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Review

Mechanisms, Applications, and Risk Analysis of Surfactant-Enhanced Remediation of Hydrophobic Organic Contaminated Soil

Lijun Wu [1,2,*], Jieru Zhang [3], Fenfei Chen [3], Junjie Li [3,*], Wen Wang [3], Shiyi Li [1] and Lifang Hu [4]

[1] Power China Huadong Engineering Corporation Limited, Hangzhou 311122, China; li_sy5@hdec.com
[2] Huadong Eco-Environmental Engineering Research Institute of Zhejiang Province, Hangzhou 311122, China
[3] Yangtze River Delta (Jiaxing) Ecological Development Corporation Limited, Jiaxing 314099, China; zhangjier1123@gmail.com (J.Z.); chen_ff@hdec.com (F.C.); wang_w3@hdec.com (W.W.)
[4] College of Quality and Safety Engineering, Institution of Industrial Carbon Metrology, China Jiliang University, Hangzhou 310018, China; lfhu@cjlu.edu.cn
* Correspondence: wu_lj2@hdec.com (L.W.); li_jj2@hdec.com (J.L.)

Abstract: Surfactant-Enhanced Remediation is increasingly being recognized for its exceptional effectiveness in eliminating non-aqueous phase liquids in soil. A comprehensive knowledge of the technique is essential for its field application. This paper provides a thorough examination of Surfactant-Enhanced Remediation incorporating insights based on the most recent advancements. Firstly, the fundamental process and major mechanisms that underpin the technology were summarized, including mobilization, solubilizing, and emulsifying. Secondly, the improvements achieved by using surfactants in soil remediation, through chemical, physical, and biological methods, have been elucidated through theoretical explanations and practical case studies. Thirdly, the risks and other limitations of Surfactant-Enhanced Remediation were discussed with an outlook for future development. This review aims to promote understanding of the effectiveness and risks holistically in field implementation of the technique.

Keywords: non-aqueous phase liquid; surfactants; mechanisms; soil remediation

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1. Introduction

The contamination of soils by organic compounds is becoming an urgent global concern with the development of industrialization [1]. Organic pollutants are mostly soluble but non-aqueous phase liquids (NAPLs) are distinct due to their volatility, toxicity and insolubility in water [1–3]. Considering the relative densities to water, NAPLs can be categorized into light non-aqueous phase liquids (LNAPLs) and heavy non-aqueous phase liquids (DNAPLs). With a density lower than water, LNAPLs are primarily composed of hydrocarbon compounds such as gasoline, diesel, kerosene, aromatic hydrocarbons, and short-chain alkanes. DNAPLs, on the other hand, notably include Trichloroethylene, Perchloroethylene, Trichloroacetic acid, Chlorophenols, Chlorobenzenes, coal tar and other highly toxic chlorinated organic substances. Toxic and chemically stable, NAPLs can infiltrate, migrate, and interact with the soil matrix or become trapped within the soil's pore spaces acting as a persistent source of contamination [4,5]. Resistant to natural degradation, NAPLs tends to accumulate and disrupt soil functionality, posing a significant risk to the environment as well as to human health [6,7].

A variety of techniques [8] have been proposed to solve the contamination problem of soil and groundwater, including Permeable Reactive Barriers, bioremediation, Air Stripping, and the Pump and Treat (P&T) technique; of which, P&T is the most common approach. However, traditional P&T is not effective for NAPL remediation due to their low solubility and low mobility. As an improvement to P&T [9], Surfactant-Enhanced Remediation (SER) was proposed, which involves the injection of water containing surfactants into the subsurface aquifer. With the aid of SER, the duration of P&T has been notably shortened while its effectiveness towards NAPLs has been amplified [10,11]. Surfactants are a class of amphiphilic substances renowned for their distinctive surface activity, which pose a unique dual-phase molecular structure, featuring a hydrophilic head and a lipophilic tail [12,13]. As shown in Figure 1, the hydrophilic head of surfactants integrates into the aqueous phase by interacting with water molecules, while their hydrophobic tails engage with nonpolar or weakly polar solvents, allowing them to be incorporated into the oil phase [14,15]. This dual interaction positions surfactants at the oil–water interface, displacing some water or oil molecules, reducing intermolecular forces, and thereby forming a stable monolayer and decreasing interfacial tension. As surfactant concentration in the solution rises, so does the adsorption at the interface, which in turn lowers the tension. Since capillary forces restrict the mobility of NAPLs, the mobilized contaminants can then be recovered in a P&T extraction well. Once the surfactant concentration surpasses the critical micelle concentration (CMC), the adsorption plateaus. Beyond CMC, hydrophobic tails of surfactant molecules self-assemble to form aggregates within the solution, known as micelles. Micelles are spherical or ellipsoidal structures that have their hydrophobic tails oriented inward and their hydrophilic heads facing outwards towards the water. This configuration endows great importance on hydrophilic heads which are often comprised of polar groups. Based on the hydrophilic head groups, surfactants can be classified into nonionic surfactants [16], anionic surfactants [17], cationic surfactants [18], gemini surfactants and special surfactants [19,20].

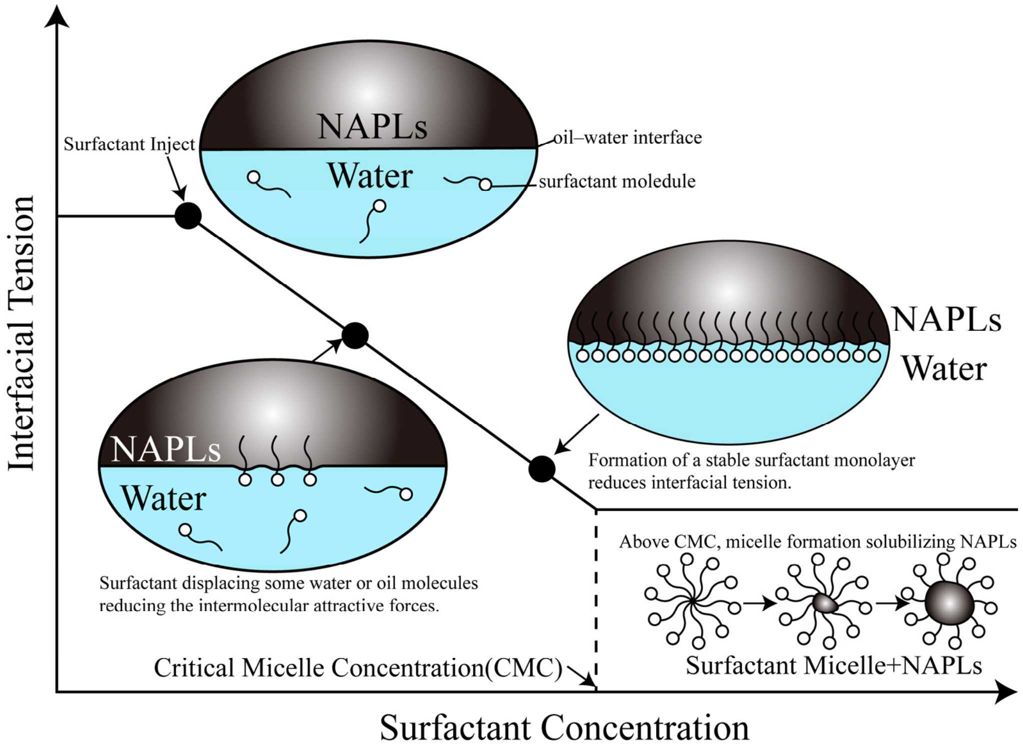


Figure 1. Schematic of Interfacial Tension Dynamics with Surfactant Concentration at the Molecular Level.

A variety of surfactants have been extensively investigated in SER, including sodium dodecyl benzene sulfonate (SDBS), Tween-80®, sodium dodecyl sulfate (SDS), hexadecyltrimethylammonium bromide (CTMAB), polyoxyethylene(10)octylphenyl ether(TX-100), cocamidopropyl hydroxysultane (CAHs) and polyethoxylate lauryl ether (Brij35) [21]. The mechanism underlying SER of NAPL contamination can be primarily categorized into solubilizing effect [22], mobilization effect [23] and emulsification [24]. The dominant mechanism varied with different types of NAPLs. The solubilization effect is often predominant in the remediation of DNAPLs, whereas the mobilization effect mostly plays the key role in the remediation of LNAPLs contamination. For example, the ratio of mobilized to solubilized oil in the porous rock was reported [25] to be 6:1 using n-Dodecyl β-D-maltoside as surfactant. A thin layer of surfactant formed and reached saturation relatively fast, which led to a reduction of the interfacial energy which favors the formation of microemulsions that promote the mobilization of NAPLs. However, the introduction of surfactants into an aquifer can also trigger complications and risks. Following the diminution of interfacial tension, unstable DNAPLs are subject to continued migration influenced by gravitational forces, hydrodynamic pressures, and capillary action, which may lead to an expansion of the contaminated area, thereby risking the contamination of previously unpolluted aquifer regions. Comprehending the mechanisms, risk, and state-of-the-art techniques is essential for the implementation of effective containment strategy. A systematic exposition of the mechanisms underpinning SER technology was reviewed followed by the examination of the synergistic applications of SER with other soil remediation methods. This paper then concluded with an analysis of the potential risks and other issues constraining the commercialization of SER in soil remediation.

2. Mechanisms of Surfactant-Enhanced Remediation Technologies

The mechanisms of Surfactant-Enhanced Remediation of NAPL-contaminated sites are primarily categorized into mobilization, emulsification, and solubilization, as depicted in Figure 2. Mobilization, which reduces the interfacial tension between NAPLs and water, thereby promoting the mobility and migration of NAPLs in porous media; emulsification, generating fine NAPL droplets stabilized by surfactant molecules, thus improving their dispersion in water; and solubilization, encapsulating hydrocarbon chains within micelles to increase the water solubility of non-aqueous solvents. The synergistic action of these mechanisms facilitates NAPLs elimination and biodegradation processes.

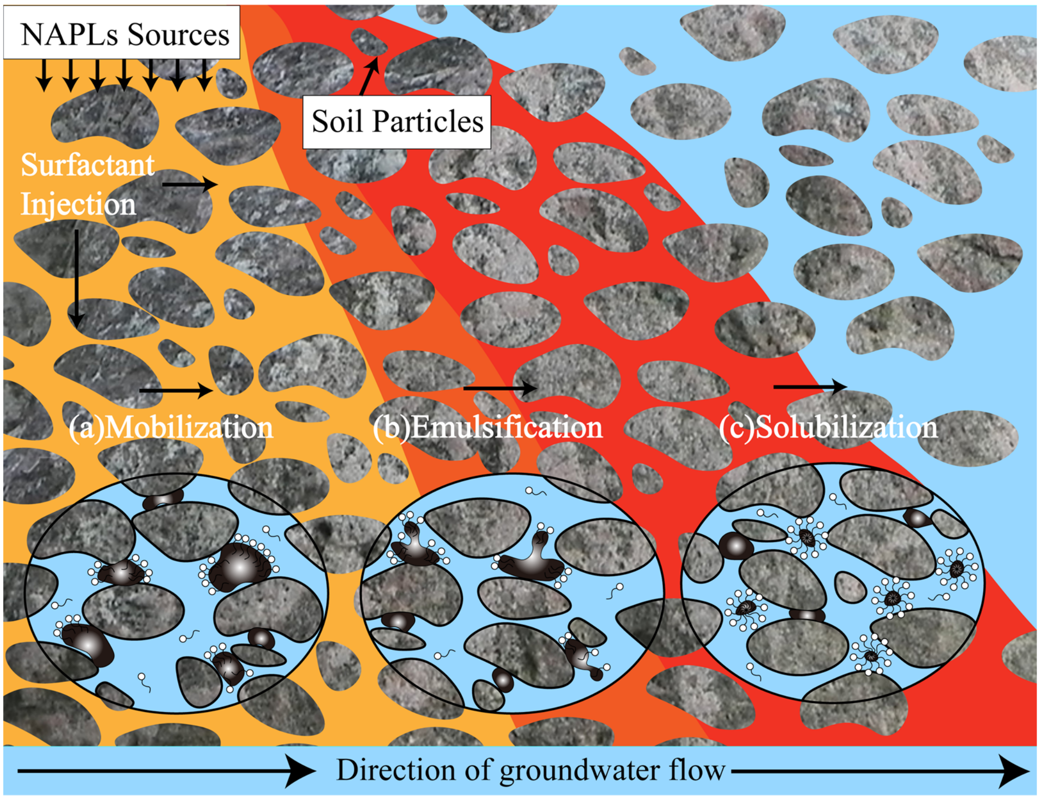


Figure 2. Surfactant-Enhanced NAPL Remediation Mechanisms: solubilization, emulsification, and flow enhancement.

2.1. Mobilization

The mechanism of the mobilization effect involves surfactant forming an adsorption layer at the water-NAPLs interface as shown in Figure 3. This reduces the interfacial tension between the water and NAPL phases, diminishing the capillary resistance within the porous media. Consequently, the stable DNAPLs are mobilized, migrating with the water flow in a liquid state. The ability of surfactant to reduce the oil–water interfacial tension determines the effectiveness of surfactant on the mobilization of NAPLs [26].

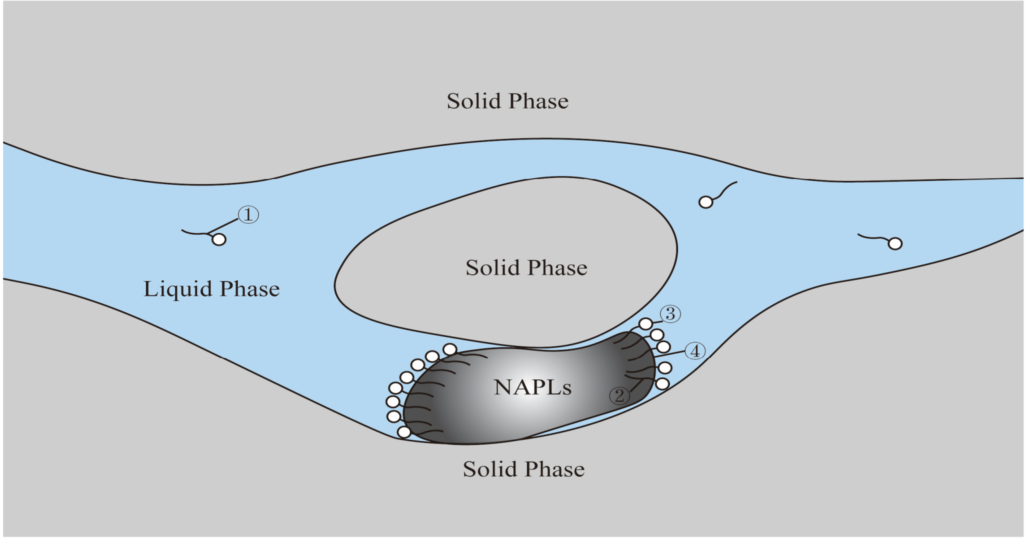


Figure 3. Schematic mobilization effect of surfactants on NAPLs (①: surfactant single molecule; ②: surfactant lipophilic group; ③: surfactant hydrophilic group; ④: oil–water interface).

To assess the critical conditions for the movement of NAPLs, Penell [27] proposed to use the total trapping number N_T to describe the state of NAPLs in porous media, as shown in the schematic diagram of the pore retention model in Figure 4 below.

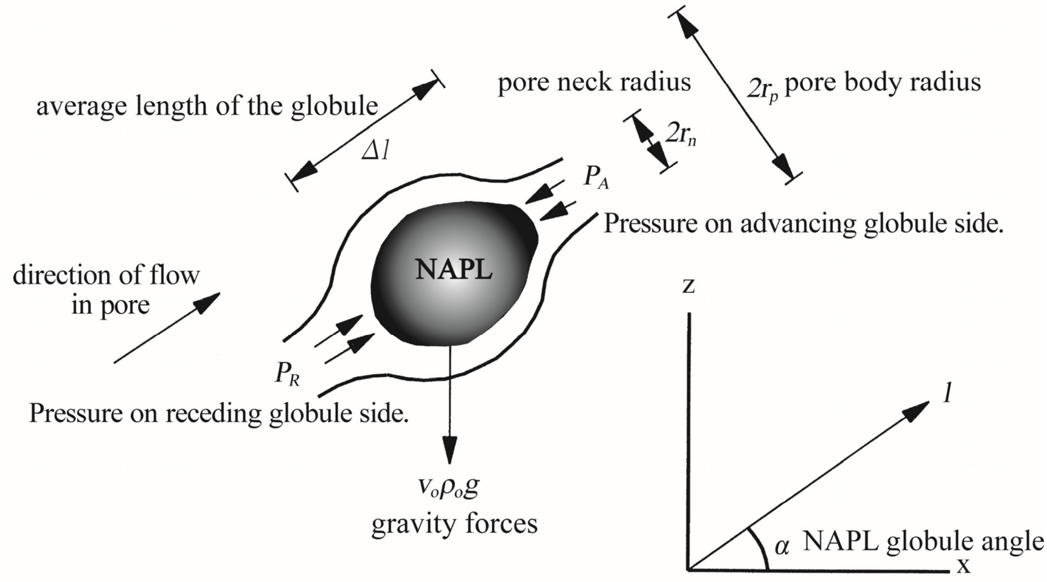


Figure 4. Schematic diagram of the pore entrapment model and corresponding coordinate system [28].

$$N_T = \sqrt{{N_{CA}}^2 + 2N_{CA}N_B \sin\alpha + {N_B}^2} \tag{1}$$

$$N_{CA} = \frac{q_{w_l}\mu_w}{\sigma_{ow}\cos\theta} \tag{2}$$

$$N_B = \frac{\Delta\rho g k k_{rw}}{\sigma_{ow}\cos\theta} \tag{3}$$

in which N_{CA} is the capillary number defined in terms of the aqueous flow component in the direction of the pore. N_B is the bond number representing the ratio of the buoyancy to capillary forces. σ_{ow} is the interfacial tension between the oil and water phases. q_{w_l} denotes the Darcy velocity of the water phase in the l direction. The angle α is measured between the flow and the positive x-axis (counterclockwise). The absolute permeability of the porous medium is characterized by k, while k_{rw} denotes the relative permeability to the aqueous phase. The dynamic viscosity of the aqueous phase is μ_w. $\Delta\rho$ signifies the difference between the density of water and the density of organic liquid, and θ is the contact angle.

The aforementioned equation quantitatively illustrated the mechanical equilibrium of gravity, viscous force, and capillary force on NAPLs in the pore space, while the generation of the mobilization effect is related to the capillary number (N_{CA}), capillary force, buoyancy force, and viscous force. When N_T exceeds a critical threshold, the NAPLs exhibit a mobilization effect [27]. The introduction of surfactants notably diminishes the interfacial tension between the oil–water phases. Concurrently, an increase in both N_B and N_{CA} facilitates the surpassing of the critical threshold of N_T. When N_{CA} is elevated, the viscous force becomes predominant, leading to a decrease in the interfacial tension within the fluid at the pore scale. In instances where the viscous force exceeds the capillary force, the mobility of NAPLs is significantly augmented [29,30]. Based on the total capture number N_T concept, Andrew et al. [31] produced migration potential maps showing how mixtures of composite multiple NAPLs are affected by viscous and interfacial tensions in both vertical and horizontal directions. Under a specified permeability condition, total trapping number influenced by surfactants that primarily operate through solubilization and emulsification mechanisms will be higher than that dominated by the mobilization mechanism.

Different types of surfactants exert varying impacts on the mobilization effect [32]. By blending multiple surfactants [30,33], the aqueous solubility of NAPLs can be significantly enhanced, thereby facilitating the occurrence of the mobilization mechanism. Increasing the concentration of surfactants can accelerate the decrease in interfacial tension [34] and low interfacial tension can help to enhance the mobilization mechanism [35], but higher surfactant concentration may also change the soil structure and flow pathway [36]. Apart from the nature of the surfactant, the nature of the porous medium, the pore water flow rate, and the environmental salinity may all affect the mobilization mechanism. For example, the alteration in the wettability of porous media leads to changes in the capillary pressure in the pores, which affects the mobilization effect to a great extend [37]. Certain surfactants have the capacity to promote the accumulation of negative charges on the surface of porous media, changing them from lipophilic to hydrophilic, which in turn intensify the mobilization effect of NAPLs [38–40]. The pore water flow rate exerts a limiting influence on the value of N_T. When the flow rate is low, N_T is diminished, making it difficult for the mobilization mechanism to manifest. Consequently, the removal efficiency of NAPLs is negligible [41]. To promote the mobilization of NAPLs, the addition of an appropriate amount of ions to the surfactant system to change the salinity is a promising strategy [25].

The mobilization effect of NAPLs offers a higher remediation rate for free-phase NAPLs, but there is a greater risk of secondary contamination due to the difficulty of controlling the movement of free-phase liquid [42], especially in the case of DNAPLs.

2.2. Solubilization

The solubilization effect involves the micellization process of surfactants, which distributes NAPLs into the hydrophobic core of the micelles. This increases the solubility of insoluble or slightly soluble NAPLs in the aqueous phase, allowing them to migrate from the porous medium to the aqueous phase through the formation of nanoscale agglomerates that encapsulate the contaminants [43,44]. The solubilizing effect of surfactants is mainly manifested in micellar solubilization, as shown in Figure 5.

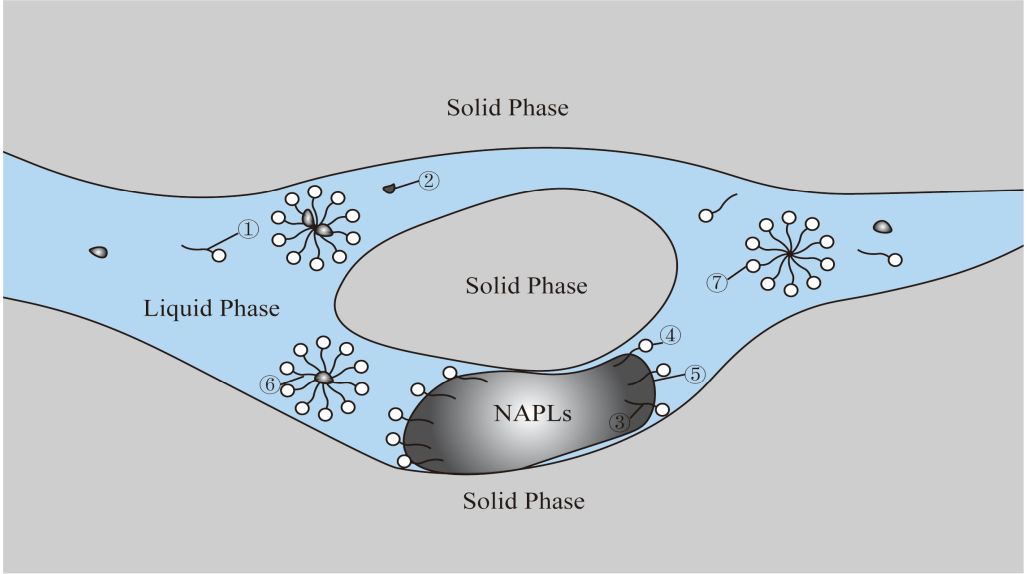


Figure 5. Schematic solubilization effect of surfactants on NAPLs (①: surfactant molecules, ②: NAPL droplets, ③: surfactant lipophilic groups, ④: surfactant hydrophilic groups, ⑤: oil–water interface, ⑥: micelles formed by surfactants and NAPLs, and ⑦: surfactant micelles).

The concentration at which a surfactant spontaneously forms micelles is called the critical micelle concentration (CMC). This pivotal concentration dictates the extent of the solubilization capacity. Surfactants exist solely as individual molecules below CMC. Once their concentrations surpass the CMC, surfactants are present both as individual molecules and as micelles, in a dynamic equilibrium between association and decomposition [45–47]. It was discovered that the CMC of nonionic surfactants in the aqueous phase decreases with an increase in the number of carbon atoms within the lipophilic group. Meanwhile, the higher the polarity of the hydrophilic group, the lower the tendency to form micelles, resulting in a higher CMC value [48].

Molar solubilization ratio (MSR) is a quantitative measure of the solubilizing ability of surfactants, which denotes the number of moles of compound solubilized per mole of surfactant [49]. It is expressed by the following formula:

$$\mathrm{MSR} = \frac{S - S_{\mathrm{CMC}}}{C_S - \mathrm{CMC}} \tag{4}$$

in which C_S is the concentration of the solution when the surfactant concentration is greater than CMC; S is the apparent solubility of the solute at a surfactant concentration of C_S; and S_{CMC} denotes the apparent solubility of the solute at a surfactant concentration of C_S as well as at the concentration of CMC.

In addition to the type and structure of surfactant, the ambient ionic strength and temperature had a significant effect on MSR [21,50]. Varied surfactants have different molar solubilization ratios. The solute partition coefficient between micellar and water phases K_{MC} can be calculated from the MSR [51] to find constant solubilizing capacity:

$$K_{MC} = \frac{\mathrm{MSR}/(1+\mathrm{MSR})}{S_{\mathrm{CMC}} V_w} = \frac{55.4 \times \mathrm{MSR}}{S_{\mathrm{CMC}}(1+\mathrm{MSR})} \tag{5}$$

On the basis of the above expression, the solubilizing effect of surfactants is related to the concentration of surfactant monomers and micelles in solution and their corresponding partition coefficients [50]:

$$S_w^*/S_w = 1 + X_{mn}K_{mn} + X_{mn}K_{MC} \tag{6}$$

where S_w^* is the apparent solubility of the solute at a total surfactant concentration of X; S_w is the solubility of the solute in pure water; X_{mn} is the surfactant monomer concentration; X_{mc} is the concentration of surfactant micelles; K_{mn} is the partition coefficient of the solute between the monomer and water phase; and K_{MC} is the solute partition coefficient between the micelle and water phase.

The solubilizing ability of a surfactant can be measured by the hydrophilic–lipophilic balance number (HLB) [23,52,53], whose value depends on the combined affinity of its hydrophilic and lipophilic groups for oil or water, respectively. High HLB values indicate strong hydrophilicity. When the HLB value exceeds 13, the solubilizing effect of the surfactant becomes even more pronounced, particularly in the case of nonionic surfactant solutions with high molecular weight and high HLB values [54].

Different surfactants have distinct CMCs. Surfactants with lower CMCs can produce stabilized polymers at low concentrations, thereby exerting a solubilizing effects [55]. It is advantageous for applications requiring a minimal surfactant dosage. Compared with single surfactants, complex surfactant systems often have more significant solubilizing effects, attributed to their reduced surface tension and CMC, coupled with the formation of more stable mixed micelles and lower adsorption and precipitation loss. Investigating the solubilizing effects of eight different types of surfactants and their complex system, Yang et al. [56] confirmed that complex systems of multiple surfactants had stronger solubilizing ability. The concentration of surfactant can also play an important role in the solubilizing effect of NAPLs [23]. Theoretically, the necessary condition for the solubilization mechanism to occur is that the concentration of surfactant is higher than CMC [23,53,57,58]. Nevertheless, even at sub-critical micelle concentrations (sub-CMC) [59,60], certain surfactants are capable of inducing solubilization. The work of Zhong [59] showed that at concentrations above CMC, the biosurfactant rhamnolipids formed micelles characterized by strong intermolecular interactions. Conversely, at concentrations below the CMC, the interactions between rhamnolipids and alkane molecules become predominant, resulting in a marked solubilizing effect. This effect is notably more pronounced than that observed at levels above the CMC, highlighting the unique behavior of rhamnolipids in facilitating the solubility of hydrocarbons.

Surfactants are easily adsorbed in soil and sensitive to the nature of porous media, and their adsorption in soil reduces the micellar solubilizing effect on NAPLs, which adversely affects remediation [61,62]. In addition, irregular soil pore structures restrict the passage of water and solute [63]. Moreover, flushing may lead to pore clogging due to the accumulation of surfactant micelles, which impede the effectiveness of remediation efforts [64].

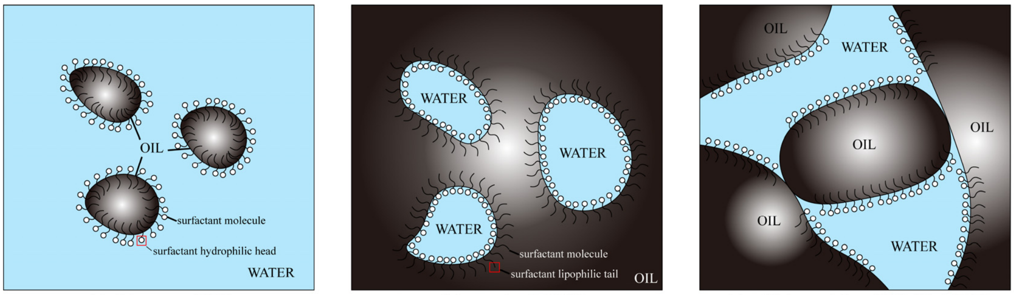
The pore water flow rate during the aggregation process has considerable impact on surfactants' solubilization mechanism. A high flow rate can diminish the surfactants' interaction with NAPLs, leading to a reduction in micelle formation and consequently weakening the solubilization effect [27]. However, concurrently, this increased flow rate can enhance the transportation of the micellar aggregates, mitigating the occurrence of pore throat plugging [23].

As one main mechanism of SER of soil contamination by NAPLs, solubilization effectiveness depends on the type of surfactant used; hence, suitable surfactants should be carefully selected according to the specific contaminants present during the remediation process in order to achieve the optimal results.

2.3. Emulsification

Surfactants play an important role in the treatment of NAPL-contaminated soil, and their emulsification is one of the key mechanisms for enhanced remediation. By adsorbing at the "oil–water interface" to form stable nanoscale oil or water droplets, surfactants achieve an emulsifying effect, promoting the dispersion of NAPLs into micro-droplets [65,66], enhancing mass transfer efficiency, and improving the mobility and recovery rate of NAPLs.

Emulsification products can be categorized into two types: microemulsions and emulsions. Microemulsions are formed through the micellar solubilization action and represent thermodynamically stable systems that are transparent or semi-transparent. On the other hand, emulsions are thermodynamically unstable systems, formed by the emulsification process that disperses the NAPL phase within an immiscible liquid phase. According to the difference between the dispersed and continuous phases, emulsion systems can be further classified into oil-in-water (O/W), water-in-oil (W/O), or multiple emulsions (W/O/W, O/W/O) [67], as illustrated in Figure 6. In porous media, the transport performance of emulsification products is lower than those of nanoscale aggregates produced by micellar solubilization [68], but moderate water-emulsion droplet size adjustments can improve the remediation efficiency [24]. Some studies indicate that enhanced emulsification of surfactants may be more advantageous than solubilization [69] in remediation applications [70].



(a)oil-in-water (O/W) (b)water-in-oil (W/O) (c)multiple emulsions (W/O/W, O/W/O)

Figure 6. Varied types of emulsion systems.

Emulsification is caused by the density difference between the oil and water phases, resulting in the formation of emulsified droplets that move in accordance with gravitational fields, Brownian motion, or applied forces, and are in a state of continuous motion. The oil–water interfacial tension was rapidly reduced to mitigate the rupture and generate fine droplets in the emulsification. However, emulsified droplets are not sufficiently stable [71–73] to overcome collision, sedimentation, coagulation, and aggregation, resulting in remediation impediment. Therefore, this stability is pivotal in ensuring the effectiveness of surfactant-based remediation strategies.

Emulsification is a dynamic process in which surface-active molecules move rapidly to the interfacial region with the destruction of emulsified droplets. The emulsion stability is not only related to the nature of the surfactant solution [74], but also affected by the type of NAPLs [75], the ratio of NAPLs to water and the water content of the system [76]. Liu et al. found that surfactant AEOSHS derived from the modification of fatty alcohol ethoxylates yielded emulsions characterized by reduced droplet sizes, increased emulsification capacity, and enhanced emulsion stability. These attributes led to increases in the mobility and recycling efficiency of emulsified droplets in porous media [74]. In addition to the modification of surfactants, the addition of auxiliary substances such as polymers can also improve the stability of emulsions. For example, the addition of xanthan gum can form a 3D network of polymers, reducing the collision rate of droplets and improving the formation and stability of emulsions [77]. The introduction of sodium carbonate solution in the emulsion system can promote the adsorption at the oil–water interface and improve the mechanical strength of the emulsion film. In the application of foam-assisted oil recovery, high emulsion stability is more beneficial than the low interfacial tension for the flow of the emulsified oil [78]. The properties of emulsion in porous media are also affected by pore structure and pore water flow rate. Emulsions exhibit the shear thinning behavior as non-Newtonian fluids when passing through porous media. Different pore structures can alter the rheology of emulsions [79]. By increasing the pore water flow rate, the retention of emulsion in porous media can be reduced [80].

However, the formation of emulsions from surfactants during remediation can have negative effects. If the emulsion traps contaminants within a low mobile phase, increasing its volume will hinder the penetration of surfactants to the soil–oil interface due to its relatively static and highly viscous properties. It may pose a risk of secondary contamination, and present challenges for subsequent remediation [81].

2.4. Other Mechanisms

In addition to mobilization, solubilizing, and emulsifying effects, surfactants have the ability to increase the bioavailability of NAPLs, thereby enhancing the bioremediation process and promoting the biodegradation of NAPLs [82]. The degradation ability of NAPLs varies among different types of surfactants [83]. The micellar system formed by surfactants helps to increase the number of microorganisms and enhance the degradation efficiency of NAPLs [84]. The uptake of NAPLs by plant roots was promoted in the presence of surfactants, enhancing the phytoremediation effect, which shows promise in the remediation of organically contaminated soil and groundwater.

However, some of the metabolites produced by surfactants during the remediation process may be toxic and inhibit microbial activity [85,86]. Further investigation in this area holds promise and merits continued exploration in the future.

3. Surfactant-Enhanced Remediation Techniques

Widely distributed in the soil environment, NAPLs are not prone to be desorbed from soil pores, being characterized by limited mobility and degradation. As a result, the remediation effect of chemical, biological, and physical remediation techniques on NAPLs in soil is often unsatisfactory. Non-traditional approaches that leverage surfactants have the potential to enhance remediation efficiency significantly, offering the added benefits of reduced costs and expedited time.

3.1. Surfactant-Enhanced Chemical Oxidative Remediation Technology

In situ chemical oxidation (ISCO) is an advanced remediation technology that employs chemical oxidants and the potent oxidizing free radicals they generate to degrade organic pollutants in soil [87], converting them into small molecules, H_2O and CO_2, and NAPL contaminants within the soil matrix. Oxidizing agents of choice include persulfate, potassium permanganate, hydrogen peroxide and ozone, among which sodium persulfate is the most widely used in soil remediation [88]. Given the oxidation reaction usually occurs solely in the aqueous phase [89], the residual non-aqueous phase NAPLs that persist within in the soil are not susceptible to oxidization, thereby inducing a rebound effect [90] in which recalcitrant pollutions continue to be emitted.

Surfactants promote the dissolution of NAPLs into the aqueous phase, and synergistically amplify the chemical oxidation on NAPLs in the remediation process. Surfactant enhanced in situ chemical oxidation (S-ISCO) as a co-elution technique [91] has been extensively studied. This technology was first developed by VeruTEK (Bloomfield, CT, USA) and later acquired by EthicalChem LLC (South Windsor, CT, USA), which sells its VeruSOL surfactant to the oil production industry as a “green” product. In S-ISCO technology, the compatibility of surfactants and oxidizers is an important factor to be considered [92]. Although extensive research has shown that the addition of surfactant has an significant promotive effect on the chemical oxidation technology, the organic nature of surfactant can lead to interactions with oxidants, potentially inactivating the surfactants [93]. Additionally, the introduction of oxidants may escalate the non-productive consumption of surfactants [94] which could compromise the overall remediation efficacy.

Wei et al. [92] selected a binary mixture of SDBS/BS-12 to synergistically enhance the remediation of the oxidizing agent $KMnO_4$, using 1.73–23.07% of the commonly used surfactant in practical experiments, with a cost reduction of more than 50%. Demiray et al. [95] found that despite Tween 80 possibly affecting the kinetics of the oxidation reaction, its overall impact is to accelerate and facilitate the remediation process. The preferential adopting of surfactants that are more compatible with the oxidant system can maximize the remediation effect and have a positive impact on soil remediation.

3.2. Surfactant-Enhanced Bioremediation Technologies

Bioremediation encompasses two primary approaches: microbial remediation and phytoremediation. The efficiency of microbial remediation technology [96] is contingent upon the functionality and abundance of the microbial community in the environment. The degradation of NAPLs in soil is achieved under the combined action of organic nutrients and oxygen, and the specificity of the microorganisms and their susceptibility to external environmental factors significantly influences the remediation efficiency [97]. The combination of biosurfactant and microbial remediation technology can not only increase the degradation rate by more than 50% [98], but also substantially mitigate the secondary contamination effects associated with chemical surfactants; but, the biodegradation mechanism of surfactants remain elusive. Moreover, severe adverse effects on remediation were discovered relating to surfactants at high concentration [99].

Phytoremediation technology [100,101] utilizes plants to adsorb pollutants in soil or shallow groundwater through their roots. However, this method is characterized by a prolonged remediation time as well as limited remediation depth [102]. Surfactants can augment the combined plant-microorganism remediation technology by significantly increasing the abundance of bacterial flora, which, in return, elevates the removal rate of NAPLs. Non-ionic surfactants and biosurfactants demonstrate optimal performance as they mitigate the root toxicity associated with cationic surfactants [103–105].

3.3. Surfactant-Enhanced Physical Remediation Technology

Soil physical remediation technologies encompass a range of methods, including aeration remediation, electric remediation, and thermal treatment technologies. These are complemented by ex situ treatment techniques and land replacement strategies.

Aeration remediation technology is suited for soil environments characterized by high permeability and a loose structure [106]. This method expels NAPLs to the surface through air flow injection. Nevertheless, the method's remediation efficacy is constrained when addressing organic pollutants with attributes of low concentration and low volatility. To solve this problem, a technique referred to as surfactant-enhanced air sparging (SEAS) was proposed by adding surfactants to increase the mobility of organic pollutants and broaden the influence area of air in the soil matrix [107]. The efficiency of NAPAL's remediation is reported to be closely related to the airflow rate, surfactant concentration, aeration pressure, and the area of remediation [108]. Although this approach shows promise in low-permeability formations, additional research is warranted to elucidate the role of NAPLs in such environments [109].

Electric Remediation Technology [110] is another well practiced method in the field of soil remediation. The anode and cathode electrodes are inserted into the soil to generate an electric field where contaminants were extracted from the soil through electro-osmosis, electro-migration and electrophoresis [111–113]. However, the heat accumulated during the process will affect the soil properties in the long run, and it is more suitable for hypotonic soils with low acid buffer capacity. Nonionic surfactants are commonly used in conjunction with electrokinetic remediation techniques. Studies have demonstrated that the synergistic application of nonionic surfactants under a periodic voltage gradient can remove individual PAHs up to 69% [114]. Arumugam et al. [115] reported the integration of natural surfactants with electrokinetic remediation technology resulted in a 98% decomposition efficiency for organic pollutants and also increased subsequent bioavailability. In practical application, it is essential to consider the secondary contamination of surfactants and to identify the optimal operating conditions for electrokinetic remediation technology to ensure the most effective remediation outcomes [116].

Thermal desorption technology [117] in soil remediation refers to a process where heat is applied to contaminated soil to increase the temperature and volatilize organic compounds, thereby separating them from the soil matrix. Thermal desorption technology can regulate the temperature and residence time to achieve the best NAPL removal rate, and has the advantages of high removal efficiency, short remediation time, and minimal likelihood of inducing secondary pollution. However, the application of this technology faces limitations due to constraints posed by soil water content, high cost, and the potential for altering the physicochemical and biological properties of the soil [118]. Coupled with surfactant use, thermal desorption can implement a dual process approach, consisting of a cleaning phase followed by thermal desorption [119]. Surfactant based pretreatment diminishes the volume of soil to be treated by thermal desorption, thereby reducing the associated energy consumption costs. However, the limited number of cases of application of this technology necessitates additional research to substantiate its feasibility and effectiveness.

4. Risk Analysis of Surfactant-Enhanced Remediation

SER technology has the capacity to augment the solubility of pollutants, thereby facilitating their removal. However, it also presents challenges, such as the potential for residual concentrations to induce secondary contamination in remediation sites. The application of surfactants may also introduce heightened toxicity to the soil. Prolonged presence within the subsurface soil system could further lead to the contamination of groundwater resources.

Cationic surfactants have been observed [17,120] to interact with the negatively charged surfaces of porous media, potentially leading to adsorption and enrichment in the subsurface environment. This interaction can burden the soil medium, induce soil toxicity, exert adverse effects, reduce soil permeability, and impair soil function. On the other hand, anionic surfactants [76,121] are more susceptible to forming precipitates with cations in the soils. As for nonionic surfactants, it is often used as a common agent in SER technology [120] because of their stronger solubilizing effect, lower cost and lower toxicity to soil microorganisms [17]. However, some studies have proved that although the content of NAPLs in soil is significantly reduced post remediation, the residual surfactants can remain toxic to the plants in subsequent years [17].

To mitigate that risk, biosurfactants were proposed as an alternative in the remediation of soils contaminated with NAPLs [122]. Unlike traditional synthesized surfactants from petrochemical industrial processes, biosurfactants are generated by biological systems such as plants and microorganisms, representing a novel class of eco-friendly agents with lower toxicity and higher biodegradability [123,124]. Also, biosurfactants have a larger molecular structure and more ligand groups, endowing them with superior performance or additional properties that their synthetic counterparts often lack. For example, biosurfactants can be utilized as a carbon source by soil-inhabiting microbes to accelerate the pollutants' biodegradation [125]. Compared with traditional surfactants, the majority of biosurfactants are more efficient and effective in SER applications due to lower CMC, surface, and interfacial tension values. However, biosurfactants are constrained by limited production scales and high selectivity for target products, resulting in higher costs than synthetic surfactants [126], which poses challenges for their commercial application. Since the substrate alone accounts for almost half of the total cost of obtaining a biosurfactant, ongoing research in the field of biosurfactants is increasingly focusing on the utilization of cost-effective substrates, particularly agricultural waste [127].

5. Conclusions

Recent years saw growing research attention in SER technology thanks to its significant role in strengthening the efficacy of chemical, physical, and biological remediation of NAPL pollution in soil by leveraging mobilization, solubilization, emulsification and other mechanisms. In chemical remediation, surfactants promote the action of chemical oxidizers, while they can be used as carbon source for the activating of microorganisms in biodegradation methods. For physical remediation techniques, the presence of surfactants can broaden the influence zone of aeration or boost the electrokinetic process to accelerate NAPL removal. Detailed examination of the case studies concerning economic analysis, influencing factors, as well as the long term impact on the environment and human health is non-exhaustive and limited by relevant references. Further research and exploration is urgent in the following two areas:

1. Surfactants: The development of new surfactants, such as bilobal surfactants and switchable surfactants, is important in reducing the potential impact while improving the remediation efficiency of NAPLs [67,128]. Another strategy is to integrate various surfactants in the remediation process, leveraging their combined action towards NAPLs. Furthermore, surfactants and reaction intermediates warrant further investigations and ongoing monitoring to ensure SER was implemented with a minimum environmental risk.
2. Remediation technology: It is of great importance to further study the synergistic mechanism of SER coupled with different remediation technologies which may surpass the limitations of one single method while concurrently maximizing the outcome, such as with reduced environmental footprint, minimized surfactant usage, and enhanced NAPL removal.

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