Remediation of an Organochlorine Compound in an Unsaturated Zone Using a DL-Limonene Microemulsion System

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Contamination of the unsaturated zone, and hence, of groundwater by non-aqueous phase liquids has become a problem that arouses great concern due to the environmental damage it causes. Several efficient and economically beneficial techniques for the *in situ* treatment of contaminated soils have been applied quite frequently, including the so-called soil flushing processes. In this study, microemulsion systems were prepared using limonene, in the search for a formulation that would remove trichloroethene in soil. Limonene, a monocyclic monoterpene, is one of the main constituents of various essential oils of citrus fruits, such as oranges, tangerines and lemons. The results indicated that using a washing fluid containing 15 % DL-limonene microemulsion enabled the removal of 98.85 % of trichloroethene present in the soil after 30 minutes of residence time in the system. Hence, it can be concluded that the use of this microemulsion system is an interesting strategy for the remediation of soils contaminated with trichloroethene.

Keywords:
contaminated soil, trichloroethene, DL-limonene microemulsion, remediation

Introduction

Throughout the 1990s and 2000s, the increasing number of sites with contaminated soils around the world was attributed mainly to improper waste disposal practices or accidental spills. This has become an extremely serious problem that affects not only the environment and human health, but also economic activities associated with land use[1]. Oily sludge, for example, was included on the list of priority pollutants by the US Environment Protection Agency (USEPA). Therefore, the treatment or removal of these contaminations is extremely important in terms of environmental protection[2].

Trichloroethene (TCE) is one of the most common organic pollutants in contaminated soils because it is widely employed in industrial activities such as dry cleaning, in insecticides, manufactories, or as a degreasing agent, among other minor uses[3]. The partitioning tendency of trichloroethene in the environment has been calculated as follows: 97.7 % air, 0.3 % water, 0.004 % soil, and 0.004 % sediment[4]. Once TCE reaches the unsaturated zone, it can lodge in the pores in its gaseous phase, or even remain in the immiscible aqueous phase[5]. Trichloroethene is carcinogenic to humans (Group 1) through ingestion or inhalation[6]. Treatment technologies for TCE include common practices as well as innovative alternatives for treating contaminated soil and source zone *in situ* remediation, including a technology that integrates electrokinetics with *in situ* treatment of chlorinated organics[7,8]. The feasibility of applying electrokinetic remediation stems, above all, from high electrical conductivity and low soil permeability, which are factors that make this method more feasible for clay soil remediation.

In environmental terminology, the immiscible liquid phase in groundwater is known as non-aqueous phase liquid (NAPL), the combination of isostatic forces and capillary pressure effects results in these being distributed across the water-table, or confined below the water-table but occurring near the top of the confined coarser grained unit. When an immiscible liquid phase of the TCE compound comes into contact with the aquifer, the product forms a non-aqueous phase liquid denser than water, known as dense non-aqueous phase liquid (DNAPL), because its specific mass (1.46 kg dm^{-3}) is greater than that of water[9]. The risk associated with DNAPL contamination is specific to the types of chemical compounds and is generally persistent in the environment[10]. The EPA has classified both TCE and PCE as likely carcinogenic to humans[11].

Microemulsion (ME) can be defined as a thermodynamically stable, optically transparent, isotropic, low viscosity system formed through the appar-

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*Corresponding author: E-mail: v.campos@unesp.br ently spontaneous solubilization of two immiscible liquids, usually water and oil, stabilized by a surfactant film located at the oil-water interface[12–14]. Microemulsions are classified as oil-in-water (O/W) ME, which are structurally similar to direct micelles, with water as a continuous medium and droplets having an organic nucleus, and water-in-oil (W/O) ME, which are similar to inverse micelles and have droplets with aqueous nuclei dispersed in organic media[15]. Microemulsion systems were first described by Hoar and Schulman[16], who produced a transparent dispersion by titrating a milky emulsion with hexanol. Microemulsions have numerous applications in a variety of areas, including drug delivery systems, cosmetics, food, fuel, lubricants and coatings, detergents, agrochemicals, analytical chemistry, nanoparticle synthesis, biotechnology, and chemical reactors[17].

The use of microemulsions in cleaning technologies is described by several authors, specifically in the areas of hard surface cleaning, with patents assigned to well-known companies such as Colgate-Palmolive and Dow Chemicals[18], laundry detergent[19], toiletries such as shampoo and body washes[20,21], and in environmental remediation applications[22], with special emphasis on surfactant-enhanced aquifer remediation. In general, two types of cleaning approaches have been identified: oil detachment or mobilization, and oil solubilization[18].

The use of microemulsions in cleaning technologies is described by several authors, specifically in the areas of hard surface cleaning, laundry, and personal cleaning formulations, as well as in environmental remediation applications, with special emphasis on surfactant-enhanced aquifer remediation. A microemulsion is a liquid substance designed specifically for *ex situ* remediation projects and targeted at compounds that are extremely persistent in the subsurface, such as organochlorines (OC), polychlorinated biphenyl, heavy crude oils, and asphalt. Microemulsions have been proposed for the treatment of DNAPL, since they can act directly from the focus of contamination. Recent studies suggest that subjecting surfactants to microemulsion prior to injection may improve their performance for several reasons. For example, Pursley[23] states that microemulsions tend to present lower propensity for adsorption in mineral rocks, while Pietrangeli[24] cites, as an advantage to other surfactant solutions, the fact that microemulsions are more stable at high temperatures and have brine pH levels. Most of these studies have demonstrated that the effectiveness of microemulsions depends on the proper selection of their chemical formulations and brine chemistry, as well as test conditions, such as mineral texture and wettability of the outcrops, and the presence of components such as those of cement, which may block water channels and interfere in oil removal[25].

Limonene, the main constituent of orange essential oil (0.92 %), is a colorless oily liquid obtained from the distillation of citrus liquor. This product, which is obtained by pressing fresh orange waste (peel, bagasse, seeds) after extracting its juice, belongs to the family of terpenes, and its molecular formula is $C_{10}H_{16}$. Limonene was selected because it is eco-friendly natural oil extracted from orange peel. Yang[26] prepared nanoemulsions, showing the phase behavior of a d-limonene/isotridecanol ethoxylate-6/isopropyl alcohol/water system, with a droplet size of approx. 40 nm. The nanoemulsions were obtained by crash-dilution of a concentrated microemulsion, which was produced by the stepwise addition of a large volume of water to a solution of a surfactant, solvent, and D-limonene mixture. On the other hand, Zelenev[27] prepared a water/d-limonene microemulsion system stabilized by a mixture of nonionic surfactant and isopropyl alcohol (cosolvent), and used it in experiments of fluid recovery from horizontally oriented shale-packed columns, as well as in studies of regained permeability in fractured cores originating from a shale formation. Ramli[28] produced a limonene-based microemulsion system that could work as a vitamin C carrier for cosmetic purposes, seeking advantages such as storage stability and delivery in both hydrophobic and hydrophilic drugs and structures.

The general aim of the research is to develop and characterize a microemulsified system containing limonene essential oil (DL-limonene) as an oily phase and active ingredient to be applied in the remediation of organochlorine compounds, specifically in TCE contaminated soils (unsaturated zone).

Materials and methods

The soil sample (Tables 1 and 2), which was collected in the city of Jundiaí, state of São Paulo, Brazil, was classified as dystrophic red latosol (DRL), according to the Brazilian Soil Classification System. The mineralogical composition of the DRL soil sample was determined by X-ray diffraction (Bruker AXS D8 Advance) with CuKα radiation and λ equal to 1.5405 Å. The angular range of 2θ was 2° to 65°, with a step of 0.020° and count time of 28 s/step.

The microemulsion system was prepared using ultrapure water (18.2 MΩ cm^{-1} resistivity at 25 ºC) obtained from a water purification system (Gehaka Master System MS2000). The reagents used in the microemulsion formulation were the surfactants sodium dodecyl sulfate, and n-butanol as cosurfactant, while DL-limonene essential oil was used as oily

Table 1 – *Textural characteristics, density, and total porosity of soil from Jundiaí, São Paulo*

Soil (cm)	Particle size distribution (g kg^{-1})			Textural classification	Density (kg m^{-3})	Total porosity
	sand	silt	clay		soil	(%)
0–34	643.02	51.43	304.1	sandy clay loam	1452.97	45.12
34–53	572.44	48.21	354.01	sandy clay	1391.9	48.27

Table 2 – *Characteristics of DRL soil from Jundiaí, São Paulo, sampled at depths of 0–34 and 34–53 cm from the surface*

Soil (cm)	Water pH	Exchangeable Al, mmol$_c$ dm^{-3}	Saturation Al (%)	Saturation bases (%)	P	K	Ca	Mg	MO
					mg dm^{-3}	mg dm^{-3}	cmol$_c$ dm^{-3}	cmol$_c$ dm^{-3}	%
0–34	4.4 – 5.1	2 – 22	2.0 – 43	20 – 62	2.7 – 29.3	19 – 147	3.8 – 4.3	1.9 – 2.7	2.7 – 3.7
34–53	4.2 – 5.1	1 – 26	1.9 – 43	18 – 60	2.2 – 27.4	13 – 144	3.1 – 3.7	1.2 – 1.8	2.0 – 2.5

phase. All the reagents and solvents were p.a. grade purchased from Merck.

The presence of limonene functional groups was investigated by means of infrared spectroscopy. The infrared spectra from the compounds embedded in potassium bromide for IR spectroscopy were obtained in the range of 4000 – 400 cm^{-1}, using a Perkin Elmer 16 PC FTIR spectrophotometer.

The volatile organic compound was analyzed using the methodology specified by US EPA method 8260. The soil samples were air dried, broken up, and sifted through a 2 mm mesh sieve. The fine material was quartered, and the samples were subjected to various laboratory techniques, including particle size analysis by the pipette method[29].

The routine analytical test was performed in a Perkin Elmer Clarus 600 GC/MAS system equipped with a DB-VRX column (60 m x 0.25 mm x 1.40 μm), using helium as carrier gas at a flow rate of 1.0 mL min^{-1}, The temperature was set at 5 ºC for 1.0 min, followed by an increase of 4 ºC min^{-1} up to 200 ºC, where it was held for 1 min, and another increase of 10 ºC min^{-1} up to 230 ºC, where it was held for 2 min. Developments were made using samples prepared from primary standards. The average droplet size of the microemulsions was determined by the dynamic light scattering technique, using a ZetaPLUS Particle Size Analyzer. The mean droplet size and polydispersity index (PI) were determined by dynamic light scattering (DLS), using a Zetasizer Nano ZS particle size analyzer (Malvern Instruments, UK).

The phase diagram was constructed using the water titration method at ambient temperature. Four ternary phase diagrams were constructed with ratios of sodium dodecyl sulfate to n-butanol of 1:1, 2:1, 3:1, and 4:1. The following ratios of the mixture of limonene used in each ternary phase diagram were 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, and 9:1, according to the authors Ramli[30] and Zainuddin[31]. At the end, formulations starting from the 4:1 diagram were selected for characterization. The stability of the formulations was evaluated according to the freeze/thaw cycle and thermal stress. In the freeze-thaw cycle, the samples were subjected to 4 °C for 24 h, and 45 °C for another 24 h. The samples were subjected to six cycles in a refrigerator and six in an oven, making a total of 12 days of analysis. During thermal stress, the samples were heated in a thermostatic bath, in the temperature range of 40 to 80 °C, with a gradual increase in temperature in 5 °C steps, holding the samples at each temperature for 30 minutes.

The ideal formulation of a microemulsion system is one that exhibits the desired physicochemical properties, such as viscosity, stability, pH, and specific area of the dispersed phase. The mixture of four components was optimized using Minitab software, which generated possible options for surfactant, providing a total of 12 formulations using sodium dodecyl sulfate. To create the initial formulations, a minimum (30 %) and maximum concentration range (47 %) were set for each reagent in the formulation, and a design of experiment (DOE) was established to obtain the best mix options, thereby favoring savings in reagents and minimizing waste. This statistical design was developed using Minitab® version 18 software, which generated 12 possible formulations. Subsequently, 50 mL of the selected formulation was prepared, weighing the components according to the percentages determined by Minitab, and then subjecting each formulation to three homogenization cycles of three minutes each at 200 W in an ultrasonic cell disruptor. After homogenization, the formulations were stored in scintillation vials and allowed to stand for 60 hours at room temperature.

Experiments in fixed-bed columns were performed to evaluate the removal of trichloroethene (Table 4). Each column was filled with 150 g of dystrophic red latosol, homogenized with trichloroethene (20 mg dm^{-3}), and stirred with a glass rod to reach the density determined for DRL (1.56 kg dm^{-3}). Then, fixed volumes (400 mL) of aqueous solution containing DL-limonene microemulsion were injected, for a total of four repetitions. After the soil was washed, the columns were disassembled, and the soil contained in each segment was removed. TCE was extracted in a shaker with 5 g of soil in 25 mL of methanol under stirring at 150 rpm for 60 minutes. The percolated liquid phase was then stored in sealed glass vials for subsequent quantification by chromatography.

Results and discussion

TCE adsorption was evaluated at two levels of ionic strength (15 and 75 mmol dm^{-3}). To carry out the adsorption experiment, soil suspensions (200 mesh) were prepared in NaCl saline solution, at two concentrations: 15 µmol dm^{-3} and 75 µmol dm^{-3}. The ionic strength of 15 mmol dm^{-3} was used because it is similar to that observed in the solution of weathered soils, such as DRL. The pH level of all the suspensions was adjusted to 5.1±0.2 using 10 mmol dm^{-3} of NaOH and HCl. The final soil: solution ratio was 1:100 (mass/volume), and all the samples were analyzed in triplicate. The contact time of the samples was 120 hours, divided into cycles of shaking and resting. After the reaction period, the suspension of each sample was centrifuged at 3,000 rpm for 30 minutes and the supernatant was removed for analysis. At 15 and 75 mmol dm^{-3} of ionic strength, the average percentage of trichloroethene adsorption was 74.2 and 75.9 %, respectively. Not only was the average percentage comparable ($p<0.05$), but similarities were also observed in the total amplitude, indicating that an increase in ionic strength had not led to a significant change in the adsorption rate. On the other hand, the desorption rate at the dose of 15 µmol dm^{-3} was less than 8 %, at the two levels of ionic strength (Table 3). An analysis of variance (ANOVA) was performed to determine if there were differences between the mean responses of the treatments. Based on this procedure, the presence or absence of differences was inferred at a confidence level of 95. The ANOVA results showed significant difference among the percentages, and, followed by a Tukey test, it was observed that the means obtained in the desorption percentage in the concentration of 75 µmol L^{-1} were significantly different.

Table 3 – *Trichloroethene (TCE) adsorption and desorption rates in DRL soil samples (0–34 cm) at two levels of ionic strength (IS) in the equilibrium solution and two concentrations of trichloroethene (15 and 75 µmol dm^{-3})**

TCE	Adsorption (%)		Desorption (%)	
	IS$_1$	IS$_2$	IS$_1$	IS$_2$
15 µmol dm^{-3}	74.2a	74.6a	7.1a	7.8a
75 µmol dm^{-3}	75.2a	75.9a	3.2b	9.2a

* Means followed by the same letter do not differ statistically from each other according to Tukey's test at 5 % probability.

Table 4 – *Formulations of DL-limonene microemulsion generated by Minitab Statistical software*

Factors	–1	0	+1
DL-limonene concentration (wt%)	10	15	20
Water volume concentration (%)	45	50	55
Centrifuge speed (rpm)	3,000	10,000	17,000
Mixing time (min)	15	30	45

Because of its moderate water solubility, trichloroethene in soil has the potential to migrate into groundwater. The relatively frequent detection of trichloroethene in groundwater confirms its mobility in soils[32]. Drinking water supplies relying on contaminated groundwater sources may contain trichloroethene. The Agency for Toxic Substances and Disease Registry (ATSDR) states that trichloroethene is the most frequently reported organic contaminant in groundwater. It estimates between 9 and 34 percent of drinking water supply sources have some trichloroethene contamination, but that most municipal water supplies are in compliance with the maximum contaminant level of 5 µg dm^{-3} [32,33].

Oil-in-water (O/W) microemulsions have proved to be an efficient vehicle for incorporating lipophilic substances into aqueous systems due to their higher solubility[34]. The use of co-surfactants enables the additional reduction in interfacial tension required for the formation and thermodynamic stability of microemulsions, and also helps fluidize the interfacial film formed by the surfactant, thereby preventing a significant increase in the system's viscosity[35]. In this work, the DL-limonene microemulsion was produced according to the statistical design offered by Minitab. The factors with their respective levels and the design matrix are presented in Table 4. Based on the design matrix, 12 samples containing sodium dodecyl sulfate were manufactured for analysis and characterization. By applying the optimum solution, the level of reagents declined from 8.3 % to 3.1 %.

The microemulsions (ME) were prepared in various combinations, after which all the solutions

Table 5 – *Parameters of pH, electrical conductivity, temperature, and refractive index, and their comparison with the literature*

Sample	Parameters			Reference
	pH	Conductivity (μS cm^{-1})	Refractive index (25 ºC)	
ME_6 Limonene	7.6 ± 0.08	6.04 ± 0.02	1.38 ± 0.01	–
ME_8 Limonene	7.5 ± 0.06	5.98 ± 0.04	1.39 ± 0.01	–
ME_{10} Limonene	7.9± 0.01	5.96 ± 0.02	1.42 ± 0.01	–
ME Rosemary oil F1	5.3± 0.01	6.05 ± 0.07	1.46	Assis[36]
ME Rosemary oil F2	6.2± 0.01	2.18 ± 0.01	1.46	Assis[36]
ME Rosemary oil F3	6.6± 0.01	6.18 ± 0.03	1.45	Assis[36]

prepared with anionic surfactant, sodium dodecyl sulfate, were discarded. Preliminary testing indicated that only three microemulsion formulations showed stability (ME_6, ME_8 and ME_{10}), so these were subjected to characterization. The ME_6 formulation with anionic sodium dodecyl sulfate (30 wt%) was the best, and the size of the droplets in the dispersed phase of microemulsions ranged from 1.8 to 5.3 nm. This system presented the formation of more organized micellar aggregates.

Of the four diagrams created, the one with the largest area of transparent systems in the ratio of 4:1 was selected. The hydrophilic-lipophilic balance (HLB) of this system was closest to that found for the oil, as it presented the largest area of ME formation, with greater diversity of structures, particularly of O/W and bicontinuous phases, which characterize the most suitable formulations to carry limonene essential oil. The last HLB value of each system varied according to the relative proportion of each surfactant. The HLB of the formulation containing limonene was found to be 10.3, since it showed the highest stability in all the analyzed parameters.

Aspects such as coloration, homogeneity, phase separation, or presence of precipitates in the microemulsion were evaluated 60 hours after the preparation of each formulation. All the formulations were evaluated in triplicate based on the parameters of pH, electrical conductivity, refractive index, freeze-thaw cycle, and thermal stress. The refractive index was determined using an ABBE benchtop refractometer, and the freeze-thaw cycle was performed by subjecting the samples to a total of six cycles of freezing and thawing to room temperature, as well as heating tests up to 80 ºC, in order to determine whether the extreme limits of cold and return to room temperature would destabilize the systems. The polydispersion index in the ME_6 formulation was determined by dynamic light scattering (DLS), a precise and suitable technique for studying the internal properties of microemulsions. This formulation presented a polydispersion index of 0.208, indicating that the droplets were distributed homogeneously, thus elucidating the possible regular behavior in the microemulsion system with droplets smaller than 100 nm.

Table 5 describes the findings of pH, electrical conductivity, temperature, and refractive index, comparing them with those reported by Assis[36]. No changes in color, turbidity, precipitation or phase separation were observed after the thermal stress and freeze-thaw cycle tests, demonstrating the preliminary stability of the formulations subjected to extreme temperature changes, thus reinforcing the hypothesis of thermodynamic stability characteristic of ME.

The purpose of this work was to develop and describe microemulsions containing citrus essential oil, i.e., limonene. The surfactant system was composed of anionic sodium dodecyl sulfate, n-butanol and limonene were used for the oily phase. The spectrum of DL-limonene as well as that of microemulsion had several similarities (Fig. 1). In the FTIR spectrum (Table 6 and Fig. 2) of the ME_6 microemulsion, note the wide band with maximum absorption at 3354 cm^{-1}, corresponding to the elongation vibrations of the different hydroxyl groups contained in the compound. The band clearly visible at 1639 cm^{-1} pertains to the vibrations of these O–H groups. The spectrum shows additional bands at 2962, 2855 and 1639 cm^{-1}, corresponding to the CH vibrations and elongation of the different groups of CH_3 and CH_2.

The presence of the peaks at 1377, 1210, and 1046 cm^{-1} can be attributed to C–O elongation vibrations. The inclusion complexes characterized by Fourier transform infrared spectrophotometry (FTIR) showed changes in several characteristic bands of limonene, reinforcing the hypothesis of complexation. A few variations were detected, mainly in the bands between 2924 and 1639 cm^{-1}, which were broader, as well as a band at 978 cm^{-1}, which is characteristic of the alkene group. In the spectrum corresponding to limonene, note the band at 3073 cm^{-1}, which corresponds to the –CH stretch-

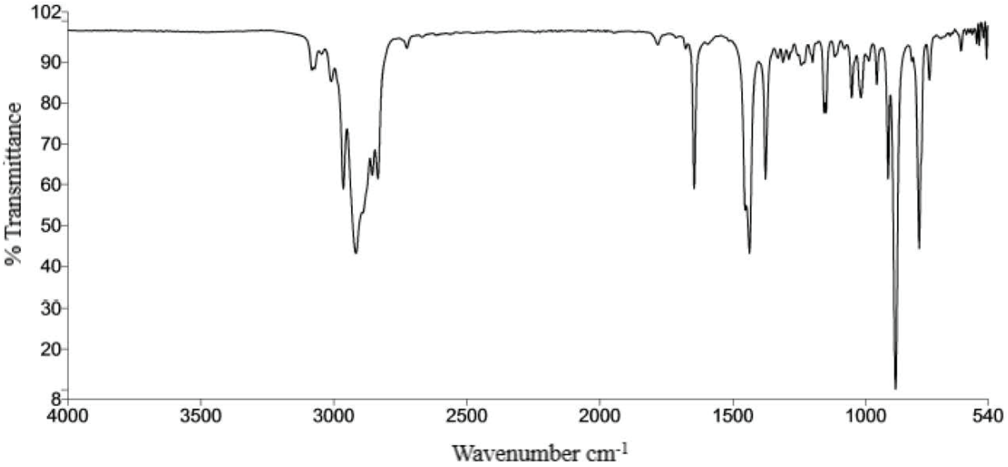

Fig. 1 – *Infrared spectra of limonene absorption bands in the range of 400–4000 cm^{-1}*

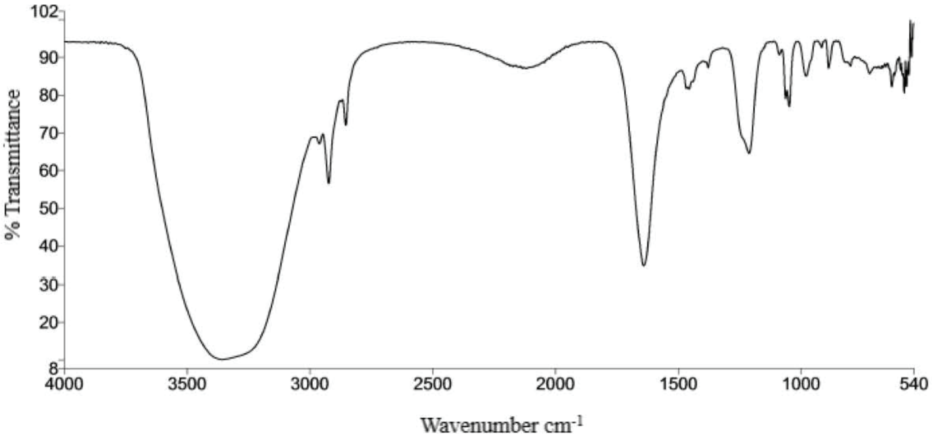

Fig. 2 – *Infrared spectra of microemulsion absorption bands in the range of 400–4000 cm^{-1}*

ing of alkene, while the peaks at 2962, 2930 and 2847 cm^{-1} correspond to CH_3 and CH_2 angular deformation, which may be linked to primary and second carbons. The presence of the peak at 1445 cm^{-1} indicates C=C stretching vibrations characteristic of cycloalkene. The peak at 1379 cm^{-1} corresponds to CH_3 angular deformation, while another peak at 892 cm^{-1} corresponds to $R_2C=CHR$, where R represents branches in the structure of the compound.

An evaluation of the physicochemical parameters of the soil revealed an extremely low cation exchange capacity of about 3.1 cmol$_c$ kg^{-1}, an organic matter content in the order of 5 %, and acid characteristics (pH 5.1). In addition, the sandy clay loam texture of the soil stood out, with its mineralogical composition consisting essentially of kaolinite $Al_2Si_2O_5(OH)_4$, hematite (Fe_2O_3) and quartz (SiO_2). Before the test, it was necessary to determine the void volume of the soil column, i.e., the pore volume. This was done by gravimetry, by weighing the dry column filled with soil and comparing it with the column filled with water. The result corresponded to 36 mL of pores per 100 mL of packed soil, i.e., 36 % of total porosity. The constant infiltration rate was 10.97 (cm h^{-1}), and the saturated hydraulic conductivity of soil was 1.64 (cm h^{-1}). Water movement in soils depends on total porosity, soil density, and hydraulic conductivity. With respect to soil compaction, it is known that Red Latosols are generally permeable due to their textural and structural characteristics, which favor the leaching process. The advantage of the sorption phenomenon in DRL is that it delays the migration rate of contaminants that will dissolve in groundwater. However, its disadvantage is the reverse process, which may also occur. In other words, part of the mass of TCE adsorbed by the soil may gradually dissolve in groundwater through molecular diffusion.

Table 6 – *FTIR absorption peaks (cm^{-1}) of the ME_6 microemulsion and the limonene used as oily phase*

Sample	–CH	CH_3–CH_2	C=C	CH_3	O–H	C–H	C–O
ME_6	2962	–	–	–	3354	1046	1455
Limonene	3084	2965	1644	1376	–	–	–

Table 7 – *Concentration and standard deviation of TCE in soil samples before and after a fixed-bed column test*

	Sample	TCE (mg dm^{-3})		Removal (%)
		Before	After	
Soil	Soil-01	18. 91	0. 19	98. 99
	Soil-02	17.83	0.23	98.71
	Mean	18.37±0.76	0.21±0.18	98.85

As may be seen in Table 7, the DL-limonene microemulsion shows a promising potential for the removal of trichloroethene from soil. In this case, the term “degradation” does not suitably describe remediation using microemulsions because microemulsion elution is a physical process rather than a chemical one, so TCE cannot be subjected to cleavage of chemical bonds. The analysis of the soil samples before and after the fixed bed column experiment revealed highly positive results in the decontamination of soil containing TCE, indicating a reduction of 98.85 %. Qin[25] attributed the good performance of the ME in solubilizing crude oil to the unique ability of d-limonene swollen micelles to penetrate into microcrystalline dolomite cements and swell the crude oil, leading to a more effective desorption. In another study, core flooding tests integrated with a high resolution X-ray micro-CT scanner showed that a D-limonene microemulsion had a greater tendency to alter the wettability of surfaces than the surfactant alone, leading to more effective NAPL removal. Hernandez[37], in turn, focused on the removal of crude oil residue from sand, using microemulsions formulated with D-limonene as the solvent. The authors clearly showed that the amount of crude oil residue removed increased dramatically as a function of the increasing amount of D-limonene in the ME. They attributed the high removal rate achieved with the ME to the fact that D-limonene diffuses and penetrates into the residue layer, softening it and thus facilitating its removal. Gu[38] studied the remediation of diesel oil contaminated sand with a microemulsion containing sodium dodecyl benzene sulfonate (SDBS) and lauryl sodium sulfate (SLS). The authors found that the oil removal rate increased with the increase in the leaching rate. The reason for this may be that the high-speed microemulsion precursor occupied the space of the oil phase in the oily sand, reducing the adhesion force between the oil phase and the sand. Therefore, it has a significant scouring effect. The oil removal rate was as high as 82.84 %, and the sand’s oil content was reduced to 2.57 %.

Conclusions

Microemulsion formation using surfactant (anionic sodium dodecyl sulfate) have been reported. This work has also demonstrated that a microemulsion can be formulated using essential oils. The ME_6 formulation with anionic sodium dodecyl sulfate (30 wt%) was the best containing phase of sodium dodecyl sulfate-n-butanol-limonene-water microemulsion system. The evaluation of the ionic strength showed significant effects for the samples with higher concentration of TCE (75 µmol L^{-1}) in the step of desorption. The ANOVA presented the higher F value for the columns’ interaction, and the Tukey test indicated that the difference between the means for ionic strength 1 and 2 in the higher concentration of TCE was significant in 95 % of confidence. Based on this study, it was concluded that the technique used for the design of experiments, which provides well-defined microemulsion formulations using Minitab software, is very simple, highly reproducible, and very useful. The technique clearly indicates the possible microemulsion formulations, facilitating the choice of the content of each component, as well as promoting savings on reagents and reducing wastes. The droplet size of the dispersed phase in a microemulsion was less than 100 nm. Vegetable oil microemulsions are commonly prepared with alcohols and a surfactant. In this work, the microemulsion was prepared with limonene. The main characteristics of this surfactant are the formation of organized structures, among which the smallest ones are micelles. Once injected into the soil, the emulsified material enters the pores, traveling by means of micellar transport and increasing its distribution to areas of lower concentration. Oil droplet sizes in microemulsions can range from 0.01 to 0.1 µm, which is compatible with soil pore size, minimizing pore clogging and accelerating transport of the contaminant. The fixed-bed column experiment removed 98.85 % of trichloroethene from the soil within a percolating solution residence time of 30 minutes. This study demonstrated the potential of an aqueous solution containing a DL-limonene microemulsion formulation for the remediation of TCE-contaminated soils in the unsaturated zone.

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