Enhancing remediation of residual DNAPL in multilayer aquifers: Post-injection of alcohol-surfactant-polymer mixtures

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HIGHLIGHTS

- Presence of 1-hexanol in AS mixture enhances 1-propanol's partitioning into DNAPL
- ASP mixtures with 1-hexanol leads to mobilization mechanism by swelling DNAPL
- ASP mixtures with solely 1-propanol exhibit a solubilization mechanism
- DNAPL Solubilization in soil is signified by a dark zone followed by a white zone
- DNAPL mobilization in soil is denoted by ganglia coalescence, and DNAPL migration

GRAPHICAL ABSTRACT
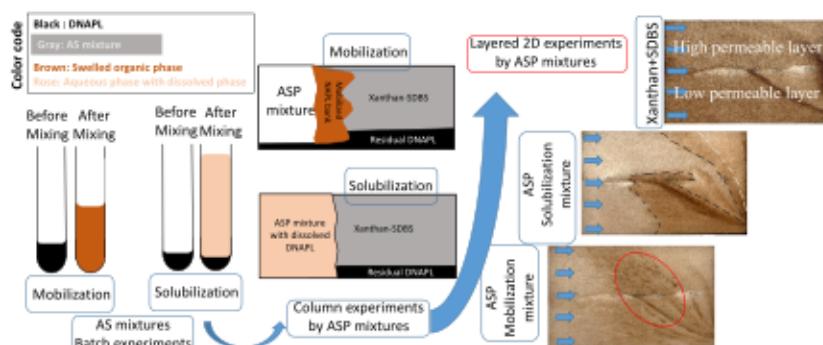
ABSTRACT

Although polymer-surfactant injection is an effective remediation technology for multilayer aquifers contaminated by Dense Non-Aqueous Phase Liquids (DNAPL), the existence of residual DNAPL after treatment is inevitable. This study evaluates the efficiency of the post-injection of alcohol-surfactant-polymer (ASP) mixtures containing 1-propanol/1-hexanol, sodium dodecylbenzenesulfonate (SDBS), and xanthan in enhancing remediation of residual DNAPL in layered systems. A range of experimental devices, including batch, rheological measurements, centimetric 1D column, and decametric 2D tank experiments, were employed.

Batch experiments revealed that the inclusion of 1-hexanol swelled the DNAPL volume due to alcohol partitioning. Conversely, with only 1-propanol present in the alcohol-surfactant (AS) mixture, DNAPL dissolved in the aqueous phase. The co-presence of 1-hexanol along with 1-propanol in AS mixture favored 1-propanol's partitioning into the DNAPL phase.

Column experiments, following primary xanthan-SDBS (XS) injections, demonstrated that ASP mixtures with 1-hexanol (regardless of presence of 1-propanol) underwent a mobilization mechanism. DNAPL appeared in the

effluent as an organic phase after the post-injection of 0.3 pore-volumes (PV), by a reduction trend in its density. In contrast, mixtures with solely 1-propanol exhibited a solubilization mechanism, with DNAPL dissolving in the aqueous phase and emerging in the effluent after approximately 1 PV.

2D tank experiments visualized mobilization and solubilization mechanisms in multilayered systems. Post-injection of the ASP mixture with solely 1-propanol led to DNAPL solubilization, demonstrated by a dark zone of varied DNAPL concentrations, followed by a clearer white zone indicating significant DNAPL dissolution. Injecting ASP mixture containing both 1-propanol and 1-hexanol mobilized swollen DNAPL ganglia throughout layers, with these droplets coalescing and migrating to the recovery point. The darkness of mobilized droplets was faded as more DNAPL was recovered. The solubilization ASP mixture enhanced the recovery factor by 0.02 while the mobilization ASP mixture led to a 0.08 increase in the recovery factor.

1. Introduction

One of the main environmental issues is the spill of chlorinated organic compounds through the soil (You et al., 2020). These highly toxic organic compounds are considered as Dense Non-Aqueous Phase Liquids (DNAPLs). They tend to penetrate downward through the aquifer and form trapped as contaminated lenses (Alamooti et al., 2022, 2024 Li et al., 2007; Pennell et al., 1996). The dissolved DNAPL in aqueous phase can enter in low permeability layers by molecular diffusion (Parker et al., 2003; Puigserver et al., 2022). Parker et al. (2003) proposed a framework for understanding the architecture of DNAPL source areas within granular aquifers, highlighting transition zones at the interface of granular aquifers and basal aquitards. These zones, situated at the base of numerous aquifers, exhibit distinct characteristics marked by the presence of numerous thin layers of silty-clay intertwined with coarser-grained layers such as sands and gravels.

In general, DNAPLs are considered as long-lasting contaminants in the groundwater environment. Surfactant injection has proven to be an effective approach in remediation of soil and aquifer contamination caused by DNAPLs (Amanat et al., 2022; Barbati et al., 2023; Colombano et al., 2020, 2021; Pennell et al., 1993; Pennell and Abriola, 2017; Taylor et al., 2001). By introducing a surfactant solution, the recovery of pollutants can be enhanced through two mechanisms: solubilization of DNAPL molecules in the aqueous phase occurring at surfactant concentration higher than critical micelle concentration (CMC) and mobilization of DNAPL by reducing the interfacial tension (IFT) between the pollutant and the aqueous phase.

The injection of a flushing solution, comprising either a surfactant or a co-solvent, can effectively reduce the residual saturation of DNAPL by mobilizing or dissolving the DNAPL. (St-Pierre et al., 2004). Alcohols with lower molecular weights such as methanol, ethanol, 1-propanol, and 2-propanol, typically function as a co-solvent which preferentially partition into the aqueous phase when in contact with the DNAPL, thus facilitating the dissolution of DNAPL molecules into the aqueous phase (Agaoglu et al., 2012; Aydin et al., 2011; Mo et al., 2023a; Oostrom et al., 2006). This aids in remediation through a solubilization mechanism. Conversely, alcohols with higher molecular weights or medium chain lengths are typically used as co-surfactants alongside water-soluble surfactants to establish a microemulsion system. When in contact with the DNAPL phase, these alcohols tend to preferentially partition into the organic phase. This leads to an improvement in DNAPL recovery through a mobilization mechanism. As the volume of DNAPL ganglia grows, they merge to create a less viscous, lighter DNAPL bank ahead of the displacement area (Fu et al., 2022; Ramsburg and Pennell, 2002; Zhou and Rhue, 2000).

Experimental studies demonstrate that the injection of these types of alcohols as cosolvents in low-volume fractions (around 1–5 % by volume) can enhance NAPL solubilization, although it necessitates numerous pore volumes of the flushing solution to substantially remove NAPL mass. In contrast, flooding with higher volume fractions (70–90 %) can lead to a complete NAPL recovery within a single pore volume (Imhoff et al., 1995).

The role of medium chain length or branched short chain alcohols in DNAPL mobilization has been the focus of several studies, particularly their ability to decrease DNAPL density by partitioning into the DNAPL phase (Fu et al., 2022; Kibbey et al., 2002; Ramsburg et al., 2003; Ramsburg and Pennell, 2002; St-Pierre et al., 2004; Wu et al., 2016) . In remedial emulsions, the presence of alcohol swells the DNAPL ganglia by partitioning into the organic phase, which in turn facilitates DNAPL movement by reducing interfacial tension, viscosity, and enhancing flow properties. Experimental studies show that the water present in the alcohol-surfactant emulsion can also partition into the organic phase causing higher swelling of DNAPL (Damrongsiri et al., 2013). This process also serves to limit uncontrolled DNAPL downward migration, which can occur during surfactant injection, by neutralizing gravitational forces (Ramsburg et al., 2003; Shook et al., 1998).

Numerous studies have assessed the performance of alcohol-surfactant emulsions in remediating DNAPL-contaminated aquifers, taking into account various factors such as the ions present in the aquifer, pH, aquifer temperature, and the temperature of the injected emulsion (Aydin et al., 2011; Mo et al., 2023a, 2023b). Other studies have evaluated the efficacy of the injection of alcohol-surfactant emulsions in heterogeneous systems, particularly where DNAPL is trapped in low permeability layers (Fu et al., 2022; Ramsburg et al., 2003; Ramsburg and Pennell, 2002).

Ramsburg et al. (2003) used a macroemulsion composed of 4.7 % Tween 80, 1.3 % Span 80, and 15 % 1-butanol for in-situ density conversion of trichloroethene (TCE) in a heterogeneous, unconfined aquifer system. After approximately 1.2 pore volumes (PV) injection of the macroemulsion, a low-interfacial-tension (low-IFT) solution with 10 % Aerosol MA (sodium bis(1,3-dimethylbutyl) sulfosuccinate which has been obtained from Cytec Industries), 6 % 1-butanol, 15 g/L NaCl, and 1 g/L CaCl$_2$ was used to displace and recover DNAPL. This process resulted in successful TCE-NAPL displacement and 93 % recovery of the introduced TCE mass after the injection of a combined 2.4 PV of the macroemulsion and low-IFT solutions. Fu et al. (2022) in an experimental study used sodium dodecyl sulfate (SDS)/1-butanol based in-situ microemulsion as the flushing solution for the remediation of soil contaminated by nitrobenzene as DNAPL, trapped in a low permeable zone surrounded by groundwater. Their findings indicated 15-fold improvement in the recovery of DNAPL compared to the SDS pure solution. Although, the efficiency of the injection of alcohol emulsions in heterogeneous soils has been discussed, their performance for remediation of a multilayer system is still inadequately understood. Indeed, the displacement of these emulsions in these systems presents unique challenges due to the existence of layers with differing permeabilities but nearly the same thicknesses. The long presence of DNAPL in subsurface can destroy the natural microbiological consortium. Although the alcohols are harmful for the few remaining bacteria, the fast biodegradability of the remaining alcohol at low concentration combined with low residual saturation of DNAPL can accelerate the natural reappearance of the bacteria in the treated zone. If necessary, the post flush of alcohol can be proceeded by injection of polymer slug.

Polymer solutions with shear thinning behavior aid in minimizing channeling and facilitate the movement of surfactant into the different layers of the heterogeneous porous medium (Alamooti et al., 2022; Martel et al., 1998, 2004). By combining polymers and surfactants,

DNAPL-saturated multilayer soils can be remediated effectively through the stabilization of the displacement front and a reduction in interfacial tension (Alamooti et al., 2023; Robert et al., 2006). Alamooti et al. (2023) showed in experimental and numerical studies that the addition of surfactant to the polymer solution improved for 0.07 the recovery of the DNAPL in the multilayer system. Nevertheless, even after the initial flushing using these methods, there may still be some DNAPL ganglia trapped in the porous media that cannot be further mobilized. While the back-diffusion of DNAPL from a less permeable zone poses challenges (Parker et al., 2003), employing a polymer solution can enhance pollutant mobilization, particularly when the solution contains alcohol for DNAPL mobilization/solubilization. In practical field applications, along with co-solvent injection, reactive biodegradation combined with polymer injection can be applied (Phenrat et al., 2011; Puigserver et al., 2023). An identified limitation of employing an alcohol-surfactant mixture in a multilayer system is the potential creation of preferential pathways in highly permeable layers; nevertheless, the use of a polymer solution provides control over channeling through these highly permeable layers (Alamooti et al., 2023; Martel et al., 1998; St-Pierre et al., 2004).

This study proposes using a mixture of polymer, surfactant, and alcohols as a post-injection remediation fluid for multilayer systems, taking advantage of the shear thinning feature of polymers and alcohol's washing properties. Specifically, the shear thinning polymer xanthan, surfactant SDBS, water-soluble alcohol 1-propanol, and water-insoluble alcohol 1-hexanol were employed. Batch experiments were conducted to assess the partitioning and solubilization properties of alcohols, considering varying surfactant concentrations, alcohol volume fractions, and DNAPL volume fractions (vol%). Rheological analyses on different ASP mixtures were also carried out. 1D-column experiments were performed to evaluate the performance of post-injection of ASP mixtures following a primary injection of polymer-surfactant in two individual DNAPL saturated sand packs. A 2D tank with two layers was used to evaluate the efficiency of injecting ASP mixtures on residual DNAPL removal in multilayer systems.

The main objectives of this study are (i) the evaluation of the performance of varying vol% of 1-propanol and 1-hexanol and various concentrations of SDBS on dissolution or swelling of DNAPL; (ii) the assessment and the comparison of the injection of solubilization and mobilization flushing solutions in different injection scenarios (injection scenarios including post-injection, primary injection, several injection consequences, and different vol% of alcohols) in 1D-column; (iii) the comparison of the performance of the post-injection of solubilization and mobilization flushing solutions on remediation of residual DNAPL in a multilayer system.

2. Materials and methods

2.1. Experimental materials

In the 1D column and 2D tank experiments, the porous media consisted of two particle-size fractions of marble sand: 0.2–0.3 mm (with a permeability of 35 ± 5 darcy) and 0.4–0.6 mm (with a permeability 105 ± 10 darcy). Prior to use, the sand were washed with deionized water, and oven-dried for 10 h at 105 °C. The DNAPL used in the study is extracted from real polluted site at Tavaux (in France) and is consisted primarily of hexachlorobutadiene-HCBD (58 %), hexachloroethane-HCA (14 %), and penta-chlorobenzene (3.5 %), as well as carbon tetrachloride (4 %). The density and viscosity of the multicomponent DNAPL are 1.66 g/mL and 4.47 mPa.s, respectively (Alamooti et al., 2022; Colombano et al., 2020). Xanthan gum, an anionic, water-soluble biopolymer, and SDBS, a biodegradable surfactant were employed in this study. Additionally, 1-propanol and 1-hexanol were used as water-soluble and water-insoluble alcohols, respectively, both with a 99 % purity. Xanthan and SDBS solid powders, and the alcohols were all sourced from Sigma-Aldrich. For analyzing the solutions' rheological

behavior, the Haake Mars 60 rotational rheometer with a cone-plate geometry was used. The concentration (mass) of DNAPL in organic phase was determined by density analysis of recovered organic phase and gas chromatography. For density analysis, the density and volume of recovered organic phase was measured and considering the densities of alcohols and DNAPL the DNAPL content was found. For DNAPL concentration in aqueous phase, only gas chromatography was used. For gas chromatography, AGILENT 8890 gas chromatograph with a thermal conductivity detector at 280 °C and an injector for chromatograph columns filled at 250 °C. Agilent CP-SIL 5 CB chromatograph columns were used with polydimethylsiloxane as the active phase and helium as the carrier gas. Gas chromatography is able to provide the concentration of alcohols and DNAPL in both aqueous and organic phases.

2.2. Batch experiment

Batch experiments were conducted to investigate the role of alcohols in the mobilization and solubilization of DNAPL. The experimental materials consisted of solutions prepared with deionized water, a mixture of 1-propanol and 1-hexanol, and the surfactant SDBS. The solutions were mixed with DNAPL, in vol% of 20 % and 10 %, within 50 mL polyethylene flasks. The SDBS was first dissolved in water at concentrations ranging from 0 to 100 g/L (specifically 0, 1, 5, 10, 25, 50, and 100 g/L) to form the aqueous phase. This aqueous phase was then mixed with the 1-propanol and 1-hexanol mixture at volume percentages of 25 % and 50 % to prepare the final mixtures. The mixtures of 1-propanol and 1-hexanol was prepared at different volume proportions of 1:0, 3:1 1:1, 1:3, and 0:1. The AS mixtures were mixed with DNAPL using a Laboshake Gerhardt® shaker and mixed continuously for a period of 24 h. Subsequently, the Sigma 3-30ks centrifuge was used to separate the phases (organic and aqueous) at a speed of 10,000 rpm for a duration of 30 min. The changes of DNAPL volume, which we will refer to as the organic phase post-process, serves as an indicator of the active remediation mechanism. Following the separation, the volume of both the organic and aqueous phases was recorded, and their respective densities were measured using pycnometers.

2.3. 1D column

The 1D-column experiments aimed to examine the displacement of DNAPL within two separate sand packs of varying permeabilities. The procedure involved an initial injection of a XS (0.8 g/L of xanthan and 1.265 g/L SDBS) mixture, followed by a post-injection of an ASP mixture. The column was made of a glass tube with a 2 cm radius and a 30 cm length (Fig. 1). It was gradually filled with sand, flushed with CO_2 for 30 min to remove trapped air, and then saturated with degassed deionized water at a steady flowrate of 0.1 mL/min using an Ismatec® Reglo ICC digital peristaltic pump. Afterward porosity and permeability were measured. Porosity was assessed using the volumetric method, involving measurements of dry weight and the fully saturated water-wet weight of the column. Permeability, on the other hand, was measured by varying the flow rate and recording the pressure drop within the framework of Darcy's law. Next, DNAPL was introduced at a fixed rate of 1 mL/min until residual water saturation was achieved. Then, the XS mixture was injected at a constant flow rate of 1 mL/min until reaching residual DNAPL saturation. Residual saturations were determined when no further recovery of the displaced phase was observed in the effluent. This was followed by the injection of an ASP mixture at the same flow rate for approximately 2 PV. The effluents were collected in 15 mL propylene tubes, while the differential pressure along the column was monitored using KELLER PR33X. The DNAPL recovery during the primary injection was measured volumetrically. For the ASP mixture post-flush, the organic and aqueous phase volumes were recorded and their densities were measured. Then, the organic and aqueous phases from every 3 to 4 tubes were individually combined, diluted, and analyzed using a gas chromatography apparatus.
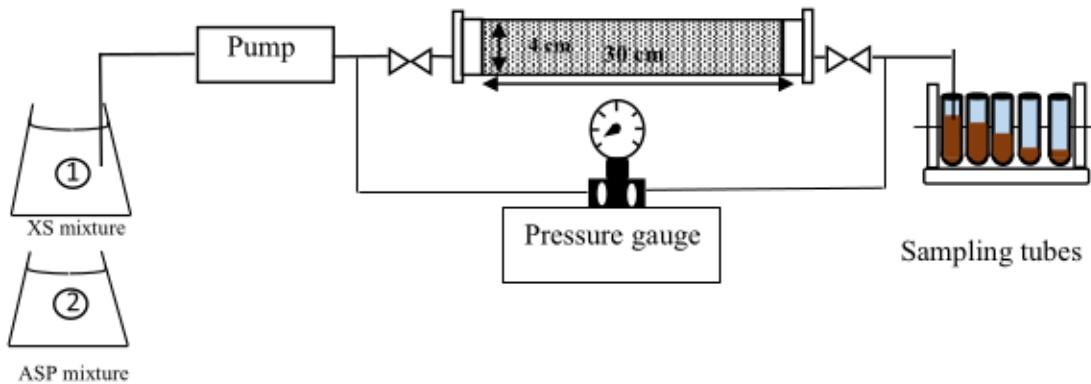
Fig. 1. Schematic represntation of polymer-surfactant injection (container 1) followed by ASP mixture injection (container 2) for DNAPL displacement in 1D column.

2.4. 2D tank

To test the efficiency of the developed flushing solutions on a multilayer system, a confined 2D tank equipped with pressure measurement transducers was employed. The tank measures 15 cm in length, 10 cm in height, and 2 cm in width. It contains two ports on the left side, three ports on the bottom, three ports on the top and one port on the right side. The 2D tank sets up with two distinct layers: a less permeable layer (35 Darcy) at the bottom with a thickness of 5 cm and a more permeable layer (105 Darcy) on top, also with a thickness of 5 cm. The layers were packed under water and then saturated by DNAPL from the ports located at the bottom of the tank, leaving a residual water saturation. In primary injection step, the XS mixture was injected using two ports (in correspondence of layers) located on the left part of the tank at the fixed injection rate of 2×0.5 mL/min, and the DNAPL was naturally recovered through the port located on the right bottom side of the tank at ambient pressure. Then two different ASP mixtures (providing improved recovery by mobilization and solubilization) were individually injected into the layers at residual DNAPL saturation (in two different experiments with similar experimental setup and initial conditions). The injection processes for the 2D system are visually represented in Fig. 2.

3. Results and discussion

3.1. Partitioning behavior alcohol-surfactant mixture and DNAPL

Our batch experiments revealed that surfactant concentration does not significantly influence the results. Therefore, for subsequent analyses, the results were averaged across all surfactant concentrations, and the error bars have been displayed on the corresponding graphs. The volumes of the organic and aqueous phases (after mixing and separation in batches) were found to be primarily influenced by the volume fractions of the alcohols, water, and DNAPL. A sort of batch experiments has been performed in the presence polymer. We found that the presence of polymer in the mixture does not significantly affect the partitioning


High permeable zone; sand size: 0.4-0.6 mm
Low permeable zone; sand size: 0.2-0.3 mm
Injection/production port

Pressure transducer
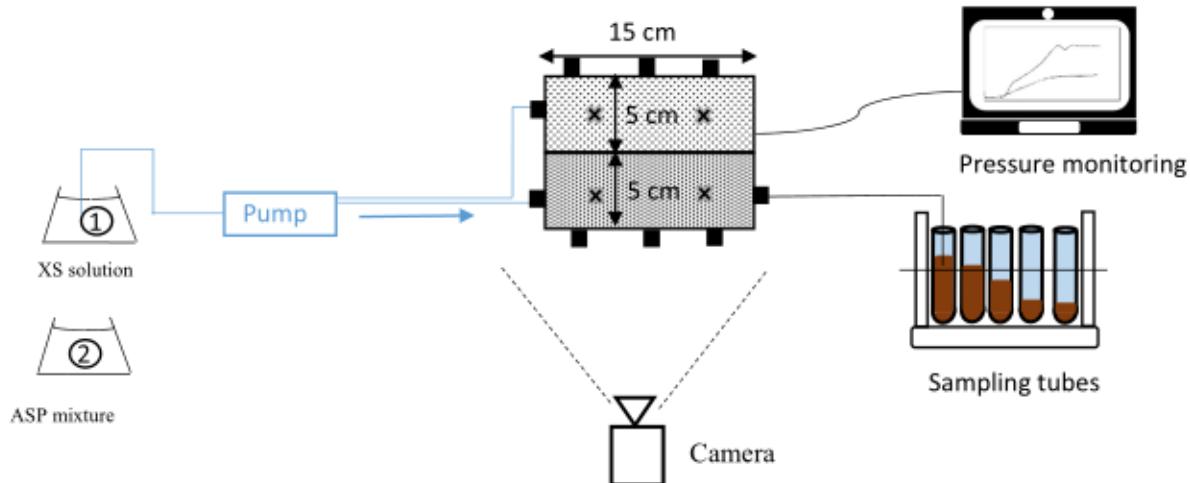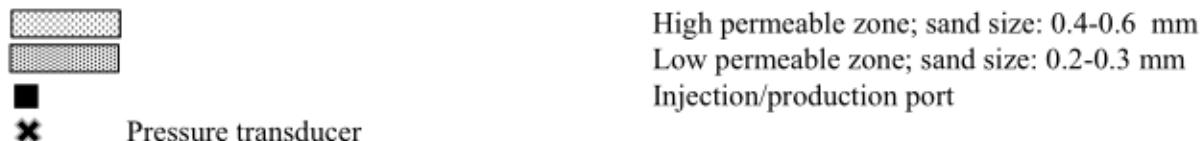
Fig. 2. Schematic representation of polymer-surfactant injection (container 1) followed by ASP mixture (container 2) injection for DNAPL displacement in the 2D tank (multilayer system).

behavior of alcohols. Also, the separation of phases by centrifuge for the mixtures containing polymer was long; therefore, the batch experiments were performed only with AS mixtures. The batch experiments showed that when 1-propanol is the sole alcohol in the AS mixture, DNAPL dissolves in the aqueous phase. As illustrated in Fig. 3a, a higher 3:1 ratio of 1-propanol to water results in increased DNAPL dissolution. Specifically, for initial volume fractions of DNAPL at 10 % and 20 %, approximately 0.97 and 0.65 of the initial DNAPL dissolves into the aqueous phase, respectively. In contrast, with a lower 1:1 ratio of 1-propanol to water, the same initial volume fractions of DNAPL lead to only about 0.27 and 0.14 dissolution, respectively. When a larger volume of the DNAPL comes in contact with AS mixture, a lower fraction of the organic phase is dissolved, owing to the AS limited solubility capacity. The results show that the solubility of DNAPL in AS mixture is around 0.27 g/mL for higher 3:1 ratio of 1-propanol to water and 0.054 g/mL for lower 1:1 ratio of 1-propanol to water. In Fig. 3b, tubes on the left represent the state before mixing, while those on the right depict the state after mixing. The gray color indicates the AS mixture prior to mixing. DNAPL is represented by the black color, and the brownish phase signifies the aqueous phase post-mixing. A darker shade of brown suggests a higher degree of DNAPL dissolution in the AS mixture.

Contrarily, when 1-hexanol is included in the AS mixture, there's an increase in the volume of the organic phase. Fig. 4 presents the swelling factor of the organic phase, defined as the ratio of the volume of the organic phase after contact with the AS mixture (mL) to the initial volume of DNAPL (mL). This is plotted against the volume ratio of 1-propanol to 1-hexanol, for various volume fractions of water in the AS mixture and of DNAPL in contact with the mixture. The results indicate that a lower volume fraction of DNAPL in contact with the AS mixture, such as 10 % (5 mL DNAPL and 45 mL AS mixture), leads to a more pronounced increase in the volume of the organic phase. Another significant factor influencing the swelling of the organic phase is the volume fraction of water in the AS mixture. A higher volume fraction of alcohol results in a greater swelling factor. For instance, when the

volume fraction of water in AS mixture is 25 % (meaning 75 % of alcohol in the AS mixture) and the volume fraction of DNAPL is 10 %, a swelling factor of more than 8 can be observed. These findings also suggest that the volume ratio of 1-propanol to 1-hexanol does not noticeably influence the partitioning of alcohols into the organic phase.

The results obtained from the swelling factor of the organic phase are consistent with those from the density analysis of the organic phase, as shown in Fig. A-1 (in supplementary materials). This analysis demonstrates that samples with a higher swelling factor (i.e., a sign of greater partitioning of alcohols into the NAPL) exhibit lower densities.

As previously mentioned, in the absence of 1-hexanol, DNAPL dissolves into the aqueous phase containing 1-propanol. However, as Fig. 4 demonstrates, when 1-hexanol is present, a substantial portion of both 1-propanol and 1-hexanol partitions into the NAPL phase, leading to a high swelling factor.

The analysis of alcohol content in the organic and aqueous phases performed by gas chromatography, shown in Fig. A-2 (in supplementary materials), reveals that when 1-hexanol is present and the volume fraction of water is lower (i.e., 25 %) in the AS mixture, the majority of 1-propanol (between 90 % to 100 %) partitions into the organic phase. Conversely, when the volume fraction of water is higher (i.e., 50 %), a smaller proportion of 1-propanol (~70 %) partitions into the organic phase. For all cases, when 1-hexanol is present in the AS mixture, all of the 1-hexanol partitions into the organic phase.

3.2. Selection of the flushing mixtures

The results obtained from batch experiments indicate that a solution containing only 1-propanol as the alcohol leads to the solubilization mechanism, while AS mixtures containing both 1-propanol and 1-hexanol, or only 1-hexanol, result in the mobilization mechanism. Consequently, three AS mixtures were selected for the remediation of soils at residual DNAPL saturation. These include mixtures consisting of 50 % volume fraction of 1-propanol and 50 % of surfactant solution, 25 % of


(a)   (b)
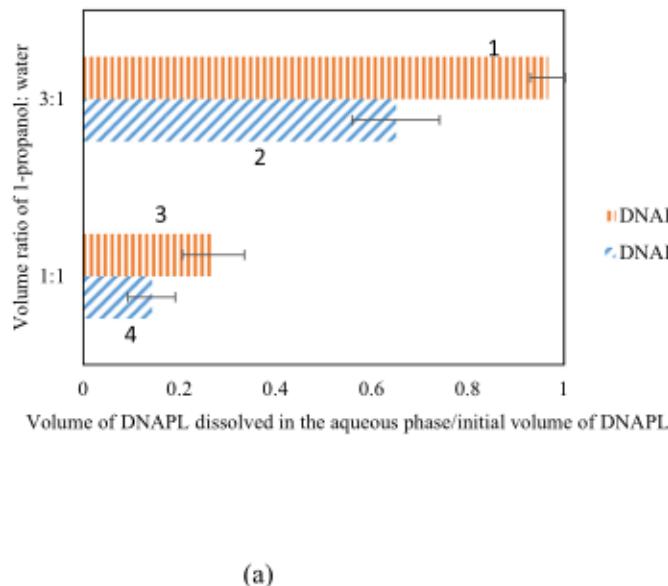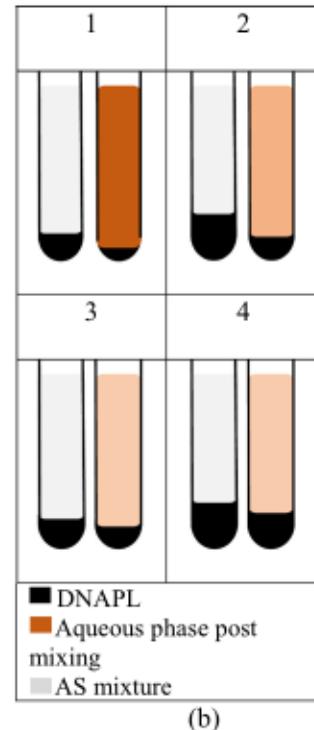
Fig. 3. Dissolution of DNAPL in contact with AS mixtures containing solely 1-propanol (a) graph showing the dissolution rates, and (b) schematic of dissolution: tubes on the left represent the state before mixing, while those on the right depict the state after mixing. The gray color indicates the AS mixture prior to mixing. DNAPL is represented by the black color, and the brownish phase signifies the aqueous phase post-mixing.
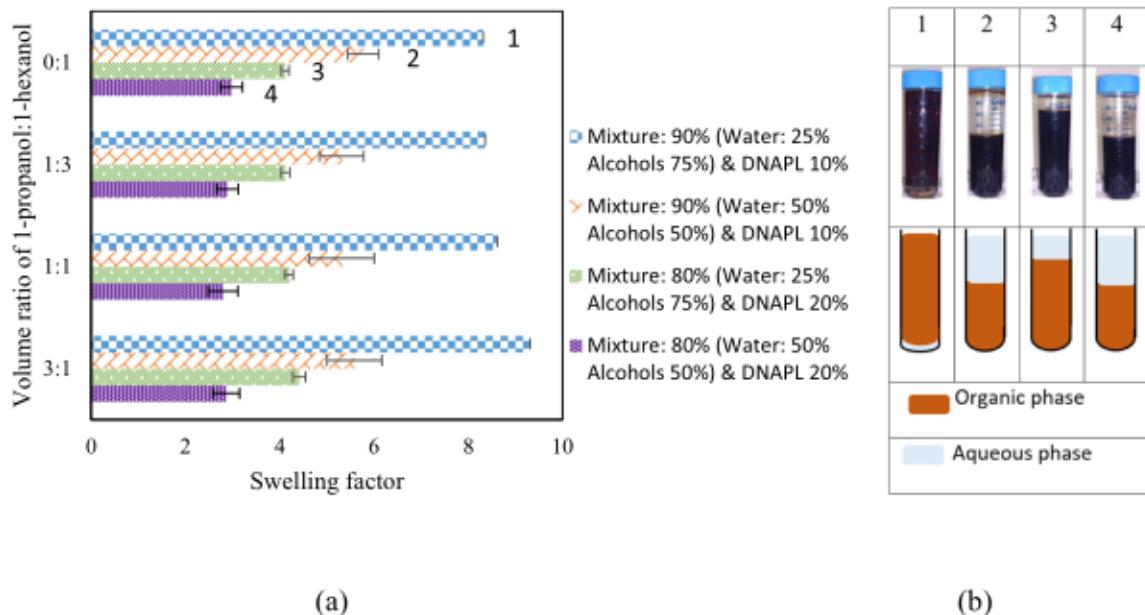
Fig. 4. a) Swelling factor of organic phase versus volume ratio of 1-propanol:1-hexanol for various water/alcohol and DNAPL volume fractions (b) schematic of dissolution for the case 0:1.

1-propanol, 25 % of 1-hexanol, and 50 % of surfactant solution, and also 50 % 1-hexanol and 50 % surfactant solution. The surfactant also helped to improve the stability of the mixture of alcohols and water, especially in the presence of 1-hexanol.

Given that the surfactant concentration does not significantly influence the partitioning behavior of alcohols, a low concentration of 1 g/L was chosen. Rheological analysis of these AS mixtures reveals that they exhibit Newtonian behavior, with a viscosity of approximately 3 mPa.s for the AS mixture containing solely 1-propanol as alcohol, and 16 mPa.s for AS mixtures containing 1-hexanol (regardless of presence of 1-propanol).

To enable the injection of the AS mixtures into a multilayer system, a polymer was added to them. The polymers have the non-Newtonain behavior and can help the displacement of DNAPL in layered system where the permeabilities are different. For this purpose, xanthan, a biopolymer, was selected. The stability of the newly formed ASP mixtures with the polymer was evaluated. It was shown that for cases where the volume fraction of water was 25 %, the ASP mixture was unstable,

either two distinct phases or visually discernible wormlike micelles appeared. While for a 50 % volume fraction of water, a highly stable mixture was formed that lasted several days. It's important to note that mixtures without surfactant in contact with the polymer immediately became unstable.

The rheological behavior of the mixtures with a xanthan concentration of 2 g/L in the surfactant solution was evaluated. As seen in Fig. 5, the addition of alcohols to the surfactant-polymer solution (1 g/L of SDBS and 2 g/L of xanthan) resulted in higher viscosities compared to the primary remediation fluid i.e. XS (1.26 g/L of SDBS and 0.80 g/L of xanthan (Alamooti et al., 2023)) mixture that was chosen to be injected into the DNAPL-saturated soil. All ASP mixtures showed a shear thinning behavior, while in the range of working shear rate i.e. around 1–10 1/s, the highest viscosity can be observed for the 25 % of 1-propanol, 25 % of 1-hexanol and 50 % of surfactant-polymer solution (C_3-C_6), and also 50 % 1-hexanol and 50 % surfactant-polymer solution (C_6), which have a viscosity approximately 17 times that of the XS mixture. The ASP mixture consisting of 50 % volume fraction of 1-propanol and 50 % of
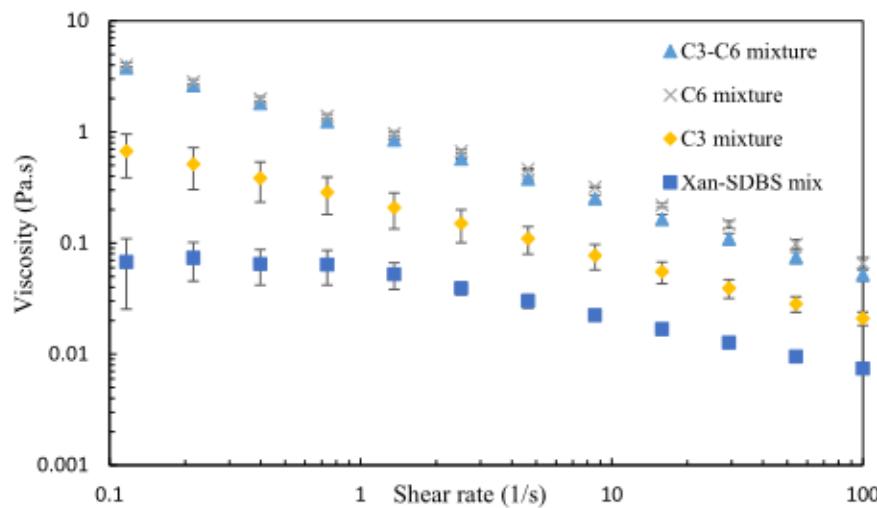

Fig. 5. Viscosities of different ASP mixtures containing xanthan with concentration of 2 g/L, as well as XS mixture

surfactant-polymer solution (C_3) also has a viscosity around 5 times that of the XS mixture.

3.3. 1 D column experiments

Column experiments were conducted to evaluate the performance of selected ASP mixtures in the remediation of soils of varying permeabilities at residual DNAPL saturation. To this end, the XS solution was first injected into DNAPL-saturated columns packed with both coarse and fine sand. Fig. 6 illustrates the recovery factor $\left(\frac{\text{volume of DNAPL recovered}}{\text{initial volume of DNAPL in porous media}}\right)$ and differential pressure for the period after 1 PV injection of the XS mixture, as well as the subsequent injection of ASP mixtures, displayed against cumulative PV, for both high and low permeable porous media.

These results indicate that the recovery curves for the post-injection of C_3-C_6 and C_6 mixtures follow a similar trend in both high and low permeability 1D columns. In the early stages of injecting alcohol solutions containing 1-hexanol, for approximately 0.3 PV of post injection (between ~2 and 2.3 PV) there is not a noticeable DNAPL recovery. However, DNAPL begins to emerge in the effluent after approximately 0.3 PV of post-injection of ASP mixture. This is attributed to alcohols partitioning into the trapped DNAPL ganglia within the pore space, causing them to swell and eventually coalesce to form larger droplets capable of migrating through the porous media (St-Pierre et al., 2004). Consequently, an organic phase, containing both DNAPL and alcohols, starts appearing in the effluent. This phase, having a density lower than
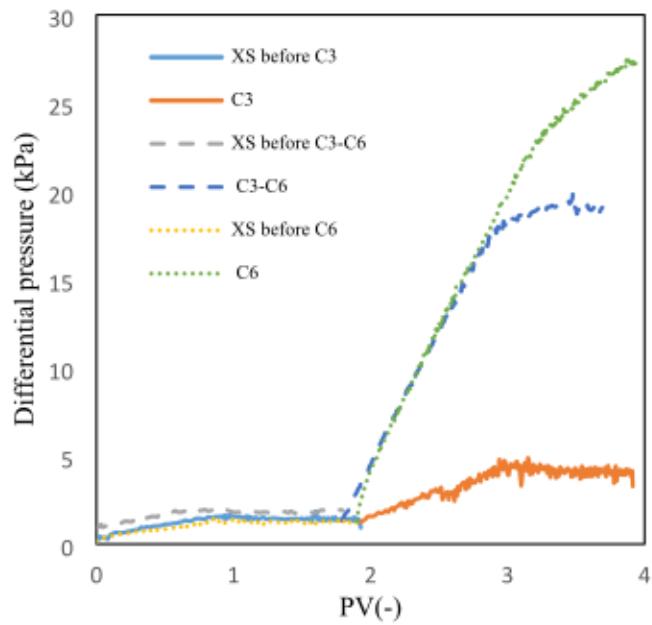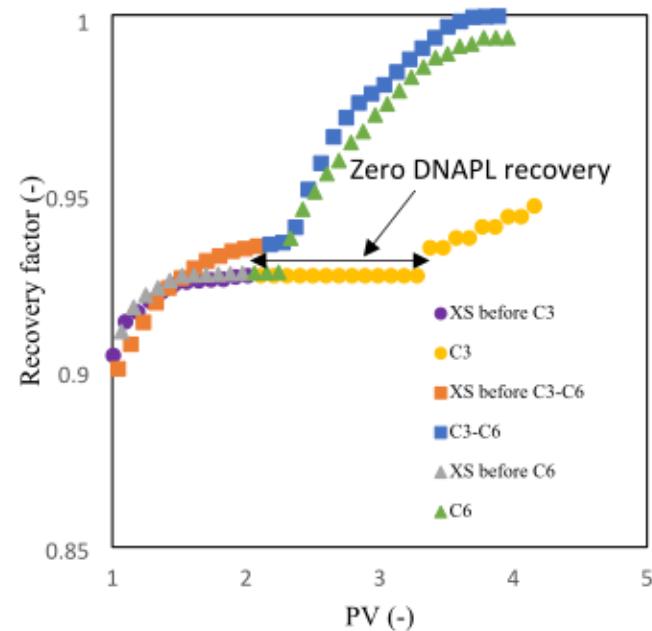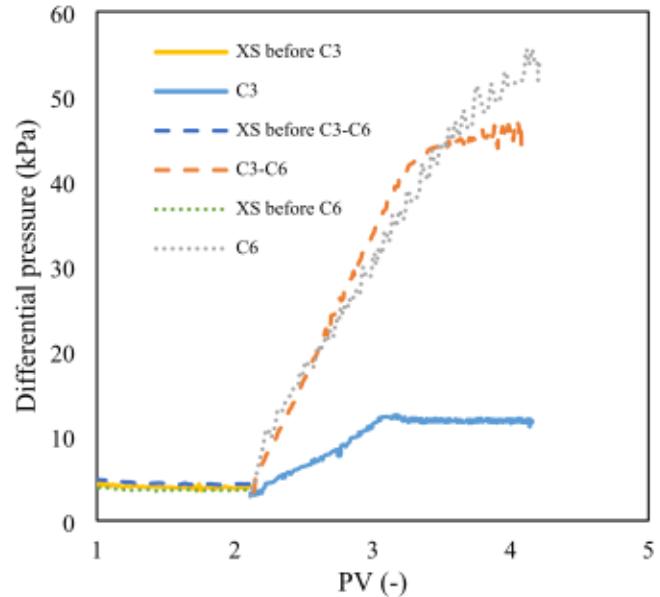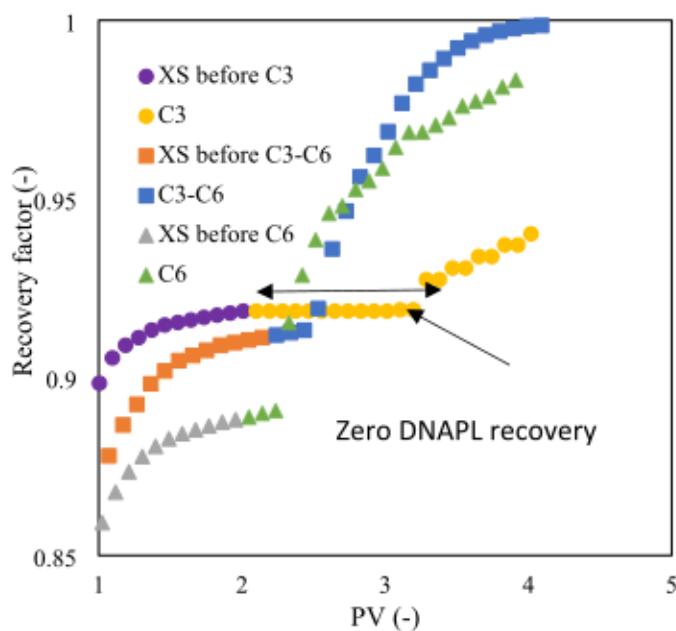

Fig. 6. Experimental results of post-injection of ASP mixtures in columns: (a) recovery factor for low permeable layer, (b) differential pressure for low permeable layer, (c) recovery factor for high permeable layer, and (d) differential pressure for high permeable layer.

the original DNAPL, eventually transitions into a LNAPL. Fig. A-3 (in supplementary materials) visually demonstrates this, as the organic phase progressively lightens in both color and density with the continued injection of the C_3-C_6 mixture in high-permeability layers. The color of the recovered organic phase in individual samples shifts from very dark initially to much lighter by the end. The differential pressure curves for the 1-hexanol containing mixtures are consistent with rheological behavior, reflecting the similar behavior observed in the C_3-C_6 and C_6 mixtures.

In contrast, the C_3 mixture, when introduced into columns at residual DNAPL saturation, leads to the emergence of the organic phase only after 1.3 PV post injection of C_3 mixture, indicating a solubilization mechanism. The C_3 mixture begins dissolving the residual DNAPL into the aqueous phase, moving through the porous media. Once maximum solubility is reached in the aqueous phase, the subsequent slug of the C_3 mixture continues this dissolution process. To see the DNAPL in the effluent, the aqueous phase containing dissolved DNAPL needs to reach the effluent. As a result, DNAPL is absent in the effluent until after 1 PV of post-injection, and then it is recovered at a constant recovery rate (fixed slope). It should be noted that in this case, no DNAPL is recovered as individual organic phase, and all NAPL is recovered through aqueous phase. The mechanisms of DNAPL recovery for different ASP mixtures in both high and low permeable porous media are similar; however, the differential pressure for low permeable porous media is around three times more than high permeable layer corresponding to their permeabilities. XS injection in the higher permeable layer led to a slightly higher recovery rate (~2 %), and displacement patterns were consistent between layers. Additionally, a two-layer system composed of both high and low permeable layers is needed to observe the preferential pathway.

As previously noted, the recovery of DNAPL through the post-injection of ASP mixtures in the columns experiences a delay (around 1 PV for the C_3 mixture and 0.3 PV for the C_3-C_6 and C_6 mixtures). Fig. A-4 (in supplementary materials) depicts the DNAPL content in effluent samples against the cumulative injected PV for both solubilization and mobilization mechanisms. The DNAPL content in effluent was determined by analysis of density of recovered organic phase as well as the gas chromatography. For the analysis of recovered DNAPL in aqueous phase, only gas chromatography has been used. The first sample in which DNAPL starts to appear in the effluent, exhibits the highest DNAPL content.

For the solubilization mechanism (using the C_3 mixture), this high DNAPL content can be attributed to the fact that the front of the ASP mixture has the most DNAPL dissolved within it. Meanwhile, for the mobilization mechanism, this elevated DNAPL content is due to the partitioned alcohols. These alcohols increase the size of trapped DNAPL droplets and mobilize a significant portion of it through the coalescence of newly swollen DNAPL ganglia. Consequently, the first sample with DNAPL has the richest DNAPL content. This observation aligns with the density measurements of the organic samples during the mobilization mechanism; samples with a higher DNAPL content show a greater density, which eventually converges to the density of the alcohols (densities of 1-propanol and 1-hexanol are 0.803 and 0.814 g/mL respectively).

3.4. Evaluating different injection scenarios for DNAPL mobilization mechanism in columns

As it is shown in the previous section, the post-injection of mobilization ASP mixtures (specifically those containing 1-hexanol) leads to a recovery factor improvement of roughly 0.09 and 0.07 for low and high permeable porous media, respectively. Notably, while the post-injection of these mixtures quickly enhanced the recovery factor by recovering more DNAPL, a plateau was observed during the latter stages of ASP mixture injection.

To further investigate, two scenarios using one of the mobilization ASP mixtures (C_3-C_6) were assessed as following;

The mixture was directly introduced to columns saturated with DNAPL at residual water saturation.

A sandwich method was employed: following an initial 2 PV injection of XS mixture, only 0.5 PV of the C_3-C_6 mixture was introduced, which was then flushed with the same XS solution as initially used.

Fig. A-5 (in supplementary materials) presents the results. For both low and high permeable layers, a 0.99 recovery efficiency was achieved after the injection of approximately 1.5 PV of direct mixture of C_3-C_6 injection. In contrast, with a full post-injection of C_3-C_6, 1.3 PV was required to attain the same efficiency. In the sandwich method, 0.5 PV of ASP mixture injection improved the recovery factor by 0.03, and subsequent flushing further improved recovery by another 0.02–0.03, after which DNAPL recovery ceased. Interestingly, the sandwich method achieved a ~ 0.06 recovery factor improvement with just 0.5 PV of ASP between two periods of XS injection. Conversely, for the full post-injection approach, approximately 1 PV was necessary to achieve comparable recovery factor improvements following the initial XS injection.

3.5. 2D tank experiments

To evaluate the efficiency of ASP mixtures in a multilayered system, 2D tank experiments were carried out as detailed in Section 2.4. To compare the solubilization and mobilization processes, two ASP mixtures were used in the post-injection phase (following an initial injection with the XS mixture) in the multilayer system. To this end, the C_3 as the solubilization and C_3-C_6 as the mobilization mixtures were chosen.

Fig. 7 illustrates the consequences of DNAPL recovery in a multilayer system, first using XS and then the C_3 mixture. This figure shows that the XS solution effectively displaces DNAPL from both layers. This displacement is influenced by density differences, where the invading solution is overriding the DNAPL, in response to density difference between the invading and defending phases (Alamooti et al., 2023). Upon subsequent injection of the C_3 mixture, two distinct zones appear: the dark and white zones. These are highlighted by white and black dashed lines, respectively.

Consistent with observations from the column experiments, the injection of the C_3 mixture initiates the dissolution of DNAPL, forming a dark zone indicative of near-maximum solubility. This dark zone advances thanks to the driving force provided by the continuous injection of C_3 mixture. The ASP mixture in the front of the dark zone is near the maximum solubility of DNAPL, where further DNAPL dissolution becomes negligible, leaving behind residual DNAPL. Behind the front of the dark zone, the ASP mixture continues the dissolution of the remaining DNAPL. This phenomenon gives rise to a transition zone, characterized by a DNAPL concentration gradient in the aqueous phase that descends from its maximum at front to nearly zero at its rear. Subsequent to this transition zone is the white zone, which represents regions where DNAPL has been largely dissolved or flushed out by the C_3 mixture. While the dark zone's propagation correlates directly with the injected pore volume (e.g., at 0.7 PV injection, the dark zone encompasses 60 % of the tank's surface area), the white zone's advancement is notably slower, covering only an additional 20 % of the surface area between 1.58 and 2.1 PV. This may be attributed to the role of boundary conditions, particularly the presence of a single outlet port. This port seems to cause a significant pressure gradient near the production area, possibly creating a preferential pathway for the C_3 mixture and bypassing some untouched zone in the layers.

Fig. A-6 (in supplementary materials) displays both the recovery factor and the differential pressure during the initial injection of XS and the subsequent injection of the C_3 mixture into the multilayer system. As observed in the column experiments, DNAPL starts to appear in the effluent after 1 PV of C_3 mixture injection and is recovered at a steady rate. Post-injection of C_3 mixture has improved the recovery factor for approximately 0.02. The differential pressure between the pressure ports in each layer as shown in Fig. 2, curves align with the injection
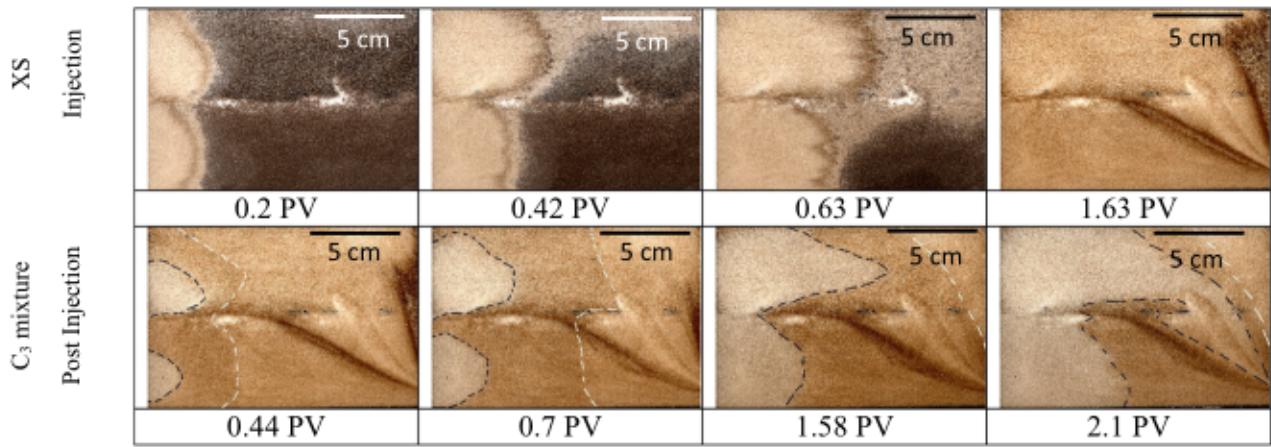
Fig. 7. DNAPL displacement in a 2D multilayer system by injection of XS solution (first row) and subsequent injection of C₃ mixture (second row) against the number of PVs injected of each solution.

process, showing a higher pressure gradient in the less permeable layer, and a notably higher gradient for the C₃ mixture post-injection compared to the XS injection which is attributed to its higher viscosity.

For the case of post-injection of C₃-C₆ mixture in the multilayered system in the 2D tank, in accordance with the column experiments the mobilization mechanism has been observed. Likewise, the C₃ mixture post-injection, firstly a XS mixture has been injected until no more DNAPL was recovered, then the C₃-C₆ mixture was introduced into the layered system at residual DNAPL saturation. As this mixture was introduced, the alcohols within it began partitioning into the DNAPL ganglia, causing them to move, therefore showing the mobilization mechanism. As it can be seen in Fig. 8, just after the injection of 0.3 PV of the C₃-C₆ mixture mobilized DNAPL droplets have arrived at the recovery point. These dark droplets gradually lightened as more of the mixture moved into the layers. This is because as the amount of the remaining DNAPL in the layers decreased, the dark color associated with it started to fade.

Fig. A-7 (in supplementary materials) presents respectively the

recovery factor and differential pressure in each layer for the C₃-C₆ mixture's post-injection into the multilayered system. It reveals that the injection of this mixture has enhanced the recovery factor by approximately 0.08. Similarly, the differential pressure curves align with the findings from the column experiments.

The injection of the C₃-C₆ mixture exhibits a higher pressure (around 13 kPa and 8 kPa at the end of post injection for low and high permeable layers respectively) than the injection of the C₃ mixture (around 3.3 kPa and 1.5 kPa at the end of post injection for low and high permeable layers respectively). It can be attributed to the higher viscosity of the C₃-C₆ mixture compared to C₃ mixture.

4. Conclusion

Experiments were carried out to assess the effectiveness of alcohol-surfactant-polymer mixtures in remediating layers polluted by DNAPL at residual saturation. Xanthan (polymer), SDBS (surfactant), and 1-propanol and 1-hexanol (water-soluble and water-insoluble alcohols)
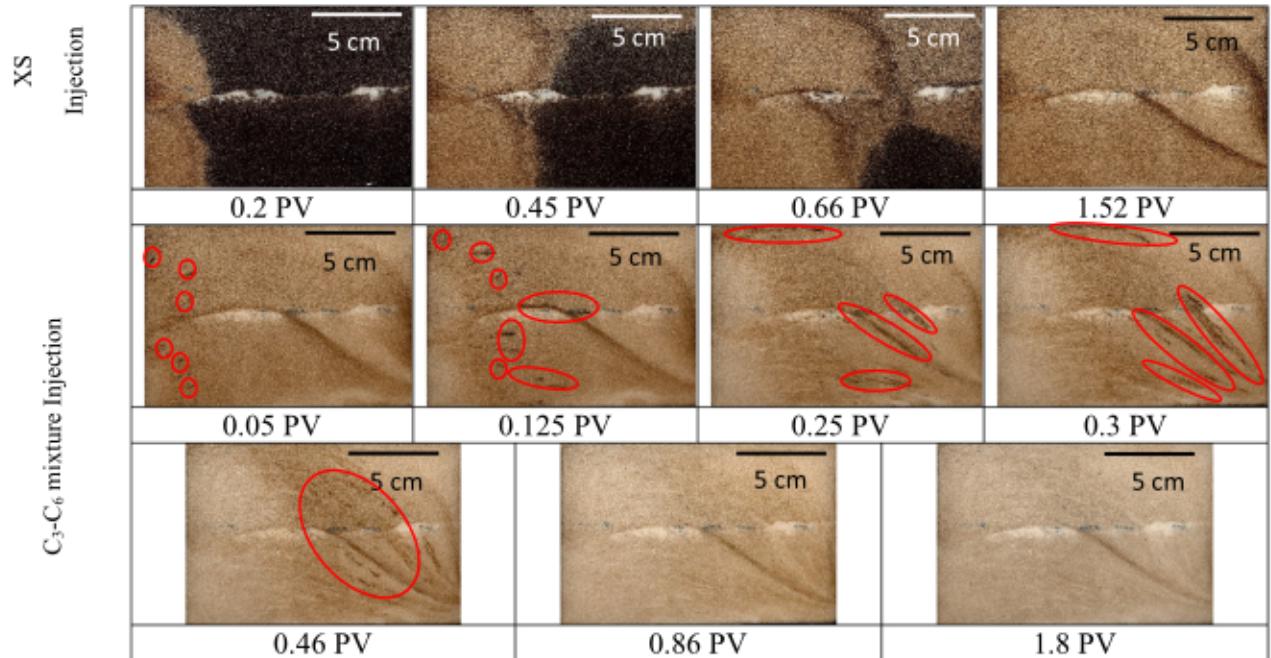

Fig. 8. DNAPL displacement in a 2D multilayer system by injection of XS solution (first row) and subsequent injection of C₃-C₆ mixture (second and third rows) against the number of PVs of each solution injected, mobilized ganglia are shown by red circles.

were incorporated in the mixtures. A variety of experimental devices, including batch, column, and 2D tank experiments, as well as rheological analysis, were used.

Batch experiments revealed that the inclusion of 1-hexanol in the AS mixture led to alcohol partitioning in the DNAPL phase, swelling the organic phase. Conversely, when 1-propanol was the sole alcohol in the mixture, DNAPL was dissolved in the aqueous phase. Rheological analysis demonstrated that for AS mixtures with 50 % volume fraction of alcohols, those containing 1-hexanol either 25 % or 50 % volume fraction could yield a viscosity three times higher than mixtures with only 1-propanol. The rheological analysis showed that the by adding the alcohols to the polymer-surfactant solution the non-Newtonian behavior has been retained.

Column experiments, performed after primary injection of the XS solution, revealed two unique mechanisms. The post-injection of ASP mixtures with 1-hexanol resulted in DNAPL appearing in the effluent after injecting 0.3 PV, indicating the mobilization mechanism due to alcohol partitioning into trapped DNAPL. In contrast, the post-injection of C_3 mixture initiated DNAPL dissolution, signifying a solubilization mechanism. Here, DNAPL only appeared in the effluent after 1 PV. In a set of individual column experiments, a sandwich method of post-injection of the mobilization mixture was proposed. This method improved the recovery factor by roughly 0.06 with only 0.5 PV injection of the mixture, compared to 1 PV in a full post-injection scenario.

2D tank experiments were conducted to visually compare the solubilization and mobilization processes. Initial injection of the XS mixture effectively displaced DNAPL from both layers. The post-injection of the C_3 mixture initiated DNAPL dissolution, forming a dark zone with the DNAPL concentration gradient, followed by a white zone where DNAPL had been largely dissolved. Post-injection of the C_3-C_6 mixture showcased the mobilization mechanism, with alcohol partitioning into DNAPL causing mobilization. This was illustrated by the formation of moving DNAPL droplets within the layers, where the swollen DNAPL ganglia became interconnected, mobilized and reached the recovery point only after 0.3 PV. As the invasion of new ASP mixture progressed, the dark color of these mobilized droplets gradually faded. The post-injection of the C_3 mixture enhanced the recovery factor by 0.02 and generated a lower pressure gradient compared to the C_3-C_6 mixture. In contrast, the C_3-C_6 mixture led to a larger improvement in the recovery factor, approximately 0.08. These results show that post-injection of ASP mixture can minimize the residual saturation of DNAPL in layered system and achieve a promising displacement efficiency.

CRediT authorship contribution statement

Amir Alamooti: Conceptualization, Formal analysis, Investigation, Methodology, Software, Visualization, Writing – original draft. **Stéfan Colombano:** Funding acquisition, Project administration, Supervision, Writing – review & editing. **Abbas Shoker:** Investigation, Validation. **Azita Ahmadi-Sénichault:** Supervision, Writing – review & editing. **Fabien Lion:** Visualization. **David Cazaux:** Investigation, Resources. **Cédric Marion:** Investigation. **Jérôme Lagron:** Investigation. **Idriss Sawadogo:** Investigation. **Dorian Davarzani:** Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

References

Agaoglu, B., Scheytt, T., Copty, N.K., 2012. Laboratory-scale experiments and numerical modeling of cosolvent flushing of multi-component NAPLs in saturated porous media. J. Contam. Hydrol. 140–141, 80–94. https://doi.org/10.1016/j.jconhyd.2012.07.005.

Alamooti, A., Colombano, S., Omirbekov, S., Ahmadi, A., Lion, F., Davarzani, H., 2022. Influence of the injection of densified polymer suspension on the efficiency of DNAPL displacement in contaminated saturated soils. J. Hazard. Mater. 440, 129702 https://doi.org/10.1016/j.jhazmat.2022.129702.

Alamooti, A., Colombano, S., Glabe, Z.A., Lion, F., Davarzani, D., Ahmadi-Sénichault, A., 2023. Remediation of multilayer soils contaminated by heavy chlorinated solvents using biopolymer-surfactant mixtures: two-dimensional flow experiments and simulations. Water Res. 243, 120305 https://doi.org/10.1016/j.watres.2023.120305.

Alamooti, A., Colombano, S., Davarzani, D., Lion, F., Ahmadi-Sénichault, A., 2024. Gravity-driven remediation of DNAPL polluted aquifers using densified biopolymer brine solution. Adv. Water Resour., 104643 https://doi.org/10.1016/j.advwatres.2024.104643.

Amanat, N., Barbati, B., Rossi, M.M., Bellagamba, M., Buccolini, M., Galantini, L., Petrangeli Papini, M., 2022. Synthetic and natural surfactants for potential application in mobilization of organic contaminants: characterization and batch study. Water (Basel) 14, 1182.

Aydin, G.A., Agaoglu, B., Kocasoy, G., Copty, N.K., 2011. Effect of temperature on cosolvent flooding for the enhanced solubilization and mobilization of NAPLs in porous media. J. Hazard. Mater. 186, 636–644. https://doi.org/10.1016/j.jhazmat.2010.11.046.

Barbati, B., Lorini, L., Amanat, N., Bellagamba, M., Galantini, L., Petrangeli Papini, M., 2023. Enhanced solubilization of strongly adsorbed organic pollutants using synthetic and natural surfactants in soil flushing: column experiment simulation. J. Environ. Chem. Eng. 11, 110758 https://doi.org/10.1016/j.jece.2023.110758.

Colombano, S., Davarzani, H., van Hullebusch, E.D., Huguenot, D., Guyonnet, D., Deparis, J., Ignatiadis, I., 2020. Thermal and chemical enhanced recovery of heavy chlorinated organic compounds in saturated porous media: 1D cell drainage-imbibition experiments. Sci. Total Environ. 706, 135758 https://doi.org/10.1016/j.scitotenv.2019.135758.

Colombano, S., Davarzani, H., van Hullebusch, E.D., Huguenot, D., Guyonnet, D., Deparis, J., Lion, F., Ignatiadis, I., 2021. Comparison of thermal and chemical enhanced recovery of DNAPL in saturated porous media: 2D tank pumping experiments and two-phase flow modelling. Sci. Total Environ. 760, 143958 https://doi.org/10.1016/j.scitotenv.2020.143958.

Damrongsiri, S., Tongcumpou, C., Sabatini, D.A., 2013. Partition behavior of surfactants, butanol, and salt during application of density-modified displacement of dense non-aqueous phase liquids. J. Hazard. Mater. 248–249, 261–267. https://doi.org/10.1016/j.jhazmat.2012.12.059.

Fu, Y., Qin, C., Gao, S., Lv, C., Zhang, C., Yao, Y., 2022. Aquifer flushing using a SDS/1-butanol based in-situ microemulsion: performance and mechanism for the remediation of nitrobenzene contamination. J. Hazard. Mater. 424, 127409 https://doi.org/10.1016/j.jhazmat.2021.127409.

Imhoff, P.T., Gleyzer, S.N., McBride, J.F., Vancho, L.A., Okuda, I., Miller, C.T., 1995. Cosolvent-enhanced remediation of residual dense nonaqueous phase liquids: experimental investigation. Environ. Sci. Technol. 29, 1966–1976.

Kibbey, T.C.G., Ramsburg, C.A., Pennell, K.D., Hayes, K.F., 2002. Implications of alcohol partitioning behavior for in situ density modification of entrapped dense nonaqueous phase liquids. Environ. Sci. Technol. 36, 104–111. https://doi.org/10.1021/es010966q.

Li, Y., Abriola, L.M., Phelan, T.J., Ramsburg, C.A., Pennell, K.D., 2007. Experimental and numerical validation of the total trapping number for prediction of DNAPL mobilization. Environ. Sci. Technol. 41, 8135–8141. https://doi.org/10.1021/es070834i.

Martel, K.E., Martel, R., Lefebvre, R., Gélinas, P.J., 1998. Laboratory study of polymer solutions used for mobility control during in situ NAPL recovery. Ground Water

Monit. Remediat. 18, 103–113. https://doi.org/10.1111/j.1745-6592.1998.tb00734.x.

Martel, R., Hébert, A., Lefebvre, R., Gélinas, P., Gabriel, U., 2004. Displacement and sweep efficiencies in a DNAPL recovery test using micellar and polymer solutions injected in a five-spot pattern. J. Contam. Hydrol. 75, 1–29. https://doi.org/10.1016/j.jconhyd.2004.03.007.

Mo, Y., Dong, J., Liang, X., Bai, J., 2023a. Influencing of hydrogeochemical conditions and engineering parameters on phase behaviors and remediation performance of in-situ microemulsion for residual PCE in aquifers. Sci. Total Environ. 872, 162253 https://doi.org/10.1016/j.scitotenv.2023.162253.

Mo, Y., Dong, J., Li, Y., Liang, X., Bai, J., 2023b. Formation of in-situ microemulsion and its efficiency for residual PCE removal in low temperature aquifers. Colloids Surf. A Physicochem. Eng. Asp. 656, 130461 https://doi.org/10.1016/j.colsurfa.2022.130461.

Oostrom, M., Dane, J.H., Wietsma, T.W., 2006. A review of multidimensional, multifluid intermediate-scale experiments: nonaqueous phase liquid dissolution and enhanced remediation. Vadose Zone J. 5, 570–598.

Parker, B.L., Cherry, J.A., Chapman, S.W., Guilbeault, M.A., 2003. Review and analysis of chlorinated solvent dense nonaqueous phase liquid distributions in five Sandy aquifers. Vadose Zone J. 2, 116–137. https://doi.org/10.2113/2.2.116.

Pennell, K.D., Abriola, L.M., 2017. Surfactant-enhanced aquifer remediation: fundamental processes and practical applications. Fundamentals and Applications. Routledge 693–750.

Pennell, K.D., Abriola, L.M., Weber Jr., W.J., 1993. Surfactant-enhanced solubilization of residual dodecane in soil columns. 1. Experimental investigation. Environ. Sci. Technol. 27, 2332–2340.

Pennell, K.D., Pope, G.A., Abriola, L.M., 1996. Influence of viscous and buoyancy forces on the mobilization of residual tetrachloroethylene during surfactant flushing. Environ. Sci. Technol. 30, 1328–1335. https://doi.org/10.1021/es9505311.

Phenrat, T., Fagerlund, F., Illangasekare, T., Lowry, G.V., Tilton, R.D., 2011. Polymer-modified Fe0 nanoparticles target entrapped NAPL in two dimensional porous media: effect of particle concentration, NAPI. saturation, and injection strategy. Environ. Sci. Technol. 45, 6102–6109. https://doi.org/10.1021/es200577n.

Puigserver, D., Herrero, J., Nogueras, X., Cortés, A., Parker, B.L., Playà, E., Carmona, J. M., 2022. Biotic and abiotic reductive dechlorination of chloroethenes in aquitards. Sci. Total Environ. 816, 151532 https://doi.org/10.1016/j.scitotenv.2021.151532.

Puigserver, D., Herrero, J., Carmona, J.M., 2023. Mobilization pilot test of PCE sources in the transition zone to aquitards by combining mZVI and biostimulation with lactic acid. Sci. Total Environ. 877, 162751 https://doi.org/10.1016/j.scitotenv.2023.162751.

Ramsburg, C.A., Pennell, K.D., 2002. Density-modified displacement for dense nonaqueous-phase liquid source-zone remediation: density conversion using a partitioning alcohol. Environ. Sci. Technol. 36, 2082–2087. https://doi.org/10.1021/es011357l.

Ramsburg, C.A., Pennell, K.D., Kibbey, T.C.G., Hayes, K.F., 2003. Use of a surfactant-stabilized emulsion to deliver 1-butanol for density-modified displacement of Trichloroethene. Environ. Sci. Technol. 37, 4246–4253. https://doi.org/10.1021/es0210291.

Robert, T., Martel, R., Conrad, S.H., Lefebvre, R., Gabriel, U., 2006. Visualization of TCE recovery mechanisms using surfactant-polymer solutions in a two-dimensional heterogeneous sand model. J. Contam. Hydrol. 86, 3–31. https://doi.org/10.1016/j.jconhyd.2006.02.013.

Shook, G.M., Pope, G.A., Kostarelos, K., 1998. Prediction and minimization of vertical migration of DNAPLs using surfactant enhanced aquifer remediation at neutral buoyancy. J. Contam. Hydrol. 34, 363–382. https://doi.org/10.1016/S0169-7722(98)00090-4.

St-Pierre, C., Martel, R., Gabriel, U., Lefebvre, R., Robert, T., Hawari, J., 2004. TCE recovery mechanisms using micellar and alcohol solutions: phase diagrams and sand column experiments. J. Contam. Hydrol. 71, 155–192. https://doi.org/10.1016/J.JCONHYD.2003.09.010.

Taylor, T.P., Pennell, K.D., Abriola, L.M., Dane, J.H., 2001. Surfactant enhanced recovery of tetrachloroethylene from a porous medium containing low permeability lenses: 1. Experimental studies. J. Contam. Hydrol. 48, 325–350. https://doi.org/10.1016/S0169-7722(00)00185-6.

Wu, B., Li, H., Du, X., Zhong, L., Yang, B., Du, P., Gu, Q., Li, F., 2016. Correlation between DNAPL distribution area and dissolved concentration in surfactant enhanced aquifer remediation effluent: a two-dimensional flow cell study. Chemosphere 144, 2142–2149. https://doi.org/10.1016/j.chemosphere.2015.11.005.

You, X., Liu, S., Dai, C., Guo, Y., Zhong, G., Duan, Y., 2020. Contaminant occurrence and migration between high- and low-permeability zones in groundwater systems: a review. Sci. Total Environ. 743, 140703 https://doi.org/10.1016/J.SCITOTENV.2020.140703.

Zhou, M., Rhue, R.D., 2000. Effect of interfacial alcohol concentrations on oil solubilization by sodium dodecyl sulfate micelles. J. Colloid Interface Sci. 228, 18–23.