

# Technologies for the treatment of contaminated soils with total petroleum hydrocarbons

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## Abstract

Soil fulfills vital functions for life on Earth and it is urgent to protect it from all sources of contamination. However, with the increase in industrial activity, environmental liabilities arising from petroleum by-products have been found. Biological, chemical, and thermal remediation techniques have been developed to remove/reduce or immobilize pollutants. Ex-situ soil washing is one of the promising ways to concentrate contaminants, allowing soil cleaning and the reuse of extracted oils. In this work, an ex-situ soil washing process using two surfactants, sodium dodecyl sulfate (SDS) and polyoxyethylene sorbitan monooleate (Tween 80), was tested in the decontamination of an artificially contaminated soil. A kinetic study of experimental parameters, such as stirring speed, liquid-solid ratio, number of washing stages, concentration, effecting soil washing was carried out. The performance of using microfoams of both surfactants was also evaluated using the same contaminated soil. The removal efficiency of total petroleum hydrocarbons (THP) was determined by gravimetry. After washing the soil, the potential for reuse of the washing solutions was also evaluated. Finally, the discharge of the washing solution was considered and activated carbon was used to ensure its safe disposal.

**Keywords:** Total petroleum hydrocarbons; soil washing; surfactants; microfoams; reuse and recycling.

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## 1. Introduction

The growth of industrial activity is motivated by population growth caused and an increase in oil exploration and extraction [1]. Thus, the number of environmental liabilities has also increased. In Europe, the main sources of contamination are related to the inappropriate use and disposal of waste (38.1%), industrial and commercial activities (34.0%), poor storage (10.7%), accidental spills (7.9%), among other sectors, such as agriculture, military, and nuclear (9.3%) [2]. According to the EEA, total petroleum hydrocarbons (TPH) contamination represents more than half of environmental liabilities, including mineral oils (23.8%), Polycyclic aromatic hydrocarbon (10.9%), monoaromatic hydrocarbons (10.2%), halogenated hydrocarbons (8.3%), and among others, and about 35% heavy metals [2]. The severity of a given soil contamination depends on several factors. First, the soil, which is predominantly made up of clay silicates, such as aluminosilicates, which are electronegative elements, and therefore, with a high capacity for cation adsorption, water retention, and some contaminants [3]. On the other hand, organic matter, consisting of humic substances resulting from secondary synthesis reactions carried out, for example, by microorganisms. These substances are composed of fulvic acids and humic acids rich in carboxylic groups that favor interactions with cationic groups [3, 4]. Humic, another fraction of organic matter, has a high hydrophobicity that favors interaction with hydrocarbons.

Depending on the texture of the soil, it may be easier to remediate if it has a high sand content that favors fluid drainage [5]. On the other hand, the high clay content increases the porosity of the soil, but with a predominance of micropores, increasing the fluid retention capacity, making the remediation process difficult [5].

### 1.1. Risk assessment

Before any remediation plan, there are a series of steps necessary to analyze the environmental liability and verify which are the risks that may jeopardize human health and the environment [6, 7].

The assessment is carried out through the regulatory authority of each country, in the case of Portugal, the APA, which collects local information, characterization of the soil, as well as its history of use, type and concentrations of contaminants present, its source of contamination, trajectory and possible receptors. In this way, the APA ranks the risk as low, medium, or high, allowing to proceed to a remediation or monitoring plan if necessary [5, 7].

### 1.2. Remediation techniques

To alleviate the problem of soil contamination, several biological, chemical, physical, and thermal techniques have been developed, both *in-situ* and *ex-situ* [5]. Biological remediation techniques include bioremediation, which involves the degradation of pollutants through microbial/enzymatic activity and

phytoremediation that is based on the natural capacities of plants to extract, filter, stabilize, degrade, and volatilize organic and inorganic pollutants from the affected land [5, 8]. These methods are suitable for soils with high levels of organic matter, such as peat soils, serving as food for living organisms. Despite the simplicity and low cost that characterize these methods, they generally do not allow very high efficiencies in soil remediation [8]. As a rule, physical-chemical methods are more intensive than biological ones and allow for better remediation efficiencies. These techniques include pump-and-treat and air sparging processes for the treatment of the saturated zone and soil vapor extraction, soil flushing, soil washing, oxidation process, containment barriers and electrokinetic separation for the unsaturated soil zone [5]. While thermal processes such as thermal desorption, pyrolysis, gasification, and incineration, involve heating the soil to different temperatures and oxygen ratios [5].

### 1.3. Soil washing

One of the methods that stands out in soil remediation is washing soil, for its versatility and capacity to remove volatile organics, semi-volatile, and non-volatile, inorganic, radioactive and heavy metal contaminants [8] [9]. This *ex-situ* technique requires a pre-treatment, with granulometric separation of the soil, separating it into a finer fraction (<2mm), which is associated with most of the contamination, and a coarser fraction, which is a cleaner fraction, may remain in place, or, if necessary, be referred to another type of less refined treatment [5, 8].

Then, the fine-grained material is washed with an aqueous solution that may contain different treatment agents such as surfactants, chelating agents, oxidizers, and even acids or bases for pH control. In the end, the soil can be returned to the site, and the contaminated washing solution proceeds to a treatment plant.

### 1.4. Surfactants

Given the extent of soil contamination caused by TPH, soil remediation has focused on the investigation of soil washing with surfactants [2, 9].

Surfactants can form three types of microemulsions, Winsor type I, II and III [10, 11]. Type I Winsor allows for the solubilization of oil in water, and forms only when surfactant concentrations are above the CMC [9, 10]. Type II Winsor is water-in-oil microemulsions, also known as inverted microemulsion that does not allow TPH solubilization, and type III Winsor which corresponds to the coexistence of 3 phases (water, surfactant, and oil) resulting from the reduction of surface tension and interfacial tension promoted by the presence of surfactant, allowing the removal of TPH by mobilization [10, 11, 12].

The choice of surfactants in soil remediation is generally made only with nonionic and/or anionic surfactants since

cationic surfactants are strongly adsorbed by clay minerals and soil organic matter [9, 13].

Furthermore, there are some characteristics that surfactants must present, such a low tendency to form precipitates, gels, or macroemulsions, fast coalescence of the surfactant with the contaminant, to reduce the remediation time [14]. On the other hand, surfactants must have a high solubilization capacity, which can be favored by low CMC values [14]. Nonionic surfactants generally have lower CMC values compared to ionic surfactants, requiring a smaller amount of surfactant to initiate micelle formation. CMC may vary depending on environmental conditions. In ionic surfactants, the CMC drops when electrolytes are present in solution, resulting in a shielding effect of the repulsive forces of the hydrophilic groups of the surfactants.

On the other hand, parameters such as toxicity and biodegradability are also considered [5, 9, 15]. Toxicity measures the adverse effects that surfactants cause in the soil while biodegradability measures the capacity of microorganisms present in the soil to degrade the applied surfactants [9, 15]. According to Cheng and Wong, Tween 80 and SDS are more than 96% biodegradable, while surfactants such as Tween 20 and SDBS are at 20% [11, 16]. Regarding toxicity, Tween 80 is slightly toxic, with an  $EC_{50}$  of 70  $mgL^{-1}$ , while SDS is quite toxic with an  $EC_{50}$  of 1.0-13.9  $mgL^{-1}$  [9, 11].

### 1.5. Foams and microfoams

In the context of soil remediation, foams can be a good alternative to the use of aqueous surfactant solutions, as the high contact area favors the mass transfer of soil contaminants to the foam, using a significantly smaller amount of surfactant, with cost reduction and less generation of effluent to be treated [5].

Foams correspond to a dispersion of gas in a liquid, in which the gas phase is surrounded by a thin film of continuous liquid and can be formed by injecting air or another gas such as  $CO_2$  or  $N_2$  into the surfactant solution [18, 19].

The most relevant characteristics of foams are stability and foaming. Stability corresponds to its ability to remain stable over time, that is, without deteriorating, while foamability is the ability to foam [9].

However, due to the high instability, transport difficulty, and high volume required, foams must be used immediately after their formation [20]. To take advantage of regular foams and avoid their inherent limitations, foams were replaced by microfoams [21].

Microfoams correspond to bubbles surrounded by multilayers of liquid, and therefore, have lower gas contents (30-60% v/v). These structures are more stable than regular foams, with the possibility of being pumped without collapsing [18].

### 1.6. Wastewater treatment

At the end of the washes, treated soil and a contaminated aqueous solution are obtained. The

treatment of the aqueous solution must be carried out with separation processes, and if necessary, followed by degradation processes [22]. In the first phase, the solution must be decanted to remove the oily fractions and some solid particles. Then, one can resort to filtration and adsorption processes with activated carbon, widely used in industry, to remove organic contaminants and dissolved heavy metals, surfactants, solvents, and organic matter that are still present, with a consequent reduction in Deficiency levels Oxygen Biochemistry (BOD) and Chemical Oxygen Demand (COD) [22, 23]. Degradation methods generally involve a biological treatment with the introduction of microorganisms capable of absorbing pollutants with the generation of a strong oxidizing species, usually the OH<sup>•</sup> radical, to degrade the pollutants [22].

## 2. Methods

### 2.1. Soil characterization

The soil was collected in a locality belonging to the municipality of Leiria (39°41'41" N 8°55'32" W). Then, the soil was sieved to remove the coarsest fraction (d>2mm). The soil sample was dried and quartered.

The soil porosity was determined through bulk density and particles. Moisture was also determined by gravimetry, weighing the soil sample before and after being kept in an oven at 105°C, until maintaining a constant weight.

The organic matter content was calculated by gravimetry, by the difference in dry mass and by the sample mass after being subjected to a maximum temperature of 700°C in the Nabertherm model P330 muffle.

### 2.2. Soil contamination

The finest fraction of the soil (<2mm) was artificially contaminated at 5% (m/m) with burnt oil supplied by the F.S. Portugal workshop. Then, the soil was mixed with the oil until it was well homogenized. Finally, the mixture was left to stand for 4 days at room temperature.

### 2.3. Surfactants

The surfactants applied in the washes were polysorbate, Tween 80, and sodium dodecyl sulfate, SDS. In table 1 the main characteristics of these two surfactants are presented.

Table 1- Characteristics of Tween 80 and SDS.

Surfactant	MW (g/mol)	$\rho$ (g/cm <sup>3</sup> )	CMC (M)	HLB	N <sup>o</sup> of aggregation
<b>Tween 80</b>	1310	1,06	9,92x10 <sup>-6</sup>	15,0	58
<b>SDS</b>	288	1,01	5,75x10 <sup>-3</sup>	51,4	84

### 2.4. Soil washing

The washing of the soil was carried out in Erlenmeyer flasks with orbital shaking in an Aralab brand Agitorb200

shaker at room temperature. Standard washing conditions were set at a Tween 80 concentration of 9.94x10<sup>-4</sup>M (100xCMC) and 5.75x10<sup>-3</sup>M SDS (0.76xCMC), a stirring speed of 150 rpm and an equal L/S at 10. Then the soil in the washing solution proceeded to decantation, with subsequent vacuum filtration followed by drying in the oven and analyzed by burning in the muffle.

### 2.5 Kinetic study

The next step is the optimization of the relevant experimental parameters such as surfactant concentration, from 9.92x10<sup>-4</sup>M (100xCMC) to 6.95x10<sup>-3</sup>M (700xCMC) for Tween 80 and from 5.75x10<sup>-3</sup>M (0.71xCMC) to 6.95x10<sup>-3</sup>M (0.86xCMC) for SDS, liquid-solid ratio at 5, 10 and 15 and stirring speed at 100, 150, and 200 rpm over time.

### 2.6 Study of regular foams and surfactant microfoams

Regular foams were formed by injecting air with a single hole or with a Hagen® brand acrylic diffuser with multiple holes, at 4 bars.

The formation of the surfactant microfoam was carried out with a high-power stirrer, T50 digital ULTRA-TURRAX® IKA, for 5 minutes at 5000rpm.

#### 2.6.1 Study of the stability of microfoams

The microfoam stability study was performed for concentrations of SDS and Tween 80 at 5.75x10<sup>-3</sup>M and 9.92x10<sup>-4</sup>M, respectively.

The stability of the microfoams was determined according to their half-life, that is, the time it takes for a given volume of aqueous surfactant solution to drain half of its initial volume of solution after being subjected to vigorous stirring.

#### 2.6.2 Determination of the volume of trapped air

The determination of the volume of air trapped in the foams formed by the air injection was carried out in a 1000 mL beaker, where the initial weight of the surfactant solution was measured. Then, the time required for foaming was measured in a volume of 500 cm<sup>3</sup>, and foaming was continued until time t, allowing the foam to escape from the beaker. By direct proportionality, the foam volume that came out was calculated, considering the foam that was contained in the beaker at the end. Through the difference of the initial and final weight of the solution, it was possible to determine the percentage of the volume of air trapped in the foam, according to equation (1).

$$V_{trapped\ air}(\%) = \left( \frac{V_{Foam\ exit} - V_{Liquid\ exit}}{V_{Foam\ exit}} \right) \times 100 \quad (1)$$

When  $V_{Foam\ exit}$  is the volume of foam that exited the beaker, and it is calculated according to equation (2) and  $V_{Liquid\ exit}$  is the volume of liquid corresponding to the foam that exited the beaker.

$$V_{Foam\ exit}(mL) = \left( \frac{500 \times t_{Final}}{t_{500}} \right) - 1000 \quad (2)$$

When  $t_{Final}$  is the time to determine the volume of foam generated,  $t_{500}$  is the time required to form a volume of 500 cm<sup>3</sup> of foam and 1000 is the volume of foam that has not come out of the beaker.

The  $V_{Liquid\ exit}$  is determined by the difference in initial and final weight of the solution.

Then, the volume of air trapped in the foam formed under the working conditions was calculated using the equation (3).

$$V_{Trapped\ air}(\%) = \left( \frac{V_{initial} - V_{final}}{V_{initial}} \right) \times 100 \quad (3)$$

When  $V_{initial}$  is the volume occupied by the microfoam after it is formed and  $V_{final}$  is the final volume, corresponding to the volume of the aqueous surfactant solution.

## 2.7. Quantification of TPH

The quantification of TPH was carried out using the gravimetric method with the aid of a muffle. For the quantification of contaminants removed after washing, the sample was kept in the oven at 105°C until it presented a constant weight. Then, the sample was placed in the desiccator until it reached room temperature and was then weighed in porcelain crucibles. The sample went to the muffle, whose conditions were submitted from room temperature to 400°C in 30 minutes, remaining at this temperature for 2 hours, then the temperature was increased to 700°C in 2 hours, remaining for 3 hours.

At the end of the chosen program, the muffle was allowed to cool down to room temperature to collect the samples for weighing.

Equations (4), (5) and (6) were used to determine the content of TPH removed in the washing.

$$\% TPH\ Removed = \frac{\% TPH_{Initial} - \% TPH_{Final}}{\% TPH_{Initial}} \times 100 \quad (4)$$

$$\% TPH_{Final} = \frac{M_{After\ kiln} - M_{After\ muffle} - M_{Organic\ matter}}{M_{After\ kiln}} \times 100 \quad (5)$$

$$M_{Organic\ matter} = \frac{M_{After\ muffle} \times \% Organic\ matter}{1 - \% Organic\ matter} \quad (6)$$

## 2.8. Kinetic models

The pseudo-first order and pseudo-second order kinetic models are the most used to analyze the mechanisms that control the adsorption processes, such as chemical reaction, diffusion, and mass transfer [17]. The pseudo-first order equation is given according to equation (7) [17].

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (7)$$

Where  $k_1$  is the pseudo-first order adsorption rate constant, independent of the concentration of

contaminants present,  $q_e$  and  $q_t$  correspond to the amounts of contaminant adsorbed by the surfactant at equilibrium and time  $t$ , respectively. By integrating equation (7) and applying the boundary conditions of  $q_t=0$ ,  $t=0$  and  $q_t=q_t$  when  $t=t$ , equation (8) is obtained.

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (8)$$

Thus, it is possible to obtain the constant  $k_1$  through the graph  $\ln(q_e - q_t) - \ln(q_e)$  as a function of  $t$ .

The pseudo-second order equation is given according to equation (9).

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (9)$$

Where  $k_2$  is the pseudo-second order adsorption rate constant dependent on the amount of contaminants adsorbed by the surfactants over time and at equilibrium. By integrating and linearizing the equation (9) the equation (10) is obtained.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

In this way, it is possible to obtain the  $q_e$  and the constant  $k_2$  through the graph  $(t/q_t)$  as a function of  $t$ .

## 2.9. Data Analysis and Optimization using STATISTICA software

An optimization of the experimental parameters through combinatorial analysis leading to the maximization of the TPH removal efficiencies using the STATISTICA for Windows version 10. Software. The different values tested for the experimental parameters were: time of the assays (1h, 2h, 5h, 16h, 24h, 36h, 48h, and 72h) stirring speed (100rpm, 150rpm, and 200rpm) and L/S ratio (5, 10 and 15) for fixed concentrations of 100xCMC for Tween 80 and 0.71xCMC for SDS. It should be noted that, at the beginning of the experiments, the data entered in the program correspond to the lines centered on a cube, instead of its vertices.

The results were obtained using an Experimental design (DOE) in central composite, non-factorial, surface designs (CCD).

It was also possible to find a relationship between the response variable ( $y$ ), that is, the TPH removal efficiency and the independent experimental variables ( $x_i$ ), time, stirring speed and L/S through a second order polynomial model given by:

$$y = b_0 + \sum_{i=1}^k b_i x_i + \sum_{i=1}^k b_{ii} x_i^2 + \sum_{1 \leq i < j}^k b_{ij} x_i x_j \quad (11)$$

Where  $k$  is the number of independent variables,  $b_0$  the intercept parameter and  $b_i$ ,  $b_{ij}$  e  $b_{ii}$  are the regression parameters for linear, quadratic and interaction effects between variables.

### 2.10. Reuse of wash solution

At the end of each wash, the contaminated aqueous solution was grouped according to the surfactant used. The treatment of these solutions went through a liquid-liquid decantation in a separating funnel. After separating the aqueous solution from the oil phase, the solution was centrifuged at 3000G for 10 minutes by the Sigma Centrifuge 4-16S.

The solution was reused in washes with and without surfactant replacement to further investigate its remaining potential.

### 2.11. Treatment of disposal solution

The effluent resulting from the washing processes proceeded to a batch washing with Arkema's Acticarbon® 830WLP Chemical Powders granular activated carbon. The treatment of the washing fluid with activated carbon was carried out under orbital stirring at 200 rpm and a liquid-solid ratio of 10 for 5 hours. At the end, a vacuum filtration was carried out, separating the treated fluid from the activated carbon. The evaluation of the efficiency of the process was carried out by measuring the COD.

## 3. Results and discussion

### 3.1. Soil classification

According to the granulometry of the soil grains, Leiria soil is classified as sandy soil, constituted by 95.5% of coarse sand, 3.9% of fine sand, 0.6% of silt and clays [24]. It also presents a porosity of 41.1% with a low content of organic matter, of 1.20%.

### 3.2. Regular foams and microfoams

The regular foam resulting from the injection of air through a single orifice formed large bubbles, with a polyhedral geometry and a very short lifespan, inherent to the associated instability, while the foam bubbles formed by the acrylic diffuser are smaller, spherical, and uniform, due to the small pores of the diffuser. The volume of air occupied in regular foams with and without acrylic diffuser for Tween 80 was 99.14% and 99.90% while for SDS it was obtained 99.19% and 99.45%, respectively. The difference in air content in the bubbles formed by the diffuser results from the greater amount of liquid needed to cover the smaller bubbles.

Regarding microfoams, a very thin foam was observed, because of the repeated breaking of the bubbles caused by vigorous stirring.

The microfoams generated by Tween 80 had a relatively short lifetime of 130 seconds and a lower air content of 45.97% compared to those formed by SDS, with 230 seconds and an air content of 54.45%, without ice bath. The low stability of Tween 80 microfoams may be associated with the non-ionic character of the surfactant, which prevents greater repulsion between the microbubbles, leading to their coalescence. On the other hand, the solubility of Tween 80 in water, at 0.123mg/mL,

is much lower than of SDS at 150mg/mL, leading to less hydration and, in turn, greater lamellar drainage [21, 25]. When placing the surfactant solutions in an ice bath, a reduction of 10°C from room temperature was observed, even with the heating caused by vigorous stirring using Turrax. The stability of both surfactants increased with the reduction of temperature, a consequence of the reduction of vibrations and shocks between the particles, and minimization of liquid evaporation, delaying the coalescence of microbubbles and their drainage. The increase in stability is associated with the increase in the half-life values of Tween 80 and SDS by 70.8% and 76.1%, respectively.

### 3.3. Washing efficiencies

For washing the soil under standard conditions, after 72 hours of washing, an TPH removal efficiency of 68.9%±2.7% and 92.2%±1.6% for Tween 80 and SDS was obtained, respectively.

The high efficiency of TPH removal with SDS at concentrations below the actual CMC of 2317.7mg/L shows that the mobilization mechanism is quite efficient for this surfactant. However, it must be considered that this CMC value is high, allowing the displacement of hydrocarbons at concentrations slightly below this, through the reduction in the interfacial tension by its monomers between the soil surface and the contaminants [26].

About Tween 80, its CMC value is low, 13.0mg/L, and therefore, at concentrations close to CMC, the number of monomers present in the solution may not be able to efficiently remove pollutants, which also shows that the mobilization and solubilization mechanisms act simultaneously at the usually used concentrations. The result was confirmed with the test performed with Tween 80, at a concentration equal to 5xCMC, at 150 rpm, L/S of 10 for 72 hours, where a removal efficiency of only 16.6%±1.4% is obtained.

When washing with milli-Q water only, there is a slight removal of organic contaminants caused by the action of mechanical mechanisms (stirring and friction between particles), since TPH is insoluble in water. In the test using milli-Q water at 200 rpm for 16 hours, there was an improvement in the removal of pollutants from 3.4%±2.1% at 100 rpm to 12.8±3.7%, which reinforces the thesis that the mechanical action is extremely important in the mechanism of mobilization of TPH, especially when they are found in large concentrations.

The results obtained using the two surfactants, under standard conditions, show that both present relatively slow removal kinetics, of about 36 hours to reach the stationary level, even working in sandy soil with low organic matter content, which indicated a less time-consuming wash.

According to Figure 1, it can be seen that when using the same concentration of  $6.95 \times 10^{-3} \text{M}$ , the removal efficiencies with the SDS solution occur with faster kinetics, between 2 and 5 hours, while with the solution

of Tween 80 there is an increase of more than 20% at the end of 72 hours of washing to the standard concentration, with a greater discrepancy in the value obtained after 16 hours of washing, with a difference of 2.4%.

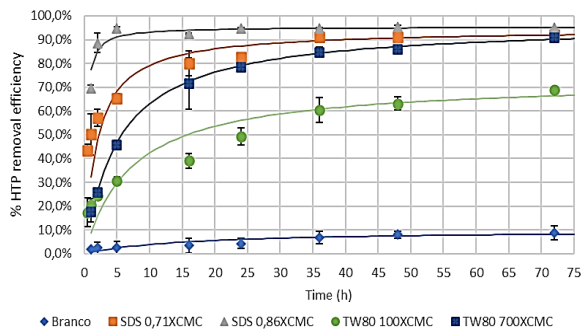


Figure 1 - Efficiencies of TPH removal with washing solutions of Tween 80 and SDS at different concentrations as a function of time.

The difference in the efficiencies reached by the two surfactants is related to the different behavior they have in solution. On the other hand, anionic surfactants, by negatively charging oil droplets, attract water molecules and positively charged counter-ions from the aqueous solution around them (forming an electrical double layer) and repel the negatively charged particles from the soil, which are little adsorbed by them. In the case of non-ionic surfactants, such as Tween 80, this repulsion effect does not occur, being more easily adsorbed by the soil particles, and, therefore, a greater amount of surfactant will be needed to remove the TPH.

The fitting of experimental data to the pseudo-second-order kinetic method is presented in Figure 1 as it was the model that presented the best fit, according to Table 2.

Table 2- Pseudo-first order and pseudo-second-order equation parameters for experimental results at different concentrations of SDS and Tween 80.

Parameters		SDS	SDS	TW80	TW80
		0,71xCMC	0,86xCMC	100xCMC	700xCMC
Pseudo-first order	$k_1$ ( $h^{-1}$ )	0,107	0,205	0,055	0,071
	$R^2$	0,948	0,741	0,975	0,972
Pseudo-second order	$q_e$	0,943	0,954	0,730	0,968
	$k_2$ ( $g \cdot g^{-1} \cdot h^{-1}$ )	0,552	4,486	0,189	0,193
	$R^2$	0,99880	0,99995	0,97720	0,99960

When comparing the  $R^2$  of the fittings of the data to pseudo-first order and pseudo-second-order models, it can be observed that, for all experiments, the pseudo-second-order model provides a better fit, except for the blank. Through the pseudo-second-order kinetic model, it is verified that the increase in the concentration of each surfactant translates into an increase in the amount of contaminants adsorbed in equilibrium ( $q_e$ ) and the adsorption rate of the contaminant in the surfactant ( $k_2$ ).

### 3.3.1. Stirring speed

Increasing the stirring speed from 100 rpm to 200 rpm resulted in a significantly higher TPH removal efficiencies of Tween 80 than SDS. According to Figure 2, after 72 hours of washing with Tween 80 aqueous solutions at 100rpm, an efficiency of  $24.2\% \pm 2.3\%$  is obtained, while at 150rpm and 200rpm values of  $68.9\% \pm 2.7\%$  and  $95.6\% \pm 2.3\%$ , were obtained, respectively.

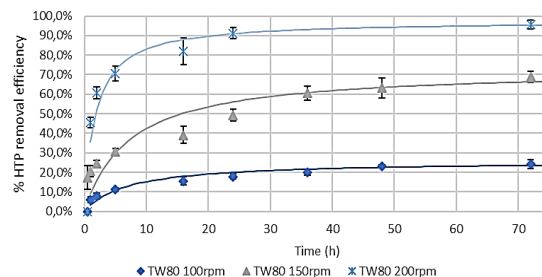


Figure 2- Efficiencies of TPH removal with Tween 80 aqueous solutions at 100, 150 and 200 rpm as a function of time. Lines correspond to the 2<sup>nd</sup> pseudo-order kinetic model.

In Figure 3, the efficiency of TPH removal obtained with SDS aqueous solutions at 100 rpm is already high. However, an increase in the stirring speed allows a greater reduction of the washing time to reach the stationary level.

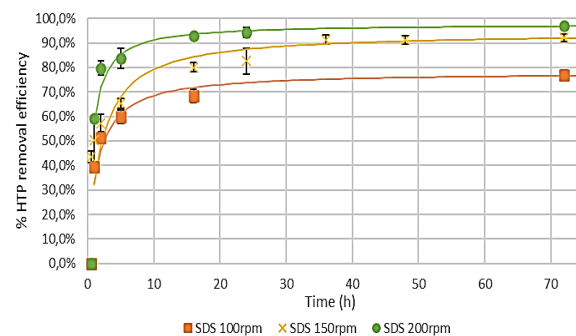


Figure 3- Efficiencies of TPH removal with SDS aqueous solutions at 100, 150 and 200 rpm as a function of time. Lines correspond to the 2<sup>nd</sup> pseudo-order kinetic model.

The fitting of the experimental data regarding the test of different stirring speeds is presented in Figures 2 and 3. The pseudo-second-order kinetic method as in Figure 1, since it was the model that best fitted, according to Table 3.

Table 3- Pseudo-first order and pseudo-second-order equation parameters for experimental results at different stirring speeds.

Parameters		TW80	SDS	TW80	SDS	TW80	SDS
		100 rpm	100 rpm	150 rpm	150 rpm	200 rpm	200 rpm
Pseudo-first order	$k_1$ ( $h^{-1}$ )	0,060	0,162	0,055	0,107	0,133	0,174
	$R^2$	0,971	0,828	0,975	0,948	0,920	0,859
Pseudo-second order	$q_e$	0,258	0,781	0,730	0,943	0,976	0,978
	$k_2$ ( $g \cdot g^{-1} \cdot h^{-1}$ )	0,553	0,917	0,189	0,552	0,584	1,407
	$R^2$	0,986	0,999	0,977	0,999	0,999	0,9999

When comparing the  $R^2$  of the fittings of the 2 models, it can be seen that the pseudo-second order model provides better fittings than pseudo-first order. For both surfactants, the increase in the stirring speed increases the amount of contaminant adsorbed in equilibrium ( $q_e$ ). However, the rate decreases when the stirring speed is increased from 100 rpm to 150 rpm, again rising to 200 rpm.

### 3.3.2. Liquid-solid ratio

The liquid-solid ratio had different results depending on if the liquid phase or the solid phase is kept. By maintaining the solid phase and changing the proportions of the aqueous solution, according to L/S 5, 10, and 15, a reduction in the efficiency of TPH removal for both surfactants was observed. These data are depicted in the Figures 4 and 5. These counter-intuitive results are justified by the deficient mixing between the two phases caused by the significant increase in the height of liquid in the container used, an Erlenmeyer flask.

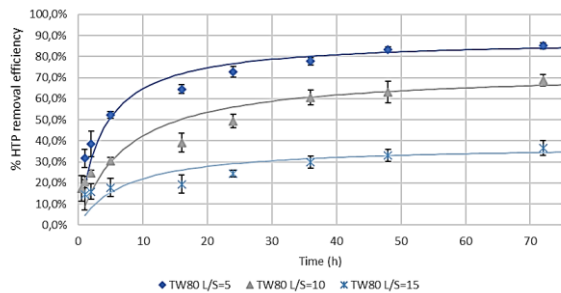


Figure 4- Efficiencies of TPH removal with Tween 80 aqueous solutions, with L/S of 5, 10 and 15, varying the amount of liquid, as a function of time.

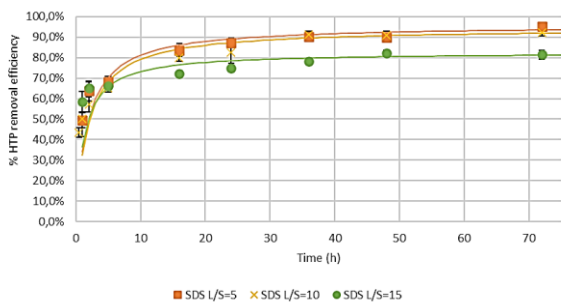


Figure 5 Efficiencies of TPH removal with SDS aqueous solutions, with L/S of 5, 10 and 15, by varying the amount of liquid, as a function of time.

If the mass of the solid phase is changed, keeping the same L/S ratios of 5, 10 and 15, an increase in the efficiency of TPH removal in washing solutions of both Tween 80 and SDS was observed. These results are shown in Figures 6 and 7. These results, although different from the previous ones, can be explained by higher contact area between the two phases, increasing the contaminant mass transfer from the aqueous solution to the solid.

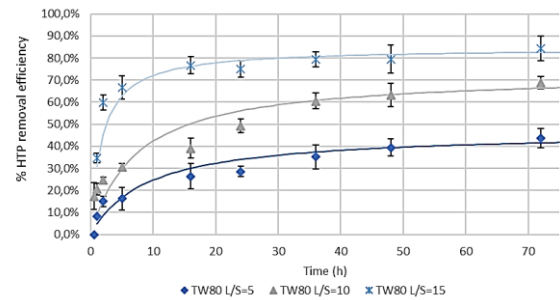


Figure 6- Efficiencies of TPH removal with Tween 80 with L/S of 5, 10 and 15, by varying the mass of solid, as a function of time. Lines correspond to the 2<sup>nd</sup> pseudo-order kinetic model.

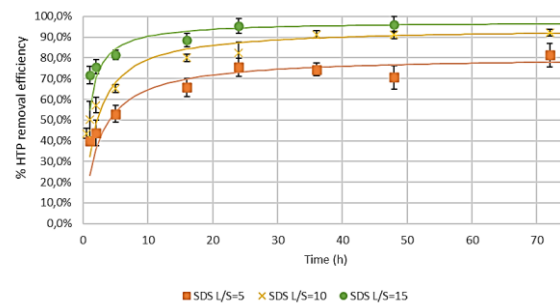


Figure 7- Efficiencies of TPH removal with SDS with L/S of 5, 10 and 15, varying the mass of solid as a function of time. Lines correspond to the 2<sup>nd</sup> pseudo-order kinetic model.

The experimental points of Figures 6 and 7 were adjusted according to the pseudo-second-order kinetic model. The values of the parameters given in both mathematical kinetic models are shown in Table 4.

Table 4- Values of pseudo-first order and pseudo-second-order equation parameters for experimental results at different liquid-solid ratios.

Parameters		TW80 L/S=5	SDS L/S=5	TW80 L/S=10	SDS L/S=10	TW80 L/S=15	SDS L/S=15
Pseudo-first order	$k_1$ ( $h^{-1}$ )	0,048	0,086	0,055	0,107	0,077	0,198
	$R^2$	0,969	0,895	0,975	0,948	0,841	0,897
Pseudo-second order	$q_e$	0,467	0,806	0,730	0,943	0,846	0,974
	$k_2$ ( $g \cdot g^{-1} \cdot h^{-1}$ )	0,241	0,503	0,189	0,552	0,683	1,328
$R^2$		0,975	0,9925	0,9772	0,9988	0,9984	0,9994

By the pseudo-second-order model is verified that in both surfactant aqueous solutions, the increase in the stirring speed increases the amount of contaminant adsorbed in equilibrium ( $q_e$ ) and the adsorption rate  $k_2$ .

### 3.3.4. Optimization of washing time

The evolution of TPH removal efficiencies for different stirring speeds and L/S ratios over time, allows to verify good results for 2-hour washes with SDS solution and 5-hour washes with Tween 80 solution, at 200 rpm and at L/S of 15. The results of these assays were  $90.7\% \pm 2.8\%$  and  $80.7\% \pm 3.2\%$ , respectively. From Figure 8, it is

possible to verify the increase in washing efficiency by combining these two parameters.

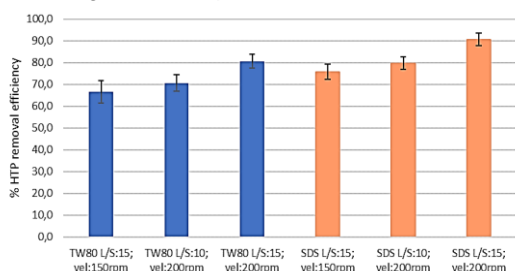


Figure 8- Efficiency of TPH removal for 5-hour Tween 80 and 2-hour SDS washes with 10 and 15 L/S combinations and stirring speeds of 150 and 200 rpm.

### 3.3.3. Optimization using STATISTICA software

Through the STATISTICA Software, it was possible to carry out a combinatorial analysis of all the parameters under study to obtain an optimization of all variables to obtain satisfactory TPH removal efficiencies. The software provides the values of the regression coefficients allowing to obtain an equation from the model. For washes with Tween 80, the percentage of TPH removal correlates with the experimental parameters through the following equation:

$$\begin{aligned} \%Remoção\ de\ HTP = & -1.04 + 6.56 \cdot 10^{-3}X_1 - 1.03 \cdot 10^{-4}X_1^2 + \\ & 4.81 \cdot 10^{-3}X_2 + 1.27 \cdot 10^{-5}X_2^2 + 6.27 \cdot 10^{-2}X_3 + 1.38 \cdot \\ & 10^{-3}X_3^2 + 3.69 \cdot 10^{-5}X_1X_2 - 6.85 \cdot 10^{-6}X_1X_3 - 3.14 \cdot \\ & 10^{-4}X_2X_3 \end{aligned} \quad (12)$$

Where  $x_1$  is the time parameter,  $x_2$  is the stirring speed and  $x_3$  is the L/S.

The model fits well the experimental data obtained in the laboratory, with  $R^2$  of 0.9556. The most relevant parameters were the stirring speed followed by the L/S ratio. The optimum point for washes with Tween 80 was reached for a wash time of 21 hours, stirring speed of 170 rpm and an L/S of 7, It should be noted that since the test values do not correspond to the extreme points represented by the model cube given by STATISTICA, the software estimated for HTP removal efficiencies greater than 100% and, therefore, it was assumed that the values optimal for the points from which the software assumes 100% efficiency.

For washes with SDS the percentage of TPH removal correlates with the experimental parameters through the following equation:

$$\begin{aligned} \%Remoção\ de\ HTP = & 2.04 \cdot 10^{-1} + 1.73 \cdot 10^{-2}X_1 - 1.40 \cdot 10^{-4}X_1^2 - \\ & 8.70 \cdot 10^{-4}X_2 + 7.04 \cdot 10^{-6}X_2^2 + 2.00 \cdot 10^{-2}X_3 - 3.48 \cdot 10^{-4}X_3^2 - \\ & 5.84 \cdot 10^{-6}X_1X_2 - 2.28 \cdot 10^{-4}X_1X_3 + 1.16 \cdot 10^{-4}X_2X_3 \end{aligned} \quad (13)$$

Again, the model provides a good description of the experimental results, with  $R^2$  of 0.9175. It was also found that the most relevant parameter was time, followed by L/S and stirring speed. The maximum of TPH removal for washes with SDS about 100% was reached for a washing time of 7 hours, stirring speed of 170 rpm and an L/S of 10.

### 3.3.3. Successive washes

The results from the washing in several stages with surfactant replacement on each one, lasting 2 hours on each stage, allow to conclude that Tween 80 aqueous solution obtained a TPH removal efficiency of  $37.8\% \pm 1.8\%$  after 2 washing stages, surpassing the efficiency of  $30.6\% \pm 1.6\%$ , obtained with 1 stage, after 5 hours, as shown in the Figure 9. With 3 stages, an efficiency of  $44.0\% \pm 4.3\%$  was obtained, similar to that obtained when only one stage for 24 hours was used,  $49.4\% \pm 3.1\%$ .

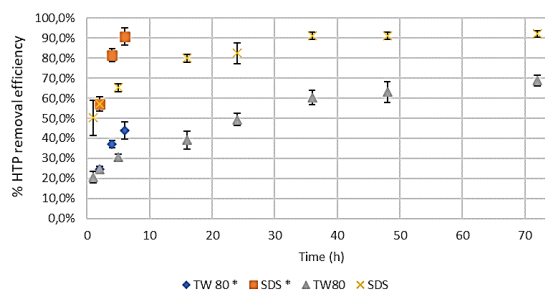


Figure 9- Efficiencies of TPH removal with Tween 80 and SDS at 150 rpm and L/S of 10 and successive washes of 2 hours each as a function of time.

In what concerns SDS, a TPH removal efficiency of  $81.6\% \pm 3.3\%$  was obtained with 2 stages washing of 2 hours each. This value is close to that obtained when using only one washing stage for 24 hours,  $82.5\% \pm 5.3\%$ , as shown in Figure 9. For a washing with 3 stages, a TPH removal efficiency of  $90.8\% \pm 4.3\%$  was obtained, a value that is close to that obtained for 72 hours of one washing stage,  $92.2\% \pm 1.6\%$ .

### 3.3.5. Microfoam washes

Washing the soil with Tween 80 microfoams did not represent a significant improvement comparing to the efficiencies achieved with the aqueous solutions of this surfactant. The values obtained for the TPH removal efficiencies of microfoams were  $15.7\% \pm 3.7\%$ ,  $22.2\% \pm 0.8\%$  and  $26.3\% \pm 2.6\%$  for 30 minutes, 1 and 2 hours of washing respectively, values that are similar with those obtained with aqueous solution of the surfactants,  $17.3\% \pm 6.0\%$ ,  $20.6\% \pm 2.7\%$  and  $24.6\% \pm 1.3\%$  for the same period of time. These results, shown in Figure 10, may be associated with the short lifespan of the microfoam.

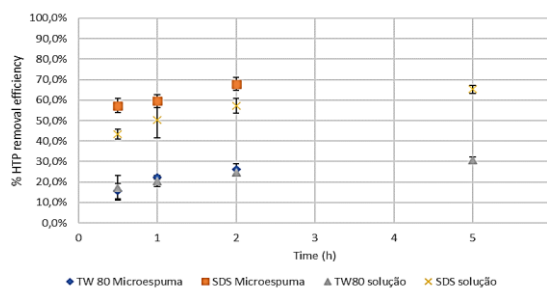


Figure 10- Efficiencies of TPH removal with aqueous solutions and Tween 80 and SDS microfoams as a function of time.



Regarding the results obtained with SDS microfoams, there is a slight increase in TPH removal efficiency. The values obtained with the aqueous solution were  $43.5\% \pm 2.5\%$ ,  $50.2\% \pm 8.7\%$  and  $57.2\% \pm 3.6\%$  in 30 minutes, 1 and 2 hours of washing respectively, while the values of  $57.3\% \pm 3.4\%$ ,  $59.6\% \pm 3.2\%$  and  $67.9\% \pm 3.2\%$  were obtained with microfoams. It is also verified that the 2-hour wash with microfoams surpasses the efficiency achieved at the end of the 5-hour wash with aqueous solution, if the microfoam stability problem is overcome.

### 3.4. Reuse of washing solutions

To impart a more sustainable character to this project, the reuse of the surfactants washing solutions was studied. Unfortunately, the reuse of the washing solution of Tween 80 shows a very weak TPH removal efficiency of  $6.1\% \pm 1.9\%$ , close to that achieved with the blank. When replacing the entire amount of surfactant in the solution, an increase in efficiency is observed to  $41.4\% \pm 3.8\%$ , a value still below the at obtained with a fresh solution, of  $49.4\% \pm 3.1\%$ . These results may indicate that most of the surfactant was lost during the first wash, probably was adsorbed by the soil and/or in decantation and centrifugation during oil separation. On the other hand, the reduction in the efficiency of the reused solution with total replacement of surfactant in relation to the fresh solution can be explained by the inhibition caused by the soluble organic matter already present in the solution.

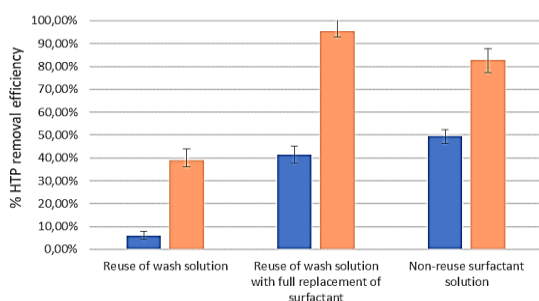


Figure 11 - Efficiencies of TPH removal by reusing the wash solution with and without full surfactant replacement and a fresh surfactant wash solution after 24 hours of

In what concerns SDS, there is still a potential to reuse the washing solution. Even with the soluble organic matter present in solution, the reuse of the washing solution allows an efficiency of  $38.8\% \pm 2.7\%$  at the end of 24 hours. When replacing all the surfactant, a TPH removal efficiency of  $95.2\% \pm 2.2\%$  is obtained, which shows an increase when compared to the fresh solution. The results also show a loss of surfactant and/or an inhibition caused by the soluble organic matter present.

### 3.5. Disposal of wash solution

After the soil washing cycles, and the removal of the TPH, the washing solutions need to be discharged in the municipal sewage system. Thus, to fulfill the legal requirements, the washing solutions were contacted with

activated carbon, and then COD values were determined. There was a reduction in COD values from  $2800\text{mg}/\text{LO}_2$  to  $22\text{mg}/\text{LO}_2$  for the washing solution containing Tween 80, while for SDS washing solution a decrease from  $3400\text{mg}/\text{LO}_2$  to  $22\text{mg}/\text{LO}_2$  was observed, allowing the flushing solutions discharge.

## 4. Conclusions

The results obtained in this work allow to conclude that soil washing using surfactants is a good strategy to remediation of soil contaminated with TPH.

According to the results obtained, it is observed that the anionic surfactant SDS is efficient in the removal of TPH by the mobilization mechanism, given that its CMC is high, of  $2317.7\text{ mg}/\text{L}$ , thus allowing that there are enough monomers in solution capable of mobilizing the organic phase. Meanwhile, the Tween 80 solution needs concentrations above the CMC, since this value is relatively low, of  $13.0\text{ mg}/\text{L}$ , being necessary enough monomers to face the amount of organic contaminants present, removing them, in this way, both by mobilization and solubilization.

The removal of contaminants from the soil to the aqueous surfactant washing solutions, under standard conditions, followed pseudo-second-order kinetics. Regarding the TPH removal kinetics using SDS aqueous washing solutions, under standard conditions (concentration:  $0.71 \times \text{CMC}$ ; stirring speed:  $150\text{ rpm}$ ; L/S: 10), it was observed that the equilibrium was achieved after 36 hours with a removal efficiency of  $91.3\% \pm 1.8\%$ , higher than that achieved with Tween 80 under the standard conditions (concentration:  $100 \times \text{CMC}$ ; stirring speed:  $150\text{ rpm}$ ; L/S:10), where the equilibrium was achieved after 48 hours, with a removal efficiency of  $63.2\% \pm 5.2\%$ .

The TPH removal efficiency was optimized using several experimental parameters, such as surfactant concentration, stirring speed, solid-liquid ratio.

The increase in the concentrations of SDS ( $0.86 \times \text{CMC}$ ) and Tween 80 ( $700 \times \text{CMC}$ ), to work in equal molar concentrations, showed a faster kinetics for SDS with stabilization after 2 hours obtaining  $88.6\% \pm 4.1\%$ , while for Tween 80 there was not such a significant improvement in kinetics, but after 16 hours an efficiency of  $71.5\% \pm 3.3\%$  was obtained.

The increase in stirring speed allowed a very significant improvement in the kinetics for the Tween 80 obtaining an efficiency of  $70.7\% \pm 3.9\%$  after 5 hours and a stabilization after 24 hours with  $91.2\% \pm 2.9\%$ .

The liquid-solid ratio had a very similar response, in kinetic terms, with the stirring speed in the SDS wash, obtaining an efficiency in the same range of values and in the same wash time. For Tween 80, the L/S had a lesser relevance than the previous parameter.

Through the prediction of results provided by the STATISTICA software, it was confirmed that the stirring speed parameter is the most relevant in obtaining better TPH removal efficiencies in Tween 80 washes, while in

SDS washes it is time. In addition, it was possible to estimate an optimal point of both washes that focused on a stirring speed, L/S, and wash times of 170 rpm, 7 and 21h for the washes with Tween 80 and 170 rpm, 10 and 7h of washing with SDS.

In another vein, microfoams of these two surfactants were also tested for the removal of TPH. It was observed that SDS microfoams were much more stable than Tween 80 microfoams, with the former reaching removal efficiencies similar to those of aqueous solutions.

The washing in several stages was also tested and it was found out that it can be more effective than one stage, saving time to reach the optimal extraction efficiency. However, the re-use of the Tween 80 washing solution was not very efficient since it was observed that most of the surfactant was lost in the first use of the washing solution.

Activated carbon was used remove the contaminants and surfactants from the washing solutions and thus to allow its discharge in of the washing solutions to sewage system.

The results obtained in this work show that the soil washing using aqueous surfactants solutions is a viable technology for the treatment of sandy soils contaminated with low volatile hydrocarbons.

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