



**Synthesis of non-ionic, cationic, and anionic surfactant from coconut oil for remediation of diesel contaminated soil**

**Síntesis de surfactante no iónico, catiónico y aniónico a partir de aceite de coco, para la remediación de suelos contaminados con diésel**

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**Abstract**

Nowadays, there is great concern about environmental pollution caused by human activity. The soil represents an ecosystem affected by oil activities. Surfactant soil washing is commonly used to remediate contaminated total petroleum hydrocarbons (TPH) soil. However, most commercial surfactants are derived from petroleum; therefore, new surfactants friendly to the environment are researched.

This work synthesized types three green surfactants from coconut oil. FTIR, and <sup>1</sup>H NMR spectroscopy indicated the proposed chemical structures. These surfactants were evaluated in the TPH remotion. The results show a more effective removal of hydrocarbons using the cationic surfactant with 99.3 %, followed by the non-ionic surfactant with 97.5 %, and the anionic surfactant, with 93.7 %.

Residual diesel in the soil was characterized and quantified using Gas Chromatography-Mass (GC-MS) and UV-Vis spectroscopy, complying with the maximum permissible limits of TPH in the soil (NOM-138-SEMARNAT/SSA1-2012). The GC results show the removal of several TPHs; however, some differ based on the type of surfactant used in the wash. Soil characterization by SEM-EDS confirmed that there was no significant particle wear. Furthermore, the cationic surfactant was not adsorbed on the soil after washing.

*Keywords:* surfactants, coconut oil, hydrocarbons, soil remediation, soil washing.

**Resumen**

En la actualidad, existe una gran preocupación por la contaminación del suelo debido a las actividades petroleras. El lavado de suelo con surfactante se usa comúnmente para remediar el suelo contaminado por hidrocarburos totales de petróleo (TPH). Sin embargo, la mayoría de los tensioactivos se derivan del petróleo; por ello, se investigan nuevos tensioactivos amigables con el medio ambiente.

En este trabajo se sintetizaron tres tipos de tensioactivos verdes a partir del aceite de coco. La espectroscopia FTIR, y <sup>1</sup>H NMR confirmó las estructuras químicas propuestas. Estos surfactantes fueron evaluados en la remoción de TPH. Los resultados muestran una mayor efectividad en la remoción de hidrocarburos utilizando el tensoactivo catiónico con un porcentaje de remoción de 98.35%, seguido del no iónico con 94% y el aniónico con 93.70%.

El diésel residual en el suelo se caracterizó mediante Cromatografía de gases-Masas (CG-MS) y espectroscopia UV-Vis, cumpliendo con los límites máximos permisible según la NOM-138-SEMARNAT/SSA1-2012. Los resultados de CG-MS muestran la eliminación de TPH conforme al tipo de surfactante utilizado en el lavado. La caracterización del suelo por SEM-EDS confirmó que no hubo desgaste significativo de partículas y que el tensioactivo catiónico no fue adsorbido en el suelo.

*Palabras clave:* surfactantes, aceite de coco, remoción, hidrocarburos, lavado de suelo.

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## 1 Introduction

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Nowadays, there is great concern about the pollution of the environment caused by human activity that threatens ecosystems and their living beings (Obida *et al.*, 2021). The global use of petroleum hydrocarbons for various applications has increased with the release of many pollutants that affect soil, surface, and groundwater (Ossai *et al.*, 2020). The petroleum products released most frequently into the environment are fuels (their production represents 80 to 83% of processed crude) (Rakowska, 2020). Oil refineries, storage tanks for crude oil and petroleum products, service stations, and industrial plants are all sources of pollution. The soil is an ecosystem that includes many toxic compounds derived from these oil activities (Mao *et al.*, 2015; Wu *et al.*, 2017). A particularly difficult pollutant is diesel, which consists of many compounds of different chemical structures and biodegradability. Also, this pollution is dangerous because some compounds can remain in the environment for a long time. Therefore, its elimination is necessary due to its toxicity and persistent harmful impact on living organisms.

Different Physico-chemical soil parameters currently assess this type of disturbance. Ecotoxicological effects are measured by biomarkers, bioindicators, or a combination of both (Brulle *et al.*, 2010), where soil organisms are helpful for quantification of the ecological impact of chemical contamination. Several studies have been reported about the effects of hydrocarbons on the composition and abundance of soil invertebrates like organisms bioindicators: nematodes, collembolans, and mites (Blakely *et al.*, 2002; Hedde *et al.*, 2012). Uribe *et al.* evaluated soil quality through the study of the collembolan invertebrates. The study area (443 hectares) is in the city of Minatitlán; it is a swamp area that works as a basin regulator of the hydrodynamics of the Coatzacoalcos River, to 30 kilometers from the mouth of the Gulf of Mexico (Uribe-Hernández *et al.*, 2010). The change caused to the structure of the collembola community found in this site can cause long-term adverse effects on the entire ecosystem.

Different hydrocarbon biodegradation technologies have been proposed for soil remediation, such as biodegradation, physical-chemical techniques, electro-remediation, soil washing, vapor extraction, solvent extraction, etc., or thermal process as pyrolysis, etc., vitrification, thermal desorption, etc.

(Martínez-Prado *et al.*, 2014). The biodegradation of contaminants can be improved using synergistic action with other techniques such as electro-remediation or biosurfactants (Martínez-Prado *et al.*, 2017; Castillo-Campos *et al.*, 2021). However, the method of petroleum biodegradation in soil depends on many factors, including the type of hydrocarbons or soil, the microbial consortium, and environmental conditions such as temperature, moisture, pH, nutrients, and oxygen (Sharma and Reddy 2004; Li *et al.*, 2019). In sites where soil conditions are unfavorable for biodegradation, such as in acid soils where organic matter is negligible, remediation with surfactant solutions is good. This technology is commonly used on contaminated sites due to its good oil removal performance, time-saving ability, and cost-effectiveness. Surfactant washing is based on the physicochemical processes between the soil particles and the washing solution. There is extensive information on soil remediation using chemical surfactants (Befkadu *et al.*, 2018; Karthick *et al.*, 2019).

On the other hand, today, there is a demand for a transition from an economy based on fossil fuels to one based on biology by the depletion of non-renewable resources. Renewable surfactants have excellent potential due to their lower environmental impact and lower consumption of fossil resources (Hou *et al.* 2014a and 2014b). They are named green surfactants, defined as biobased amphiphilic molecules obtained from nature or synthesized from renewable raw materials. This new class of biodegradable and biocompatible products responds to the increasing consumer demand for less toxic and more efficient (Benvegnu and Sassi 2010).

This work proposes the green synthesis of three types of surfactants (anionic, non-ionic, and cationic) from a natural source of raw material: coconut oil. This is an important raw material for producing plant-based surfactants in the oleochemical industry worldwide (Gervajio *et al.*, 2005). Today, in the production of biodiesel as an energy resource. However, due to the search for new sustainable products derived from natural sources, another added value is the use of coconut oil-based surfactants in soil technology. The coconut oil-based surfactants synthesized were studied in the soil technology to remove diesel from acid soils where microbiological remediation is not feasible.

## 2 Materials and methods

### 2.1 Chemicals/reagents

N, N-dimethyl-1, 3-propilendiamina (99%), diethanolamine ( $\geq 98\%$ ), methyl iodide (99.5%), Chlorosulfonic acid (99%), DL-Malic acid (99%), sodium hydroxide ( $\geq 98\%$ ), hydrogen peroxide (30%) and all the solvents (reagent grade) were purchased from Merck Company. The coconut oil was acquired from "oleofino" Corporation and the distilled water from Theisser Company.

### 2.2 Synthesis of coconut oil based biodiesel

The methyl cocoate was obtained by transesterification of the triglyceride from coconut oil. The

coconut oil was placed in three parts of methanol (w/v), then NaOH was added to catalyze the reaction (0.5 % w). The mixture was set at 70 ° C for one h 30 min, and after this time, the triglyceride was not observed by thin-layer chromatography (TLC). The TLC was performed on silica gel and used as an effluent, a combination of Heptane-AcOEt (9:1). Subsequently, the solvent was evaporated, and the product was placed in a separation funnel to separate the glycerol. The methyl cocoate was washed with a saturated NH<sub>4</sub>Cl solution to obtain pH = 7. Then, the organic phase was dried with anhydrous sodium sulfate to obtain a colorless coconut-scented liquid with a 92 % yield. This product was characterized by IR spectroscopy and Gases Chromatography. The methyl cocoate was used to prepare the surfactants, as illustrated in Figure 1.

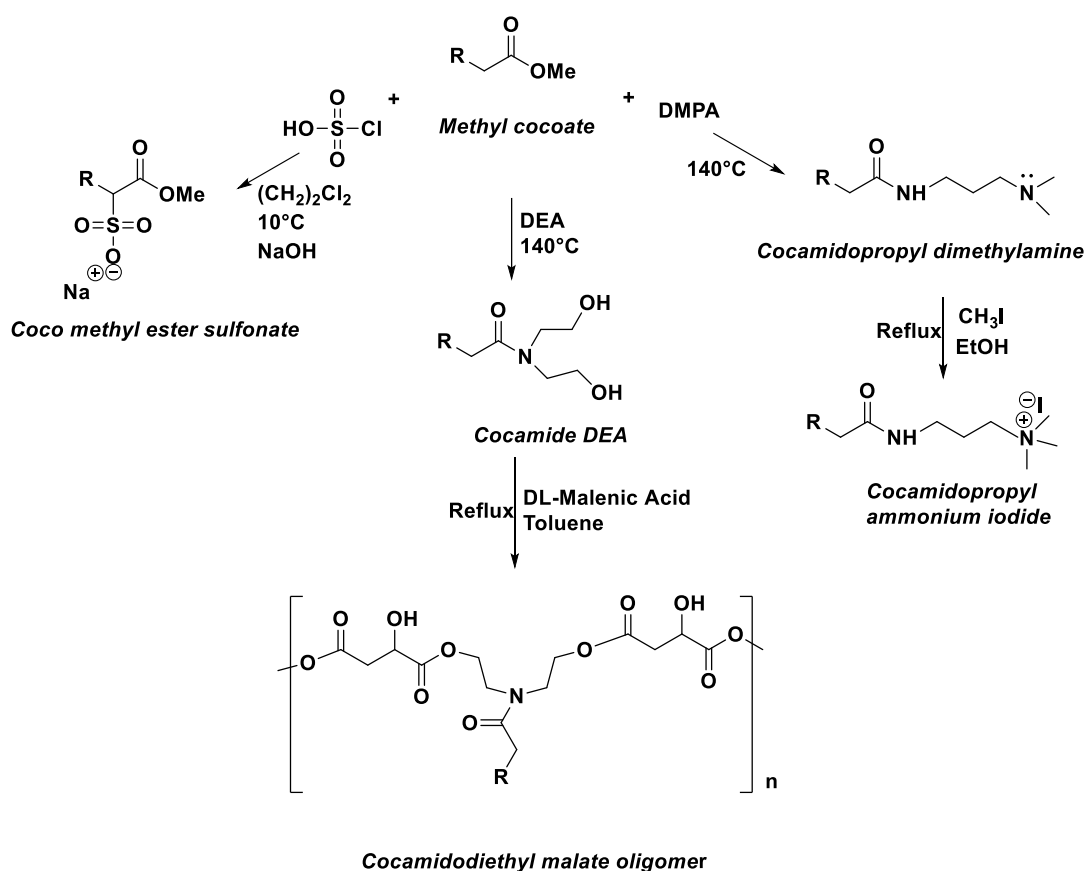


Figure 1. Synthesis of surfactants from coconut oil-based methyl cocoate. R= alkyl chains from coconut oil.

### 2.3 Coconut oil-based anionic surfactant synthesis

The anionic surfactant (coco methyl ester sulfonate) was synthesized from the sulfonation reaction to the  $\alpha$ -carbon to the carbonyl of the methyl cocoate following the method reported for the methyl ester derived from palm oil with some modification (Saxena *et al.*, 2017). Chlorosulfonic acid (2 mol) was added dropwise to coconut methyl ester (1 mol) dissolved in 2-dichloroethane (70 mL) at 10 °C. After two hours, the reaction reached room temperature, and TLC revealed the complete sulfonation. Subsequently, 50 mL of methanol was added to ensure the methylation of the methyl cocoate. Finally, the dark solution was bleached by adding a quantity of 5 mL of hydrogen peroxide at 30 % and placed at 60 °C with vigorous stirring until the whitening of the reaction was observed (3 h). Then, a 30 % NaOH solution was added dropwise to form the sulfonated sodium salt until pH = 7. Subsequently, the methanol solvent was evaporated, and the phase aqueous was separated. The organic phase was dried with anhydrous sodium sulfate to remove traces of water. The solvent was evaporated under reduced pressure on a rotary evaporator to obtain a slightly yellow liquid in an 89 % yield, which was analyzed by FTIR and H-NMR spectroscopy.

### 2.4 Coconut oil-based non-ionic surfactant synthesis

The synthesis of the non-ionic surfactant: Cocamidodiethylmalate oligomer was carried through the aminolysis of methyl cocoate (1 mol) with diethanolamine (DEA, 1.1 mol) at 140 °C following the same method previously reported for the direct aminolysis of coconut oil (Vázquez-Vélez *et al.*, 2022). TLC monitored the reaction until the complete formation of the product (2 hours). After, the cocamide DEA was dissolved in toluene (1:7, w/v) with DL-malic acid (2 mol) to carry out a condensation reaction between alcohol and carboxylic acid. The mixture was placed in a Dean-Stark system at reflux. The reaction was monitored by TLC every 15 min until the disappearance of the cocamide DEA (2 h 30 min), using as an effluent a mixture of dichloromethane-methanol (85:15). Subsequently, the solvent was evaporated under reduced pressure on a rotary evaporator to obtain a highly viscous yellow liquid in a quantitative yield, which was characterized by FTIR and H-NMR spectroscopy.

### 2.5 Coconut oil-based cationic surfactant synthesis

The cationic surfactant Cocamidopropyl ammonium iodide was synthesized through an aminolysis reaction of 1 mol methyl cocoate with 1 mol of N, N-dimethyl-1, 3-propilendiamina (DMAPA) at 140 °C for 3 hours, to give the Cocamidopropyl dimethylamine (CPAB). After, exhaustive Hoffman methylation was carried out to obtain a quaternary ammonium salt as a product. 1 mol of CPAB was solved in absolute ethanol (1:7 w/v), 2 mol of methyl iodide was added, and the mixture was placed at reflux. The reaction was monitored by TLC, using as an effluent a mixture of dichloromethane-methanol (85:15) until the complete disappearance of the CPAB (4 hours), observing only one product formed. The solvent was then evaporated under reduced pressure on a rotary evaporator to obtain a yellow liquid in quantitative yield. The reaction crude was characterized by FTIR and H-NMR spectroscopy.

### 2.6 Molecular characterization

The methyl cocoate mixture was analyzed in a Gas Chromatograph (Agilent 6890) using a flame ionization detector (FID) to know the fatty acid content in coconut oil. The mixture was separated in a capillary column (75 m  $\times$  0.18 mm, 0.14  $\mu$ m) using hydrogen as carrier gas with a flow of 1.6 ml min<sup>-1</sup>. The oven temperature was 140 °C for 5 min. and a gradient of 4 °C until reaching 240 °C for two min. The chromatogram peaks were identified with the commercial standards of methyl esters (C10-C18) according to their retention time, as reported in previous work [Vázquez-Vélez *et al.*, 2022]. All products were analyzed by FTIR Spectroscopy, using the film technique in Bruker Tensor 27 equipment. Surfactants were analyzed by visible UV spectroscopy, using water as a solvent, in Ocean View UV-vis spectrophotometer. Besides, each surfactant was analyzed by Nuclear Magnetic Resonance Spectroscopy (<sup>1</sup>H) in 300-MHz Jeol E equipment (300 MHz, D<sub>2</sub>O  $\delta$  = 4.75 ppm).

### 2.7 Soil preparation and soil contamination

The soil type and its physicochemical parameters were simulated based on the affected site characterized by Uribe-Hernández *et al.*, 2010. The total concentration of petroleum hydrocarbons (TPH), soil type, pH, cation exchange capacity (CEC), organic carbon

Table 1. Physic-chemistry parameters of contaminated soil.

	pH	OM (%)	CEC (meq/100g)	Sand (%)	Silt (%)	Clay (%)	TPH (mg/kg)
Uribe 2010	4.7-6	0.5-3	20	39	30	31	214515
<b>Here</b>	5.2	-	≥15	40	30	30	214515

(OC), and moisture content (MC) were reported and simulated in this work. Two parameters were negligible: the OC, which is minimal due to the acidic pH because it does not favor the growth of microorganisms; and the cation exchange capacity (CEC) which is a function of the type of clay in the soil (Velázquez-Vázquez *et al.*, 2022). Here, kaolin was used with a low CEC of 15 meq/100g. The soil parameters reported and simulated in this work are presented in Table 1.

The soil type was prepared as follows: the sand was sieved through an 18-mesh screen (10 %) and a 30-mesh screen (30 %). This sand mixture was washed three times, leaching all the calcium, magnesium, and potassium carbonates, obtaining pH=6. Then, the pH was adjusted with a 1N HCl solution to pH=3, and the resulting sand was dried in an oven at 85 °C for 48 h. The silt and clay were added to this mixture, neutralizing the active acidity. The Ca<sup>++</sup> ion replaces the H<sup>+</sup> ion to restore the original level of vibrant acidity to obtain a pH=5.2. Soil acidity can be related to the content of minerals present in the type of clay. However, soil acidity is also associated with aluminum and iron content (Yzquierdo-Ruiz *et al.*, 2022). The aggregate silt (200 mesh) was characterized as low-quartz (SiO<sub>2</sub> α-quartz) and the clay as triclinic kaolinite (Al<sub>2</sub>(OH)<sub>4</sub>Si<sub>2</sub>O<sub>5</sub>) by X-ray powder diffraction analysis using Brucker equipment.

The contaminated soil (5 Kg) was prepared as follows: the diesel was weighed (214515 mg/Kg) and dissolved in dichloromethane (1 L) to be added to the soil. The mixture was left for two days under a hood to evaporate the solvent. Once the diesel was adsorbed on the soil, a Soxhlet extraction was carried out every month for three consecutive months using hexane-dichloromethane in a 1:1 ratio. The hydrocarbons obtained by the Soxhlet method were characterized by UV-Vis spectroscopy using a Hitachi UV-Vis US5100 spectrophotometer.

## 2.8 Batch desorption experiments

Batch desorption experiments were performed by mixing 20 g of contaminated soil and 20 ml of

surfactant solution in a centrifuge tube (50 mL). Three anionic, cationic, and non-ionic synthesized surfactants were tested. The best concentration for the removal of hydrocarbons from the soil was investigated. Three concentrations were tested for each surfactant: 0.125 %, 0.25 %, and 0.5 %, above the critical micellar concentration (CMC) reported for similar surfactants. The samples were shaken on a rotary shaker at 150 rpm at 26 °C for 48 hours. After the test, the tubes were centrifuged at 400 rpm, at 26 °C, for 20 minutes. After the solution was decanted, the soil was washed with distilled water (1:2). The soil was dried in an oven at 60 °C for 48 h. The removal efficiency (RE %) was obtained by weight difference. All tests were performed in triplicate. The standard deviation statistical analysis was used to obtain the standard error.

The effect of surfactant volume was also investigated using the following ratios of m/v = 1:1, 1:2, 1:3 to 1:4 for a mass of 10 g. Stirring speed in rpm was determined using the best concentration and volume previously found. The rpm used in this study were 50, 100, and 150 under the same agitated batch conditions. Finally, the temporal kinetics of diesel desorption was performed every 24 h for 120 h with a solution of each type of surfactant and water as a target.

## 2.9 Analytical methods

To quantify residual diesel in the soil after washing with the surfactant, a sample of 1g of soil was taken to which 5 mL of 1,2-dichloroethane were added, mixed vigorously, and the phases were allowed to separate. The organic phase was measured by UV-Vis spectroscopy, previously preparing a calibration curve, according to Beer's Law. The diesel absorbance spectrum presents two significant peaks at 242 nm and 278 nm wavelengths. UV-Vis spectroscopy is an accessible and versatile method for quantifying TPH (Mansouri *et al.*, 2019).

On the other hand, the soil washed by each surfactant was placed in a Soxhlet system to desorb the residual diesel and characterize it by GC-Mass

spectrometry in a Leco Inc. - Pegasus III GC-TOF-MS equipment. 1.0  $\mu\text{L}$  (1:10 diesel:cyclohexane) of the sample was injected into a midpolar column (BPX-50, 30 m, 0.25 mm i.d., 0.25  $\mu\text{m}$ ), at 250  $^{\circ}\text{C}$  at constant pressure of 325 kPa using He. The oven temperature was programmed at 60-250  $^{\circ}\text{C}$ , ten  $^{\circ}\text{C min}^{-1}$ , in a runtime of 18min. The types of petroleum hydrocarbons were described based on the hydrocarbon standards at different retention times.

### 2.10 Morphological characterization of the soil

The morphology of the soil washed with surfactant solution was characterized by scanning electron microscopy (SEM) using SEM JEOL JSM-5900LVO equipment. The soil washed with cationic surfactant was marked by a punctual analysis of Energy Dispersive Spectroscopy (EDS) to rule out contamination with Iodine because of cation exchange in the soil.

## 3 Results and discussion

### 3.1 Coconut oil-based surfactants

The biodiesel was synthesized by trans-esterifying coconut oil with methanol using basic catalysis. The reaction yield was high (92 %) compared to other synthesis methods reported in the literature (Jung *et al.*, 2017, Olusegun *et al.*, 2016). Firstly, biodiesel was characterized by GC; methyl laurate was found in a more considerable proportion (56 %), followed by methyl myristate in 19%. We previously reported these results (Vázquez-Vélez *et al.*, 2022), which are in accord with the literature (Jung *et al.*, 2017), excluding other virgin oils (Qadariyah *et al.*, 2022). Then, the three kinds of synthesized surfactants are obtained as a mixture of fatty acids in coconut oil.

On the other hand, coconut oil and its biodiesel were characterized by FTIR spectroscopy (figure 2), which we have reported previously (Vázquez-Vélez *et al.*, 2022). Both spectra observed the stretching signals of the group C = O of ester at 1741  $\text{cm}^{-1}$  and the C-O bond at 1167  $\text{cm}^{-1}$ , a signal that presents greater intensity for the triglyceride. Symmetric stress vibration signals from the methylene and methyl groups are also observed at 2923 and 2853  $\text{cm}^{-1}$ ; and at 1437-1461  $\text{cm}^{-1}$ , the methyl

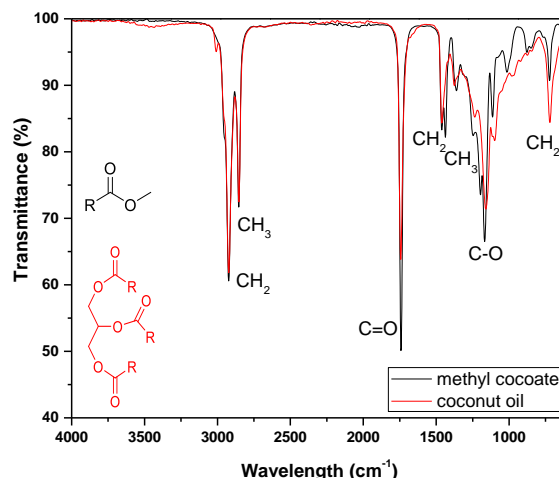


Figure 2. FTIR spectra of coconut oil and methyl cocoate.

flexing vibration ( $\text{CH}_3$ ) and scissors of the groups -  $(\text{CH}_2)_n$ - respectively; finally, at 722  $\text{cm}^{-1}$  the signal corresponding to the balancing of the methylene groups  $(\text{CH}_2)_n$ .

### 3.2 Coconut oil-based cationic surfactant

Cocamidopropyl ammonium iodide was synthesized in two stages from coconut oil-based biodiesel. First, a typical process of aminolysis with methyl cocoate and N, N-Dimetil-1,3-propilendiamina (DMAPA) was carried out as a green reaction without solvents. In previous work, we reported a similar synthesis to coffee oil (Velázquez-Torres *et al.*, 2018). The product obtained from the first stage is Cocamido propyl dimethylamine, used as a raw material in cosmetic use (Rhein *et al.*, 2007). Its industrial synthesis is an aminolysis direct of coconut oil after distillation to eliminate the glycerol (Patent, 2007). In the second synthesis stage, a conventional Hoffman methylation reaction was carried out to obtain an ammonium salt. Commonly the methylation of amines to form their ammonium salts is through methylation with alkyl halides and alkyl sulfates (Reck, 1985). The cationic surfactant synthesized has not been studied in soil remediation. The study of this kind of cationic surfactant in soil washing is interesting because the fatty acids contained in the molecule and its amide group give it biodegradability in low concentrations like in cocamido propyl dimethylamine (Rhein *et al.*, 2007); and linear quaternary ammonium salts are biodegradable too (Wennberg *et al.* 2017).

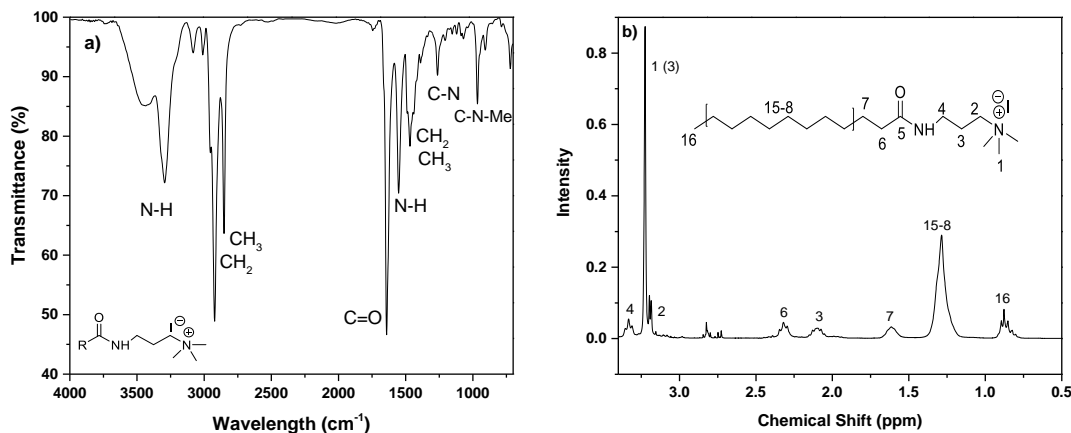


Figure 3. FTIR (a) and  $^1\text{H}$  NMR (b) spectra of a Cocamidopropyl ammonium iodide.

In the molecular characterization of the cationic surfactant mixture by FTIR spectroscopy (figure 3a), the characteristic vibration signal of the symmetric stretching of the C=O is observed at  $1643\text{ cm}^{-1}$  for the amide functional group. The vibration signal of the C-N bond appears at  $1000\text{ cm}^{-1}$  for the ammonium group. At  $3289\text{ cm}^{-1}$ , the tension vibration of N-H from the amide functional group and its bending vibration at  $1549\text{ cm}^{-1}$ . Finally, the vibration signals of the methylene and methyl groups are observed at  $2800\text{--}2900\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum confirms that it corresponds to Cocamidopropyl ammonium iodide. Integration was performed for the major compound derived from methyl laurate. The other minority compounds are contained in the same signals because they have the same chemical environment and, therefore, the same displacement. Figure 3b shows the spectrum whose signals and integration correspond to the following groups according to their chemical shift  $\delta$  (ppm) = 0.88 (t,  $J = 6.9\text{ Hz}$ , 3 H,  $-\text{CH}_3$  (16)), 1.29 (s, 16H,  $-\text{CH}_2$  (15-8)), 1.61 (m, 2H,  $-\text{CH}_2$  (7)), 2.10 (m, 2H,  $-\text{CH}_2$  (3)), 2.32 (t, 2H,  $-\text{CH}_2$  (6)), 3.20 (t, 2H,  $-\text{CH}_2$  (2)), 3.23 (s, 9H, 3  $-\text{CH}_3$  (1)), 3.33 (t, 2H,  $-\text{CH}_2$  (4)). The second spectrum corresponds to  $^{13}\text{C}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 14.18$  ( $\text{CH}_3$  (16)), 22.90 ( $-\text{CH}_2$  (3)), 23.33 ( $-\text{CH}_2$  (15)), 26.15 ( $-\text{CH}_2$  (7)), 29.79 ( $-\text{CH}_2$  (8,9)), 30.13 ( $-\text{CH}_2$  (13-10)), 32.23 ( $-\text{CH}_2$  (14)), 36.38 ( $-\text{CH}_2$  (6)), 36.65 ( $-\text{CH}_2$  (4)), 54.37 ( $-\text{CH}_3$  (1)), 65.32 ( $-\text{CH}_2$  (2)). 176.56 (C = O (5)).

### 3.3 Coconut oil-based anionic surfactant

Due to their lower cost, anionic surfactants are the most studied in the remediation of contaminated soils (Trellu *et al.*, 2016, Mao *et al.*, 2015). Sodium lauryl

sulfate (Ishiguro *et al.*, 2016) and other straight-chain, cyclic, benzyl, or dialkyl sulfonates have been studied (Mao *et al.*, 2015). The anionic surfactant synthesized in this work was the product of the sulfonation of methyl cocoate, obtained in a yield of 86 %. The sulfonation reaction has been reported for palm oil methyl ester using base catalysis to get a 76 % of the palm yield of methyl ester sulfonate (P-MES) (Saxena *et al.*, 2017). MES from virgin coconut oil has been reported using the  $\text{Al}_2\text{O}_3$  catalyst through the sulfonation process using microwave radiation [Qadaryyah *et al.* 2022]. The coco methyl ester sulfonate (C-MES) synthesized here was obtained without a catalyst through a more straightforward procedure with a better yield of 86%. Methyl ester sulfonates (MES) are biodegradable cleaning products (Maurad *et al.*, 2020), so studying C-MES in soil washing is remarkably interesting.

The C-MES spectrum (figure 4a) shows the signal for the symmetric stretching  $-\text{C}=\text{O}$  of the ester functional group is shifted at  $1637\text{ cm}^{-1}$  due to the interaction of sulfonate ion. The C-O tension vibration signal appears at  $1095\text{ cm}^{-1}$ . The strong signal for the S=O bond is at  $1153\text{ cm}^{-1}$ . At  $3435\text{ cm}^{-1}$ , the broad and intense signal corresponds to the sulfonated salt-finally, the symmetric vibration of the methylene and methyl groups at  $2923$  and  $2853\text{ cm}^{-1}$ . The molecular characterization by  $^1\text{H}$  NMR confirms the C-MES compound. The integration corresponds to the fatty chain main (C12). Figure 4b shows the spectrum whose signals and integration correspond to the following groups according to their chemical shift  $\delta$  (ppm) = 0.58 (t, 3 H,  $-\text{CH}_3$  (13)), 0.99 (s, 16 H,  $-\text{CH}_2$  (5-12)), 1.95 (t, 2H,  $-\text{CH}_2$  (4)), 3.46 (s, 3H,  $-\text{OCH}_3$  (1)), 3.51 (dd, 1H, CH (3)).

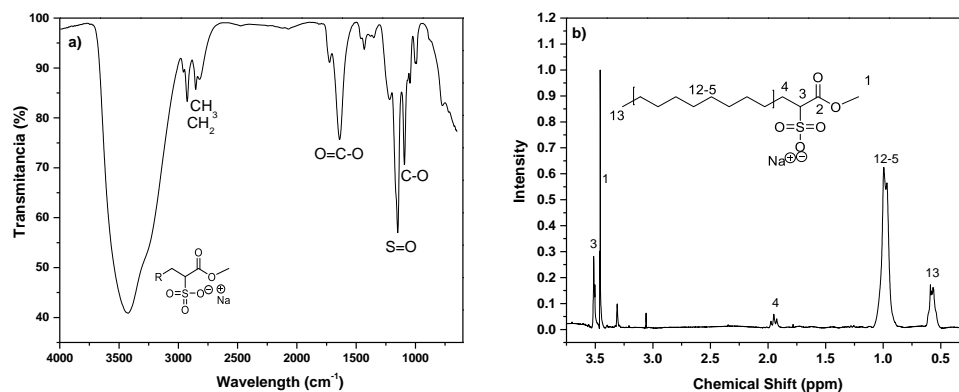


Figure 4. FTIR (a) and <sup>1</sup>H NMR (b) spectra of coco methyl ester sulfonate (C-MES).

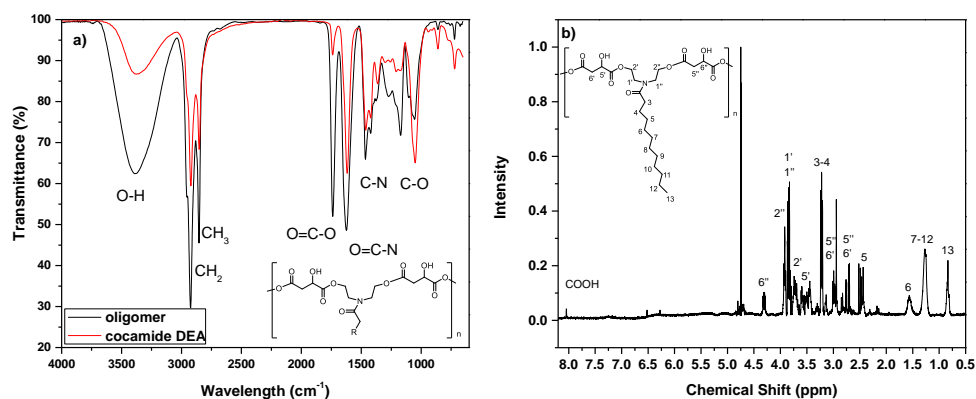


Figure 5. FTIR (a) and <sup>1</sup>H NMR (b) spectra of Cocamidodiethyl malate oligomer.

The second spectrum corresponds to <sup>13</sup>C NMR (300 MHz, D<sub>2</sub>O):  $\delta = 14.56$  (CH<sub>3</sub> (13)), 23.44 (-CH<sub>2</sub> (12)), 25.66 (-CH<sub>2</sub> (5)), 30.58 (-CH<sub>2</sub> (6-10)), 32.78 (-CH<sub>2</sub> (11, 4)), 56.34 (-OCH<sub>3</sub> (1)), 66.82 (-CH (3)), 167.47 (C=O (2)).

### 3.4 Coconut oil-based non-ionic surfactant

Non-ionic surfactants are also commonly used in the remediation of soils due to their low CMC, solubility capacity, and toxicity (Zheng *et al.*, 2012). The most widely used non-ionic surfactants are polyoxides, polyesters, polyalcohols, and polysaccharides (Mao *et al.*, 2015). In this work, the Cocodiethanolamide (CDEA) was synthesized from the aminolysis of the methyl cocoate with diethanolamine (DEA), whose process has been previously reported (Vázquez-Vélez *et al.*, 2022). CDEA is widely used as a surfactant in the cosmetic industry (Rhein *et al.*, 2007) and has been studied in soil remediation (Mao *et al.*, 2015), but its toxicity increases at high concentrations (Ishiguro *et al.*, 2016). Then, we decided to introduce

this molecule's ester groups to decrease its toxicity and facilitate biodegradation (Wennberg *et al.*, 2017). The cocamidodiethylmalate oligomer was obtained by condensing Cocamide DEA and malic acid as mixture without purification.

The FTIR spectrum of Cocamide DEA (figure 5a) showed the vibration signal of the -O-H bond at 3325 cm<sup>-1</sup> and 1640 cm<sup>-1</sup>, the signal corresponding to the C=O bond of the amide functional group. The -OH signal increased for cocamidodiethylmalate oligomer (figure 5a) derived from the condensation with malic acid, and the signal corresponding to the symmetric tension vibration of the -C-O bond at 1100 cm<sup>-1</sup> too. The -C=O of the ester functional group signal appeared at 1745 cm<sup>-1</sup>, and the signal of the amide functional group decreased. Finally, the tension vibration signals of the methylene and methyl groups of the alkyl chains derived from coconut oil are 2800-2900 cm<sup>-1</sup>. The molecular characterization of the oligomer by <sup>1</sup>H NMR showed an oligomer mixture being the main compound cocamidodiethylmalate oligomer from methyl laurate. But it is observed



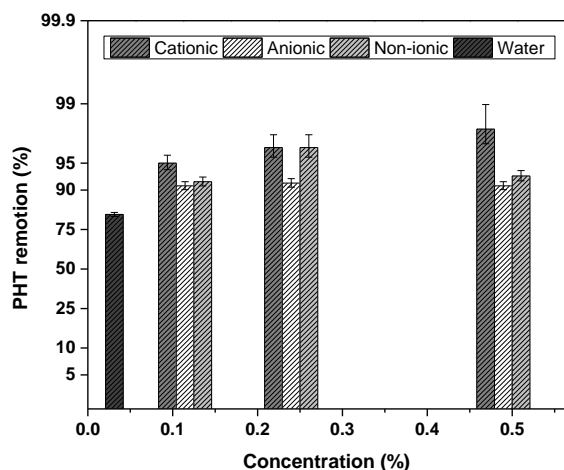


Figure 6. Log Graphic of TPH remotion depending on the concentration.

other signals at 3.5 ppm corresponding to a non-pure compound. The spectrum (Fig. 5b) signals and integration correspond to the following groups according to their chemical shift  $\delta$  (ppm) = 0.86 (t, 3 H,  $-\text{CH}_3$  (13)), 1.30 (s, 12 H,  $-\text{CH}_2$  (7-12)), 1.6 (t, 2H,  $-\text{CH}_2$  (6)), 2.5 (m, 2H,  $-\text{CH}_2$  (5)), 2.7 (dd, 2H, 2-CH (5'', 6')), 3 (dd, 2H, 2-CH (5'', 6')), 3.2 (t, 4H,  $-\text{CH}_2$  (3-4)), 3.6 (dd, 1H (5')), 3.7 (m, 2H,  $-\text{CH}_2$  (2'')), 3.84 (t, 4H,  $-\text{CH}_2$  (1', 1'')), 3.92 (t, 2H,  $-\text{CH}_2$  (2'')), 4.31 (dd, 2H,  $-\text{CH}$  (6'')). The H integration at eight ppm from the terminal acids corresponds to  $n=33$ .

### 3.5 Effect of parameters on Batch desorption

#### 3.5.1 Determination of the concentration-effect

The critical micelle concentration (CMC) is a common physical parameter to characterize the surfactants and to know the minimum concentration at which the micelle is formed. Based on the CMC reported for similar compounds, we decided to investigate the TPH remotion at three concentrations 0.125 %, 0.25 %, and 0.5 % w/v in a relationship of 1: 4 (m: v). The results are shown in figure 6. The highest removal of hydrocarbons from the soil was 98 %, using the cationic surfactant at a concentration of 0.5 % w/v. For a concentration of 0.25 %, the removal was 96.7 % followed by 95.0 % for a concentration of 0.125 %. The results show that concentrations between 0.25 - 0.5 % present a similar removal percentage. The non-ionic surfactant presented a good removal efficiency of 95 %, at a concentration of 0.25 % w/v. But for a concentration of 0.5 % and 0.125 %, the efficiency

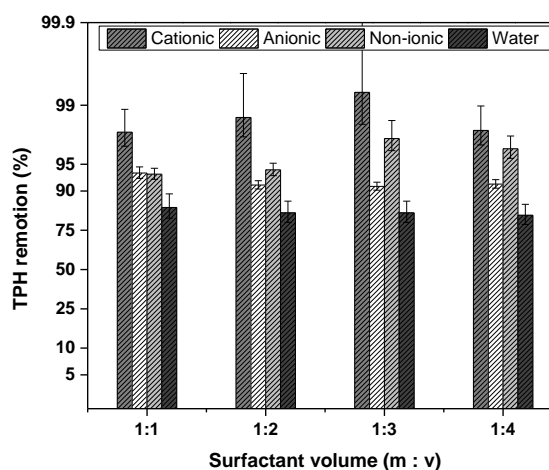


Figure 7. Log Graphic of TPH remotion efficiency from the soil as a function of the volume of the surfactant solution.

dropped to 93.0 % and 91.9 %, respectively. The anionic surfactant presented similar efficiencies of 90.7 %, 91.6 % and 91.3 % for the concentrations of 0.125 %, 0.25 % and 0.5 %, respectively. These results indicate that a higher concentration of the anionic surfactant solution does not significantly affect its removal efficiency because the error percentage is 1 %. The water had an 82 % of TPH remotion. The high removal of TPH with water is due to its polarity, which removes polar compounds such as hydrocarbons with hydroxyl groups, amines, and acids (see table 2). In addition, the adsorption of some TPH is low in soils with negligible OC content is directly related to the type of kaolinite clay (Velázquez-Vázquez *et al.*, 2022). These results agree with those described in the literature, which shows that cationic-type surfactants have good removal efficiency in acidic pH soil. Contrary to this type of soil, the efficiency is low in using anionic surfactants, commonly used in soil washing (Befkadu *et al.*, 2018).

#### 3.5.2 Determination of the volume effect

The effect of the surfactant solution volume on TPH desorption from the soil is shown in Fig. 7. Based on the results of the best concentration, for the volume influence test on washing efficiency, the cationic surfactant solution was used at 0.5 %, and for anionic and non-ionic, it was 0.25 %. The surfactant with the highest removal of TPH was the cationic one with an efficiency of 99.3 %, in a 1:3 m:v ratio. However, no significant difference is observed in the volume used. Therefore, for water savings, the efficiency of 97.9

% in a ratio of 1:1 m: v is considerable. The non-ionic surfactant presented a higher efficiency in a 1:3 m/v relationship of 97.5 %. But the anionic surfactant showed its best efficiency of 93.3 % at a lower volume ratio (1:1 m/v), which coincides with the concentration tests. A higher amount of anionic surfactant causes a deficiency in its removal due to charge interaction with the acid soil. However, for the non-ionic surfactant, it is observed that the efficiency is a function of a more significant amount of solution until it becomes saturated, and its efficiency begins to decrease.

### 3.5.3 Determination of the time and rpm effect

Based on the volume and concentration results, the time and rpm varied in the batch test. The results found for the TPH removal time were not significant. The cationic surfactant's removal efficiency was 98.8 % at 24 h, 99.3 % at 48 h, 72 h, and 98 % at 96 h and 120 h. The non-ionic surfactant had a slight increase in its efficiency of 96.5 % in 24 h, 98.3 % at 72 h, and was maintained up to 120 h. Batch test time for anionic surfactant and water did not significantly influence.

On the contrary, the rpm parameter has a significant influence due to the requirement of a larger contact area of the washing solution with the TPH. All the above tests were performed at 150 rpm, but when this power was reduced to 100 rpm and 50 rpm, the TPH removal efficiency decreased by 10%. These results are shown in Figure 8.

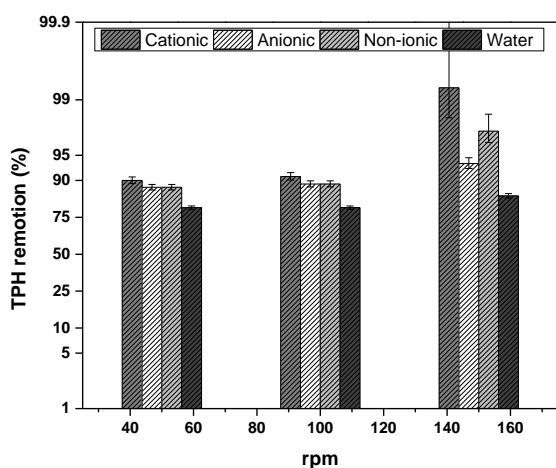


Figure 8. Log Graphic of TPH remotion efficiency from the soil as a function of rpm.

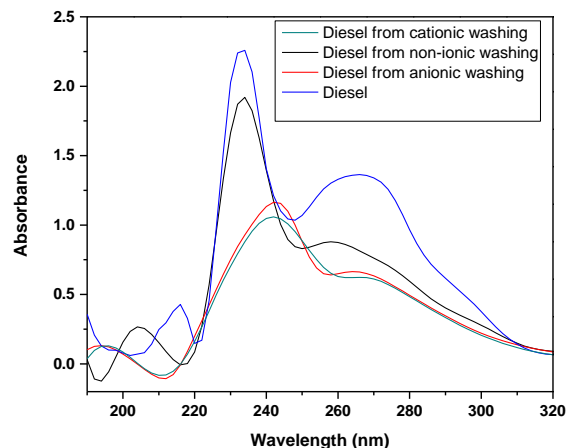


Figure 9. UV-Vis spectrum of diesel desorbed from the soil after surfactant washing.

### 3.6 Characterization and quantification of residual diesel

This was characterized by UV-Vis spectroscopy to determine the concentration of the residual diesel in the soil after washing, performing a calibration curve previously at different concentrations of diesel. Figure 9 shows the diesel and residual diesel spectra after washing with each type of surfactant. The composition of diesel is alkyl chains from C7 to C24, substituted and unsubstituted aromatic and polyaromatic compounds. In the UV-Vis spectrum of diesel, a small peak is observed at 190 nm corresponding to the alkyl chains, and another small peak at 216 nm corresponds to mono and diaromatics. The prominent peak at 233 nm corresponds to aromatic compounds with alkyl substitution, unsaturation, or polyaromatic. The peak at 266 nm corresponds to aromatic compounds substituted with polar groups that absorb at longer wavelengths (Weber *et al.*, 2016). After washing treatment using the cationic surfactant, the diesel concentration desorbed was 455.4 ppm. For the anionic surfactant was 545.8 ppm, and 992.7 ppm for washing with the non-ionic surfactant. A similar spectrum is presented for diesel desorbed from soil washed with the cationic and anionic surfactant. However, diesel desorbed from the soil washed with the non-ionic surfactant showed the absorption peak at 233 nm is more intense than at 266 nm. These results indicate that the compounds with higher chromophore groups are removed by the cationic surfactant, followed by the anionic one.

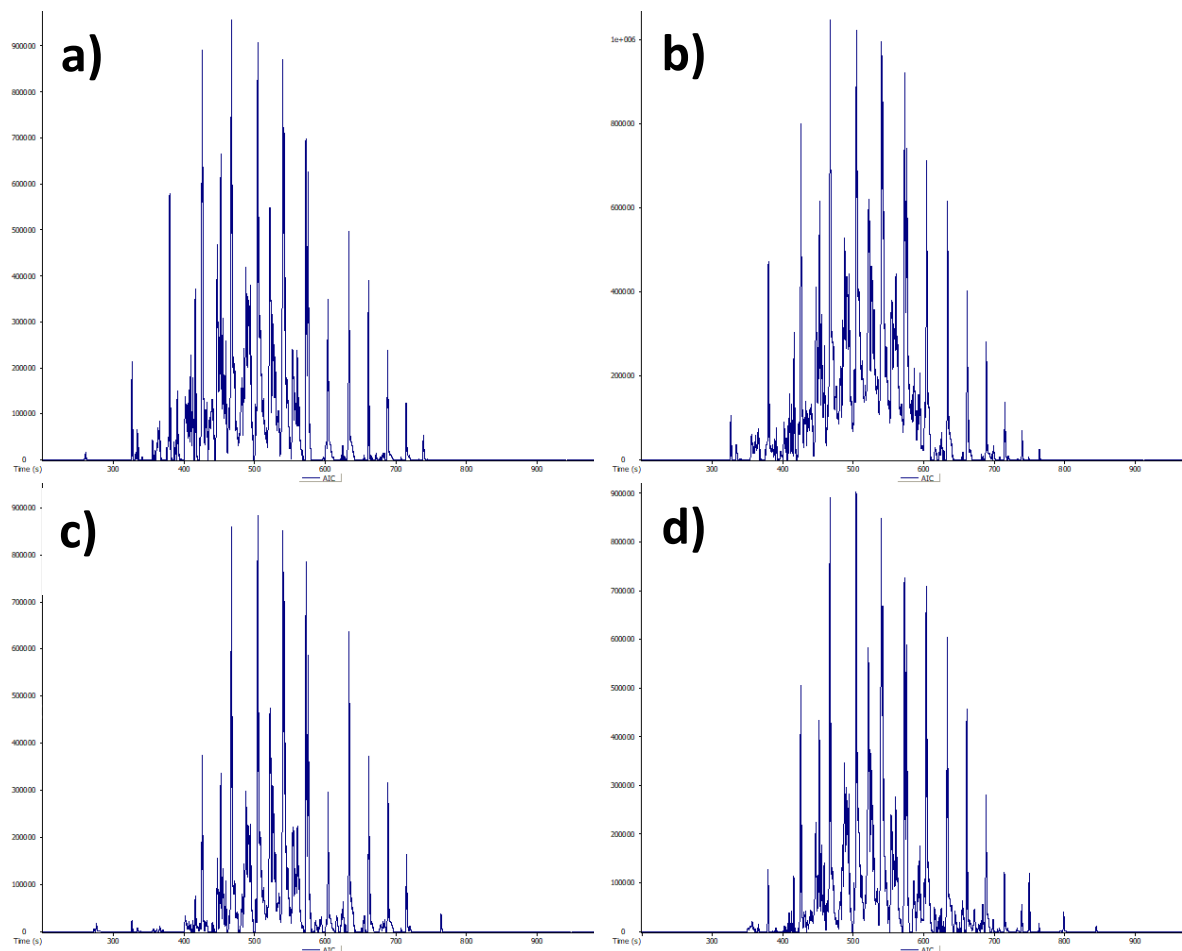


Figure 10. Chromatograms of the diesel a) before treatment, and after treatment with surfactant b) cationic, c) anionic and d) non ionic.

The remediation treatment with the three types of surfactants complies with the maximum permissible limits established for agricultural soils (1200 ppm) according to the NOM-138-SEMARNAT/SSA1-2012 (SEMARNAT, 2013).

On the other hand, the residual diesel was desorbed from the soil after washing by the Soxhlet method. This method is one of the most conclusive in the determination of hydrocarbons (Yzquierdo-Ruiz *et al.* 2022). The residual diesel quantification obtained by this method is similar to those found by UV-Vis spectroscopy. GC-MS analyzed the desorbed diesel to determine the diesel compounds before and after washing with surfactant. GC-MS is a powerful technique for the separation and identification of unknown components. The significant advantage is the compound class separation based on their parent

masses. Table 2 shows the most abundant compounds (> 2 %) in diesel detected by GC-MS, before and after washing. The results of the compounds found in diesel are comparable to those reported (Wang *et al.*, 2005). Figure 10 shows diesel chromatograms before washing and after washing with surfactants. The results show that the light fraction hydrocarbons were removed. 1,4-Butanediol and 1-Bromo-3-butene-2-ol are significant compounds contained in diesel that was released after washing with surfactants. However, Benzene 1-methyl-3-hexyl- was challenging to remove by its stability, and compounds such as Tetracosane and Heneicosane were left in the soil washed with anionic and non-ionic surfactants. So, cationic surfactant presented a better removal efficiency.

Table 2. Abundant compounds (&gt; 2 %) in diesel detected by GC, before and after washing treatment.

Diesel compounds	Area (%)	R time	Formula	Cationic	Anionic	Non-Ionic
<i>Tetradecane</i>	-	<b>379.87</b>	<b>C14H30</b>	<b>2.1</b>	-	-
<i>5,14-dibutyl-Octadecane</i>	1.79	380.07	C26H54	-	-	-
<i>Trichlorooctadecylsilane</i>	-	380.17	C18H37Cl3Si	2.1	-	-
<i>4-Ethylphenethylamine</i>	1.69	400.37	C10H15N	-	-	-
<i>n-Amyl Cyclohexane</i>	1.69	401.22	C11H22	-	-	0.48
<i>(2-methylpropyl)-Cyclohexane</i>	-	401.17	C10H20	-	2.19	-
<i>1-(1-methylethenyl)-3-(1-methylethyl)-Benzene</i>	1.69	402.97	C12H16	0.39	-	-
<i>5-ethyl-1,2,3,4-tetrahydro-Naphthalene</i>	-	424.37	C12H16	2.09	-	-
<i>3-hydroxy-2-butyl 1-(p-tolyl) ethyl Ether</i>	3.42	424.47	C13H20O2	-	-	-
<i>1,2,3,4-tetrahydro-1,4-dimethyl-Naphthalene</i>	3.42	424.97	C12H16	2.09	2.53	2.22
<i>Heptadecane</i>	-	425.87	C17H36	-	2.51	-
<i>Tetradecane</i>	3.42	426.27	C14H30	2.09	-	2.22
<i>6-ethyl-2-methyl-Decane</i>	1.66	446.37	C13H28	-	-	-
<i>Heneicosyl-Cyclopentane</i>	1.66	447.97	C26H52	-	-	-
<i>1,2,3,4-tetrahydro-1,5,7-trimethyl-Naphthalene</i>	2.19	449.22	C13H18	-	-	1.532
<i>Hexadecane</i>	2.19	452.27	C16H34	-	-	-
<i>5,14-dibutyl-Octadecane</i>	-	467.1	C26H54	-	-	4.41
<i>1-isocyanato-Octadecane</i>	-	467.22	C19H37NO	4.61	-	-
<i>Tetracosane</i>	<b>4.22</b>	467.37	C24H50	-	3.49	-
<i>Decyl-Cyclopentane</i>	-	487.77	C15H30	-	2.64	-
<i>(4-methylpentyl)-Cyclohexane</i>	2.1	487.82	C12H24	-	-	-

<i>[4.1.0] heptane-2-ol, 1-phenyl-, endo-Bicyclo</i>	2.1	488.62	C13H16O	-	-	1.751
<i>1-methyl-3-hexyl-Benzene</i>	<b>4.77</b>	489.87	C13H20	4.34	3.36	-
<i>2-(p-tolyl)ethylamine</i>	-	489.8	C9H13N	-	-	4.47
<i>7-hexyl-Eicosane</i>	-	490.9	C26H54	-	3.36	2.74
<i>3,3'-Dimethylbiphenyl</i>	-	503.82	C14H14	4.2		
<i>2-tetrahydrofurylmethyl ester Valeric acid</i>	-	503.8	C10H18O3	-	-	<b>5.54</b>
<i>1,4-Butanediol</i>	<b>5.18</b>	503.72	C4H10O2	-	-	-
<i>Tetracosane</i>	<b>5.18</b>	504.57	C24H50	-	<b>5.02</b>	<b>5.54</b>
<i>1-isocyanato Octadecane</i>	-	504.72	C19H37NO	4.2	-	-
<i>2-pentadecylester Dichloroacetic acid</i>	-	505.47	C17H32Cl2O2	4.24	-	-
<i>1-Bromo-3-butene-2-ol</i>	<b>5.18</b>	505.77	C4H7BrO	-	-	-
<i>2,2'-Dimethylbiphenyl</i>	2.05	507.52	C14H14	1.37	0.99	1.54
<i>Hexadecane,2,6,11,15-tetramethyl</i>	-	521.92	C20H42	-	2.72	-
<i>2,6,10-trimethyl-Pentadecane</i>	-	521.95	C18H38	-	-	3.34
<i>Cyclotridecane</i>	-	525.22	C13H26	2.28	-	-
<i>Undecyl-Cyclohexane</i>	-	525.72	C17H34	2.28	2.7	
<i>Decyl-Cyclohexane</i>	-	525.7	C16H32	-	-	3.12
<i>1,2,3,4-tetrahydro-8-methyl-1-Naphthalenemethanol</i>	2.05	528.02	C12H16O		3.03	
<i>Tetracosane</i>	<b>4.83</b>	539.77	C24H50	<b>5.02</b>	<b>6.37</b>	<b>5.72</b>
<i>1-bromo-3-butene-2-ol</i>	-	540.82	C4H7BrO	<b>5.02</b>		-
<i>2,6,10,14-tetramethyl-Hexadecane</i>	-	541.72	C20H42	<b>5.02</b>	<b>6.37</b>	-
<i>Hexadecyl ester Trichloroacetic acid</i>	-	560.12	C18H33Cl3O2	2.11	2.61	-
<i>Eicosyl-Cyclohexane</i>	2.14	560.92	C26H52	-	2.61	2.8
<i>1H-2-Benzopyran, 3,5,8,8a-tetrahydro-6-methyl-</i>		561.77	C10H14O	2.11	-	-

<i>Heneicosane</i>	2.44	572.62	C <sub>21</sub> H <sub>44</sub>	2.5	3.16	3.2
<i>2,6,10,14-tetramethyl-Hexadecane</i>	-	575.75	C <sub>20</sub> H <sub>42</sub>	-	2.56	3.03
<i>N-methyl-2-propyn-1-amine</i>	-	592.85	C <sub>4</sub> H <sub>7</sub> N	-	-	3.39
<i>5,14-dibutyl-Octadecane</i>	-	603.7	C <sub>26</sub> H <sub>54</sub>	3	-	<b>5.17</b>
<i>1-bromo-3-butene-2-ol</i>	-	604.55	C <sub>4</sub> H <sub>7</sub> BrO	-	-	<b>5.19</b>
<i>Heneicosane</i>	<b>2.18</b>	603.72	C <sub>21</sub> H <sub>44</sub>	-	<b>5.09</b>	-
<i>7-hexyl-Eicosane</i>	-	633.35	C <sub>26</sub> H <sub>54</sub>	-	-	<b>3.2</b>
<i>5,14-dibutyl-Octadecane</i>	-	633.37	C <sub>26</sub> H <sub>54</sub>	2.49	<b>4.01</b>	-

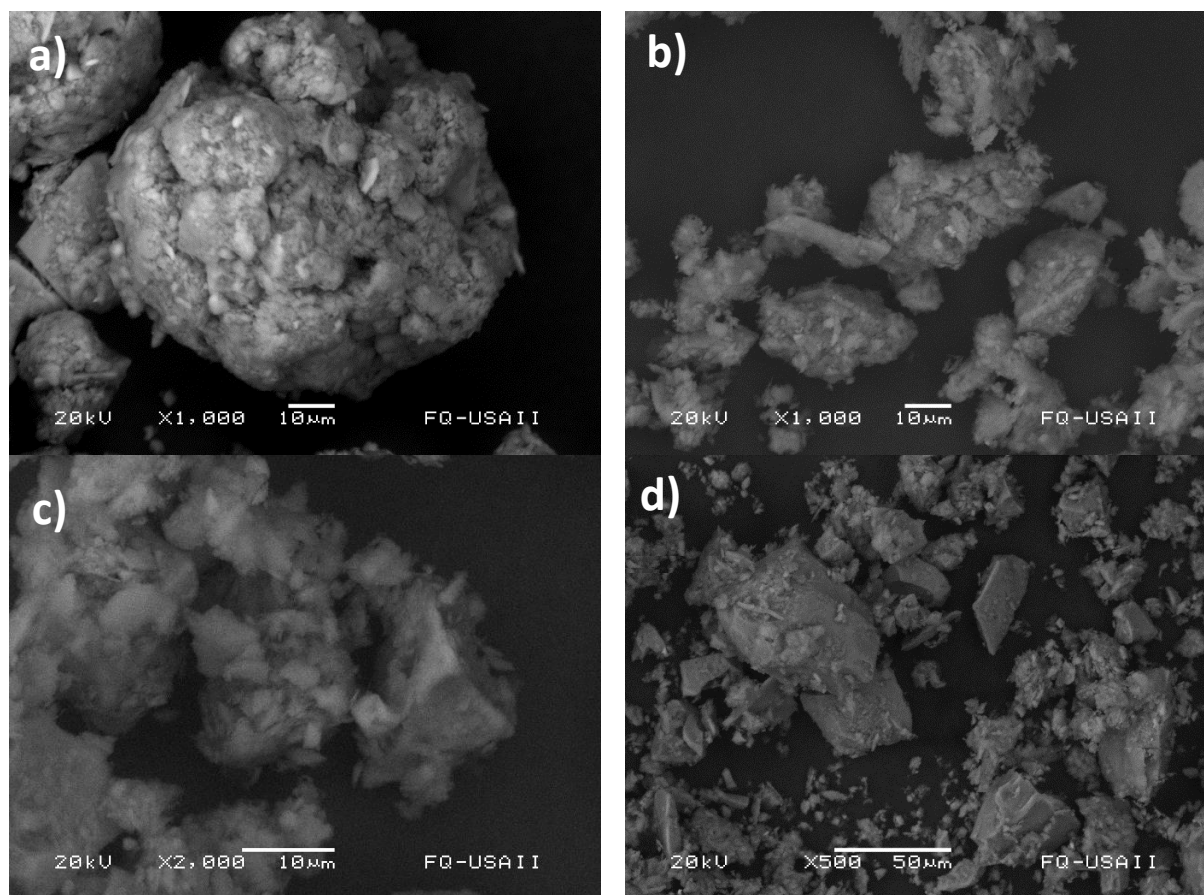


Figure 11. SEM images of a) contaminated soil, and soil after washing with b) cationic, c) anionic and d) non-ionic surfactant.

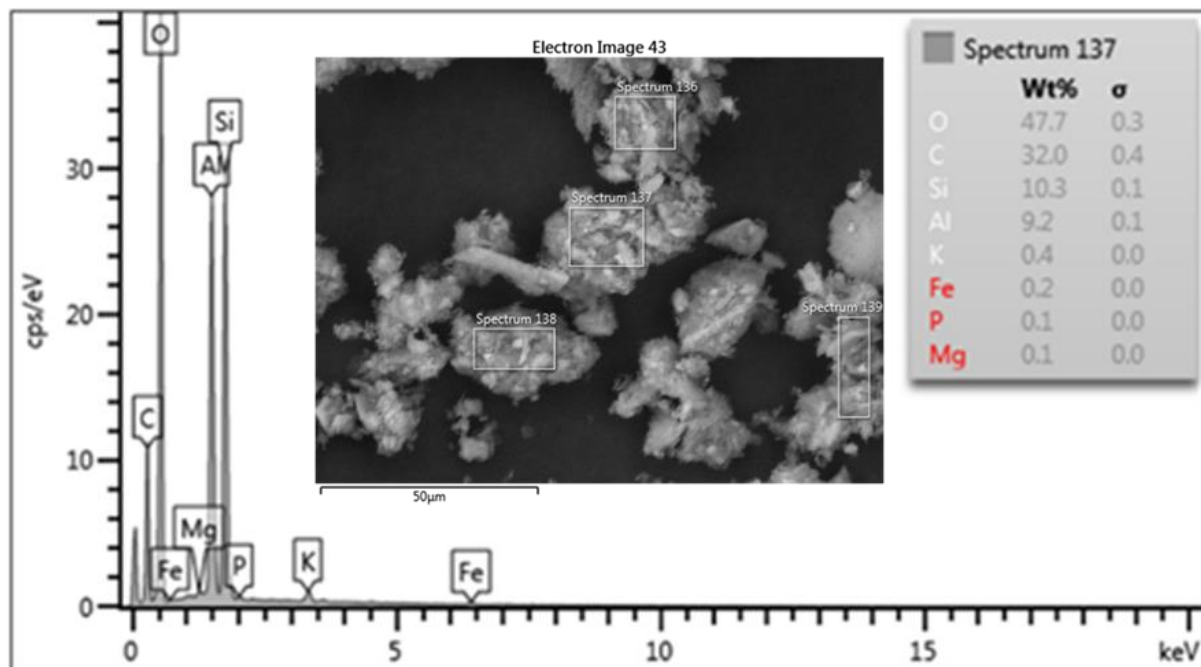


Fig. 12. SEM-EDS point analysis of the soil washed with the cationic surfactant.

On the other hand, compounds different from the reference ones were found in the soil after washing. For example, 1-Bromo-3-butene-2-ol and 2,6,10,14-tetramethyl- were discovered after washing with cationic surfactant; the second was also found in a high percentage after washing with the anionic surfactant. The 2-tetrahydrofurylmethyl ester Valeric acid was found in the soil after washing with the non-ionic surfactant in a substantial portion. These compounds can be resulted from intramolecular rearrangements between the TPH and the washing surfactants.

### 3.7 Characterization of soil after washing treatment

The soil was characterized by scanning electron microscopy (SEM) to determine the effect on the morphology and wear of the particle after treatment by the Batch method.

The morphology of the clay loam soil contaminated with diesel is observed in image 11a. The morphology is variable but is slightly observed due to the saturation of TPH in the particles. Micrographic 11 b, c, and d show the morphology of the particles after washing with their respective surfactant. In them, a difference in the wear of particles is not appreciated, so it can be said that the surfactant does not influence the wear of particles; only the

centrifugation process that was carried out for the separation of the soil at 4500 rpm.

Fig. 12 shows the SEM-EDS analysis for the soil after washing with a cationic surfactant. The result indicates that the surfactant was not adsorbed in the soil, and there is no presence of any cation exchange, although kaolinite has a low ionic content.

## Conclusions

Coconut oil-based surfactants were synthesized from coconut oil via the formation of methyl cocoate. Molecular characterization of the reaction crude by FTIR and NMR spectroscopic indicates that the molecules without significant impurities were obtained, except for non-ionic surfactant. The three types of surfactants were evaluated in removing hydrocarbons in clay loam soil. The mobility and solubility influence of the coconut oil-based surfactants in the medium were determined through the concentration of each surfactant, the volume of the solution washing, the kinetic energy through the rotational movement, and the time required for washing. Based on the results, the cationic surfactant always presented a more excellent removal in all the tests. However, the anionic and non-ionic surfactant

mixture also offer a considerable efficiency with a difference below 2 to 3 %, obtaining a percentage error of 1 % in the tests. The characterization of residual diesel in the soil and its quantification indicates that the remediation treatment with the three types of surfactants complies with the maximum permissible limits established for agricultural soils (1200 ppm) for the official Mexican standard.

Finally, one of the most critical parameters in the choice of the surfactant and its biodegradability is that it is not adsorbed on the soil. The UV-Vis spectroscopy analyzes of the residual diesel indicate that the soil is free of surfactant after the remediation treatment, and the SEM-EDS analysis for the cationic surfactant.

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