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Treatment of Motor Oil-Contaminated Soil with Green Surfactant Using a Mobile Remediation System

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Abstract: Leak of fuels and lubricants occurring during exploration, distribution, refining and storage operations is the major cause of environmental pollution due to petroderivatives dispersion. The quick use of a series of physicochemical and biological techniques is needed to drastically reduce the magnitude of damage provoked by these pollutants. Among them, soil washing proved to be an effective alternative to the remediation of hydrocarbon-polluted sites, mainly if combined with surfactant utilization. However, the direct use of surfactants can lead to problems related to the toxicity and dispersion of the resulting by-products, as the majority of marketed surfactants are produced from oil derivatives. In this context, green surfactants appear as a promising alternative to their synthetic counterpart. In the present study, two green surfactants, i.e., a chemically synthesized biobased surfactant and a *Starmerella bombicola* biosurfactant, were applied in soil decontamination tests using a concrete mixer-type Mobile Soil Remediation System (MSRS). The system was designed and developed with 3D printing based on bench-scale results. A commercial biosurfactant was formulated based on the microbial surfactant, which was compared with the biobased surfactant in various experimental conditions. A set of factorial designs combined with Response Surface Methodology was used to select the optimal conditions for pollutant removal using the prototype. The following variables were tested: Surfactant type, Surfactant volume, Surfactant dilution, Contaminant concentration, Soil type, Soil mass, Washing duration, Tank tilt angle, Mixing speed, and Type of basket. Under the optimized experimental condition, the commercial biosurfactant allowed to remove 92.4% of the motor oil adsorbed in the sand. These results demonstrate the possibility of using natural surfactants and the development of novel mechanical technologies to degrade hydrocarbons with economic earnings for oil industry.

Keywords: green surfactants; biosurfactants; biobased surfactants; soil washing; soil remediation; petroleum; 3D printing; response surface methodology

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1. Introduction

Oil is among the most significant energy sources worldwide, whose utilization as a fuel directly contributes to world socioeconomic development [1]. For this reason, there is still a great demand on the exploration, production, refining, transport and consumption of petroderivatives [2]. Incorrect management practices, natural disasters, wars and accidents during production, storage, marketing and transport bring severe environmental problems, generating contamination of large areas of soil and consequent leaching of petroderivatives into water bodies [3].

Spills of petrochemicals cause extensive ecosystem contamination owing to their high toxicity, and are one of the primary soil pollution causes. The most harmful contaminants are organic compounds such as aromatics and isoprenoids [4]. The BTEX group of pollutants, which comprises Benzene, Ethylbenzene, Toluene, and the three Xylene isomers, are especially harmful as they are mutagenic, carcinogenic, immunotoxic, and teratogenic to all forms of life, including microorganisms [5]. Soil contamination by petrochemicals also causes significant changes in its microbiological and physicochemical properties. When contaminants are released, they occupy the spaces among the soil pores, altering their behavior [4]. These spills primarily affect soil and groundwater, causing severe and large-scale environmental impacts that are almost impossible to contain after the pollutant reaches the groundwater [6].

Soil remediation techniques are divided into physical, chemical and biological ones, which, in turn, can be applied inside (in situ) or outside (ex situ) the contaminated site [7].

Currently, most efforts for clean-up of petroderivatives spills on land and coastal regions resort to physical or mechanical methods applied in situ [8]. However, there are many disadvantages associated with these methods. For example, using high-pressure washing to remove oil can destroy microbial populations, while chemical dispersants can be harmful to the environment. Furthermore, these mechanical methods are time-consuming and are only able to remove contaminants from oil to a certain extent, leaving a large amount of adsorbed oil in the soil. Since these conventional actions are not capable of promoting efficient oil cleaning in a short period, it is important to investigate other environmentally friendly remediation methods to remove soil contaminants.

Soil washing is a type of ex situ physicochemical technique that involves several steps such as excavation, fragmentation, granulometric separation, washing of different fractions, and disposing of final residues. It is an effective technique for removing organic and inorganic compounds, metals, and radioactive substances from soil. The efficiency of soil washing can be improved by adding chemical additives such as surfactants. Surfactants not only help to remove contaminants from the soil but also enhance the solubility of oils. This allows the hydrocarbons to be dissolved and easily assimilated by microbial cells, aiding in their degradation [9].

Surfactants of synthetic origin are used as cleaning agents in many of these areas, although their use often brings toxicity problems to the local environment [1,10]. Alternatively, green surfactants can be used to restore hydrocarbon-polluted sites. Green surfactants are amphiphilic molecules either of natural origin or produced from renewable resources. They are considered safe for use and provide a sustainable alternative to traditional surfactants.

A green surfactant is produced from renewable resources by chemical reaction or using the synthetic apparatus of living organisms (plants, microorganisms, etc.). The best known green surfactants applied in the oil industry are those produced by microorganisms, known as biosurfactants [11,12]. Green surfactants are preferable to synthetic ones because they are less toxic, biodegradable, more active and resistant to extreme temperatures, pH values and salinity. They can also have less critical micelle concentrations (CMCs) compared to the synthetic counterparts, which enhances their effectiveness in several uses [1,11,12].

In this work, two green surfactants with proven removal efficiency [13] were applied to different soils under different operating conditions using a mobile soil treatment system built to enable the in situ restoration of sites contaminated by petroderivatives.

The scientific problem addressed in this study is the contamination of the environment by petroleum derivatives. An effective technique for restoring contaminated areas is washing the soil with surfactants, but direct application of synthetic surfactants can be toxic and result in chemical buildup. Therefore, this study evaluated the use of two "green" surfactants, such as a biobased surfactant and a microbial surfactant produced by a yeast, in a 3D-printed mobile prototype for soil remediation. The study proposes the hypothesis that the use of natural surfactants and new mechanical technologies can be an economical and innovative solution for the oil industry.

2. Materials and Methods

2.1. Materials

All chemical reagents were of analytical grade. Cultivation media were acquired from Difco Laboratories (Detroit, MI, USA). Motor oil was an exhausted lubricant oil with a kinematic viscosity of 15 cSt collected in a mechanical workshop for vehicle repairs in Recife, PE, Brazil.

2.2. Biobased Surfactant

A commercial biobased surfactant with surface tension of 29.70 ± 0.64 mN/m composed of fatty acid esters, a natural biopolymer and long chain alcohols (Instituto Avançado de Tecnologia e Inovação, Recife, PE, Brazil) was tested as a soil cleaning agent [13].

2.3. Production of Microbial Surfactant (Biosurfactant)

The biosurfactant was produced by *Starmerella bombicola* ATCC 22214, a yeast strain acquired by Plast Labor Ind. e Com. de Equip. Hosp. e Laboratorio Ltda (Rio de Janeiro, RJ, Brazil) from the American Type Culture Collection (ATCC). Yeast Mold Agar (YMA) medium composed of (g/L) 10 glucose, 3 yeast extract (YE), 5 peptone and 2 agar (pH 7.0) was used to maintain the strain, while Yeast Broth (YMB) composed of (g/L) 10 glucose, 3 YE and 5 peptone (pH 7.0) to cultivate it.

To prepare the inoculum, young cells were suspended in YMB (500 mL) contained in flasks and orbitally shaken (200 rpm) at 30 °C for 48 h. Dilutions were then carried out to achieve a constant biomass density of 10^6 cells/mL.

Biosurfactant production was conducted in a broth composed of 50 g/L of cottonseed oil as lipophilic ingredient, 25 g/L of glucose, 1 g/L of YE, 0.5 g/L of potassium phosphate monobasic, 0.5 g/L of magnesium sulfate heptahydrate and 0.3 g/L of sodium nitrate. After solubilization in water, constituents were subjected to sterilization at 121 °C for 20 min.

Cultivations were performed at 30 °C in 1 L of culture broth inoculated with pre-inoculum suspension (10% *v*/*v*). For this purpose, 2 L Erlenmeyers were incubated for 8 d under orbital agitation (200 rpm).

After fermentation, the biosurfactant produced was recovered using the extraction procedure reported elsewhere [14]. After washing twice, the precipitate of the fermented broth containing the biosurfactant with 1:1 (*v*/*v*) ethyl acetate in a separatory funnel, the hydrophobic phase was subjected to centrifugation at 4000 × *g* for 25 min and filtered in a filter paper (Whatman n. 1, Maidstone, UK). The filtered fraction rich in biosurfactant was dried at 40 °C to withdraw the remaining solvent and determined by weight.

2.4. Commercial Biosurfactant Formulation

Formulation of the green surfactant based on *Starmerella bombicola* ATCC 22214 biosurfactant was performed using the following constituents (% *w*/*v*): 1.0 surfactant, 0.4 hydroxyethyl cellulose as a phase stabilizer, 1.0 ethylenediaminetetraacetic acid (EDTA) as a chelator, and 0.2 potassium sorbate as a preservation agent. All constituents were mechanically stirred (Tecnal, Piracicaba, SP, Brazil) at 3000 rpm for 15 min under heating, and then the formulation was kept at rest for 24 h followed by storing in sterile hermetically sealed containers [13].

2.5. Construction of the Concrete Mixer-Type Mobile Soil Remediation System (MSRS)

In this study, the mixer was completely designed using Autodesk Inventor CAM 2017. As several experiments were carried out to establish the best working conditions able to make the removal of contaminants as effective as possible, it was necessary to consider the flexibility of the prototype. Therefore, instead of developing a customary concrete mixer with several pieces welded together, the plug-in multi-piece concept was applied. This made it possible to increase the speed of cleaning, maintenance, replacement of failed components and ease of performing multiple experiments [15,16].

The detailed construction and operation of the prototype cannot be described in detail since the system is being patented. The technique chosen to generate the prototype was 3D printing. In recent years, this technology has demonstrated its usefulness in various fields of science by providing faster, easier and more adaptable solutions, as well as the ability to build a variety of complex three-dimensional products [15]. For printing, the Sethi3D printer, model S3, was used. The MSRS is composed of the following:

- Cylindrical tank with circular opening, driven by a logic system (source, motor and rotary axis), which promote a rotational displacement of the tank around the rotor axis.
- A basket added inside the drum, with specific mesh (0.053 mm/μm).
- Addition of the components of the mixture (contaminated soil + surfactant) inside the basket. The soil is contaminated after mixing the contaminant (engine oil) with soil, in the proportion of 100 g of soil to 10 g of engine oil. This mixture is inserted through a manual shovel inside the basket.
- Addition of a specific volume of surfactant, which submerges the mixture and, due to the rotation of the tank, washes the contaminated soil.

With drum rotation, the contact surface between the components expands, thus promoting greater homogenization and possibly higher contaminant removal rate [16].

2.6. Soils Selected for Removal Tests

Removal tests were performed on soils with different consistency, that is, one sandy, one silty, one clayey soil and beach sand collected in the state of Pernambuco, Brazil in locations corresponding to the following latitude/longitude coordinates and municipalities: 7°38′249″ S 34°57′21.6″ W (municipality of Goiana), 8°23′54.7″ S 35°03′42.2″ W (municipality of Ipojuca), 8°23′53.8″ S 35°03′39.8″ W (municipality of Ipojuca), and 8°05′42.8″ S 34°52′55.3″ W (Praia do Pina, municipality of Recife), respectively.

Specimens of each soil stored in 5 kg nylon bags were subdivided into four identical cross-shaped parts, in which the top and right cross arms were repeatedly mixed with the bottom and left ones, respectively, until reaching full sample homogenizing. Afterwards, specimens were left to dry out for 4 d in the open air and were stored before use.

2.7. Conditions of Application of Surfactants and Soil Washing in the MSRS

Table 1 lists the sources of variation considered and the range of values studied for each independent variable. In addition, it informs all sources of variation (input variables) that could possibly influence the response variable (output variable), i.e., the removal percentage.

Table 1. Variables and levels initially considered in the study.

Independent Variables	Level (−1)	Level (+1)
Surfactant type	Biobased surfactant	Commercial biosurfactant
Surfactant volume (mL)	500	600
Surfactant dilution (%) *	50	100
Contaminant concentration (%)	10	20
Four soil types	Sandy and Sea Sand	Silty and Clay
Soil mass (g)	100	250
Washing duration (min)	10	20
Tank tilt angle (°)	40	60
Mixing speed (rpm)	25	50
Seven types of baskets (mm/μm)	2, 1, 0.5, 0.3, 0.25	0.212, 0.053

* Surfactant dilution (%): describes the dilution performed between the surfactant and water. The lower level (−1) corresponds to the 50% surfactant and 50% water proportion, while the higher one (+1) to 100% surfactant and 0% water.

The following sources of variation were defined in the preliminary study [13]:

- The types of surfactants were chosen based on the comparison of removal efficiency.
- The contaminant concentration values and the chosen soils. Soil contamination with engine motor oil was carried out by manually saturating 100 g of soil contained in a

beaker with 10 g of engine oil previously weighted for level −1 and 20 g of engine oil for level +1. Level −1 of soil mass (100 g) was also based on a previous study [13], while level +1 (250 g) was chosen to study the MSRS ability to remove larger quantities of soil. These levels will be explained in detail below.

- In the analysis of the mixture rotation time, two different time intervals were considered (10 and 20 min) in such a way that it was possible to identify what happens to the system in regard to homogenization.
- Rotation speed was tested at 2 different levels, 50 and 100 rpm [13], based mainly on recommended speed limits when using the Permanent Magnet Motor (Bosch CEP F 006 WM0 310) DC 24V 46W.

The following sources of variation were defined through empirical observations:

- Surfactant volumes were defined from observations made during the MSRS operation, and the volumes of 500 and 600 mL were sufficient to cover the soil inside the equipment, promoting a greater probability of washing and removal of the contaminant.
- The minimum volume for the contaminated soil to be covered by the surfactant was 500 mL. Surfactant dilution aimed to evaluate the possibility of using less product. Thus, it was decided to use the pure surfactant and the surfactant diluted with water (1:1, v/v).
- The variation in contaminant concentration aimed to evaluate the removal capacity under different contamination conditions using four types of soils (sand, beach sand, silt and clay).
- Lower energy costs and greater removal productivity are considered fundamental positive aspects both for treatment of contaminated environments and for scale-up necessary for industrial application [17].
- The range of tank inclination angle was established from preliminary experiments with the MSRS, taking into account the angles that generated a greater coverage of the soil contaminated by the surfactant.
- After consecutive MSRS tests, the basket that exhibited a good soil retention capacity, with consecutive permeability of the contaminant plus surfactant, had Mesh 0.053 mm/µm.

After the development of preliminary studies, 8 independent variables from Table 1 were maintained in Table 2.

Table 2. Variables and levels considered in the $2^{8\text{-}4}$ fractional factorial design. Decoded variables.

Independent Variables	Level (−1)	Level (+1)
Surfactant type	Biobased surfactant	Commercial biosurfactant
Surfactant volume (mL)	500	600
Surfactant dilution (%)	50	100
Contaminant concentration (%)	10	20
Soil mass (g)	100	250
Washing duration (min)	10	20
Tank tilt angle (°)	40	60
Mixing speed (rpm)	25	50

Table 2 shows the factors and levels studied through the $2^{8\text{-}4}$ fractional factorial design with IV resolutions (16 experimental runs) to obtain information on which factors were actually relevant for the analysis (statistically significant) to increase removal efficiency (%). Surfactant type, Surfactant volume (mL), Surfactant dilution (%), Contaminant concentration (%), Soil mass (g), Washing duration (min), Tank tilt angle (°) and Mixing speed (rpm) were evaluated. The type of sandy soil, the mesh size (0.053 mm/µm) and the levels of other factors were defined from preliminary experiments [13], as described above.

Table 3 lists the Aliases (confusions of the fractional factorial experiment).

Table 3. Alias structure (only order 2) considered in the 2^{8-4} fractional factorial design [a].

AB + CG + DH + EF + (. . .)
AC + BG + DF + EH + (. . .)
AD + BH + CF + EG + (. . .)
AE + BF + CH + DG + (. . .)
AF + BE + CD + GH + (. . .)
AG + BC + DE + FH + (. . .)
AH + BD + CE + FG + (. . .)

[a] Influence of independent variables on removal efficiency. Individual effects: (A) Surfactant type; (B) Surfactant volume (mL); (C) Surfactant dilution (%); (D) Contaminant concentration (%); (E) Soil mass (g); (F) Washing duration (min); (G) Tank tilt angle (°); (H) Mixing speed (rpm). Multiple letters refer to interaction effects among the independent variables.

The legend below Table 3 can be used for ease of interpretation of the meaning of each letter. Letters that appear alone refer to the individual effects of each independent variable. For example, the letter "A" alone refers to the individual (main) effect of "Surfactant type" on the "Removal efficiency" selected as the dependent (response) variable. When joined to one or more letters, the acronym refers to the interaction effect of the independent variables on the same response.

Two response variables were evaluated for each experimental run, namely the Efficiency of removal of contaminant (Engine Oil) (%) and the Electrical power (W) consumed by the engine. The experiments were randomly performed to avoid the association of atypical errors with certain combinations.

After applying the Fractional Factorial Design, significant factors were selected to evaluate ways to increase contaminant removal. Thus, a complete factorial design followed by a Central Composite Rotational Design (CCRD) was used to optimize SRMS parameters.

A 2^2 full factorial design associated with Response Surface Methodology (RSM) has been selected to study the main effects and interactions among factors or independent variables, i.e., Washing duration (min) and Soil mass (g), on the same response variables. Four runs were carried out, in addition to 4 repetitions at the central point, to obtain an estimate of the variability as a function of the experimental error and to carry out a first-order model adequacy test to experimental results [18]. Runs were carried out randomly to prevent the association of atypical errors to certain combinations. The factor levels defined from preliminary experiments are presented in Table 4.

Table 4. Independent variables and levels considered in the 2^2 full factorial design. Decoded values.

Independent Variables	Level	
	−1	**+1**
Soil mass (g)	250	350
Washing duration (min)	15	25

After evaluating the factorial experiment, a CCRD with α = 1.41421 was applied to optimize the SRMS operating parameters. Table 5 shows the levels evaluated in the experiments.

Table 5. Variables and levels considered in the CCD 2^2 factorial design. Decoded variables.

Independent Variables	Level				
	−1.414	**−1**	**0**	**+1**	**+1.414**
Soil mass (g)	229.289	250	300	350	370.711
Washing duration (min)	12.928	15	20	25	27.071

As noted by Montgomery [18], it is important that a design has a reasonable stability of the variance distribution of the predicted response values. To obtain such a distribution, Box and Hunter [19] proposed the concept of rotationality as a criterion for choosing the value of α. Central composite designs (CCDs) are considered rotational when the variances of the response predictions depend only on the distance from the central point. So, a CCD is CCRD when it is

$$\pm\,\alpha = \pm\,\sqrt[4]{2^k}\ (k = \text{number of factors}). \tag{1}$$

It is the value of α that particularizes the CCD, as it can be chosen to make the regression coefficients orthogonal, to minimize the deviation of the response surface adjusted to its true form, if it is not quadratic, or to offer the design the property to be rotational [20]. Diamond [21] stated that any value can be adopted for α and for the number of repetitions of the central point.

2.8. Soils Characterization

Physical features of soils have been described on the basis of determinations of granulometry [22], liquidity limit [23], plasticity limit [24], specific grain mass [25] and compaction [26] performed following the ABNT procedures. Table 6 shows the results of the granulometry tests, consistency limits and compaction of the soils analyzed by da Silva et al. [13].

Table 6. Granulometry, consistency, compaction and soil classification [13].

Parameter	Soil			
	Beach sand	Sandy	Silty	Clayey
Granulometry (%)				
Sand	98	56	30	26
Silt	1	5	39	30
Clay	1	39	31	44
% Liquidity–plasticity (LP) < 2 µm	0.6	37	45	53
Consistency				
Liquidity limit (%)	0	47	71	66
Plasticity index (PI) (%)	0	10	26	13
I_a [1]	0	0.29	1.0	0.59
Compaction				
Optimal moisture content (%)	6.5	34	26	22
μ_{dmax} [2] (kN/m^3)	14.7	26.5	27.6	26.8
Unified Soil Classification	SP *	SC *	MH *	CH *

[1] I_a: activity index. I_a = PI/≤2 µm activity. [2] μ_{dmax}: maximum apparent specific dry mass. * SP = poorly graded sand; SC = clay sand; MH = high-plasticity silty soil; CH = inorganic clay of high compressibility.

2.9. Quantification of the Oil Removed

The starting and final quantities of lipophilic contaminant have been quantified in both the surfactant-containing washing solution and the soil after extraction using hexane as a solvent. The solvent (10 mL) was added either to the washing solution or the washed soil in a separation funnel under stirring for ten minutes. This operation was repeated until the organic phase absorbance was reduced to the one of pure hexane. Both solvent solution and oil extract were then centrifuged at 3000 rpm for 20 min to remove eventual suspended sand/soil particles.

The motor oil removal efficiency (Y_R, %) was estimated by the equation

$$Y_R = \frac{C_0 - C_f}{C_0} \times 100, \tag{2}$$

where C_0 is the starting oil concentration in soil (%) prior to washing and C_f is the final one after washing (%).

Removal efficiency has also been gravimetrically determined, as described above, after treating the pollutant-containing washing surfactant solution with hexane.

2.10. Statistical Analysis

Different experimental design techniques were used. Analysis of variance (ANOVA), regression coefficients estimation, tables and curves were performed with Minitab® version 20.3. A confidence interval of 95% and a significance level of 5% were used. In the ANOVA tables, independent variables with p-values < 0.05 are considered statistically significant, i.e., they significantly influence the response variable [18].

3. Results and Discussion

The growing interest in innovations in the treatment of oily contaminants stems from the fact that the petroleum industry is the biggest polluter of the environment. Even though different types of treatments can be performed, technologies based on natural materials, such as green surfactants, constitute innovative and sustainable solutions with expressive potential for the remediation of sites polluted by petroderivatives [27].

3.1. Construction of the Mobile Soil Remediation System

A concrete mixer is a device that originally combines substances such as cement, gravel, sand and water to form concrete. Drum rotation allows the contact surface of mixed components to increase, thus favoring homogenization [16]. This was the case for over 50 years; however, since the 1980s, soil mixers have gradually been adopted for environmental remediation, becoming a widely accepted method in the United States for treating, stabilizing and remediating soils contaminated with a variety of pollutants [28,29].

After evaluating the prototype, some ranges of parameters were defined in order to increase washing capacity:

Surfactant volume: between 500 and 600 mL;
Soil mass: between 100 and 250 g;
Washing duration: between 10 and 20 min;
Tank tilt angle: between 40 and 60°;
Mixing speed: between: 25 and 50 rpm;
Mesh size: 0.053 mm/µm.

3.2. Application of Surfactants in Mobile Soil Remediation System

Subsequent experimental runs were carried out continuously and interdependently in order to identify the input variables and levels able to maximize the output MSRS variables, that is, to define the best way to use the equipment. Therefore, they were used in the following order.

First, a fractional factorial design was applied in order to identify, among more than 10 sources of variation, which were the significant variables, i.e., those that actually have a significant influence on the MSRS operation.

Second, a full factorial design with center points was carried out to define optimal values of the significant variables found above capable of improving the MSRS operation.

Lastly, a CCRD response surface design was used to mathematically model MSRS behavior and drive operating parameters able to optimize the use of equipment.

3.2.1. 2^{8-4} Fractional Factorial Design

The idea of adopting a fractional factorial design allowed a considerable reduction in the number of runs, thus saving experiment time and avoiding unnecessary resource and material expenses [30].

Table 7 shows that experimental runs were performed in the fractional factorial design. The sequence of runs is described in a non-random way. As shown in Table 7 and Figure 1 (surfactant + oil removed), the MSRS was effective in contaminant removal from sand. The highest removal capacity was obtained in runs 2, 3, 4, 8, 10, 11, 13, 14, 15 and 16, and experiments performed with the commercial biosurfactant showed that it was able to remove the contaminant for most of the time in all operating configurations.

Table 7. Removal efficiency and energy consumption according to the evaluated factors. Results generated from the experiments described with the variables described in Table 2.

Runs	Removal (%)	Electrical Power (Watt)
1	37.52	6300
2	73.90	10,584
3	80.20	19,032
4	55.60	18,788
5	19.83	16,836
6	8.17	22,448
7	3.27	9324
8	45.17	8316
9	9.67	19,276
10	45.89	16,836
11	60.94	7560
12	9.32	10,332
13	68.98	9324
14	67.98	8694
15	48.00	14,640
16	78.80	24,888

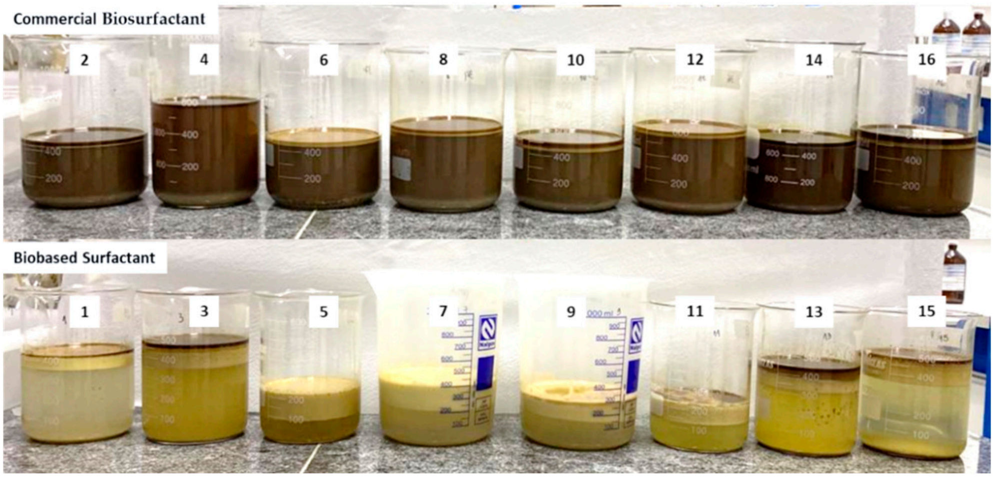

Figure 1. Images of surfactants washing solutions after the experiments of motor oil removal (liquid part: sand + removed contaminant). Numbers (1–16) correspond to experimental runs performed in $2^{8\text{-}4}$ Fractional Factorial Design.

Figure 2 shows the solid portion (sand + non-removed contaminant) recovered after the experiments. Visual inspection demonstrates that the biobased surfactant led to a higher amount of contaminant in the soil, even after washing. The apparent differences in the amount of liquid between the lower and upper part of Figure 2 occurred due to the better ability of sand to adsorb biobased surfactant compared to commercial biosurfactant.

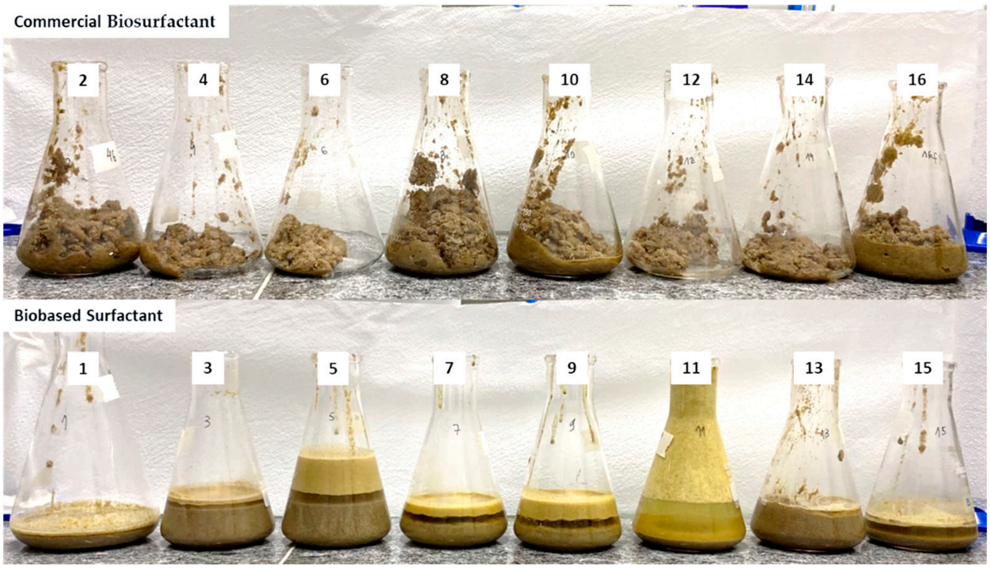

Figure 2. Images of solid portion after the experiments of motor oil removal (solid part: sand + non-removed contaminant). Numbers (1–16) correspond to experimental runs performed in $2^{8\text{-}4}$ Fractional Factorial Design.

As for the ranges of investigated factors, it is noteworthy that the commercial biosurfactant ensured a greater removal efficiency. Other researchers have already observed this type of behavior, working under similar environmental conditions [13]. The results of removal efficiency (Y_R) obtained in runs conducted according to the $2^{8\text{-}4}$ fractional factorial design (Table 6) were fitted to the following first-order model:

$$Y_R = -0.347 - 0.227\ \mathrm{ST} + 0.000617\ \mathrm{SV} - 0.00411\ \mathrm{MRT} + 0.00824\ \mathrm{CC} + 0.000669\ \mathrm{SD} + 0.001951\ \mathrm{SW} - 0.000793\ \mathrm{ST} \times \mathrm{SV} + 0.00796\ \mathrm{ST} \times \mathrm{MRT} + 0.007718\ \mathrm{ST} \times \mathrm{SD}, \quad (3)$$

where ST = Surfactant type, SV = Surfactant volume (mL), MRT = Washing duration (min), CC = Contaminant concentration (%), SD = Surfactant dilution (%), SW = Soil mass (g), while ST × SV, ST × MRT and ST × SD are significant second-order interactions among the independent variables.

According to ANOVA, the model showed a high coefficient of determination (R^2 = 0.9657), demonstrating that 96.57% of the variability in the removal efficiency was explained by the independent variables. This result is of great importance, since the backward elimination model with evaluation of Lenth's Pseudo Standard Error (PSE) was applied [31].

The Pareto diagram (Figure 3) and the marginal mean graph (Figure 4) for a confidence level of 95% (p = 0.05) confirm that, under the investigated conditions, any increase in the level of factors, i.e., Contaminant concentration (%) and Soil mass (g), had statistically significant positive individual effect on the motor oil removal, while the interaction influences between the two factors were confounded, thus requiring further evaluation to determine which of them were actually significant.

Specifically, the AF interaction was confounded with the BE, CD and GH ones (Table 3). There was little probability of statistical significance between BE and CD, since individually the factors were little or not significant. Despite the high probability of significance of both AF and GH, the latter interaction was chosen considering the great individual influence of the G factor (Soil mass). The AC interaction was confused with the BH, DF and EH ones (Table 3). There was little probability of statistical significance among AC, BH and EH, since individually the factors were not significant. In this case, we chose to consider DF because of the individual influence of the D factor (Contaminant concentration). The AB interaction was confused with the CG, DG and EF ones (Table 3). In the same way, there was little probability of statistical significance between AB and EF, since individually the factors were not significant. On the other hand, there was a high probability of significance of both CG and DG. In this case, we chose to consider GC not only in view of the large individual influence of G (Soil mass), but also because the literature findings showed that the longer the run, the higher the probability of removing contaminants [32–36].

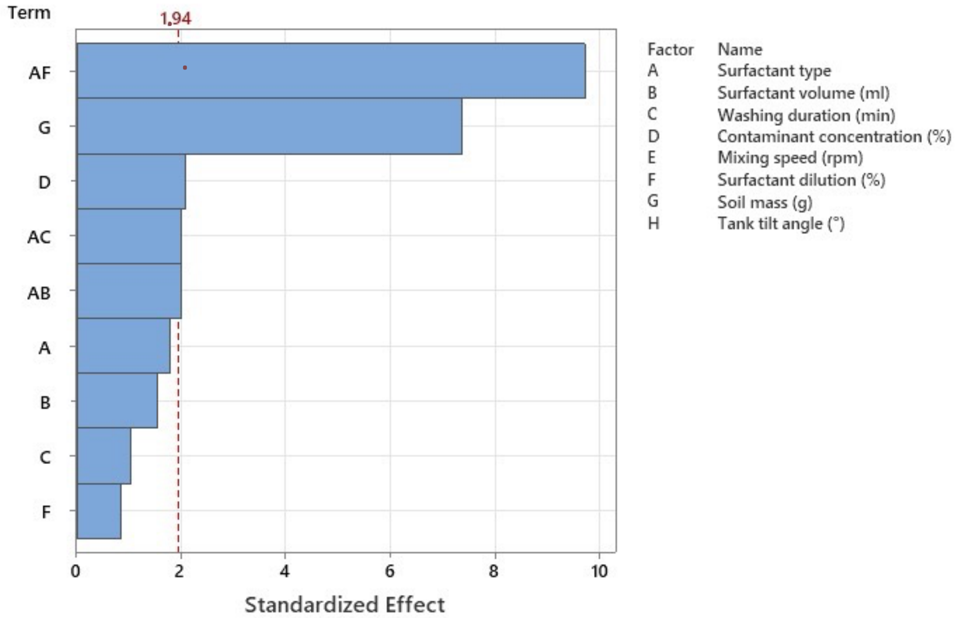

Figure 3. Pareto Chart of the standardized effects of the independent variables on the oil removal (%), α = 0.1.

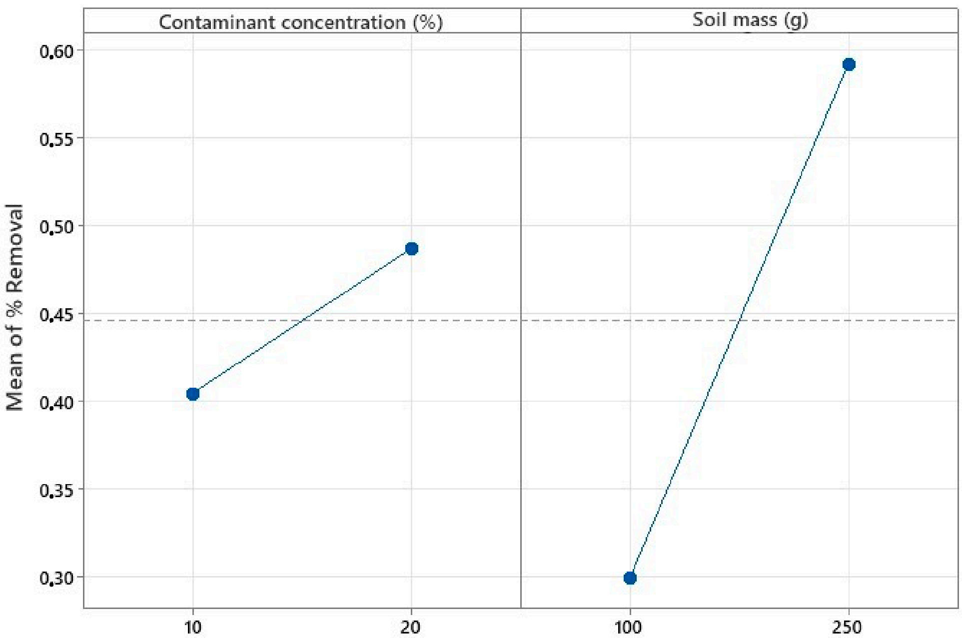

Figure 4. Main effects plot for oil removal (%) (fitted means).

Resuming, the interactions considered significant were GH (Soil mass and Tank tilt angle), DF (Contaminant concentration and Surfactant dilution), and CG (Soil mass and Washing duration).

Figure 5 illustrates the contour surface plot of the significant interaction between CG (Soil mass and Washing duration). The appearance of a dark green region is evident in the upper right corner, with the highest values of contaminant removal above 85%.

Therefore, with the aim of evaluating the SRMS performance to remove the contaminant with commercial biosurfactant, a 2^2 + 4CP (central point) full experimental design was implemented. Figure 6 shows the desirability graph, which suggests the values of levels to be adopted in order to maximize removal efficiency [37].

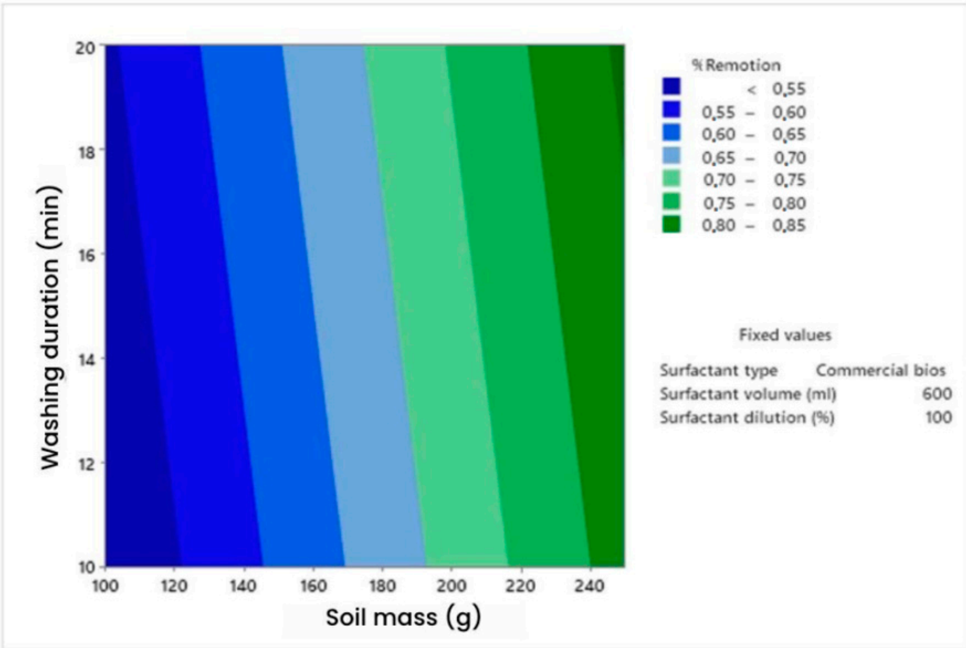

Figure 5. Contour plot of oil removal (%) vs. Soil mass (g) and Washing duration (min).

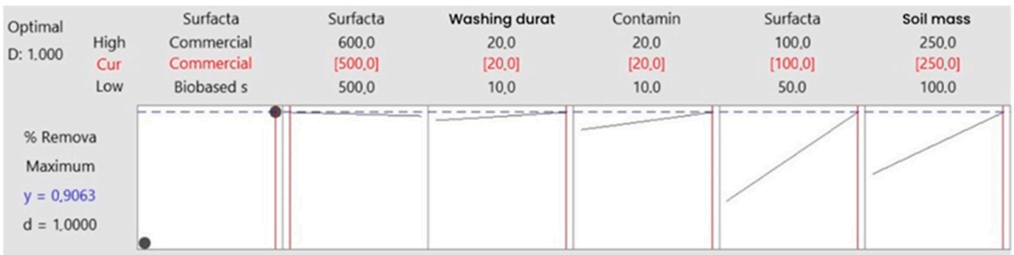

Figure 6. Multiple response prediction for optimization of oil removal (%) by the desirability function related to the 2^{8-4} fractional factorial design.

3.2.2. 2^2 Full Factorial Design

A 2^2 full factorial design combined with Response Surface Methodology was used to investigate the main effects and interactions of factors or independent variables—Washing duration (min) and Soil mass (g)—on the responses: Efficiency of Engine Oil removal (%) and Electrical power (W) consumed by the engine. All other factors and levels were kept under the best conditions described in Figure 6. Four tests were carried out, in addition to four replicates at the central point, to obtain an estimate of the variability as a function of the experimental error and to carry out a test of first-order model adequacy to the experimental data [18]. The experiments were conducted in random order to avoid the association of atypical errors to certain combinations. The factor levels were defined from the preliminary experiments.

Figure 7 shows that the interaction between Soil mass (g) and Mixture Rotation Time (min) was statistically significant for engine oil removal followed by the individual effect of Soil mass (g).

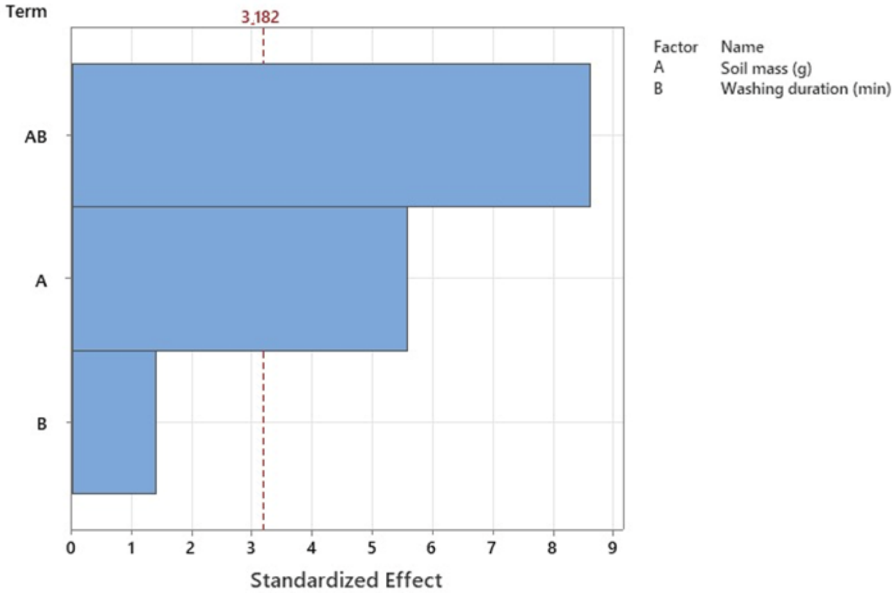

Figure 7. Pareto Chart of the standardized effects of Soil mass and Washing duration on the oil removal (%).

The effect of curvature was also significant (*p*-value = 0.001), which points to the possibility of adding quadratic terms to the regression model, indicating proximity to an optimization region, with permissiveness for the application of the response surface experiment model (CCRD). The value of coefficient of determination (R^2), which indicates the goodness-of-fit for the model, was 0.9890, that is, more than 98% of the variability of the mathematical regression model can be explained by the studied factors. Since the adjusted R^2 (R^2_{adj}) considers the number of predictors in the model, it is often used to compare models with different numbers of predictors. In this case, the value of R^2_{adj} (0.9743) indicates that 97.43% of the total variations are explained by the regression model below (in the equation bellow, CP means central point):

$$Y_R = 2.853 - 0.007915\ \mathrm{SW} - 0.0994\ \mathrm{MRT} + 0.000341\ \mathrm{SW} \times \mathrm{MRT} + 0.1778\ \mathrm{CP}. \quad (4)$$

Figure 8 shows the interaction graph between the two significant factors, i.e., Soil mass (g) and Mixture rotation time (min). In addition to the runs performed at the central point, lower levels of Soil mass (250 g) and Washing duration (15 min) showed higher values of removal efficiency (>65%).

Figure 9 shows that runs 1, 4 and the central point replicates ensured the highest removal efficiency. The top images, "Commercial Biosurfactant + Engine oil removed", visually indicate the ability to remove the contaminant (Engine oil) from soil, while the bottom ones, "Sand + Engine oil not removed", show the contaminant, which even after washing remained trapped in the soil. The two liquid phases ("Commercial Biosurfactant + Engine oil removed") can be seen in the image. The dark upper supernatant phase (engine oil) separated from the less dark lower phase (biosurfactant). Through the image, we can see that runs 1 and 4 have a higher engine oil phase than runs 2 and 3, that is, more volume of contaminant was removed by the surfactant. In the darker central point runs, there was some reaction between the components that made it difficult to see the difference between the phases. However, with a careful look, it is possible to observe a considerable volume of phase (engine oil).

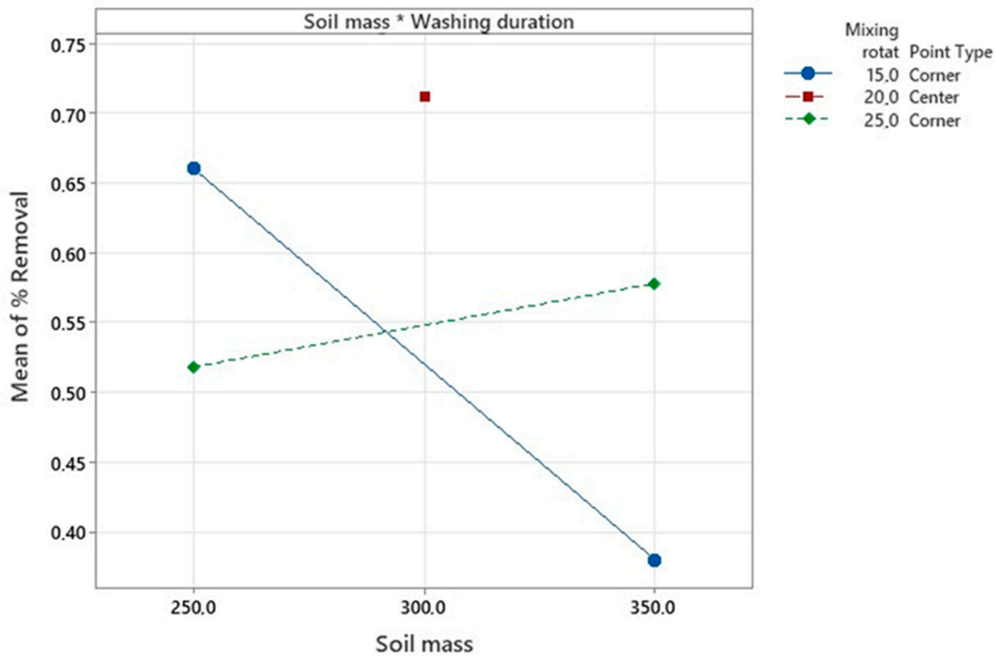

Figure 8. Interaction plot for oil removal (%) (fitted means). Soil mass * Washing duration refers to the interaction effect between these two variables.

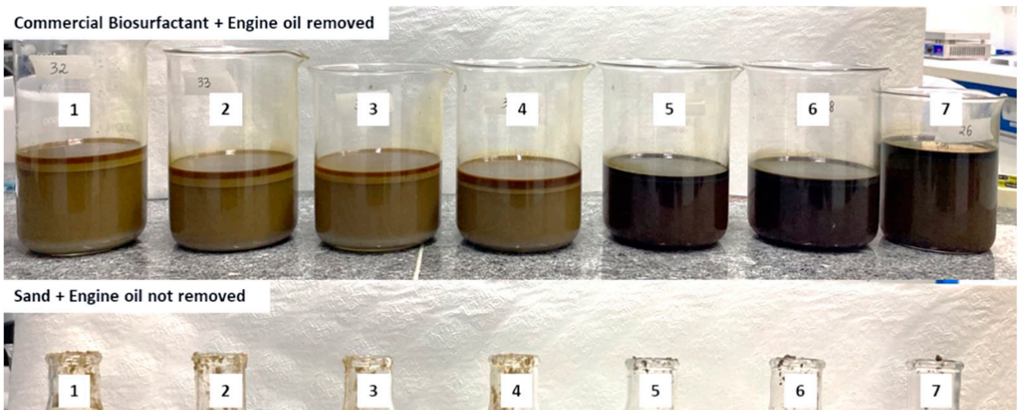

Figure 9. Images of washing solutions containing commercial surfactant (**top**) and sand (**bottom**) after contaminant removal runs carried out according to the full factorial design. Numbers (1–7) correspond to experimental runs.

3.2.3. Response Surface Methodology (RSM): Central Composite Rotational Design (CCRD)

The central composite rotational design (CCRD) is one of the most popular designs for fitting up to second order models [38]. In the present case, it included a total of 13 experimental runs, with four cube points, five central points and four axial points (α = 1.41421). The model showed a satisfactory R^2 value (0.7582), indicating that 75.82% of the variation in oil removal was explained by the following polynomial mathematical model:

$$Y_R = 0.92 - 0.00141\ SW + 0.0389\ MRT - 0.000013\ SW^2 - 0.00369\ MRT^2 + 0.000341\ SW \times MRT. \quad (5)$$

Figure 10 depicts the Normal graph of the standardized effects, which indicates the significant variables and interactions. As expected, there was the appearance of the significant quadratic influence of the Washing duration, which, together with the individual influence of the Soil mass, caused a significant change in the response variable, i.e., the higher the levels of these two sources of variation, the lower the removal rate.

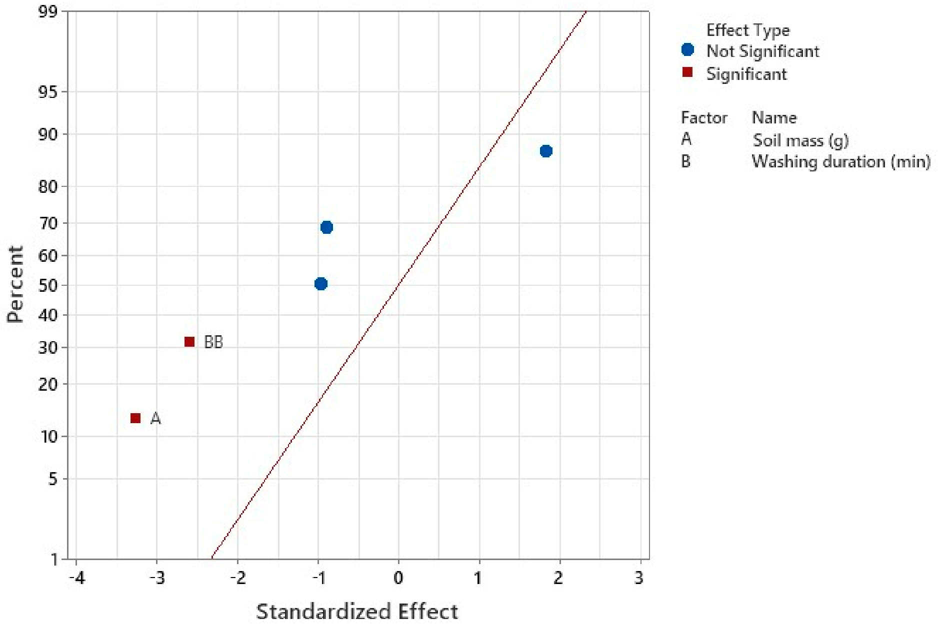

Figure 10. Normal plot of the standardized effects on oil removal (%); α (significance level) = 0.05.

The CCRD analysis considers that the residuals are commonly and independently distributed with the same variance in each treatment or factor level [39]. This assumption was checked by residual plots for oil removal (Figure 11). Since the residuals lie approximately along a straight line and no pattern, such as sequences of positive and negative residuals, is clear, it could be concluded that the residuals were normally and independently distributed.

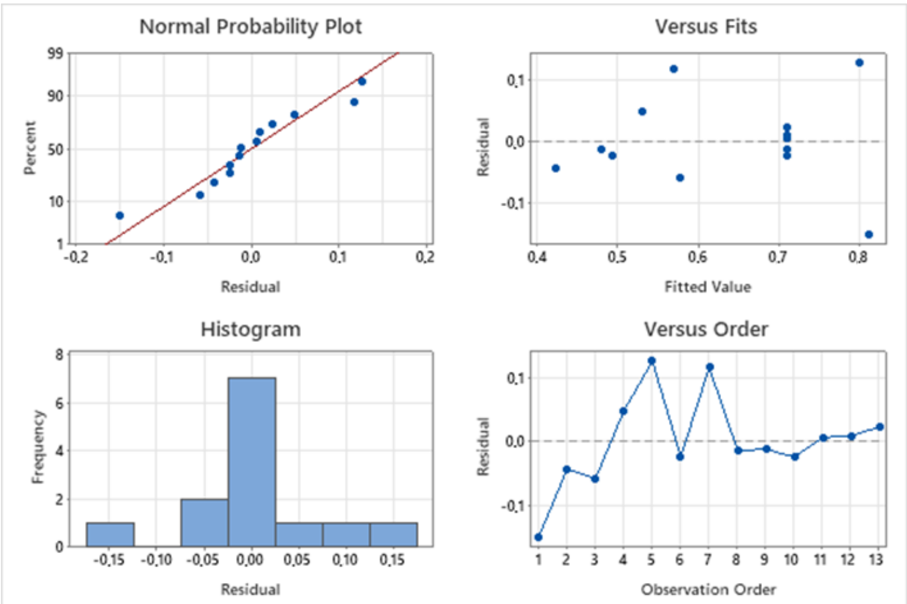

Figure 11. Residual plots for oil removal (%).

The contour surface in Figure 12 shows that there is a region where oil removal is greater than 90%.

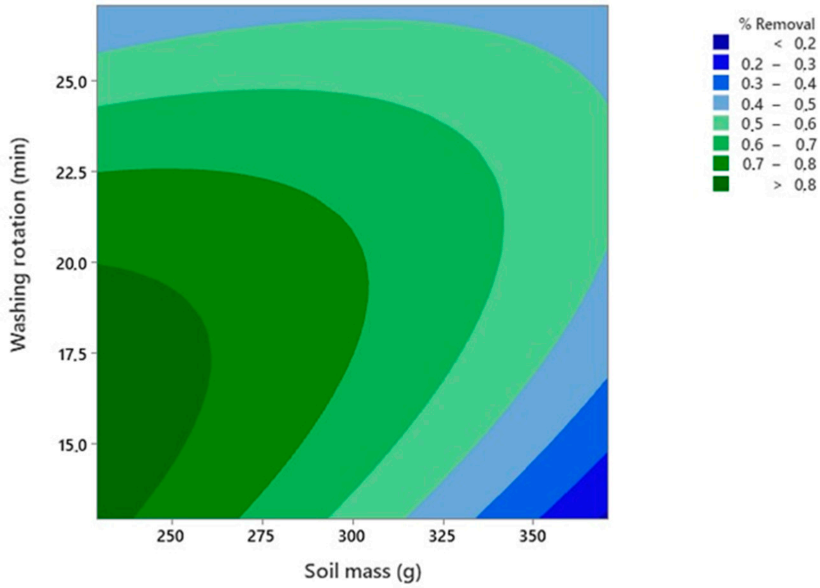

Figure 12. Contour plot of oil removal (%) vs. Washing duration (min) and Soil mass (g).

The ideal composition for contaminant removal is Soil mass between 240 and 250 g and Washing duration between 15 and 20 min. Application of the RSM reveals that the composition able to optimize the removal of the contaminant from the sandy soil is 229.28 g for 15.86 min (Figure 13). For run 5 (Soil mass of 228.289 g and Washing duration of 20 min), oil removal reached its maximum value of 92.47%. Similarly, Chaprão et al. [40] observed the highest motor oil removals from sand using *Candida sphaerica* and *Bacillus* sp. biosurfactant crude extract (93% and 43%, respectively). It can be seen in Figure 14 that the amount of contaminant remaining in the soil after washing was lower than in the other axial runs, which suggests that this contaminant was dragged by the surfactant.

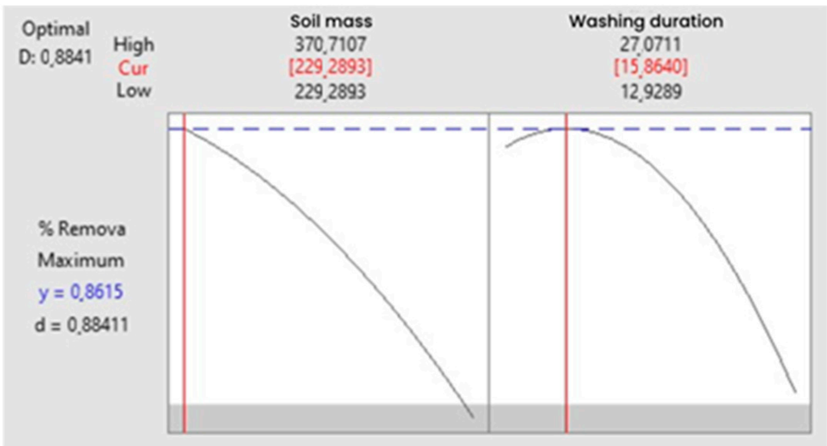

Figure 13. Multiple response prediction for optimization of oil removal (%) by the desirability function related to the Central composite rotational design (CCRD).

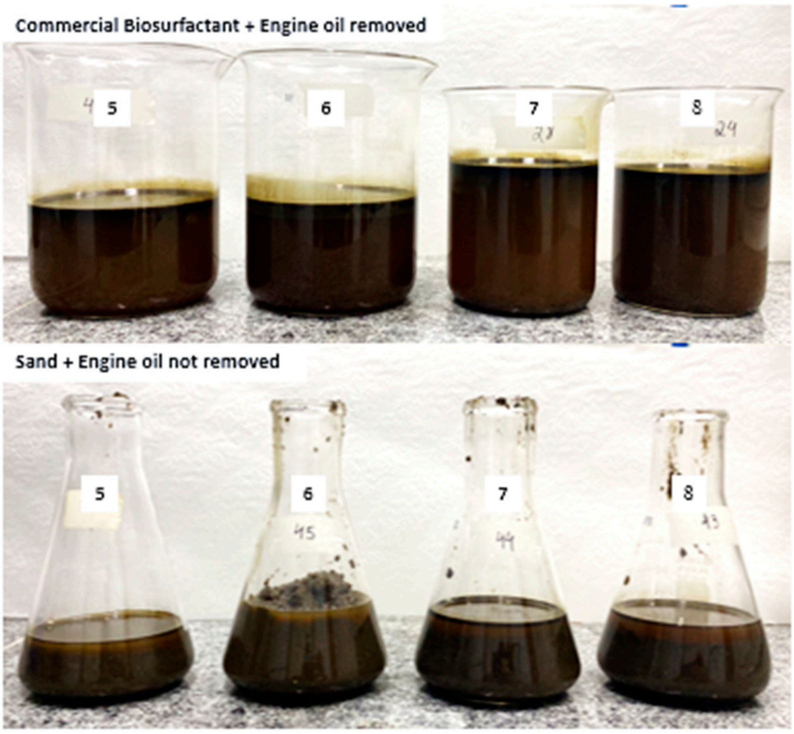

Figure 14. Images of washing solutions containing commercial surfactant (**top**) and sand (**bottom**) after axial runs of contaminant removal carried out according to the Central composite rotational design (CCRD) design. Numbers (5–8) correspond to experimental runs.

Evaluating the condition that simultaneously optimizes both response variables, minimizing energy consumption and maximizing removal efficiency, the best configuration was shown to be Soil mass of 249.28 g and Washing duration of 20.98 min (Figure 15).

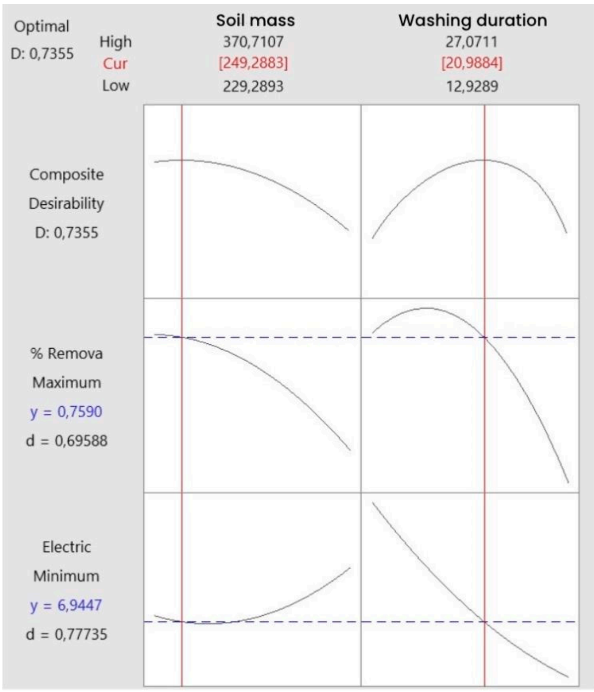

Figure 15. Multiple response prediction for simultaneous optimization of oil removal (%) and energy consumption related to the Central composite rotational design (CCRD).

3.3. Application of Surfactants in the Removal of Motor Oil Adsorbed on Soils

Surfactants act as contributors in bioremediation processes, as they can increase the mobility and availability of hydrophobic pollutants [39]. The hydrophobic moiety of the surfactant chemically binds to the hydrophobic coating of the soil particles, making it accessible through wettability, while the hydrophilic moiety attracts water molecules, allowing them to pass through the soil and increase infiltration [41].

To evaluate the MSRS operation with different kinds of soils, the experimental tests were carried out under the conditions described in Figure 6, i.e., 500 mL Surfactant volume, 100% Surfactant dilution, 20% Contaminant concentration, 250 g Soil mass, 20 min Washing duration, 60° Tank tilt angle and 50 rpm Mixing speed, and the engine oil removal efficiency was checked in four types of soils (Clay, Sandy, Silty and Sea Sand) using both the biobased surfactant and the commercial biosurfactant.

Figure 16 shows that the commercial biosurfactant obtained from *Starmerella bombicola* ATCC 22214 allowed the highest motor oil removal in the SRMS. The highest results were obtained for sand (81.3 ± 1.60%) and beach sand (65.2 ± 0.84%), likely because sandy soils have high permeability that facilitates percolation. On the other hand, tests conducted with silty and clay soils showed worse results.

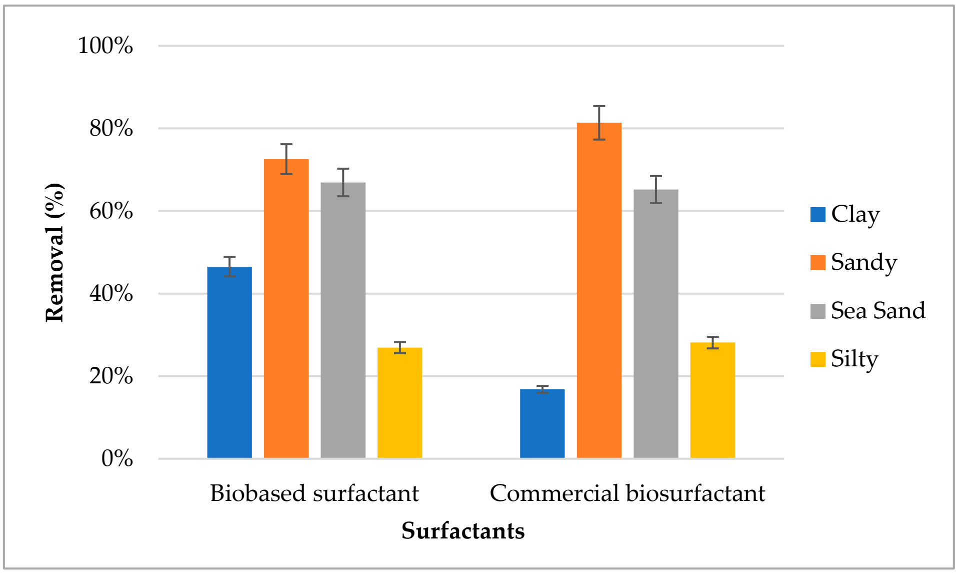

Figure 16. Removal of motor oil adsorbed to four types of soils in SRMS using both the biobased surfactant and the commercial biosurfactant.

In a general mode, the tested surfactants were not able to remove the contaminant from the clay soil due to some soil characteristics such as high liquid retention and low permeability. Nonetheless, the biobased surfactant showed a higher-than-expected yield of contaminant removal in the clayey soil (46.5 ± 1.47%). This type of soil has very small particles and interstices among them, so they retain more water [42]. This may have difficulted the complete percolation of the surfactants and, thereafter, led to the low removal of the contaminant. This result is shown in Figure 17, where it is possible to identify a small percolated volume of clay soil compared to the other soils.

On the other hand, the silty soil demonstrated a low removal yield regardless of the surfactant used (26 to 28%). Furthermore, in addition to behaving similarly to clay soil, it turned into mud due to its plasticity [43]. It is likely that the contaminant was held in this soil, which made its removal by the surfactants difficult.

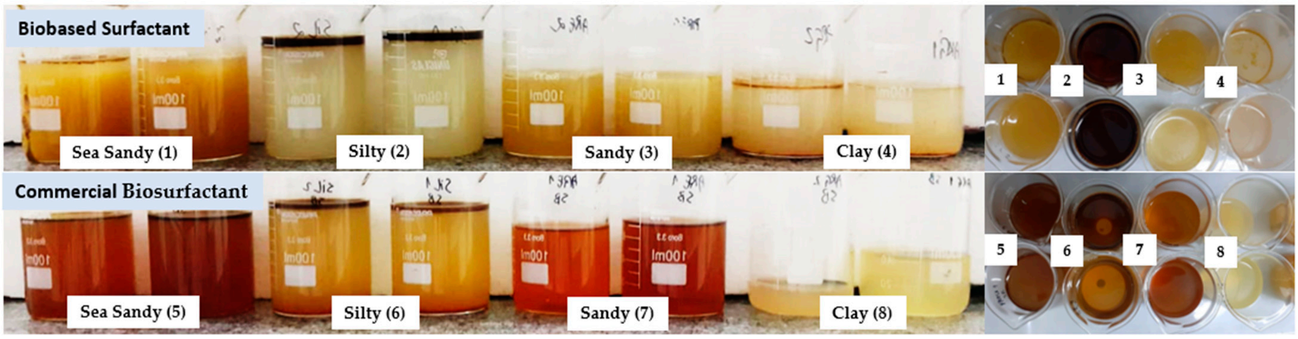

Figure 17. Images of surfactants washing solutions after contaminant removal from soils through static treatment. The removal of motor oil from the contaminated soil was carried out through the saturation of 100 g of soil with 10 g of motor oil.

As for the difference in contaminant removal evident in Figure 17, it was due to the physicochemical interactions between liquid (surfactant) and solid (soils). As already mentioned, the high retention of liquids and low permeability observed for clayey soil can be ascribed to its very small particles (micropores) and spaces among grains (pores), which make it saturated [42]. The physicochemical interaction between surfactant + soil + contaminant led to a difference in removal efficiency. On the other hand, the different colors of solutions were due to the different colors of soils, given that clay is red, silt darker and beach sand yellow, while motor oil is essentially black.

Rufino et al. [44] showed the removal of lubricating motor oil adsorbed onto three types of soils by the biosurfactant from *Candida lipolytica* UCP0988. The oil removal results obtained were 31.2 ± 0.4% in clay, 33.1 ± 0.5% in sand, and 30.0 ± 0.6% in silt. Chaprão et al. [40] reported similar removal yields using *Bacillus* sp. and *C. sphaerica*. Using the biosurfactant from *Paenibacillus* sp. D9, Jimoh and Lin [45] obtained a removal of engine oil (73%) quite higher than using sodium dodecyl sulfate as chemical surfactant (58%). The biosurfactant produced by *Pseudomonas aeruginosa* UCP0992, on the other hand, showed removal yields around 80% when crude biosurfactant (cell-free broth) was used, but less than 60% when using the isolated biosurfactant [46]. Durval et al. [47], using the biosurfactant from *Bacillus cereus* UCP1615 as a remediation agent, reported a lower removal yield (63.0 ± 2.1%) for an oil adsorbed on sand than the one obtained with the biosurfactant from *S. bombicola* ATCC 22214 (81.3 ± 1.60%), which contrasts the capability of the commercial biosurfactant in removing hydrophobic contaminants.

4. Conclusions

The tested green surfactants showed specificity for each kind of application, exhibiting promising results as agents to remove hydrophobic contaminants. The commercially formulated biosurfactant produced by *Starmerella bombicola* was more efficient in removing engine oil than the biobased surfactant. The innovation contained in this study is related to the planning, development, and optimization of the operational parameters of a new prototype applied in the removal of motor oil in four types of soils. The Mobile Soil Remediation System (MSRS) proposed in this study showed a good performance with many kinds of soils, proving to be a viable solution for application in the removal of hydrophobic contaminants from soils. Through the study of physicochemical and structural parameters, the SRMS can be optimized to work in operational regions that simultaneously maximize the contaminant removal yield and minimize the consumption of electric energy. The advantages of applying the system include carrying out remediation in loco (no expenses with transporting contaminated soil), versatility to move the equipment in areas of difficult access, treatment of contaminated material in loco and the possibility of treating large contaminated areas. However, the speed of cleaning contaminated soil and the cleaning ability of the prototype itself need to be improved. We believe that scale up will ensure the best system performance. Future studies may involve scaling up targeting industrial applications.

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Data Availability Statement: The data presented in this study are available on request from the corresponding authors. The data are not publicly available due to privacy.

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