Environ Geochem Health (2025) 47:366
https://doi.org/10.1007/s10653-025-02678-4

ORIGINAL PAPER

Eco-friendly cleaning agent applied for ex situ remediation of beach sand contaminated with crude oil

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Received: 16 April 2025 / Accepted: 20 July 2025 / Published online: 8 August 2025

Abstract Coastal oil spills cause significant adverse effects, and removing weathered crude oil mixed with sand remains a considerable challenge. To address this, an environmentally friendly cleaning agent was formulated using a vegetable oil-based microemulsion for sediment cleaning. The relationship between microemulsion composition and its efficiency in cleaning oil-contaminated sediments in coastal environments was investigated. Component selection followed criteria of low toxicity and high biodegradability, including pine oil as the oily phase, distilled water as the aqueous phase, saponified coconut oil as the surfactant, and isopropyl alcohol as the cosurfactant. Pseudoternary phase diagrams were constructed using a cosurfactant/surfactant ratio of 10. The microemulsified cleaning agents were characterized and optimized using Scheffé's simplex lattice design, with refractive index, viscosity, conductivity, and specific gravity as response variables. Biodegradable microemulsion systems were successfully applied to remediate oil-contaminated beach sand, where higher proportions of the oily phase, specifically 30% and 60%, demonstrated excellent oil removal performance. The remediation process effectively incorporated the crude oil contaminant into the oily phase of the microemulsion, achieving a maximum removal efficiency of 90%. Additionally, the microemulsion exhibited stability for

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Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10653-025-02678-4.

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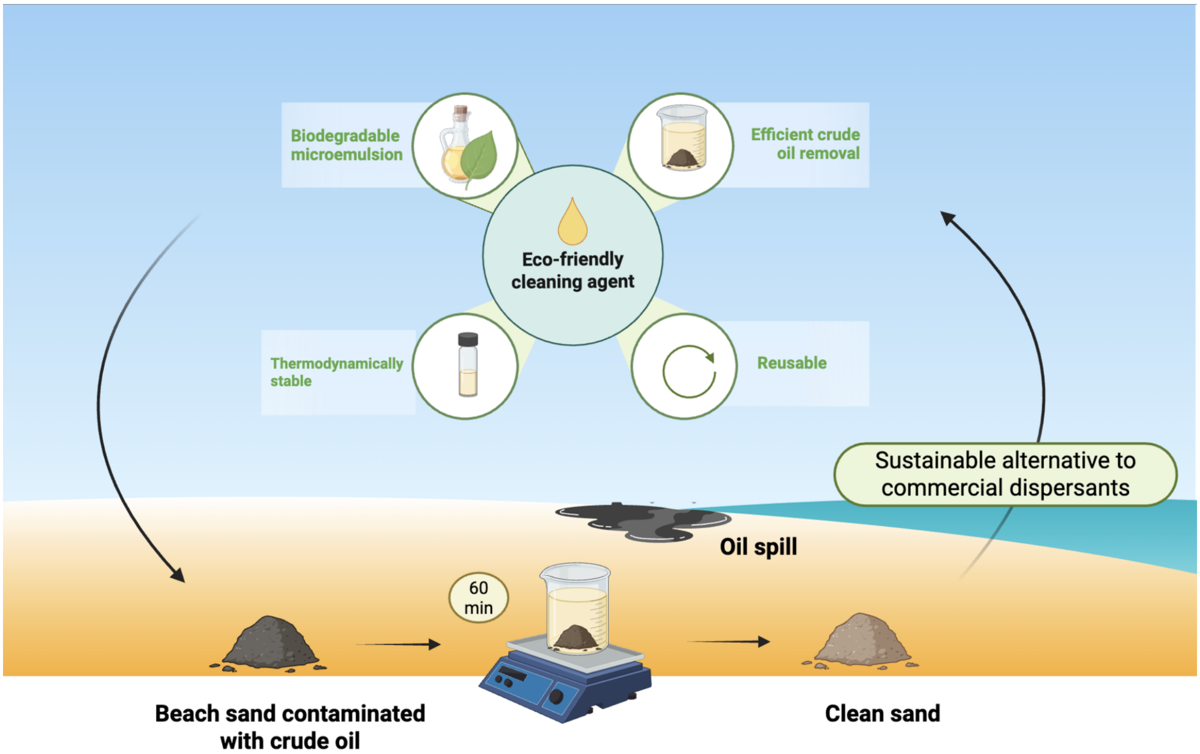
30 days and maintained efficiency for up to five reuse cycles. This study highlights the potential of environmentally friendly microemulsions derived from vegetable oils for effective remediation of beach sand contaminated with crude oil, particularly through in situ soil washing or soil flushing, reinforcing the viability and sustainability of these cleaning agents.

Graphical abstract



Keywords Crude oil spill · Soil flushing · Vegetable oil-based microemulsions · Reuse microemulsion

Introduction

Oil spills constitute a constant threat to coastal ecosystems, causing significant environmental damage (Head et al., 2006; Lim et al., 2016; Short, 2017), and the contamination of beaches and sediments requires effective decontamination measures. Recent events in Brazil and Peru in 2019 and 2022 (Pena et al., 2020; Velasquez Cokche et al., 2023) have highlighted the urgency for efficient and environmentally responsible solutions, given that natural phenomena contribute to the dispersion and burial of oil in coastal sediments (Santos et al., 2023; Wang et al., 2010). Conventional cleanup presents ecological challenges, and in this context, microemulsions (MEs) emerge as a practical, ecological, economical, and efficient alternative (Karthick et al., 2019), especially with plant-derived surfactants.

MEs act by enhancing the separation and removal of oil adhered to solid surfaces (Chen et al., 2020, 2022; Li et al., 2022) and are promising for the remediation of contaminated sands due to greater penetration and efficient oil solubilization (Gu et al., 2020; Hernandez et al., 2019a), reducing the water–oil interfacial tension (Bi et al., 2023; Chen et al., 2020; Gu et al., 2020). Winsor IV type MEs are preferred for solubilizing the extracted hydrophobic component (Amiri-Rigi et al., 2016; Jalali-Jivan and Abbasi 2019; Jalali-Jivan and Abbasi 2020; Jalali-Jivan et al. 2021).

Some studies report the use of other MEs for various purposes (e.g., soil remediation, enhancing oil bioavailability for bacteria during bioremediation, pharmaceutical removal, cosmetics, etc.) that have been formulated with environmentally friendly oil phases, including vegetable and essential oils such as castor oil, pine oil, olive oil, and sunflower oil (Bi et al., 2023; Mahdi et al., 2021; Pakkang et al., 2018; Wang et al., 2024), d-limonene (Campos et al., 2022; Hernandez et al., 2019a), methyl esters of coconut oil, and the saturated fraction of palm oil (Bragato & El Seoud, 2003; Bragato et al., 2002). Terpenic oil phases, such as pine oil, are well-documented for their exceptional solubilization properties, particularly for contaminants rich in asphaltenes and resins, which are characteristic of heavy crude oil (Al-Taq et al., 2019; Berry, Boles, Cawiezel, 2007). Studies using d-limonene-based MEs demonstrated the effective removal of asphaltenic residues even at low concentrations (Hernandez et al., 2019b), and Oliveira et al. (2004) corroborated these findings, reporting removal efficiencies of up to 93% for asphaltenic compounds from sand grains. These findings reinforce the selection of pine oil, a terpenic compound, as the oil phase in the ME system developed in this study.

Despite the documented use of MEs for washing crude oil and its derivatives, and the exploration of plant-derived surfactants (Bragato & El Seoud, 2003; Bragato et al., 2002; Dantas et al., 2007; Haegel et al., 1999; Zhao et al., 2005), few studies have focused on replacing organic phases and surfactants with plant-derived alternatives. Dantas et al. (2007) formulated MEs with saponified coconut oil. Studies have demonstrated the use of methyl esters of coconut oil and the saturated fraction of palm oil from MEs for ex-situ decontamination (Bragato et al., 2002; Hernandez et al., 2019b), and more unsaturated vegetable oils such as babassu oil have also been tested (Santos et al., 2019). The main components of the cleaning agents in the present study, pine oil and saponified coconut oil, are biodegradable.

Previous studies on MEs for remediation of contaminated soils and sediments employed toxic organic solvents such as diesel (Dantas et al., 2007; Gu et al., 2020), benzene (Tolmacheva et al., 2017), kerosene (Pérez et al., 2012), and mixtures of decane, toluene, and cyclohexane (Oliveira et al., 2004), raising environmental and health concerns (Ahmed et al., 2018; Alexander, 1995; Winterton, 2021). Some green MEs have been synthesized for food applications (Qi et al., 2023).

This study presents an innovative approach to remediate crude oil contamination in beach sand using an environmentally friendly ME, formulated with saponified coconut oil as a surfactant and pine oil as the organic phase. This ME is considered environmentally friendly due to its low health and safety risks and its biodegradability (Bi et al., 2020; Capello et al., 2007; Yue et al., 2022), being derived from plant-based sources. Saponified coconut oil is a common and stable anionic surfactant (Phaodee et al., 2020), while pine oil is biodegradable and effective in removing dirt (Prakash et al., 2019). Isopropyl alcohol was selected as a co-surfactant due to its amphiphilic nature, which allows for a reduction in interfacial tension between the aqueous and oil phases and viscosity, its low molecular weight, commonly used to minimize the precipitation of ionic surfactants (Harwell, 1992; Li et al., 2010; Mansell et al., 1996), and its safety profile (Henderson et al., 2011; Volkov et al., 2024).

The ideal formulation of a ME system exhibits desirable viscosity, stability, and pH, among other physicochemical properties (Campos et al., 2022). The effectiveness of microemulsions lies in their unique physical and chemical characteristics (Wang et al., 2019; Zheng et al., 2011). While surfactant solutions often result in unstable macroemulsions in porous media (Oliveira et al., 2004), these systems tend to be highly viscous and may contain relatively large oil droplets that can clog sediment pores (Karthick et al., 2019; Zhou et al., 2000). In contrast, MEs offer significant advantages, such as high stability, superior solubilization capacity, a narrow size distribution of the dispersed phase, and low viscosity (Mahboob et al., 2022; Santos et al., 2023). These properties provide enhanced performance and compatibility of the cleaning agents for their intended application in sediment remediation.

To the best of our knowledge, this is the first comprehensive investigation of vegetable oil-based MEs for the removal of oil from contaminated beach sand using an eco-friendly cleaning agent, exploring the effects of conductivity, viscosity, refractive index, and specific gravity on ME efficiency, along with stability and reusability tests. The low toxicity and high biodegradability of the individual components were also evaluated. Unlike previous studies that used petrochemical solvents or synthetic surfactants, this study introduces a fully plant-based ME, systematically optimized using a simplex lattice design, and evaluates its reusability and long-term stability, distinguishing itself by an integrated and environmentally responsible approach.

Materials and methods

Materials and synthesis of the surfactant

Coconut vegetable oil was purchased from local markets in Salvador, Bahia, Brazil. Saponified coconut oil (soap) was synthesized in the laboratory. The formulation consisted of coconut oil (100 g), sodium hydroxide (NaOH, 18.78 g, Vetec, 100%), calculated stoichiometrically based on the saponification index of the oil following the methodology described by Mascarenhas et al. (2022), and 300 mL of absolute ethyl alcohol (Neon, 99.5%). The NaOH was first dissolved in 80 mL of distilled water and then added to the mixture.

The reaction mixture (coconut oil + NaOH solution + ethanol) was maintained under reflux using a condenser at the boiling point of ethanol (78–80 °C) for 2 h to ensure complete saponification. After reflux, the mixture was transferred to a beaker and gently heated on a hotplate until visible evaporation of ethanol and water ceased and the formation of solid soap began. Final drying was carried out in a convection oven at 40 °C for 24 h to ensure complete removal of residual moisture. The resulting solid soap was ground using a mortar and pestle to facilitate its use as a surfactant in subsequent formulations.

Saponified coconut oil (Figs. S1 and S2, Supplementary Material) was used as the surfactant (S). Isopropyl alcohol (propan-2-ol, C_3H_8O, 98.5%, Vetec) was used as the cosurfactant (C), selected due to its amphiphilic properties and its ability to reduce interfacial tension, as supported by its favorable Hansen Solubility Parameters (HSP: $\delta d \approx 15.8$, $\delta p \approx 6.1$, $\delta h \approx 16.4$ $MPa^{1}/^{2}$). These values indicate effective partitioning at the oil–water interface, thus contributing to ME stability. The cosurfactant/surfactant ratio (C/S = 10) refers to a mass ratio, in which 10 parts by weight of isopropyl alcohol were added for each 1 part of saponified coconut soap. Commercial pine oil was used as the oil phase (OP) and distilled water as the aqueous phase (AP) to prepare the ME.

The sand used in the remediation experiments was collected from a beach near Ondina (Salvador, Bahia, Brazil), sieved through a 40 mesh screen, and dried at 100 °C for 24 h prior to use. The crude oil employed in this study was supplied by Petrobras and originated from the Tangará Field, Recôncavo Basin, Bahia, Brazil. Its properties were as follows: API gravity of 12.78, pour point of 24 °C, specific viscosity of 1298.5 cP, and relative density of 0.9807 at 20 °C (Table S2, Supplementary Material) (Souza et al., 2022). The crude oil was fractionated at the Petroleum Studies Laboratory (Lepetro) using column chromatography with silica gel, resulting in the following composition: saturated hydrocarbons (66%), aromatic hydrocarbons (11%), and polar compounds, including resins and asphaltenes (23%). Analytical-grade hexane was obtained from Synth.

Pseudoternary phase diagram

A pseudoternary phase diagram was constructed to identify ME regions by mixing four components: saponified coconut oil (used as surfactant), pine oil (oil phase), isopropyl alcohol (cosurfactant), and distilled water (aqueous phase). A mixture of surfactant and pine oil was initially prepared using a magnetic stirrer (IKA C-MAG HS) at approximately 300 rpm. The ratio between saponified coconut oil and pine oil varied among formulations, depending on the targeted ME region. In ME1, for example, the ratio was approximately 1:1.83 (w/w), whereas in ME5 it reached 1:22 (w/w).

A known amount of isopropyl alcohol was added to the surfactant phase in all formulations, maintaining a fixed mass ratio of 10:1 relative to the mass of saponified coconut oil. This ratio was defined based on preliminary trials to ensure effective emulsification and stabilization of the MEs. All components were weighed precisely using an analytical balance (Shimadzu AUY220), and each formulation was prepared with a total mass of 30 g. Distilled water was added dropwise to the oil/surfactant/cosurfactant mixture using a syringe until an optically transparent system was obtained. The volume of water added varied depending on the formulation, ranging from 3.0 g in ME5 to 15.0 g in ME3. Throughout the process, the four-component mixture was continuously stirred to allow equilibration, while visual changes from cloudy to transparent were monitored. Once a homogeneous, transparent phase was observed, the system was designated as a stable, single-phase ME.

The compositions of the five selected microemulsions (ME1–ME5) were determined based on mass measurements and are presented in Table 1. Each formulation consists of isopropyl alcohol (co-surfactant), saponified coconut oil (surfactant), pine oil (oil phase), and water (aqueous phase). These were selected from the pseudoternary phase diagram to optimize crude oil solubilization for environmental remediation. The selected points fall within the Winsor IV region, based on their physical stability and potential for oil removal. An experimental mixture design approach (Scheffé, 1963) guided the formulation process for subsequent physicochemical characterization and application in the treatment of crude oil-contaminated sand.

Table 1 Mass-based compositions (in grams) of the selected microemulsions (ME1–ME5) formulated as eco-friendly cleaning agents

Microemulsion	Isopropyl alcohol	Saponified coconut oil	Pine oil	Water
ME1	16.3636	1.6364	3.0000	9.0000
ME2	10.9091	1.0909	9.0000	9.0000
ME3	10.9091	1.0909	3.0000	15.0000
ME4	12.5455	1.2545	5.1000	11.1000
ME5	8.1818	0.8182	18.0000	3.0000

Experimental design for optimization of the ME composition

Experimental design aids in determining the optimal composition based on the relationship between the formulation and oil removal efficiency in sand. Mixture planning was carried out within the stable region of the ME components, and the results were analyzed to determine the ideal formulation (in terms of the best properties for oil solubilization).

Scheffé network statistical planning for mixtures was adopted to optimize the amount of oil (OP), cosurfactant/surfactant ratio (C/S), and distilled water (AP) in the ME. In this study, the levels of the three independent variables, OP, C/S, and AP, were chosen based on the pseudoternary phase diagrams already explained. The planning intended to study the proportion of each component in MEs because they are mixtures whose properties depend on the relative proportions of the components present and not on their concentrations.

After defining the region of interest with the points that constitute the network, the responses of each point were measured according to the techniques presented in Sect. "Characterization of the microemulsified systems" of Microemulsified Systems Characterization. Upon obtaining the model, it was tested, and the more accurately it reflects the behavior of the response variable (Y), the better the model represents the system. Response surfaces were plotted, leading to a more comprehensive evaluation of the properties.

The selection of response variables in this experimental design, conductivity, viscosity, specific gravity, and refractive index, was based on their direct relevance to the physicochemical performance of the ME formulations in oil removal applications. Although other physicochemical properties such as interfacial tension and droplet size distribution are also relevant, these were analyzed independently outside the statistical model (e.g., Table 2 and Sect. "Removal of crude oil from sand"). The selected variables were thus prioritized for their ability to reflect formulation performance in a statistically robust and interpretable model.

Statistica 7.0 software was used for statistical calculations of estimated effects, errors, analysis of variance (ANOVA), and generation of response surfaces with a confidence level of 95%. First, the modeling process applied the Scheffé network (Eq. 1), resulting in a linear system of equations with three unknown variables.

$$Y_i = AX_1 + BX_2 + CX_3 \tag{1}$$

Table 2 Physicochemical characterization of different microemulsion compositions (ME1 to ME5)

Formulation	Composition			Physicochemical properties								
	C/S (%)	Distilled water (%)	Pine Oil (%)	Dynamic viscosity (mPa.s)	Specific gravity (g/cm^3)	Particle Size (nm)	Zeta potential (mV)	Polydispersity	pH	Refractive index	Conductivity (µS/cm)	Interfacial Tension (mN/m)
ME1	60	30	10	3.93	0.88	2.97 ± 0.07	− 3 ± 2	0.39 ± 0.09	9.04 ± 0.01	1.376 ± 0.007	890 ± 30	0.3 ± 0.1
ME2	40	30	30	5.15	0.90	5.7 ± 0.2	− 0.4 ± 0.3	0.19 ± 0.01	8.8 ± 0.1	1.358 ± 0.004	750 ± 40	0.2 ± 0.1
ME3	40	50	10	4.09	0.92	5 ± 1	− 8 ± 2	0.188 ± 0.006	8.74 ± 0.06	1.367 ± 0.009	1800 ± 100	0.5 ± 0.2
ME4	46	37	17	4.48	0.90	2.8 ± 0.3	− 1.7 ± 0.7	0.17 ± 0.08	8.82 ± 0.01	1.37 ± 0.01	1297 ± 7	0.33 ± 0.05
ME5	30	10	60	5.48	0.89	6.5 ± 0.7	− 0.1 ± 0.4	0.22 ± 0.03	9.14 ± 0.01	1.41 ± 0.04	36 ± 3	0.21 ± 0.01

The cleaning agents ME1 to ME5 were formulated using varying proportions of pine oil, distilled water, isopropyl alcohol (C, representing the cosurfactant), and saponified coconut oil (S, representing the surfactant). The C/S values refer to the mass ratio between isopropyl alcohol and saponified coconut oil

where Y represents the response variable, which can encompass conductivity, refractive index, specific gravity, or viscosity. Coefficients A, B, and C signify the relative contribution of each predictor variable (X_1, X_2, X_3) to the response variable Y_i. Factors X_1, X_2, and X_3 correspond to the mass proportions of aqueous phase composition (AP) (%), oil phase composition (OP) (%), and cosurfactant/surfactant ratio composition (C/S) (%), respectively.

Characterization of the microemulsified systems

The physicochemical properties of the ME formulations were analyzed to evaluate their stability and suitability for remediation. Mean particle sizes and polydispersity index (PDI) were measured using Dynamic Light Scattering (DLS) with a Zeta Nano Series instrument equipped with a 4-inch He–Ne laser (633 nm, 4 mW) at 25 ± 0.1 °C. Conductivity, viscosity, refractive index, and pH were measured using a conductivity meter (Atra DS-703A-BI), viscometer (Anton Paar SVM 3000), refractometer (Anton Paar Abbe Mat RXA), and pH meter (Bel Engineering PHS3BW), respectively. For the interfacial tension measurements, we used a KSV CAM 101 tensiometer (KSV Instruments Ltd., Finland). To determine the critical micelle concentration (CMC) of the synthesized surfactant, we measured the surface tension of surfactant solutions at different concentrations at 25 °C using the same tensiometer. Centrifuge stability tests (Quimis Q222T) were performed over 30 days, monitoring visual clarity, phase separation, and color changes.

The toxicity and biodegradability of each component in the cleaning agent formulation were evaluated using data from their respective Safety Data Sheets (SDS), information from recognized official toxicity and biodegradability standards and databases (e.g., OECD guidelines, ECHA database), and corroborated by consulting relevant scientific literature (Chen et al., 2020; Rial et al., 2010; Von Lau, 2014; Winterton, 2021). This comprehensive assessment, drawing from multiple authoritative sources, was conducted to ensure the overall environmental compatibility of the ME formulation.

Remediation studies of sand contaminated with crude oil using ME

Ten grams of sand was contaminated with 0.15 g of crude oil in a beaker. The mixture was homogenized with hexane and transferred to a drying oven (Tecnal TE 393/2) to evaporate the hexane at 30 °C. For the remediation tests, 30 mL of ME of the selected formulations was added to the 10 g of contaminated sand.

The samples were then stirred vigorously using a magnetic stirrer for 1 h at room temperature. After the treatment time was completed, the supernatant was collected with the aid of a graduated pipette. It was then centrifuged at 3000 rpm for 10 min, so that any solid in suspension was decanted and did not influence the reading. The contaminant content present in the sand was determined by extracting the sand with ME and quantifying it on a UV–vis spectrometer based on a predetermined analytical curve (Fig. S3). The ME system was decanted, and distilled water was used to slowly rinse the oiled sand and flask three times to remove the ME residue. The rinsed sand was placed in an oven at 50 °C for 3 h to evaporate the water content, and then the remaining oil was extracted with solvent (hexane/heptane) through vacuum filtration until the sand was thoroughly cleaned. The volume of solvent used varied according to the ME formulation. Approximately 70 mL of solvent were used for sand samples treated with ME1 to ME4, while only 30 mL were required for samples treated with ME5, due to its lower water content and higher oil solubilization efficiency.

All remediation experiments were performed in triplicate, and the mean values ± standard deviation (SD) are reported for each experiment to ensure reproducibility and statistical reliability.

Reuse studies of ME

For this experiment, 10 g of crude oil contaminated sand was combined with 30 mL of fresh ME (formulation ME1) to conduct the remediation test under the specified parameters (60 min wash period, 300 rpm spin speed, and at 25 °C). The petroleum-laden ME was separated from the remediated sand using a syringe, and insoluble impurities were subsequently removed using PTFE filters with a 0.45 µm pore size. The previously used ME was then mixed with an equivalent amount of new crude oil-contaminated sand to repeat the remediation procedure. This process was performed across five consecutive reuse cycles, without intermediate treatment between cycles.

The reuse studies were also conducted in triplicate, following the same parameters, to evaluate the reproducibility and robustness of the ME formulations under multiple remediation cycles.

Analytical methods

Given that the ME is oil-based and contains pine oil, saponified coconut oil, isopropyl alcohol, and water, the analytical methods were selected to focus on quantifying the crude oil removed by the ME. Fourier Transform Infrared (FTIR) spectroscopy (Shimadzu IRP Prestige-21) was used to identify functional groups in pristine sand, crude oil-contaminated sand, and ME-remediated sand. Solid samples were analyzed using potassium bromide pellets, and liquid samples, including ME and its extract, were evaluated by ATR-FTIR (ZnSe crystal). Spectra were recorded over the range of 4000–400 cm^{-1}. The technique enabled the detection of crude oil residues and verification of ME component stability after remediation (Bi et al., 2023; Feng et al., 2023; Zhang et al., 2021). The FTIR spectrum of the synthesized saponified coconut oil is shown in Figure S2, and band assignments are provided in Table S1 (Supplementary Material).

For quantitative analysis, UV–Vis spectroscopy (Shimadzu UV-3600 Plus) was used to measure the crude oil content in sand samples (Hernandez et al., 2019b). Calibration curves were developed using crude oil solutions (10–90 mg/L) in hexane at room temperature (25 ± 1 °C). The absorbance versus concentration curve provided the basis for quantification. A total of 0.15 g of crude oil was used to contaminate each 10 g sand sample. The mixture was homogenized with the assistance of a glass rod and hexane solvent to prevent oil impregnation on the beaker walls. Subsequently, the mixture was placed in an oven at 40 °C for 1 h to enhance oil impregnation into the sand and completely remove the solvent.

The remediation efficiency was calculated using Eq. 2, where %E represents the percentage of oil removed relative to the initial oil content.

$$\%E = \left(C_i - C_f / C_i\right) * 100 \tag{2}$$

where %E is the oil removal efficiency, C_i (mass%) is the original oil content in the sand, and C_f (mass%) is the oil content after washing with the ME.

This approach ensures a robust evaluation of the ME's efficiency in crude oil removal while addressing the study's primary objective. Although a more detailed characterization of the ME components was beyond the scope of this work, the methodology provides reliable data to support the environmental compatibility and effectiveness of the formulation. All experiments were performed in triplicate for each ME, and the average values ± standard deviation (SD) were used for data analysis.

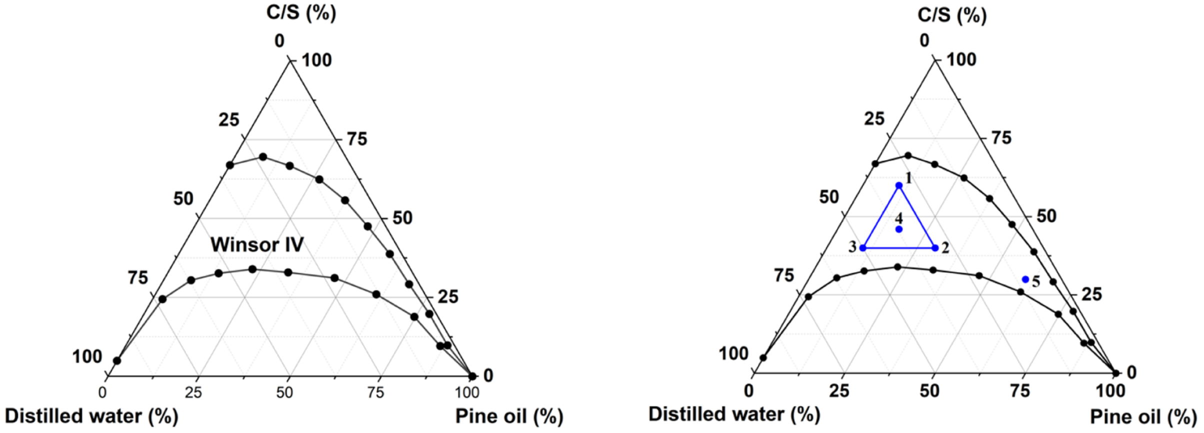
Results and discussion

Pseudoternary phase diagram

The construction of the pseudoternary phase diagram (Fig. 1) revealed that the monophasic region of the microemulsion (ME), characterized as Winsor IV, represents a stable system in which pine oil, the cosurfactant (isopropyl alcohol), and water are fully solubilized with the saponified coconut oil surfactant. This region is significant due to the high population of micelles, which is critical for the efficient solubilization of hydrophobic components (Silva et al., 2020). The CMC of the saponified coconut oil surfactant was calculated to be 0.83 g/L, closely matching the value of 0.8 g/L reported by Curbelo et al. (2020), further validating the surfactant's efficiency in microemulsion formation. The main finding of this section is that the Winsor IV region provides a foundation for selecting optimal ME formulations tailored for crude oil remediation.

Experiment planning helps to determine a model that determines the relationship between variables and identifies the optimal composition for the ME. ME formulations were developed through statistical planning of the Scheffé network to optimize the amount of pine oil (OP), the cosurfactant/surfactant ratio (C/S), and distilled water (AP) in the ME. The levels of the three independent variables, OP, C/S, and AP, were chosen based on the pseudoternary phase diagram presented in Fig. 1. The optimization study was performed in the stable region of the ME components.

The Scheffé model was employed to select points within the Winsor IV region. Utilizing a first-degree



(a)

(b)

Fig. 1 Pseudoternary diagram using C = Isopropyl alcohol, S = Saponified coconut vegetable oil, AP = Distilled water, OP = Pine oil (C/S = 10). **a** Monophasic region of Winsor IV; **b** Microemulsions points (ME1 to ME4) belonging to the Scheffé network, and ME5, which is the most oil-rich formulation. ME1 (10% OP, 60% C/S, 30% AP), ME2 (30% OP, 40% C/S, 30% AP), ME3 (10% OP, 40% C/S, 50% AP), ME4 (17% OP, 46% C/S, 37% AP), ME5 (60% OP, 30% C/S, 10% AP). The blue triangle in diagram (**b**) outlines the experimental region for the Scheffé simplex lattice design, with vertices at ME1, ME2, and ME3, and the centroid at ME4 linear model, an equilateral triangle was constructed within the targeted region under study, where each vertex (ME1, ME2, and ME3) represents a point under investigation, and the central point (ME4) within the triangle serves for system validation (Fig. 1b). Point ME5, located outside the Scheffé network, was also selected to investigate the formulation of the ME with the highest oil content.

Physicochemical characterization of the microemulsions

The physicochemical characterization of the microemulsions (MEs) revealed that ME5 stood out as the most effective formulation for environmental remediation, combining the lowest interfacial tension (0.21 ± 0.01 mN/m), a relatively small particle size (6.5 ± 0.7 nm), and the highest dynamic viscosity among the formulations (5.48 mPa.s). Despite its higher viscosity, ME5's composition, rich in pine oil and with a low aqueous content, enhances its ability to solubilize hydrophobic contaminants and facilitates efficient interaction with oil trapped in sediment pores. Its water-in-oil (W/O) structure, low conductivity (36 ± 3 µS/cm), thermodynamic stability, and eco-friendly components further support its application in the remediation of crude oil-contaminated sandy environments. The physicochemical properties of the formulations, including specific gravity, viscosity, conductivity, refractive index, pH, particle size, zeta potential, and polydispersity, were measured and are presented in Table 2. All measurements were conducted at a constant temperature of 25 °C.

The physicochemical properties of the formulated MEs were systematically evaluated to elucidate their structural characteristics and potential effectiveness for environmental remediation. All formulations exhibited ultra-low interfacial tension (IFT) values (0.21–0.5 mN/m), a key parameter for efficient oil removal. ME5, which contained the highest pine oil content (60%), showed the lowest IFT value (0.21 ± 0.01 mN/m). This is particularly advantageous, as IFT values in the range of 0.1–0.2 mN/m are considered optimal for mobilizing and solubilizing trapped oil (Tanthakit et al., 2008, 2009). The low IFT observed, especially for ME5, highlights its strong potential for effective spreading and solubilization of oil from contaminated matrices.

Electrical conductivity measurements provided insights into the internal microstructures of the MEs. Conductivity ranged from 36 ± 3 µS/cm (ME5) to 1800 ± 100 µS/cm (ME3). The high conductivity of ME3 (50% aqueous phase) indicates an oil-in-water (O/W) structure (Callender & Wettig, 2021), in which the continuous aqueous phase facilitates ionic transport. Conversely, the very low conductivity of ME5 (10% aqueous phase, 60% pine oil) suggests a water-in-oil (W/O) structure, where dispersed water droplets are insulated by the continuous oil phase. Intermediate values for ME1, ME2, and ME4 (750–1297 µS/cm) suggest bicontinuous systems. These structural transitions, influenced by the water content, are consistent with percolation phenomena described in the literature (Bera et al., 2011; Giustini et al., 1996). The presence of isopropyl alcohol, acting as a hydrophilic cosurfactant, likely enhances ion transport across interfaces, particularly in formulations with continuous or co-continuous aqueous phases.

Nanostructure confirmation was supported by dynamic light scattering (DLS), which revealed average particle sizes ranging from 2.8 to 6.5 nm. ME4 (2.8 ± 0.3 nm) and ME1 (2.97 ± 0.07 nm) had the smallest droplets. This ultra-fine size distribution is attributed to the synergistic effects of: (i) the efficient interfacial activity of saponified coconut oil, rich in lauric acid (a short-chain fatty acid), and isopropyl alcohol at the selected C/S ratio (C/S = 10), which together create a highly flexible interfacial film; (ii) the physicochemical nature of pine oil, which may facilitate the formation of smaller aggregates compared to more viscous oils; and (iii) the spontaneous emulsification process yielding thermodynamically stable, nanoscale droplets. PDI values (0.17–0.39) confirmed good monodispersity, with ME4 exhibiting the most uniform distribution. Zeta potential values ranged from –0.1 to –8 mV. Although relatively low, the negative surface charges, particularly in ME3 and ME4, may enhance colloidal stability by reducing droplet aggregation. These small particle sizes are favorable for environmental remediation, as they enable deeper penetration into porous matrices such as contaminated sediments.

All formulations demonstrated low viscosity, ranging from 3.93 mPa.s (ME1) to 5.48 mPa.s (ME5). These values are significantly lower than those typically reported for MEs in the literature, particularly those based on more viscous oils or higher surfactant content, as described by Santanna et al. (2009), and Bi et al. (2023). The low viscosity is likely a result of: (i) the effective role of isopropyl alcohol in reducing interfacial tension and disrupting micellar packing; (ii) the relatively low viscosity of pine oil compared to other common oil phases; and (iii) the spherical morphology of nanodroplets, which reduces flow resistance. MEs with higher isopropyl alcohol content (ME1, ME3, ME4) exhibited the lowest viscosities. Low viscosity is a critical parameter in practical applications, enabling easier handling and improved mobility through porous media.

Refractive index measurements were consistent across all MEs (1.358–1.41), confirming isotropic, transparent systems characteristic of true microemulsions. Centrifugation and 30-day storage tests confirmed their long-term stability, with no signs of phase separation or visual changes, further supporting their classification as Winsor IV systems.

Regarding novelty and environmental relevance, while various studies have explored MEs with environmentally friendly oil phases (see Table S5), many still rely on petroleum-derived surfactants or yield less favorable physicochemical profiles, such as high viscosity. The MEs developed in this study are fully plant-based, employing saponified coconut oil as the surfactant, pine oil as the oil phase, and isopropyl alcohol as the cosurfactant. All components exhibit low toxicity and high biodegradability (as detailed in Sect. "Evaluation of the stability, homogeneity, and biodegradability/toxicity of microemulsion ingredients based on Safety Data Sheets" and Table S6). To our knowledge, this is the first study to report such a formulation that combines ultra-low IFT, exceptionally small droplet size, and notably low viscosity, key parameters for maximizing efficiency in in situ sediment remediation. These findings represent a substantial advancement toward developing sustainable, high-performance microemulsion-based systems for the treatment of oil-contaminated environments (Childs et al., 2004).

Evaluation of the stability, homogeneity, and biodegradability/toxicity of microemulsion ingredients based on safety data sheets

The MEs maintained stability and homogeneity for more than 30 days at room temperature without phase separation (Fig. S4 and S5 in the supplementary material). After this period, the coloration changed from transparent to yellow, possibly due to the oxidative degradation of pine oil (Amiri-Rigi et al., 2020). Theoretical assessment, based on Safety Data Sheets (SDS) and regulatory references, indicates that formulations containing pine oil and saponified coconut oil exhibit high biodegradability and low toxicity within the regulatory criteria for environmentally safe formulations.

Unlike conventional dispersants, which contain synthetic surfactants and petrochemical solvents that pose risks to marine fauna (Mingxin et al., 2014; Okeke et al., 2022; Rebello et al., 2014), MEs utilize plant-based surfactants and oil phases without hazardous co-solvents. ME5 stood out for balancing stability and exhibiting biodegradability characteristics in crude oil remediation. Table S6 summarizes the characteristics of the components based on data from the European Chemicals Agency (ECHA) and Sigma-Aldrich, indicating that saponified coconut oil has high biodegradability, meets the criteria of Regulation (EC) No. 648/2004, and is classified as non-persistent, non-bioaccumulative, and non-toxic (non-PBT/vPvB), reinforcing its environmental compatibility. Pine oil also demonstrates rapid biodegradation. In contrast, isopropyl alcohol, although biodegradable, does not meet the 10-day window criterion and exhibits moderate toxicity at high concentrations. However, its non-PBT or vPvB classification justifies its application in environmentally safe formulations. While this study evaluated individual components, assessing the effects of complete formulations on living organisms requires ecotoxicological testing (Kulikova et al., 2021), which is beyond the scope of this research. Table S7 compares the toxicity and biodegradability of saponified coconut oil, Triton X-100 (Bi et al., 2023), and ethylene glycol monobutyl ether (Shang et al., 2024), reinforcing the necessity of replacing potentially harmful compounds with more environmentally compatible alternatives.

SDS data indicate that the toxicity of ME1 to ME5 formulations depends on the proportions of their components, with higher concentrations of pine oil and isopropyl alcohol increasing the risk of residual toxicity. Pine oil, essential for solubilizing hydrophobic contaminants, exhibits moderate aquatic toxicity at high concentrations, as in ME5 (60% pine oil). In contrast, ME1 (10% pine oil) has lower toxicity due to greater dilution of the oil phase. Isopropyl alcohol, although biodegradable, also exhibits moderate toxicity at high concentrations. However, in ME1, its higher water content potentially reduces this impact compared to ME5. The balance between the oil and aqueous phases directly influences the ecological compatibility of the formulations. The composition of ME5 suggests greater efficiency in crude oil removal but with a potential risk of higher residual toxicity due to its higher content of pine oil and isopropyl alcohol. On the other hand, ME1 and ME2, with lower oil phase content, have lower predicted toxicity but may compromise remediation efficiency.

MEs minimize the use of large volumes of organic solvents, offering a viable and more sustainable alternative to conventional remediation methods (Qin et al., 2022). Pine oil, used as the oil phase in this study, demonstrated effective solubilization of hydrophobic contaminants due to its physicochemical properties. Although pine oil may present moderate toxicity to aquatic organisms, its performance and biodegradability justify its application when compared to petroleum-based solvents. The assessment of solvent performance should consider not only removal efficiency but also environmental compatibility and operational safety (Hessel et al., 2022). Therefore, future investigations should incorporate targeted ecotoxicity tests to validate the environmental safety of the ME formulations, supporting their application in specific remediation contexts (Balaraman et al., 2021; Queffelec et al., 2024).

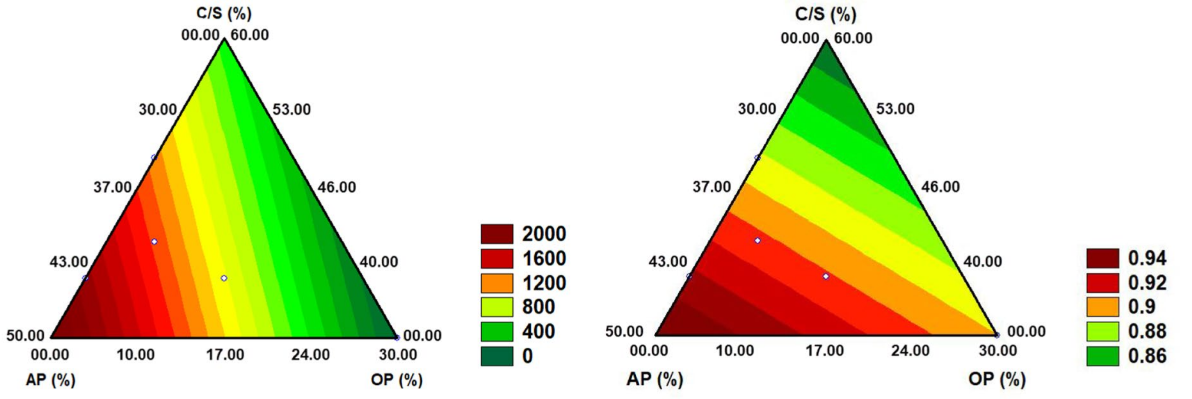
Experimental planning of mixtures for selected microemulsions

The experimental design of mixtures successfully established the relationship between the composition of microemulsions (MEs) and their physicochemical characteristics, revealing that aqueous phase content predominantly influences conductivity, while pine oil concentration significantly affects viscosity and specific gravity. Among the key findings, formulations with higher water content, such as ME3, exhibited higher conductivity and specific gravity values closer to water, indicative of oil-in-water (O/W) systems. Conversely, ME5, with its higher pine oil content, demonstrated lower conductivity and increased viscosity, characteristic of water-in-oil (W/O) systems. The statistical models for conductivity, specific gravity, and dynamic viscosity were validated, with F-values and p-values indicating high reliability, highlighting the robustness of the experimental approach for designing eco-friendly MEs tailored for environmental remediation.

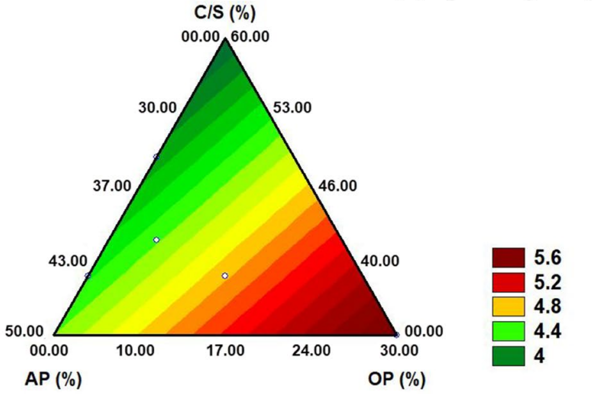
A four-run mixing design was performed in an experimental region defined by constraints on three components: aqueous (distilled water, AP), oil (pine oil, OP), and C/S ratio. From the results of conductivity, refractive index, specific gravity, and dynamic viscosity for the different compositions of MEs (ME1 to ME5), it was possible to generate regression equations according to the linear model, choosing those that satisfy a level of significance of 5%. The statistical model equations for the investigated physicochemical parameters of the MEs are presented in Table S3 in the supplementary material.

Analysis of the key statistical parameters (F-test, *p*-value, coefficient of multiple determination, predicted R^2, and adjusted coefficient of multiple determination, adjusted R^2) reveals that the equation models for the response variables conductivity, specific gravity, and dynamic viscosity are statistically significant at the stipulated level (p-value ≤ 0.05).

A high *p*-value (greater than 0.05) indicates that the regression for the refractive index response variable is not statistically significant. Consequently, the corresponding model should not be used to draw conclusions about the behavior of this variable. Furthermore, since the calculated F-value is lower than the tabulated F-value, the model for describing the refractive index is deemed not significant. Additionally, the ANOVA table (Table S4 in the supplementary material) also shows that all model components, AP, OP, and C/S, are significant terms in the models because their *p*-values are less than 0.05, except for the OP term for the conductivity model. This exception can be attributed to the



(a) Condutivicty **(b) Specific gravity**



(c) Dynamic viscosity

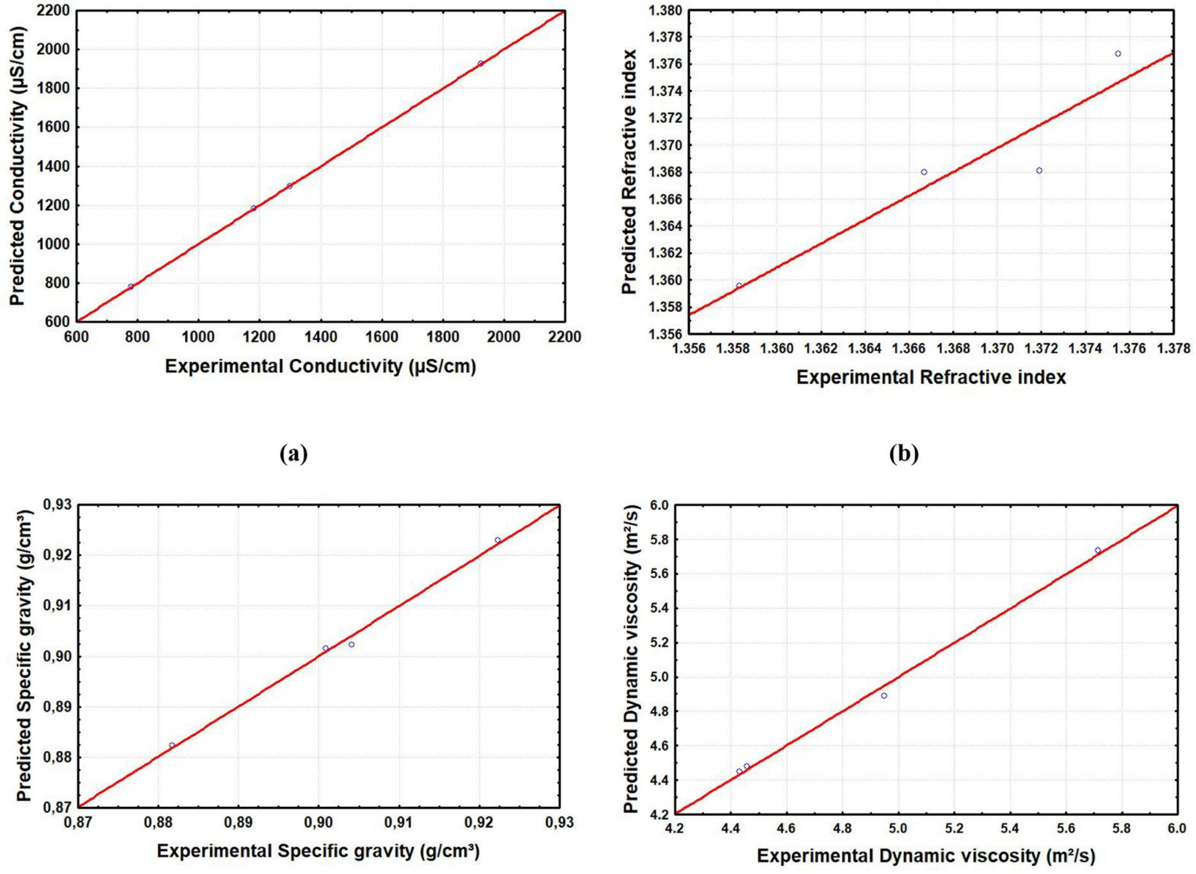
Fig. 2 Contour plot with the equations of the physicochemical parameters of the studied MEs: **a** effect of variables on the conductivity response; **b** effect of variables on the specific gravity response; **c** effect of variables on the dynamic viscosity response. The compositions of the microemulsions are as follows: ME1 (10% OP, 60% C/S, 30% AP); ME2 (30% OP, 40% C/S, 30% AP); ME3 (10% OP, 40% C/S, 50% AP); ME4 (17% OP, 46% C/S, 37% AP); ME5 (60% OP, 30% C/S, 10% AP)

low polarity and non-ionic character of pine oil, which has minimal influence on ionic conduction. Electrical conductivity in ME systems is primarily affected by the aqueous phase, which contains mobile ions, and by the composition of the surfactant and cosurfactant. Therefore, the stronger influence of AP and C/S on conductivity is consistent with their role in modulating the ionic environment of the microemulsions.

The cotour plots depicted in Fig. 2a illustrate that conductivity is predominantly affected by MEs with higher aqueous phase concentrations. Higher pine oil concentrations lead to lower conductivity of the ME, as shown in Fig. 2a. Formulations with low conductivity are classified as water-in-oil (W/O) microemulsions, according to the classification criteria established by Qi et al. (2023) and Gradzielski et al. (2021).

Figure 2b presents the specific gravity for the ME formulations. As observed, the specific gravity values are quite close to the specific gravity of water at the same temperature, which is 0.97 g/cm^3. This is particularly evident for ME3, which has a high-water content in its composition, while ME5 has a specific gravity closer to that of the organic phase. This observation is aligned with the percolation theory, which suggests that the density of MEs is influenced by the continuous phase within the system. In O/W MEs, where water is the continuous phase, the specific gravity is expected to be close to the one of water.

Additionally, Fig. 2c indicates that the viscosity of the ME increases proportionally with the inclusion of



(a) (b)

(c) (d)

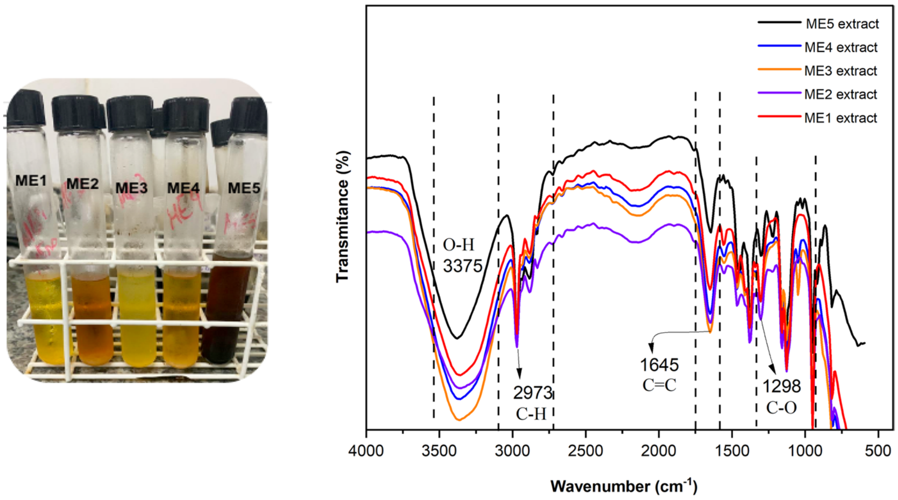
Fig. 3 Predicted versus observed physical properties of: **a** conductivity, **b** refractive index, **c** specific gravity, **d** dynamic viscosity

pine oil in the mixture. The plot comparing the predicted and experimental physical properties of the MEs is shown in Fig. 3.

The results in Table 2 and Figs. 2 and 3 suggest that the experimental design of mixtures successfully estimated the response surface that describes the relationship between the ME composition and its physicochemical characteristics, except for the refractive index model. These physicochemical properties, modeled through the experimental design, are directly related to the performance of the microemulsions in crude oil removal, as further discussed in Sect. "Removal of crude oil from sand". For example, lower viscosity and interfacial tension facilitate microemulsion penetration into sand pores and enhance the solubilization of hydrophobic contaminants, guiding the selection of the most effective formulations for remediation.

Removal of crude oil from sand

The evaluation of crude oil removal from contaminated sand demonstrated that MEs with higher oil-phase content, particularly ME5, achieved superior performance, with an oil removal efficiency of 93.46%. This effectiveness is attributed to the optimized composition of ME5, which combines a high pine oil content (60%) with a balanced aqueous phase, resulting in low interfacial tension (0.21 ± 0.01 mN/m, Table 2), enhanced solubilization of hydrophobic compounds, and improved penetration into sediment pores. Despite ME5's higher viscosity (5.48 mPa·s, Table 2), its exceptional removal



(a)

(b)

Fig. 4 **a** Photograph of extracts from ME1 to ME5 after remediation with oily sand, illustrating variations in color intensity. Darker colors correspond to higher crude oil content extracted, reflecting the efficiency of each formulation. **b** FTIR spectra of ME extracts after remediation, showing key peaks corresponding to functional groups such as O–H, C–H, and C–O, which highlight the differences among the formulations. The compositions of the microemulsions are as follows: ME1 (10% OP, 60% C/S, 30% AP), ME2 (30% OP, 40% C/S, 30% AP), ME3 (10% OP, 40% C/S, 50% AP), ME4 (17% OP, 46% C/S, 37% AP), and ME5 (60% OP, 30% C/S, 10% AP). These compositions represent varying ratios of pine oil, saponified coconut oil, isopropyl alcohol, and distilled water, influencing their performance in crude oil extraction

efficiency suggests that mass transfer limitations were minimal. This is likely due to the experimental conditions applied during the remediation process, which involved controlled mechanical mixing at 300 rpm and a sufficient contact time of 1 h (Sect. "Remediation studies of sand contaminated with crude oil using ME"). Together with the low interfacial tension, these conditions ensured effective interaction between the microemulsion and the contaminated sand.

FTIR analysis confirmed ME5's efficiency in hydrocarbon removal, evidenced by the significant reduction of hydrocarbon-related peaks in the treated sand and the presence of characteristic peaks from ME compounds incorporated during the process. Furthermore, ME5 demonstrated significant advantages compared to the use of 60% pine oil in its formulation, as the microemulsion system combines greater solubilization capacity with properties that promote environmental remediation. These findings highlight the effectiveness of Winsor IV-type MEs in remediating crude oil-contaminated environments, outperforming traditional solvents in both performance and environmental adaptability.

The solubility of crude oil in contaminated sand was investigated using different extraction media, including MEs formulated as cleaning agents (ME1 to ME5) (Fig. 4a). The FTIR spectra of the cleaning agents extracted after remediation were analyzed to evaluate the performance of these MEs (Fig. 4b).

The FTIR spectra identified characteristic functional groups associated with crude oil and ME components. The intense bands in the 3000–2700 cm^{-1} range correspond to C–H stretching vibrations, indicating hydrocarbons, while peaks between 1300 and 900 cm^{-1} suggest the presence of C–O bonds from acid groups, alcohols, phenols, ethers, and esters. These interpretations are based on our experimental data and are consistent with the findings reported by Lovatti et al. (2019). Among the tested formulations, ME5 exhibited the most intense bands, demonstrating a superior capability to extract hydrophobic compounds. ME3, on the other hand, showed stronger O–H stretching vibrations in the 3000–3500 cm^{-1} range, indicative of a higher water content.

The use of Winsor IV-type MEs represents a promising approach, as such systems are preferred

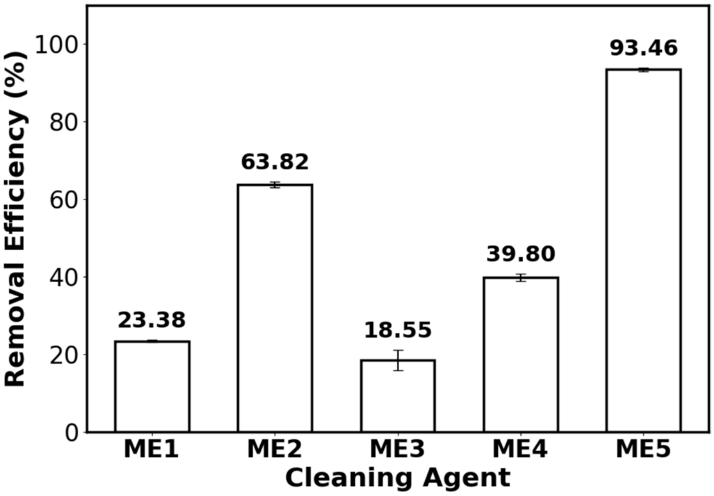


Fig. 5 Crude oil removal efficiency of microemulsions (ME1 to ME5) under identical remediation conditions. Error bars represent the standard deviation of three replicates. The efficiency increases with a higher oil-phase content in the ME composition. The formulations are as follows: ME1 (10% OP, 60% C/S, 30% AP), ME2 (30% OP, 40% C/S, 30% AP), ME3 (10% OP, 40% C/S, 50% AP), ME4 (17% OP, 46% C/S, 37% AP), and ME5 (60% OP, 30% C/S, 10% AP). These variations in composition highlight the relationship between oil-phase content and crude oil removal performance

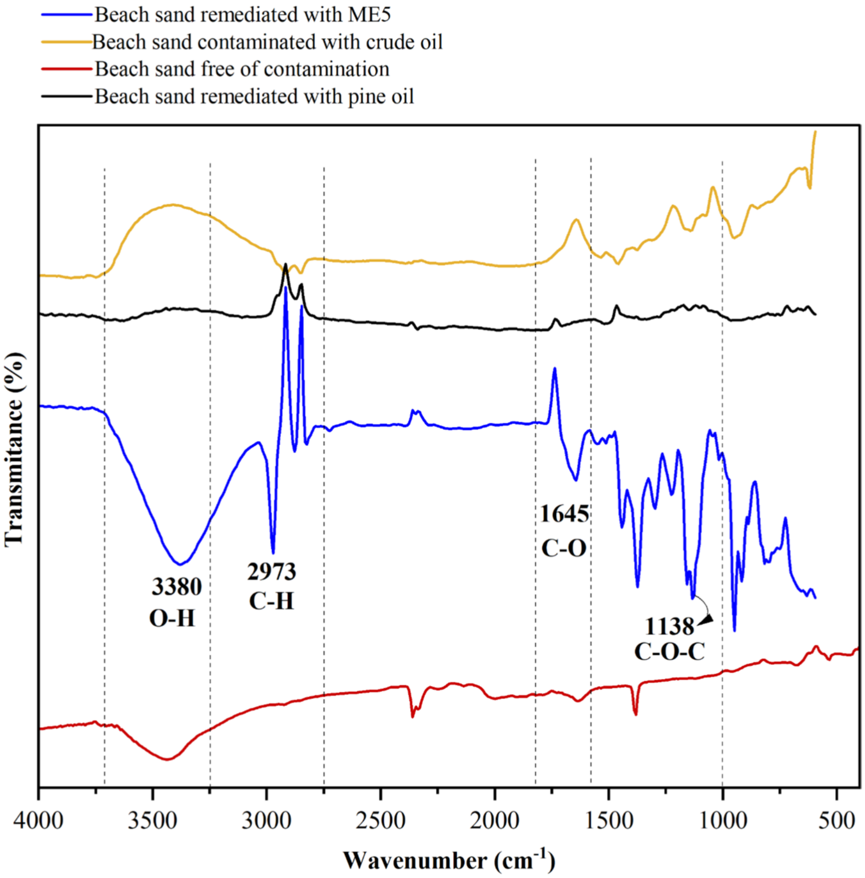


Fig. 6 FTIR spectra of beach sand under various conditions: before contamination, after contamination with crude oil, after cleaning with pine oil, and after cleaning with ME5. Key functional groups (e.g., O–H, C–H, C–O–C, C–O) are labeled to illustrate the hydrocarbon reduction

for solubilizing or utilizing extracted hydrophobic components in a microemulsified form (Amiri-Rigi et al., 2016). All washing experiments were performed under identical conditions, as described in Sect. "Remediation studies of sand contaminated with crude oil using ME". The results showed that the oil removal efficiency increased with a higher oil phase content in the ME composition (Fig. 5).

The results in Fig. 5 highlight the solvent role of MEs in oil extraction. Visual comparison of ME samples before and after washing (Figures S4, supplementary material, and Fig. 4a) revealed distinct color changes, confirming the solvent action. ME5, initially yellow due to its high pine oil content, turned black after extraction, signifying effective crude oil removal. FTIR results supported these observations, showing ME5's ability to extract hydrophobic compounds efficiently. For additional details on sand remediated with ME followed by solvents (hexane or heptane), refer to Fig. S6.

FTIR analysis of ME5-remediated sand (Fig. 6) confirmed, based on our experimental data, the presence of hydrocarbons, such as paraffins and olefins, along with carboxylic and aromatic acids. Absorption peaks in the 3000–2800 cm^{-1} range correspond to C-H stretching vibrations, while peaks at 1700–1600 cm^{-1} indicate carbonyl compounds. These assignments are consistent with the spectral interpretation criteria reported by Feng et al. (2023). Compared to crude oil-contaminated sand, ME5-treated sand showed reduced hydrocarbon-related peaks, while new peaks in the 1300–1000 cm^{-1} range suggested the incorporation of ME compounds during the cleaning process.

For comparison, pine oil also reduced hydrocarbon-related peaks in the contaminated sand, as shown in Fig. 6. However, CH absorption peaks (2920–2850 cm^{-1}) revealed residual pine oil components, indicating limited desorption and solubilization compared to ME5.

The efficiency of crude oil removal increased with a higher oil phase content in the ME composition (Hernandez et al., 2019b). Among the tested formulations, ME5 and ME2 demonstrated superior performance due to their enhanced solubilization of oil, as evidenced by their high removal efficiencies shown in Fig. 5. Conversely, ME3 and ME4 exhibited behavior more consistent with the mobilization or displacement of contaminants rather than complete solubilization, resulting in lower removal percentages. These findings align with previous studies, which emphasize the preference for Winsor IV MEs in scenarios requiring efficient solubilization of hydrophobic contaminants (Amiri-Rigi et al., 2019).

MEs, such as ME5, offer significant advantages over neat pine oil due to their ability to reduce interfacial tension between oil and water, facilitating hydrocarbon release from sediment matrices. ME5's low viscosity promotes deeper penetration into sand pores, improving contact with embedded hydrocarbons, while its thermodynamic stability ensures consistent performance over time (Bragato et al., 2002; Qin et al., 2022).

Studies by Wang et al. (2024) and Bi et al. (2023) showed that MEs formulated with anionic and nonionic surfactants and vegetable oil as the oil phase achieved oil removal efficiencies of 73.6% and 86.8%, respectively, for crude oil and diesel oil in soils and sediments. However, the efficiency obtained in this study (93.46%) surpasses these values. Importantly, the high efficiency of ME5 was achieved at 25 °C, consuming less energy compared to the elevated temperatures (e.g., 35 °C) required in other studies (Wang et al., 2024). Additionally, Bi et al. (2023) required a higher surfactant content (62.5% C/S), which increased the viscosity of the cleaning agent, highlighting the optimized formulation of ME5.

The terpenic oil-phase ME demonstrated high solubility for the contaminants studied, particularly those rich in asphaltenes and resins (66%), characteristic of heavy crude oil. Terpenic compounds are well-known for their exceptional ability to disperse asphaltenes (Al-Taq et al., 2019; Berry, Boles, Cawiezel, 2007). Recent studies further validate the effectiveness of eco-friendly solvents like terpenes. For example, d-limonene-based MEs have shown promising results in removing asphaltenic residues even at low solvent concentrations (Hernandez et al., 2019b). Oliveira et al. (2004) corroborated these findings, demonstrating that terpenic MEs can remove up to 93% of asphaltenic residue from sand grains.

Microemulsions (MEs) incorporating a terpenic oil phase are recognized for their effectiveness in solubilizing and removing various crude oil contaminants. For the Tangará crude oil used in this study, which is predominantly composed of saturated hydrocarbons (66%) alongside aromatic (11%) and polar (23%) fractions, terpenic MEs offer a potent approach for remediation. While terpenic compounds are widely acclaimed for their exceptional ability to disperse and solubilize more challenging components like asphaltenes (Al-Taq et al., 2019; Berry, Boles, Cawiezel, 2007), their strong solvent action is also highly effective for other hydrocarbon fractions, including saturates. The mechanism often involves the terpene penetrating the oil residue, reducing its viscosity, and facilitating its mobilization and dispersion by the microemulsion system.

Recent studies further validate the effectiveness of eco-friendly solvents like terpenes in such applications. For example, Hernandez et al. (2019b) demonstrated that d-limonene-based MEs achieved significant removal of crude oil residues from sand. They attributed this to d-limonene's ability to diffuse into and soften the residue layer, a mechanism that would be beneficial for mobilizing a saturate-rich oil as well. Corroborating the general efficacy of these systems for petroleum contaminants, Oliveira et al. (2004) showed that MEs formulated with terpenic oil phases (such as orange oil or other terpenes) could remove up to 93% of an asphaltenic residue from sand grains, underscoring the potent cleaning action of terpenic microemulsions. Thus, the use of a terpenic oil-phase ME is well-justified for enhancing the removal of the saturate-rich Tangará crude oil.

FTIR analysis was performed on sand samples remediated with ME5, and the resulting spectra are presented in Fig. 6. These spectra revealed characteristic absorption bands, including C–H stretching (around 2973 cm^{-1}) and C–O stretching (near 1298 cm^{-1}), indicating the presence of residual ME compounds in the treated sand. While these findings confirm the efficacy of the ME system in crude oil removal, they also raise important considerations regarding the environmental interaction of leftover components. Notably, ME5 exhibited the highest removal efficiency (93.46%) but also contained a greater proportion of pine oil, which may influence toxicity levels. To address potential concerns about residuals, our approach leverages the inherent biodegradability of all ME constituents, saponified coconut oil, pine oil, and isopropyl alcohol, which were specifically selected for their low toxicity and environmental compatibility (Sect. "Evaluation of the stability, homogeneity, and biodegradability/toxicity of microemulsion ingredients based on Safety Data Sheets"; Table S6). As such, any remaining residues are expected to degrade naturally over time through microbial activity. In addition, a post-remediation water rinse may be employed to remove loosely bound ME fractions, further minimizing environmental persistence. These strategies, combined with natural attenuation processes such as tidal action or water percolation in coastal settings, provide a sustainable framework for managing potential residues associated with ME-based remediation.

The variation in oil-phase content among the formulations (ME1 to ME5) significantly impacted both performance and potential environmental risks. For instance, formulations with higher oil-phase content (e.g., ME5) achieved superior solubilization of crude oil, but may leave higher residual concentrations of hydrophobic components. These observations align with previous studies (Hernandez et al., 2019b; Oliveira et al., 2004), which demonstrated the effectiveness and environmental implications of terpenic solvents.

The extraction efficiency of MEs for hydrophobic fractions of crude oil, such as saturated hydrocarbons, resins, and asphaltenes, is higher than that observed for pure pine oil or nonpolar solvents. This superior performance is attributed to the nanostructured organization of MEs, which facilitates penetration into porous media and promotes the solubilization of lipophilic compounds. By reducing interfacial tension and enabling more effective dispersion of oil residues, MEs not only enhance remediation efficiency but also minimize the volume of organic solvents needed, reinforcing their classification as sustainable and eco-friendly alternatives (Qin et al., 2022).

Reuse of ME

The reuse evaluation of ME5 demonstrated its initial effectiveness in crude oil removal across five consecutive remediation cycles, without the need for intermediate regeneration. In the first cycle, ME5 achieved a removal efficiency of 93.46%; however, this value gradually declined over subsequent cycles, reaching 25.01% by the fifth cycle. These values were obtained through gravimetric analysis, as detailed in Sect. "Remediation studies of sand contaminated with crude oil using ME" (Eq. 2). The declining trend is illustrated in Figure S8 (Supplementary

Material), which presents UV–Vis absorbance values at 271.5 nm for each cycle. These values, adjusted to reflect residual oil content, serve as quantitative indicators of progressive oil accumulation, with intermediate efficiencies of 76.12%, 55.38%, and 41.75% recorded in cycles 2 to 4. In parallel, Figure S7 visually documents the gradual saturation of the microemulsion, as evidenced by the darkening of its appearance with each cycle. The decline in efficiency is primarily attributed to the increasing saturation of the system with solubilized crude oil, which reduces its solubilization capacity. Furthermore, partial loss of the active microemulsion due to retention within the porous sand matrix further diminishes its effectiveness. This cumulative loss over time ultimately limits the overall remediation performance, explaining the efficiency drop to 25.01% observed in the final cycle.

Despite the decline in efficiency across cycles, ME5's ability to maintain significant oil removal performance over multiple applications underscores its potential for ex situ remediation processes. These results align with key criteria for green solvents, including renewability, technical performance, and biodegradability (Aluyor et al., 2009; Amiri-Rigi & Abbasi, 2019; Winterton, 2021).

In addition to its reusability and efficiency, the ME5 formulation demonstrated performance comparable to, or even superior to, that of conventional synthetic dispersants such as Corexit 9500A. Commercial dispersants, like Corexit 9500A, commonly contain substances such as sodium dioctyl sulfosuccinate and hydrocarbon-based solvents, which are known to pose ecotoxicological risks to marine organisms and may persist in aquatic environments (Giwa et al., 2023). In stark contrast, our ME5 system is distinguished by its composition, being formulated exclusively with plant-derived ingredients: saponified coconut oil (surfactant), pine oil (oil phase), and isopropyl alcohol (cosurfactant). These components are recognized for their biodegradability and lower toxicity profiles compared to the synthetic chemicals often found in commercial alternatives. This inherent environmental compatibility, coupled with its demonstrated reusability and stability, positions ME5 as a promising, more sustainable option for oil spill remediation, aligning with the increasing demand for greener cleanup technologies.

Application to an industrial scale: use of ME in enhanced soil flushing and treatment and disposal of liquid effluents

The application of the ME formulations as solvents to be used in the remediation of crude oil-contaminated sand, particularly at a large industrial scale, by in situ soil washing/soil flushing will enhance the efficiency and sustainability of the remediation process when compared to the use of other solvents (Santos et al., 2023; Song et al., 2007; Zhao et al., 2005). This technology aims to accelerate the mobilization of the contaminants at the remediation site to promote their treatment/recovery, using aqueous solutions (simply water in the conventional version) or solvents introduced through injection wells from the surface to dissolve/extract the contaminants present in the infiltration zone, which are then extracted through extraction wells using pumps. In the first phase, enhanced soil flushing using MEs as solvents will be applied, followed by the conventional process using seawater (or freshwater).

Surfactants and vegetable oils are used in soil washing processes for the removal of crude oil and its derivatives (Kwon et al., 2023). However, using MEs, which are thermodynamically stable systems formed by micelles, can result in greater contaminant removal efficiency compared to using surfactants or vegetable oils alone, thus enhancing the remediation process. MEs allow for better solubilization of hydrocarbons, facilitating the mobilization and emulsification of oily contaminants trapped in sand pores. This process improves the extraction efficiency of contaminants and reduces the need for subsequent treatment of liquid effluents, as MEs can be regenerated or reused within the remediation system.

However, as most of the remediation the processes, cleaning crude oil-contaminated beach sand using vegetable oil-based MEs generates liquid effluents, the saturated ME (when their reuse is no longer possible) and the aqueous effluent that results from the sand washing with water. Therefore, proper treatment and disposal of these effluents are essential to ensure environmental protection and to prevent secondary pollution (Fig. 7). The separation (and recovery) of the cleaning agent from the crude oil becomes necessary. A possible approach, depending on the contaminated site location, is to direct the residual effluent to nearby refineries, where the crude oil can be

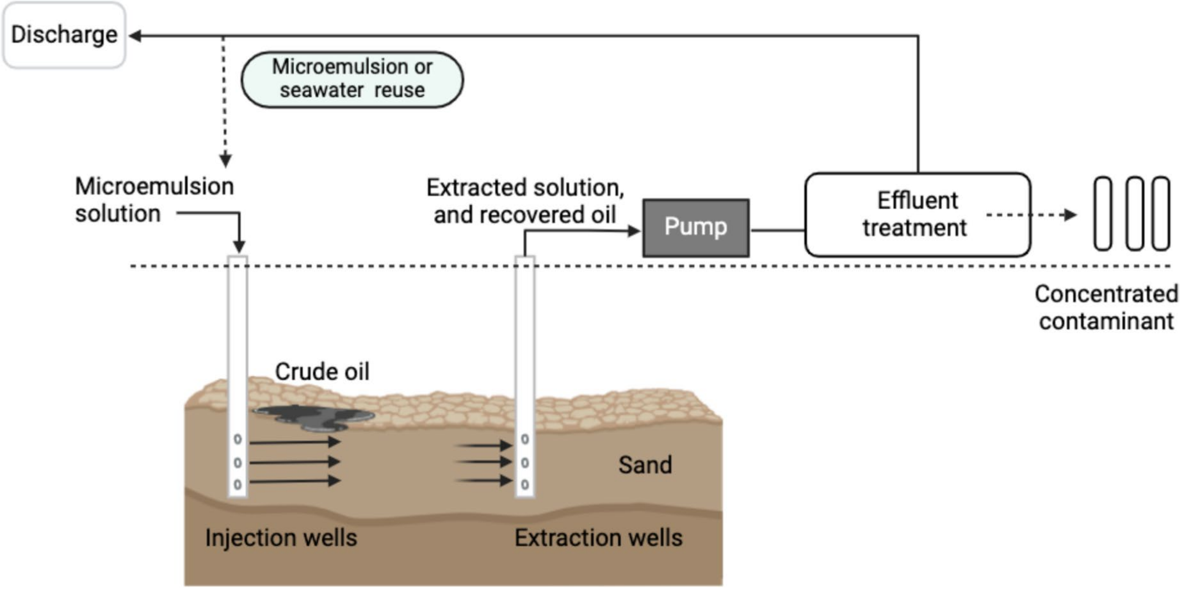


Fig. 7 In Situ treatment with extraction wells using ME for remediation of crude oil-contaminated sand (adapted from Quintero et al., 2013; Rulkens et al., 1995)

separated and recovered, thus minimizing the negative impact of untreated materials.

Alternatively, a compact wastewater treatment plant may be used to promote the treatment of the liquid effluents (Fig. 7), which will be based on the separation of the ME from the crude oil (first remediation phase), where a skimmer or oil trap can be used to physically separate and recover the oil floating on the surface, and from water (second remediation phase). The use of seawater, due to its increased salinity, can assist in phase separation, making the ME responsive to environmental conditions (Li et al., 2024; Pal et al., 2023). Anionic surfactants, such as saponified coconut oil, may be helpful as they are considered environmentally responsive in the presence of increased salinity due to their ability to rapidly dissociate within the microemulsion, leading to complete phase separation (Huang et al., 2024). The aqueous phase can be recovered and reused for sand washing, contributing to the sustainability of the process, while the recovered crude oil accumulates at the surface, completing a closed and environmentally conscious effluent management cycle. In coastal environments, the natural increase in salinity from seawater supports this process. The high salinity in the effluent promotes the coalescence of oil droplets, facilitating the separation of the microemulsified system from the crude oil.

However, it is important to highlight that directing the effluents to nearby refineries for treatment may not always be viable, especially when the crude oil spill occurs in remote or isolated locations. In such scenarios, the use of compact or mobile wastewater treatment units may represent a more practical and operationally feasible alternative (Ryazantsev et al., 2022). These units can be adapted to local conditions, enabling the on-site separation of the microemulsion from the recovered oil and the treatment of the aqueous phase. This strategy would minimize the need for long-distance transport of effluents, reducing operational costs and environmental risks, while maintaining the sustainability and efficiency of the remediation process.

Conclusion

This study investigated the development and application of microemulsion (ME) formulations composed of pine oil, saponified coconut oil, water, and isopropyl alcohol for the remediation of beach sand contaminated with crude oil. Pine oil was identified as a key component due to its terpenic composition, which contributed to enhanced solubilization and removal of the contaminant. The theoretical assessment based on safety data sheets (SDS) and regulatory references indicated that the tested formulations have low predicted toxicity and high biodegradability, reinforcing their potential environmental compatibility.

Pseudoternary phase diagrams were used to identify the most effective ME compositions within the single-phase Winsor IV region, guiding the selection of appropriate formulations for contaminant removal. The experiments demonstrated that formulations with higher oil-phase content, such as ME5, achieved crude oil removal efficiencies of up to 93.46% under controlled laboratory conditions. Physicochemical characterizations, including conductivity, particle size, refractive index, and FTIR analysis, confirmed the stability of the formulations over multiple cycles of use. Additionally, ME5 maintained consistent performance over five consecutive remediation cycles, highlighting its applicability in practical scenarios.

The analysis of MEs underscored significant advantages over traditional solvents. Their enhanced capacity to extract lipophilic compounds, combined with lower viscosity and interfacial tension, enabled better penetration into sediment matrices and solubilization of hydrocarbons. These findings suggest that MEs can be applied in combination with other techniques, such as passive barriers, to confine remediation sites and expand their use in integrated treatment strategies.

Future evaluations should include detailed ecotoxicological studies to investigate the potential impacts of ME residues on aquatic ecosystems. Testing with aquatic organisms across different trophic levels is essential to determine long-term effects and validate the safety of these formulations. Additionally, to better approximate real-world conditions, future studies should also evaluate the performance of the microemulsion in weathered oil-contaminated soils. Such soils present a more chemically complex matrix due to aging and environmental exposure, which can hinder the effectiveness of remediation strategies. Testing under these more challenging conditions is crucial to fully assess the robustness and practical applicability of the proposed ME system.

The results indicate that microemulsions based on plant-derived components represent a technically robust alternative for removing crude oil from contaminated sand. Their physicochemical properties enhance performance in the remediation process while minimizing associated environmental impacts.

Acknowledgements The authors would like to express their gratitude for the use of the facilities at the Laboratório de Termodinâmica Aplicada, the Centro Interdisciplinar de Energia e Ambiente (CIEnAm), and LEPETRO, all part of the Federal University of Bahia (UFBA). We extend our sincere thanks to technician Valtinei Silva and Professor Elaine Christine de Magalhães Cabral Albuquerque for their invaluable assistance with the DLS analyses, as well as to the LEPETRO technicians, particularly Sarah Adriana Soares.

Author contribution All authors have made substantial contributions to this manuscript. AVS conceived the study, designed the experiment, and wrote the manuscript. AVS and VFBS performed the experiments. AVS, VCF, CG, SAF, GS, and LCLS edited and critically reviewed the manuscript. CDM and LCLS supervised and secured funding for the project. All authors read and approved the final version of the manuscript.

Funding The authors would like to express their gratitude to the Coordination for the Improvement of Higher Education Personnel – Brazil (CAPES) – Finance Code 001, the National Council for Scientific and Technological Development (CNPq), and the financial support provided through the JOVEMPESQ/PRPPG/UFBA Call for Proposals. We also acknowledge the Human Resources Program of the National Agency of Petroleum, Natural Gas, and Biofuels (PRH/ANP – PRH36/UFBA), funded by investments from qualified oil companies under the R&D Clause of ANP Resolution N. 50/2015. This work received financial support from the PT national funds (FCT/MECI, Fundação para a Ciência e Tecnologia and Ministério da Educação, Ciência e Inovação) through the project UID/50006 - Laboratório Associado para a Química Verde - Tecnologias e Processos Limpos.

Data availability No datasets were generated or analysed during the current study.

Declarations

Conflict of interest The authors declare no competing interests.

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