat.* 306 (2016) 149–174.
- M.S. Álvarez, A. Rodríguez, M.A. Sanromán, F.J. Deive, Simultaneous biotreatment of polycyclic aromatic hydrocarbons and dyes in a one-step bioreaction by an acclimated *Pseudomonas* strain, *Bioresour. Technol.* 198 (2015) 181–188.
- R. López-Vizcaíno, C. Sáez, P. Cañizares, M.A. Rodrigo, The use of a combined process of surfactant-aided soil washing and coagulation for PAH-contaminated soils treatment, *Sep. Purif. Technol.* 88 (2012) 46–51.
- Y.J. Shih, P.C. Wu, C.W. Chen, C.F. Chen, C.D. Dong, Nonionic and anionic surfactant-washing of polycyclic aromatic hydrocarbons in estuarine sediments around an industrial harbor in southern Taiwan, *Chemosphere* 256 (2020), 127044.
- V.E. Wolf-Márquez, M.A. Martínez-Trujillo, G. Aguilar Osorio, F. Patiño, M. S. Álvarez, A. Rodríguez, M.A. Sanromán, F.J. Deive, Scaling-up and ionic liquid-based extraction of pectinases from *aspergillus flavipes* cultures, *Bioresour. Technol.* 225 (2017) 326–335.
- H. Benkhedja, J.P. Canselier, C. Gourdon, B. Haddou, Phenol and benzenoid alcohols separation from aqueous stream using cloud point extraction: scaling-up of the process in a mixer-settler, *J. Water Process. Eng.* 18 (2017) 202–212.
- L. Bulgariu, D. Bulgariu, Extraction of metal ions in aqueous polyethylene glycol–inorganic salt two-phase systems in the presence of inorganic extractants: correlation between extraction behaviour and stability constants of extracted species, *J. Chromatogr. A* 1196–1197 (2008) 117–124.
- L. Bulgariu, D. Bulgariu, Selective extraction of Hg(II), Cd(II) and Zn(II) ions from aqueous media by a green chemistry procedure using aqueous two-phase systems, *Sep. Purif. Technol.* 118 (2013) 209–216.
- M.S. Álvarez, L. Gómez, R.G. Ulloa, F.J. Deive, M.A. Sanromán, A. Rodríguez, Antibiotics in swine husbandry effluents: laying the foundations for their efficient removal with biocompatible ionic liquids, *Chem. Eng. J.* 298 (2016) 10–16.
- F.J. Deive, A. Rodríguez, (Liquid + liquid) equilibrium of aqueous biphasic systems composed of 1-benzyl or 1-hexyl-3-methylimidazolium chloride ionic liquids and inorganic salts, *J. Chem. Thermodyn.* 54 (2012) 272–277.
- M.S. Álvarez, F. Moscoso, F.J. Deive, M.A. Sanromán, A. Rodríguez, On the phase behaviour of polyethoxylated sorbitan (Tween) surfactants in the presence of potassium inorganic salts, *J. Chem. Thermodyn.* 55 (2012) 151–158.
- F.A. Vicente, J. Bairos, M. Roque, J.A.P. Coutinho, S.P.M. Ventura, M.G. Freire, Use of ionic liquids as cosurfactants in mixed aqueous micellar two-phase systems to improve the simultaneous separation of immunoglobulin G and human serum

- albumin from expired human plasma, *ACS Sustain. Chem. Eng.* 7 (2019) 15102–15113.
- [25] C.N. Haidar, G. Martini, L.P. Malpiedi, B.B. Nerli, Rhamnolipids biosurfactants as potential modulators of phase and partitioning behavior in micellar systems of aliphatic alcohol ethoxylate surfactants, *J. Mol. Liq.* 309 (2020), 113125.
- [26] P.A. Albertsson, *Aqueous Polymer-Phase Systems*, John Wiley and Sons, New York, 1986.
- [27] J.C. Merchuk, B.A. Andrews, J.A. Asenjo, Aqueous two-phase systems for protein separation: studies on phase inversion, *J. Chromatogr. B* 711 (1998) 285–293.
- [28] M.S. Álvarez, F. Moscoso, A. Rodríguez, M.A. Sanromán, F.J. Deive, Triton X surfactants to form aqueous biphasic systems: experiment and correlation, *J. Chem. Thermodyn.* 54 (2012) 385–392.
- [29] Y. Marcus, Effect of ions on the structure of water: structure making and breaking, *Chem. Rev.* 109 (2009) 1346–1370.
- [30] T. Mourão, A.F.M. Cláudio, I. Boal-Palheiros, M.G. Freire, J.A.P. Coutinho, Evaluation of the impact of phosphate salts on the formation of ionic-liquid-based aqueous biphasic systems, *J. Chem. Thermodyn.* 54 (2012) 398–405.
- [31] L.I.N. Tomé, F.R. Varanda, M.G. Freire, I.M. Marrucho, J.A.P. Coutinho, Towards an understanding of the mutual solubilities of water and hydrophobic ionic liquids in the presence of salts: the anion effect, *J. Phys. Chem. B* 113 (2009) 2815–2825.
- [32] A.F.M. Cláudio, A.M. Ferreira, S. Shariari, M.G. Freire, J.A.P. Coutinho, Critical assessment of the formation of ionic-liquid-based aqueous two-phase systems in acidic media, *J. Phys. Chem. B* 115 (2011) 11145–11153.
- [33] J.L. Li, B.H. Chen, Equilibrium partition of polycyclic aromatic hydrocarbons in a cloud-point extraction process, *J. Colloid Interface Sci.* 263 (2003) 625–632.
- [34] K.C. Hung, B.H. Chena, L.E. Yu, Cloud-point extraction of selected polycyclic aromatic hydrocarbons by nonionic surfactants, *Sep. Purif. Technol.* 57 (2007) 1–10.
- [35] A.K. Rathankumar, K. Saikia, P.S. Kumar, S. Varjani, S. Kalita, N. Bharadwaj, J. George, V.K. Vaidyanathana, Surfactant-aided mycoremediation of soil contaminated with polycyclic aromatic hydrocarbon (PAHs): progress, limitation, and countermeasures, *J. Chem. Technol. Biotechnol.* 97 (2022) 391–408.
- [36] H. Heo, M. Lee, Surfactant-enhanced soil washing using tween and tergitol series surfactants for Kuwait soil heavily contaminated with crude, *J. Soil Groundw. Environ.* 20 (2015) 26–33.