

Review

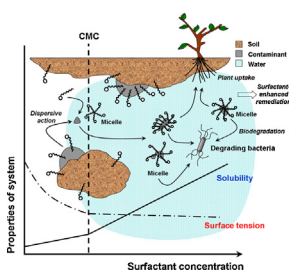
Use of surfactants for the remediation of contaminated soils: A review

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HIGHLIGHTS

- The recent advances in use of surfactant for soil remediation are reviewed.
- The mechanisms of surfactant-based soil remediation are discussed.
- A review on the application of different types of surfactants is made.
- The future research direction of surfactant-based technologies is suggested.

GRAPHICAL ABSTRACT



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ABSTRACT

Due to the great harm caused by soil contamination, there is an increasing interest to apply surfactants to the remediation of a variety of contaminated soils worldwide. This review article summarizes the findings of recent literatures regarding remediation of contaminated soils/sites using surfactants as an enhancing agent. For the surfactant-based remedial technologies, the adsorption behaviors of surfactants onto soil, the solubilizing capability of surfactants, and the toxicity and biocompatibility of surfactants are important considerations. Surfactants can enhance desorption of pollutants from soil, and promote bioremediation of organics by increasing bioavailability of pollutants. The removal of heavy metals and radionuclides from soils involves the mechanisms of dissolution, surfactant-associated complexation, and ionic exchange. In addition to the conventional ionic and nonionic surfactants, gemini surfactants and biosurfactants are also applied to soil remediation due to their benign features like lower critical micelle concentration (CMC) values and better biocompatibility. Mixed surfactant systems and combined use of surfactants with other additives are often adopted to improve the overall performance of soil washing solution for decontamination. Worldwide the field studies and full-scale remediation using surfactant-based technologies are yet limited, however, the already known cases reveal the good prospect of applying surfactant-based technologies to soil remediation.

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1. Introduction

Soil contamination is a global concern and can be considered a major barrier to sustainable development. It ruins the balance of the ecosystem, and causes increasing economic loss and human health damage. Soil contamination is mainly caused by inadequate or irresponsible disposal measures, such as improper industrial discharge, mining tailings, waste disposal, and stockpiles. The prevailing soil contaminants include heavy metals, toxic organics, and radionuclides [1]. Increased heavy metal levels in soil have been reported in many industrialized countries and areas. The metals and their metalloids, such as chromium, cadmium, mercury, and lead, can threaten the ecosystem and human health through food chains or direct exposure to the contaminated soil/water [2]. Organic pollutants, e.g., volatile chlorinated solvents, polychlorinated biphenyls (PCBs), and petroleum products are another pervasive concern due to their toxicity, mobility, and abundance of species. These organic pollutants hardly degrade in soil, being damaging to human being and the environment through toxicity to animal and plant species [3]. Human activities also make radionuclides to contaminate the soil [4], such as the fallout from atmospheric testing of nuclear weapons, the leakage of radioactive waste, and radiological events like the Chernobyl and Fukushima accident. Soils contaminated with low levels of radionuclides can pose a long-term radiation hazard to human health via food chains and other pathways [5].

Due to the high risk on human health and ecological security, contaminated soils need to be remediated for their reclamation. Many remedial attempts, including some cutting-edge technologies, have been made to achieve an environmentally sound and cost-effective remediation of contaminated lands. Among these technologies, soil washing/flushing is a time-efficient and versatile method, and attracts increasing attentions in recent years. Soil washing is a mechanical process that uses liquids, usually aqueous solutions, to remove chemical pollutants from soils. In practical remediation, because contaminants adhere to the surfaces of soil particles and usually have low water solubility, additives like acids, surfactants, and chelating agents are often added into eluents to solubilize contaminants from the soil. Surfactants are a group of amphiphilic chemicals which contain both hydrophilic and hydrophobic parts in the molecular structure simultaneously. The unique molecular structure of surfactant allows to enhance the water solubility of soil contaminants, especially for the hydrophobic organic compounds. Variety of surfactants, e.g., anionic, cationic, zwitterionic, and nonionic surfactants, have been tested and/or applied for soil remediation [6]. For an ex-situ soil washing using surfactant aqueous solution, the general procedure is schematically illustrated in Fig. 1a. The excavated contaminated soil is pretreated and mixed with the water containing surfactants, and agitated. After washing, the clay particles are allowed to settle out, and the eluents (i.e., the washing solutions) can be separated and regenerated for next round use [7]. The ex-situ soil washing can treat a broad range of influent contaminant

concentrations, and allow for the return of clean coarse fractions of soils to the site at a relative low cost [8]. In-situ soil flushing with surfactant eluents is another strategy for practical application [9], as shown in Fig. 1b. Flushing solutions, e.g., liquids containing surfactants, are injected into the area of contamination via injection wells. The soil contaminants are mobilized by solubilization (e.g., formation of micelles with the assistance of flushing solutions) or chemical interactions. After passing through the contamination zone, the contaminant-bearing fluid is collected and brought to the surface for disposal, recirculation, or on-site treatment and reinjection [10]. So far, the soil washing is one of the few treatment routes which can thoroughly separate heavy metals, organics, and radionuclides from contaminated soils. Surfactant is a frequently used additive for soil washing or other remedial technologies, such as surfactant-enhanced bioremediation [11], surfactant-enhanced phytoremediation [12], and surfactant-enhanced electrokinetic remediation [13].

In this review, the considerations for a surfactant-enhanced soil washing, and the mechanism for the removal of different types of contaminants from soils are summarized and discussed, with purposes of providing an overview of the influence of surfactants' properties on the remediation process and the interactions between soil contaminants and surfactant-containing eluents. The progresses in the past 15 years on the application of surfactants for the remediation of contaminated soils/sites are accordingly reviewed and discussed, including ionic surfactants, nonionic surfactants, gemini surfactants, biosurfactants, and mixed surfactants. The scope of the article includes not only surfactant-enhanced soil washing, but also surfactant-enhanced bioremediation and phytoremediation. Particular attentions are given to the recent advances on the removal of radionuclides using surfactants, to gemini surfactants, biosurfactant, and to the mixed use of surfactants for soil remediation. For the readers' reference, the basic information of the surfactants mentioned in this article, is shown in Table 1.

2. Consideration of surfactant-enhanced soil remediation

When surfactant molecules are present in a water–soil heterogeneous system, they could adsorb onto the surface of soil particles and interactions take place, as shown in Fig. 2. Normally, the hydrophilic groups (or head groups) are apt to enter into aqueous phase and the lipophilic groups (or tail groups) tend to combine with hydrophobic contaminants or soil particles. Therefore, surfactants at a low concentration mainly accumulate at solid–liquid or liquid–liquid interface in the form of monomers. With increasing concentrations, surfactant molecules gradually replace the interfacial solvent like water, resulting in a lower polarity of the aqueous-phase and decreased surface tension. At the same time, dissolution of the contaminants, e.g., the non-aqueous phase liquid (NAPL) contaminant, could be accelerated. When surfactant concentration further increases, ellipsoidal or spheroidal micelles

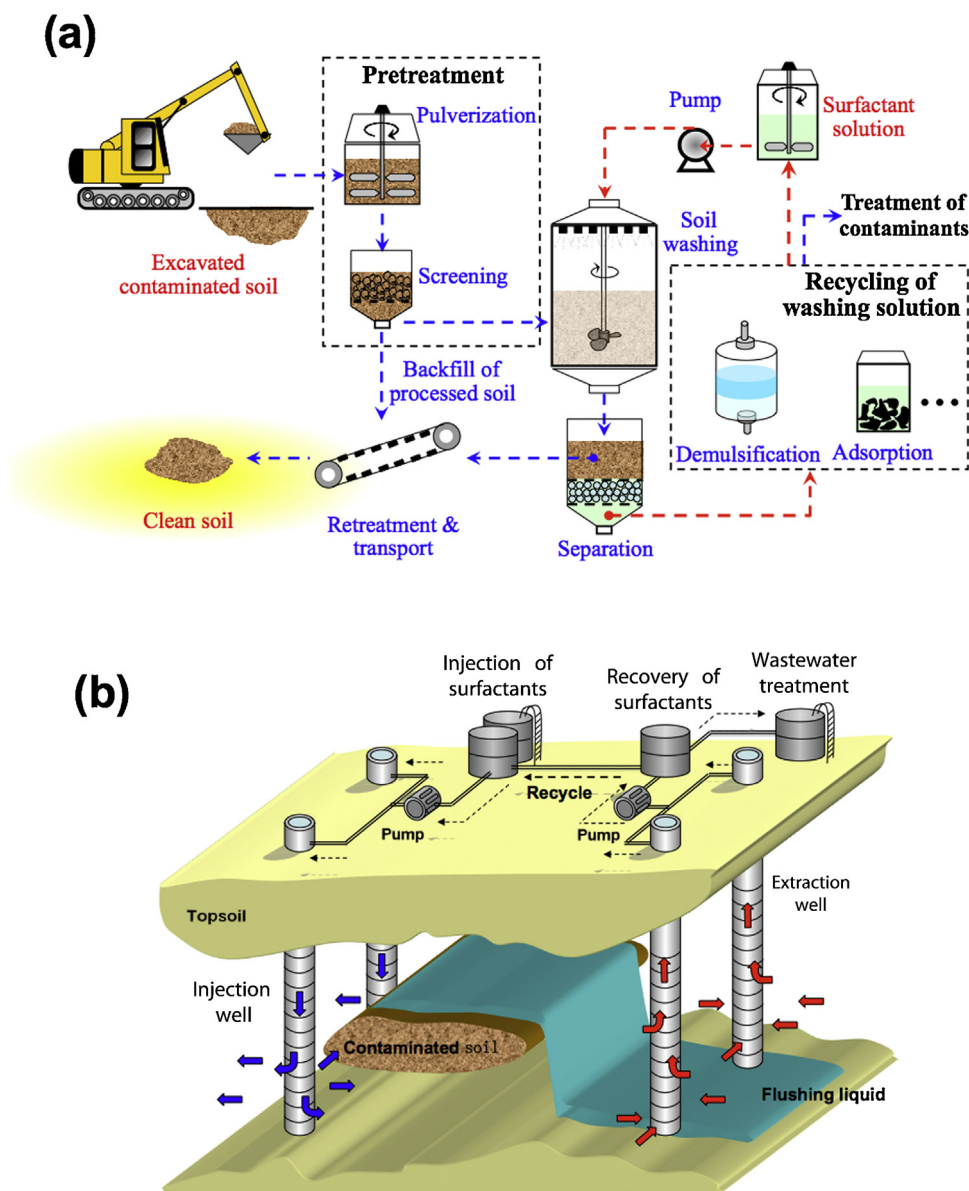


Fig. 1. General procedure of (a) ex-situ washing [14] and (b) in-situ flushing for soil remediation [15].

form and the threshold surfactant concentration at which micelles begin to form is termed the critical micelle concentration (CMC) [16]. These micelles with hydrophilic surfaces and lipophilic cores can easily disperse the contaminants like NAPLs, and dramatically improve their solubility in water phase, thereby further promote desorption of contaminants from soil. The dissolved contaminants in aqueous phase have better mobility, being conducive to the subsequent removal of contaminants via either biotic routes (e.g., plant uptake and microbial degradation shown in Fig. 2) or abiotic routes (e.g., soil washing and subsequent separation [17]).

In order to successfully implement a surfactant-enhanced remediation of contaminated soils, there are some scientific factors worth considering, including the adsorption behavior of the surfactants onto soil, the solubilizing/elution ability of surfactants on the target contaminants, the toxicity and the biodegradability of surfactants. Some nonscientific factors such as the cost of surfactants and scale of the contaminated land should also be considered in parallel. Ideally, in addition to the strong ability to desorb contaminants, an applicative surfactant should possess a lower CMC and function at a small dosage for washing solutions, in order to

reduce the cost of remediation processes and further ensures the economy of the overall process.

When surfactants are added into the water–soil system, a certain amount of surfactants will inevitably be adsorbed by soil particles. The more the adsorbed surfactants, the less the surfactants contribute to the solubilization of pollutants. Moreover, the hydrophobicity of the soil is increased as the surfactants adsorbed onto soil particles. As a result, removed solubilized organic will be re-adsorbed on soil surface [15]. Therefore, the adsorption behavior of the surfactant onto soil particles is a critical concern for selecting appropriate surfactants. The molecular structure of surfactants, which governs the properties of surfactants, is the dominating factor for adsorption behavior. For example, the sorption of a perfluorosulfonate on sludge was much stronger than the perfluorocarboxylate analog, and sorption also increased with increasing the alkyl chain length for C5–C15 perfluoroalkyl surfactants [18]. In addition to the properties of the surfactant itself, the adsorption of a surfactant is also associated with soil properties. The adsorption of a cationic surfactant dodecylpyridinium chloride (DPC) onto soil was found to increase linearly with the cationic exchange capacity val-

Table 1
Basic information of the surfactants mentioned in the article.

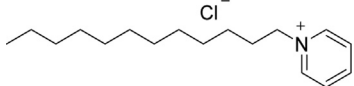
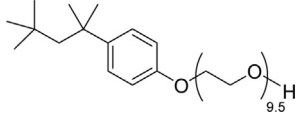

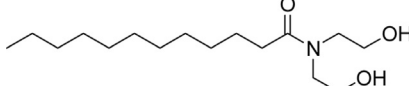
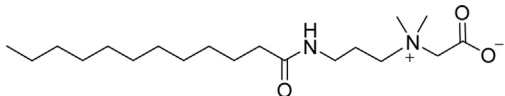
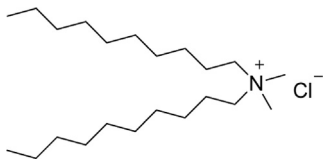
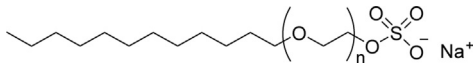
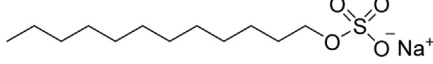
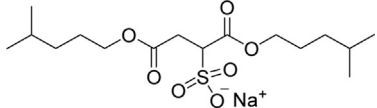
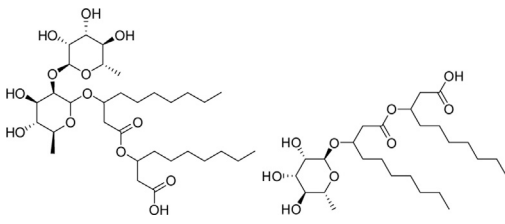
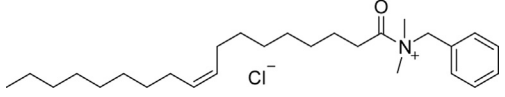
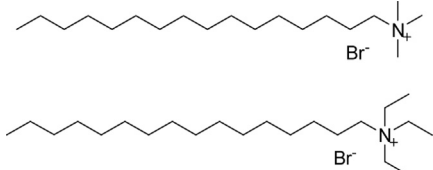
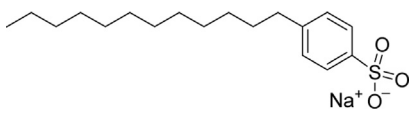
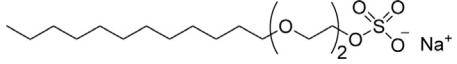
| Surfactant | Name/components | Type | General structural formula/examples of typical structure | Molecular formula/mol. wt. |
|-------------|---|-------------------------|--|---|
| DPC | 1-dodecylpyridinium chloride | Cationic surfactant |  | C ₁₇ H ₃₀ ClN/283.88 |
| TX-100 | <i>P</i> -tertiary-octylphenoxy polyethyl alcohol | Nonionic surfactant |  | C ₈ H ₁₇ C ₆ H ₄ O(OCH ₂ CH ₂) _{9.5} H/628 |
| PFOA | Perfluorooctanoic acid | Anionic surfactant |  | C ₇ F ₁₅ COOH/414.07 |
| NINOL 40-CO | Cocamide DEA | Nonionic surfactant |  | C ₁₆ H ₃₃ NO ₃ /287.44 |
| CAPB | Cocanut amide propyl betaine | Zwitterionic surfactant |  | C ₁₉ H ₃₈ N ₂ O ₃ /342.52 |
| DDAC | Didecyl dimethyl ammonium chloride | Cationic surfactant |  | C ₂₂ H ₄₈ ClN/362.08 |
| SLES | Sodium laureth sulfate | Anionic surfactant |  | C ₁₂ H ₂₅ (OCH ₂ CH ₂) _n OSO ₃ Na |
| SDS | Sodium dodecyl sulphate | Anionic surfactant |  | CH ₃ (CH ₂) ₁₁ OSO ₃ Na/288.38 |
| SDHS | Sodium dihexyl sulfosuccinate | Anionic surfactant |  | C ₁₆ H ₂₉ NaO ₇ S/388.45 |
| JBR-425 | Rhamnolipid | Nonionic biosurfactant |  | C ₃₂ H ₅₈ O ₁₃ and C ₂₆ H ₄₈ O ₉ /504.6 and 650.8 |
| Ammonyx KP | Oleyl dimethyl benzyl ammonium chloride | Cationic surfactant |  | C ₂₇ H ₄₆ ClNO/436.11 |
| CTAB | Cetyltrialkyl Ammonium Bromide | Cationic surfactant |  | C ₁₆ H ₃₃ (CH ₃) ₃ NBr and C ₁₆ H ₃₃ (CH ₂ CH ₃) ₃ NBr/364.45 and 406.53 |
| SDBS | Sodium dodecyl benzene sulfonate | Anionic surfactant |  | C ₁₈ H ₂₉ NaO ₃ S/348.48 |
| Texapon-40 | Sodium lauryl ether sulfate | Anionic surfactant |  | C ₁₆ H ₃₃ NaO ₆ S/376.48 |

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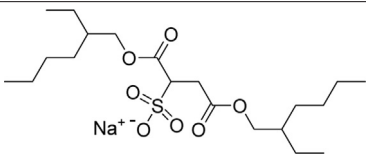
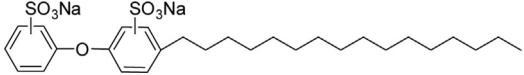
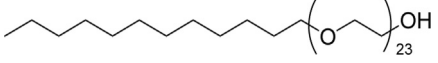
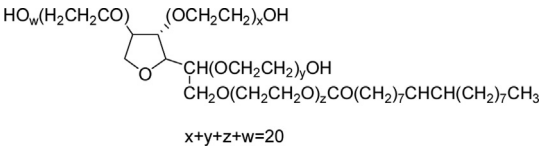
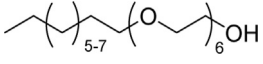
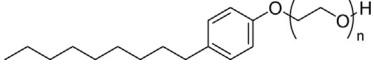
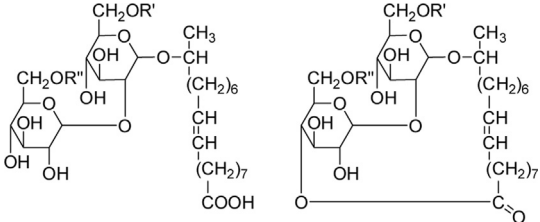
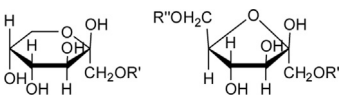
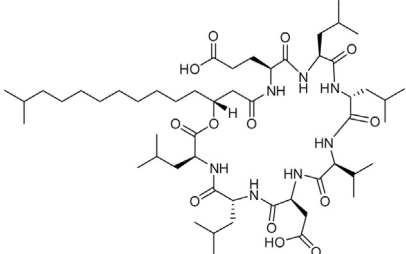
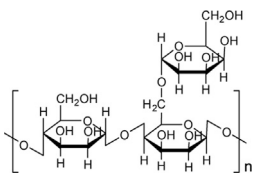
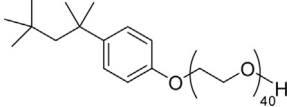
| Surfactant | Name/components | Type | General structural formula/examples of typical structure | Molecular formula/mol. wt. |
|---------------------------|---|----------------------------|---|--|
| AOT | Bis(2-ethylhexyl) sulfosuccinate sodium | Anionic surfactant |  | C ₂₀ H ₃₇ NaO ₇ S/444.56 |
| Calfax 16L-35;Dowfax 8390 | Sodium hexadecyl diphenyl ether disulfonate | Anionic gemini surfactant |  | C ₂₈ H ₄₀ Na ₂ O ₇ S ₂ /598.72 |
| Spolapon AOS 146 | Linear sodium alkene sulfonates and hydroxyalkanesulfonates (C12–C16) | Anionic surfactant | $R-CH=CH-SO_3Na \quad R-\overset{OH}{\underset{H}{C}}-CH_2-SO_3Na$ $R = C_{10}\text{--}C_{14}$ | CH ₃ (CH ₂) _{9–13} CH=CHSO ₃ Na & CH ₃ (CH ₂) _{9–13} CH(OH)CH ₂ SO ₃ Na |
| Brij-35 | Poly(oxyethylene) ₂₃ dodecyl ether | Nonionic surfactant |  | C ₁₂ H ₂₅ (OC ₂ H ₄) ₂₃ OH/1198 |
| Tween 80 | Polyoxyethylene sorbitan monooleate | Nonionic surfactant |  $x+y+z+w=20$ | C ₆₄ H ₁₂₄ O ₂₆ /1310 |
| Empilan KR6 | Alcohols, C9–C11, ethoxylated | Nonionic surfactant |  | CH ₃ (CH ₂) _{8–10} (OCH ₂ CH ₂) ₆ OH |
| Tergitol NP-10 | Polyoxyethylene nonyl phenyl ether | Nonionic surfactant |  | No record (N. R.) |
| Sophorolipid | Sophorolipid | Nonionic biosurfactant |  | N. R. |
| Fructoselipid | Mixture of fructoselipid with different structure | Nonionic biosurfactant |  | N. R. |
| Surfactin | Cyclic lipopeptide | Zwitterionic biosurfactant |  | N. R. |
| Guar gam | Galactomannan | Nonionic biosurfactant |  | N. R. |
| TX-405 | Polyoxyethylene (40) isooctylphenyl ether | Nonionic surfactant |  | C ₁₄ H ₂₁ (OCH ₂ CH ₂) ₄₀ OH |

Table 1 (Continued)

| Surfactant | Name/components | Type | General structural formula/examples of typical structure | Molecular formula/mol. wt. |
|------------|----------------------------------|-------------------------|--|---|
| Brij-58 | Polyoxyethylene (20) cetyl ether | Nonionic surfactant | | C ₁₆ H ₃₃ (OCH ₂ CH ₂) ₂₀ OH/1123.5 |
| Brij-98 | Polyoxyethylene (20) oleyl ether | Nonionic surfactant | | C ₁₈ H ₃₅ (OCH ₂ CH ₂) ₂₀ OH/1149.5 |
| Saponin | Pentacyclic triterpene saponin | Nonionic biosurfactant | | N. R. |
| CAS | Cocamidopropyl hydroxysultaine | Zwitterionic surfactant | | CH ₃ (CH ₂) ₁₃ -N(OH)- (CH ₂) ₃ -N ⁺ (CH ₃) ₂ - CH ₂ -CHOH-CH ₂ SO ₃ ⁻ /452.69 |

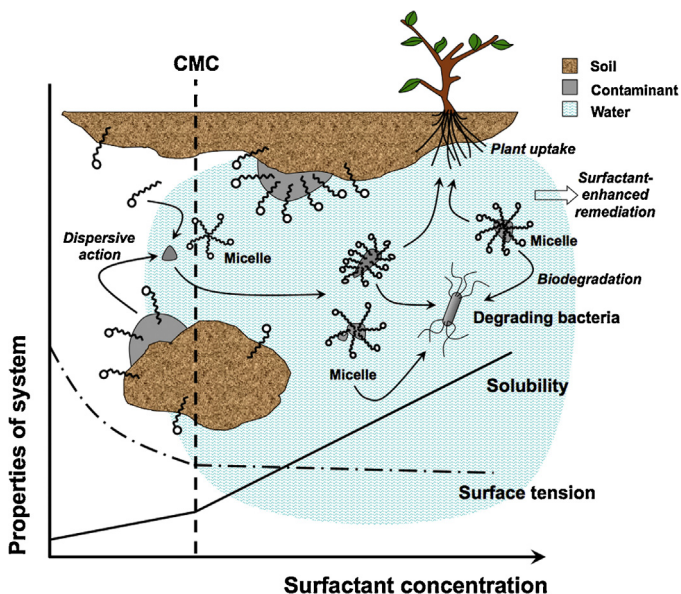


Fig. 2. Schematic of surfactant enhanced-remediation of contaminated soils [10].

ues of soil, suggesting that the adsorption of DPC depended on the net negative charges of soil surface. The investigation on the correlation between the maximum sorption of TX-100 and the content of soil organic matter, also indicated that the soil organics altered the interfacial properties of the soil–water system, therefore affected the adsorption behavior of nonionic TX-100 [19].

Surfactants for soil washing should have good solubilization potentials while maintaining less adsorption onto soil. Studies show that the type of surfactants, and the molecular structure (e.g., length of hydrophobic chain [18,20–22], number of hydroxyl groups [23], and presence of different substituent groups [24]), can greatly influence the molar solubilization ratio (MSR) of contaminants. The MSR is defined as the moles of contaminant solubilized per mole of surfactant. It corresponds to the straight line slope above the CMC on a plot of aqueous contaminant solubility versus

surfactant concentration. Namely, the MSR can be calculated by the equation below,

$$\text{MSR} = \frac{C_{\text{mic}} - C_{\text{CMC}}}{C_{\text{surf}} - \text{CMC}} \quad (1)$$

where C_{mic} is the total apparent solubility of the organic contaminants (in moles per liter) in micellar solution at a particular surfactant concentration greater than the CMC, C_{CMC} is the apparent solubility of the contaminant (in moles per liter) at CMC which may be approximated as the aqueous solubility of the contaminant, and C_{surf} is the surfactant concentration at which C_{mic} is evaluated in moles per liter [25].

Introduction of surfactants into soils may change the physicochemical and biological properties of soil through initiating a range of surface reactions [26]. For instance, the sorption of certain surfactants on the soil particles proved to change the hydraulic conductivity of soils [27]. Toxic surfactants directly incur harmful effects on soil ecosystem. For example, perfluorooctanoic acid (PFOA) is a surface active agent that was once extensively used in manufacturing industry. Now there are evidences that perfluorooctanoic acid can persist indefinitely in soil environment and show toxic and carcinogenic effects in animals [28]. Concerns about toxicity of surfactants mainly arise from the residual surfactants in soil after soil washing if they are not readily biodegradable. Excessive presence of surfactants in the soil/pore water system may adversely affect the ecosystem due to the biological activities of surfactants. Anionic surfactants can bind to bioactive macromolecules such as peptides, enzymes, and DNA, changing the biological function of microorganisms [29]. Cationic surfactants can affect the cytoplasmic membrane of bacteria [30]. Some nonionic surfactants exert antimicrobial activity by binding to various proteins and phospholipid membranes [31]. Bailey et al. [32] studied the influence of different surfactants on the growth and development of *Shewanella oneidensis* MR-1, revealing that NINOL 40-CO at all testing concentrations could inhibit bacterial growth while cocamidopropyl betaine (CAPB), and sodium laureth sulfate (SLES) (concentrations ranging from 20 to 100 mM) showed lower inhibitory effects. Linear alkylbenzene sulfonate (LAS) is revealed to interact with cell membranes of bacteria and disturb their proper functioning [33], therefore showing certain inhibitory effect on the growth and viability of various soil microorganisms [34]. By contrast,

sodium dodecyl sulphate (SDS) (20–500 μM) can be utilized by the bacteria as a carbon source [32]. The better biocompatibility and biodegradability of the SDS make it feasible to accomplish a surfactant-enhanced bioremediation. Chang et al. [35] studied the effects of TX-100 and Brij-35 on the physiological and enzymatic properties of indigenous degradation bacteria in a polycyclic aromatic hydrocarbons (PAHs) biodegradation system. The results indicated that the addition of the non-ionic surfactants altered the profiles of the microbial populations and the produced exoenzymes. For plants, a proper surfactant application was reported to enhance the water and nutrient uptake because the surfactant could reduce the dry zone in sandy soils by decreasing water surface tension [36]. Meanwhile, excessive accumulation of some surfactants in soil may produce negative impact on the plants [37]. Oros et al. [38] confirmed the phytotoxicity of sulfosuccinic acid esters to *Tradescantia bicolor*. The alkyl chains of sulfosuccinic acid esters are thought to insert into the lipophilic part of the phospholipids bilayers, causing membrane disorder and malfunction.

In general, research shows that the cationic surfactants, e.g., quaternary ammonium compounds (QACs), are more hazardous, and their limits, such as half maximal effective concentration (EC50) and lethal concentration (LC50), are the lowest among the commonly used surfactants [30]. A typical example is didecyl dimethyl ammonium chloride (DDAC), which is used as a disinfectant cleaner for a broad spectrum of bacteria and fungi [39]. Although the toxicity of surfactants to soil ecosystem is associated with many factors [40], selection of surfactants with favorable biocompatibility is obviously important for achieving a sustainable and green soil remediation. Biosurfactants, which are derived from biotic processes, are thought to have better biocompatibility than chemically synthesized surfactants. Use of biosurfactants and the synthetic surfactants with good biocompatibility and biodegradability is the future direction for soil remediation.

3. Mechanism of soil pollutants removal

3.1. Removal of hydrophobic organic pollutants

Surfactant-enhanced soil washing for hydrophobic organic pollutants can result from two distinct mechanisms: soil roll-up mechanism (occurs below the CMC) and solubilization (occurs above the CMC) [41]. Surfactant monomers before the CMC are responsible for the soil roll-up mechanism. Surfactant monomers accumulate at the soil–contaminant and soil–water interfaces, and change the wettability of the system by increasing the contact angle between the soil and the hydrophobic contaminants. Surfactant molecules adsorbed on the surface of the contaminant cause a repulsion between the head groups of the surfactant molecules and the soil particles, thereby further promoting the separation of the contaminants from the soil particles [41]. When the concentration is above the CMC, the surfactant can enhance the solubilization of hydrophobic organic pollutants in the micelles, and the partition of pollutants in the aqueous phase thereby remarkably increases.

For a soil washing process, the contaminants that partition in the micellar phase can be further separated and treated, e.g., via adsorption by activated carbon [42], electrochemical treatment [43], and demulsification [44,45], to realize the recycle of washing solutions, or the final disposal. Recycling of the surfactants is desired to decrease the cost of overall remedy. On the other hand, surfactants in soil affect the bioremediation of organics by increasing the bioavailability of pollutants [46]. Mathurasa et al. [47] found that the addition of the ionic surfactant sodium dihexyl sulfosuccinate (SDHS) contributed to the interaction between the tributyltin (TBT) and the soil bacteria, thereby benefited the bacterial degradation of TBT. Seo and Bishop [48] allowed the formation of a *Pseu-*

domonas biofilm on the surface of phenanthrene-contaminated soil beforehand, then added a certain amount of non-ionic surfactant TX-100 (nontoxic to *Pseudomonas*) to the soil. The results confirmed a significant improvement of phenanthrene biodegradation. It is believed that the physiological properties of the attached microbial film changed when the TX-100 concentration in pore water was higher than its CMC. Moldes et al. [49] compared the bioremediation of hydrocarbon-contaminated soil under different conditions, and suggested a positive role of biosurfactants on the biodegradation of pollutants. The biosurfactant produced by *Lactobacillus pentosus* bacteria significantly accelerated the biodegradation of soil contaminants after 40 days of incubation. It should be pointed out that surfactants may also retard, or have no effect on biodegradation of organic hydrocarbons. The toxicity of surfactants may cause inhibitory effects on pollutant degrading bacteria and retard the biodegradation.

Surfactant-enhanced phytoremediation for organics contaminated soil is also reported. Pot culture experiments were conducted to evaluate the combined effects of biosurfactant rhamnolipid, mushroom dregs, and alfalfa on the degradation of PAHs [50]. After 60 days of culture, 14.43% of organic matter could be digested by alfalfa alone, while the removal rates respectively, increased to 32.64% and 36.95% with the addition of 125 and 250 mg/g rhamnolipid surfactant in the combined remediation processes. The added rhamnolipid surfactants are believed to change the permeability of root cell membranes, which enhanced the nutrient uptake and facilitated the growth of alfalfa. On the other side, the solubilization effect of rhamnolipid is conducive to the desorption of PAHs from contaminated soils, further improving the bioavailability of pollutants.

3.2. Removal of heavy metals

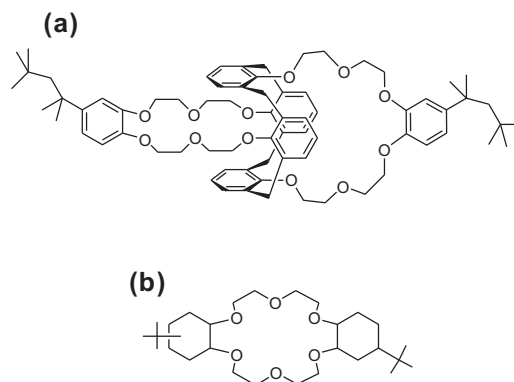
Heavy metals in soil mainly adsorb on the surface of soil in the form of ions or precipitation of metal compounds [51]. Different from the organic soil contaminants, heavy metals are mainly removed from the soil via surfactant-associated complexation [52] and ionic exchange [53]. Therefore, surfactant-enhanced washing and surfactant-enhanced bio-extraction can be applied to the remediation of heavy metal contaminated soils. Slizovskiy et al. [54] studied the enhanced remediation of heavy metal contaminated soils by cationic surfactant DPC, nonionic surfactant Ammonyx KP, and ionic biosurfactant JBR-425. It was found that the JBR-425 had the best elution effect for Zn (39%), Cu (56%), Pb (68%), and Cd (43%). Surfactants contribute to the bio-extraction of soil heavy metals as well. Lipopolysaccharide (LPS, a unique ingredient in the cell walls of Gram-negative bacteria), consisting of hydrophilic polysaccharide and hydrophobic phospholipids, was investigated as a biosurfactant for the extraction of heavy metals. The research by Langley and Beveridge [55] showed that LPS enhanced the hydrophilicity of the outer cell walls and further coordinated with metal cations by means of O-side-chain and phosphoryl, thus, assisted the bacteria to absorb heavy metals. Almeida et al. [56] studied the impact of surfactants on the removal of Cu by salt marsh plant *Halimione portulacoides*. TX-100 and SDS used in the experiments were both favorable for Cu harvesting and transportation in plant roots, but did not influence the transportation of Cu in stem and leaves. This study suggested that surfactants promoted the phytoremediation by changing the membrane permeability of the root cells. Meanwhile, the added surfactants could promote the desorption of metals and uptake of metals by plant [57].

For the removal of heavy metals, it should be pointed out that the common forms of chromium and arsenic are negatively charged anionic complexes. Such oxyanions may combine with cationic surfactants to cause more stable retention in soils. Li

et al. [58] investigated how cationic surfactant sorption onto clay might retard chromate migration. It was observed that the cationic surfactant with a longer tail group significantly increased the chromate retention in soils. This observation indicates that the cationic surfactants can be anchored onto clay surface via hydrophobic attraction between their tail groups and clay, and further fixed the negatively charged Cr(VI) (e.g., dichromate, found at a pH below 5, and chromate, found at a pH above 6) via the electrostatic attraction between Cr(VI) and the positively charged head groups. This fixation effect is obviously detrimental to the mobility of Cr(VI), and impedes the subsequent removal of Cr(VI). More recently, bio-surfactants, such as soapberry-derived saponin and rhamnolipids, are found to be able to remove chromium and arsenic oxyanions from spiked soils or mine tailings [59–61]. Wang and Mulligan [62,63] pointed out that several mechanisms might be involved for the mobilization of arsenic/chromium oxyanions by negatively-charged rhamnolipids: (1) rhamnolipids compete with arsenic oxyanions for the adsorption sites on soil particles, therefore suppressing arsenic and mobilizing the metal ions, (2) anion exchange between arsenic anions and rhamnolipids may contribute to the mobilization, and (3) adsorption of rhamnolipids could increase the negative zeta potential of the soil particles, therefore further mobilizing arsenic through electrostatic repulsive interactions. Considering the complexation ability of saponin and rhamnolipids on metal cations, they can be developed as washing agents capable of simultaneously removing mixed heavy metals.

3.3. Removal of radionuclides

Important man-made soil radionuclides include caesium (^{137}Cs), uranium (^{238}U), and strontium (^{90}Sr), which have similar properties to heavy metals. Therefore, they can be remediated through the same mechanism including dissolution, ionic exchange, and complexation [64,65]. Cationic surfactants, particularly hexadecyltrimethylammonium, have been successfully applied as a flushing additive to clean Cs^+ contaminated soils [66]. Whereas, due to the great harm of soil radionuclides, their desorption from soil should be enhanced by more powerful complexation for a more thorough decontamination [67,68]. Some macrocyclic compounds, such as crown ether, cyclodextrin and calixarene, possess a unique selectivity for cations. The coordination atoms (e.g., nitrogen and oxygen atoms with lone pair electrons) can coordinate to a cation within the cavity, and the denticity of cavity influences the affinity/selectivity of a macrocyclic compound for cations [69]. Fig. 3 shows the complexations of typical cavum structures with cations. The crown ether can match with the cations with different coordination modes, such as 1:1 complex (Fig. 3a) and 2:1 sandwich complex (Fig. 3b) [70], depending on the properties of cations. Calixarenes (Fig. 3c,d) are a family of phenol-formaldehyde cyclic oligomers [71], and they combine the characteristics of both ordinary crown ether and cyclodextrin. The calathiform structural frame of calixarene can be designed to extract different sized ions. In addition, some flexible chain compounds with coordinating atoms, as illustrated in Fig. 3e, also show coordinating capability for ions [72]. Considering the above features of macrocyclic compounds, researchers introduce hydrophobic groups (e.g., alkyl and phenyl) into the rings of annular polyoxyethylene, or link calixarene to hydrophilic poly(oxyethylene) and polyether [73], to obtain a group of macrocyclic compounds-based surfactants, which have better washing performances on radionuclides contaminated soils and radioactive waste. Bonnesen and co-workers [74,75] found that calixcrown ether (BOBCalixC6, see Scheme 1a) had a good performance for the extraction of radioactive cesium compounds. Boda et al. [76] further confirmed the superior selectivity of macrocyclic hybrid calixcrown ether toward Cs^+ by a density functional theory (DFT) calculation. Raut et al. [77] studied the selective



Scheme 1. Molecule structure of (a) BOBCalixC6 [74,75] and (b) DTBCH18C6 [77].

extraction of radio-strontium from acidic media by a supported liquid membrane method. The supported liquid membrane consisted of the mixture of 1 M crown ether-type surfactant DTBCH18C6 (Scheme 1b), 2-nitrophenyl ether and *n*-dodecane absorbed into a microporous polytetrafluoroethylene film. After 24 h of extraction, about 98.25% of Sr was separated out. These crown ether-type surfactants show good prospects on the remediation of radionuclides contaminated soils, but field tests on radionuclides contaminated sites are still needed to determine their practical efficiencies.

4. Remedial applications of surfactants

Generally, surface-active agents consist of four categories in terms of the hydrophilic group: cationic, anionic, nonionic, and zwitterionic surfactants [15]. Surfactants with different structures and properties can serve for different decontamination purposes. In this section, the application cases of surfactants for soil remediation in recent years are reviewed and discussed in terms of the types of surfactants.

4.1. Ionic surfactants

Ionic surfactants include cationic, anionic, and zwitterionic surfactants. Most soil colloidal particles are negatively charged, and they can bind with cationic and anionic surfactants by ion exchange and ion matching [15]. The consequent decrease of the interfacial tension between soil and water facilitates the migration of pollutants. Biodegradable SDS, one of the most common ionic surface-active agents, features an efficient removal of hydrophobic contaminants from soil [78]. Davezza et al. [79] extracted 4-methylphenol, 4-ethylphenol, and 4-*tert*-butylphenol from sandy clay using SDS, and obtained 89.1%, 65.3%, and 55.1% of removal efficiencies, respectively. Likewise, SDS has the capacity to elute heavy metals. Ramamurthy et al. found that the best removal efficiencies of Cu(II) and Zn(II) were obtained with the addition of 1.25 CMC of SDS, and the highest removal amounts of Cu(II) and Zn(II) by SDS reached 1.25 mg/L and 36.8 mg/L, respectively [80]. Due to the sulfur-containing groups in SDS molecules, SDS can bind with heavy metals and facilitate their desorption from soils [81]. Other commonly used surfactants include cetyltriethyl ammonium bromide (CTAB), sodium dodecyl benzene sulfonate (SDBS), and cocamidopropyl betaine. In comparison with anionic surfactants, cationic surfactants are more likely to adsorb onto the surface of negatively charged soil particles and aquifer materials, which inevitably increased the consumption of surfactants. Therefore, more cases that use anionic surfactants, instead of cationic surfactants, for soil washing or aquifer flushing were reported. In Table 2, cases of using ionic surfactants for the remediation of site-specific contaminated soils (laboratory-scale, field demonstration and full-scale) after year 2000 are summarized. It is noted that ionic

Table 2
Application cases of ionic surfactants for the remediation of contaminated soil (HTAB, hexadecyl trimethyl ammonium bromide; CTAB, cetyltrimethylammonium bromide; TCA, trichloroacetic acid; TCE, trichloroethylene; BTEX, benzene series; TPH, total petroleum hydrocarbon; DNAPL, dense non-aqueous phase liquids; and LNAPLs, light non-aqueous phase liquids).

| Soil source/ contaminated sites | Soil texture | Scale of remediation | Major contaminants | Surfactant and use | Effectiveness of remediation | Refs. |
|--|---|------------------------|--|---|---|-------|
| Agricultural soil from Crete island, Greece | 56% sand, 35.5% silt, and 8.5% clay | Laboratory | Cd(II) | 10 ⁻² M SDS, 38 V electrokinetic leaching for 18 days | 94% Removal efficiency of Cd after 18 days | [82] |
| Heavy metals contaminated soil from a metallurgy plant, Mexico | 39% clay, 36% loam, and 24% sand | Laboratory | Heavy metals like Cd, Zn, Cu, Ni | 20 mL 0.5% Texapon-40 mixed with 6 g soil, 24 h stirring | Cd, Ni, and Zn were removed by 83.2%, 82.8%, and 86.6% | [83] |
| Organics contaminated soil in Pyeongtaek, Korea | Sandy soil with 0.8% clay | Laboratory | 1,2,4-trichlorobenzene (TCB) | 4 wt% SDS + 10 wt% NaCl, the volume of leachate was 3750 mL | 97% Removal efficiency for TCB | [84] |
| Soil from the campus of Nankai University, Tianjin, China | – | Laboratory | Aldicarb (carbamate pesticide) | 50 mL HTAB (200 mg/L) to 5 g contaminated soil | 56% Desorption ratio of aldicarb | [85] |
| Clay soil collected from Meachitoba Province, Canada | Crushed and screened clay soil | Laboratory | Benzene series, naphthalene and phenanthrene | 1.5% (w/w) CTAB, the hydraulic gradient was 2.8 | Organic pollutants were removed by 58.8–98.9% | [86] |
| Fuel oil contaminated soil near Algiers, Algeria | 94% silt, 2.4% sand, and 2.9% clay | Field demonstration | Diesel | 8 mM SDS, 48 h leaching at 3.2 ml/min flow velocity | 97% Removal efficiency for diesel | [87] |
| Underground Storage Tank Site in Oklahoma | Sandy silt, silty clay, and silt | Full-scale remediation | Diesel fuel and gasoline fuel NAPL | AOT/Calfax 16L-35 (0.94 wt% total concentration) 0.2–0.4 wt% NaCl | 75–99% Benzene reduction, 65–99% TPH reduction | [88] |
| An incinerator plant in Czech Republic | 80% sand, 17% silt, and 3% clay | Field demonstration | PCBs | Spolapon AOS 146 solution (40 g/L CMC value) | 56% Efficacy for PCBs decontamination | [89] |
| Alameda Point Naval Air Station Site, Alameda, CA | Homogeneous sands and clay | Field demonstration | DNAPL, especially TCA and TCE | Dowfax (5 wt%), sodium dihexyl sulfosuccinate (2 wt%), NaCl and CaCl ₂ | 95% DNAPL removal and 93% surfactant recovery | [90] |
| Millican Field, Pearl Harbor, Hawaii | Geological layers of highly fractured volcanic tuff | Field demonstration | Petroleum, LNAPLs | 4 wt% Isalchem 123 (PO) _{7.7} sodium ether sulfate with 8% SBA cosolvent | 87.5% of the LNAPL in soil was recovered | [90] |
| Chevron Cincinnati Facility in Hooven, OH. | Fine sand and silt, clay | Full-scale remediation | BTEX, LNAPLs | Mixture of Alforterra 123-4-PO sulfate, 8% 2-butanol, Emcol-CC-9 and calcium chloride | LNAPL reduced from 8% to less than 1% residual saturation | [91] |

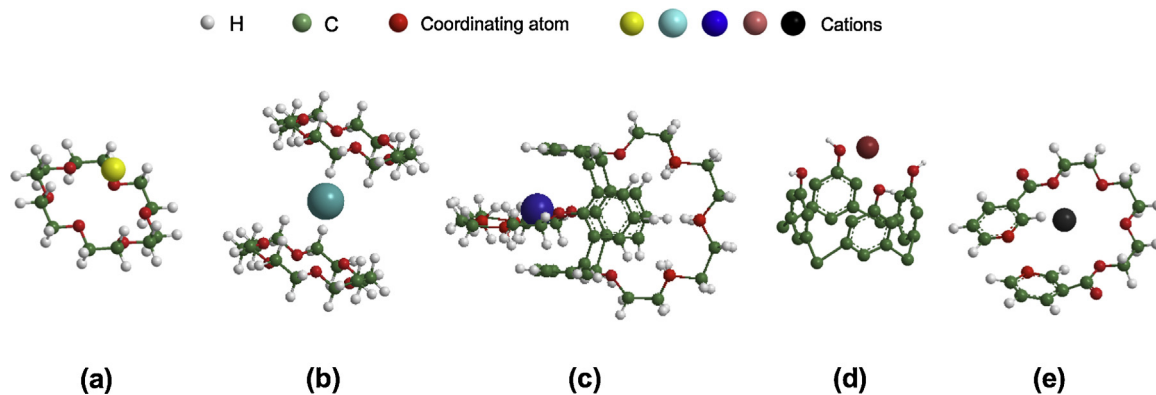


Fig. 3. Complexations of (a) one crown ether 18-crown-6, (b) two crown ether 18-crown-6, (c) calixcrown calixarene-bis(crown-5), (d) calixarene, and (e) flexible chain compound ethylene glycol isonicotinic acid derivative with the corresponding cations [70–72].

surfactants is successfully applied for the removal of a variety of contaminants, such as PCBs, petroleum, dense NAPLs, light NAPLs, BTEX, and heavy metals from site-specific soils at pilot scale or full scale. However, the field demonstration of in-situ flushing is yet limited. The toxicity concerns relative to ionic surfactants and the uncertainty of containment of a flushing remediation, are recognized as the major reasons that confine the field application of in-situ flushing. Development of low-toxicity, biodegradable surfactants will be helpful to address this concern.

4.2. Nonionic surfactants

Nonionic surfactants hardly ionize in water, and their hydrophilic portions are usually made up of oxygen-containing groups such as hydroxyl and polyoxyethylene. Nonionic surfactant molecules dissolve in aqueous phase via the formation of intermolecular hydrogen bonds between the hydrophilic groups and water molecules. Micellization is easier for nonionic surfactants because the aggregation takes place mainly due to the hydrophobic attraction among non-polar chains whereas, hydrophilic chains are easily separated in an aqueous phase. Ionic surfactants are more difficult to form micelles than the nonionic surfactants of identical alkyl chain length, because higher concentrations are necessary to overcome the electrostatic repulsion between the head groups of ionic surfactants during aggregation [92]. Therefore, nonionic surfactants usually have low critical micelle concentrations. Owing to their solubilization capacity and low toxicity, nonionic surfactants are widely applied into the research on remediation of contaminated soil [93]. Mulligan and Eftekhari reported on the effect of surfactants on the leaching of pentachlorophenol. The results showed that, using the 1% (w/w) TX-100 washing solution, more than 84% of pentachlorophenol could be extracted from fine sandy soil and silt [94]. In Torres et al.'s research, 88% of methyl parathion in soil was removed under the same TX-100 concentration [95]. Rios et al. [96] inspected the efficiencies of two kinds of nonionic surfactants on the desorption of dichloro diphenyl trichloroethane (DDT) from soils. When 2% Brij-35 solution was used as extractor solvent and the uninterrupted washing time was 86 min, the removal ratio reached 76.7%, while 56.3% of DDT could be eluted by 2% Tween 80 solution after 118 min of washing. In Table 3, cases regarding the use of nonionic surfactants for the remediation of site-specific contaminated soils are summarized.

4.3. Gemini surfactants

In recent years, some novel surfactants with particular structure and functions become the focus of attentions. Gemini surfactants are a group of surface active compounds possessing more than

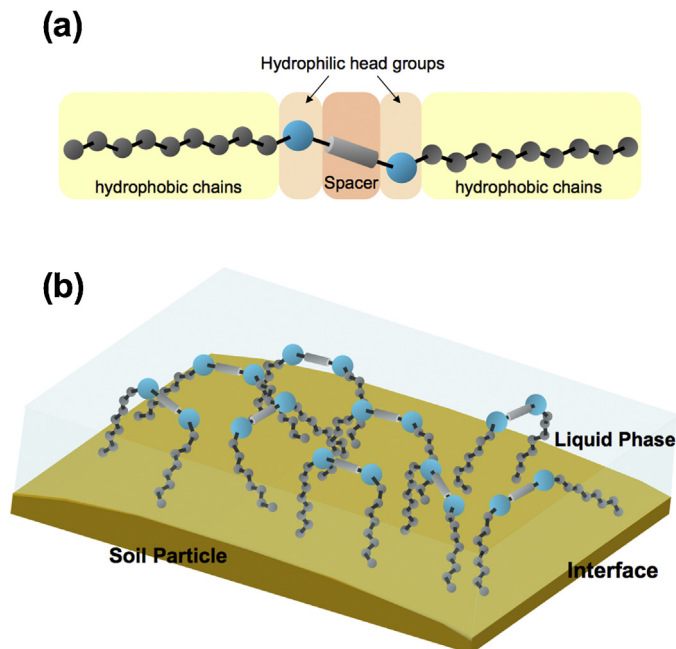


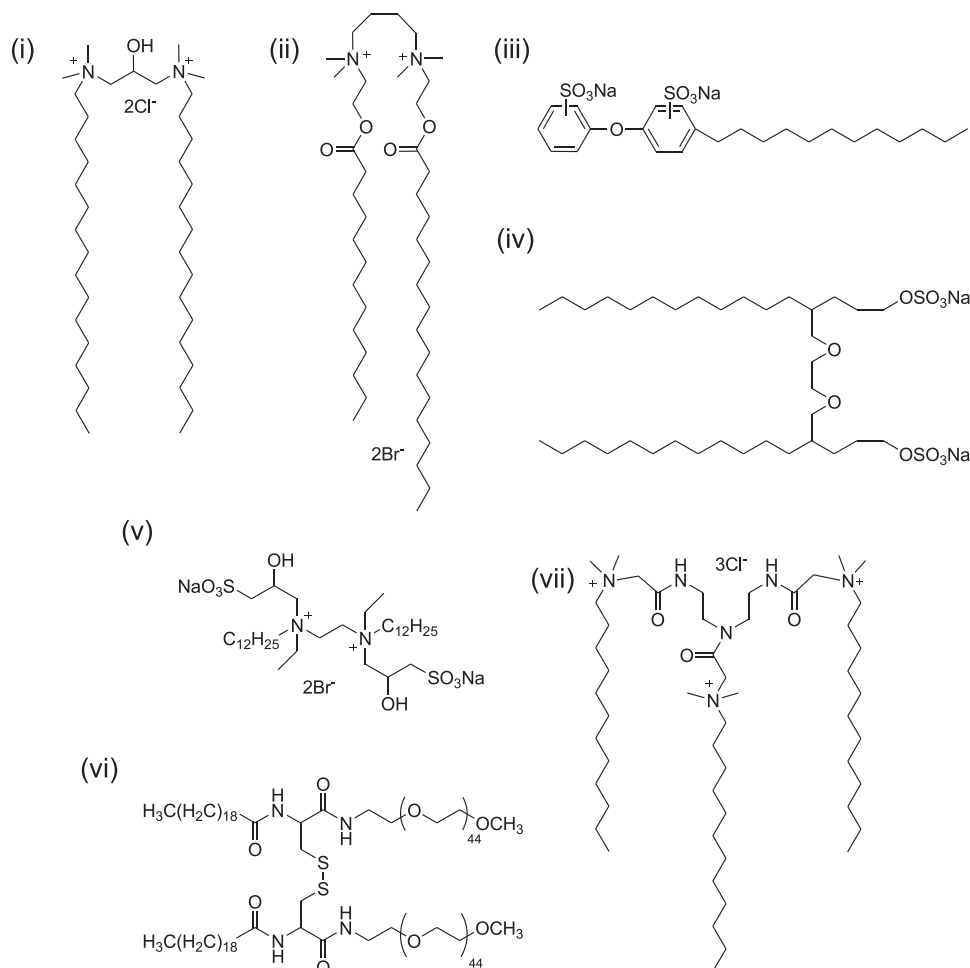
Fig. 4. (a) Schematic of a symmetrical gemini surfactant and (b) a monolayer film formed at the water–soil interface due to the adsorption of gemini surfactant molecules [107].

one hydrophobic and hydrophilic groups [105]. They are of great value to soil remediation due to their lower CMC values compared to the corresponding monomeric surfactant [106]. In the structure of a gemini surfactant, two conventional single chain surfactants are strung together by a spacer chain, and even more functional groups can be added for a certain purpose. Schematic of a symmetrical gemini surfactant is shown as an example in Fig. 4a. The design of spacer can be flexible, alkyl carbon chains, rigid phenyl groups, polystyrene chain and polar polyethers being candidates for spacers. The hydrophilic portions can be anionic sulfates, carboxylates, phosphates, cationic quaternary ammoniums, nonionic polyethers, polysaccharides, and complicated hydrophilic oligomers. The hydrophobic portions are usually long hydrocarbon chains [107,108].

Fig. 4b depicts the adsorption of a monolayer of gemini surfactant onto the surface of a soil particle. The hydrophobic tails inward bind with soil particles, while the hydrophilic heads linking with spacers extend to aqueous phase, forming a unique binding mode. The performance of a gemini is affected not only by the hydrophobic/hydrophilic groups, but also by the spacer. First, the bridging

Table 3Application cases of nonionic surfactants for the remediation contaminated soil (MGDA, methyl glycine diacetic acid and MTBE, methyl *tert*-butyl ether).

| Soil source/ contaminated sites | Soil texture | Scale of remediation | Major contaminants | Surfactant and use | Effectiveness of remediation | Refs. |
|--|--|----------------------------|--|--|--|-------|
| Loamy sand in Madrid, Spain | Soil particle <2 mm | Laboratory | <i>P</i> -cresol | Tween 80, solid-to-liquid ratio (W/V _L) was 2.5 mg/L, mixing time was 48 h | >70% Extraction efficiency | [97] |
| Soil prepared in the laboratory | 50–55% sand, 40–43% silt, and 4–5% clay | Laboratory | Hydrophobic aromatic compounds | 25 mL 0.05 M Brij-35 solution to 2 g soil, 5 h stirring | 43–69% Removal efficiency | [98] |
| Heavy metals contaminated soil from a metallurgy plant, Mexico | 39% clay, 36% loam, and 24% sand | Laboratory | Cd, Zn, Cu, Ni, Pb, and other heavy metals | 20 mL 0.5% Tween 80 to 6 g soil, 23 h stirring | Removal efficiency: 85.9% Cd, 85.4% Zn, and 81.5% Cu | [83] |
| Bachman Road site in Oscoda, northeast Michigan, US | Shallow, unconfined sandy aquifer | Field demonstration | Tetrachloroethylene | 68,400 L of an aqueous solution of 6% (wt) Tween 80 | Washing out 19 L tetrachloroethylene | [99] |
| Crude oil contaminated soil in refinery | Silt and clay | Field demonstration | Petroleum hydrocarbon | 0.15% (v/v) Empilan KR6 and 1.6 mg/kg bioaugmentation commercial product MicroSolv-400, phytoremediation by <i>Scirpus maritimus</i> | Total petroleum hydrocarbon removal increased from 15% to 28% in the soil layer with higher root density (5–10 cm). | [100] |
| Soil from a pilot-scale site in Pusan, Korea | Landfill soil (top layer), silt, and sand clay | Field demonstration | Diesel, coal oil and lubricating oil | 2% of sorbitan monooleate (POE 20), in situ flushing | 88% of total petroleum hydrocarbon in soil was removed by POE 20 | [101] |
| An old wood preservation site in Elnaryd, south east Sweden | Particle size distribution: 17% sand, 36% silt, and 28% clay | Laboratory and pilot scale | PAH and As | A combination of 0.213 M MGDA and 3.2 CMC of alkyl glucoside surfactant at pH 12 | Concentrations of As and PAH were reduced from 105 ± 4 and 27 ± 0.7 mg/kg to 25 and 10 mg/kg after washing, respectively | [102] |
| An out-of-service oil distribution and storage station, Mexico | 38% porosity | Pilot/field demonstration | Polluted by gasoline and diesel, like MTBE, benzene, toluene, BTEX | 0.5% Canarcel TW80 at pH 7.8 | Initial concentration was 4600 mg/kg of TPH, average TPH removal was 87.1% | [103] |
| A horizon of Heverlee bos' after removal of the surface litter, Belgium | 54% sand, and 33% silt, 13% clay | Laboratory and pilot scale | Diesel | Tergitol NP-10 (10 ⁻⁶ –10 ⁻³ mol/L), 50 g soil/L | Diesel oil was removed by 50% | [104] |



Scheme 2. (i) A symmetric cationic gemini (dimeric); (ii) an asymmetric cationic gemini (dimeric); (iii) an asymmetric anionic gemini (dimeric); (iv) a symmetric anionic gemini (dimeric); (v) a zwitterionic gemini surfactant; (vi) a nonionic gemini (dimeric); and (vii) a gemini-type surfactant with three hydrophobic and hydrophilic groups [114–120].

function of the spacer reduces the electrostatic repulsion between the similarly-charged ionic groups, leading to forming tightly-packed micelles than the corresponding monomeric surfactant [109]. Therefore, dimeric surfactants often have better solubilization capability. Next, change of spacer type or spacer length also affects the nature of gemini surfactants [110,111]. According to the literature [110], the shorter the spacer chain, the greater the micellar aggregation number as well as the surface-excess values on silica–water interface. Therefore, the spacer is directly relevant with the surfactivity and the CMC of geminis. Wei investigated the enhanced solubilization of three gemini surfactants with varied length spacers, observing increased solubilities of naphthalene and pyrene as more methylene groups were added in the spacer [112]. Longer spacer resulted in a lower surface excess and a lower CMC value, thereby accelerating the dissolution of organics. Zhu et al. [113] studied a homologous series of anionic geminis with different spacer nature, and found that a hydrophilic, flexible spacer was more conducive to the formation of micelle than a hydrophobic, rigid spacer, thus, giving more stable micelles and a better surfactivity. In Scheme 2, several gemini (dimeric) surfactants with different structures and a gemini-type surfactant with three hydrophobic and hydrophilic groups are given [114–120]. These molecular structures demonstrate the variability of gemini surfactant chemistry and their potential for high-performance soil washing surfactant. However, due to the relatively complicated synthetic process, the cost of gemini surfactants is still the primary obstacle for their extensive application in soil remediation.

4.4. Biosurfactant

Biosurfactants are bio-available surface-active compounds mainly generated in the vital movement of bacteria, fungi and yeast. Biosurfactants can also be extracted from the metabolites of plants and animals [15]. For instance, rhamnolipid can be secreted by *Pseudomonas aeruginosa* [121], and *Candida* can produce a large amount of sophorolipid in the fermentative process [122]. The hydrophilic parts of biosurfactants can be polysaccharides, phosphates, amino acids, carbohydrates, polyhydroxy structures, and cyclic peptide, while the hydrophobic parts are usually made up of aliphatic hydrocarbons [11,121,123]. Technically, biosurfactants can also be categorized as ionic and nonionic ones. The biosurfactants commonly used for soil remediation include glycolipid (e.g., rhamnolipids, fructose lipids, sophorolipids), lipopeptide (e.g., surfactin, polymyxin) compounds and humic substances. As the most widespread natural organic matter, humic acids (HAs) exhibit amphiphilic properties, which can be conveniently used as environmentally friendly biosurfactants [124]. Extraction of HAs from natural soils is laborious with low yields for prefigured industrial applications. Nevertheless, biomasses offer the opportunity to get HAs from renewable sources at a good yield. This fact recently encouraged scientific community and industry, to consider biomasses, such as agricultural waste biomass and municipal solid wastes, to be used as source of HAs [124].

The environmental compatibility of biosurfactant [125] facilitates the biodegradation of contaminants, whilst promotes the

self-degradation of surfactants [126]. In addition to the positive impact on solubilization and desorption of soil pollutants, biosurfactants also stimulate microbes to decompose the contaminants, which is favorable to the in-situ bioremediation of soil pollutants. In comparison with synthetic surfactants, biosurfactants often have larger molecular structure and more ligand groups, which endows biosurfactants with extraordinary surface activity for the decontamination of both hydrophobic organics and heavy metals [127]. Song et al. [128] investigated the performance of saponin for the simultaneous removal of cadmium and phenanthrene. Using 3750 mg/L saponin solution as washing agent, 87.7% Cd(II) and 76.2% phenanthrene were synchronously removed. The external carboxyl groups of saponin micelles are believed to coordinate with cadmium to improve the mobilization. Mulligan et al. [129] investigated the effectiveness of biosurfactants on the removal of heavy metals from soils. Less than 1% of Cu and Zn were extracted with pure water, while 25% of Cu and 6% of Zn could be removed by an alkaline aqueous solution of 0.25% surfactant. The removal efficiencies of Cu and Zn can be further improved to 70% and 22% after five times washing. Mulligan et al. [130] also found that 4% sophorolipids acidic solution can achieve nearly 100% removal of Zn after consecutive washing. Bordas et al. [131] conducted a series of dynamic column elution tests, suggesting that rhamnolipids at a high concentration (5.0 g/L) could remove ~70% of the pyrene in soil. At a low dose of 0.1 wt%, locust bean gums washing liquid was able to extract 99.5–99.7% of methyl parathion from contaminated soil, and the removal efficiency obtained by gums was 84.2–99.7% [95]. Jorfi et al. [132] used the biosurfactant extracted from *P. aeruginosa* SP4 to enhance pyrene removal from the contaminated soil. The results showed that, at the addition of 250 mg/L biosurfactant, the pyrene removal of 84.6% was obtained compared to 59.8% for control sample without any surfactants. Unlike synthetic surfactants, biosurfactants can be produced in-situ and takes effect with less follow-up management, being effective with regard to technique and cost. If the artificially improved soil environmental allows the bioaugmented cultures to out-compete the indigenous microorganisms, the less labour and transport would be required and the remedial process would be ecologically acceptable. Martienssen and Schirmer [126] implemented a field experiment of in-situ remediation of oil-contaminated soil by adding a mixture of commercial biosurfactant BioVersal FW and microbial suspension (contain various obligate strains). About 50 g hydrocarbon compounds were degraded in one kilogram of soil after 15 months.

HAs have been used as well to solubilize organic pollutants using the soil washing technique. HA surfactants isolated from leonardite and water used at a concentration of 10 mg/L, were able to remove a similar amount of PAHs and thiophenes contaminants [133]. At the same concentration of 10 g/L, HAs derived from lignocellulosic biomass plus food wastes, was reported to be more effective than SDS in the removing of PAHs using soil washing technique [134]. The additional advantage of HAs as surfactant for soil remediation is its versatility. The solubilization effect on hydrophobic organics and complexation effect on heavy metal ions make HAs suitable to the remediation of soils with mixed contaminations. Considering the readily availability of biosurfactant, the engineering application of biosurfactants to the remediation of different types of soils will be the focus in the future.

4.5. Mixed surfactants and combined use

Combination of different types of surfactants can incur a synergistic effect for washing solutions. Therefore, the use of mixed surfactants for soil remediation is very common. For example, mixture of ionic and nonionic surfactants tends to give a stronger solubilization effect than single surfactants, because nonionic surfactants disperse the ionic surfactants and reduce the electrostatic

repulsion between molecules of ionic surfactants to some extent [15]. Therefore, a small amount of nonionic surfactant in the ionic surfactant solutions can significantly decrease the CMC of the mixed surfactant system [135]. Besides, an appropriate mixing of several surfactants could inhibit the adsorption of individual surfactant onto soil each other, so the loss of surfactant caused by the adsorption onto soil in a mixed system is relatively low. Such a scenario thereby strengthens the capability of mixed surfactants for pollutant desorption. For example, a study showed that the lowest total adsorption quantity (15 mg/g) of surfactants was obtained when TX-100 and SDBS were mixed at a mass ratio of 1:9 (the total concentration was 7 g/L). Such a value was much less than the adsorption loss of individual TX-100 (70 mg/g) and individual SDBS (50 mg/g) [136]. Due to the above reasons, the mixed surfactant often shows a better solubilizing capability to soil contaminants than the individual surfactant [137]. For instance, in comparison with the use of pure TX-100, the apparent solubility of phenanthrene in the mixed micelle increased by 12–66%, depending on the molar ratio of SDS to TX-100 in the mixed surfactant solution. Moreover, the order of the effects of four mixed anionic-nonionic surfactants on the dissolution of PAHs was SDS/TX-405 > SDS/Brij-35 > SDS/Brij-58 > SDS/TX-100, namely the solubility of contaminants increased with the increasing of the hydrophile-lipophile balance (HLB) value of nonionic surfactants [138]. It should be noted that, mixed surfactant is also alternative way to improve the biocompatibility the surfactant system for soil remediation. For example, the presence of a little amount of SDS in an anionic-nonionic mixed surfactant system is proved to promote the biodegradation of phenanthrene [139].

Combined use of surfactants with other additives, such as organic solvents, chelating agents, and ligand ions, can also provide a stronger capability to remove soil contaminants. Alcohol is one of the common additives. Zheng et al. [140] found that a mixture of 2.0 g/L rhamnolipid, 10 g/L NaCl, and 5.0 g/L *n*-butyl alcohol had the highest oil extraction rate of 74.55%. Childs et al. [141] studied the supersolubilization of tetrachloroethylene (PCE) in the mixed solution of sodium dihexyl sulfosuccinate, isopropanol (IPA) and CaCl₂ (wt. 3.3%: 3.3%: 0.4%), confirming a significantly increased concentration of PCE in the surfactant micelles. Zheng et al. [93] mixed the Tween 80, 1-pentanol, and linseed oil to formed oil-swollen micelles. When the micelle concentrations of mixed solution were higher than the CMC of Tween 80, the oil-swollen micelles showed a considerable increase in the solubility of two organochlorine pesticides (DDT and γ -HCH) compared to the empty surfactant micelles (without oil). Chelating agents are also good synergists for the surfactant-enhanced remediation of contaminated soils. Combined use of surfactants and chelating agents is often adopted to enhance the mobilization of metallic contaminants. Wen and Marshall [142] attempted to probe the simultaneous removal of trace metal elements and PAH in the soil with a mixed solution of Brij-98 and [S,S]-ethylenediaminedisuccinic acid (EDDS). It was found that almost all of the benzopyrene and chrysene as well as a part of heavy metals (Cd, Cr, Mn, Ni, Pb, and Zn) can be eliminated by the combined use of Brij-98 and EDDS. An electrokinetic washing of contaminated soils revealed that 73% of phenanthrene and 82% of Pb could be removed with the combined use of 1% Tween 80 and 0.1 M EDTA [143]. Cao et al. [144] reported that the mixture of saponin and EDDS provided the best desorption rates of Pb, Cu, and PCBs from the soil. EDDS is thought to facilitate the complexation of saponin with metals, and to improve the solubility of PCBs in the saponin solution. Mouton et al. [145] evaluated the simultaneous removal of PAHs and Pb using the surfactant cocamidopropyl hydroxysultaine (CAS). Their results suggested that the addition of EDTA significantly enhanced the Pb solubilization. Surfactants can be also used in conjunction with some ligand ions for soil remediation. Lima et al. found that, with the addition of 0.336 mol/L of

iodine ions in the TX-100 surfactant solution, the removal rates of Cd²⁺ and phenanthrene can be improved by 36.3% and 15.2% [146]. In addition to above mentioned additives, biological additives [100,126], water-soluble polymers [147], and inorganic salts [148] were reported as the admixtures of surfactant solution for soil remediation.

5. Concluding remarks and future prospect

Soil contamination is worldwide concerned due to its great harm to human and ecosystem. Surfactant plays an important role in the remediation of contaminated soils due to its unique function capable of enhancing the desorption pollutants from soils. In the present manuscript, the fundamental aspects of use of surfactants for the remediation of contaminated soil are summarized and the application cases of surfactant-enhanced remediation are reviewed and discussed. For a successful surfactant-enhanced remediation, the adsorption of surfactants onto soils is expected to be low, but surfactants have strong solubilizing capability on target contaminants. The surfactants are biocompatible and favorable to the subsequent utilization of soils. The presence of surfactant enhances the partition of pollutants in the aqueous phase, it could also promote the bioremediation of organics by increasing the bioavailability of pollutants. Heavy metals and radionuclides in soils can be removed via surfactant-associated complexation and ion exchange process. Macrocyclic compound-based surfactants, which have superior selectivity on radionuclides, are promising to the remediation of radionuclide-contaminated soil.

Gemini surfactants are of great value to soil remediation due to their lower CMC values and better solubilizing capability compared to the corresponding monomeric surfactant. Biosurfactants have good environmental compatibility, and they not only have the capability of desorbing and dissolving contaminants, but also facilitate the biodegradation of contaminants. Mixed surfactants or combined use of surfactants with other agents are alternative ways to further improve the overall performance of soil washing solution. Although limited field studies are available in comparison to many laboratory-scale studies, but the reported pilot field studies and full-scale remediation projects show that surfactant based remedial technology can be used to successfully remediate a variety of contaminated soils and sites.

Even though further research regarding the behavior of biosurfactant in the fate and transport of soil contaminants is still required, biosurfactant appears an attractive choice for surfactant-based soil remediation technology. The data currently available indicate that, the potential monetary value of biosurfactants is between 1 and 60 €/kg compared with a production cost of 0.10 to 0.30 €/kg [124], depending on the degree of purity and product specifications required by the desired application. Considering the huge production of synthetic surfactants and their lower average price (1–2 €/kg surfactant), biosurfactant is currently not a cost-competitive substitute in the marketplace. Therefore, a massive and cost-effective production of biosurfactant is very crucial to promoting its extensive use. Innovations on surfactant chemistry, biotechnology and remedial engineering technology are necessary to spur the application of biosurfactants and other surfactant-based techniques in the future.

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