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Assessment of a novel alcohol-in-biopolymer emulsion for enhanced remediation of diesel-contaminated soils

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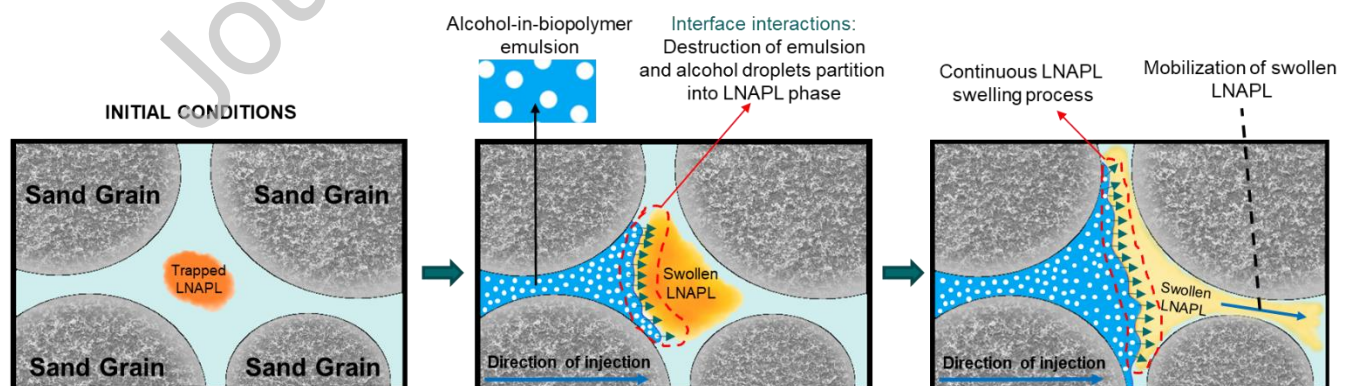
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Highlights

- Novel biopolymer-based emulsion enhances LNAPL removal from contaminated soils
- 1-pentanol induces diesel oil swelling, improving its mobilization in porous media
- Shear-thinning emulsion ensures stable and uniform displacement in porous media
- Porous media studies confirm complete diesel removal with minimal fluid injection
- Promising approach for sustainable soil cleanup, minimizing environmental impact

1 Graphical abstract

Sketch illustrating LNAPL displacement by emulsion at pore-scale



Abstract

Conventional pump-and-treat technologies have demonstrated limited effectiveness in remediating soils contaminated with light non-aqueous phase liquids (LNAPLs), such as petroleum hydrocarbons. Non-conventional in-situ flushing with shear-thinning fluids, such as polymers, offers a promising alternative. However, even with polymer flushing, residual LNAPL ganglia may remain trapped in porous media, requiring further improvement of the flushing fluid to enhance remediation efficiency.

In this study, we present a novel alcohol-in-biopolymer emulsion developed to enhance the recovery of residual diesel oil from porous media. Batch experiments were conducted to evaluate the partitioning behavior of fifteen different alcohols between the aqueous and diesel phases. The results revealed that 1-pentanol preferentially partitions into the diesel phase rather than the aqueous phase, leading to an increase in diesel oil volume via a swelling mechanism. Furthermore, 1-pentanol forms a stable and homogeneous emulsion when combined with an aqueous solution of the biopolymer xanthan gum, and the surfactant sodium dodecyl sulfate. The emulsion demonstrated stability over 30 d, ensuring its suitability for prolonged remediation processes. Rheological experiments confirmed the emulsion's shear-thinning behavior, which ensures stable and uniform displacement within porous media.

A two-dimensional cell packed with silica sand was used to evaluate the efficiency of the emulsion in removing residual diesel oil. The results demonstrated that the emulsion propagates uniformly throughout the porous media, effectively achieving complete removal of residual diesel within 1.15 pore volumes of injection. Pore-scale visualizations revealed the swelling and subsequent mobilization of entrapped diesel ganglia induced by the emulsion, further confirming its efficacy. These findings highlight the potential of this novel alcohol-in-biopolymer emulsion to significantly improve diesel oil recovery from contaminated soils.

Keywords: Diesel; xanthan gum; surfactant; emulsion; alcohol partitioning; swelling mechanism; soil remediation.

2 Introduction

Light-refined petroleum products, such as gasoline, diesel, engine oil, etc., are among the most widely spread environmental pollutants, representing light non-aqueous phase liquids (LNAPL) (Charbeneau, 2006; Tomlinson et al., 2017). The primary source of pollution of terrestrial and aquatic ecosystems with petroleum hydrocarbons is anthropogenic activity. When released into the soil, LNAPLs infiltrate downward through the vadose zone under gravitational and capillary forces, eventually accumulating on top of the groundwater table due to their lower density. The persistence of LNAPL in soil and groundwater poses a significant threat to plants, animals, microorganisms, and human life due to their mutagenic and carcinogenic properties (Akinpelumi et al., 2023; Cavelan et al., 2022; Wu et al., 2011). Therefore, finding effective ways to remediate LNAPL-contaminated soil and groundwater is essential.

Conventional pump-and-treat (PT) or waterflooding (WF) techniques are commonly used for pumping and removing a significant fraction of LNAPL to the surface. However, these methods were found to have limited efficiency where recovery yields typically do not exceed 60%. This limitation is due to site complexity, such as limited access to polluted zones, the extent of contaminants both horizontally and vertically, soil heterogeneity and anisotropy, and LNAPL's physicochemical properties such as high hydrophobicity, low water solubility, high viscosity, high interfacial tension with water, and adsorption to soils and aquifer sediments (Colombano et al., 2020; National Research Council et al., 1994). Since the injected water mainly mobilizes contaminants from larger pores, significant residuals of LNAPL remain trapped in smaller pores due to the dominance of capillary forces over viscous and buoyancy forces (Jawitz et al., 2001). Moreover, these methods proceed slowly, which is not beneficial due to its prolonged duration, which leads to increased operating costs (Mackay & Cherry, 1989). Therefore, non-conventional in-situ remediation methods are being widely developed, particularly through soil flushing, which complements and may potentially replace PT and WF to address the latter challenges.

In-situ remediation techniques can also be challenging due to soil heterogeneity and anisotropy, which may hinder access to contaminants. Soil heterogeneity causes fluids to bypass low permeability zones,

creating preferential pathways in higher-permeability areas. To overcome this issue, viscous shear-thinning (non-Newtonian) fluids, such as aqueous foam (Baigadilov et al., 2024; Forey et al., 2020; Hirasaki et al., 1997; Karthick et al., 2019; Omirbekov et al., 2020, 2022) and aqueous polymers (K. E. Martel et al., 1998; R. Martel et al., 2004), have been proposed to prevent fluid bypass and ensure stable, uniform displacement (Bouزيد & Fatin-Rouge, 2022; Maire et al., 2015, 2018). However, only a limited number of studies have investigated the use of polymers for the remediation of LNAPL-contaminated soil (Hernández-Espriú et al., 2013; Karthick et al., 2019; K. E. Martel et al., 1998), as this technology was inspired by Enhanced Oil Recovery methods. The recovery yield of these technologies often exceeds 70%. For instance, K. E. Martel et al. (1998) studied polymer flooding in a bench-scale setup and achieved an LNAPL recovery of approximately 80%, outperforming conventional pump-and-treat. Maire et al. (2015, 2018) and Bouزيد & Fatin-Rouge (2022) demonstrated that polymer and foam injection can result in recoveries of up to 90%, which is significantly higher than conventional methods. Nevertheless, it is important to note that challenges like elevated injection pressure or soil uplift remain (Omirbekov et al., 2023), recovery yield of these technologies often exceeds 70%. For instance, K. E. Martel et al. (1998) studied polymer as these innovative fluids inspired by EOR technologies have limitations when applied to soil remediation. The higher viscosity of these complex fluids can result in high injection pressures, which may harm the aquifer ecosystem. Therefore, careful technology selection is critical for effective soil remediation.

To enhance in-situ remediation techniques, polymer solutions can be combined with various additives, including chemical compounds, surfactants, and alcohols. Polymer solutions, particularly xanthan solutions, are known to improve the delivery of remedial amendments into low-permeability zones, enhancing sweeping efficiency in porous media (Zhong et al. (2008, 2011)). Surfactants, when added to these solutions, can mobilize and solubilize NAPLs (Barbati et al., 2023, 2024; Javanbakht & Goual, 2016; Jawitz et al., 1998; Lee et al., 2007), although the use of a single surfactant has been proven to have poor solubilizing performance. Consequently, incorporating co-surfactants or co-solvents, such as alcohols, has been explored to enhance the solubilization and mobilization of NAPLs (Bernardez & De Andrade Lima, 2021; Fu et al., 2022).

In contrast to the mobilization (IFT reduction) and solubilization mechanisms, some higher molecular weight alcohols exhibit a displacement mechanism through swelling or expanding the NAPL phase, which can also be considered a form of mobilization. Typically, this mechanism occurs when less polar alcohols preferentially partition into the NAPL phase rather than the aqueous phase, promoting its swelling (St-Pierre et al., 2004). These partitioning alcohols convert residual NAPL ganglia into a continuous phase through the swelling mechanism, making them less dense, less viscous, and much easier to mobilize compared to discontinuous NAPL residuals (Brandes & Farley, 1993; Damrongsiri et al., 2013; Hayden et al., 1999, 1999; Hofstee et al., 2003; Kibbey et al., 2002; Lunn & Kueper, 1997; Ramsburg et al., 2004; Ramsburg & Pennell, 2002a, 2002b; St-Pierre et al., 2004; Talawat et al., 2013; Van Valkenburg & Annable, 2002). Previous studies have demonstrated that effective displacement of residual trichloroethylene (TCE) via the swelling mechanism can be achieved by partitioning *tert*-butanol (Brandes & Farley, 1993), *n*-propanol at higher concentrations (Brandes & Farley, 1993; Hayden et al., 1999; St-Pierre et al., 2004), and *n*-butanol (Ramsburg & Pennell, 2002a, 2002b) diluted in aqueous solution. Ramsburg & Pennell (2002a) reported that *n*-butanol was effective in swelling of chlorobenzene (CB). Similarly, the swelling of tetra/perchloroethylene (PCE) was facilitated by *tert*-butanol at higher concentrations (Brandes & Farley, 1993; Van Valkenburg & Annable, 2002) and *n*-butanol (Damrongsiri et al., 2013; Lunn & Kueper, 1997, 1999; Talawat et al., 2013). However, according to Hayden et al. (1999), *n*-propanol resulted in very little swelling of PCE, while Brandes & Farley (1993) observed no swelling at all, suggesting a solubilization mechanism. This shows that some lower molecular weight alcohols, specifically at lower concentrations, tend to partition into the aqueous phase due to reduced swelling properties or affinity for NAPL (Hofstee et al., 2003; Lunn & Kueper, 1997). In contrast, higher molecular weight alcohols with long-chain carbon atoms preferentially partition into the NAPL phase rather than the aqueous phase due to their lower polarity and strong affinity for NAPLs. However, these alcohols are generally water-immiscible, posing challenges in controlling and delivering them into the trapped NAPL phase in the subsurface.

In remedial emulsions, the incorporation of oil-swelling alcohols can further enhance NAPL displacement by inducing swelling and promoting stable mobilization within porous media. While

emulsions are inherently thermodynamically unstable systems, as the immiscible fluids tend to separate over time. However, the inclusion of surfactants, which form a stabilizing barrier around the dispersed droplets, can impart kinetic stability to the system, enabling the emulsion to remain homogeneous for extended periods (Becher, 1983; Ravera et al., 2021). These stabilized emulsions serve as an efficient delivery system for dispersed droplets of oil-swelling alcohols, facilitating the density-modified displacement of DNAPLs (Kibbey et al., 2002). For instance, Ramsburg et al. (2003) used a 15% (v/v) 1-butanol oil-in-water (O/W) macroemulsion, stabilized with two non-ionic surfactants — Tween 80 (4.7% v/v) and Span 80 (1.3% v/v) — to deliver dispersed droplets of oil-swelling 1-butanol into a contaminated zone within heterogeneous two-dimensional aquifer cell. This approach facilitated the density conversion of trichloroethylene (TCE) and perchloroethylene (PCE). Following the injection of 1.2 pore volumes (PV) of macroemulsion, an additional 1.2 PV of a post-injection solution containing 10% (v/v) Aerosol MA, 6% (v/v) 1-butanol, 15 g.L⁻¹ NaCl, and 1 g.L⁻¹ CaCl₂ was applied to reduce interfacial tension (IFT), resulting in a 93% recovery of DNAPLs.

Although oil-swelling alcohols have primarily been used for DNAPLs, their application to LNAPLs presents significant potential for enhancing in-situ remediation strategies. However, the use of oil-swelling alcohols for LNAPLs has been limited, with only a few studies exploring their efficacy in LNAPL removal (Falta et al., 1999; Jeong et al., 2009). This limited research is likely due to the physical property similarities between oil-swelling alcohols and LNAPL, despite their promising potential to enhance LNAPL removal. To our knowledge, only two studies have investigated the use of oil-swelling alcohols for LNAPL removal. Jeong et al. (2009) studied the swelling phenomenon of benzene residuals (LNAPL) by image analysis using a two-dimensional glass pore network micromodel with dimensions of 15 cm × 10 cm. The injection of 30% *tert*-butanol and 30% 1-propanol resulted in the swelling of the benzene residuals. Furthermore, co-injection of airflow enhanced the mobilization of the swollen benzene residuals. Meanwhile, Falta et al. (1999) conducted a pilot-scale field test in a 5 m × 3 m confined cell, using a mixture of 15% hexanol combined with 80% *tert*-butanol for subsurface remediation of LNAPL, which was composed of a complex mixture of aromatic and aliphatic hydrocarbons, chlorinated solvents, and other compounds. The injection of

four pore volumes of this mixture removed 90% of the more soluble contaminants (toluene, trichloroethane, xylenes, ethylbenzene, trimethylbenzene, naphthalene) and 80% of the less soluble contaminants (decane and undecane) from the soil. The pollutants were remediated through both enhanced solubilization and mobilization (swelling) mechanisms, although the relative contribution of each was not quantified.

Our study aims to address the critical research gap in LNAPL remediation by developing a novel shear-thinning emulsion formulation specifically designed to enhance hydrocarbon removal from porous media. The alcohol-in-biopolymer emulsion presented in this paper overcomes the limitations of traditional pump-and-treat methods and other unconventional techniques. Its highly viscous, shear-thinning properties ensure uniform propagation through porous media, minimizing bypassing and enhancing delivery to low-permeability zones. Moreover, the incorporation of a swelling alcohol enhances the mobilization of residual diesel ganglia by inducing a swelling mechanism that converts disconnected ganglia into a continuous phase, making them easier to displace. These combined mechanisms provide a targeted approach to address the limitations of traditional methods, particularly in complex soil environments. The emulsion formulation consists of a biopolymer-surfactant aqueous phase solution with dispersed droplets of oil-soluble swelling alcohol. Xanthan gum (XG) and sodium dodecyl sulfate (SDS) were chosen as the foundation for the aqueous phase of the emulsion. Since the swelling behavior of alcohols is NAPL-specific, fifteen different alcohols were tested at the bench scale to assess their partitioning behavior and ability to form a stable emulsion when mixed with the aqueous XG + SDS solution. Based on these two criteria, the most suitable alcohol was selected as the base for the remediation emulsion. Thus, the main objectives of our research are: (i) to develop a stable, homogeneous emulsion at the bench scale using a biopolymer/surfactant/oil-swelling alcohol mixture; (ii) to assess the performance and efficacy of this emulsion in removing residual LNAPL in a sand-packed two-dimensional (2D) cell; and (iii) to investigate the swelling and distribution of LNAPL within the pore space of a real porous medium (sandpack) using the same 2D cell.

3 Materials and methods

3.1 Materials

The porous medium used in this study was extra-siliceous sand with grain size (D_g) in the range of 0.4 to 1.5 mm ($D_{50} = 1.0$ mm), provided by Sibelco France. The sand's chemical composition consisted predominantly of SiO_2 (> 99%), with minor amounts of Fe_2O_3 (0.011%), Al_2O_3 (0.300%), TiO_2 (0.010%), and CaO (0.010%). We selected a porous medium to replicate the characteristics of a contaminated plurimetric-scale pilot site (BRGM's PRIME platform in Orléans, France), including permeability, grain size, and porosity.

The LNAPL used was a diesel oil (Excellium Truck Diesel) provided by TotalEnergies, a complex mixture of hydrocarbons. The diesel primarily consists of alkanes, cycloalkanes, and a minor fraction of aromatic hydrocarbons (polycyclic aromatic hydrocarbons $\leq 8\%$ by mass), along with additives such as anti-foaming agents. The high alkane content of the diesel fuel ensures compatibility with selected alcohols used in the emulsion, which are capable of partitioning effectively into the diesel phase. To enhance the visualization of diesel oil within porous media, Oil-Red-O (Sigma-Aldrich) was used as an oil-soluble dye at a concentration of 0.2 g.L^{-1} . The addition of the dye to the diesel oil did not result in any noticeable changes in its physical properties. The measured physical properties of the diesel oil are presented in Table 1.

Table 1. Physical properties of diesel oil at 20°C .

LNAPL	Density, ρ (g.cm^{-3})	Dynamic viscosity, μ (mPa.s)	LNAPL/deionized water interfacial tension, σ (mN.m^{-1})
Diesel	0.824 ± 0.002	3.15 ± 0.05	21.8 ± 0.5

A biopolymer xanthan gum (XG), which is an anionic polysaccharide sourced from *Xanthomonas campestris*, was selected as the solution base for its low environmental impact and high biodegradability (Berninger et al., 2021; Katzbauer, 1998; Nsengiyumva & Alexandridis, 2022). XG solution is known for its highly viscous shear-thinning rheology, which effectively overcomes displacement instabilities caused by unfavorable viscosity ratios and the physical heterogeneity of porous media (Alamooti et al., 2023; Dekker et al., 2022; Zhong et al., 2008). Additionally, XG acts as

an emulsifier, stabilizer, thickening, and gelling agent, significantly enhancing emulsion stability by retarding destabilization mechanisms such as creaming and sedimentation (Dickinson et al., 1994; Kaur et al., 2024). Following Lenormand et al. (1988), we set a minimum XG concentration of 1 g.L^{-1} (with respect to the aqueous phase) to overcome capillary and viscous fingering and ensure a uniform displacement front within porous media at a 1 mL.min^{-1} flow rate. The XG used in this study was supplied in powder form by Sigma-Aldrich.

Sodium dodecyl sulfate (SDS), a commonly used anionic surfactant, was selected for its low toxicity, high biodegradability, and dual functionality as both a surfactant and an emulsion stabilizer (Karthick et al., 2019; Mao et al., 2015). Its surface charge reduces the rate of droplet coalescence through electrostatic repulsion, ensuring long-term emulsion stability (Demetriades & Julian McClements, 2000). Furthermore, the anionic nature of both SDS and XG minimizes their adsorption onto the negatively charged silica soil used in this study, reducing material loss and maintaining the effectiveness of the flushing fluid throughout remediation. SDS was used at a fixed concentration of 5 g.L^{-1} in the aqueous phase, which is twice its theoretical critical micelle concentration (CMC) of 8.2 mM (2.3 g.L^{-1}) at ambient temperature (Rosen & Kunjappu, 2012), to ensure sufficient surfactant availability and stable emulsion performance. SDS powder, with a purity of $\geq 98.5\%$, was supplied by Sigma-Aldrich.

Fifteen alcohols (ranging from ethanol to n-octanol) supplied by Sigma-Aldrich were used in batch experiments to create polymer-surfactant-alcohol mixtures. These alcohols are known for their application in alcohol flushing studies aimed at soil remediation (Bernardez & De Andrade Lima, 2021; Falta et al., 1999; R. Martel et al., 1993; St-Pierre et al., 2004). They were specifically selected for this study to cover a broad range of molecular structures and physicochemical properties, such as chain length, branching, and functional groups, which influence their partitioning behavior and interaction with diesel. Furthermore, this selection enabled the evaluation of their compatibility and ability to form stable, homogeneous mixtures with the polymer-surfactant solution. The physical properties of these alcohols at 20°C provided by the supplier are shown in Table 2.

Table 2. Physical properties of the chosen alcohols at 20°C .

№	Trade name	Molecular structure	Density, ρ (g.cm ⁻³)	Dynamic viscosity, μ (mPa.s)
1	Ethanol	CH ₃ CH ₂ OH	0.789	1.200
2	1-propanol	CH ₃ CH ₂ CH ₂ OH	0.804	2.210
3	2-propanol	CH ₃ CH(OH)CH ₃	0.785	2.200
4	1-butanol	CH ₃ (CH ₂) ₃ OH	0.810	2.950
5	2-butanol	CH ₃ CH(OH)CH ₂ CH ₃	0.808	4.703
6	Isobutanol	(CH ₃) ₂ CHCH ₂ OH	0.801	3.103
7	Tert-butanol	(CH ₃) ₃ COH	0.775 (at 30°C)	3.300 (at 30°C)
8	2-methyl-1-butanol	CH ₃ CH ₂ CH(CH ₃)CH ₂ OH	0.815	5.505
9	1-pentanol	CH ₃ (CH ₂) ₄ OH	0.811	3.441
10	2-pentanol	CH ₃ CH(OH)CH ₂ CH ₂ CH ₃	0.812	4.100
11	3-pentanol	CH ₃ CH ₂ CH(OH)CH ₂ CH ₃	0.815	6.626
12	1-hexanol	CH ₃ (CH ₂) ₅ OH	0.814	5.300
13	1-heptanol	CH ₃ (CH ₂) ₆ OH	0.822	7.317
14	1-octanol	CH ₃ (CH ₂) ₇ OH	0.827	9.000
15	2-octanol	CH ₃ CH(OH)CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	0.819	6.200

We used deionized water (with a resistivity of 18.2 M Ω .cm) produced by Milli-Q water purification system to prepare all aqueous solutions. All the experiments performed in this study were conducted at 20°C.

3.2 Bulk experiments: setups and procedures

This subsection outlines the setups and procedures for bulk experiments used in this study. The primary objectives were to develop and select the most stable and homogeneous alcohol-in-biopolymer emulsion exhibiting non-Newtonian shear-thinning behavior for subsequent LNAPL removal experiments in porous media. To achieve this, batch tests were conducted to evaluate the partitioning behavior of the alcohols between the aqueous and LNAPL phases and to develop stable and homogeneous emulsions by mixing these alcohols with an aqueous solution containing 1 g.L⁻¹ XG and 5 g.L⁻¹ SDS. Rheological experiments were carried out to assess the bulk dynamic viscosity of the emulsions across a wide range of shear rates. Additionally, stability and droplet size distribution experiments were performed to ensure the long-term stability and uniformity of the selected emulsion.

3.2.1 Batch tests

Batch experiments were conducted in 20 mL glass vials. The systems were prepared by mixing alcohol, diesel, and deionized water in each vial at a volume ratio of 2:1:2. Each sample underwent thorough shaking for 180 min using an orbital shaker (Laboshake Gerhardt®), followed by a 24-h

settling period. The volumes of the separated aqueous and organic phases were recorded to determine the partitioning behavior of alcohol between water and diesel.

The following stage of batch experiments was to ensure the development of a stable and homogeneous mixture of polymer (XG) solution and alcohol. Since we employed both water-soluble and oil-soluble alcohols, surfactants play a crucial role in generating and stabilizing emulsions (Goloub & Pugh, 2003; Ravera et al., 2021).

The polymer-surfactant solution was prepared by first adding 5 g.L^{-1} of SDS powder to deionized water. The mixture was stirred using an overhead stirrer (DLAB OS40-S) at 300 rpm for 1 h. After the SDS was completely dissolved, 1 g.L^{-1} of XG powder was gradually added to the surfactant solution, and the mixture was stirred at 500 rpm for 6 h. Subsequently, the vial tests were performed by mixing the fifteen alcohols with the aqueous solution containing 1 g.L^{-1} XG and 5 g.L^{-1} SDS at a 1:1 volume ratio. The vials were thoroughly shaken using an orbital shaker for 180 min, followed by a 24-h settling period for system stabilization. Considering the use of both water-soluble and oil-soluble alcohols in this study, the most stable and homogeneous alcohol-containing solution or emulsion, capable of enhancing mobilization efficiency through diesel oil swelling, will be selected for further experiments.

3.2.2 Emulsion stability and droplet size distribution

The stability of the selected emulsion was evaluated by measuring the volumes of the cream layer and the serum layer separated as a function of storage time. The experiments were performed using 50 mL graduated cylinders sealed with capping.

The droplet size and distribution of the selected emulsion were characterized using an upright microscope (Nikon Eclipse with an Andor Neo sCMOS 5.5 Megapixel camera) equipped with 20X and 100X objectives. A drop of the freshly formed emulsion was placed between two coverslips for examination. The microscope images were analyzed using ImageJ Fiji, a Java-based image processing software, to determine the size of the emulsion droplets.

3.2.3 Rheological measurements

The rheological behavior of the selected emulsion was investigated using a Haake Mars 60 Thermofisher rheometer. The rheology of 1 g.L⁻¹ XG solutions (with and without 5 g.L⁻¹ SDS) was also measured the obtained rheograms were used as reference for comparative analysis with that of the emulsion. The rheometer was equipped with a plate-plate geometry (C60/Ti and TMP60), featuring a minimum torque rotation of 0.02 μN.m and a torque resolution of 0.1 nN.m. Two milliliters of the emulsion/solution were loaded onto the geometry, ensuring optimal assessment conditions by effectively filling the 0.054 mm shear gap. Viscosity was measured by applying shear rates in the range of 0.01 to 100 s⁻¹. Each recorded value was taken when the variation in shear stress fell below a predetermined tolerance. The maximum allowable measurement time for shear rate was set to 60 s. All experiments were conducted in triplicate. The Carreau-Yasuda model (Yasuda et al., 1981) was used to fit the measured rheological curves and can be expressed as:

$$\mu(\dot{\gamma}) = \mu_{inf} + (\mu_0 - \mu_{inf})[1 + (\lambda\dot{\gamma})^a]^{\frac{n-1}{a}} \quad (1)$$

where, μ_0 (Pa.s) and μ_{inf} (Pa.s) are the viscosity at zero and infinite shear rates, n (-) is the power index, a (-) is a transition parameter, and λ (s) is the relaxation time, identified as the point on the viscosity-shear rate curve where the transition occurs from the lower Newtonian region to the Power Law region of flow.

3.3 2D cell experiments

The main objectives of the experiments conducted using a two-dimensional (2D) cell filled with silica sand were: (i) to assess the effectiveness of the selected fluid formulation in removing residual LNAPL trapped within the porous media, and (ii) to reveal the mechanism involved in the displacement of LNAPL in porous media by the injected fluid formulation.

3.3.1 Setup and procedures

A conceptual illustration of the 2D (Hele-Shaw) cell experiment setup is presented in Figure 1. This setup has been successfully used to study two-phase flow in porous media (Colombano et al., 2020; Philippe et al., 2020). The cell, measuring 5 cm in height, 5 cm in length, and 2 cm in width, was made

of polyvinylidene fluoride (PVDF). Two metallic mesh grids with a pore size of 250 μm were placed at the cell's inlet and outlet to hold the sand in place. The cell was covered on both sides with two transparent glass plates for photography. Images from the 2D cell experiments were captured using a Nikon D810 camera (34 Mega Pixels) with NIKKOR LENS 105 (Nikon®). The camera was installed at the center of the vertically positioned 2D cell, at a distance of 50 cm from the cell. Imaging experiments were conducted in a dark room with two 300-W spotlights (Broncolor®). The fluid was injected into the sand-packed cell using a Reglo ICC Ismatec® digital peristaltic pump with a resolution of 0.01 rpm. The effluent sample was collected in a 100 mL graduated cylinder and weighed with a Scout STX6201 OHAUS® digital scale (± 0.1 g precision).

Initially, the silica sand was first thoroughly washed with demineralized water and then dried in an oven at 100°C for 48 h to ensure complete moisture removal. The dried sand was then gradually packed into the vertically positioned cell. To remove any trapped air, the cell was then flushed with CO₂ for 1 h, as the solubility of CO₂ in water helps prevent air entrapment within the porous medium. Following this, the cell was saturated with degassed and demineralized water, introduced from the bottom to the top at a constant flow rate of 1 mL.min⁻¹. The cell was weighed both before and after water saturation to calculate the porosity and PV of the porous medium.

In the subsequent stage, drainage experiments were performed by introducing diesel oil into the water-saturated sand cell from top to bottom at a fixed flow rate of 1 mL.min⁻¹ until irreducible water saturation S_{wi} (%) was achieved. Following this, imbibition experiments were carried out by injecting 2 PV of demineralized and degassed water from bottom to top at the same flow rate of 1 mL.min⁻¹. This vertical injection setup was used to minimize gravitational effects caused by density differences between diesel and water, ensuring uniform residual diesel saturation S_{or} (%) throughout the porous medium. Irreducible water saturation and residual diesel saturation were determined by measuring the displaced water and diesel from the This high recovery efficiency is primarily attributed to the physicochemical porous medium, respectively. Overall, the measured properties of the cell's porous media are listed in Table 3.

Table 3 Properties of porous media

Porous media	Grain size diameter, d (mm)	Porosity, ϕ (%)	Permeability, k (m^2)	Pore Volume, PV (mL)	Irreducible water saturation after drainage test, S_{wi} (%)	Residual diesel saturation after imbibition test, S_{or} (%)
Silica sand	0.4-1.5	35 ± 1.0	$280 (\pm 20) \times 10^{-12}$	17.5 ± 0.5	16 ± 0.5	33 ± 2.4

Diesel oil recovery experiments were subsequently conducted by injecting the flushing fluid horizontally from left to right (inlet to outlet), mimicking field-scale remediation configurations. To enhance the recovery of residual diesel ganglia within the porous medium, 2 PV of the selected fluid formulation were injected at a constant flow rate of $1 \text{ mL} \cdot \text{min}^{-1}$, maintaining a pressure gradient of $250 \text{ mbar} \cdot \text{m}^{-1}$ across the experimental setup. The fluid formulation was prepared under controlled stirring conditions at 500 rpm for 3 h at 20°C to ensure homogeneity and stability. Photographs of the porous medium within the 2D cell were captured at 5-s intervals during the injection process for subsequent image analysis.

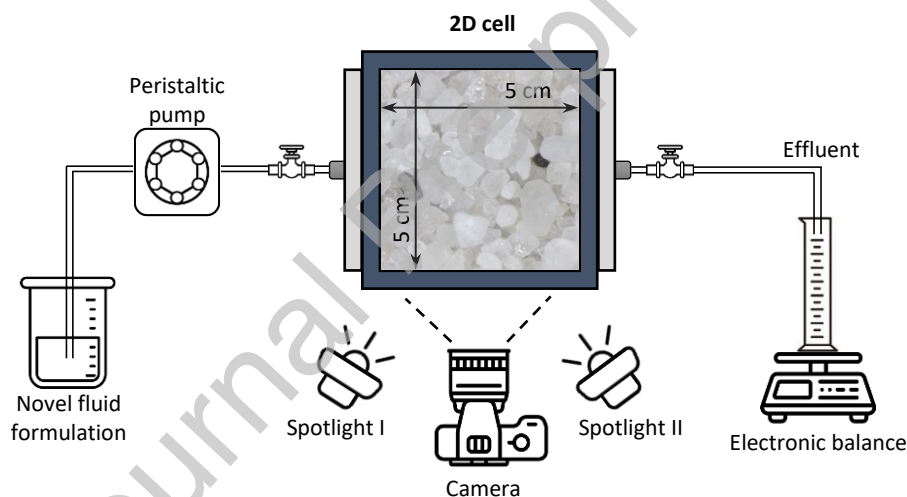


Figure 1. Schematic diagram of the experimental setup used to study LNAPL recovery through the injection of the selected fluid formulation into a 2D sand-packed cell.

3.3.2 Image analysis

The purpose of the image analysis was to estimate diesel oil saturation in the porous medium and to examine the mechanisms involved in the recovery of residual diesel oil during the injection of the selected fluid formulation. Residual diesel oil saturation was determined by estimating the fraction of area occupied by diesel oil relative to the total area of the porous medium in the image. Image analysis was conducted using Fiji ImageJ software.

First, all images were cropped on all sides before analysis to eliminate the wall shade effect. The resulting cropped images measured 3.24 cm in length and 2.16 cm in height, differing from the original dimensions of the 2D cell's glass surface. Using these measurements, we set the image scale. Subsequently, the images were adjusted for contrast and brightness to enhance the visibility of the diesel oil and then converted into RGB format. A "color threshold" technique was applied to distinguish the diesel phase from the rest of the image based on adjusting the color hue and saturation. Once the diesel phase was isolated, the area occupied by diesel oil was measured, and total diesel content θ (%) on the 2D surface was calculated as follows,

$$\theta = \frac{\text{Area of Diesel Oil}}{\text{Total Area}} \quad (2)$$

With the initial residual diesel content on the 2D surface known, the final residual diesel content after injecting 2 PV of the selected fluid formulation was determined to estimate the diesel oil removal.

The subsequent stage of image interpretation focused on investigating the mechanisms involved in the recovery of diesel oil ganglia within the pore space. We used the method proposed by Colombano et al. (2021) for DNAPL/water saturation estimation in the 2D tank and adapted it to estimate the LNAPL volume fraction in a targeted ganglion. Initially, the images were converted to an 8-bit format. A specific area of interest (AOI) was then defined, focusing on regions where a diesel ganglion was trapped. The impact of the selected fluid formulation on the displacement of the diesel ganglion was assessed by measuring changes in their initial area and optical density over time. The linear relationship between the optical density and the diesel volume fraction was determined using two known reference zones: the first containing pure diesel fuel ganglia before treatment, representing a diesel volume fraction of unity, and the second containing only the flushing fluid, representing a diesel volume fraction of zero.

4 Results

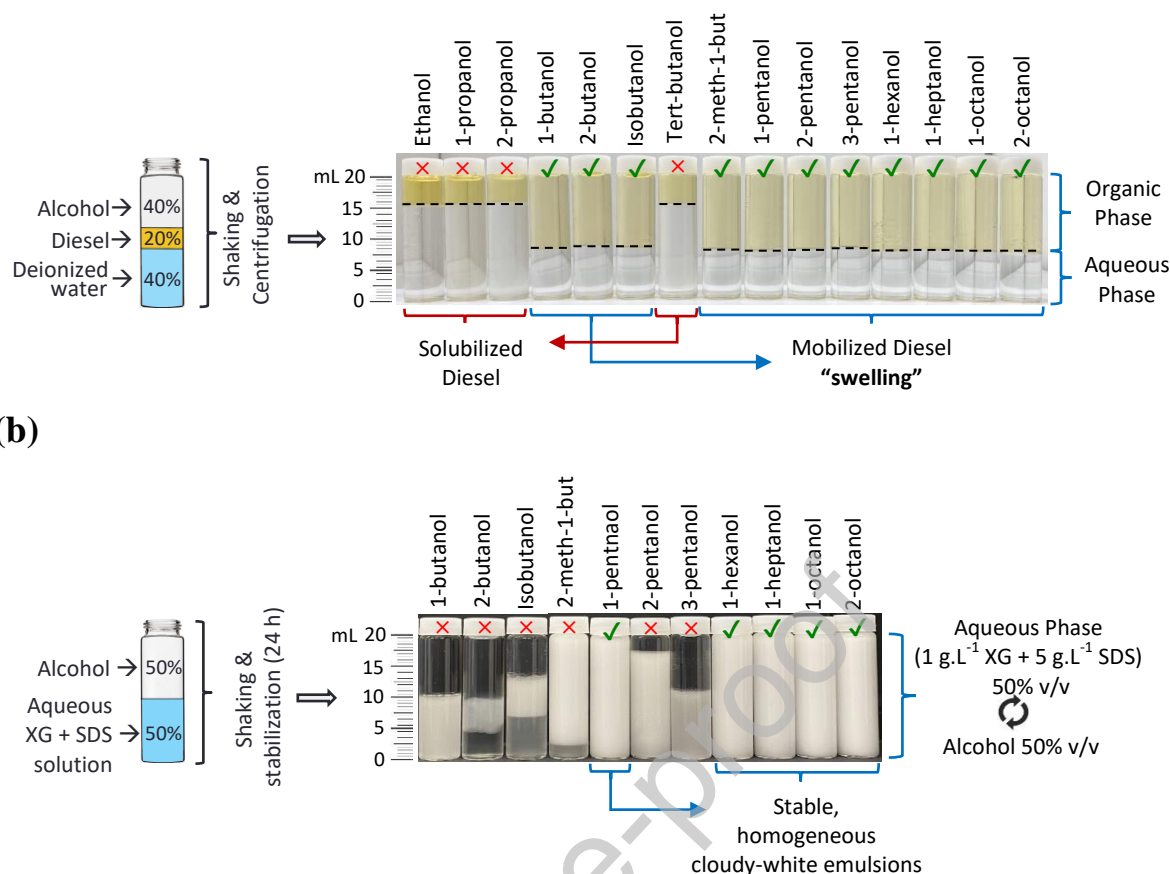
4.1 Development and selection of injection fluid based on batch tests

4.1.1 Alcohol partitioning test

Figure 2a presents the partitioning behavior results of each alcohol (40% v/v) between deionized water (40% v/v) and diesel oil (20% v/v). Based on the phase behavior results, ethanol, 1-propanol, 2-propanol, and tert-butanol were preferentially partitioned into the aqueous phase, further promoting the solubilization mechanism of diesel oil in the aqueous phase. The volume of solubilized diesel oil was not quantified due to its insignificant solubility, making accurate measurements impossible. However, Jeong et al. (2009) reported that in a two-dimensional glass pore network pattern, 30% 1-propanol (v/v) and 30% tert-butanol (v/v) increased the area of trapped benzene-LNAPL blobs through a swelling mechanism, as detected via image analysis. As a result, the partitioning behavior of alcohols in the presence of both aqueous and organic phases depends on the type of organic phase and the polarity of its molecules. Consequently, ethanol, 1-propanol, 2-propanol, and tert-butanol, which facilitate the solubilization of diesel oil into the aqueous phase, were not selected for further investigation as it is beyond the scope of our study.

In contrast, the oil-soluble alcohols 1-butanol, 2-butanol, 2-methyl-1-butanol, 1-pentanol, 2-pentanol, 3-pentanol, 1-hexanol, 1-heptanol, 1-octanol, and 2-octanol were predominantly partitioned into the diesel phase. As a result, the volume of the diesel phase was increased due to swelling, indicating a mobilization mechanism. These alcohols, with their non-polar part, tend to partition into the non-polar diesel phase rather than the polar aqueous phase. Therefore, these “oil-swelling alcohols” were selected for further batch tests to develop a new formulation by mixing with the 1 g.L⁻¹ XG + 5 g.L⁻¹ SDS solution.

(a)



(b)

Figure 2. a) Partitioning of alcohols between the aqueous and diesel phases ('✓': selected oil-soluble alcohols that promote the swelling mechanism of diesel fuel, 'x': unselected water-soluble alcohols that promote diesel solubilization mechanisms), and b) Development and selection of a stable and homogeneous formulation by mixing selected diesel-swelling alcohols with 1 g.L^{-1} XG + 5 g.L^{-1} SDS solution ('✓': stable and homogeneous oil-in-water emulsions, 'x': unstable emulsion formulations).

4.1.2 Development of a novel formulation

Subsequent batch experiments aimed at developing homogeneous and stable mixtures of the 1 g.L^{-1} XG + 5 g.L^{-1} SDS solution with various oil-swelling alcohols. The results of the eleven mixtures are depicted in Figure 2b. Among the oil-swelling alcohols, only 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, and 2-octanol formed homogeneous oil-in-water (O/W) emulsions upon mixing with 1 g.L^{-1} XG + 5 g.L^{-1} SDS solution. These emulsions remained stable after a 24-h settling period, demonstrating their suitability for further investigations.

In contrast, emulsions based on 2-methyl-1-butanol, 2-pentanol, and 3-pentanol exhibited instability within 24 h, leading to phase separation. This instability can be attributed to the reduced

hydrophobicity of branched-chain alcohols, which makes them more soluble in water than their straight-chain isomers (Jin et al., 2019). Branching in the molecular structure decreases the surface area available for intermolecular interactions within the hydrophobic part of the molecule, thereby limiting the alcohol's ability to stabilize emulsions effectively. Consequently, branched-chain alcohols like 2-pentanol and 3-pentanol were found to be unstable due to their intermediate molecular structures and polarity, which disrupted the balance required for stable emulsions. Since unstable emulsions are unsuitable as injection fluids for LNAPL remediation, as they must remain homogeneous to ensure constant rheological properties throughout the application process, these alcohols were excluded from further consideration.

Similarly, 1-butanol, 2-butanol, and isobutanol failed to form homogeneous emulsions upon mixing with the 1 g.L⁻¹ XG + 5 g.L⁻¹ SDS solution, further narrowing the range of suitable candidates. In contrast, emulsions prepared using 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, and 2-octanol exhibited similar stability (24 h) and diesel swelling ability, making them suitable candidates for further investigations. Ultimately, we selected 1-pentanol among all oil-swelling alcohols for the rest of the study as a component of the injection emulsion based on toxicity (Patočka & Kuča, 2012; PubChem) and biodegradability criteria (Babeu & Vaishnav, 1987; Vaishnav et al., 1987). This newly formulated emulsion, consisting of 1 g.L⁻¹ XG, 5 g.L⁻¹ SDS, and 50% (v/v) 1-pentanol, was named "COCKTAIL" due to its cloudy white appearance.

4.2 Characterization of COCKTAIL emulsion

4.2.1 Stability and drop size distribution

Figure 3 shows the stability results of COCKTAIL emulsion over time in sealed graduated cylinders. The results reveal that the COCKTAIL emulsion exhibited no phase separation, maintaining constant apparent stability throughout the 30-d observation period. Generally, emulsion instability is caused by various physicochemical mechanisms, including gravitational separation (creaming/sedimentation), flocculation, coalescence, and Ostwald ripening (Friberg et al., 2003; Langevin, 2019; McClements, 2004; Taylor, 1998). However, the stability of emulsions depends on the stabilizers and their function as either "emulsifiers" or "texture modifiers" (McClements, 2007). In the case of the COCKTAIL emulsion, an anionic SDS surfactant (at 2 CMC) was assigned as an emulsifier. SDS reduces

interfacial tension between phases, and its negatively charged molecules adsorb onto the surface of 1-pentanol droplets, thereby preventing their aggregation due to electrostatic repulsion (Kundu et al., 2019). As for the XG biopolymer, it acted as a “texture modifier” of the COCKTAIL emulsion. According to Stokes’ law, emulsion droplets’ sedimentation or creaming rate is inversely dependent on the viscosity of the continuous phase. Dickinson et al. (1994) observed that the presence of XG in the aqueous phase of an emulsion, particularly when its concentration exceeds the overlap concentration ($\sim 1 \text{ g.L}^{-1}$), retards the creaming mechanism. Therefore, in the COCKTAIL emulsion, XG promoted an increase in the viscosity of the continuous phase, thereby retarding the upward migration of 1-pentanol droplets due to density differences. This retardation is associated with the immobilization of dispersed droplets in the viscous surrounding phase. Thus, the high stability of the COCKTAIL emulsion is due to the increased viscosity of the continuous phase, facilitated by XG, and the electrostatic repulsion between dispersed droplets induced by SDS.

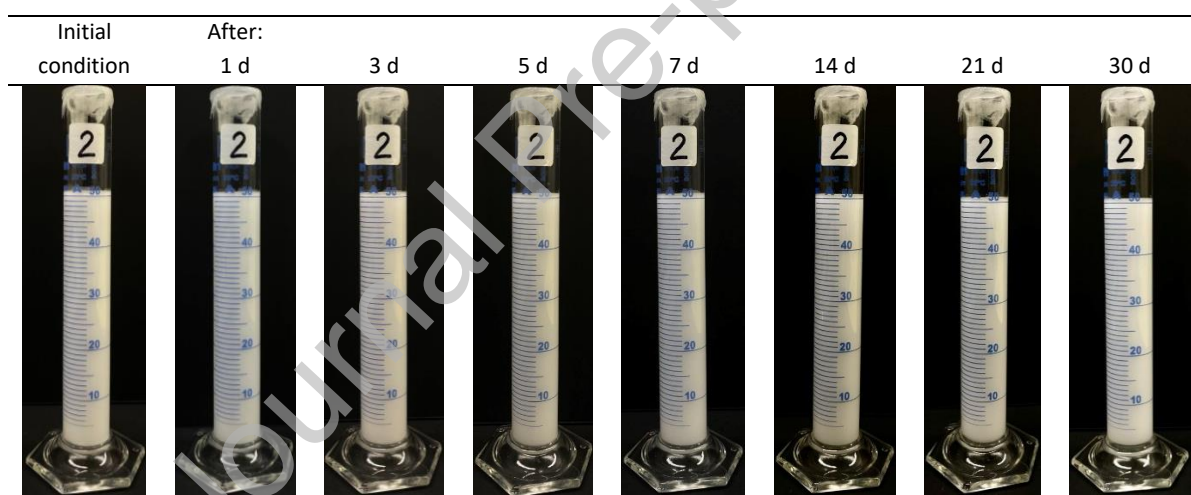


Figure 3. Stability of COCKTAIL emulsion over time.

Drop Size Distribution (DSD) analysis is essential for a comprehensive understanding of the stability and destabilization processes of the COCKTAIL emulsion. Figure 4 illustrates the DSD of a polydisperse COCKTAIL emulsion over time. The DSD of freshly prepared COCKTAIL emulsion (Figure 4a) and after 30 d (Figure 4b) were monomodal. The droplet size of the freshly prepared COCKTAIL emulsion ranged from 5 to 18 μm , while the 30-d-old emulsion ranged from 5 to 100 μm . The mean drop diameter of the freshly prepared and 30-d-old COCKTAIL emulsion was about 11 ± 3

μm and $23 \pm 18 \mu\text{m}$, respectively. Thus, a significant increase in droplet diameter was observed for the 30-d emulsion compared to the maximum droplet diameter of the freshly prepared emulsion.

Moreover, the 30-d emulsion contained a larger number of droplets measuring less than 5 microns in size compared to the freshly prepared emulsion. This indicates a structural change in the emulsion over time, which the coarsening of the droplets can explain. Emulsions are generally prone to coalescence and Ostwald ripening phenomena, contributing to their overall coarsening over time (Aronson & Petko, 1993; Taylor, 1995). According to Fick's law of diffusion, the molecules of smaller dispersed droplets diffuse into surrounding larger droplets, driven by the pressure difference between them. This phenomenon elucidates the mechanism behind Ostwald ripening (Fischmeister & Grimvall, 1973; Ostwald, 1897).

Additionally, the solubility of the dispersed phase in the continuous phase influences Ostwald ripening. In the COCKTAIL emulsion, Ostwald ripening may occur due to the low solubility of 1-pentanol (the dispersed phase) in the 1 g.L^{-1} XG + 5 g.L^{-1} SDS solution (the continuous phase). Hence, besides droplet coalescence, the Ostwald ripening phenomenon explains the presence of numerous droplets smaller than 5 microns and larger coarsened droplets exceeding $18 \mu\text{m}$ in the 30-d-old emulsion. However, similar to creaming and sedimentation mechanisms, Ostwald ripening can be retarded by the viscosity or elasticity of the continuous phase. In the COCKTAIL emulsion, the viscosity of the continuous phase containing 1 g.L^{-1} XG polymer significantly retards Ostwald ripening. Thus, the changes in the DSD of the COCKTAIL emulsion over time are primarily due to the creaming mechanism of the dispersed phase, followed by coalescence and Ostwald ripening.

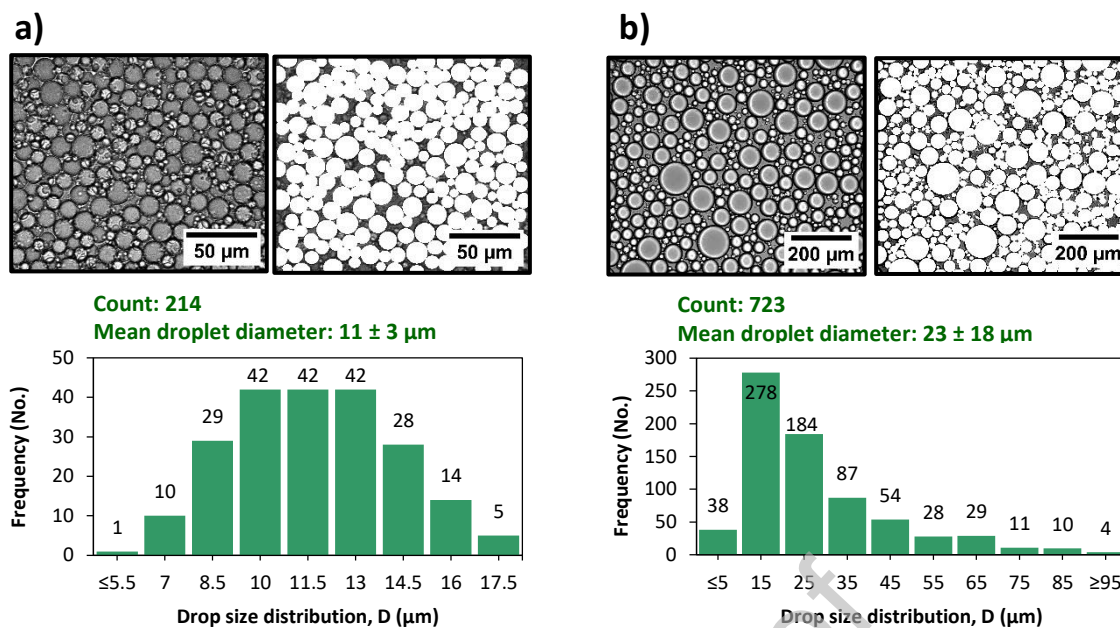


Figure 4. Drop size distribution histograms of COCKTAIL emulsion over time based on microscopic images and size quantification using Fiji ImageJ: **a)** freshly prepared and **b)** after 30 d.

The stability of the emulsion plays a critical role in determining its effectiveness for diesel removal. Emulsions that are prone to phase separation or coalescence over time are unsuitable for injection due to their inability to maintain constant rheological properties during flow through porous media. The results of the stability experiments demonstrated that emulsion containing 1-pentanol exhibited high stability over 30 d, maintaining its homogeneous structure without phase separation. This stability is essential for ensuring the uniform propagation of the emulsion within the porous medium and the effective delivery of 1-pentanol to trapped diesel ganglia.

4.2.2 Rheology: effect of alcohol on emulsion behavior

Although 1-pentanol was selected as a component of the injection emulsion, we also evaluated and compared the rheological behavior of all stable emulsions formed by other diesel-swelling alcohols, including 1-hexanol, 1-heptanol, 1-octanol, and 2-octanol. Figure 5a presents the viscosity of these emulsions as a function of shear rate. All the emulsions exhibited non-Newtonian shear-thinning behavior across a wide range of shear rates. The rheological behavior of the emulsions was very similar, confirming the choice of 1-pentanol as the component of the COCKTAIL emulsion based solely on its lower toxicity and higher biodegradability compared to other alcohols.

Figure 5b illustrates the viscosity of the COCKTAIL emulsion and reference solutions as a function of shear rate. 1 g.L^{-1} XG and 1 g.L^{-1} XG + 5 g.L^{-1} SDS solutions and COCKTAIL emulsion (a mixture of 1-pentanol and 1 g.L^{-1} XG + 5 g.L^{-1} SDS at a volume ratio of 1:1) behaved as non-Newtonian fluids, exhibiting shear-thinning behavior over a wide range of shear rates. However, despite all fluids exhibiting shear-thinning rheology, 1 g.L^{-1} XG, and 1 g.L^{-1} XG + 5 g.L^{-1} SDS showed a Newtonian region at low shear rates in the $0.01\text{-}0.04 \text{ s}^{-1}$ range.

Based on the rheological curves, the viscosity of the XG solution decreases with the presence of SDS surfactant. This phenomenon is associated with microstructural changes in XG molecules due to their interaction with SDS. The explanation lies in the electrostatic repulsion between similarly charged molecules (Krstonošić et al., 2019). Additionally, it is assumed that SDS in the XG solution may induce wall-slip effects between the two parallel plates where the solution was previously loaded. Consequently, the appearance of slip velocity on the walls affects the true shear values (Omirbekov et al., 2022).

In contrast, incorporating the oil-soluble 1-pentanol into the 1 g.L^{-1} XG + 5 g.L^{-1} SDS solution increased the viscosity, which is attributed to the formation of O/W emulsion (Pal, 1992). The viscosity of the COCKTAIL emulsion increased by approximately threefold compared to its continuous aqueous phase represented by the 1 g.L^{-1} XG + 5 g.L^{-1} SDS solution. Furthermore, the viscosity of the COCKTAIL emulsion was approximately 1.7 times higher than that of the XG solution at the same concentration (1 g.L^{-1}).

(a)

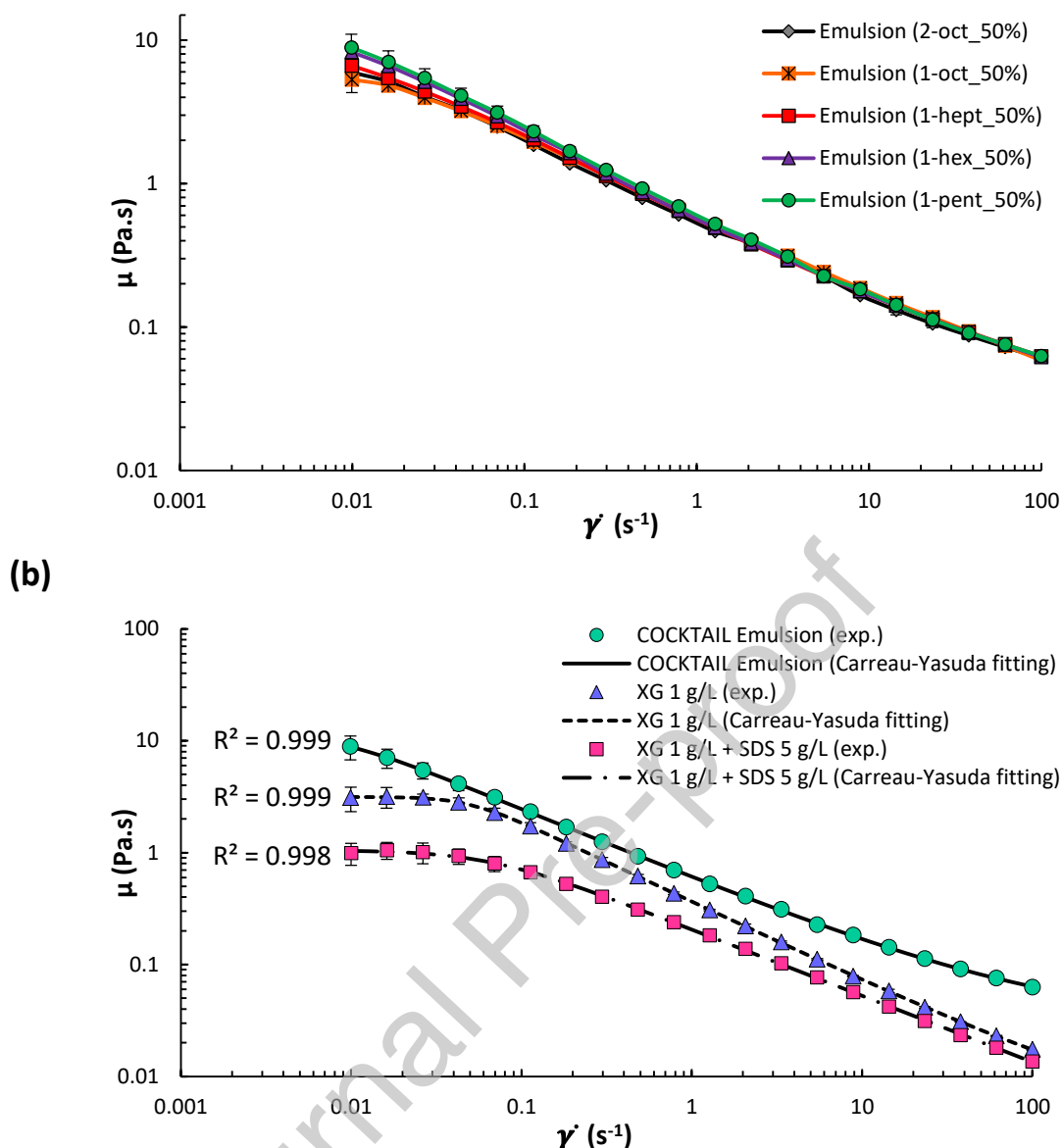


Figure 5. Viscosity as a function of shear rate: (a) comparison of various stable emulsions containing 50% v/v swelling alcohol and an aqueous solution of 1 g.L⁻¹ XG + 5 g.L⁻¹ SDS, and (b) comparison of the “COCKTAIL” emulsion (1-pent_50%) with reference solutions of 1 g.L⁻¹ XG, 1 g.L⁻¹ XG + 5 g.L⁻¹ SDS, including fitting curves based on the Carreau-Yasuda model.

The Carreau-Yasuda model effectively fits the measured rheological curves of both polymer solutions and COCKTAIL emulsion. The coefficients of determination and the fitting parameters obtained by nonlinear regression are presented in Table 4. The coefficient of determination is above 99% in all cases, indicating an excellent fit for the model. The dynamic viscosities of all fluids at zero (μ_0) and infinite (μ_{inf}) shear rates were positive values. The viscosity at zero shear rate refers to the viscosity of

a fluid when no shear stress is applied. Hence, the COCKTAIL emulsion had the highest viscosity at zero shear rate ($\mu_0 = 11.922$ Pa.s), indicating resistance to flow at low shear rates compared to 1 g.L^{-1} XG and 1 g.L^{-1} XG + 5 g.L^{-1} SDS solutions. As the shear rate increases, the dynamic viscosity decreases towards the lower limit at the infinite shear rate (μ_{inf}), exhibiting a shear-thinning rheology. The power law index of the COCKTAIL emulsion ($n = 0.379$) indicates a significant shear-thinning behavior over a wide range of shear rates. However, the power law index of the 1 g.L^{-1} XG solution ($n = 0.285$) exhibits more significant shear-thinning behavior compared to both the COCKTAIL emulsion ($n = 0.379$) and 1 g.L^{-1} XG + 5 g.L^{-1} SDS solution ($n = 0.407$). The COCKTAIL emulsion has a higher value of a relaxation time ($\lambda = 129.453$ s) compared to 1 g.L^{-1} XG ($\lambda = 20.518$ s) and 1 g.L^{-1} XG + 5 g.L^{-1} SDS ($\lambda = 15.671$ s) solutions. The relaxation time shows that the COCKTAIL viscosity takes 129.45 s to adjust and reach a steady state after changing the shear rate. The higher relaxation time suggests that the COCKTAIL emulsion is a more viscous and complex two-phase fluid with slower structural rearrangement under applied stress. Meanwhile, the COCKTAIL emulsion exhibits the lowest transition parameter ($a = 0.235$) between the zero-shear rate and power law region. The low transition parameter implies that COCKTAIL shows a relatively gradual transition between its high and low shear rate viscosity regimes. Its viscosity varies smoothly with changes in shear rate, in contrast to the more pronounced changes observed in 1 g.L^{-1} XG and 1 g.L^{-1} XG + 5 g.L^{-1} SDS solutions with higher transition parameters.

Table 4. The Carreau-Yasuda fitting parameters for different fluids in bulk form.

Media	Bulk form		
	Fluids	XG 1 g.L^{-1}	XG 1 g.L^{-1} + SDS 5 g.L^{-1}
μ_0 (Pa.s)	3.146	1.052	11.922
μ_{inf} (Pa.s)	0.004	0.002	0.030
λ (s)	20.518	15.671	129.453
n (-)	0.285	0.407	0.379
a (-)	3.253	1.713	0.235
R^2	0.999	0.998	0.999

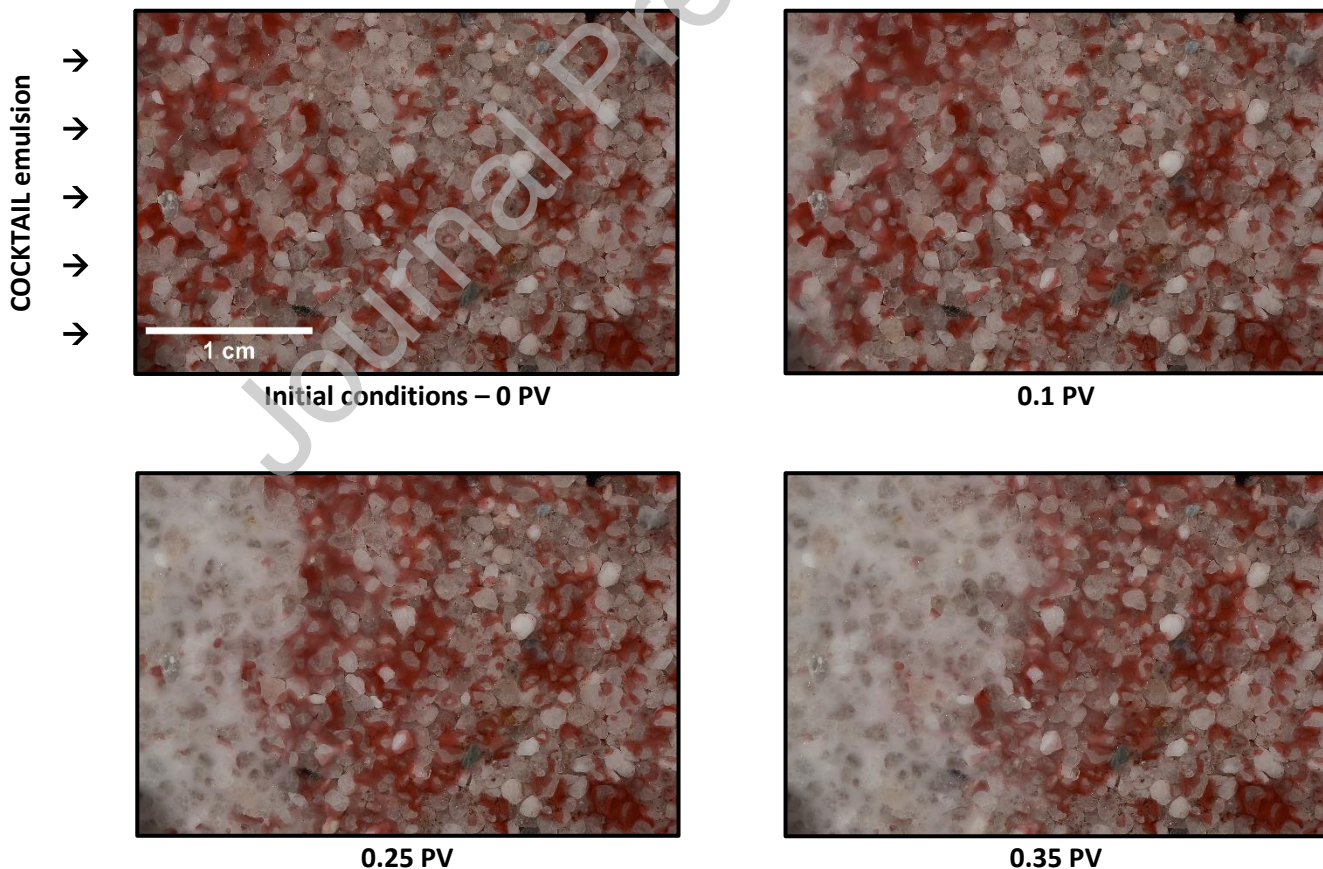
4.3 Assessment of LNAPL swelling and displacement

Figure 6 illustrates the diesel removal efficiency of the COCKTAIL emulsion as a function of injected pore volume (PV) in the 2D cell (see Supplemental Video 1). Following the drainage-imbibition

experiments, residual diesel saturation was achieved in the porous medium, which was then defined as the initial condition for the COCKTAIL injection. Injecting the viscous, shear-thinning COCKTAIL promoted stable and uniform displacement within the porous medium. Image analysis revealed that the residual diesel content observed on 2D image surfaces was completely removed within just 1.15 PV of COCKTAIL injection. Unlike traditional pump-and-treat techniques, which often leave significant residual diesel due to bypassing in low-permeability zones, the emulsion ensures uniform propagation and enhanced mobilization of trapped diesel ganglia. For further comparison, unconventional methods such as surfactant flushing studied by Hernández-Espriú et al., (2013) achieved recovery rates of 40–78%, while cosolvent-enhanced flushing reported by Falta et al. (1999) reached efficiencies of 70–90%. Similarly, studies by Omirbekov et al. (2023) and Alamooti et al. (2023) using polymers and surfactant-polymer solutions achieved recovery rates of 85–92%. In contrast, the COCKTAIL emulsion achieved complete diesel recovery under comparable laboratory conditions, highlighting its superior performance and potential as a highly effective remediation technique.

This high recovery efficiency is primarily attributed to the physicochemical interactions between 1-pentanol and diesel, which facilitate the swelling mechanism observed in diesel ganglia during emulsion injection. The hydrophobic alkyl chain and polar hydroxyl group of 1-pentanol enable its preferential partitioning into the diesel phase rather than the aqueous phase. This partitioning results in the lower polarity of the diesel oil, which aligns well with the hydrophobic interactions of 1-pentanol molecules. Once partitioned into the diesel phase, 1-pentanol molecules reduce intermolecular interactions within the diesel oil, causing the ganglia to expand in volume—a phenomenon known as swelling. This swelling mechanism enhances recovery efficiency by converting them into a continuous phase that the emulsion can more easily displace. The physicochemical compatibility between 1-pentanol and diesel oil thus plays a crucial role in enhancing the mobilization and removal of residual diesel from the porous media. The diesel oil-swelling behavior of 1-pentanol was comprehensively studied during batch experiments (see Section 3.2.1), and its effectiveness in promoting diesel mobilization was confirmed in porous media.

In addition to the physicochemical interactions, the rheological behavior of the COCKTAIL emulsion is equally significant for achieving high diesel removal efficiencies from porous media. Composed of XG in the continuous phase, the emulsion exhibits high viscosity and shear-thinning rheology (see Figure 5), which facilitate the targeted delivery of 1-pentanol droplets into low-permeability zones where diesel ganglia are trapped. The shear-thinning behavior, characterized by a significant reduction in viscosity with increasing shear rate, may offer considerable advantages for large-scale field applications. This property allows the emulsion to maintain low viscosity during high-pressure injection, minimizing energy requirements and operational costs associated with pumping. Once in the subsurface, the emulsion's viscosity increases under low-shear conditions, which helps ensure uniform propagation and prevents bypassing in low-permeability zones. Moreover, the shear-thinning behavior also reduces the risk of soil uplift or fracturing during injection, as it allows better control of injection pressure. This property is particularly advantageous in heterogeneous porous media, where maintaining a stable displacement front is critical for achieving efficient remediation.



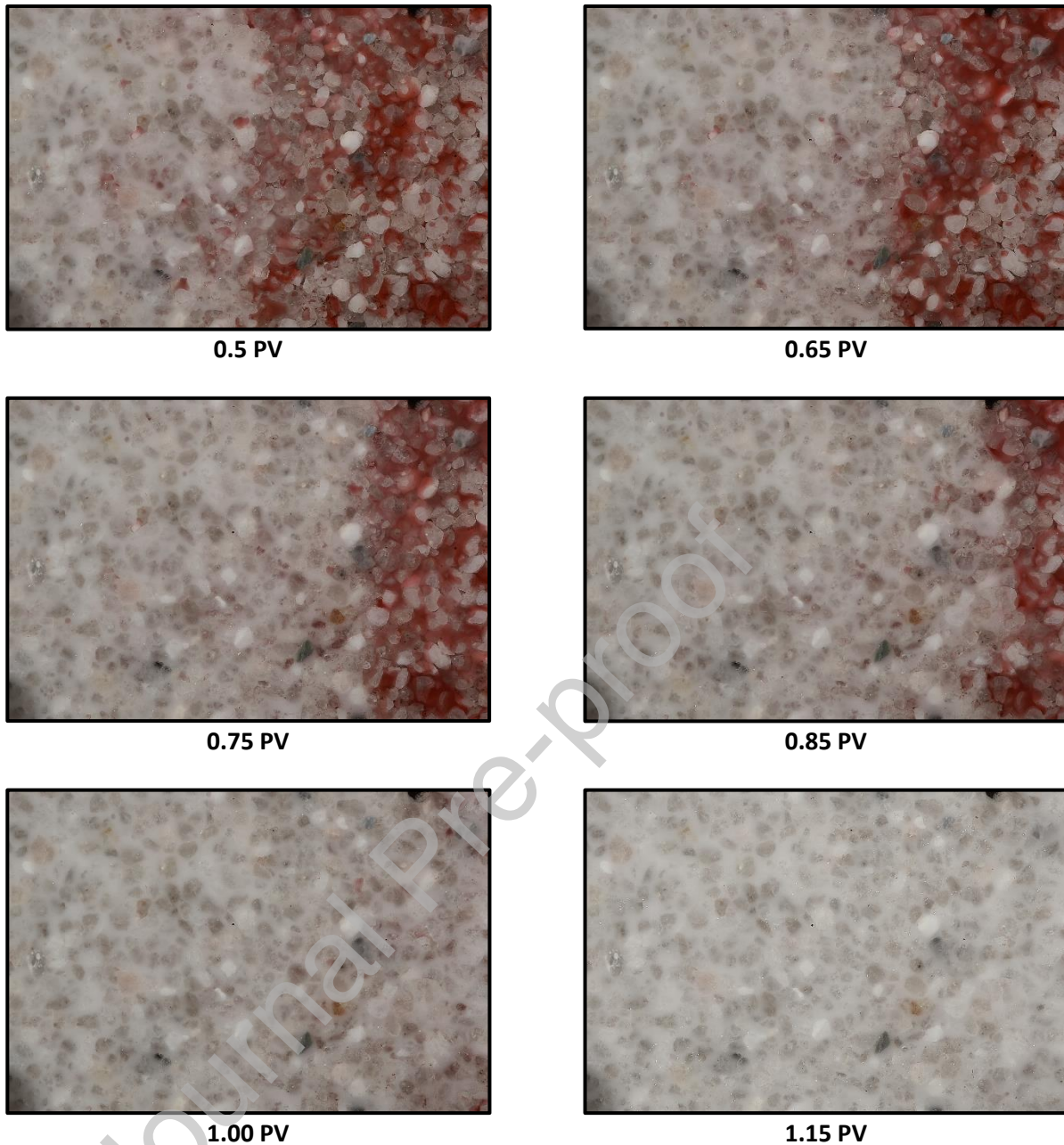


Figure 6. Cropped images of LNAPL removal as a function of PV using COCKTAIL emulsion flushing in the sand-packed 2D cell (red: diesel oil; white: COCKTAIL emulsion; gray: sand).

Figure 7 complements the findings presented in Figure 6 by providing a visual representation of the diesel recovery process in the 2D cell at 0.5 PV injection. The image highlights three distinct fluid displacement zones, separated by yellow dashed lines, offering detailed insights into the emulsion's behavior in porous media.

Zone I represents the pure COCKTAIL emulsion, where the injected emulsion fully occupies the pore spaces, effectively displacing any residual diesel oil that was previously present. Zone III depicts the residuals of pure diesel oil (free product), distinguished by its dark red color in the image. In contrast to Zones I and III, Zone II exhibits more complex displacement behavior, characterized by a miscible fluids bank alongside more stable displacement. This middle zone between the two yellow dashed lines represents the miscible displacement bank of the emulsion and residual diesel oil.

The complex behavior in Zone II can be explained by the partial destruction of the COCKTAIL emulsion at the interface upon contact with diesel ganglia. Dispersed 1-pentanol droplets are released from the COCKTAIL emulsion and preferentially partition into the entrapped diesel ganglia, causing them to swell. Once the emulsion partially or fully collapses at the interface, the viscous $1 \text{ g.L}^{-1} \text{ XG} + 5 \text{ g.L}^{-1} \text{ SDS}$ solution, with its shear-thinning behavior, continues to displace the swollen diesel ganglia while maintaining a relatively stable displacement front, highlighted by the dark dashed line. Moreover, partitioning occurs mainly at the interface, while the COCKTAIL emulsion invading from behind displaces both the separated $1 \text{ g.L}^{-1} \text{ XG} + 5 \text{ g.L}^{-1} \text{ SDS}$ and the swollen diesel ganglia. This swelling mechanism increases the diesel ganglia area, facilitating the mobilization of previously immobile ganglia. The swollen diesel phase, distinguished by its light red (or pink) color, can be observed at the front of the emulsion flow, clearly different from the pure diesel oil depicted in dark red in Zone III.

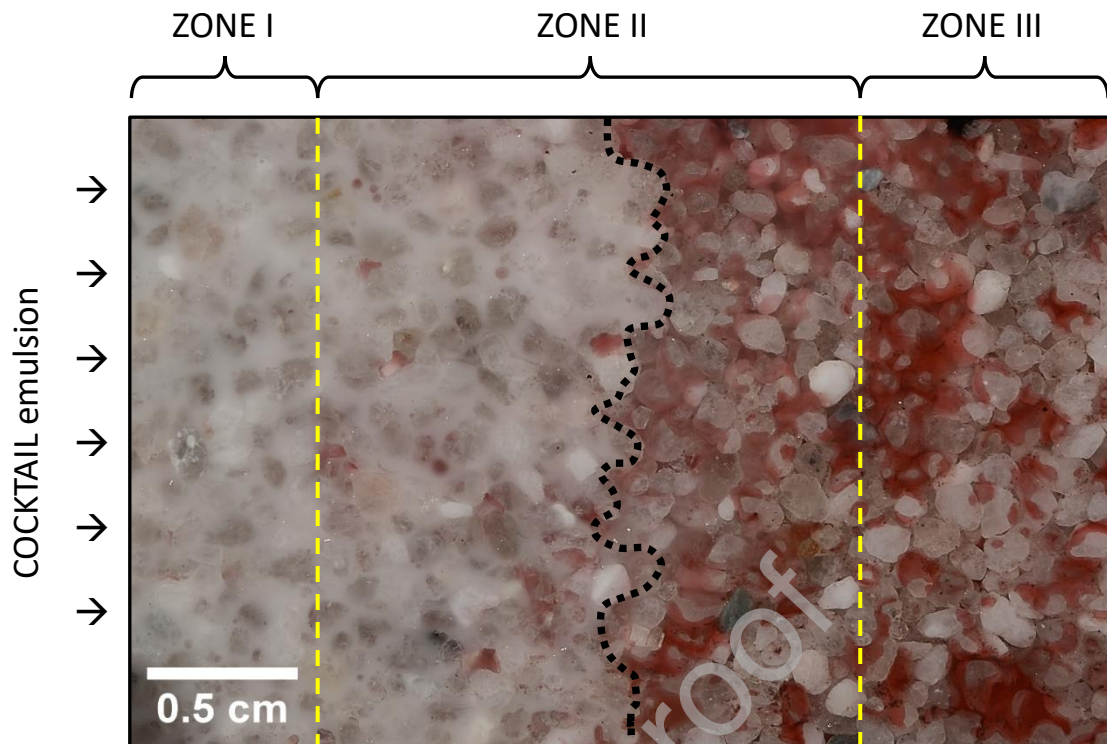


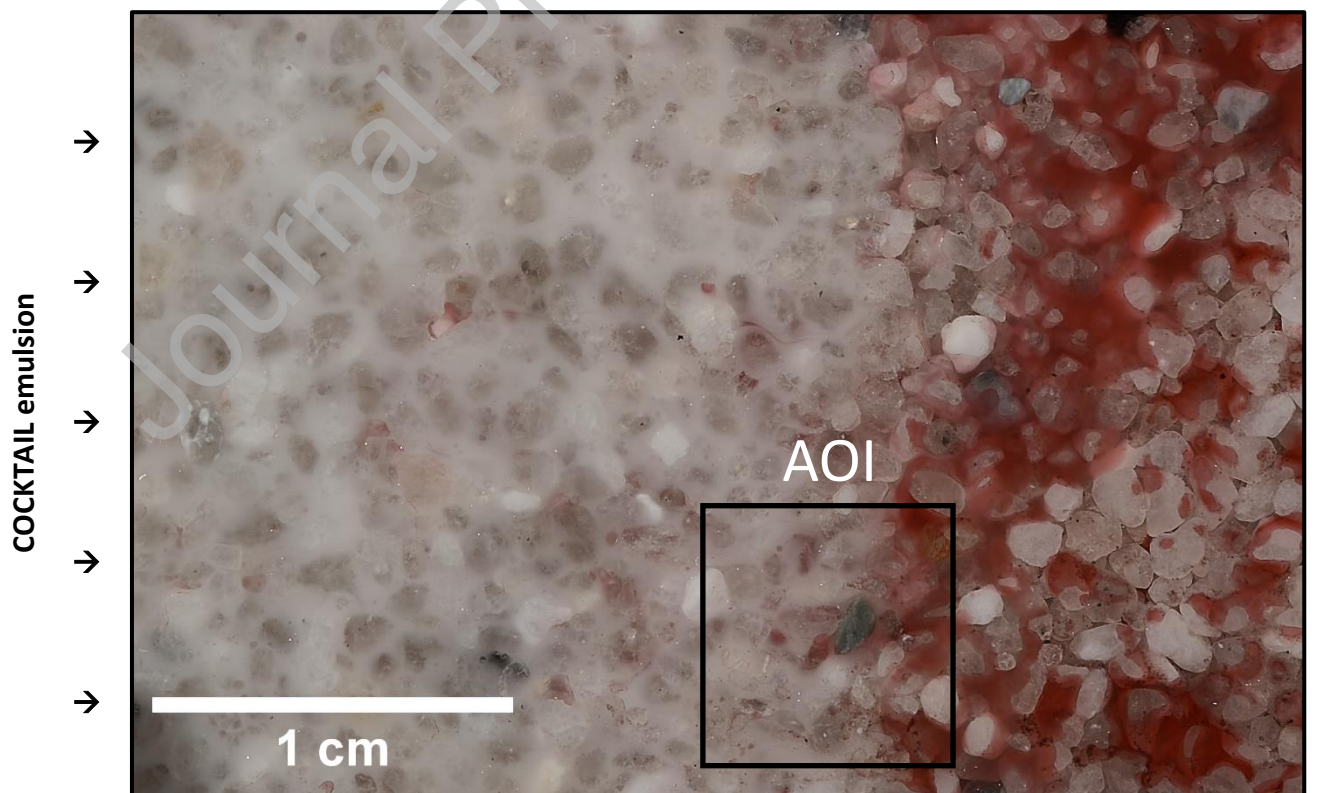
Figure 7. Visual representation of diesel oil displacement zones at 0.5 PV COCKTAIL emulsion injection - Zone I: pure COCKTAIL emulsion, Zone II: residual diesel oil swelling induced by COCKTAIL emulsion containing 1-pentanol, Zone III: trapped residual diesel oil.

Overall, the complex behavior in Zone II, particularly the interaction between the COCKTAIL emulsion and the residual diesel ganglia, highlights the need for a thorough investigation of the swelling mechanism in the pore space. To better understand the pore-scale mechanism of diesel swelling, an area of interest (AOI) was determined (see Figure 8a), representing a single entrapped diesel ganglion within the pore space (see Supplemental Video 2). The AOI was selected at the interface between the 0.65 PV of injected COCKTAIL and the resident diesel oil, where a clear photographic illustration of diesel ganglion swelling was observed. Figure 8b illustrates the results of the changes in surface area and diesel volume fraction of a single trapped ganglion as a function of time during the COCKTAIL emulsion flow through the AOI.

At the initial condition of 0 s (0.65 PV), a trapped diesel ganglion (outlined in pink) was observed, representing the state before 1-pentanol has partitioned into the ganglion during the COCKTAIL emulsion flow. Initially, the diesel ganglion appeared as a small droplet with a well-defined shape,

where no partitioning of 1-pentanol had yet been observed. However, after 5 s, the diesel ganglion's shape and surface area began to change slightly, indicating a swelling mechanism as 1-pentanol starts to partition into it. By 10 s, the swelling became more pronounced as the ganglion enlarged, indicating increased partitioning of 1-pentanol. Following this, a gradual increase in the diesel ganglion area and a decrease in the color intensity were observed over 15 and 20 s, leading to continuous swelling. This swelling caused the diesel ganglion to deform slightly from its original shape, becoming more elliptical. Finally, a significant increase in diesel ganglion area and color intensity occurred after 25 s. As a result, the diesel ganglion's shape became irregular and deviated from its original round form. The pink outline shows that the diesel ganglion became a continuous phase within the porous medium, facilitating easier displacement. This observation is consistent with the findings of Brandes & Farley (1993), who reported that the alcohol-induced DNAPL globules become a relatively continuous phase within the porous medium, making them easier to displace than disconnected residuals.

(a)



Initial conditions determined at 0.65 PV of COCKTAIL injection: Defining the area of interest (AOI)

(b)

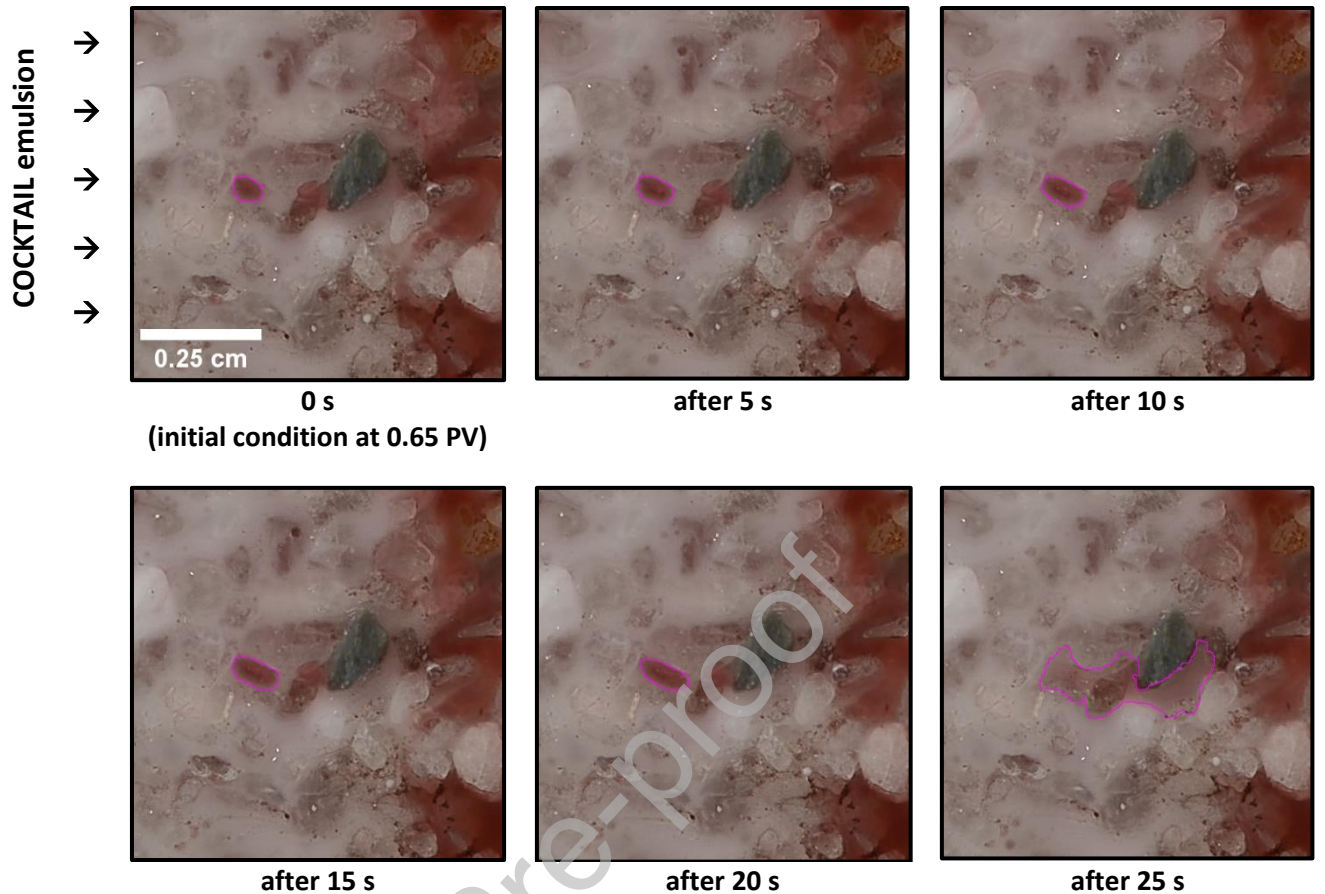


Figure 8. LNAPL removal in the 2D cell through emulsion injection: a) Initial conditions after drainage-imbibition experiments, including AOI determination for investigating diesel oil swelling, and b) swelling behavior of the trapped diesel ganglion as a function of emulsion injection time (red: diesel fuel; white: COCKTAIL emulsion; pink line: ganglion's border).

Figure 9 presents a quantitative assessment of the relationship between the normalized diesel ganglia area and the corresponding diesel volume fraction within that area as a function of emulsion injection time. The analysis of diesel ganglia swelling induced by the 1-pentanol-containing emulsion was conducted in triplicate, systematically evaluating trapped diesel ganglia from different experimental runs. To account for variations in initial conditions at $t = 0$, such as the diesel ganglia area among the analyzed samples, the results are presented as normalized diesel ganglia areas to ensure comparability. The area of the diesel ganglia increased by more than 14-fold from its initial state at $t = 0$ s to its final state at $t = 25$ s. Concurrently, the diesel volume fraction in the studied ganglia, which initially represented pure diesel oil at $t = 0$ s, varied over time due to the continuous partitioning of 1-pentanol

into the ganglia. As a result, the diesel volume fraction decreased from 1.00 ± 0.00 ($100\% \pm 0\%$) to 0.23 ± 0.07 ($23\% \pm 7\%$) within 25 s. This decrease is attributed to the observed swelling of the diesel ganglion, suggesting that 1-pentanol has significantly partitioned into the ganglion, thereby facilitating its mobilization from the AOI. Thus, the transition from a diesel droplet to a significantly swollen and irregular continuous diesel phase within the porous medium indicates the effect of 1-pentanol partitioning into the diesel ganglion over time, facilitating its subsequent mobilization.

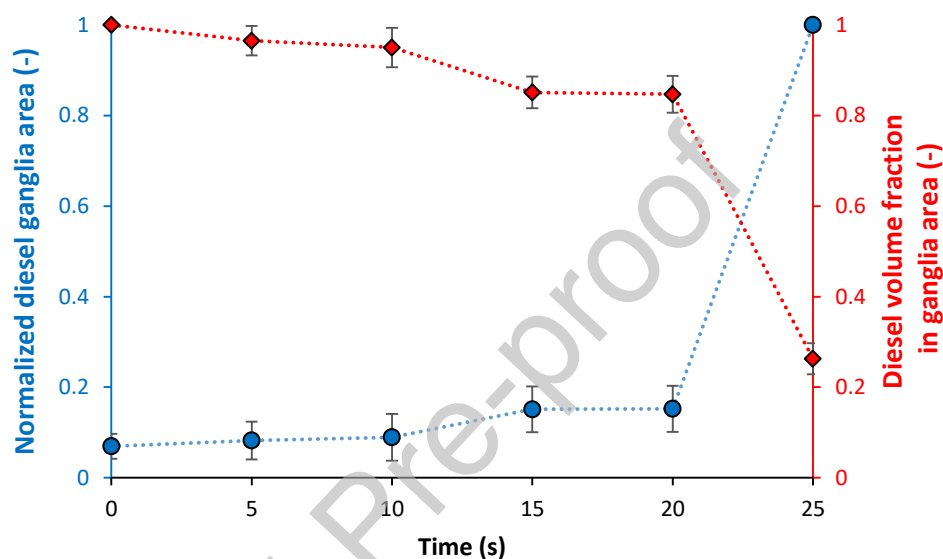


Figure 9. Normalized diesel ganglia area and corresponding diesel volume fraction as a function of COCKTAIL emulsion injection time.

5 Conclusions

In this study, we present a novel alcohol-in-biopolymer emulsion designed to improve the removal of LNAPL, specifically diesel fuel, from contaminated sandy soil. The concept behind developing this emulsion is based on two mechanisms that improve diesel oil removal: first, the alcohol component induces the swelling of diesel oil residuals, converting them into a continuous phase within the porous media that can be more easily displaced. Second, combining the diesel-swelling alcohol with a biopolymer-surfactant solution into a single flushing emulsion facilitates stable and uniform displacement within the porous media while ensuring the efficient delivery of the alcohol to low-permeability zones where diesel oil residuals are trapped. To assess this approach, numerous experiments were conducted at various scales.

Batch experiments revealed that five of the fifteen tested alcohols - 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, and 2-octanol - preferentially partition into the diesel phase rather than the aqueous phase. Moreover, these alcohols form stable and homogeneous emulsions when combined with a solution of 1 g.L⁻¹ XG and 5 g.L⁻¹ SDS in a 1:1 volume ratio. Rheological experiments revealed that these emulsions exhibited very similar viscosities, behaving as non-Newtonian shear-thinning fluids. Their viscosity was approximately three times higher compared to their continuous aqueous phase, represented by the solution of 1 g.L⁻¹ XG and 5 g.L⁻¹ SDS. Despite their comparable performance, 1-pentanol was selected for further experiments as the diesel-swelling alcohol in a flushing emulsion. Stability tests showed that 1-pentanol-based emulsion, dubbed “COCKTAIL,” maintained high stability throughout the 30-d testing period, confirming its applicability for injections at any point within that timeframe. Subsequent 2D cell experiments filled with sand demonstrated that injecting the shear-thinning COCKTAIL emulsion ensures stable and uniform displacement within the porous medium while completely removing the entrapped diesel oil residuals with just 1.15 PV of injection. Pore-scale visualizations revealed the swelling and subsequent mobilization of an entrapped diesel ganglion induced by 1-pentanol, further confirming the COCKTAIL emulsion’s efficacy.

The proposed novel emulsion, “COCKTAIL,” comprising an aqueous solution of 1 g.L⁻¹ XG and 5 g.L⁻¹ SDS with oil-soluble 1-pentanol in a 1:1 volume ratio, offers a promising approach for enhancing the remediation of diesel-contaminated soils. Our laboratory findings suggest that combining a swelling alcohol with a shear-thinning biopolymer-surfactant solution into a single flushing emulsion is an effective strategy that addresses a critical research gap in the remediation of soils contaminated with LNAPLs. To further elaborate on our results, prospective research should focus on scaling up experiments to field or pilot-scale tests to validate the emulsion performance under real environmental conditions. Such investigations would offer a deeper understanding of the emulsion’s effectiveness in complex and heterogeneous environments, helping to bridge the gap between laboratory findings and field applications. Key parameters, including injection pressure, flow rate, and subsurface heterogeneity should be carefully evaluated to optimize the technology for large-scale applications. In addition, exploring alternative alcohols by considering the physicochemical properties of other

LNAPLs, such as gasoline or lubricants, could extend the applicability of this approach to different types of contaminants. Moreover, future studies should focus on optimizing the alcohol ratio in the COCKTAIL emulsion to balance efficacy with financial considerations.

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