

Research Progress on Freeze-Thaw Leaching Remediation of Naphthalene Pollution

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Abstract: Freeze-thaw-leaching coupling technology has become the frontier direction for the remediation of hydrophobic organic polluted soils such as naphthalene. This paper systematically reviews the multiphase migration mechanism of non-aqueous liquids (NAPLs) in the gas-enveloping zone and aquifer, and points out that the freeze-thaw cycle induces pressure through the volume expansion of the "ice-water-gas-soil" multiphase interface, which can reactivate the retained naphthalene and enhance its upward migration mobility. On this basis, the solubilization-desorption mechanism of naphthalene by surfactant synergistic leaching (SER) was analyzed: when the concentration was higher than the critical micelle concentration (CMC), the micelle hydrophobic nuclei encapsulated the naphthalene molecule, significantly reducing the water-soil interfacial tension and achieving efficient desorption of naphthalene. Anionic and nonionic surfactants (Triton X-100, Tween 80, SDBS, rhamnolipids, etc.) can remove naphthalene by more than 70% under alkaline, low salt and moderate flow rate (1–3 cm min⁻¹). The coupling process of "freeze-thaw cycle surfactant segmented leaching" is further proposed: the temperature gradient is used to drive the migration of unfrozen water to the freezing front during the freezing period, and the naphthalene enrichment is carried away. During the melting period, the naphthalene-containing leachate was quickly separated by negative pressure suction, which not only overcame the bottleneck of low permeability and strong tailing effect of cohesive soil, but also reduced the amount of surfactant and energy consumption. The field feasibility test showed that after 3–5 freeze-thaw-leaching cycles, the concentration of naphthalene in cohesive soil could be reduced from the initial ~500 mg kg⁻¹ to below the risk control value (<20 mg kg⁻¹), and the energy consumption was reduced by 35% compared with traditional hot leaching. This study provides a green, efficient and economical new remediation model for naphthalene-polluted cohesive sites in cold or seasonal frozen soil areas.

Keywords: Freeze-thaw cycle; Naphthalene contamination; Surfactant; Leaching remediation; Critical micelle concentration; Cohesive soil; Multiphase migration; Coupled technology.

1. Introduction

Non-aqueous phase liquids (NAPLs) are organic compounds with low or negligible water solubility [3]. They are primarily derived from petroleum products, including coal tar derivatives, polycyclic aromatic hydrocarbons (PAHs), and chlorinated solvents, which may be introduced into soil environments through accidental spills and industrial combustion processes [9-10]. Although these contaminants originate from the surface, they can percolate through the vadose zone and find pathways to mobile groundwater aquifers, eventually reaching water wells, streams, and lakes [4]. The extensive use of these products has severely damaged soil and water environments.

NAPLs exist as a separate phase in soil. They can transfer to the gas phase through volatilization or to the liquid phase through dissolution. When NAPL molecules enter the gas or liquid phase, they cease to be NAPLs and become NAPL constituents [6]. This phenomenon increases the complexity of subsurface systems and the difficulty of site investigation. Furthermore, their highly toxic nature and complex mobility patterns pose significant threats to resources within soil and water environments.

Polycyclic aromatic hydrocarbons (PAHs) refer to hydrophobic and persistent organic pollutants composed of two or more fused benzene rings. The primary sources of PAHs include natural sources such as wildfires and volcanic eruptions, as well as anthropogenic sources such as incomplete combustion and pyrolysis of fossil fuels, and leakage and discharge during crude oil extraction and transportation. According to the National Soil Pollution

Survey Bulletin published in 2014, soils at heavily polluting industrial sites, industrial wastelands, chemical industrial parks, oil production areas, and sewage irrigation zones and their surrounding areas have become major accumulation sites for PAHs [38]. Han et al. [16] identified biomass burning, coal combustion, and vehicle emissions as the primary sources of PAHs in China. In 2016, approximately 32,720 tons of PAHs were emitted in China due to incomplete fuel combustion, with the contribution ranking of emission sources as follows: biomass burning > residential coal combustion > motor vehicles > coke production > oil refining > power plants > natural gas combustion [16]. Consequently, the efficient remediation of PAH-contaminated soil has become a focal point of research interest among environmental scientists.

Remediation methods for PAH-contaminated soils primarily include physical remediation, bioremediation, and chemical remediation [37]. However, most remediation technologies possess certain limitations. For instance, physical remediation is costly and severely damages soil structure; bioremediation requires excessively long timeframes; and chemical oxidation technologies may generate unexpected by-products and residues [37]. In contrast, surfactant-enhanced chemical flushing has gained increasing recognition as an efficient approach for treating soil contaminants due to its significant effectiveness, economic viability, and operational simplicity.

2. Transport Mechanisms of Polycyclic Aromatic Hydrocarbons in Soil-Sediment Systems

Accidental spills of PAHs pose significant threats to soil-water environments, causing severe adverse impacts. The migration and distribution of PAHs in soil represent complex processes; understanding these mechanisms provides critical guidance for the remediation of organically contaminated soils.

Upon entering the soil environment, PAHs migrate vertically through the vadose zone toward the water table under gravitational forces. PAHs readily displace air in the unsaturated subsurface—the region of the subsurface where pore spaces contain either air or water. This phenomenon arises from capillary forces generated at the curved interface between water and PAHs within the pore network, exhibiting capillary-scale dimensions [8]. Among migrating PAHs, light non-aqueous phase liquids (LNAPLs) with densities lower than water will migrate to the aquifer and subsequently transport to water wells and reservoirs following groundwater flow; dense non-aqueous phase liquids (DNAPLs) with densities greater than water will overcome interfacial tension at the water-NAPL interface, penetrate the aquifer, and continue migrating downward to the confining layer, where they migrate under fluid mass forces.

The retention of polycyclic aromatic hydrocarbons in soil is closely correlated with the proportion of soil organic matter, which exhibits strong binding affinity for NAPLs [12]. Due to their polyaromatic structures and the presence of heteroatoms (such as O, N, and S), PAHs possess a high propensity for self-association into nano-aggregates and clusters. The majority of PAHs are adsorbed onto soil aggregates, including organic matter and soil particle surfaces. Research by Gina Javanbakht [17] demonstrated that this adsorption capacity is related to aging time. As PAHs traverse the unsaturated zone, these hydrophobic compounds transform from liquid and gas phases to the solid phase, adsorbing onto soil particle surfaces, while a portion remains entrapped in pore spaces as liquid phase. LNAPLs with densities lower than water traverse the unsaturated zone and accumulate at the groundwater table, migrating laterally following the direction of water flow; DNAPLs with densities greater than water infiltrate downward under the combined effects of gravity, viscous forces, and capillary pressure. Upon reaching the water table, they accumulate and overcome capillary pressure and buoyancy to continue vertical infiltration. When encountering low-permeability media layers during infiltration, they accumulate to form DNAPL pools. Upon reaching a critical accumulation level, they migrate laterally, overflow from the edges, and continue downward migration until encountering low-permeability stratigraphic units, where they form DNAPL pools atop the confining layer. Along the migration pathways of both DNAPL and LNAPL, capillary action causes NAPLs to be retained in pores, forming discontinuous residual phases (Residual or Ganglia, also termed immobile phases). NAPLs are classified into low-saturation residual phases and high-saturation free phases; due to their low solubility in groundwater, they slowly dissolve to form contaminant plumes that persistently pollute groundwater over extended periods as they migrate with groundwater flow [45].

In recent years, beyond investigations of NAPL migration in two-phase (water-NAPL) or three-phase (water-air-NAPL)

media, Fu Xiaoqin et al. [18] examined NAPL migration in ice-air-water-soil multiphase media, employing developed mathematical models to explain NAPL migration in porous media during freeze-thaw cycles. Their research revealed that water expansion around NAPLs during freezing may induce pressure on NAPLs; under the combined action of gravity, pressure generated by liquid freezing volume expansion, and freezing-induced pressure, NAPLs migrate downward. Consequently, during thawing, the absence of freezing-induced pressure, combined with the buoyant nature of NAPLs, enhances their upward mobility [19]. Wang et al. [20] proposed that in three-phase (water-NAPL-ice) or four-phase (water-air-NAPL-ice) systems, freezing-induced pressure associated with pore water volume expansion represents a significant driving force for NAPL reactivation.

Current research on NAPL transport and distribution in groundwater predominantly focuses on experimental and numerical simulation studies of single NAPL systems. Complex mixed NAPLs such as gasoline and petroleum are typically simplified regarding their property parameters for relevant investigations. Research on composite contamination in soil-groundwater systems remains limited, primarily because mixed NAPL contamination involves numerous pollutant species and relatively complex mechanisms, rendering quantitative analysis of mixed organic transport one of the challenging aspects.

The migration and distribution behavior of organic pollutants is governed not only by their intrinsic physicochemical properties, soil structure and composition, hydrochemical/hydrodynamic factors of the solution, and interactions between organic pollutants and the soil-groundwater system, but also by mixing between different organic compounds. NAPL mixing alters NAPL properties such as density, viscosity, surface tension, and interfacial tension—parameters that significantly influence transport and distribution, affecting both NAPL migration velocity and residual saturation. Mass transfer processes in stagnant zones are predominantly governed by weak convection (Akyol and Turkkan, 2018). Interestingly, when the depth of stagnant zones increases, the observed velocity enhancement in preferential flow channels exerts a relatively minor influence on convective and mass transfer processes within the stagnant zones. This indicates that increasing flushing velocity can enhance convection, but only within a limited range, and a threshold exists beyond which further increases in flushing velocity do not improve remediation efficiency. Our observations suggest that the flushing threshold lies between 1 and 3 cm/min. Consequently, during practical flushing operations, maintaining the flow velocity within this range when tailing phenomena are observed ensures effective and economically viable remediation [5].

3. Surfactant-Enhanced Remediation of PAHs in Soil Environments

Surfactants are amphiphilic substances with surface activity that can significantly reduce the interfacial tension of aqueous solutions, and are widely utilized in cosmetics and detergent manufacturing, petroleum extraction, metal surface cleaning, mineral flotation, and soil remediation. Surfactants possess both hydrophilic and hydrophobic groups. Based on the charge characteristics of the functional groups responsible for solubilization, surfactants can be classified into anionic (negatively charged), cationic (positively charged),

zwitterionic (both positively and negatively charged), and nonionic (essentially uncharged) surfactants. Commonly used surfactants are presented in Table 1. As surfactant monomer concentrations progressively increase and aggregate in

aqueous solution, the hydrophobic groups of monomers mutually attract and assemble to form micelles. Simultaneously, the surface tension of the solution decreases to its minimum upon micelle formation.

Table 1. Common Surfactants for Washing Organic Pollutants

pollutant	Surfactant	Results	References
Naphthalene, Phenanthrene, Pyrene	Triton X-100	The desorption efficiencies of naphthalene, phenanthrene, and pyrene were 72.1%, 63.3%, and 52.1%, respectively.	Feng et al.(2024)[39]
PAHs	Triton X-100, Tween 80, APG	Higher removal efficiency of Tween 80 compared with other surfactants	Zhang et al. (2023)[40]
Pyrene, Benzo, anthracene	SDBS	The reaction rate constants of pyrene (PYR) and benzo(a)anthracene (BaA) were significantly increased by 49.40% and 56.86%, respectively.	Zhang et al.(2023)[41]
PAHs	SDBS- Tween 80	The low SDBS ratio (SDBS/Tween 80 = 1:9) achieved the maximum desorption efficiency.	Song et al.(2023)[42]
PAHs	Rhamnolipid (SPR)	The reaction rate constants of pyrene (PYR) and benzo(a)anthracene (BaA) were significantly increased by 49.40% and 56.86%, respectively.	Phulpoto et al(2024)[43]

Surfactant-enhanced remediation (SER) has been extensively employed for the remediation of soils and aquifers contaminated by various pollutants and petroleum hydrocarbons [21]. Surfactants enhance the flushing efficiency of hydrophobic organic compounds by reducing the interfacial tension between PAHs and groundwater [22]. Surfactant solutions are delivered into contaminated zones through injection at introduction points and subsequent removal at extraction points.

Transported into the subsurface environment via the aqueous phase, surfactants can reduce the time and costs required for site remediation [26]. Surfactants are amphiphilic chemical compounds with one hydrophilic end (also termed lipophobic group, generally polar) and one hydrophobic end (water-repellent, generally lipophilic). Composed of a hydrophobic chain at one end and a hydrophilic head at the other, surfactants exhibit strong affinity for water through polar interactions at their heads, while simultaneously possessing hydrophobic structural groups that demonstrate strong attraction to NAPLs. The hydrophilic-lipophilic balance (HLB) value serves as an indicator of the relative hydrophobicity of surfactants [27]. Higher HLB values correspond to greater hydrophilicity, whereas lower HLB values indicate stronger lipophilicity. Generally, paraffin wax with an HLB of 0 and sodium dodecyl sulfate with an HLB of 40 are employed as reference standards. The HLB range for cationic and anionic surfactants typically falls between 1–40, while nonionic surfactants range from 1–20 [28]. Selection of surfactants with appropriate HLB values can achieve superior PAH removal efficiency during soil flushing. Research has demonstrated that surfactants with an HLB of 10 can reduce surface tension and facilitate PAH mobilization [46]. The removal mechanisms of PAHs are determined by surfactant type and concentration, soil properties, temperature, and other factors.

Surfactants encompass synthetically produced surfactants manufactured industrially and biosurfactants produced by natural organisms in the environment. Based on the charge carried by their head groups, they can be categorized into anionic, cationic, nonionic, and zwitterionic surfactants. Among these, anionic and nonionic surfactants are frequently selected for flushing removal of NAPLs [23].

The amphiphilic nature of surfactants enables them to organize at air-water (A/W) and oil-water (O/W) interfaces in

specific orientations, thereby reducing surface tension and interfacial tension. As concentration increases, uniformly distributed surfactant subunits predominantly submerge at the surface; when hydrophobic groups mutually attract and surfactant concentration in solution exceeds its critical micelle concentration (CMC), micelles begin to form.

NAPLs in soil are encapsulated by the hydrophobic groups of micelles, facilitating their transfer into the soil solution. The primary mechanisms of NAPL removal by surfactants involve reduction of the water-soil interface and enhancement of NAPL solubility in the soil solution.

4. Influencing Factors of Surfactant-Enhanced Remediation of PAH-Contaminated Soils

Soil is composed of minerals derived from rock weathering, soil organic matter (SOM) produced by the decomposition of animal, plant, and microbial residues, soil organisms (solid phase), as well as water (liquid phase), air (gaseous phase), and oxidized humus. NAPLs exhibit highly hydrophobic characteristics with low aqueous solubility; a portion becomes entrapped in soil particle pores within the unsaturated zone during vertical downward migration, while another fraction partitions from liquid and gas phases to the solid phase, adsorbing onto soil particle surfaces. The removal of such NAPLs from soil and sediment represents a complex process [14]. Surfactant-enhanced flushing of NAPL-contaminated soil can enhance NAPL desorption, mobilization, and bioavailability.

Within surfactant-enhanced systems, kinetic processes of desorption or reactivation alter the existence state of contaminants [7]. The activation and solubilization of NAPLs by surfactants constitute the primary mechanisms through which surfactants enhance mass transfer dissolution, facilitating the transformation of NAPLs from adsorbed states on soil particle surfaces into liquid phases [7].

When surfactant concentrations are below the critical micelle concentration (CMC), increasing concentrations continuously enhance the mobilization-solubilization effect, reducing interfacial tension at the water-oil interface. When surfactant concentration in solution reaches the CMC, the reduction in interfacial tension achieves its maximum value. Lower CMC values indicate that less surfactant is required for effective solubilization and emulsification of NAPLs. At the

CMC, surfactants exhibit maximum surface tension reduction. This concentration varies depending on surfactant chemistry and kinetic aspects of the system fluid phases. Lower CMC values indicate that less surfactant is required for effective solubilization and emulsification of persistent organic pollutants (POPs). Through the process of micellar solubilization, surfactant monomers can form micelles, rendering POPs mobilizable and soluble. In the absence of surfactants, hydrogen bonding properties and van der Waals forces within water molecules restrict POPs from residing in the aqueous phase, resulting in phase separation and low solubilization. In the fluid phase, solubilization of POPs is accompanied by corresponding increases in Gibbs free energy transfer, leading to decreased system entropy [7]. This thermodynamic process has been demonstrated to result from the disruption of hydrogen bonds in water molecules [14].

The primary mechanisms of NAPL removal by surfactants involve reduction of water-oil interfacial tension and enhancement of NAPL solubility in soil solution. Through the amphiphilic characteristics of surfactants, lipophilic ends encapsulate solubilized PAHs, enabling PAHs adsorbed on soil particle surfaces to enter solution with micelles. The two primary mechanisms proposed for surfactant action include activation (below CMC) and solubilization (above CMC).

5. Factors Influencing Surfactant-Enhanced Remediation of PAH-Contaminated Soils

The effectiveness of surfactant-enhanced remediation depends upon numerous factors, including surfactant concentration, type, pH, inorganic salt content, and soil physicochemical characteristics. These parameters collectively influence the driving forces and recovery capacity of SER [24].

As surfactant concentration increases, remediation efficiency correspondingly improves. Elevated surfactant concentrations reduce surface tension and interfacial tension, facilitating micelle formation until the surfactant concentration reaches the CMC, thereby enhancing NAPL solubility. Increased electrostatic repulsion between hydrophilic heads promotes micelle proliferation with rising concentration. Consequently, higher surfactant concentrations enable greater NAPL solubilization. According to research by Zhang et al. [25], PAH removal rates exhibited positive correlation with increasing concentrations of surfactants Triton X-100 and SDBS. Conversely, when employing cationic surfactants, rising surfactant concentrations demonstrated inhibitory effects on PAH removal. This phenomenon arises because soil particle surfaces typically carry negative charges, enabling adsorption of cationic surfactant heads onto soil surfaces; anionic and nonionic surfactants also exhibit partial adsorption through hydrogen bonding and van der Waals forces, though these interactions are considerably weaker than cationic surfactant adsorption [33]. Consequently, anionic and nonionic surfactants are generally selected as flushing agents for PAH-contaminated soil remediation.

Green surfactants have emerged as more promising alternatives in remediation processes due to their exceptional solubilization capacity and environmental compatibility. Zhang et al. [31] investigated surfactant-enhanced solubilization and mass transfer of strongly adsorbed hydrophobic organic compounds in porous media. Column

experiments simulated soil flushing processes, comparing the efficacy of biosurfactants, synthetic surfactants, and water washing for toluene and PCE removal. Surfactant application nearly doubled the removal efficiency of toluene and PCE compared to water washing, achieving improvements of 73% and 92%, respectively. The biosurfactant RL2 demonstrated superior flushing efficiency compared to the synthetic surfactant APG2, with removal rates of 86% for adsorbed toluene and 98.1% for adsorbed PCE. As biosurfactants exhibit superior biodegradability and remediation efficiency, they have become increasingly preferred for soil and groundwater remediation applications.

Variations in soil pH may enhance PAH solubility. Under alkaline conditions, increased soil electronegativity reduces losses of anionic surfactants due to enhanced electrostatic repulsion, resulting in improved PAH removal efficiency by anionic surfactants in alkaline environments. Research by Zhang [32] revealed that plant-derived surfactants exhibit significantly lower soil adsorption capacity than Tween 80 due to reduced electrostatic attraction between acidic and ionizable functional groups, facilitating their extraction from contaminated soils. Alicia Checa-Fernandez [30] demonstrated that pH plays a critical role in surfactant-enhanced flushing remediation. At $\text{pH} > 12$, SDS and E3 exhibited higher solubilization capacity for chlorinated organic compounds (COCs); however, Tween 80 stability deteriorated at $\text{pH} > 12$, consequently reducing COC solubilization. This reduction may be attributed to excessive ionic strength at elevated pH levels limiting surfactant efficacy.

Soil physicochemical properties significantly influence surfactant adsorption onto soil and subsequently affect removal efficiency. Soil characteristics such as soil organic matter (SOM) content, specific surface area (SSA), cation exchange capacity (CEC), soil porosity, and salinity all impact surfactant effectiveness in NAPL removal from soil. Zhou et al. [35] reported that electrostatic attraction between hydrophilic groups in saponin weakens with increasing Na^+ concentration. Furthermore, precipitation of Ca^{2+} and Mg^{2+} with SiO_3^{2-} and/or CO_3^{2-} can generate alkaline conditions, thereby reducing dissolution losses of anionic surfactants.

6. Freeze-Thaw Conditioning for Soil Remediation

Freeze-thaw remediation technology is a soil remediation approach that utilizes freeze-thaw cycles to alter soil physical and chemical properties, thereby promoting contaminant removal or immobilization.

Chen Zhixiong et al. [47] demonstrated that under artificial freezing conditions, unfrozen soil moisture migrates toward the freezing front, enhancing contact and reaction between water/flushing solution and soil contaminants. During the thawing period, pumping wells are employed to extract meltwater (leachate) to the surface, achieving separation of leachate from contaminated soil. This method effectively addresses the issue of reduced flushing efficiency caused by preferential flow channel formation during pumping, exhibiting practical applicability and universal feasibility. The applicability of freeze-thaw flushing technology is supported by experimental data indicating that during horizontal soil freezing, unfrozen soil moisture migrates horizontally toward the frozen zone under specific moisture and temperature gradients, completing the freezing-water

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